COLL 1

Cytosolic internalization of luminescent quantum dots

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The remarkable progress made over the past two decades to grow inorganic nanomaterials, combined with careful surface functionalization strategies offer an opportunity to develop novel platforms for use in molecular imaging and as diagnostic tools. A successful integration into biological systems requires devising strategies to promote their intracellular uptake while circumventing endocytosis. We report on the use of an amphiphilic anti-microbial peptide as means of promoting the cytosolic uptake of luminescent QDs. The peptide is synthesized with a terminal cysteine to allow conjugation onto QDs that have been coated with multifunctional metal-coordinating ligands. Using fluorescence imaging and flow cytometry we find that incubating cells with the QD-peptide leads to delivery into the cytoplasm without affecting the cellular morphology or viability. We observed a homogeneous distribution of QD staining throughout the cytoplasm and without co-localization with labelled endosomes. Additional experiments where endocytosis has been eliminated (such as pre-treatment with specific inhibitors) have shown minimal effects on the intracellular QD uptake.

COLL 2

Influence of PEGyalation on the interaction of colloids with cells

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Several homologous nanoparticle libraries were synthesized in which inorganic nanoparticles (Au, FePt) were coated with polyethylene glycol (PEG). In the first series the molecular weight of the PEG was systematically increased. In the second series the diameter of Au cores as well as the thickness of the shell of polyethylene glycol was varied, keeping the resulting diameter constant. Basic physicochemical parameters of this two-dimensional nanoparticle library, such as size, z-potential, hydrophilicity, elasticity, catalytic activity, as well as protein adsorption were determined. Uptake of the nanoparticles by cells lines, and their effect on basic structural and functional cell parameters was determined.

COLL 3

Engineered nanomaterials for protein and nucleic acid delivery

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Therapeutic delivery of proteins and nucleic acids is a difficult goal. Of the many challenges in the delivery process, perhaps the most demanding is providing these biologics with access to the cytosol. Most delivery strategies employ endosomal uptake, requiring endosomal escape for the payload biologics to be effective. In our research, we have developed an alternative strategy that uses nanoparticle-stabilized nanocapsules (NPSCs) to deliver proteins and nucleic acids (siRNA and DNA) directly to the cytosol. These NPSCs use a membrane fusion process to bypass the endosomal pathway, providing highly effective payload delivery. The direct access to the cytosol makes NPSCs effective tools for therapeutic delivery, particularly in conjunction with intracellular targeting. Applications in vitro, in vivo, and mechanistic studies of these vehicles will be discussed.

COLL 4

Supramolecular bioactive nanostructures for cell signaling

***Samuel I. Stupp**, s-stupp@northwestern.edu.* Northwestern University, Evanston, Illinois, United States

Signaling pathways and other cell functions mediated by the extracellular matrix involve filamentous nanostructures that interact with receptors. This lecture will describe supramolecular nanostructures that mimic these nanostructures, created with biomolecular structural units including modified peptides, glycans, and nucleic acids. The systems to be described have the capacity to signal cells and promote biological adhesion, proliferation, and differentiation of stem cells. The lecture will demonstrate the functionality of these structures both *in vitro* and *in vivo* in the context of regenerative medicine and also systemic targeted therapies. The lecture will also discuss the design of dynamic bioactivity in these nanostructures that can be switched “on” or “off” using soluble chemical signals. Other features to be discussed include their capacity to bind multiple proteins for complex signaling, and also their ability to control cell signaling by changing the properties of cell membranes.

COLL 5

Optimizing passivation of interfaces with zwitterions

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Zwitterionic functionality at an interface is known to be highly effective at reducing interactions with (bio)macromolecules. Such “nonfouling” surfaces are found in nature and are increasingly being used to moderate interactions of nanoparticles with the in vivo environment. In particular, a nonfouling background decorated with ligands of high specificity is frequently a target of nanoparticle synthesis. Several morphologies for passivating nanoparticles with zwitterions are available, ranging from a monolayer of functional units to a thick brush of zwitterionic polymer. To prepare these zwitterion coatings, the chemistry for surface attachment, ligand density and zwitterion chemistry must be optimized. This talk will address various ways of anchoring zwitterions to surfaces and the performance against aggregation of the resulting planar and nanoparticle materials. Fundamental understanding of the mechanism for zwitterion nonfouling properties will be highlighted. At least one example of counterintuitive/surprising zwitterion behavior will presented.

COLL 6

Nanoparticles interactions with viruses

Francesco Stellacci, *francesco.stellacci@epfl.ch.* Institute of Materials, EPFL, Lausanne, Switzerland

Viruses perform many roles when interacting with humans. They are responsible for millions of deaths worldwide due to a plethora of transmissible diseases that they create. At the same time they are key components in vaccines and are used as transfection agents in modern medicine. These amazing self-assembled biological objects are nanoscale in size and hence potentially could interact with nanoparticles in a variety of -mostly unexplored- ways. In this talk, I will show how most functions of viruses can be affected by the interaction with small gold nanoparticles, leading to innovative ideas in medicine.

COLL 7

Smart and bright: Functional luminescent nanoparticles for bioimaging and therapy

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Functional luminescent nanoparticles are promising materials for in vitro and in vivo optical imaging and therapy due to their unique optical and chemical properties. In this talk, I will present two new types of biocompatible luminescence nanoparticles.
The first type of materials is upconversion nanoparticles (UCNPs). They absorb low energy near-infrared (NIR) light and emit high-energy shorter wavelength photons. Their special features allow them to overcome various problems associated with conventional imaging probe at both single molecule and ensemble levels. I will present new developments regarding engineering UCNPs towards deep tissue imaging, photodynamic therapy, optogenetic applications in neuroscience and immunotherapy.
The second type of nanoparticles is persistent luminescence nanoparticles (PLNPs). They are bioluminescence-like and possess unprecedented in vivo deep tissue energy rechargeability, outstanding signal-to-noise-ratio with no need for an excitation resource

(light) during imaging, and they can be directly detected with existing imaging systems. These nanoparticles continue to emit light for minutes or hours and, in some cases, days, after turning off the excitation source. These long-lasting, light-emitting nanocrystals can provide noninvasive imaging technology for evaluating structural and functional biological processes in living animals and patients.

COLL 8

Ionic functionalization of hydrophobic colloidal nanoparticles to form ionic nanoparticles with enzyme-like properties

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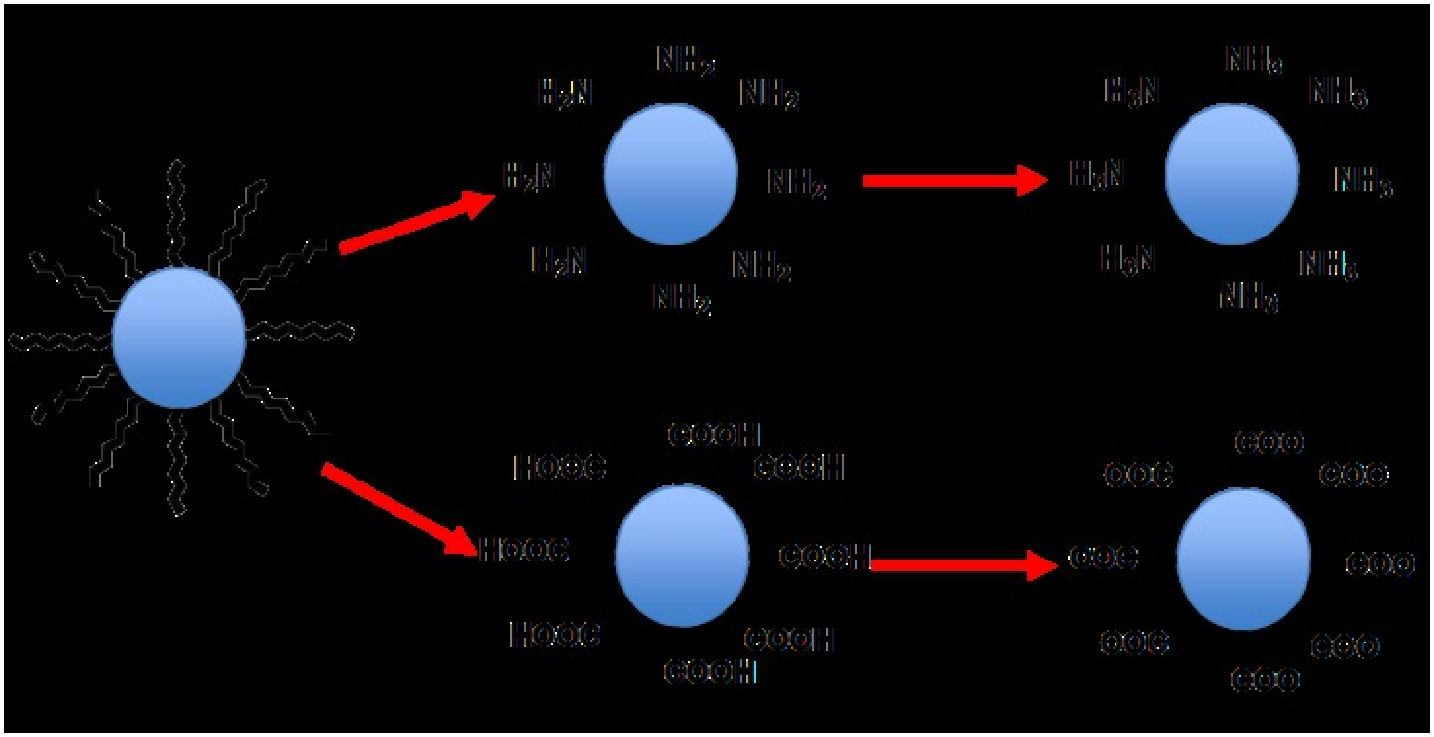
Inorganic colloidal nanoparticles (NPs) stabilized by a layer of hydrophobic surfactant on their surfaces have poor solubility in the aqueous phase, thus limiting their application as biosensors under physiological conditions. Here we report a simple model to ionize various types of hydrophobic colloidal NPs, including FePt, cubic Fe_3O_4, Pd, CdSe, and $NaYF_4$ (Yb 30%, Er 2%, Nd 1%) NPs, to multicharged (positive and negative) NPs via ligand exchange. Surfaces of neutral hydrophobic NPs were converted to multicharged ions, thus making them soluble in water. Furthermore, peroxidase-like activity was observed for ionic FePt, Fe_3O_4, Pd, and CdSe NPs, of which FePt and CdSe catalyzed the oxidation of the colorless substrate 3,3′,5,5′-tetramethylbenzidine (TMB) to the blue-colored product in the absence of H_2O_2, while Pd and Fe_3O_4 catalyzed the oxidization of TMB in the presence of H_2O_2. With the benefit of the ionic functionalization protocols described herein, colloidal NPs should gain wider use as biomarkers, nanozymes, and biosensors.



COLL 9

Understanding the overall surface charge of single-walled carbon nanotubes through point of zero charge measurements

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Since their discovery in 1991, carbon nanotubes (CNT) have been used for many applications such as solar cells, catalyst support, water filtration membranes, and drug delivery. For a lot of these applications, post-synthesis processing of CNT are needed in order to functionalize the surface with oxygen groups, metal particles, or drugs. The charge of the CNT in an aqueous solution will depend on its point of zero charge (PZC). In this work, we study how the PZC of different diameter distribution single-walled carbon nanotubes (SWCNT) is affected by two oxidative treatments: ozonation and nitric acid treatment. The functionalization treatment affects what functional groups are on the surface of the SWCNT and in turn their PZC.Transmission electron microscopy (TEM), near edge x-ray absorption fine structure spectroscopy (NEXAFS), and photoluminescence spectroscopy (PL) are used to study this affects.

COLL 10

Insights into the kinetics and thermodynamics of shape- and composition: Control of bimetallic metal nanocrystals on surfaces

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The vast appeal of metal nanocrystals stems from the fact that their size, shape, and composition determines their overall physicochemical properties, and subsequently, their relevance to a given application. To date, the most effective means for engineering these property-defining features relies primarily on seed-mediated strategies where preformed templates (or seeds) serve as nucleation centers for metal atoms arriving from the solution phase. This approach has been used to derive an immense collection of intricate nanocrystals while at the same time serving as a model platform for cultivating our understanding of how atoms nucleate, diffuse, and then assemble on the surface of seeds. However, the complexity of the colloidal platform has made the elucidation of mechanisms guiding the nucleation and growth processes extremely difficult. Ambiguity emanates from the large number of chemical species present in the colloidal system (*e.g.*, stabilizers, ligands) coupled with the fact that many of these species can be multifunctional in nature. Ligands, for example, can simultaneously re-define the surface energy landscape of the seed surface while at the same time modulate the rate at which atoms are added to the surface. Instead of attempting to disentangle the various roles these species can take, we completely avoid their use by implementing an alternative platform based on ligand-free templates (immobilized to a surface) that act as seeds for the nucleation and growth of metal atoms arriving from the solution- or vapor-phase. Having such a simplified platform not only provides a model system for characterizing nucleation and growth, but also gives rise to a new set of substrate-based nanostructures that exhibit unique and interesting catalytic and photocatalytic properties.

COLL 11

Thermosensitive microgels as "active" nanoreactors for tuning the catalytic activity of metal/metal oxide nanoparticles

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Environmentally responsive microgels have been subjects of great interest in the last two decades due to their versatile applications in fields like drug delivery, chemical separation and catalysis. In our previous study, thermosensitive polystyrene core-shell microgel particles, in which the core consists of polystyrene whereas the shell consists of a poly (N-isopropylacrylamide) (PNIPA) network, have been used as “nanoreactors” for the deposition of metal nanoparticles (such as Ag, Au, Pd, and Pt). We demonstrate that the catalytic activity of the metal nanoparticles can be tuned by the volume transition within the microgel by using the catalytic reduction of 4-nitrophenol as the

model reaction. In addition to this, thermosensitive Au-PNIPA yolk-shell microgel systems in which a single Au-nanoparticles is immobilized in a hollow shell of PNIPA have been developed. The catalytic selectivity of this hybrid system can be tuned by temperature as is shown by the competitive reduction of the hydrophilic 4-nitrophenol and the hydrophobic nitrobenzene by borohydride.
In the present study, we report a facile and novel method for the fabrication of Cu_2O@PNIPA core-shell nanoreactors using Cu_2O nanocubes as the core. The PNIPA shell not only effectively protects the Cu_2O nanocubes from oxidation, but also improves the colloidal stability of the system. The Cu_2O@PNIPA core-shell microgels can work efficiently as photocatalyst for the decomposition of methyl orange under visible light. A significant enhancement in the catalytic activity has been observed for the core-shell microgels compared with the pure Cu_2O nanocubes. Most importantly, the photocatalytic activity of the Cu_2O nanocubes can be further tuned by the thermosensitive PNIPA shell. A theory for the diffusion- and solvation-controlled contribution to the reaction rate of such a "nanoreactor" has been also discussed. Hence, the microgel particles present an "active" carrier system for applications in catalysis.

COLL 12

Dual catalyst with diagnostic power for probing stepwise reduction and oxidation reactions

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Aromatic azo compounds are high-value chemicals extensively used as pigments, drugs, and food additives, but their production typically requires stoichiometric amounts of environmentally unfriendly metals or nitrites. There is an urgent need to develop a dual catalytic system capable of reducing nitroaromatics to aromatic amines, followed by their oxidation to azo compounds. Here we report such a dual catalyst based on Ag@Pd-Ag core-frame nanocubes for the stepwise conversion of 4-nitrothiophenol to *trans*-4,4'-dimercaptoazobezene under ambient conditions. Our *in-situ* surface-enhanced Raman spectroscopy study reveals three sequential processes that include the Pd-catalyzed reduction of 4-nitrothiophenol to 4-aminethiophenol by hydrogen, a period during which the 4-aminothiophenol remain unchanged until all hydrogen has depleted, and the Ag-catalyzed oxidation of 4-aminothiphenol to *trans*-4,4'-dimercaptoazobezene by the O_2 from air. This work will lead to an environment-friendly and sustainable approach to the production of aromatic azo compounds.

COLL 13

Ordered mesoporous carbon/metal oxide for adsorption and decomposition of dimethyl methylphosphonate

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In this study, different kinds of ordered mesoporous carbons (OMC), *i. e.* the hexagonal structured FDU-15, the reversed hexagonal structured CMK-3, and cubic structured CMK-8 have been synthesized as host materials. Using a simple impregnation-decomposition method, several metal oxide nanoparticles, such as copper oxide, zinc oxide, molybdenum oxide, and aluminum oxide, were grown inside the porous systems of the OMCs. These composites have controllable chemical composition, uniform mesostructure, large pore volume and surface area, as confirmed by ICP-AES, TEM, SEM, and N_2 adsorption–desorption. XRD and XPS shows that the crystal phase and valence state of the metal oxides are adjustable by controlling the annealing temperature. The activity of these different OMC/metal oxides were systematically investigated by NMR using the chemical warfare agent simulant dimethyl methylphosphonate (DMMP). The results revealed the importance of the mesostructures, crystal phases, and metal compositions, during gas phase transportation for the activity of the guest nanoparticles.

COLL 14

Size dependent catalytic activity of iron (0) nanoparticles as hydrogenation catalysts

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The synthesis and application of less expensive base metal catalysts as appropriate substitutes for costly, noble metal catalysts is of great importance in catalysis. Iron-based catalysts are highly appealing due to being significantly cheaper, the large abundance of iron in Earth's crust, and their low toxicity. Iron nanoparticles were synthesized by thermal decomposition with weakly coordinating surfactants, allowing for a magnetically recoverable unsupported catalyst which also retains catalytic activity. This method allows us to reproducibly obtain a large volume of highly magnetic Fe (0) nanoparticles with sizes ranging from 6-18 nm.

Precisely controlling the size and loading of these nanoparticles allows us to systematically study the catalytic behavior as a function of particle size. Hydrogenation of olefins was chosen as the catalytic process to study due to utility in organic chemistry and robust techniques available to analyze these systems. Experimental techniques such as nuclear magnetic resonance, high performance liquid chromatography, transmission electron microscopy, and small-angle X-ray scattering allow us to quantify percent conversion, calculate relative activity of nanoparticles as a function of size, and monitor the efficacy or altered properties of the nanoparticles after multiple cycles at various temperatures and partial pressures.

COLL 15

Hybrid catalytic nanoparticles based on zirconium oxocluster

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The catalytic properties of organic-inorganic hybrid nanoparticles based on zirconium oxoclusters are exploited for the oxidation of sulfur-containing substrates. The structurally well-defined methacrylate-functionalized zirconium oxocluster Zr_4O_2(methacrylate)$_{12}$ is copolymerized with stimuli-responsive monomers by free-radical copolymerization in the confined space of miniemulsion droplets. The formation of a strong covalent chemical bond between the organic and the inorganic counterparts has the advantage of providing a homogeneous distribution of the guest species (oxoclusters) in the polymer particles, overcoming problems related to phase separation, aggregation, and migration of oxoclusters in the matrix. Peculiar is the dual role of Zr_4 in the nanoparticles network, acting both as catalytically active species and as cross-linking units, thus endowing a high potential of for heterogeneous catalysis. The oxidation of methyl p-tolylsulfide by hydrogen peroxide to the corresponding sulfoxide and sulfone has been investigated as a model reaction, showing a high selectivity towards the oxidation of the sulfoxide.

COLL 16

Energetics of sorption of water, carbon dioxide, and ethanol on oxide surfaces

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In the natural and technological environment, water, carbon dioxide, and organic molecules compete for sorption on reactive oxide surfaces, and in pores. especially of nanoparticles. Using gas adsorption calorimetry, we have measured the energetics of sorption of H_2O, CO_2, and C_2H_5OH on silica, alumina, and calcite nanoparticle surfaces. The adsorption energetics of water and carbon dioxide follow a relatively simple pattern with comparable energetics but that of ethanol shows more complex behavior, reflecting the difference in hydrophobicity between the hydroxyl and ethyllll ends of this model small organic molecule. The strong interaction of the OH-end of the ethanol molecule with the hydrophilic mineral surface leaves the hydrophobic ends of the molecules unable to bond fully with the next layers of ethanol. We view this as a step in a gradual transition from simple adsorption to the formation of protective capping layers on nanoparticles.

COLL 17

Thermal analysis and calorimetry applied to the studies of nanomaterials

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The particle size decrease affects the reactivity and stability, the functions, and subsequently the applications of the nanomaterials. Being their main advantage, the high surface area and the complex interfaces require a special methodology to characterize them and investigate their properties.

Decreased particle size affects reactivity, stability, functionality and, subsequently, the applications of nanomaterials. Particle size decrease, hence increase in specific surface area, also results in the formation of complex interfacial regions, all of which provide nanophases with advantages over bulk phases. These high surface areas and complex interfaces require special methodologies to investigate their properties as well as reactions occurring at the nanophase surfaces.

Thermal analysis and calorimetry have been used to characterize the stability of nanoparticle phases, their phase purity, oxidation states of constituent metals, the type and amount of functional groups, as well as adsorbed surface gases and aqueous ions. Of these, the complex coupled manometric-calorimetric technique is crucial for understanding and guiding nanocatalyst applications, as it is the only direct method to measure the heats of gas adsorption on solid nanoparticles. Additionally, a coupled technique that combines evolved gas analysis and thermogravimetry (TGA, TG-DSC), provides information about the amounts and types of adsorbed surface gases generated during the desorption or decomposition process. Experimental thermodynamics combining these two complex, coupled microcalorimetry techniques (gas adsorption and TG-DSC) along with high temperature oxide melt solution calorimetry allows examination of difficult questions regarding nanophase materials involved in environmental and industrial settings. The high temperature oxide melt solution calorimetry

The thermomechanical analysis is the main technique used to investigate the sintering and the densification kinetics of nanomaterials and nanocomposites.

Thus, in addition to study of the energetics of nanophase surfaces and sorption, overcoming interfacial energetics for the formation of nanocomposites has implications for industrial applications as well as for high temperature natural environments. Each of the techniques will be explained and examples will be given to illustrate their applications using different materials (oxides, alloys, 2D carbon nanocomposites).

COLL 18

Thermodynamics of nanophase manganese oxides: Sodium, potassium, and calcium birnessite and cryptomelane

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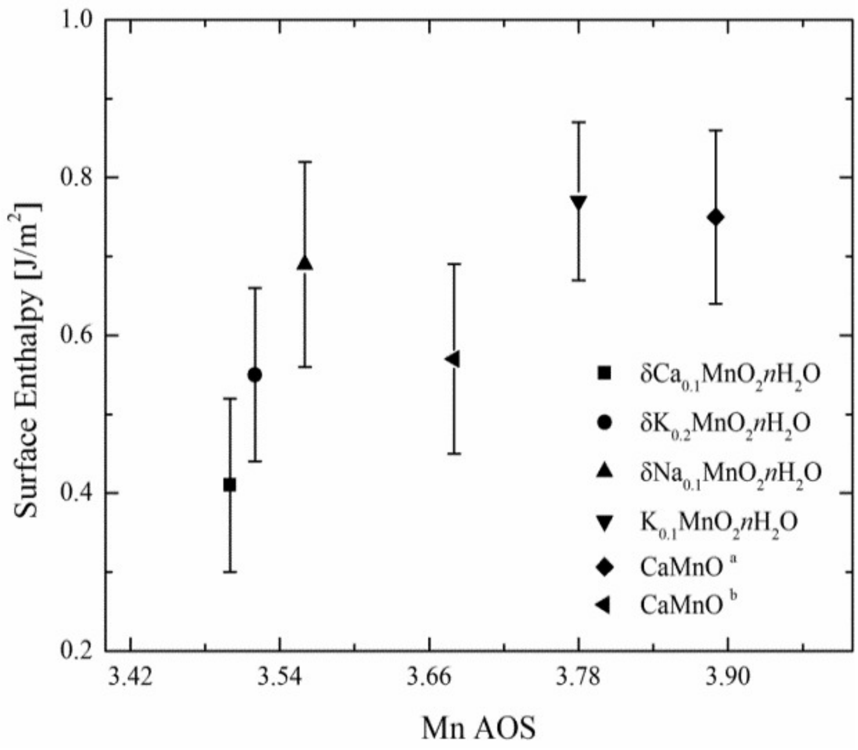
Layered (birnessite) and tunneled (cryptomelane) manganese oxides contain Ca, Na, and/or K, in addition to water. They are typically nanophase, and charge balance is achieved by interlayer or tunnel cations and by vacancies. Earlier studies determined the energetics of formation these phases but did not consider the effects of particle size and surface energy. Thus we returned to these materials with the hypothesis that they, like the nanosheet calcium manganese oxide catalysts, have low surface energies which help stabilize them as fine-grained materials. For the birnessites, cryptomelane, and calcium manganese oxide (*CaMnO*) nanosheets an increase in the counter cation content has a thermodynamically stabilizing influence on the enthalpy of formation, in accord with our earlier work. The surface energies for hydrous surfaces and overall manganese average oxidation state (AOS) (value in parentheses) for complex manganese oxides are: cryptomelane 0.77 ± 0.10 J/m^2 (3.78), sodium birnessite 0.69 ± 0.13 J/m^2 (3.56), potassium birnessite 0.55 ± 0.11 J/m^2 (3.52), and calcium birnessite 0.41 ± 0.11 J/m^2 (3.50). Surface enthalpies of hydrous surfaces of the calcium manganese oxide nanosheets as $Ca_{0.39}MnO_{2.3}nH_2O$ 0.75 ± 0.10 J/m^2 (3.89) and $Ca_{0.43}MnO_{2.3}nH_2O$ 0.57 ± 0.12 J/m^2 (3.68). Surface energy of the complex manganese oxides appears to decrease with decreasing manganese average oxidation state, that is, with greater mixed manganese valence (Fig. 1). The surface energies of the layer and tunnel structured complex manganese oxides are confirmed to be significantly lower than those of binary manganese oxide phases, which were previously measured as: hausmannite 0.96 ± 0.08 J/m^2 (Mn_3O_4), bixbyite 1.29 ± 0.10 J/m^2 (Mn_2O_3), and pyrolusite 1.64 ± 0.10 J/m^2 (MnO_2).



Variation of surface energy with manganese average oxidation state (AOS). Birkner and Navrotsky, in preparation.

COLL 19

What one can do with flow microcalorimetry: Applications to studies of the surface reactivity of oxides

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Flow adsorption microcalorimetry (FAMC) provides a direct, quantitative measure of the heat evolved during a reaction. Besides providing information of thermodynamic significance, i.e., heats of reactions and enthalpy changes (DH in kJ.mol^{-1}), FAMC can also provide information about changes that occur in the properties of a surface or a mineral-water interface, e.g. chemical bonding, heterogeneity of surface functional groups as well as charging behavior, with varying experimental conditions. FAMC is thus a technique ideally suited for measuring interactions occurring at the liquid/solid interface; it is an excellent and unique probe of surfaces. The purpose of this talk is present methodologies that we developed to directly probe the interfacial reactivity of oxides. Illustrative examples will be provided to showcase the usefulness of calorimetrically collected data on surface charge in general sorption studies as well as in theoretical modeling frameworks correlating oxide structure, charge distribution and reactivity.

COLL 20

Ab initio thermodynamnics of metal oxide surfaces

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Oxidation of metal oxides and minerals is a surface-mediated process that is important for performance of sensors, catalysts, and electronic components as well as mitigating corrosion and promoting surface activation or passivation. The performance of the surface and its redox characteristics is highly dependent upon the environmental conditions. *Ab initio* thermodynamics -in which density-functional theory calculations are linked to macroscopic chemical potentials of redox species, water, or other components in the environment – enables the prediction of how surface structure and reactivity change as conditions change. Applications discussed in this presentation will focus on 1) determining optimum pulsed-laser deposition conditions for growth of mixed Ti-Mn oxides on rutile, and 2) how the surface orientation and electron transfer process between uranium and oxygen determines the nanoscopic subsurface arrays of interstitial oxygen atoms in subsurface oxidation of UO_2.

COLL 21

Surface structure and reactivity of ferrihydrite scaling from nucleus to nanoparticle: Oxyanion adsorption and surface energetics

Tjisse Hiemstra*, tjisse.hiemstra@wur.nl.* Wageningen University, Wageningen, Netherlands

Ferrihydrite (Fh) is one of the most important Fe (hydr) oxides in nature. Fh particles can be extremely small leading to a high reactive surface area that changes its chemical potential, strongly affecting solubility, nucleation, and chemical stability. According to thermochemistry, Fh has an exceptionally low interfacial Enthalpy and Gibbs free energy in comparison to all other iron (hydr) oxides making Fh to the most stable iron (hydr)oxide at the nanoscale despite the relatively high instability of the mineral lattice. In general, the surface Gibbs free energy of iron (hydr) oxides increases with the mean coordination number of oxygen in the lattice. However, Fh is an exception due to surface stabilization of the unstable core by additional Fe, changing the polyhedral composition as proposed by the surface depletion (SD) model for Fh.

Surfaces can be stabilized by the adsorption of oxyanions. In the present study, the adsorption of phosphate by freshly prepared Fh has been measured for a large range of conditions. The charge distribution (CD) approach has been applied to describe the data. For modeling, the surface structure of Fh has been analyzed and further quantified

as a function of particle size. For downscaling of the CD model to an ultra-small cluster size, spherical double layer theory has been implemented.

Interpretation of the phosphate adsorption behavior of Fe hydroxide, produced by ultra-fast neutralization of a Fe(III) solution, shows formation of very small Fh clusters with on average 62 ± 5 Fe that have a solubility product of logQso = -37.5. The corresponding critical size of nucleation matches very well with the smallest imaginable Fh cluster with a Keggin structure that has only 13 Fe. In the presence of phosphate, critical nuclei can be stabilized by adsorbed phosphate ions that decrease of the surface Gibbs free energy. Depending on the solution conditions, it may affect the pathway of nanoparticle formation. The Fe(III) ion by itself may also contribute to the stability of ferrihydrite nuclei by decreasing the surface Gibbs free energy via adsorption to the mineral core in agreement with the SD model.

COLL 22

Glucose sensing with SERS

***Richard P. Van Duyne**, vanduyne@northwestern.edu.* Chemistry, Northwestern University, Evanston, Illinois, United States

Surface-enhanced Raman spectroscopy (SERS) is a highly sensitive and selective technique which allows for the detection and characterization of low concentration analytes in complex biological environments, both *in vivo* and i*n vitro*. Due to the rising incidence of diabetes, one of the primary in vivo small molecule targets is glucose. It is projected that the number of people with diabetes in the U.S. will double or even triple by 2050. Although various *ex vivo* and implantable blood glucose monitoring instruments exist, most are severely inaccurate in measuring hypoglycemic blood glucose levels (<80 mg/dL).
In this lecture we discuss our recent progress towards direct sensing of glucose in physiologically relevant concentrations by SERS on gold film-over-nanosphere (AuFON) substrates. For these studies, customized bisboronic acid analogs were synthesized and used as capture ligands for glucose. Importantly, AuFONs functionalized with bisboronic acid analogs showed selectivity for glucose over fructose. In order to analyze our data, we utilized computational modeling to assign the normal modes and vibrational frequencies for the monoboronic acid base of our bisboronic acids, glucose and fructose; as well as multivariate statistical models. Multivariate statistical analysis of SERS measurements indicates that our sensors can detect glucose accurately in the 1-10 mM range and distinct hypoglycemic, normal, and hyperglycemic ranges. Based on our results, AuFONs functionalized with bisboronic acid are promising platforms for the further development of an *in vivo* SERS-based glucose sensor.

COLL 23

Surface enhanced hyper Raman scattering for bio-applications

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Multi-photon excitation of optical processes has many advantages over one-photon excitation. Spontaneous, two-photon excited Raman scattering in the local fields of plasmonic nanostructures, termed surface-enhanced hyper Raman scattering (SEHRS), is a particularly interesting approach for vibrational probing of bioorganic molecules due to the high electromagnetic field enhancement that takes place because of the non-linear process, and because of the complementary vibrational information that is obtained. We discuss resonant and non-resonant SEHRS spectra of important organic molecules, measured with different types of plasmonic nanoparticles. Furthermore, mapping and imaging using SEHRS will be demonstrated. Our results show that the SEHRS signals strongly depend on the type of plasmonic substrate. This also has consequences for applications in live cells, where the SERS/SEHRS substrate is usually being processed and its plasmonic properties are altered.

A combination of SERS and SEHRS is very useful for the construction of SERS/SEHRS nanosensors that can be used in complex biological environments. We compare one- and two-photon excited non-resonant Raman spectra of reporter molecules and typical biomolecules in the local fields of different plasmonic nanostructures under changes in chemical environments, for example at different pH. Applying pH sensitive molecules, we observe that the combination of SERS and SEHRS spectra excited at 1064 nm allows more robust pH sensing than SERS measurements in the visible excitation range. Investigating the plasmonic properties under different experimental conditions, we find that the multimodal SERS/SEHRS based sensing is possible in the low femtoliter range with extremely high enhancement factors, and without multiple tagging.

COLL 24

Adsorption behavior of mixed thiols on SERS active single crystal gold nanoplatelets

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The functionalization of SERS active plasmonic nanocrystals are of critical importance to the biomedical application of Raman enabled molecular detection and labeled imaging. Because of the noble metal composition of plasmonic nanocrystals, thiol surface chemistry has been the dominate functionalization strategy. It has long been assumed that thiol molecules efficiently and completely replaces residual (post-synthetic) surfactant covering Au or Ag colloidal nanocrystals during ligand exchange process to produce surface assembled monolayers (SAMs). However, we observed complex displacement behavior of polymer surfactant on single crystalline Au nanoplatelets, even after long exposure in agitated solutions. Experimental results on nanoscale surface morphology, chemical composition and SERS characteristics will be

presented. Proposed mechanism of thiol-surfactant interactions and the potential utilization of this discovery on SERS hotspot engineering will be discussed.

COLL 25

Surface-enhanced Raman spectroscopy for biodetection: From mechanism to application

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Surface-enhanced Raman spectroscopy (SERS) is particularly powerful for biological study because it can obtain the fingerprint information of the system under the aqueous and ambient conditions, but with a much higher sensitivity. To obtain SERS signal of biomolecules with good reproducibility and high sensitivity is extremely important for a wide application of SERS in biological systems and is also a great challenge for SERS. We first addressed this issue by investigating the plasmon shaping effect and SERS background issue. We demonstrated with well controlled single nanorods experiments that the inevitable background of SERS is indeed not from the fluorescence of dye molecule or the surface impurities but from the photoluminescence of the metallic nanostructure. We proposed a way to correct the relative Raman intensity of molecular species with the SERS background and bulk photoluminescence, which is able to remove the influence of plasmon shaping effect and allows us to recover the original Raman spectra. In this way, the corrected Raman spectra can faithfully reflect the chemical interaction of the molecules with the substrate.

We further address the issue of quantitative analysis of SERS which is severely bothered by the heterogeneous enhancement in nanoaggregates that give the strongest signal. We developed core-molecule-shell nanoparticles (CMS NPs) with two components in the molecular layer, a framework molecule to form the shell and a probe molecule as Raman internal standard, for the quantitative SERS analysis. The signal of the embedded Raman probe provides an effective feedback to correct the fluctuation of samples and measuring conditions. Meanwhile, the shell can be completely adsorbed by target molecules with different affinities. This method allows the quantitative analysis of target molecules over a large concentration range.

We then address the issue of reliability of SERS detection by controlling the interaction of probe molecules with the metal nanoparticles. We modify the SERS-active nanoparticles or solid SERS substrates with some halide ions to remove the surface impurities. Thereby, we can enhance the interaction of biomolecules with the SERS substrate. The method was successfully used for label-free detection of proteins and DNAs.

COLL 26

Designer nanoparticle rattles for SERS detection

***Amanda J. Haes**, jha444@gmail.com.* Chemistry, University of Iowa, Iowa City, Iowa, United States

Directly detecting low concentrations of small molecules in biological and environmental samples is often limited by similar molecular structures and function of the target species as well as complex sample matrices. In addition, understanding molecular orientation is important in the detection of small molecules using SERS as adsorption processes can influence the measured signals. In this presentation, internally etched silica stabilized, gold coated silver nanoparticles are synthesized for their use as SERS substrates to ensure electromagnetic stability of the metal cores and surface accessibility for molecular adsorption and systematic SERS studies. The implications of molecular identity and concentration on molecular adsorption and SERS intensity are evaluated using localized surface plasmon resonance (LSPR) spectroscopy, SERS, and Langmuir adsorption isotherm modeling. Synergistic results suggest molecule-dependent tilt angles on the nanoparticle surfaces play a big role in small molecule quantification. These findings are confirmed through Langmuir adsorption isotherm modeling in which equilibrium constants and free energies of adsorption suggest that London dispersion force stabilization between the ligands and the metal surface induce these differences and the overall detectable SERS signals.

COLL 27

Ultrastrong, transparent and conductive freestanding reduced graphene oxide nanomembranes with SERS functionality

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Ultrastrong freestanding reduced graphene oxide (rGO) nanomembranes with as low as 3 nm thickness were fabricated via a novel solvent-assisted layer by layer (LbL) technique. Unlike the typical LbL technique requires two different components to provide the strong interactions to ensure the uniform growth of the nanocomposites film, the facile approach proposed here relies on solvent promoted hydrophobic-hydrophobic interactions to assemble single component GO sheets without any additional binders. These uniform and ultra-smooth nanomembranes with high transparency (up to 93% at 550 nm) and electrical conductivity (up to 3000 S/m) also exhibit outstanding mechanical strength of 500 MPa and Young’s modulus of 120 GPa, which are several times higher than those of traditional GO or rGO ultrathin films. Furthermore, as high as 94 wt% micro-level size silver nanoplates can be sandwiched into as-prepared 10 nm nanomembranes to construct a unique freestanding rGO surface enhanced Raman scattering (SERS) substrate, which isolates the direct contact of metal-molecular to get cleaner enhanced Raman signals (more flat baseline and better signal-to-noise ratio). This approach gives a unique strategy for the further design and fabrication of the desire SERS substrate.

COLL 28

Beyond biomarkers: Array-based profiling for diagnostics and high-throughput screening

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The "chemical nose/tongue" approach presents a potential alternative to specific biomarker approaches. In this strategy a sensor array is generated to provide differential interaction with analytes via *selective* receptors, generating a stimulus response pattern that can be statistically analyzed and used for the identification of individual target analytes and also for profiling of complex mixtures. In our research, we have applied this methodoloy to sensing of proteins and cell surfaces, focusing on areas of biomedical importance. In this talk we will discuss applications of array-based sensing for diagnostics (Figure 1), as well as the use of high-content cell-based sensing for both drug discovery and environmental monitoring.

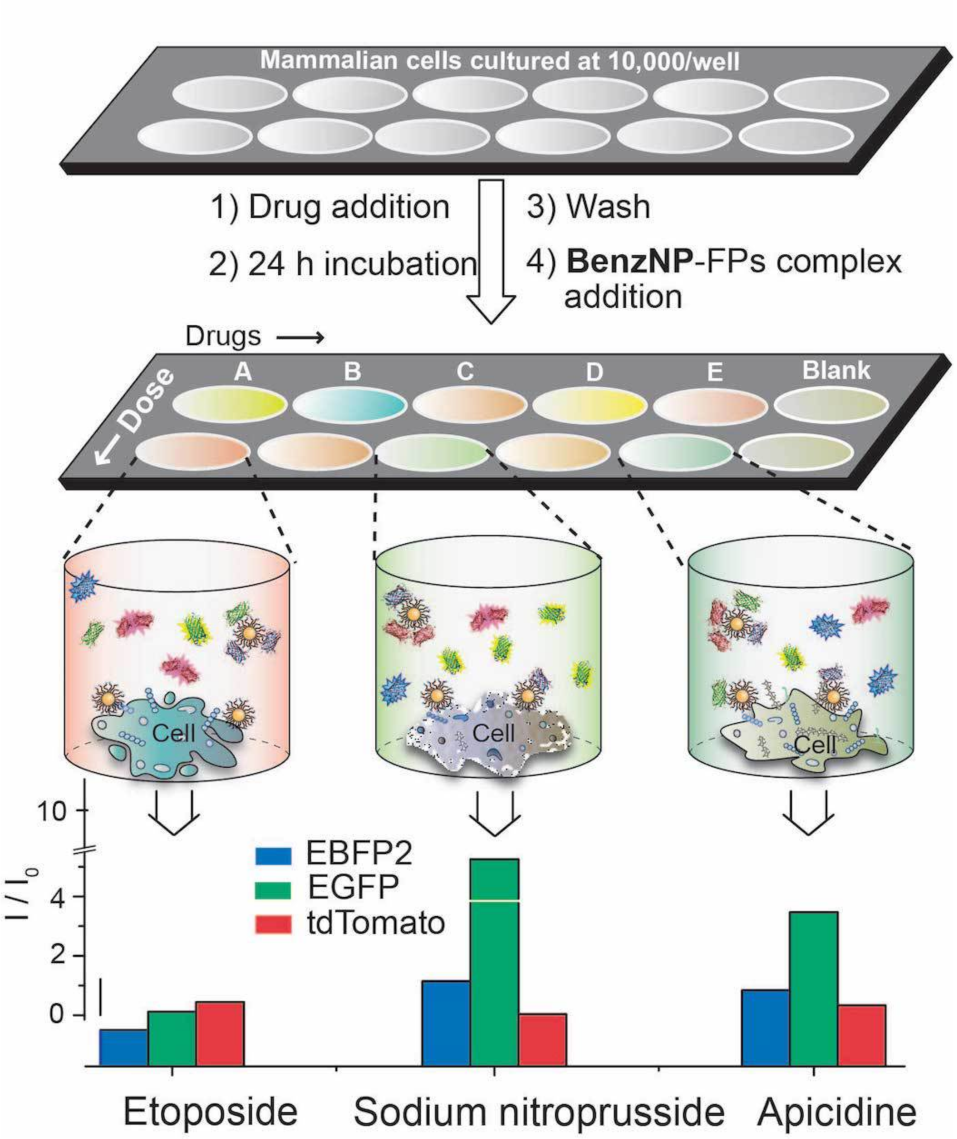

Figure 1. Multichannel nanosensor for high content/high throughput screening applications.

COLL 29

Scaling principles for understanding and exploiting adhesion

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A grand challenge in the science of adhesion is the development of a general design paradigm for adhesive materials that can sustain large forces across an interface yet be detached with minimal force upon command. Essential to this challenge is the generality of achieving this performance under a wide set of external conditions and across an extensive range of forces. Nature has provided some guidance through various

examples, e.g. geckos, for how to meet this challenge; however, a single solution is not evident upon initial investigation. To help provide insight into nature's ability to scale reversible adhesion and adapt to different external constraints, we have developed a general scaling theory that describes the force capacity of an adhesive interface in the context of biological locomotion. We have demonstrated that this scaling theory can be used to understand the relative performance of a wide range of organisms, including numerous gecko species and insects, as well as an extensive library of synthetic adhesive materials. We will present the development and testing of this scaling theory, and how this understanding has helped guide the development of new composite materials for high capacity adhesives. We will also demonstrate how this scaling theory has led to the development of new strategies for transfer printing and adhesive applications in manufacturing processes. Overall, the developed scaling principles provide a framework for guiding the design of adhesives.

COLL 30

Design of brush-like polymer surfaces through spontaneous segregation of bottlebrush polymer additives

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Bottlebrush polymers are based on a linear backbone with densely-grafted side chains. Bottlebrush polymer coatings can offer many of the unique surface functions that are associated with end-grafted polymer brushes, such as controlled adhesive interactions and switchable wettability. However, the synthesis of bottlebrush polymers is more complex than linear polymers, so we are interested in their potential as *surface-active additives* for commodity thermoplastics. In our first studies, we examined the thin film phase behavior of linear polystyrene with 10% bottlebrush polystyrene additive. We demonstrated that short linear chains will disperse the bottlebrush additive throughout the film, while long linear chains will drive bottlebrush segregation at surfaces and interfaces. This entropy-controlled behavior is very similar to the thermodynamics in athermal blends of linear polymers and polymer-grafted nanoparticles. Building on these results, we designed bottlebrush copolymer additives that can tailor the surface properties of a film. The bottlebrush copolymers were synthesized with a random sequence of two side-chain chemistries: one type serves as a compatibilizer with the linear matrix, and the other type delivers a desired surface function. This approach was demonstrated with linear polylactic acid (PLA) containing 1-5% bottlebrush PLA-co-polydimethylsiloxane (PDMS) additive. The bottlebrush copolymer rapidly segregates to the top of the coating, and the PDMS side-chains generate a low-energy surface that is useful for fouling release.

COLL 31

Importance of surface chemistry to enhance wet adhesion during peeling of soft materials

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Using a custom-built apparatus we investigate the interplay between surface structure, elasticity, and dwell time on the peeling force between two surfaces in a viscous fluid. We create films with equivalent bending rigidity but different elasticity to highlight and characterize the relationship between the shape of the peeling front and the work of separation. We also highlight the contribution of surface deformation and compare our results to a model based on hydrodynamics and bending beam. Finally we determine the surface, mechanical, and fluid properties that are necessary for surface structures to enhance adhesion. In particular we highlight the importance of van der Waals forces and viscoelasticity. We show that in absence of these two effects the presence of surface structure does not lead to enhancement in adhesion (and in many cases reduces the adhesion), even with highly compliant surfaces.

COLL 32

Energy dissipation and adhesive failure of acrylic emulsion-based pressure sensitive adhesives

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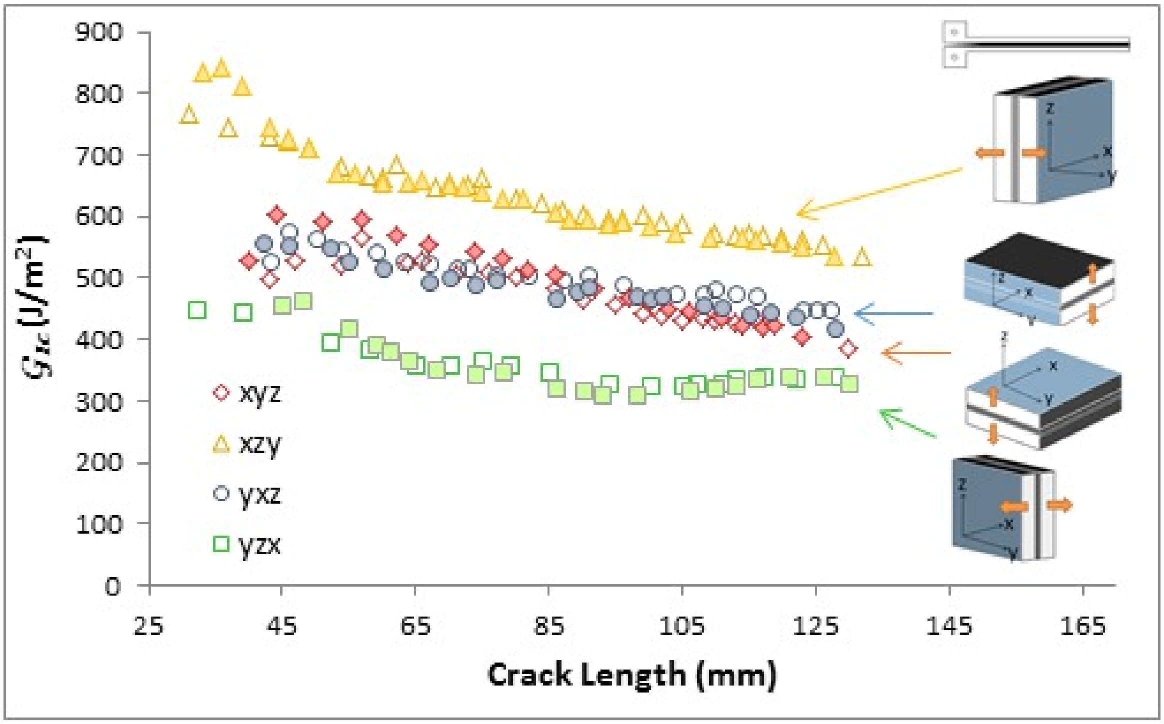
The performance of pressure sensitive adhesives (PSAs) depends strongly on both the linear and non-linear viscoelastic properties of the adhesive material. In this work we use an oscillatory test that is able to quantify the mechanical response of adhesive materials in the linear regime, and also in the highly strained regime where the adhesive layer has cavitated to form mechanically isolated fibrils. The experiments involved the use of hemispherical glass or polyethylene indenters, brought into contact with a thin adhesive layer and then retracted. A set of model acrylic emulsion-based PSAs were used in the experiments. The adhesives have a surprising degree of elastic character at high strains, with subsequent loading/unloading cycles giving overlapping results and suggesting that an adhesive failure criterion based on the stored elastic energy is appropriate for these systems. The primary effect of the substrate is to slightly modify the maximum strain at which adhesive detachment from the indenter occurs.

COLL 33

Investigating effect of print orientation on integrity of multi-material interfaces in polyjet additive manufactured materials

***David A. Dillard**, dillard@vt.edu, Ivan Q. Vu, Anthony DiBerardino, Logan Sturm, Nickolas A. Meisel, E. Bruce Orler, Christopher B. Williams.* Virginia Tech, Blacksburg, Virginia, United States

Deposition in additive manufacturing processes creates numerous interfaces, between the adjacent roads and sequentially applied layers, that can affect the resulting properties of the fabricated component. Depending on the specific manufacturing system, the structural integrity of these interfaces between the discretely deposited materials can be affected by the degree of wetting, molecular interpenetration, porosity, and/or curing histories. Recent progress in additive manufacturing capabilities for polymer jetting systems allows multiple materials, and even blends of materials, to be deposited in a single manufacturing process, offering new opportunities for design flexibility. This study investigates the fracture behavior of multi-material interfaces fabricated using an Objet printer to produce UV-cured configurations consisting of a soft acrylic layers (TangoBlack) sandwiched by two stiffer acrylic strips (Verowhite). Several test configurations based on double cantilever beam DCB and T-peel specimens were fabricated and evaluated to characterize the fracture resistance of the assembled layers. Failures nominally occurred at the interface between the two types of materials, though dramatically different fracture resistances were observed, depending on the print build orientation used to fabricate the specimens. An illustration of the dependence on print orientation is shown, revealing that the multi-material interface between simultaneously deposited and cured layers (xzy orientation) exhibits a higher fracture resistance than for sequentially applied layers (xyz and yxz orientations). These studies also suggest opportunities for designing printed interfaces with alternate architectures to achieve improved performance for multi-material additive manufacturing products.



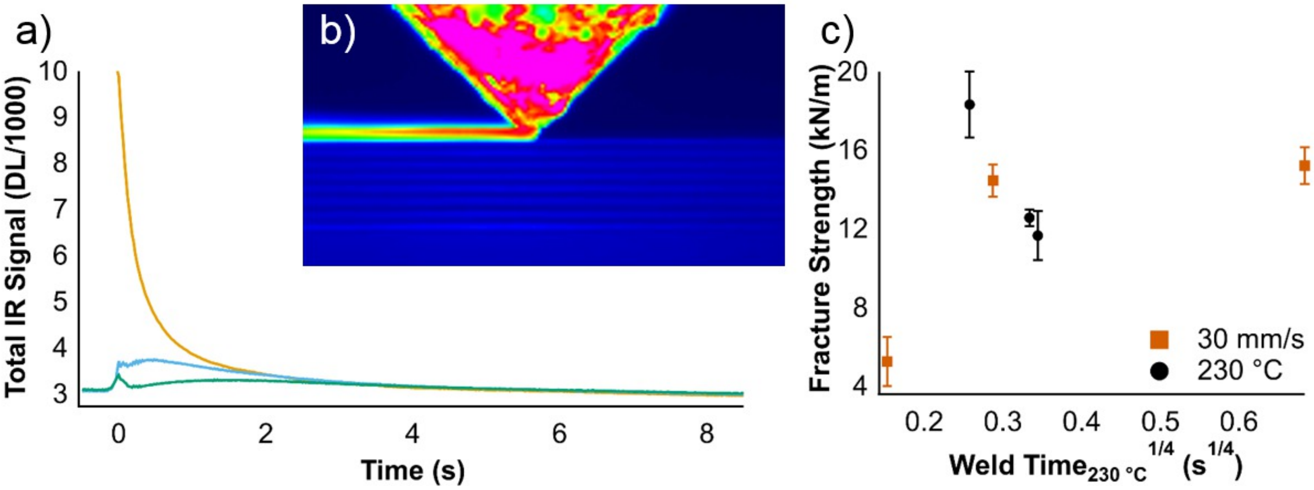
COLL 34

Fundamental characterization of polymer extrusion additive manufacturing processes

Jonathan E. Seppala[3], *jonathan.seppala@nist.gov, Seung Hoon Han*[1,3], *Kaitlyn E. Hillgartner*[2,3], *Chelsea S. Davis*[3], *Kalman B. Migler*[3]. (1) Mathematics, Montgomery College, Rockville, Maryland, United States (2) Chemical and Biological Engineering, Colorado School of Mines, Golden, Colorado, United States (3) Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland, United States

Additive manufacturing (AM) is an important and disruptive production method. In traditional manufacturing techniques customized tooling for a given part requires a large initial investment which is offset by large volume production. In AM no tooling investment is needed and per unit productions costs are flat, which is a huge boon for individualized production. This is especially important in the medical industry where many devices are custom designed for the individual. Although interest in AM seems recent, development has been ongoing for a few decades. AM is now at a point where research and development can focus on understanding and improving the process at a fundamental level.

In polymer extrusion 3D printing, a material extrusion AM method, thermoplastic filament is extruded though a rastering nozzle on the previous layer. The resulting strength of the 3D produced part is limited by the strength of the weld between each layer. While numerous factors can affect the weld strength, the temperature of the extrudate and the previous layer dictate the amount of interdiffusion and thus the weld strength. Temperature measurements were performed using forward looking infrared imaging. Interdiffusion estimates were calculated from temperature profiles, normalized using horizontal shift factors from offline rheological measurements of the neat polymer. Weld strength was measured directly by Mode III Fracture using a simplified geometry limiting the measurement to a single weld. Since the processing conditions are known *aprioi* this approach provides the data needed to estimate the final build strength at time of design. The resulting agreement between interdiffusion estimates and weld strength for a range of printing conditions and thermoplastics are discussed.



a) Total infrared (IR) signal from printed layer (orange), first sublayer (blue), and second sublayer (green). b) False color IR image of polymer extrusion process. c) Fracture strength for various weld times based on polymer extrusion process conditions.

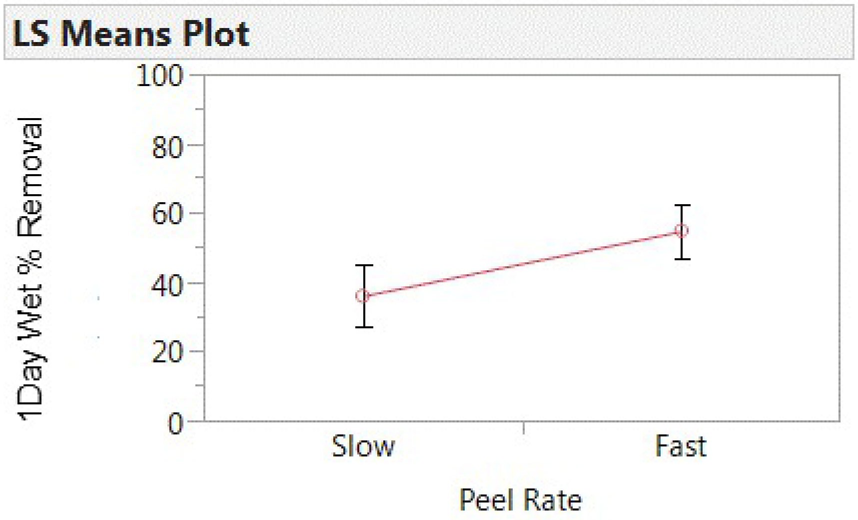
COLL 35

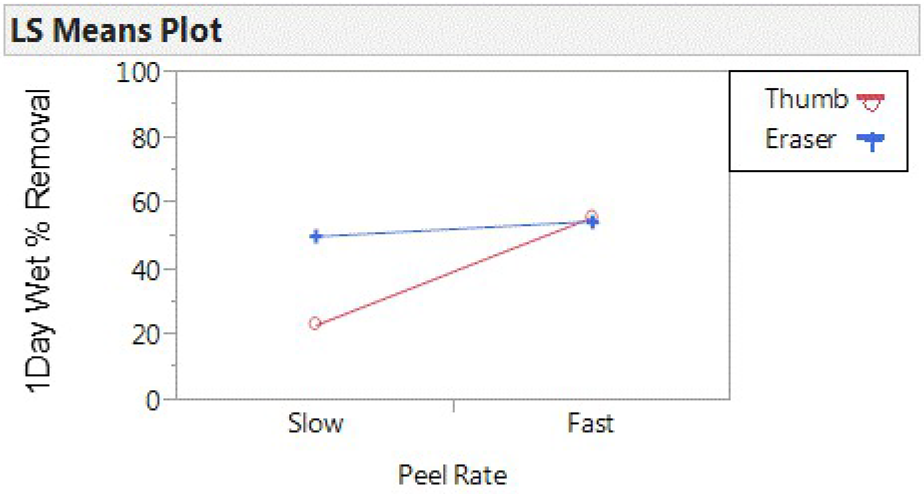
Understanding the adhesion of latex paints over alkyd surfaces

Partha S. Majumdar[1], *psmajumdar@dow.com, Jeff Sweeney*[2], *Christopher Kozak*[1], *Scott Carpenter*[1], *Sonya Eberly*[1], *William Howell*[1], *Louis C Fioravanti*[1]. (1) Dow Coating Materials, Dow Chemical, Collegeville, Pennsylvania, United States (2) R&D Statistics, Dow Chemical, Midland, Michigan, United States

Alkyd chemistry still dominates a considerable portion of the global architectural paint market. As the paint industry is shifting towards latex paints, one of the key properties of interest is their ability to adhere to previously painted alkyd substrates. In order to differentiate latex paints based on their adhesion over alkyd surfaces, a thorough understanding of the variability associated with the test method is required to improve data reproducibility.
This study utilized six sigma methodologies and design of experiments (DOE) based

approach to investigate the variability in alkyd adhesion following ASTM D3359. A set of ten variables were identified as potential root causes and were separated into two DOE plans for validation. DOE plan 1 focused on the variables associated with the procedure such as peel angle and peel rate, while DOE plan 2 explored the variables associated with the conditions such as alkyd substrate curing time and temperature. The data collected from the complex designed experiment (DOE) plans allowed estimation of Taylor-Series Expansion models involving main effect and two factor interaction terms. Within the analysis of the data, predictive models were developed to estimate the trends in the adhesion responses associated with the variables. Finally, optimized levels of each of the significant factors were identified which minimized test method variability and improved differentiation among latex paints.





COLL 36

Colloidal In_2Se_3 nanosheets and their enhanced photoresponse

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Two-dimensional semiconductors have recently emerged as an alternative to complement the zero band gap shortcomings of graphene for technological applications like photodetectors, sensors and photovoltaic devices. In this presentation, we will describe the colloidal synthesis of phase-pure nanosheets of In_2Se_3 (which exhibits large lateral dimensions, of the order of 1 - 2 microns) and their resulting optoelectronic properties. The synthesis of these nanosheets undergoes a two-stage hot injection process wherein the oriented attachment of pre-formed In-Se nanocrystals (during the first injection) is triggered by the addition of cyanamide during the second injection step. The synthesis is scalable and a reasonable level of control on the morphology can be exercised through the ligand chain length-solvent interplay. We will also demonstrate the enhanced photoresponsivity of these nanosheets under white light illumination, through optoelectronic transport measurements performed on devices fabricated by electron-beam lithography.

COLL 37

First electronic transition of interfacial water on alpha-alumina studied by far-ultraviolet spectroscopy

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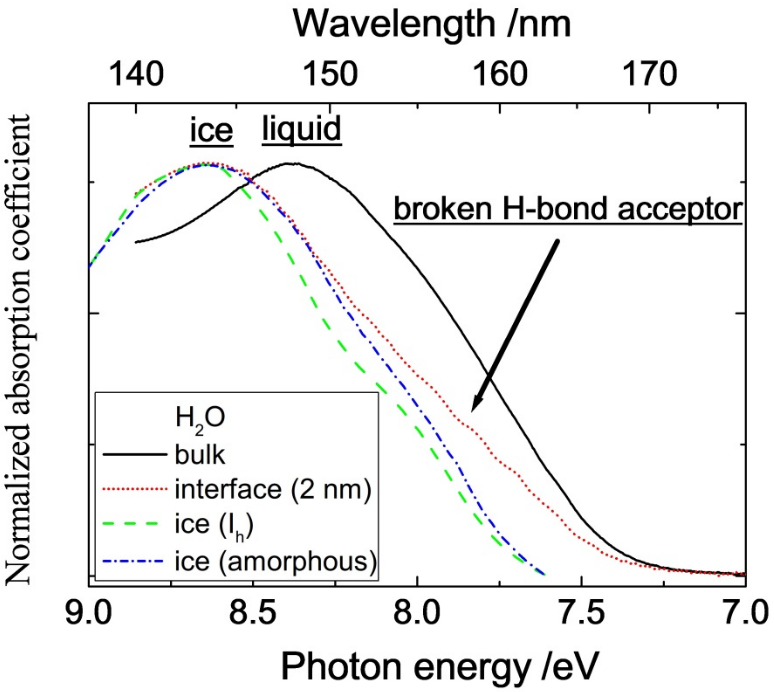
First electronic transition (A←X) of interfacial water on an α-alumina substrate was studied using attenuated total reflection far-ultraviolet (ATR-FUV) spectroscopy (wavelength: 140–180 nm or 8.86–6.89 eV). The interfacial water was examined for a liquid water-alumina interface and an ultra-thin water layer (>10 nm) on the alumina surface. For the liquid water-alumina interface, a variation in the penetration depth of the evanescent wave of the probe light (25–19 nm) provided individual FUV spectra associated with bulk water (distance from the alumina surface > 2 nm) and interfacial water (<2 nm). The A←X band of the interfacial water was markedly blue-shifted and red-tailed relative to bulk water, indicating that the hydrogen bond (H-bond) network of the interfacial water involves an ice-like structure with broken H-bond acceptors. This reveals that the first layer might be hydrophobic to the subsequent layers, because the strong H-bond structure in the first layer makes fewer dangling OH bonds to the second layer. For the thin water layer on the alumina surface, the A←X band was red-shifted relative to bulk water, indicating that the H-bond network of the adsorbed water is very disordered. These electronic state differences of the interfacial water from bulk water mainly arise from the H-bond structure and hydration energy affected by the alumina surface.



COLL 38

Synthesis and efficient Z-scheme electron transfer of ZnO/CdSSe tree-like nanostructure

Zhengxin Li[2], *lizx@udel.edu, Jesus Nieto-Pescador*[1], *Alexander Carson*[1], *Jolie Blake*[2], *Lars Gundlach*[2,1]. (1) Physics and Astronomy , University of Delaware, Newark, Delaware, United States (2) Chemistry and Biochemistry, University of Delaware, Newark, Delaware, United States

We present a vertically-aligned ZnO/CdSSe tree-like nanostructure and discuss its unique electronic properties. The tree-like nanostructure was prepared by growing CdSSe branches onto vertically-aligned ZnO nanowires. Branches and arrays of ZnO nanowires were grown via chemical vapor deposition. The CdSSe branches sensitize the nanostructures to visible light absorption. ZnO/CdSSe nanotrees show a type II heterojunction at the interface between CdSSe branch and ZnO. Time-resolved fluorescence measurements show efficient electron transfer from CdSSe branches to ZnO stems as well as the possibility for Z-scheme charge transfer in the structure. The unique combination of hierarchical structure as well as optical and electronic properties makes the ZnO/CdSSe nanotree structure a promising candidate for applications that benefit from a Z-scheme charge transfer mechanism, for example in solar energy conversion, opto-electronics, and photo catalysis.

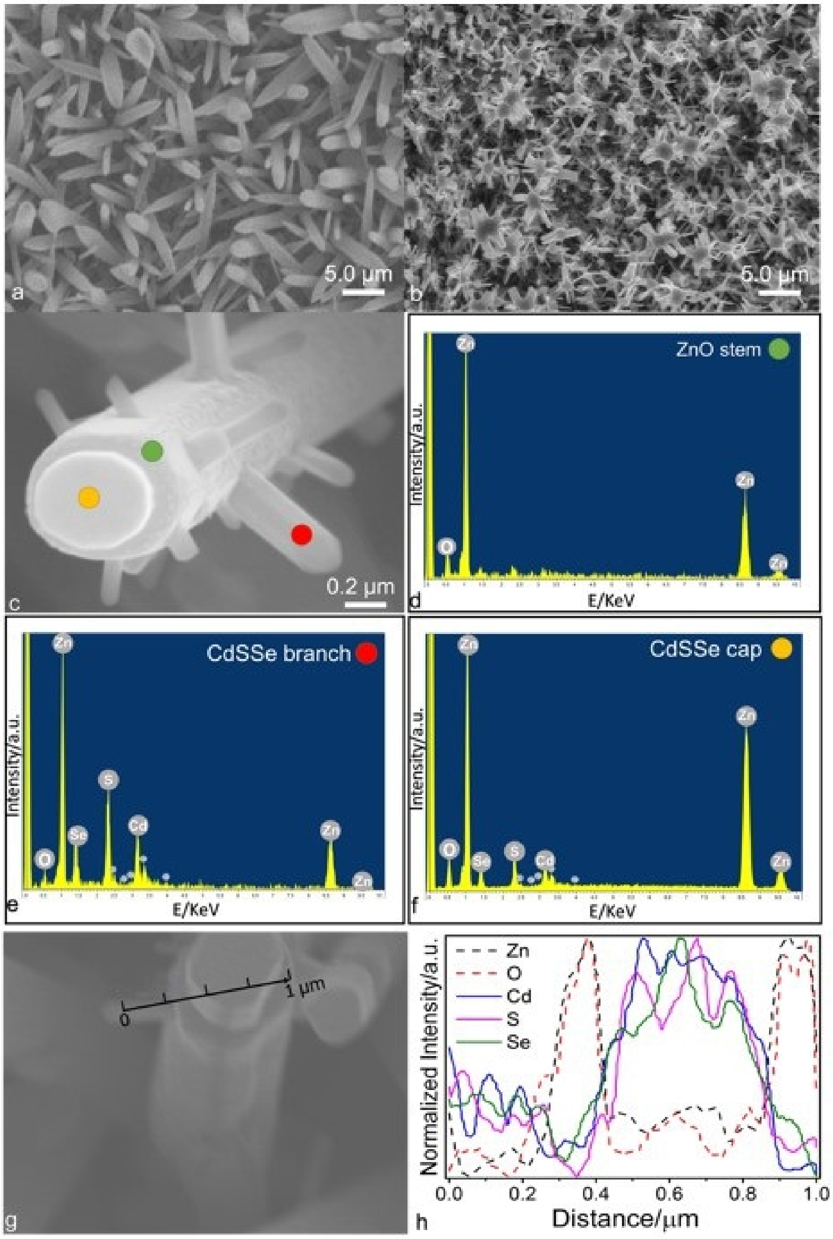


Figure 1(left): SEM image
nanowires prepared via CVD .
SEM images of ZnO/CdSSe NTs
via CVD. EDS spectra of ZnO ste
cap, and CdSSe branch of ZnO/C
are shown in d), e), and f), respe
shows an element line scan alon
shown in g).

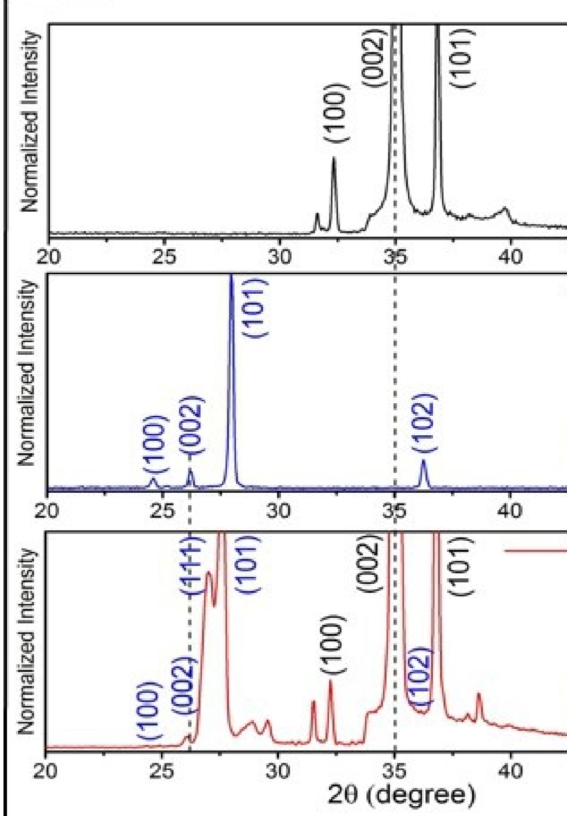


Figure 2(up): XRD spectra of Zn
and ZnO/CdSSe NTs

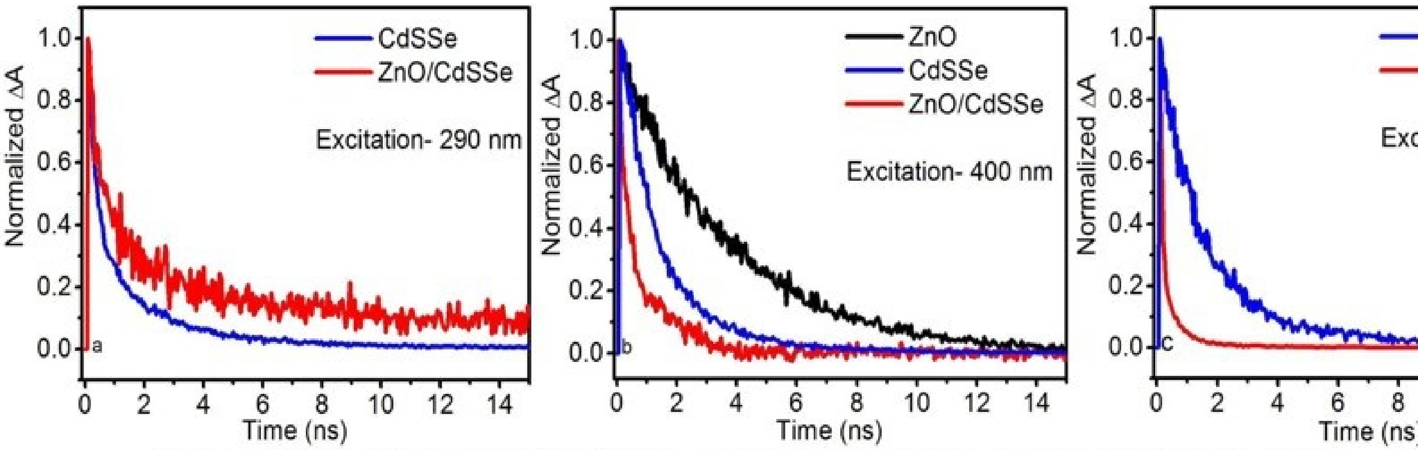


Figure 3(up): Time-resolved fluorescence measurements of ZnO, CdSSe, and

COLL 39

Tailoring of oxide nanoparticle superstructures through deposition method, temperature and ligand behavior

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The hierarchical assembly of nanoparticle (NP) building blocks into ordered superstructures holds promise for providing unique properties for the production of new nanostructured materials and devices. While several technologies that utilize individual NPs have emerged, superstructures can offer further distinct physical and chemical properties, which arise from the collective properties of NPs. Importantly, analogous to crystals, these properties are dependent on superstructure crystallographic phase. In order to provide insights into the self-assembly process and the resulting phases, this study explores the direct self-assembly process by using oleate-covered CeO_2 nanoparticles (cubic and polyhedral shapes), through the correlation of experimental and theoretical investigations. By tuning the temperature and evaporation rate in the colloid deposition, several crystallographic structures could be identified by high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) (e.g., Figure 01), and then correlated to the Gibbs free energy variation of the system. The analysis of the total potential energy of each ordered structure showed that the effective NP ligand size and its Flory-Huggins parameter (solubility) controlled the overall structure. This study provides fundamental understanding of how the control of simple physiochemical parameters affects the resulting superstructures morphologies.

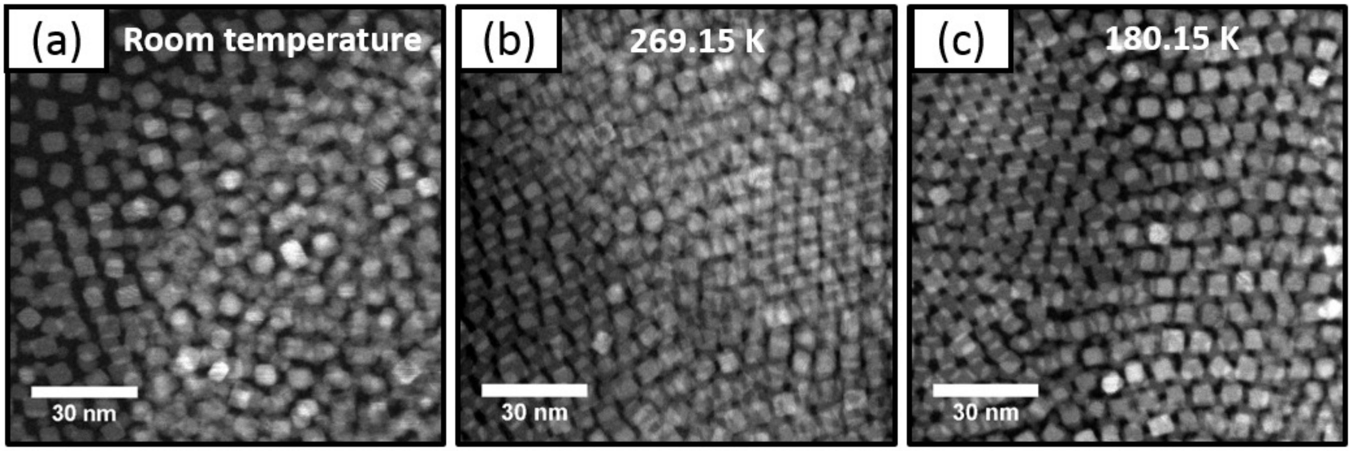

Figure 01- HAADF-STEM images of cubic CeO_2 NP prepared by delaying colloid evaporation and at several temperatures (inserted). (a) Non-ordered, (b) FCC and HCP and (c) FCC structures.

COLL 40

Biphasic synthesis of metal sulfide nanoparticles at room temperature

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Due to their unique optical and semiconducting properties, metal sulfide nanoparticles are excellent candidate materials for photovoltaic, catalytic, labeling, and sensing applications. In this work, small (1- 10 nm) metal sulfide (Ag_2S, PdS, or CdS) nanoparticles were synthesized in toluene at room temperature. Tetraoctylammonium metal complexes of Ag, Pd, or Cd were first prepared and characterized. These complexes were then dissolved in toluene, and aqueous solutions of Na_2S were added, forming biphasic mixtures. Upon phase transfer of the sulfide ion, relatively monodisperse metal sulfide nanoparticles capped with tetraoctylammonium bromide were generated in the toluene phases. UV-visible absorption, fluorescence emission, infrared absorption, and Raman scattering spectroscopies, as well as X-ray diffraction and transmission electron microscopy were used to characterize the synthesized metal sulfide nanoparticles.

COLL 41

Methanol adsorption on monocrystalline ceria surfaces

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Due to the oxygen mobility and the reducibility of cerium ions, ceria and related materials have extensive catalytic applications. Studying the interaction of methanol with ceria surfaces taking the so-called surface science approach is of crucial importance to gain a fundamental understanding of the oxidation of alcohols to aldehydes. We have studied the adsorption of methanol on the (110) and (111) surfaces of bulk ceria (CeO_2) single crystals using infrared reflection-absorption spectroscopy (IRRAS). To assign the experimentally observed features, density functional theory (DFT) has been applied. For ceria (110), only a single intense band at 1108 cm^{-1} is observed, which is assigned to a monodentate methoxy species. For the fully oxidized ceria (111) surface, a more complex spectrum has been obtained: the small band at 1108 cm^{-1} is attributed to methanol adsorption at a small amount of (110) facets exposed at step edges in the (111) surface. The strong bands at 1085 and 1060 cm^{-1} are assigned to a methanol monolayer that consists of H-bonded methoxide as well as molecularly adsorbed methanol species. These assignments are derived from molecular dynamics simulations for several adsorption structures with low and high methanol coverage. Surface defects were also considered. Our results reveal that a simple relation between the redshift in the methoxy CO stretching mode and the number of

cerium cations coordinated to the methoxide oxygen atom (as often used in previous work) does not apply.

COLL 42

Distance dependent triplet energy transfer between CdSe nanocrystals and surface bound anthracene

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Here we investigate triplet energy transfer (TET) across variable-length aromatic oligo-*p*-phenylene and aliphatic bridges in a covalently linked CdSe nanocrystal (NC)-bridge-anthracene hybrid system. Photon upconversion measurements in saturated 9,10-diphenylanthracene hexane solutions under air-free conditions at room temperature provided the steady-state rate of TET (k_{et}) across this interface. For flexible transmitters, k_{et} is similar for different lengths of aliphatic bridges, suggesting the ligands bending backwards. For the rigid phenylene spacer, triplet sensitization of anthracene transmitter molecules by CdSe NCs shows a strong distance dependence, with a Dexter damping coefficient of 0.50±0.07 Å^{-1}. The anthracene transmitter bound closest to the NC surface gave the highest QY of 14.3% for the conversion of green to violet light, the current record for a hybrid platform.

COLL 43

Anisotropically shaped perovskite nanostructures synthesis and photovoltaic applications

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The organic-inorganic hybrid materials known as perovskites have been the focus of much research recently due to their unmatched solar energy conversion efficiency that could reach up to 20%. These materials have shown the ability to redefine the field of photovoltaics, however, little is known about their growth and formation kinetics in the colloidal state. Herein, we present a first-time study of the growth mechanism of methyl ammonium lead halide quantum wires. It was determined that the surface ligand chemistry plays a critical role in the shape control of these nanomaterials. Our long-term objective is to develop a fundamental understanding of how nanostructure organic-inorganic hybrid materials can be rationally synthesized from the bottom up with shape control and unique properties, and enhance the performance of perovskite-based solar cells by designing first perovskite nanostructure-based photovoltaics.

COLL 44

Accelerating Förster resonance energy transfer (FRET) between PbS quantum dots (QDs) with organic chromophore bridge

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Efficient space-separated coupled energy transfer can help extract the multiexciton states from semiconductor quantum dots before they annihilate through the Auger recombination. To approach this objective, we fabricate self-assembled aggregates of PbS QDs with different sizes in aqueous solution by employing coordination between surface ligands, glutathione, and Zn^{2+} cations. Dynamic light scattering and cryo-STEM characterization show that the aggregates have diameters of 40 - 60 nm. Steady-state and time-resolved photoluminescence experiments demonstrate efficient FRET from the QDs with smaller sizes to the larger ones. However, in these QD assemblies, the energy transfer rates are too slow (0.02 - 0.1 ns^{-1}) to compete with the Auger recombination (5 - 100 ns^{-1}). We then insert organic chromophores that can serve as FRET bridges between donor/acceptor QDs. The two-step FRET (from QD donors to dye bridges, then to QD acceptors) happens much faster than FRET between directly coupled donor/acceptor QDs.

COLL 45

Understanding photovoltaic properties of PbS quantum dot solids via solution contacting

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Photovoltaic (PV) devices based on PbS quantum dot (QD) solids demonstrate high photon-to-electron conversion yields. However, record power conversion efficiencies remain low, in part due to small photovoltages, which in turn are affected by both bulk and interfacial defects. Their relative impacts on limiting the photovoltaic performance of QD solids are not known. Interfacial defects can be formed when contacting a semiconductor and may dominate the semiconductor/metal or metal-oxide junction properties. The objective of this study is to explore whether electrochemical contacting using liquid electrolytes provides means of contacting QD solids without introducing interfacial defects. We have initially focused on the relationship between photovoltages of QD solids and energetics of the contacting electrolytes. We have investigated electrochemical contacting of PbS QD solids using anhydrous liquid electrolytes containing fast, outer-sphere redox couples. Depending on the energetics of a redox couple, rectifying or non-rectifying PbS QD solid/electrolyte junctions were formed. Results were consistent with electrochemical contacting being a “soft” contacting method that did not introduce interfacial defects as the open-circuit voltage (V_{oc}) varied ideally with solution potential (E), $\Delta V_{oc}/\Delta E = 1.08 \pm 0.04$. Using this method, we are currently investigating how ligand chemistry of QD solids affects their photovoltages.

COLL 46

Colloidal plasmonic nanocrystals

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Colloidal plasmonic nanoparticles have proven to be of an enormous potential in a wide range of applications. To fully realize their technological potential and further explore their fundamental plasmonic properties relies on the ready availability of high-quality, high-performance nanocrystal samples at different amount scales. We have made tremendous efforts over the past ten years on the development of synthetic methods for colloidal metal nanocrystals. We have developed methods for the synthesis of several types of highly uniform colloidal Au and Ag nanocrystals, investigated their plasmonic properties and applications. They are Au nanospheres, Au nanorods, Au nanobipyramids (NBPs), Ag nanorods, AuAg nanostructures and Au nanoplates. Their sizes and therefore their localized plasmon energies can be readily varied over broad spectral ranges by carefully controlling the synthetic conditions. The syntheses of these nanocrystal samples are all based on seed-mediated growth. Fine size tuning is realized through mild oxidation and anisotropic overgrowth, which allows for precise control of the plasmon resonance energies. Precise control of the plasmon resonance is very important for many plasmon-enabled applications.

Specifically, we have been able to grow Au nanospheres from ~20 nm to ~300 nm in diameter. Due to the simple geometry and the availability of analytical solutions for nanospheres, Au nanospheres are preferred for assembly and for checking experiments/simulations with theories. We can tailor the diameter and aspect ratio of Au nanorods. The former can be employed for adjusting the relative contributions of scattering and absorption to the total extinction, and the latter can be used for adjusting the longitudinal plasmon energy. Compared to Au nanorods, Au NBPs exhibit larger field enhancements, narrower plasmon peak widths and higher refractive index sensitivities. From Au NBPs, we can grow Ag nanorods with excellent control on both diameter and length, and synthesize Ag nanostructures with extremely narrow plasmon peak widths. Moreover, we have been able to synthesize Au nanoplates with narrow distributions on both side length and thickness. The thickness of these nanoplates can be varied from ~10 nm to ~50 nm. Such thickness control has rarely been demonstrated before.

COLL 47

Kinetic control of the nucleation and growth of colloidal metal nanocrystals

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The reduction kinetics plays a pivotal role in controlling the synthesis of colloidal metal nanocrystals, including those widely used for plasmonic applications. Recent studies indicate that the reduction rate not only determines the internal structure (including single-crystal, singly-twinned, multiply-twinned, and stacking-fault lined) of a seed formed in the nucleation step but also controls the growth pattern or mode of the seed in the following steps. In this talk, I will first describe our recent studies with regard to the quantitative measurements of kinetic parameters (including rate constant and activation energy) for a number of systems and then illustrate how this knowledge can be applied to achieve a deeper understanding of the nucleation and growth processes, moving toward the goal of achieving a precise control over the products.

COLL 48

Colloidal metallic nanocrystals with unusual morphologies

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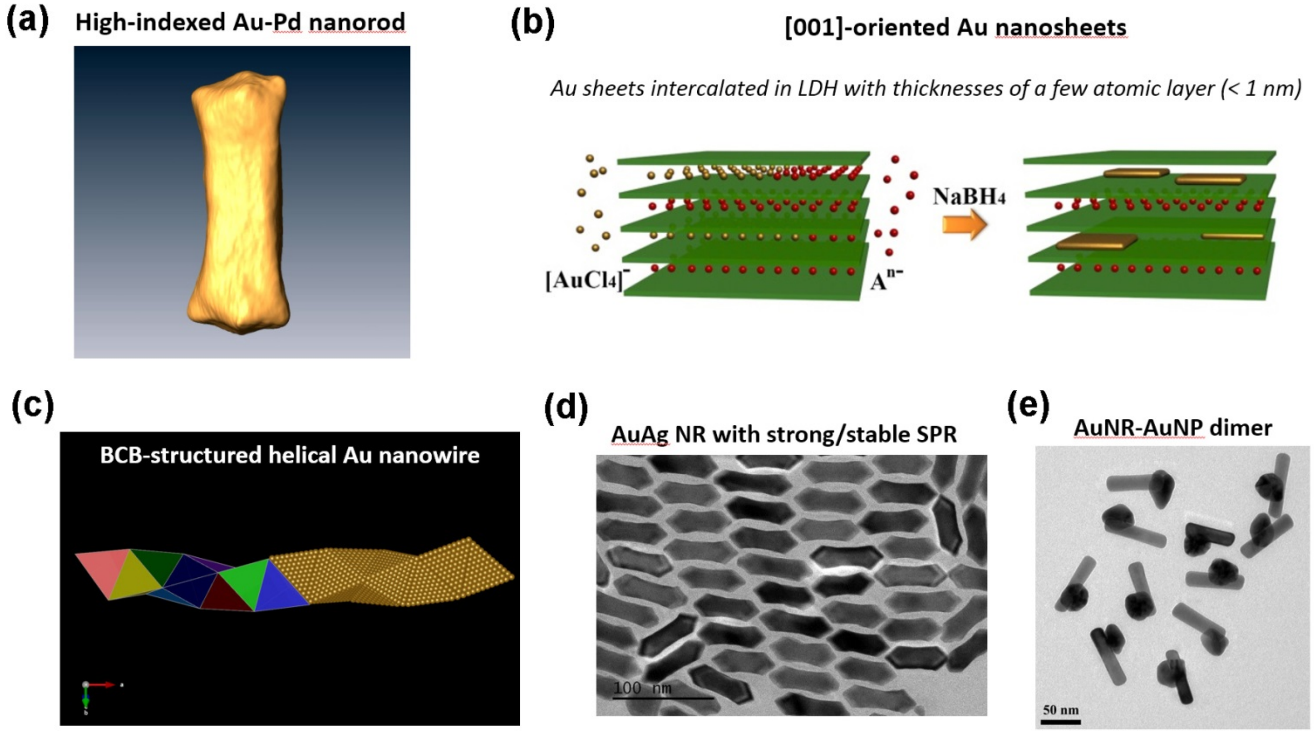
Metallic nanocrystals usually show highly symmetrical particle morphologies, as dictated by their intrinsic crystallographic symmetries. Breaking this morphological symmetry is fundamentally challenging for synthesis, but practically significant because it would allow the introduction of new properties into nanocrystals, enriching their applications for plasmonics, photonics, sensing, and catalysis. In this presentation, I will brief the development of new synthetic routes to metallic nanocrystals with exotic (unusual) morphologies that we developed in the last 3 years. Some interesting results are highlighted in the Figure below.



COLL 49

Stress induced fabrication of new plasmonic nanostructures

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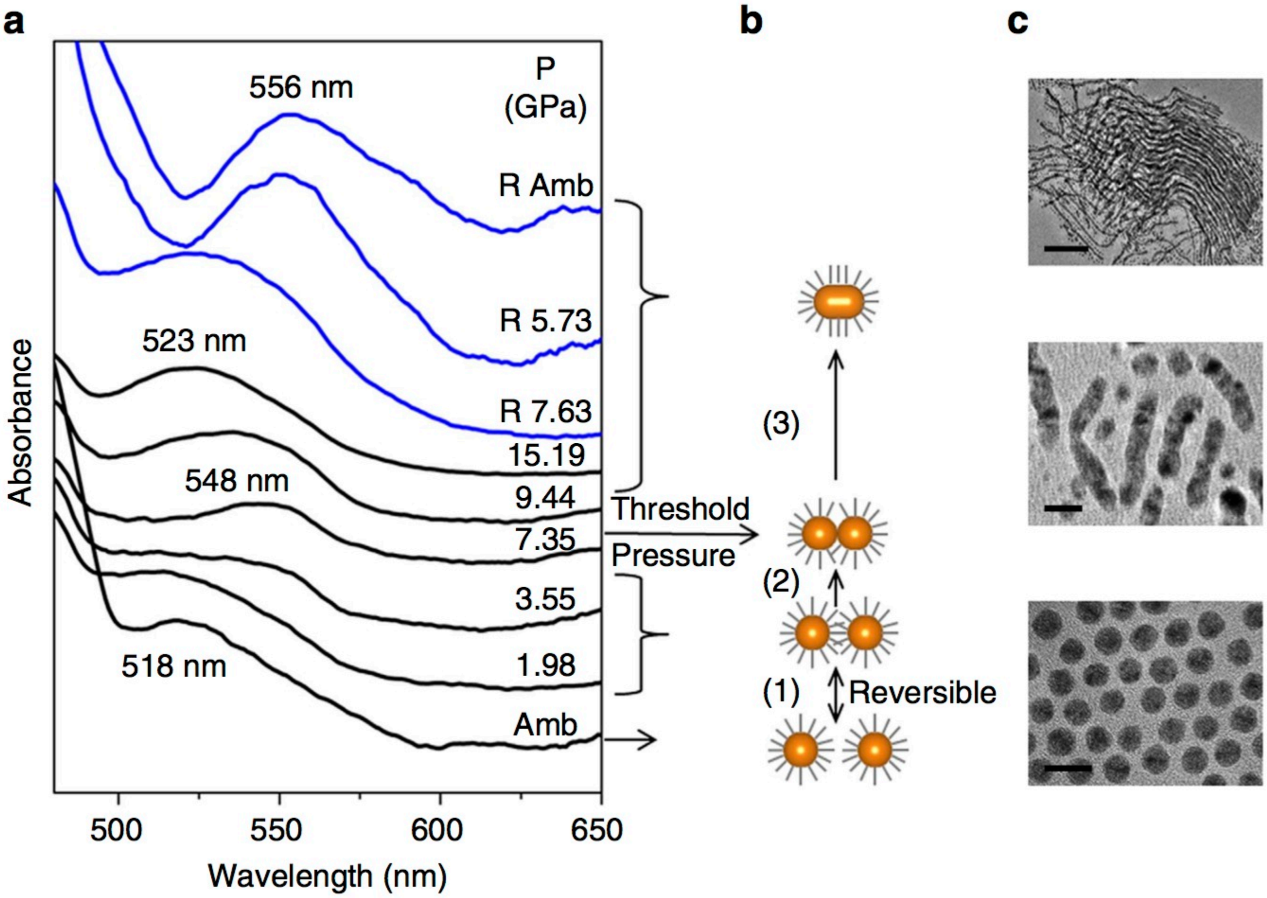
One of the outstanding challenges in the emerging fields of nanophotonics is the ability to achieve precise control in macroscopic nanoparticle (NP) superlattices of structural characteristics such as interparticle distance so as to enhance efficiency of charge/energy transfer. To this aim, both top-down processes such as e-beam and ion-beam lithography and bottom-up methods such as self-assembly of colloidal NPs have been vigorously pursued. While these methods have provided certain success, they have essential fundamental limitations. The top-down processes are limited by their spatial resolutions of ~10nm by the e-beam/ion-beam size and by their inability to fabricate complicated and tunable 3D nanostructures. Bottom-up methods have been limited to 2nm interparticle distances by the NP surface ligands. Here we show a new stress-induced fabrication method to produce new classes of 1-3D plasmonic nanostructures with precisely and systematically controlled structural characteristics for strong and tunable collective optical properties. The method allows reversible manipulation of structural characteristics such as interparticle distance under stress and offers unique robustness for *in situ* interrogation of both chemical and physical coupling in NP assembly, which has not been possible for both top-down and bottom up methods.



Stress-induced structure and optical property correlation of Ag nanoparticles superlattice under pressure. (a) In-situ UV-vis spectra of Ag nanoparticles superlattice. (b) Schematic of nanoparticle assembly and consolidation under high pressure. (c) TEM images of Ag corresponding nanostructures to different stages of Ag nanoparticle aggregation in b and optical signature in a. Scale bars, 100, 10 and 10 nm (c, from top to bottom).

COLL 50

When colloidal chemistry meets substrate-immobilized seeds: New synthetic schemes, new architectures, and new capabilities

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Seed-mediated colloidal chemistry has proven to be one of the most effective means for exerting the architectural and chemical controls needed to direct noble metal nanostructure synthesis along pathways yielding structures with highly tunable optical properties. Seeds can act as (i) platforms upon which material is deposited, (ii) sculpted through its partial dissolution into the adjacent liquid medium, or (iii) exposed to reaction environments which both add and subtract material through sequential or parallel processes. Here, we describe our efforts to integrate the competencies of colloidal chemistry with substrate-based techniques in a manner yielding organized surfaces of complex noble metal nanostructures which are unobtainable through other means. The synthetic strategy is reliant on the fabrication of periodic arrays of noble metal nanostructures which act as seeds for solution-based protocols adapted from well-studied colloidal syntheses such as galvanic replacement, selective etching, and the heterogeneous nucleation of reduced metal ions. Collectively, these syntheses have generated an entire class of substrate-based architectures which include nanocubes, truncated octahedra, nanocrescents, nanoprisms, core-shell nanocubes, and truncated octahedra confined within a nanoshells, nanocages, or nanoframes. The nanostructures differentiate themselves from those produced through colloidal syntheses in that (i) seed epitaxy with the substrate facilitates nanostructure alignment, (ii) architectural asymmetries originate from a substrate which sterically hinders deposition and negates reactions with the underside of the seed, and (iii) the formation of core-void-shell structures where substrate immobilization preserves a well-defined gap between the inner core and outer shell. With such structures offering unique properties, synthetic flexibility, and high degree of tunability, they are intriguing candidate materials for such application as biological and chemical sensors and as catalytic nanoreactors powered by plasmonic near-fields or the localized heating generated by plasmon decay.

COLL 51

Noble metal nanocube, nanoshell, nanocage, and nanoframe syntheses reliant on citrate as a (100) capping agent

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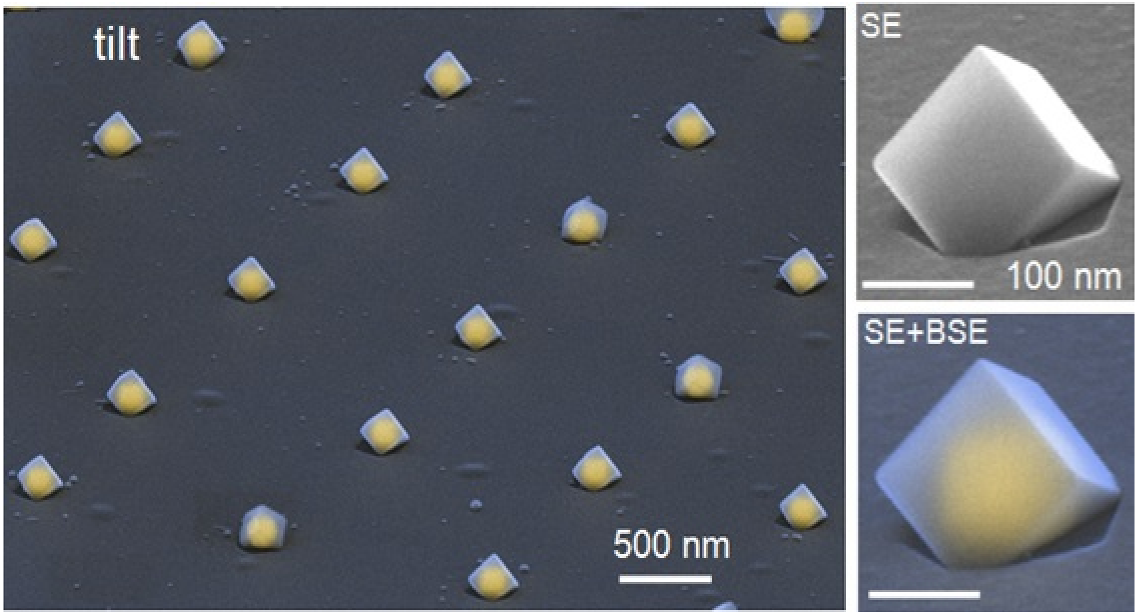
The foremost synthetic protocol for the synthesis of noble metal nanostructures shaped as (111)-faceted octahedra involves the reduction of metal ions onto preexisting seeds in the presence of citrate and ascorbic acid. It is generally accepted that the growth mode is facilitated by the selective capping of (111) facets by citrate, with ascorbic acid remaining passive in terms of directing the shape. Here, we present results which are contrary to this understanding and, hence, warrant a reexamination of the role of citrate as a shape-directing capping agent. A synthesis is demonstrated in which Ag^+ is reduced onto Au seeds where citrate acts as both the capping and reducing agent. The expectation of an octahedron-shaped reaction product, founded on the premise that citrate would cap (111) facets, proved inaccurate. Observed instead was a robust nanocube growth mode able to withstand wide variations in the growth parameters. The seeming contradiction between these results and the aforementioned octahedral growth mode is reconciled through experiments which demonstrate that the nanocube geometry gives way to an octahedral growth mode when small quantities of ascorbic acid are included in the synthesis. The implication of these results is that citrate, or one

of its oxidation products, caps (100) facets, but where this capability is compromised by an interplay between it and ascorbic acid. In addition to this mechanistic discovery, the work presents synthetic achievements which include (i) the formation of substrate based M@Ag nanocubes where M =Au, Pd, and Pt, (ii) the fabrication of periodic arrays of Au@Ag core-shell nanocubes which are epitaxially aligned with the underlying substrate (Figure 1), and (iii) the transformation of these nanocubes into nanoboxes, nanocages and nanoframes using galvanic replacement reactions. Such syntheses could advance a growing list of potential applications which take advantage of substrate-based nanostructures with the nanocube geometry.



COLL 52

Short cell penetrating peptides for stem cell engineering and targeting

*Geunwoo Jin, **Won H. Suh**, whs@temple.edu.* Bioengineering, Temple University, Philadelphia, Pennsylvania, United States

Cell Penetrating Peptides (CPPs) actively transport into mammalian cells across the lipid bilayer plasma membrane barrier. Examples include sequences derived from naturally occurring proteins such as HIV-1 transcriptional activator (TAT). We recently invented a short cell penetrating peptide (herein PepB) as a platform technology for stem cell engineering and cellular targeting. We have currently reduced the CPP sequence to PepB (<10-mer) and tested their efficiency in the delivery specific bioactive compounds such as retinoic acid into human neural stem cells. In the presentation, we will present new data showing dye functionalized PepB sequences with specific lipid moieties. The results of neural stem cell differentiation below and above the critical micelle concentration (CMC) will be presented as well as the matching physicochemical properties associated with the self-assembly (or cooperative assembly) processes. Time lapse live-cell imaging and fluorescence microscopy data, RT-qPCR, and

immunocytochemistry data will be presented to show the effectiveness of our CPP PepB in the derivation of neurons from human neural stem cells.

COLL 53

Assembly of nanoparticles containing biologics and other soluble therapeutics by flash nanoprecipitation

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Biologics are the most rapidly growing segment of the pharmaceutical market, however there are still unmet needs in delivery. Nanoparticle and microparticle formulations of peptide and protein therapeutics have been developed in an effort to prolong release, target tissues of interest, and evade degradation and immune responses. Current particle-based formulation technologies for biologics and other soluble therapeutics are limited in their encapsulation efficiencies, maximum loadings, ability to maintain sustained release, and scalability. We have adapted Flash Nanoprecipitation (FNP), a nanoparticle synthesis method traditionally used in the formulation of hydrophobic therapeutics, to the formulation of hydrophilic therapeutics including biologics. Initially “inverted” nanoparticles are formed. These particles are stabilized through non-covalent methods. Finally, they are either coated to form nanoparticles or incorporated into a PLGA matrix to form microparticles. Here we discuss important processing parameters in our new FNP system, and demonstrate the synthesis of both nanoparticles and microparticles with high loadings and encapsulation efficiencies compared to other formulation technologies.

COLL 54

Modeling self-assembly of nucleic acid containing bionanoparticles

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Nucleic acid interactions with polymers, proteins, and nanomaterials to generate structured material systems is of interest to varied applications such as biosensing, DNA and siRNA delivery, and the creation of crystalline materials with interesting optical or electronic properties. The ability to control the size of the nanoparticles and/or the spacing between them is important to the performance of these materials in different applications. A promising approach to nucleic acid delivery that has been demonstrated in the literature is by generating nucleic acid containing bionanoparticles via the complexation of the polyanionic nucleic acid with a double hydrophilic block copolymer containing a nonionic and polycationic block. While both the block copolymer and the nucleic acid have high water solubility, the complexation creates a reduction in charge and increased hydrophobicity for the complex and promotes the formation of multimolecular aggregates by self-assembly. Although the formation of self-assembled aggregates from a block copolymer such as polyethylene oxide - poly L lysine with DNA or siRNA is intuitively obvious, currently there is no quantitative treatment to predict the size of the resulting bionanoparticles as a function of the molecular weight and composition of the block copolymer and the charge ratio between the cationic block and the nucleic acid. In this work, we develop a simple molecular thermodynamic model building upon our earlier work on uncharged block copolymer micelles, but now considering the polyelectrolyte complexation in detail. The aggregate size and shapes are predicted from the model as a function of the molecular properties of the block copolymer and the nucleic acid. The model is also extended to a triblock copolymer such as polyethylene oxide – poly L lysine – poly L leucine, the added block being a nonionic hydrophobe, because of the recent interest in such a system from the point of view of enhancing the stability of the nucleic acid containing bionanoparticles.

COLL 55

Controlling the physicochemical and self-assembling properties of pyridinium amphiphiles at molecular level for efficient nucleic acid delivery

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Self-assembled synthetic vectors based on synthetic amphiphiles constitute an alternative to viral vectors but their efficiency must be improved by adapting their supra-molecular structure to extracellular and intracellular delivery barriers. In this context it was recognized that pyridinium amphiphiles with different packing parameters – simple surfactants, gemini surfactants, lipophilic polycations, lipids and their formulations can act as efficient nucleic acid delivery systems in vitro and in vivo.

We will present our latest synthetic and formulation efforts towards the generation of new pyridinium amphiphiles able to efficiently pack and deliver DNA, siRNA and mRNA in vitro and in vivo, alone, without the help of co-lipids. This represents an important step towards the simplification of formulations, enhancement of formulation reproducibility and a more linear translation from in vitro to in vivo.

COLL 56

Evaluation of nanolipoprotein particles (NLPs) as an *in vivo* delivery platform for biomedical applications

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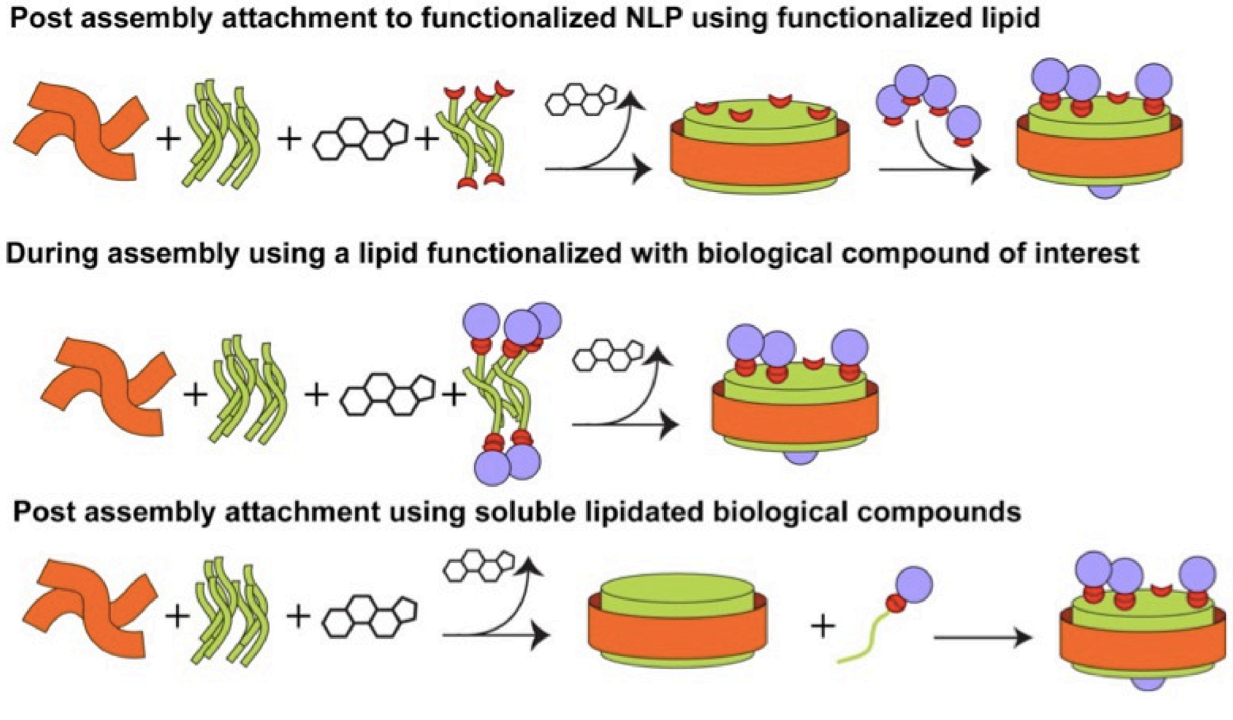
Nanoparticles hold great promise for the delivery of therapeutics. One emerging class of these materials are nanolipoprotein particles (NLPs), which are mimetics of naturally occurring high-density lipoproteins (HDLs). NLPs are attractive for drug formulation applications since they: (1) can be loaded with hydrophobic "cargo" molecules, (2) have high water solubility and (3) are easily modified for targeted delivery to specific tissues. However, their widespread adoption has been limited by poor in vivo stability, likely due rapid exchange with lipoproteins in blood, and a perceived liability of immunogenicity for human use. We report herein progress towards loading NLPs with several classes of therapeutically relevant molecules and drastic improvement of NLP in vivo stability. Additionally, we have evaluated the functionality, stability, cytotoxicity, toxicity, immunogenicity and in vivo biodistribution of NLPs. We found that a wide range of molecules with disparate chemical properties could be reliably conjugated to NLPs, including proteins, single-stranded DNA, and small molecules. We also report an optimized NLP formulation that is highly stable in human serum, with a half-life greater than 24 hrs and no cytotoxicity to human cell cultures at doses as high as 320 µg/ml—the equivalent of 24 grams of NLP dosed to a 75 kg human. In mice, we did not observe significant weight loss or organ toxicity after administration of NLP daily for 14 days. NLPs did not display overt immunogenicity with respect to antibody generation when administered through the intranasal and intraperitoneal route, which is important considering they are partially composed of protein. Finally, we present initial evidence that NLPs cross the blood brain barrier for delivery of therapeutics to the brain. These findings are supportive of NLPs as a versatile platform that holds promise for use as a delivery vehicle for a range of therapeutics.



COLL 57

pH responsive supramolecular hydrogels of β-amino acid derivatives

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In the past two decades supramolecular self-assembly has stimulated the research efforts on the rational design of smart materials that could provide robust routes for the development of myriad of applications in biomedical area. Hydrogel-that is, the most fascinating arena in self-assembly system to the keen chemists, is ubiquitous in biology, because of their enormous use in regenerative medicine, drug delivery, biosensing, a 3D matrix for cell culture etc. Among these smart materials, low-molecular-mass gelators (LMMGs) comprised of peptide/amino acid have acclaimed as one of the most convincing hydrogelators owing to their synthetic customizability, ease of availability and cost.

For the sake of invention of new hydrogelators, here in this work we intend to present two tripeptide based hydrogelators containing β-amino acid (β-alanine) which were observed to show pH responsive gelationr. All the hydrogels were characterized by various techniques including field emission scanning electron micropy (FESEM), transmission electron microscopy (TEM), Fourier transformed infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), circular dichroism (CD), and rheological studies. FESEM and TEM images revealed formation of nano-fibrillar three dimensional networks (3D) which entrapped a large amount of water molecules into the gel matrix. FTIR and other studies demonstrate hydrogen bonding interaction of the amide groups and π-π stacking interaction between the hydrogelators were the main driving forces for the hydrogelations. Moreover, drug solubilization with the hydrogels at psychological pH (pH 7) and release study have been done by taking one non-steroidal anti-inflammatory drug (diclofenac sodium). It is to be mentioned that these hydrogelators have potential to resist hydrolysis against proteolytic enzymes due to the presence of β-alanine residue. Therefore, it is believed that these hydrogelators with their proteolytic resistant property might be attracting in biomedical application, and also might expand the ranges of application as biomaterials.

COLL 58

Biocompatible nanoparticles for a selective drug release at cancer cells

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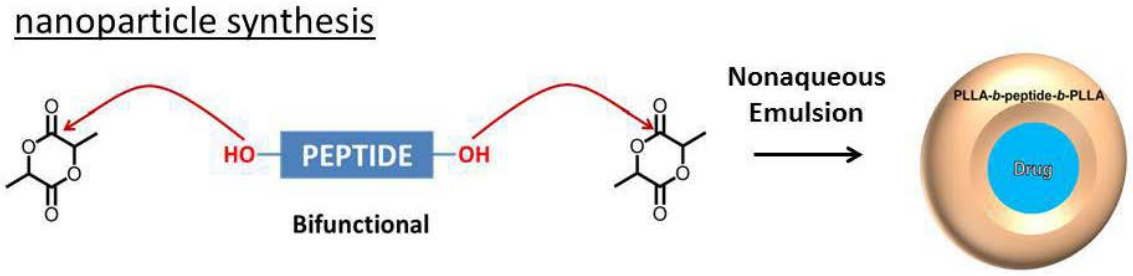
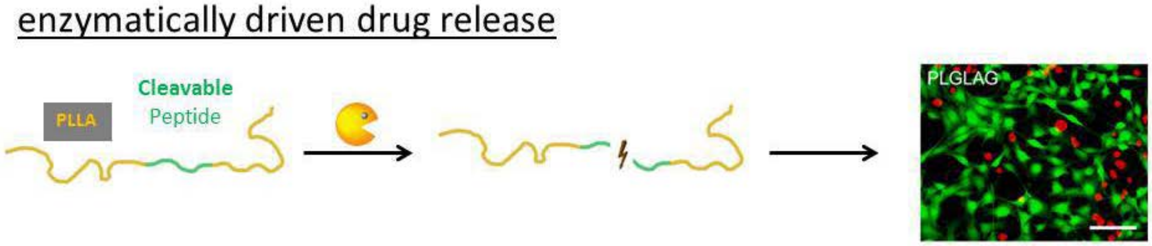
For nanoparticles that are used as intravascular drug delivery systems, aggregation resulting in carrier sizes >250 nm is a serious issue as those systems are removed from the blood stream by Kupffer cells.

Herein, we describe nanoparticles which consist exclusively of non-toxic biodegradable polymers (polylactide and polypeptides) making them suitable candidates for medical

applications in particular for cancer therapy.

A light sensitive PEG-*block*-poly((1-pyrenyl methyl) glutamate) (PEG-*b*-PGlu(Pyr)) copolymer is synthesized and used as emulsifier in a non-aqueous emulsion polymerization of lactide. Poly(L-lactide) (PLLA) nanoparticles were synthesized via ring-opening polymerization of L-lactide with a moisture-sensitive catalyst in a non-aqueous emulsion consisting of acetonitrile, cyclohexane, and the PEG-*b*-PGlu(Pyr) copolymer as emulsifier. Upon UV irradiation, hydrophobic pyrenyl methylene units are cleaved from the block copolymer, resulting in a polarity reversal of the particle surface from hydrophobic to hydrophilic. The product particles have a fully hydrophilic and biocompatible PEG-*b*-PGlu shell and can be dispersed in water without aggregation. Furthermore, introducing MMP-3 cleavable peptide sequences in the nanoparticles allows for a full degradation of the particles when they are getting close to tumor cells. This offers the opportunity to selectively release drugs which have been incorporated during the particle formation. In the area of non-cancer cells the particles are non-toxic as control experiments reveal.





COLL 59

Directed evolution of peptide nanomaterials

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The tremendous functionality of living systems is based on sequence-specific polymers and it is increasingly clear that much simpler oligomers, such as peptides, are suitable building blocks for supramolecular nanomaterials with myriad applications. However, the design and selection of self-assembling sequences is challenging due to the vast combinatorial space available. We demonstrate methodology that enables the peptide sequence space to be searched for self-assembling structures. In this approach, dipeptides are subjected to continuous enzymatic condensation, hydrolysis and sequence exchange with the free energy change associated with the assembly process itself giving rise to selective amplification of self-assembling candidates. By sequentially changing conditions, different sequences and consequent nanoscale morphologies may be selected- thus demonstrating discovery of peptide nanostructures by directed evolution. Applications in the discovery of peptide nanoparticles for therapeutic applications and peptide hydrogels for cell culture will be discussed.

COLL 60

Bioactive glycopolypeptide self-assembled biohybrid nanomaterials

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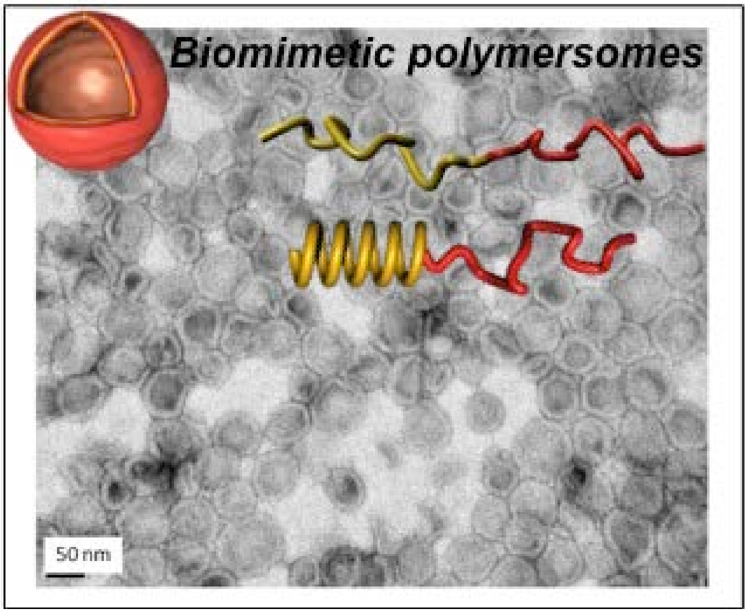
The field of synthetic polypeptides has seen many significant advances in recent years, including studies on block and hybrid copolypeptides that form vesicles, fibrils, and other structures with potential applications in medicine and materials chemistry. However, the development of glycosylated polypeptides has not kept pace, primarily due to the inability to readily synthesize glycopolypeptides in a controlled manner. Glycosylation of natural proteins provides diverse functionality such as mediation of recognition events, modification of protein conformations, ect, that may find interest and application in biomedical field. In this context, we developed over the last years synthetic strategies for the design of glycosylated polypeptides and polysaccharide-polypeptide biohybrids with controlled placement of sugar functionality. We were especially interested in designing amphiphilic copolymers able to self-assemble into well-defined micelles and vesicles that can advantageously be loaded with drugs and present a surface with multivalent presentation of bioactive saccharides or oligosaccharides. The ability of these nanoparticles for different biomedical applications, from drug-delivery to inhibitor, will be presented.



COLL 61

Strain-promoted oxidation-controlled cyclooctyne–1,2-quinone cycloaddition (SPOCQ) for fast and activatable protein conjugation

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A main challenge in the area of bioconjugation is to devise reactions that are both activatable and fast. Here, we introduce a temporally controlled reaction between cyclooctynes and 1,2-quinones, induced by facile oxidation of 1,2-catechols. This so-called strain-promoted oxidation-controlled cyclooctyne–1,2-quinone cycloaddition (SPOCQ) shows a remarkably high reaction rate when performed with bicyclononyne (BCN), outcompeting the well-known cycloaddition of azides and BCN by three orders of magnitude, thereby allowing a new level of orthogonality in protein conjugation. This reaction is not only highly efficient in protein conjugation and labeling, but can also be extended to the synthesis of peptide-containing hydrogels. Gelation is induced by oxidation, which is performed both chemically using sodium periodate and enzymatically using mushroom tyrosinase. Due to the fast reaction kinetics, SPOCQ-formed hydrogels can be functionalized in one-pot with an azide-containing moiety using the strain-promoted azide-alkyne cycloaddition.

COLL 62

Polyplexes formed from cationic block polymers: investigating the role of block length, chemistry, and nucleic acid size on biological delivery

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The development and thorough characterization of polymeric delivery vehicles for nucleic acid and genome editing therapies are of high interest to the field of nanomedicine. Synthetic delivery vehicles offer the ability to tune chemical architecture/biological activity and readily package
nucleic acids of various sizes and morphologies for a variety of applications. DNA and RNA can spontaneously bind with polycations to form polyelectrolyte complexes termed polyplexes. When the polycation is a diblock copolymer with a cationic block (i.e., primary, secondary, tertiary amines) and a neutral hydrophilic block (i.e., PEGs or glycopolymers), the polyelectrolyte complexes formed with plasmid DNA (pDNA) are often colloidally stable and show great promise for in vivo systemic delivery applications. While the resulting properties (size, stability, and toxicity to biological systems) of the complexes have been studied for numerous polyplexes formed with cationic diblock polymers, the fundamentals of the pDNA-diblock binding process have not been extensively investigated. Herein, we report how the cationic block content of a diblock polymer influences the pDNA-diblock interactions. DNA of various sizes (21-9000 base pairs) and morphologies (linear or circular) has been complexed with a variety of cationic diblock polymers. The chemistry, composition, and molecular weights of the hydrophilic and cationic blocks have been systematically varied. We show that the enthalpy change from pDNA-diblock interactions is dependent on the cationic diblock composition, and is closely associated with both the binding strength and the pDNA tertiary structure. We have correlated these parameters with the biological delivery properties in vitro and in vivo.

COLL 63

Silica-phthalocyanine-antibody conjugate-based near infrared photoimmunotherapy: A newly established physico-chemical cancer therapy

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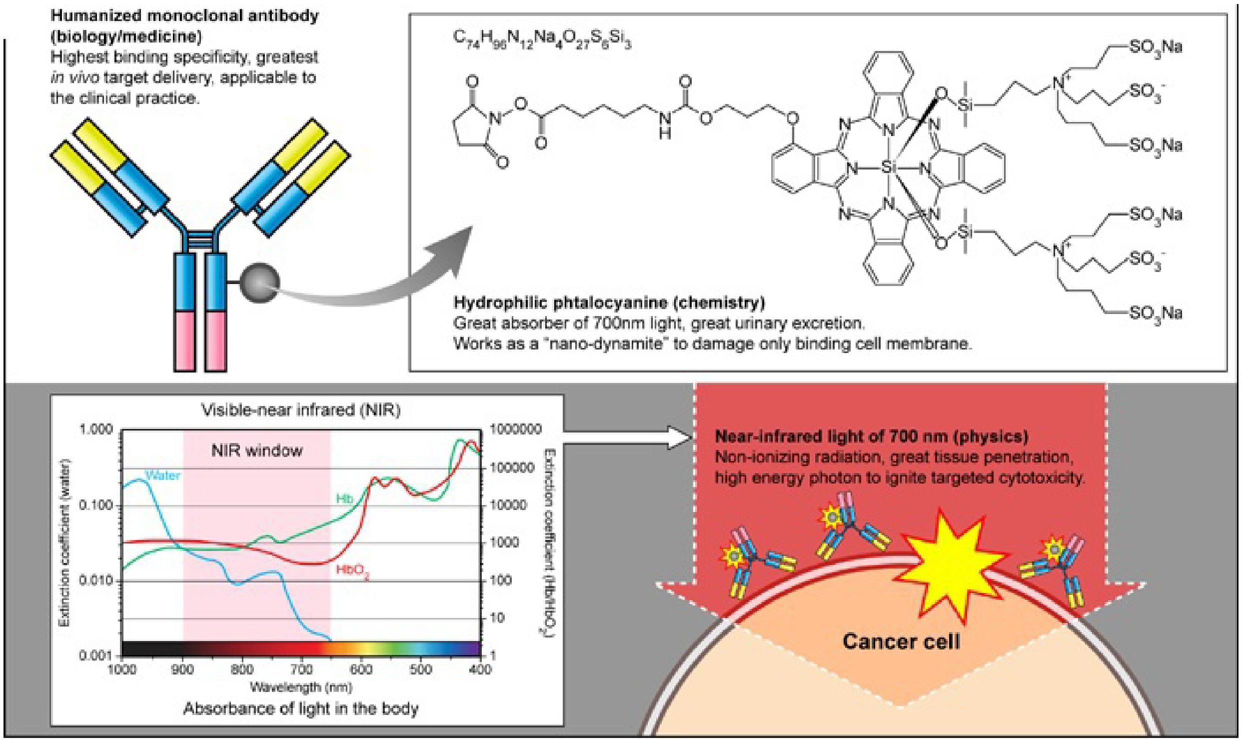
Near infrared (NIR) photoimmunotherapy (PIT) is a newly developed, molecularly-targeted cancer photo-therapy based on conjugating a near infrared silica-phthalocyanine dye, IRdye700DX (IR700), to a monoclonal antibody (MAb) thereby targeting cancer-specific cell-surface molecules. A phase I study of cetuximab-IR700 (RM-1929), for the treatment of inoperable head and neck cancers is ongoing (NCT02422979). When exposed to NIR light, the conjugate rapidly induces a highly-selective, necrotic/immunogenic cell death only in antigen-positive MAb-IR700-bound cancer cells. Immunogenic cell death occurs as early as 1 minute after exposure to NIR light and results in irreversible morphologic changes on target-expressing cells including cellular swelling, bleb formation, and rupture of vesicles due to membrane damage. Meanwhile, immediately adjacent receptor-negative cells are totally unharmed. NIR-PIT-induced cellular membrane damages were investigated from the physical, chemical and

biochemical perspective. Three-dimensional dynamic observation of tumor cells undergoing NIR-PIT along with quantitative phase microscopy and selective-plane illuminating microscopy showed rapidly swelling in treated cells immediately after light exposure suggesting rapid water influx into cells. Even after maximally damaging the cell membrane, minimal oxidative changes were found in 16-1 phosphatidylchorine by a high sensitivity lipid mass spectroscopy. However, by exposing the cell to NIR light, the IR700 ligated and released a side chain containing sulfonic acid that converted IR700 from highly hydrophilic to strongly hydrophobic. The photo-induced ligand exchange reaction led to loss of fluorescence and aggregation of the conjugate along with all directly associated proteins that leads to a compromise in the membrane pressure and an imbalance in the osmotic pressure between inside and outside of cells. This theory could explain the high cellular specificity of NIR-PIT-induced cytotoxicity.


Humanized monoclonal antibody (biology/medicine)
Highest binding specificity, greatest *in vivo* target delivery, applicable to the clinical practice.

Hydrophilic phtalocyanine (chemistry)
Great absorber of 700nm light, great urinary excretion.
Works as a "nano-dynamite" to damage only binding cell membrane.

Near-infrared light of 700 nm (physics)
Non-ionizing radiation, great tissue penetration, high energy photon to ignite targeted cytotoxicity.

Absorbance of light in the body

COLL 64

Programmable pre-assembly of near-infrared fluorescent multivalent molecular probes for biological imaging

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A programmable pre-assembly method is used to produce near-infrared fluorescent molecular probes with tunable multivalent binding properties. The modular assembly process threads one or two copies of a tetralactam macrocycle onto a fluorescent PEGylated squaraine scaffold containing a complementary number of docking stations.

Appended to the macrocycle periphery are multiple copies of a ligand that is known to target a biomarker. The threaded complexes are effective multivalent molecular probes for fluorescence microscopy and in vivo fluorescence imaging of living subjects. The pre-assembly method is extremely versatile and can be used in a parallel combinatorial manner to produce libraries of near-infrared fluorescent multivalent molecular probes for different types of imaging and diagnostic applications, with incremental structural changes in the number of targeting groups, linker lengths, and degree of PEGylation.

COLL 65

Tuning mechanics via structural interplay in polymer-peptide hybrids

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Inspired by natural materials, such as spider silk, bone, and collagen, we have also designed a series of polymer-peptide polyurethanes/ureas to explore the hierarchical arrangement critical to energy absorption and mechanical enhancement. We have addressed design strategies for hierarchical assembly and the influence of the interfacial region on mechanical behavior via the incorporation of ordered regions. Multi-block copolymers, which mimic the microstructure of numerous natural materials, are ideal systems with which to explore ‘soft’ domain ordering via variations in secondary structure of nature’s building blocks – peptides. The sheet-dominant hybrid materials were typically tougher and more elastic due to intermolecular H-bonding facilitating load distribution, while the helical-prevalent systems generally exhibited higher stiffness. Recently, we have explored peptide assembly within covalently crosslinked motifs as an additional hierarchical handle toward enhanced mechanics. Fiber manufacturing of these hybrid materials has also led to variations in peptide organization and stimuli-responsive behavior. It is envisioned that these peptide-polymer platform materials will advance technologies related to biomedical devices, and smart coatings/fibers.

COLL 66

Size-controlled synthesis of thermal stable Ru@*H*-SiO_2 core-shell nanoparticles and their catalytic applications

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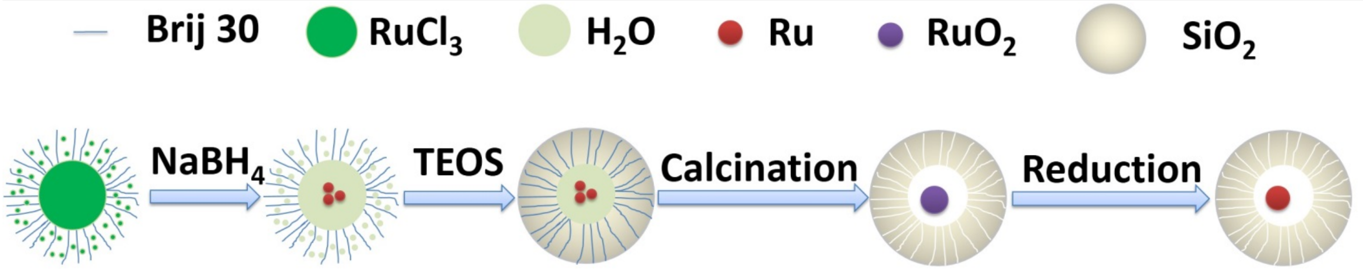
Single-cored Ru@*H*-SiO_2 (H: hollow) core-shell nanoparticles (NPs) with around 4.3 nm Ru cores and hollow SiO_2 shells were prepared successfully. In this synthetic process, we obtained multi-cored Ru@SiO_2 NPs initially, single-cored RuO_2@*H*-SiO_2 NPs during treatment, and single-cored Ru@*H*-SiO_2 NPs in the end. The Ru@SiO_2 NPs were prepared by water-in-oil microemulsion method, and the

size and core number of Ru@SiO_2 NPs can be controlled by the adjustment of the concentration of tetraethyl orthosilicate (TEOS) and $RuCl_3$. Single-cored RuO_2@*H*-SiO_2 NPs and Ru@*H*-SiO_2 NPs were successively obtained by calcination and reduction. The structure showed promising aggregate-resistant performance during the high temperature reducing process, and catalysis performance of Ru@*H*-SiO_2 at ammonia synthesis and hygrogenation of p-nitrophenol were also carried out.



Scheme 1 Synthesis procedures of Ru@*H*-SiO_2 NPs

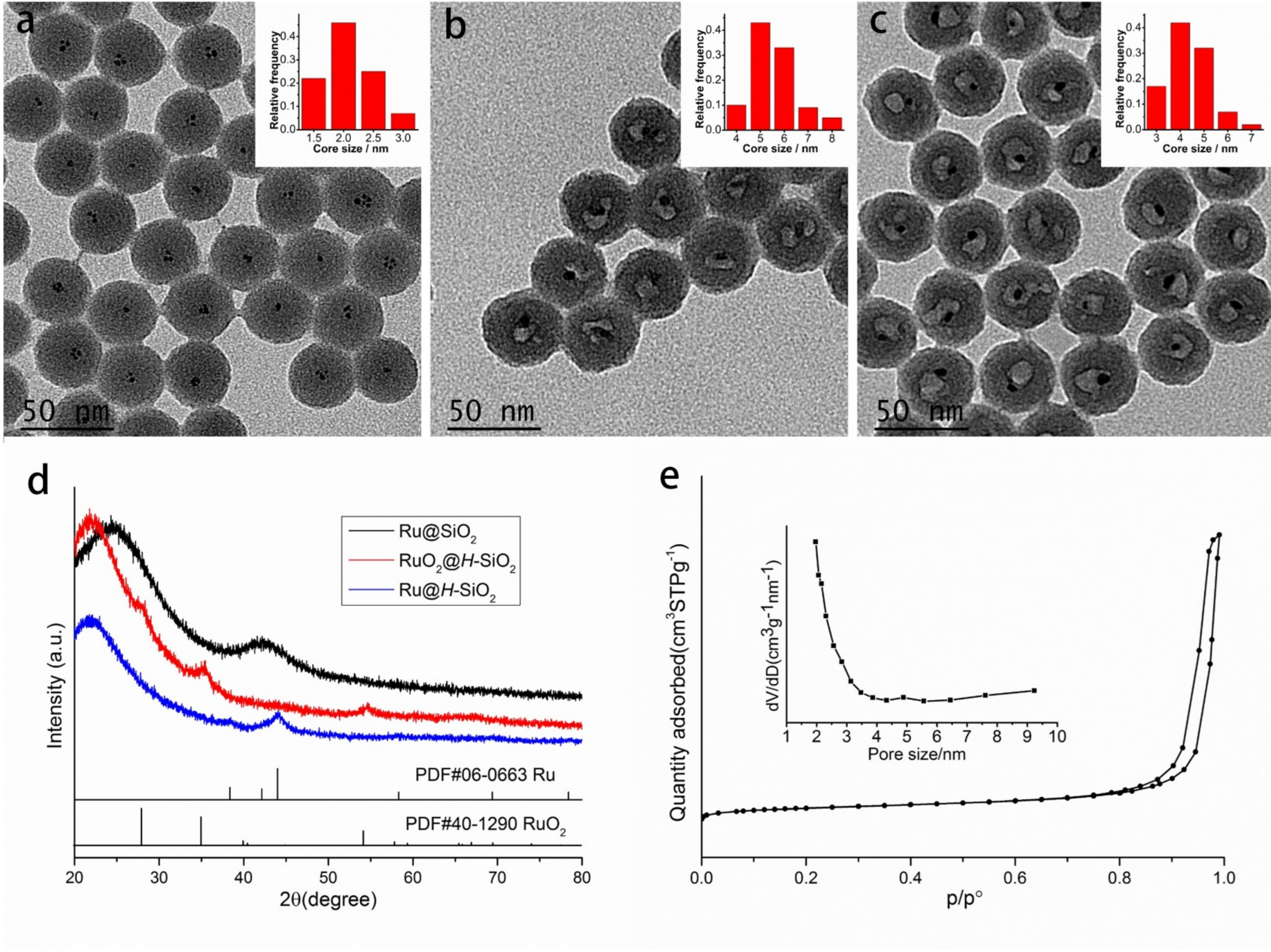


Figure 1 (a)(b)(c) TEM images, (d) of XRD patterns of Ru@SiO_2, RuO_2@*H*-SiO_2, Ru@*H*-SiO_2 NPs; (e) N_2 sorption/isotherms and pore size distribution of Ru@*H*-SiO_2 NPs

COLL 67

Controlled anisotropic growth of Co-Fe-P nanostructures as an efficient catalyst for the oxygen evolution reaction

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Phase-pure nanostructured cobalt-iron phosphides $(Co_xFe_{1-x})_2P$ were synthesized by phosphidation of ~30 nm cobalt-iron oxide nanoparticles (NPs) with trioctylphosphine at 300 °C. Through anion-exchange, uniquely tailored compositions and structures were obtained. The dimensions of the resulting nanostructures (nanorods and sea-urchin like NPs) were controlled by x, with smaller x (Fe-rich ferrites) yielding longer (up to 450 nm) and thinner (down to 2 nm) rods or branches. The Co-Fe-P nanostructures, especially the sea-urchin like, show Co/Fe-composition dependent catalysis for the oxygen evolution reaction (OER) in 0.1 M KOH. The $(Co_{0.54}Fe_{0.46})_2P$ is the most efficient OER catalyst, reaching 10 mA/cm^2 at an overpotential of 0.37 V (vs. RHE). The report offers a new synergistic approach to tune and optimize electrocatalysis for OER.

COLL 68

Comparative analysis of new metal-impregnated nanomaterials and their recyclable catalytic properties

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Nanogels have shown various applications in various fields ranging from optoelectronics to catalysis. In our previous works, the silica-coated metallic nanoparticle's size and shape was specifically tailored to be utilized as nanocatalysts. Successful synthesis of noble metal nanoparticles using a silylated-PEI polymer, trimethoxysilylpropyl polyethylenimine (TMSP-PEI), as the host material was investigated.

In this poster, we present our recent results for creating a series of silane-based metal-impregnated nanogels and their individual catalytic properties. This research included the one-pot process of forming a mesoporous siloxy network around the noble metal nanoparticles resulting in the formation of hybrid nanogels using various copolymerizing agents, and the comparative analysis of each nanogel as a recyclable catalyst. We will

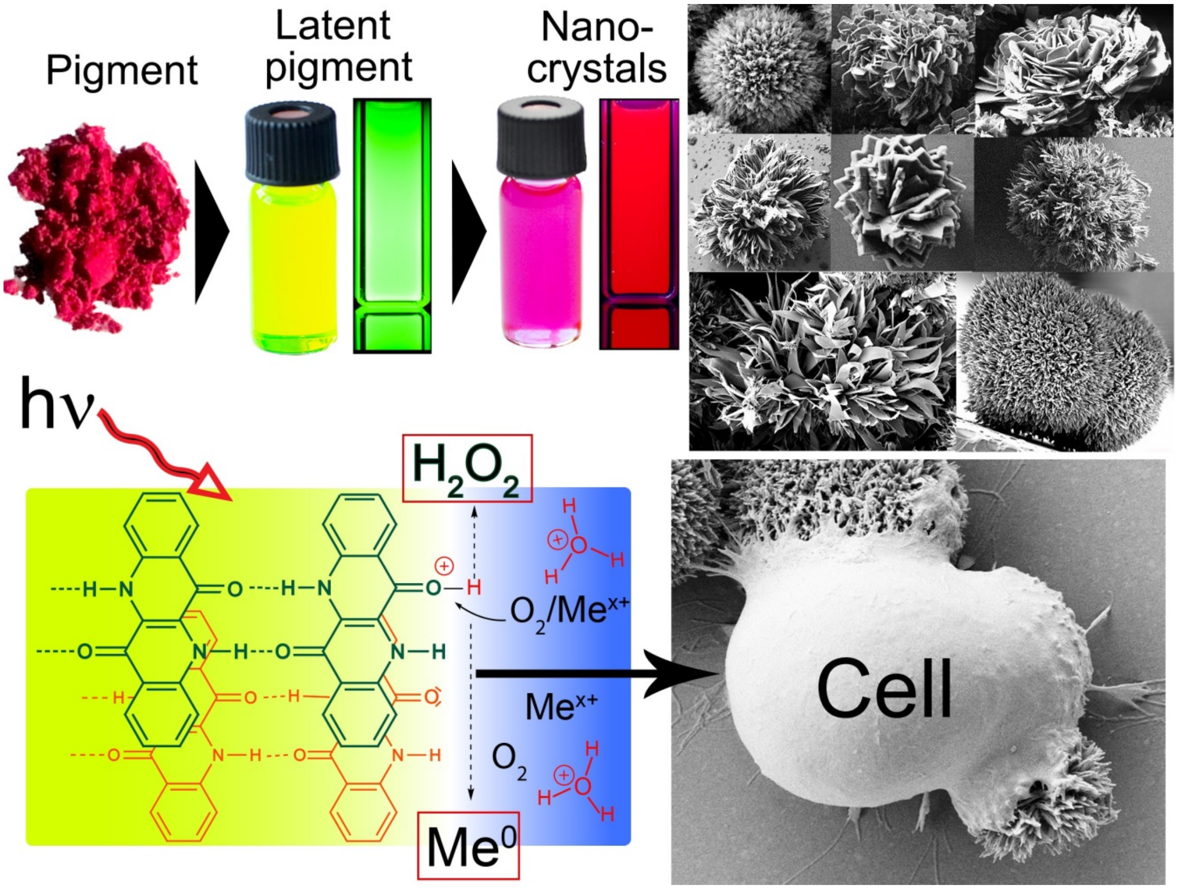
also present the detailed characterization and comparison of the physical and chemical properties using UV-Vis spectroscopy, FT-IR, TEM, and SEM/EDS.

COLL 69

Hydrogen-bonded organic pigment nanoarchitectures for photocatalysis: From photosynthesis of hydrogen peroxide to metal reduction

***Eric D. Glowacki*[1], *glowacki.eryk@gmail.com, Marie Jakesova*[1]*, Dogukan Apaydin*[1]*, Mykhailo Sytnyk*[2]*, Wolfgang Heiss*[2]*, Serdar Sariciftci*[1]*.* (1) Physical Chemistry, Johannes Kepler University, Linz, Austria (2) i-MEET, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

Photocatalytic materials which are cheap and readily-available and environmentally benign are an important focus of sustainability research. We discuss the recent discovery that several hydrogen-bonded organic pigments, mass-produced industrial colorants, are directly suitable for several photo- and photoelectrocatalytic applications, most notably oxygen reduction to hydrogen peroxide and the reduction of dissolved metal cations to zerovalent metal. Colloidal chemical techniques are used to generate a range of crystalline micro and nanoarchitectures from these materials, enabling efficient use as photoelectrodes in photoelectrochemical cells as well as colloidal materials that make use of a sacrificial electron donor for photoelectrochemistry. In this respect, several materials were found to act as artificial enzyme mimics, oxidizing glucose in aqueous solution while reducing O2 to H2O2, thereby mimicking glucose oxidase. In the presence of metal salts, they can act as metal reductases, oxidizing chloride while reducing metal cations. We have employed this to photochemically scrub harmful Pb2+, Hg2+, Cd2+, and Ni2+ from water. The key enabling property shared by these pigments is a combination of high-energy LUMO energy (typically more positive than -3 eV) with exceptional stability in aqueous environments. We demonstrate photocatalytic properties in a range from pH 1 to pH 14, with unprecedented stability under continuous illumination, and show experiments conducted at interfaces with living cells. This work highlights, for the first time, that organic semiconductors can be directly suitable as robust heterogenous photocatalysts in a wide range of aqueous environments.



COLL 70

Explorations in metal particle catalysis using silicon stabilized nanosized metals

***Bhanu P. Chauhan**, chauhan.cepm@gmail.com.* Department of Chemistry, William Patterson University, Wayne, New Jersey, United States

In this presentation, we present a new class of nanoparticle based catalysts which were found to be highly active and selective for various transformations. Our synthetic strategy is unique in terms of stabilization mechanism, where a very weak passivation is used to produce dispersible but highly active nanoparticles. This method also opens a new door for “on demand” organic dispersions of nanoparticles, which are very appealing for catalysis. Following specifics will be discussed in this presentation.

1. We developed a new synthetic approach to stable yet highly active metal particles in organic solutions “organosols” and devised a scheme, where the generation and stabilization is carried out in one pot.
2. We found that the metal nanoparticles synthesized in our laboratory were very active, highly selective, very efficient, regiospecific, and recyclable catalyst.
3. We investigated the impact and role of the stabilizing agents in the catalytica activity of the stabilized metal nanoparticles.

4. We developed rational and general guidelines for the large scale production of metallic particles for catalytic aplications.

COLL 71

Self-propelling cellulose nanocrystal based nanobots with high catalytic activity

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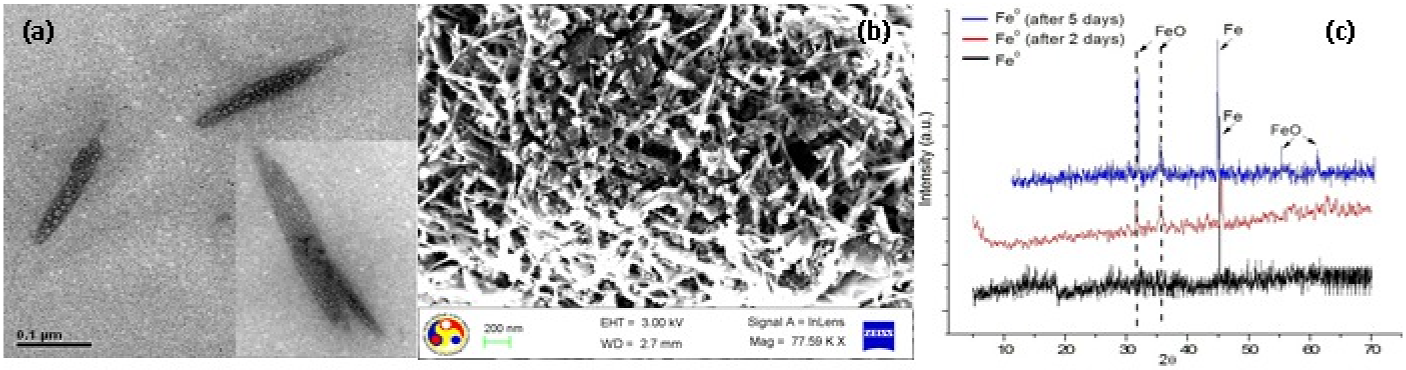
We report an environmental-friendly single step approach for synthesis of zerovalent iron(ZVI) supported on cellulose nanocrystals (CNCs) fabricated from bamboo pulp as precursors. Abundant hydroxyl functional groups on CNC surfaces acts as an anchor point for simultaneous reduction and stabilization of the ZVI. XRD studies of ZVI showed single, distinct, highly crystalline peak at 44.9°, which is a fingerprint of bcc-lattice of iron nanoparticles. CNCs also act as corrosion inhibitor, which enhances the zero state life of supported ZVI thereby enhancing the catalytic activity as it retains zero state even after five days of exposure to air. Both UV and XRD analysis were carried out after 5 days to confirm the presence of zero iron, however small intensity peaks corresponding to oxides were present. The chemical composition of synthesized ZVI was studied using Raman and FTIR spectroscopy, to understand the interactions with the supporting CNCs. Further, CNCs supported ZVI are found to be negatively charged with improved dispersion stability in water as confirmed from the zeta potential studies. This innovative approach reduces the usage of harmful reducing agents and with abundant resources of cellulose available, provides an attractive cost effective option for large scale fabrication of ZVI-CNCs. It is noteworthy to mention that the synthesized ZVIs shows high catalytic activity towards rapid degradation of the model pollutant dye methylene blue (MB) and conversion of toxic 4-nitrophenol (4-NP) to nontoxic products. We next highlight another application where CNCs acts as nanomotors which can move under the influence of chemically induced pH-gradient and magnetic field. On increasing the magnetic field strength (~60 mT) at a constant pH (~4), the CNCs supported ZVI attained the maximum speed reaching as high as ~7 mm/s(~35body lengths per second). Such self-propelled CNCs, are reported for first time which, will be an ideal candidate for drug delivery, MRI contrast agents, design of biomedical devices because of their nontoxicity and biocompatibility as well as an active biocatalyst.



(a) TEM images, (b) FESEM micrographs and (c) XRD patterns of ZVI-CNCs.

COLL 72

Synthesis and characterization of halloysite-TiO_2 hybrid nanocomposites for the photocatalytic degradation of organic dye pollutants in industrial wastewater

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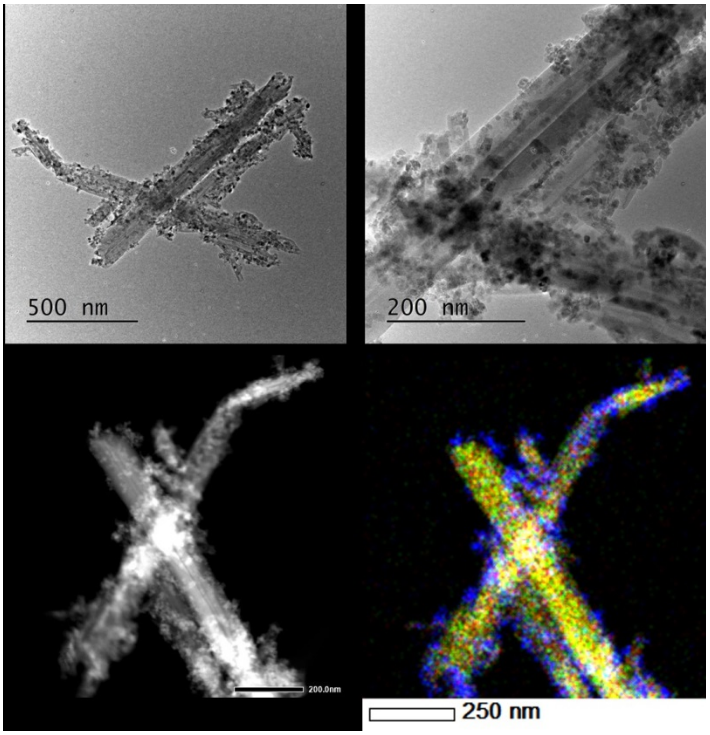
Halloysite nanotubes (HNTs) are novel 1D natural nanomaterials and possess attractive characteristics such as large surface area, hollow structure and abundance of hydroxyl groups. On the other hand, with excellent photochemical stability and low cost, nano-sized TiO_2 particles offer a great potential for the removal of organic pollutants in wastewater by photocatalytic degradation. In this study, conventional and microwave hydrothermal treatment methods were utilized to synthesize TiO_2 nanoparticles in the presence of HNTs in order to obtain hybrid nanostructures, in which HNTs were uniformly decorated with TiO_2 nanoparticles of controlled size. The morphology and structure of resulting hybrid HNT/TiO_2 nanostructures were confirmed using SEM, TEM, EDX, XRD, Raman and FT-IR spectroscopies. Chemical analysis was performed using XRF, whereas the phase analysis was performed by applying Rietveld refinement method on the XRD data. The photocatalytic activity of these hybrid nanostructures was evaluated in a fluidized bed reactor set-up by the degradation of methyl orange, Reactive Red 120 and Reactive Orange 16 dyes in model wastewater systems. HNT/TiO_2 nanostructures exhibited significantly higher photocatalytic activity compared to HNTs or TiO_2 alone, as evidenced by periodic UV-Vis spectrometric measurements, which was attributed to the presence of uniformly distributed TiO_2 nanoparticles of controlled size on the hydrophilic HNT surface.



HRTEM and STEM-EDX images of HNT/TiO_2 hybrid nanostructures

COLL 73

Morphology control in polyolefin synthesis via self-assembled hybrid supports

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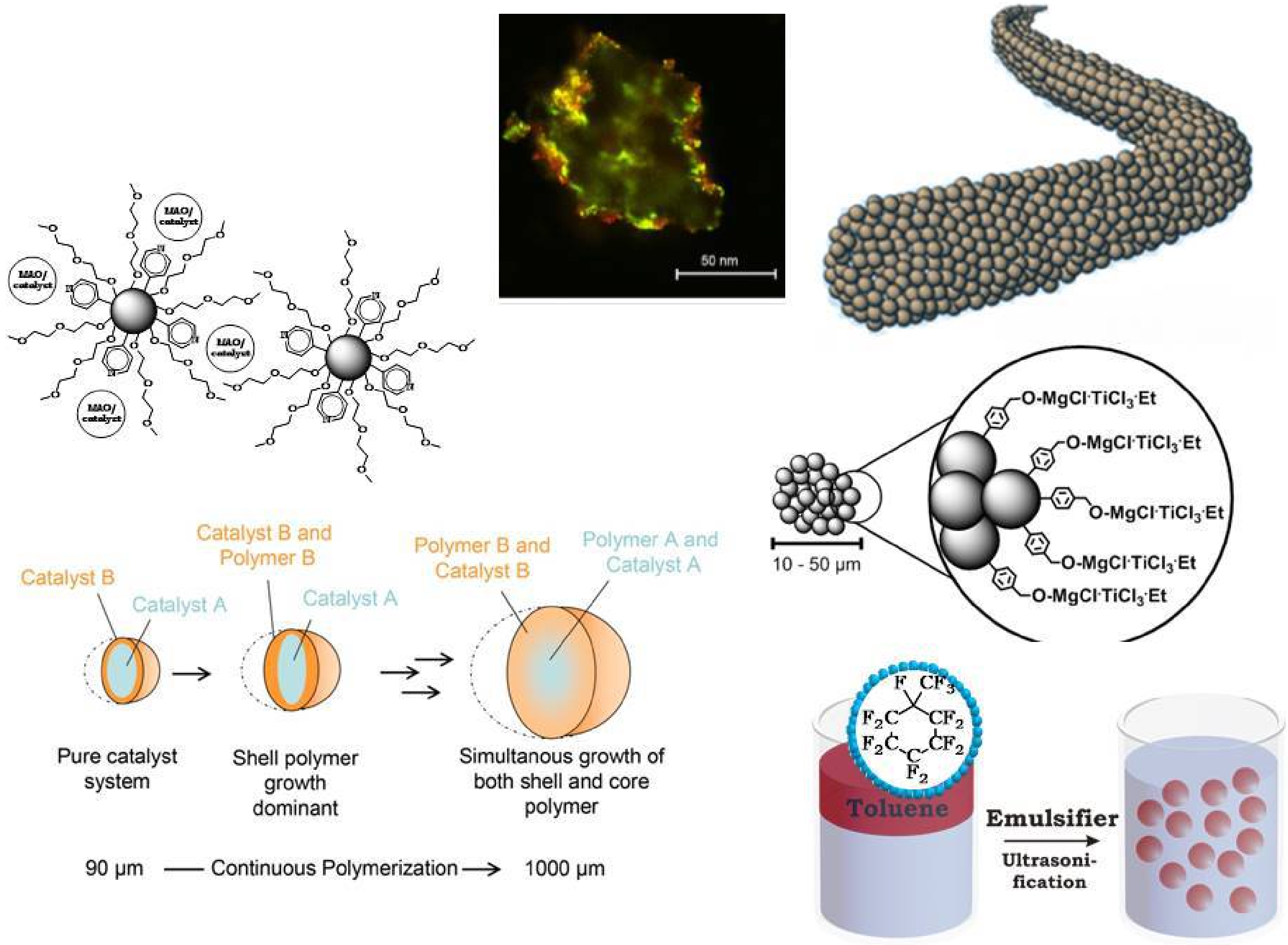
Immobilization of catalysts on inorganic and organic support particles has become well-established nowadays in order to achieve morphology control in the olefin polymerisation.
Latexparticles with different functionalities such as hydroxy, pyridyl and and PEG-chains are presented in the metallocene and Ziegler-Natta catalysed olefin polymerisation. Furthermore our approach enables a targeted synthesis of well-defined core-shell structures of polyolefin materials by spatially resolved supporting of different catalysts. As both, the catalysts and the polymers are migrationally stable, the final product represents the core-shell structure of the initial shape. In particular, two different metallocene catalysts were separately immobilized on silica particles and an organic support consisting of nanoparticles. Subsequently polymerization of propylene led to well-defined core-shell particles consisting of low M.W. atactic (core) and high M.W. isotactic (shell). The minimum particle size lies in the range of micrometers.
In order to obtain polyolefin particles also on a smaller length scale (< 1 µm) and to non-aqueous emulsions based on a perfluorinated solvent as the continuous phase and a

hydrocarbon as the dispersed phase have been developed. These oil-in-oil systems are stabilized by high molecular weight block copolymers. As the metallocene catalyst is predominantly soluble in the dispersed droplets, the reaction takes place there and yields polyolefin particles with an average diameter of approximately 50 nm.
In a third examples shape anistropic supports like fibers obtained by electro spinning are loaded with different olefin polymerization catalysts. Due to the replication of the shape of the support polyolefin fibers of e.g. UHMWPE are obtained directly out of the reactor.



COLL 74

Adsorption of CO_2, CH_4 and H_2O on clay surfaces: Density functional theory calculations of structure and dynamics

***Lorena Tribe**, lut1@psu.edu, Michael D. Kilmer.* Penn State Berks, Reading, Pennsylvania, United States

Electronic structure calculations free of adjustable parameters can provide insight into the structure and dynamics of surface complexes relevant to Enhanced Gas Recovery, a process in which supercritical carbon dioxide (sCO_2) is used to increase the yield of natural gas from shale reservoirs. A comprehensive understanding of the interplays of CH_4, CO_2 and H_2O molecules with the surfaces will help to provide a basis for gas-in-place estimations by accounting for the contribution to production of CH_4 adsorbed to the mineral surfaces.
First principles Molecular Orbital/Density Functional Theory was used in this work to model two clay minerals, Na-montmorillonite and kaolinite, and their interactions with CO_2 and CH_4 molecules. Energy minimizations were performed with the M06-2X functional, well suited for non-bonding interactions, followed by determination of the infrared vibrational frequencies. The free energies of adsorption of the clay models, the adsorbates, and the adsorbate-substrate clusters were determined, and the difference provided results for ΔG_{ads}. The values obtained are contrasted with data derived from experimental adsorption isotherms.
Selected input structures indicated that the adsorption of CH_4 to a clay surface is less favored that that of CO_2 and that the presence of water molecules, modeled explicitly, leads to significant differences in ΔG_{ads}. The outcomes depend strongly on the clay model, the adsorbate, and the initial adsorbate-substrate cluster. Small differences in the initial geometry did not produce much change in the adsorption of CO_2 on kaolinite, which remained unfavorable, but significantly changed the interaction of this adsorbate with Na-montmorillonite with outcomes as different as physisorption and mineralization. The vibrational frequencies for adsorbed CO_2 were compared to experimental data and to calculations in the literature using Molecular Dynamics simulations.
Energy scans for adsorbate moving away from the surface were performed to determine the activation energy and the rate constant of adsorption, finding a strong dependence on the position and nature of the surface complex as well as the number and distribution of the water molecules with respect to the surface.

COLL 75

Characterisation of silica and silicate nanoparticulate films using surface science methodologies

*Diane Baird[1], Skandar Taj[1], Alexander Rosu-Finsen[1], Victoria Frankland[1,2], Mark Collings[1], **Martin R. McCoustra**[1], m.r.s.mccoustra@hw.ac.uk.* (1) Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, United Kingdom (2) Department of Chemistry, University of Leeds, Leeds, United Kingdom

Silicate nanoparticles with stoichiometries derived from materials with olivine ($Mg_{2-x}Fe_xSiO_4$) and pyroxene ($Mg_{2-x}Fe_xSi_20_6$) compositions are believed to play a highly significant role in the chemical evolution of the Universe; catalysing the formation of small hydrogen rich molecules and providing a substrate for icy film growth in which

complex organic species are ultimately synthesised in the cold, dense environments where stars begin to form. Understanding the surface physics and chemistry of such systems is therefore crucial if we are to understand the chemistry of space.

We will report on preliminary studies of model silica nanoparticulate films produced on a copper substrate by electron-beam evaporation in ultrahigh vacuum using a combination of temperature programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS) at temperatures down to 18 K. We will describe TPD studies of the distribution of binding energies for CO on these particles and how this can be used to explain inhomogeneous line broadening of the CO RAIR spectra and provide a new window on to the relaxation dynamics of vibrationally excited CO on such nanoparticle surfaces. We will also describe RAIR studies of H_2O diffusion on these particle surfaces and outline our future plans to utilise these small molecules and others (C_2H_2 and C_6H_6) to probe silicate nanoparticles produced by pulsed laser deposition in collaboration with colleagues from the Department of Physics and Astronomy at the University of Jena.

COLL 76

Energetics of smectite clay swelling

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Smectite clay minerals are colloidal particles ubiquitous in terrestrial weathering environments. Because of their large specific surface area and negative structural charge, these minerals swell extensively when exposed to water. This swelling strongly influences the microstructure, mechanics, and fluid transport properties of clayey soils, sediments, and sedimentary rocks (shale, mudstone). The swelling pressure of clay minerals is thought to result from a combination of short-range (steric packing, hydrogen bonding), intermediate-range (London dispersion), and long-range interactions (electrical double layer overlap). However, the exact importance of the different interactions is not well constrained by existing measurements. Here, we present molecular dynamics (MD) simulations that aim to quantify the different components of the swelling pressure of smectite clay minerals. We compare our simulation predictions with theoretical models of the pore-size and salinity-dependence of the different components of smectite swelling pressure.

COLL 77

First-principles discovery of shape-reactivity relationships in adsorption onto Keggin-type aluminum hydroxides

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Keggin-based aluminum nanoclusters have been noted to be efficient sorbents for the removal of arsenic of water. Obtaining a molecular-level understanding of the adsorption processes associated with these molecules is of fundamental importance, and could pave the way for rational design strategies for water treatment. Due to their size and the availability of experimental crystal structures, Al nanoclusters are computationally tractable at the density functional theory (DFT) level. Here, we compare the reactivity of three aluminum polycations: $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (Al_{13}), $[Al_{30}O_8(OH)_{56}(H_2O)_{26}]^{18+}$ (Al_{30}), and $[Al_{32}O_8(OH)_{60}(H_2O)_{30}]^{20+}$ (Al32). We model both inner-shpere and outer-sphere adsorption of various environmentally relevant ionic species, and discuss how the molecular shape of the Keggins strongly influences adsorption trends. We relate our results to experimental structures where available, and also make direct comparisons of reactivity between the molecular models and single crystal alumina surfaces. By comparing the Keggin species to surfaces, we can further demonstrate the unique shape-reactivity relationships present in the former.

COLL 78

Adsorption energy, binding mode and geometry of toxic chemicals on TiO_2(110) using density functional theory

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Developing technologies for potable water, clothing and shelter for Warfighters requires approaches to handling toxic industrial chemicals and chemical warfare agents. Depending upon the application, we have to either remove or sequester the toxic chemicals, chemically or biologically degrade them or prevent their entry through material systems. Metal oxides offer one of the effective means for adsorbing as well as catalytically degrading these toxic chemicals. Understanding the interactions of these highly toxic materials during the adsorption on the metal oxide surface is essential in order to develop technologies to handle these chemicals. Because of the high toxicity of chemicals, often laboratory experiments are conducted with model molecules designed to simulate in relevant ways the properties of the toxic compound. An example is the use of dimethyl methyl phosphonate (DMMP) as a simulant for the highly toxic nerve agents such as Sarin, Soman and VX. Computational tools offer an important way to determine the appropriateness of the simulant to represent the toxic chemical, with respect to how they interact with the metal oxide surface. In this work, we study the adsorption of Sarin, Soman, VX and DMMP on TiO_2(110) using density functional theory (DFT). The properties of the different molecule/TiO_2 systems such as adsorption energy, binding mode and geometry will be discussed. In addition, we will consider the effect of the environmental conditions on the stability and structure of the systems due to hydroxylation. These results will allow a detailed comparison between the different properties of the toxic chemical and the simulant when adsorbed on TiO_2(110).

COLL 79

Acidity of a TiO_2-ZrO_2 adsorbent modified with phosphate or tungstate species

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Solid acids are promising adsorbents for removal of base contaminants from effluents. In this study, a series of tungstate- and phosphate-modified ZrO_2-TiO_2 composites were prepared through impregnation or incorporation methods and the influences of the two modifiers on the surface acidity were clarified systematically. The ZrO_2-TiO_2 substrate exhibited a high surface area of 195 m^2/g and acidic sites of 859 µmol/g. Compared to impregnation, higher surface acidity was obtained by incorporation of the modifiers. After incorporating phosphate and tungstate species into the substrate matrix with the optimal P/M and W/M raito of 0.44 and 0.16, respectively, the amounts of acidic sites increased to 1547 and 972 µmole/g, respectively. The W^{6+} ions, which have a high coordination number and high electronegativity, resulted in substantial amounts of oxygen vacancies and strong Lewis acid sites, while P^{5+} ions mainly introduced Bronsted acidity. The incorporated phosphate species improved the thermal stability of the ZrO_2-TiO_2 substrate, thus increasing the surface area to 270 m^2/g and maintaining the small pore size of 3.5 nm after calcination at 500°C. The phosphate-modified oxides performed high recoverability in repeated NH_3-TPD tests and exhibited higher NH_3 adsorption capacity than commercial zeolites NAY and ZSM-5. These results reveal that the phosphated ZrO_2-TiO_2 solid acids are highly potential for advanced pollution control.

COLL 80

Implications of shape-reactivity relationships on the crystallization of aluminum polycations

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A variety of aluminum hydroxide nanoparticles and heteroatom analogs have been identified through experimental methods, with applications ranging from sorbents for water treatment to templates for materials design. However, a molecular-level understanding of the structure-property relationships of these materials is lacking, and questions remain about how to optimize synthesis and how to harness reactivity. We report on theoretical studies of different polycation structures including, the flat $[Al_{13}(\boldsymbol{\mu}_3\text{-OH})_6(\boldsymbol{\mu}\text{-OH})_{18}(H_2O)_{24}]^{15+}$ (f-Al_{13}) and the Keggin-type $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (Al_{13}), as well as forms with substituted cations present in the structure. Using outer-sphere adsorption of anions as a probe, we model outer-sphere complexes with tetrahedral SO_4^{2-} and trigonal planar NO_3^-. Computational results reveal electrostatic potential gradients and adsorption-induced structural deformations as key factors governing reactivity, and provide insights about which counterions are the most effective in crystallization experiments.

COLL 81

SERS tags for multiplex immunophenotyping cellular receptors

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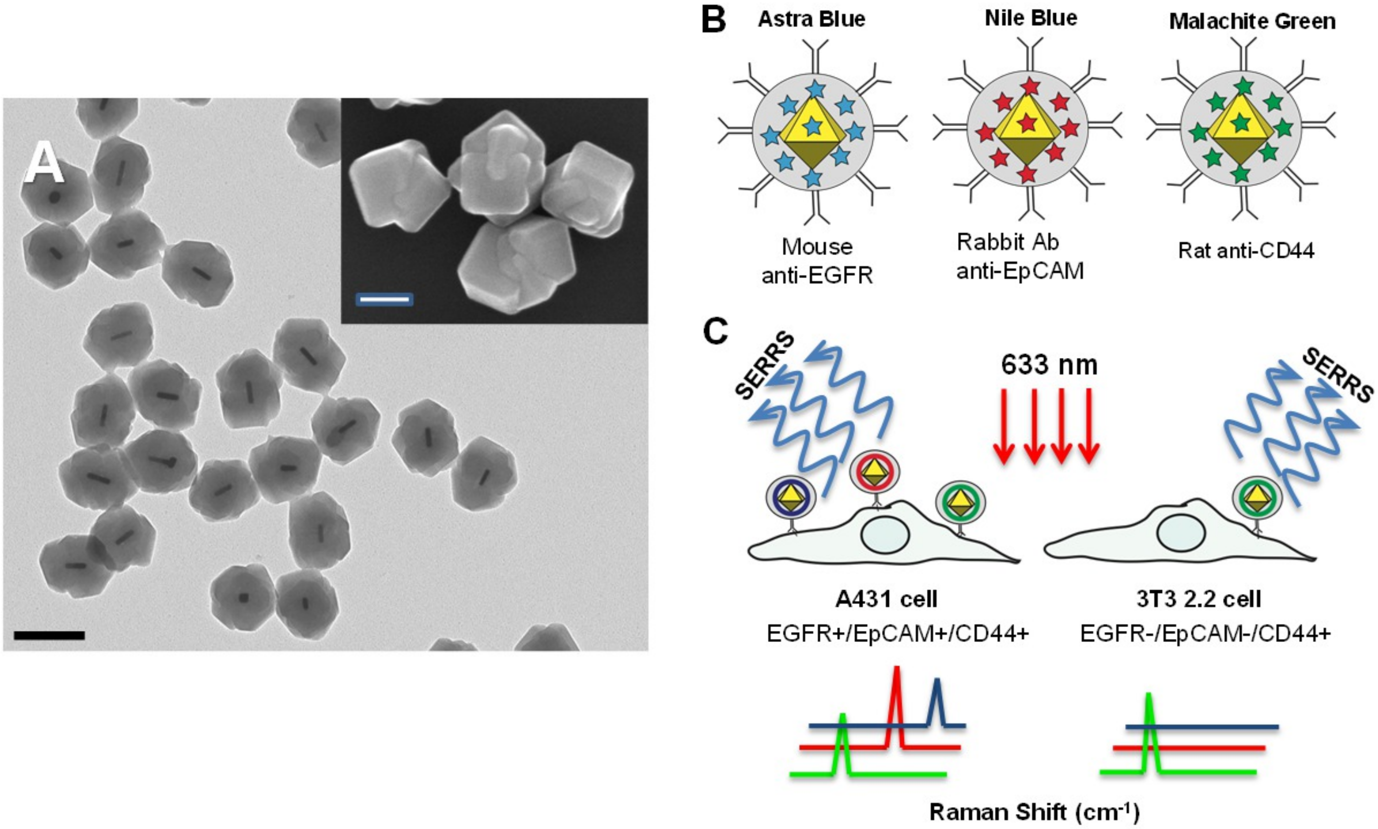
Detection technologies employing optically encoded particles have gained much interest toward clinical diagnostics and drug discovery, but the portfolio of available systems is still limited. We report the fabrication and characterization of highly stable surface enhanced Raman scattering (SERS)-encoded colloids, for the identification and imaging of proteins expressed in cells. Two different approaches were developed to synthesize the plasmonic nanostructures; a) gold octahedra coated with poly(isopropylacrylamide) (Au@pNIPAM) microgels, that can be readily encoded with Raman active dyes while retaining high colloidal stability in biofluids, and b) plasmonic nanoparticles encapsulated within zeolitic imidazolate frameworks (ZIF-8) that can be easily doped with different Raman reporters (see Figure A)

A layer-by-layer polyelectrolyte coating was used to seal the outer surface of the pNIPAM encoded particles and to provide a reactive surface for covalent conjugation with antibodies. On the other hand, the ZIF-8 coating of the particles allowed its direct bio conjugation with His-tagged proteins.

The targeted multiplexing capabilities of the SERS tags was demonstrated by the simultaneous detection and imaging of three tumor-associated surface biomarkers EGFR, EpCAM and CD44 by Raman spectroscopy (see Figure B and C). The plasmonic microgels were able to discriminate tumor A431 (EGFR+/EpCAM+/CD44+) and non-tumor 3T3 2.2 (EGFR-/EpCAM-/CD44+) cells while co-cultured *in vitro*.



(A) Representative TEM image of ZIF-8 coated nanoparticles. (B) Au@pNIPAM SERRS tags indicating their Raman codification and targeting entities. (C) Schematic representation of the SERRS immunophenotype detection of A431 and 3T3 2.2 cells.

COLL 82

Protein detection at cell surfaces and characterization of amyloid oligomers within phospholipid bilayers using SERS nanoparticles

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SERS nanoparticles offer platforms for finding cell surface receptors and spectroscopy on membrane embedded proteins. Both examples will be discussed in this talk. In the first example, we compare dark field imaging of the resonances between coupled plasmonic particles, along with SERS multiplexed labelling of distinct receptor types on individual cells. The role of particle size, shape and aggregation number will be contrasted with methods to couple excitons with the plasmonic nanoparticle responses, all in the goal of making reliable, bright labels for SERS-based flow cytometry. The second example will be the use of phospholipid bilayer encapsulation, to enhance NP stability and targeting, but also to host proteins for spectroscopy of their conformations. In particular, the detection of oligomers of beta amyloid will be discussed.

COLL 83

Stability and targeting properties of glycan-decorated plasmonic Au nanoparticles: Toward a selective SERS-based nanosensor

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Gold nanoparticles (AuNPs) with asymmetric shapes and different morphologies have attracted interest because of their unique optical properties due to anisotropy. Among these properties, the appearance of a plasmon band in the near infrared (NIR) region and the promising performance as surface-enhanced Raman scattering (SERS) substrates are being exploited for ultrasensitive detection. However, to selectively detect specific analytes in complex biological environments (culture media, cells, blood stream, etc…), nanoparticles must be decorated with ligands able to prevent aggregations of Au NPs and target selected biomolecules even in the presence of protein-rich media.

Poly(ethylene glycol) (PEG) has become the gold standard for stabilization of plasmonic nanoparticles (NPs) in biofluids, because it prevents aggregation while minimizing unspecific interactions with proteins. In this study we demonstrate that the functionalization with low-molecular-weight glycans ensures high colloidal stability and biocompatibility to anisotropic gold nanoparticles, prevents phagocytosis by macrophages and exhibits excellent selectivity toward carbohydrate binding proteins (lectins) both in serum and in *in vitro* cultured cells. The intracellular gold nanoparticles would serve as probes for SERS allowing for biochemical characterisation of their cellular environment. In particular, in this work we compare the intracellular accumulation of PEGylated and glycan-decorated gold nanoparticles and their ability to differentiate cell phenotypes. The carbohydrate shell on the surface of plasmonic nanoparticles affords lectin targeting on tumoral cells while avoiding phagocytosis by macrophage-like cells. Finally, the selectivity of the glyco-NPs toward lectins shows that the chemical structure of the glycan-stabilizing agent dramatically changes protein-particle interactions, and thereby opens new strategies in the fields of self-assembly or SERS-based biosensing.

COLL 84

Controlling the synthesis and assembly of silver nanocrystals for SERS application

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Silver nanoparticles have been widely explored as SERS substrates from the very beginning in the development of this analytical tool. By switching to silver nanocrystals with a well-defined and precisely controlled size, shape, or morphology, one can further enhance and optimize the detection sensitivity. In this talk, I will discuss how silver nanocrystals can be synthesized with a broad range of sizes and a variety of shapes, including cubes, bars, and rods. I will also discuss how these nanocrystals can be assembled into dimers to enable the formation hot spots for SERS. At the end, I will illustrate some examples related to SERS sensing and imaging with silver nanocrystals, together with a brief discussion on the stability issue and the potential solution.

COLL 85

Nanophotonics-based theranostics of cancer and heart disease: From *in vivo* diagnostic chemical imaging to phototherapy of heart disease

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In recent years, the use of nanoparticles has advanced from its original utilization to study cells in vitro to application in animal models for cancer diagnostics and therapy. No such advances have been reported concerning the number one killer, heart disease. Here we report on in vivo photon based diagnostics as well as therapy for both diseases. It is well known that the chemistry of the extracellular tumor environment differs from that of healthy organs in two major respects: oxygen depletion and acidosis, i.e. lower pH. The latter may affect the efficacy of therapy, e.g. radiation therapy, chemotherapy and photodynamic therapy. It would thus be advantageous for precision medicine to have this information. We have shown that nanoparticle based photoacoustic imaging can quantify both tissue oxygen as well as pH, and note that this photon and ultrasound based imaging technique is both non-invasive and relatively inexpensive. Regarding photon based therapy, photodynamic therapy (PDT) has been used clinically for skin cancers. Previous animal model tests have also indicated its potential use for internal organs and even brain cancer. We now show that PDT can also serve to fix arrhythmia, possibly the most critical aspect in heart disease. Starting with *in vitro* tests, continuing with rodent models and culminating with large animal models (sheep), we have shown that *cell selective* photoablation has major advances compared to the traditional modes of treatment. The latter approach is based on the use of targeted photoactive nanoparticles. Notably, the latter have to be of a much smaller size (below 10 nm) compared to the photodynamic nanoparticles used for the treatment of cancer, which can be of the order of 100 nm.

COLL 86

Biomedical imaging using SERS tags: The future beyond fluorescent dyes

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Surface enhanced Raman scattering (SERS) has been historically considered a tool for physical scientists. Recently however it has emerged as a powerful technique for biomedical imaging and biodetection. One of the major drivers of this evolution has been the development of the concept of SERS tag. SERS tags are nanostructured reporter systems comprising a plasmonic nanoparticle for electric field enhancement, a Raman reporter molecule, a capping layer to impart stability and biocompatibility, and a tagging moiety. They serve the role in SERS that fluorescent dyes have in fluorescence microscopy, i.e. to detect, indirectly, the presence of a specific target molecule. Because of the high sensitivity and selectivity afforded by SERS, SERS tags can be employed to selectively detect molecules of biological interest, such as oligonucleotides and proteins. In particular, they can be used to target surface- or integral proteins expressed in healthy and diseased cells providing a unique identification tool at the hand of the biomedical scientist or the physician.

During my talk, I will introduce the audience to the concept of SERS tags and their potential in early disease diagnosis. Starting from our earlier studies, in which dimer-based SERS tags were used for cancer cell identification, I will move on to more recent results obtained with SERS tags synthesized starting from gold nanostars. In particular, I will focus on the synthesis and characterization of the nanoparticles, provide a detailed analysis of their plasmonic properties, from both the experimental and computational standpoint, and demonstrate how these particles possess extended stability in the intracellular environment thus promising to retain their SERS activity *in vivo*. Finally I will show how their cytotoxicity is equal to or lower than that reported for spherical gold nanoparticles, using a multiparametric analysis and four different types of cytotoxicity assay. Compared to fluorescent tags, which suffer from photobleaching and limited multiplexing capability, SERS tags promise to become a much-improved tool in biomedical imaging.

COLL 87

Orientation and binding of near infrared absorbing dyes at a gold surface

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Surface Enhanced Raman Scattering (SERS) in the near-infrared (NIR) is an attractive technique for the in-situ detection of tailored nanoprobes in biomedical applications due to the greater depth of penetration in of NIR light in biological tissue and reduced interference when compared to SERS in the visible region. While a great deal of attention has been given to dye molecules that absorb light in the visible region, less

work has been devoted to the development and characterization of Raman reporters with absorption maxima resonant with common NIR lasers. A key challenge is the understanding of the surface layer formed when a specific label is anchored to the SERS substrate. Here we present thiophene- and selenophene-substituted chalcogenopyrylium (CP) dyes as a new class of ultra-bright, NIR-absorbing Raman reporters. We make use of surface-selective sum frequency generation vibrational spectroscopy (SFG-VS) to examine the affinity of the reporter for the gold surface and to define the surface orientation and manner of attachment for the CP dyes. This novel approach offers new opportunities for the development of designer rules for NIR Raman reporters. We present SERS spectra taken at different wavelengths and theoretical analysis that indicate plausible surface atomic arrangements at the surface.

COLL 88

Lysosomal sensing

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Analyte responsive nanoparticles are introduced to cells. Readout is carried out via fluorescence or SERS. Both modalities will be compared.

COLL 89

Supramolecular polymers for self-assembly in adhesive design

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Nature broadly utilizes a diverse selection of noncovalent interactions in the design of biomacromolecules, from hydrogen bonding to ionic interaction. These dynamic noncovalent interactions prove vital to the unique, complex self-assembled structures of many biological systems, such as the deoxyribonucleic acid (DNA) double helical structure. DNA employs a synergy between hydrogen-bonding and ionic bonding interactions to encode genetic information and stabilize the supramolecular structure, which inspires the rational design of novel monomers with ionic group and hydrogen bonding donor/acceptor. The reversible noncovalent interactions contribute to physically crosslinked supramolecular networks with stimuli responsiveness to external triggers, such as pH, temperature, and salt concentration. Furthermore, this transient physical crosslinking provides mechanical reinforcement for the cohesive strength of these supramolecular polymers, benefiting their performance as adhesives and coatings. Novel quadruple hydrogen-bonded, acrylic ureido-cytosine (UCy) monomers and doubly-charged DABCO salt-containing styrenic monomers allow the synthesis of supramolecular copolymers for adhesive applications. Relatively strong physically crosslinks from UCy and DABCO salt units significantly impact the self-assembly and

transient network formation, which leads to enhanced cohesive strength and stimuli-responsive adhesive performance. DABCO salt units associate and form ionic aggregates, while UCy groups π-π stack into quadruply hydrogen-bonded hard domains. Both functional monomers contribute to supramolecular polymers with microphase-separated morphologies, and enable potential applications in adhesives and thermoplastics.

COLL 90

Significant adhesion and toughness enhancement by bio-inspired nano-priming

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We developed bio-inspired catecholic primers that enhances adhesion performance of dental/medical/electronic adhesives up to an order of magnitude between mineral/metal surfaces compared to conventional primering techniques, e.g., silane- and phosphate-based graftings. A combination of experimental and computational studies has confirmed the ~1 nm thick monomolecular self-assemblies of the primers.The significant conceptual and practical advances have been made by (1) forming a perfect mono-molecular layer in 10-30 sec from a “water” solution of uniquely designed molecules, and (2) showing the highest bonding performance. This green and high performance priming technology can replace the conventional silane-based priming techniques, involving heat, toxic chemicals, and difficulties in quality controls. The toughness of dental and medical cements was also significantly increased with this catecholic priming technology. The bonding and toughness enhancement was shown in a million-fold stiffer (~4 GPa) polymeric materials than previously reports.

COLL 91

Designing high performance adhesives using principles learned from marine biology

Courtney Jenkins[1], *Michael Johnston*[2], *Taylor A. Jones*[1], *Heather Meredith*[2], *Michael North*[1], *Amelia Putnam*[1], *Heather Siebert*[1], ***Jonathan J. Wilker***[1,2], *wilker@purdue.edu.* (1) Department of Chemistry, Purdue University, West Lafayette, Indiana, United States (2) School of Materials Engineering, Purdue University, West Lafayette, Indiana, United States

Adhesives have been in use since well before ancient Egyptian society. Despite centuries of development, we still have a lot to learn about this topic. Marine organisms including mussels, barnacles, and oysters stick themselves to wet rocks quite well, yet man-made glues do not function when applied underwater. Our research group is working to both characterize biological adhesives and use the resulting insights to design new synthetic materials. Here we will show how functional proteins can be

represented by synthetic polymers if the proper adhesion chemistry is incorporated therein. By exploring several aspects of polymer design, properties including high strength bonding, curing underwater, tunable flexibility (or modulus), degradability, and cytocompatibility can all be achieved. These biomimetic materials are now being explored for uses ranging from the joining of structural materials (e.g., metals, plastics, woods) to biomedical repair of soft and hard tissues.

COLL 92

Novel adhesives based on biomimetic approach

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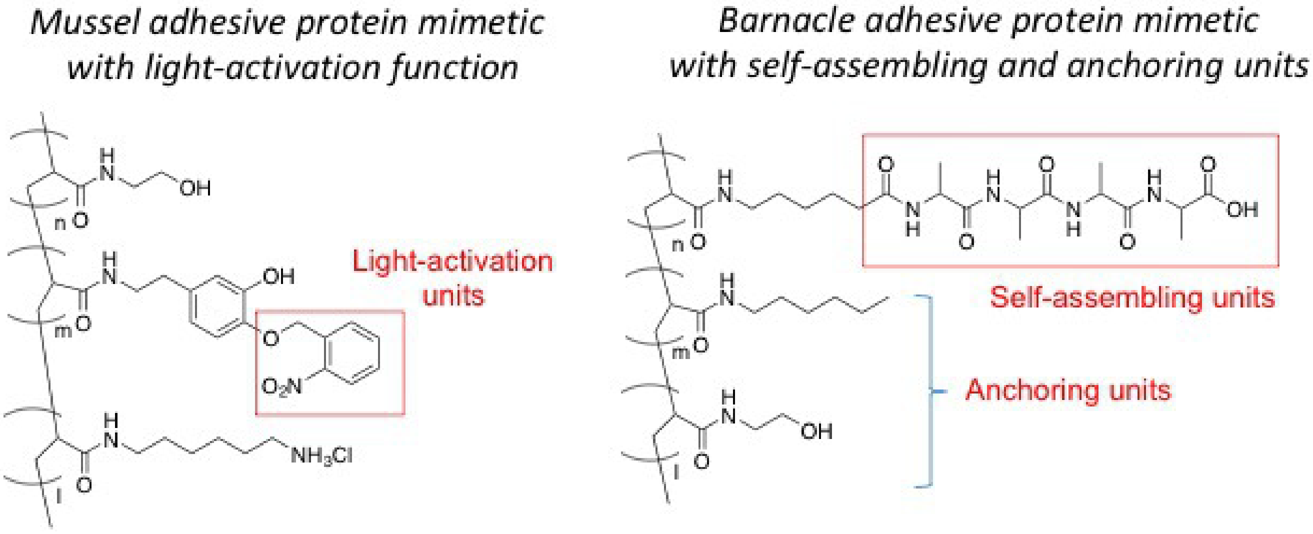
Novel biomimetic adhesives were designed based on adhesive proteins of marine organisms. An acrylamide-type copolymer containing hydroxyl, amino and caged catechol groups was synthesized as a functional mussel adhesive protein (MAP) mimetic, which shows light-activated gelation and adhesive properties. A polyacrylamide composed of self-assembling and surface-anchoring groups was synthesized as a mimetic of barnacle underwater adhesive proteins. Gelation of the aqueous polymer solution was observed through introduction of hydrophobic alkyl tail into self-assembling oligo-alanine groups. The hydroxy and hexyl groups were effective for anchoring to the substrate to prevent interfacial peeling. Metal and resin plates adhered by gelation of the adhesive polymer aqueous solution.



COLL 93 – Withdrawn.

COLL 94

Elucidating T_g and polarity effects in bioinspired catechol synthetic adhesives towards improved interfacial adhesion

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Inspired by the versatile adhesion of marine mussel foot proteins and the high concentration of Dopa residue (3,4-dihydroxyaniline) expressed therein, a significant amount of research involving catechol based polymeric materials have been reported. As a class, the synthetic polymers have shown potential as modest adhesives with broad substrate applicability. Initial fundamental studies sought to elucidate the local chemical environment (e.g. pH, electrostatics, polarity) of the catechol moiety to improve the toughness and adhesion mechanisms, although many of the fundamental polymer physics aspects have not been examined. To clarify the impacts of polarity and T_g effects in catechol based polymeric systems, we have synthesized a series of polyacrylates with pendent catechols in order to correlate T_g to adhesion on alumina substrates. Furthermore, surface spectroscopy was explored to analyze the mechanism of action by which the polymeric materials interact with the substrate. It is hoped that our work can lead to an improved understanding of the catechol functionality, and may allow utility in high performing adhesives under extreme environments that include broad temperature and humidity ranges.

COLL 95

Hybrid aminopropyltriethoxysilane-polydopamine coatings and adhesive properties

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The presence of water generally leads to deterioration in performance of synthetic polymer adhesives, particularly at organic-inorganic interfaces. We hypothesized that incorporation of catechol moieties in coupling agents would improve adhesive bonding in a moisture-rich environment without adversely affecting the adhesive properties of coupling agents under drier conditions for the following reasons: (1) polydopamine coats a broad range of materials, (2) catechols are capable of chemisorption on a variety of metal oxides in the presence of water, (3) and dopamine moieties are known to provide mussels with strong adhesion in underwater environments. In this presentation, we demonstrate the incorporation of 3-aminopropyltriethoxysilane (APTES) coupling agents, which are capable of covalent substrate binding to metal oxides, into

polydopamine coatings. Variable energy X-ray photoelectron spectroscopy (VE-XPS), conventional XPS, near-edge X-ray absorption fine structure (NEXAFS), Fourier transform infrared-attenuated total reflectance (FTIR-ATR), infrared spectroscopy and ellipsometry measurements were used to investigate changes in coating composition and thickness, which suggest covalent incorporation of APTES into polydopamine. These coatings can be deposited either in tris buffer or by using an aqueous APTES solution as a buffer without tris. APTES-dopamine hydrochloride deposition from solutions with molar ratios between 0:1 and 10:1 allowed us to tune the coating composition across a broad range. Preliminary lap shear studies showed enhanced adhesive properties for surfaces treated with aminopropyltriethoxysilane-polydopamine coatings.

COLL 96

Reverse micelles from hydrogen bonding surfactants

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This presentation will describe the formation of reverse micelles that consist of hydrogen bonding cationic surfactants paired with anionic sugar acids or other carboxylate containing counterions. The resulting structures are uniform and stable under ambient conditions. Hydrogen bonding interactions between cationic amphiphiles and their counterions promotes reverse micelle formation and in many cases eliminates the need for cosurfactants. One member of this class of cationic surfactants is hexadecyldimethylammonium acetamide that forms amide-carboxylate hydrogen bonds with glucuronate in chloroform. Related systems will be described.

COLL 97

Multiscale modeling of hairy vesicles

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We develop a computational model by coupling implicit solvent coarse-grained dry martini model with a lattice-Boltzmann fluid in order to design and characterize nanostructured soft materials. The long range hydrodynamic effects are included in the system through the implementation of the Lattice-Boltzmann fluid. This removes the necessity of using explicit solvent molecules. The particle dynamics is resolved via the Molecular Dynamics simulation method. Our objective is to generate a stable vesicle composed of single (DPPC) and multiple (DPPC and Pegylated DPPC) phospholipid

species through the use of implicit solvent coarse-grained model with long range hydrodynamics in order to investigate physiological processes occurring on the mesoscopic spatio-temporal scales. By using a four to one mapping scale of Martini model, the DPPC molecule is represented by four head beads and eight tail beads. The twelve beads are further divided into four types, each with different interaction energies and length scales. Analogous models are developed for the other phospholipids. The vesicle is initially equilibrated using the Dry Martini force field without Lattice-Boltzmann fluid. In order to couple Dry Martini model with Lattice-Boltzmann fluid, node particles are placed on the surface of the hydrophilic head beads of the phospholipid molecules. These nodes and the surrounding head beads are treated as a rigid particle so that hydrodynamic forces can be transferred from fluid to lipid molecules. We investigate the dynamical, structural and morphological properties of the resulting hybrid aggregates. The results of our investigations can be used for the design and prediction of novel hybrid soft and bio-materials at the mesoscale for various applications in medicine, sensing and energy.

COLL 98

Structure-function relationships of bio-inspired rhamnolipid surfactants

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Monorhamnolipids are a class of biosurfactants with outstanding surface activity. Rhamnolipids are 2-3 orders of magnitude more potent than SDS based on critical micelle concentration (CMC) values. They are potential candidates for biodegradable and non-toxic replacements of current specialty synthetic surfactants. The structure of the most abundant rhamnolipid is comprised of a *double tailed* lipid unit of (***R***,***R***)-β-hydroxyalkanoyl-β-hydroxyalkadecanoic acid, trans-1,2-O-glycosylated by monocarbohydrate L-rhamnopyranosyl units (Rha-C10-C10). Their relative structural complexity has precluded their commercialization on scales comparable to simpler related materials such as polyalkylglucosides until recently. The exploration of the structure-function relationships in these materials is crucial for 1) the design and manufacturing of glycolipids that are synthetically more readily accessible with similar or better performance, and 2) demonstrating the tailorability of rhamnolipid properties. In this work, we have addressed questions related to such structure-function relationships by systematically modifying the hydrophobic moieties of monorhamnolipids. Here, we explore the effect of lipid tail symmetry on the surface activity and aggregation behavior of diastereomeric mixtures of a series of monorhamnolipids. Access to pure materials at the gram scale with specific structural features that are bio-inspired but either not found in nature, impossible to harvest and isolate from microbial colonies, or impractical to produce by means of the synthetic methodologies previously reported, required development of an original method to obtain them in pure form and with the desired lipid tails. The thermodynamics of their surface activity are described by surface tensiometry at the air-water interface at pH 8. Characteristics of their aggregation behavior in

aqueous solutions including hydrodynamic radius, aggregation number, and aggregate morphology are determined using dynamic light scattering and time resolved fluorescence quenching.

COLL 99

Some effects of surface heterogeneity on the morphology of surfactant self-assembled aggregates

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Surfactants are ubiquitous chemicals in academia, industry, and consumer products. Just in the oil and gas industry, these compounds can be used for enhanced oil recovery and environmental remediation strategies. In consumer-care products, surfactants find wide use in soaps, shampoos, and many other products. Fundamental investigations have been focused on surfactants for many years, not only because self-assembling systems present a number of questions that are intrinsically interesting, but also for the expected positive impacts in a variety of industrial sectors, including nanotechnology and drug delivery. However, most studies have concentrated on homogeneous systems, either in the bulk, or at contact with pristine surfaces. A number of recent discoveries suggest that perhaps the behavior of surfactants on heterogeneous surfaces differs compared to that expected based on results obtained on homogeneous substrates. In this presentation we will present recent results obtained using multiple computational strategies to unveil the effects of heterogeneous surface properties on the morphology of self-assembled surfactant aggregates. We will also discuss how our results can be explained by an expression for the system free energy that accounts for the elastic deformation of the self-assembled surfactant film.

COLL 100

NMR investigations of the sphere to rod phase transition for cationic gemini surfactants

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Ionic gemini surfactants are known to adopt various aggregation morphologies that depend on the structure of the surfactant, the surfactant concentration, and the structure and concentration of counterions. We are studying the transition from spherical to rodlike micelles of several cationic gemini surfactants, alkanediyl-alpha-omega-bis(dodecyldimethylammonium) bromide, 12-*n*-12 2Br, with n = 2, 3, and 4. The three surfactants have a similar CMC (around 1 mM), but become viscous (implying tangled rodlike micelles) at very different concentrations: ~5 mM for 12-2-12, ~40 mM for 12-3-12, and >100 mM for 12-4-12. One major difficultly in this project is a lack of methods for precisely determining the sphere-to-rod transition. To that end, we will describe our work identifying nuclear magnetic resonance (NMR) measurements that indicate the sphere to rod transition, such as chemical shift, relaxation, and pulsed-field-gradient diffusion. We will also discuss our experiences using probe molecules for NMR diffusion measurements on these systems. Nonpolar probe molecules are necessary to

distinguish the diffusion of the micelle from the (faster) diffusion of the surfactants themselves, since the surfactants rapidly exchange between free and aggregated states. Curiously, some probe molecules (e.g. ferrocene) that are effective for single-chain surfactants seem to be unsuitable for use with gemini surfactants.

COLL 101

Molecular insights into the structure of nanoemulsions

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Nanoemulsions have attracted a growing interest due to their potential applications with drug delivery, in the production of nanomaterials, and more. However, the advancement of applications of nanoemulsions has preceded a molecular level understanding of their behaviors, such as stability, surface adsorption, and solvent confinement. We focus on two surfactant systems at both the planar oil-water interface, and the curved regular emulsion and reverse emulsion interfaces. This presentation will report on recent work in our lab towards understanding the similarities and differences of these different oil-water systems, in particular, the behaviors and effects of interfacially adsorbed surfactants in different interfacial geometries. These studies combine vibrational sum-frequency spectroscopy in the scattering and reflective geometries, light scattering, surface tension and molecular dynamic simulations.

COLL 102

Effects of constituent block size on the interfacial dynamics of $C_i(EO)_n(PO)_m$ block copolymer surfactants

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Block copolymer surfactants have well documented uses in both industrial detergents as well as novel laboratory applications. Their increased use demands thorough characterization of their interfacial behavior. Measurements of equilibrium behavior and discernment of interfacial transport of these surfactants is not only crucial to their application but also allows for analysis of fundamental surfactant characteristics. The effects of varied chemistry and varying constituent block size on the interfacial behavior of this family of surfactants is lacking in the literature. Moving forward, understanding the interfacial dynamics of these surfactants gives opportunities to expand their areas of application and the ability to fully characterize their behavior.

This study explores three commercial alkyl-poly(ethylene/propylene glycol) surfactants (LS-36, LS-54, LS-24) at the air-water interface. Dynamic interfacial tensions are measured on the micro-scale using the technique of microtensiometry, allowing for

examination of behaviors at interfaces of varying size, concentration, and mixture composition. The analysis of dynamics is then used within a theoretical framework to quantify adsorption and ascertain relevant parameters. The data is then compared with data for surfactants of varied chemistries to study the effect of the additional polymer block on the interfacial behavior.

COLL 103

Alkyl thioglycoside green surfactant properties: Effects of various disaccharide and monosaccharide headgroup and alkyl tail length

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The relationship between surfactant molecular structure and solution phase properties is investigated for a series of thioglycoside surfactants. Glycolipid surfactants are attractive greener alternatives to current commercial nonionic surfactants due to high biodegradability, low toxicity, renewable feedstock sourcing, and sensitive structure and property tuning. The surfactancy and application is related to molecular structure which can be tailored for specific function. This work investigates the solution phase properties of thioglycosides with disaccharide (cellobiose, maltose, lactose) and monosaccharide (galactose, glucose) headgroups and varying straight-chain alkyl tails of 8-12 carbons linked through a *S*-glycosidic bond, rather than the more widely studied *O*-glycosides. These thioglycosides form a range of phase properties from gel-like to micellar solutions at low concentrations (<1% w/w) depending on the headgroup and tail length. For example, thioglycosides with cellobiose and lactose headgroups and decyl or dodecyl chains form gel-like phases in the dilute concentration regime, whereas those with lactose headgroups and octyl chains do not. The microenvironments of these surfactant phases are investigated by optical microscopy and fluorescence spectroscopy. For surfactants that form isotropic micellar solutions, the critical micelle concentrations, minimum surface tensions, and micellar environments are investigated by surface tensiometry, dynamic light scattering, fluorescence spectroscopy, and crossed polarized imaging. Vast solution phase changes are observed with modifications of the headgroup, alkyl tail length, and glycosidic bond type documenting the sensitivity of surfactant performance attributes to subtle changes in molecular structure.

COLL 104

Molecular simulations of SPAN80 desorption from the squalene-water interface

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Extensive all-atom molecular dynamics calculations on the water-squalane interface for nine different loadings with sorbitan monooleate (SPAN80), at T = 300K, are analyzed for the surface tension equation of state, desorption free energy profiles as they depend on loading, and to evaluate escape times for absorbed SPAN80 into the bulk phases. These results suggest that loading only weakly affects accommodation of a SPAN80 molecule by this squalane-water interface. Specifically, the surface tension equation of state is simple through the range of high tension to high loading studied, and the desorption free energy profiles are weakly dependent on loading here. The perpendicular motion of the centroid of the SPAN80 head-group ring is well-described by a diffusional model near the minimum of the desorption free energy profile. Lateral diffusional motion is weakly dependent on loading. Escape times evaluated on the basis of a diffusional model and the desorption free energies are 7 × 10^−2 s (into the squalane) and 3 × 10^2 h (into the water). The latter value is consistent with irreversible absorption observed by related experimental work.

COLL 105

Specific ion effects on the reduction of interfacial tension by ionic surfactants

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Surfactant flooding is an oil recovery process in which an aqueous surfactant solution is injected into a reservoir to improve recovery relative to water flooding. While the degree of improvement afforded by surfactants is impacted by the salinity of the injected solution and reservoir brine, the mechanisms by which dissolved salts affect the chemical and transport processes in the reservoir remain poorly understood. In this study, we address one of several potential mechanisms: the effect of specific ions on the reduction of hydrocarbon/brine interfacial tension (IFT) by ionic surfactants. To help quantify this effect, we develop a predictive molecular thermodynamic model and validate it against experimental data. In the thermodynamic model, we capture the adsorption of an ionic surfactant at the fluid-fluid interface using a surface equation of state, and we capture the counter-ion distribution profiles of dissolved salts near the interface using a modified Poisson-Boltzmann equation. This equation permits modeling of specific-ion effects by incorporating ionic dispersion interactions, which depend on the polarizabilities and sizes of ions. To test the model, we calculate the IFT of dodecane/water at different concentrations of NaCl and CsCl, and compare with experimental measurements using force tensiometry. Initial results from the model and experiments agree well, with both showing that specific ions (NaCl and CsCl), in addition to total salinity, impact the efficiency of the surfactant in reducing IFT.

COLL 106

Microenvironment of monorhamnolipid aggregates and their synthetically produced diastereomers as a function of solution conditions

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Rhamnolipids have relatively low toxicity, high biodegradability, and surfactant properties that make them of interest as green replacements for more toxic synthetic surfactants. Typically produced by strains of *Pseudomonas aeruginosa*, rhamnolipid biosurfactants have been studied previously using a wide variety of techniques. However, little is known about their detailed phase behavior as a function of solution conditions such as ionic strength, pH, surfactant concentration, and temperature. To better understand these properties, steady-state fluorescence spectroscopy methods are utilized to probe surfactant microenvironment using the solvatochromic properties of the fluorogenic dyes prodan and laurdan with the native monorhamnolipid (mRL) mixture harvested and purified from *P. aeruginosa* ATCC 9027, an exclusive producer of mRLs. By dissolving these dyes within mRL aggregates and observing their solvatochromic behavior, detailed insight into surfactant phase can be attained. Both experimental evidence as well as computational evidence from all-atom molecular dynamics simulations indicate that mRLs form spherical micelles at high pH and low surfactant concentration, whereas elongation and/or vesicle formation characteristic of lamellar phases is observed at low pH and moderate to high surfactant concentration. A unique synthetic method has also allowed the production of mRL variants with very high purity but with an expanded set of diastereomers and hydrophobe chain length. Similar studies are performed on these synthetic variants as a function of solution conditions and compared with the properties of the native mRLs to gain insight into structure-function relationships resulting from changes in stereochemistry and hydrophobe characteristics.

COLL 107

Hierarchical assembly of gold nanoparticles for SERS biosensing

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The integration of nanoparticle superstructures into daily life applications faces major challenges including the simplification of the self-assembly process, reduced cost and scalability. It is however often difficult to improve on one aspect without losing on another. Stamping and templated assembly have been used to create single- and multi-particle patterns, but these are typically limited to a small number of particles. We have recently developed a bench-top method that allows patterning a macroscopic substrate with gold nanoparticle supercrystals in a one-step process. The method allows parallelization and patterned substrates can be made with high throughput. The self-assembly of a variety of building blocks into crystalline superstructures takes place upon solvent evaporation and their precise placement over millimeter scale areas is induced by confinement of the colloidal suspension in micron sized cavities. We mainly focus on gold nanorods and demonstrate their hierarchical organization up to the device scale. The height of the formed nanorod supercrystals can be tuned by simply varying nanorod concentration, so that the topography of the substrate and the resulting optical properties can be readily modulated. The crystalline order of the nanorods results in homogeneous and high electric field enhancements over the assemblies, which is demonstrated by surface enhanced Raman scattering spectroscopy detection *in vitro*.

COLL 108

Colorimetric stress sensor based on plasmonic nanostructures

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Plasmonic metal nanostructures have received considerable attention due to their broad applications in optoelectronics, sensing, catalysis and photothermal therapy. In this presentation we report the development of plasmonic nanostructure-based stress-responsive colorimetric sensors that can memorize the stress that the system has experienced. We will use two examples to demonstrate the design principles of the plasmonic stress sensors: one is based on the orientational dependence of localized surface plasmon resonance of gold nanorods, and the other takes advantage of the plasmonic shift associated with the disassembly of one-dimensional gold nanoparticle chains. In both cases, the plasmonic shifts are caused by the plastic deformation of the surrounding polymer matrix. These stress-responsive materials can be used to capture and record the pressure distribution and magnitude between two contacting or impacting surfaces by outputting color information.

COLL 109

Optical analysis of the orientational order parameter in gold nanorod composites

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The development of modern nanotechnology over the past decade has enabled fabrication of various subwavelength structures that give rise to novel mechanical and physical properties not normally found in natural materials. Among them, composites of

nanoparticles embedded in a polymer matrix have brought intensive interest. With a combination of superior mechanical, electrical and plasmonic properties from metallic nanoparticles, processability and flexibility of polymers, and a low cost bottom-up chemical fabrication process, these structures are widely considered as competent candidate for novel devices. However, since many of these properties are sensitive to spatial distribution and orientation of the nanoparticle building blocks, it is important to develop tools and models that can effectively characterize and describe the inhomogeneous structure as well as orientation of the building blocks.

In this presentation, we propose a new approach to characterize the orientation distribution of the uniformly dispersed nanorods embedded in PMMA matrix through spectroscopy ellipsometry. The composite thin films are produced under conditions that produce thin films with a preferred in-plane rod orientation. Under the coupling between the localized surface plasmonic resonance (LSPR) within individual rods, we treat the composites as a homogeneous amorphous metamaterial with uniaxial birefringence and use ellipsometry to measure both the film thickness and the birefringent index of refraction. Finite-difference time-domain (FDTD) simulations and effective medium theory calculations are performed to relate the measured optical anisotropy to the out-of-plane order parameter. This new approach can be potentially applied to other common nanoparticle composite systems to replace the commonly used, but more complicated and costly electron microscopy analysis.

COLL 110

Magnetic field induced symmetry breaking in anisotropic plasmonic nanostructures

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Anisotropic noble metal nanostructures have attracted tremendous interest among scientists due to their geometry modulated plasmonic properties. Understanding the direct relationship among geometry, the nature of the plasmonic mode and resultant optical response will significantly benefit the further development and applications of plasmonic metamaterials. Herein, by using magnetic circular dichroism (MCD) spectroscopy, we explore the geometry induced symmetry breaking of the magnetoplasmonic response in gold nanorods (GNRs). In GNRs, surface plasmon resonance (SPR) along different directions exhibit distinct MCD response, which can be further manipulated by changing the aspect ratio of GNRs. Furthermore, GNR assemblies with different configuration (end-to-end and side-by-side) show conformation dependent plasmonic MCD response. Theoretical model and simulation elucidate the intrinsic relationship among the symmetry of SPR modes in GNRs, geometry factors and the resultant plasmonic MCD response. This work opens the way to design and fabricate nanostructures with tunable magnetoplasmonic response.

COLL 111

High-strength magnetically-switchable plasmonic nanorods assembled from a binary nanocrystal mixture

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Next-generation ‘smart’ nanoparticle (NP) systems call for the synthesis of NPs that are precisely engineered in size, shape, and composition and that introduce multiple functionalities. Here, we synthesize size- and shape-engineered, multifunctional NPs by combining the best of top-down fabrication technologies and bottom-up nanocrystal (NC) self-assembly. We synthesize these NPs by templating them in the shape of nanorods (NRs) from mixtures of superparamagnetic $Zn_{0.2}Fe_{2.8}O_4$ NCs and plasmonic Au NCs. Exchange of surface ligands drives Au NC fusion and forms a NC network in the NRs that imparts the NRs with high mechanical strengths, and with polarization-dependent, infrared surface plasmon resonances characteristic of Au NRs. The combination of the strong magnetic and plasmonic response enables the infrared transparency of suspensions of these hybrid NRs to be modulated by an external magnetic field, which is then exploited to demonstrate ‘smart’ windows.

COLL 112

Surface modification of silver nanomaterials for extraction-surface enhanced Raman spectroscopy

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Surface enhanced Raman spectroscopy (SERS), which could provide the enhanced Raman spectra of target molecules with the enhancement factors with the order of million magnitudes, has been developed into a reliable platform for rapid and sensitive analysis. The distance from analytes to substrates is crucial for SERS detection because SERS could only strongly enhance the Raman signal of molecules close to the substrates. However, Persistent Toxic Substances (PTS) show weak affinity to the surfaces of traditional SERS substrates for their chemical inertness. The modification of the SERS substrates, which could enrich PTS onto the substrate surface, could greatly improve the SERS performance for PTS sensing.

Due to the low concentration of analytes and the complexity of the sample matrix, efficient extraction technique is essential for reliable and accurate analysis. Coupled with membrane extraction, SERS could overcome these shortages as an integrated novel analytical technique. The membrane extraction media, such as SERS active filter

paper, disordered silver nano-wire filter membrane, have been fabricated for the combination of sample preparation and SERS detection, which realize the qualitative and quantitative detection of various water contaminants. To reduce the occurrence of analytic error and shorten the overall analysis time, solid phase extraction (SPE) has been combined with SERS to develop a SPE-SERS device. Silver nanodendrites, which have a relatively large surface area and porous structure, were modified by alkanethiols to fabricate SERS-active SPE column. The total analysis time for one sample including extraction, spectral acquisition, elution and intermediate process will be less than 1 minutes. This will greatly benefit the in-field and in-situ analysis of environmental contaminants. To realize the rapid analysis of PTS, especially on-site detection after the emergent environmental accidents, the integrated hyphenated technique combining solid phase microextraction (SPME) and SERS for the rapid analysis of PTS has been established. The micro-extraction fiber, such as sliver nanoparticles aggregates/Ag-Cu fiber, silver nanoplate-decorated copper wire, have been realized the detection of the environmental pollutants on site. The integrated hyphenated fiber could be further confirmed by GC-MS.

COLL 113

Ag@Au concave cuboctahedra for monitoring Au-catalyzed reduction and oxidation reactions by surface-enhanced Raman spectroscopy

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We report a facile synthesis of Ag@Au concave cuboctahedra by titrating aqueous $HAuCl_4$ into a suspension of Ag cuboctahedra in the presence of ascorbic acid (AA), NaOH, and poly(vinyl pyrrolidone) (PVP) at room temperature. Initially, the Au atoms derived from the reduction of Au^{3+} by AA are conformally deposited on the entire surface of a Ag cuboctahedron. Upon the formation of a complete Au shell, however, the subsequently formed Au atoms are preferentially deposited onto the Au{100} facets, resulting in the formation of a Ag@Au cuboctahedron with concave structures at the sites of {111} facets. The concave cuboctahedra embrace excellent SERS activity that is more than 70-fold stronger than that of the original Ag cuboctahedra at an excitation wavelength of 785 nm. The concave cuboctahedra also exhibit remarkable stability in the presence of an oxidant such as H_2O_2 because of the protection by a complete Au shell. These two unique attributes enable *in-situ* SERS monitoring of the reduction of 4-nitrothiophenol (4-NTP) to 4-aminothiophenol (4-ATP) by $NaBH_4$ through a 4,4'-dimercaptoazobenzene (*trans*-DMAB) intermediate and the subsequent oxidation of 4-ATP back to *trans*-DMAB upon the introduction of H_2O_2.

COLL 114

DNA-based plasmonic and photonic metamaterials

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This talk will emphasize recent theory and experiments in collaboration with Chad Mirkin in which DNA-functionalized nanoparticles are used to create superlattices of plasmonic and photonic nanoparticles. The synthetic work involves a bottom-up assembly technique in which DNA hybridization drives the self-assembly of nanoparticle superlattices with exquisite control over the atomic, nano and micron level structure of the materials. We show that the array structures lead to new kinds of hybrid optical modes in which localized surface plasmon resonances in the nanoparticles are coupled with photonic modes of the lattices, including Bragg modes, Fabry-Perot modes and other modes. These hybrid modes are often much narrower than the isolated particle plasmons, and films composed of these superlattices have unusual metamaterials properties related to strong interactions between photonic modes and plasmons, and between excitons and plasmons.

COLL 115

Filomicelles self-assembled from degradable di-block copolymers circulate longer in vivo, and deliver retinoids & chemotherapeutics to irreversibly control carcinoma cell fate

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Conventional injection of semi-soluble drugs hit both healthy and tumor cells, causing side effects that limit dose. This approach might be broadened with better delivery, and herein, flexible ‘filomicelles’ demonstrate effective delivery of two very different hydrophobic compounds. Retinoic acid (RA) and other retinoids regulate RA receptor transcription factors that induce differentiation and arrest proliferation of many cell types. Paclitaxel, on the other hand, stabilizes microtubules and induces aneuploidy by blocking mitosis at the metaphase-anaphase transition, which greatly increases cell death. When cancer cells are treated with either of the drugs alone over several periods of the normal cell cycle, cancer cell populations revert back to the original proliferative state, consistent with relapse commonly seen after chemotherapy. Combining RA with select chemotherapeutics has produced durable cures of select cancers, notably pro-myeloblastic leukemia (PML), where RA differentiates cells while chemotherapeutic kills the cancer stem cell. With carcinoma lines, we find dual treatment with RA plus Paclitaxel increases, aneuploidy, Lamin-A (a marker of differentiation) levels and cell death beyond those achieved by either drug single-handedly, with effects being durable. A month after treatment, relapse rates are low for RA-Paclitaxel treated cells (15%), compared to almost all (92%) for cells treated with Paclitaxel alone. Trends with the key cell cycle factor Cyclin-D1 and proliferation marker Ki-67 help clarify the basis for drug synergy. These effects are greatly enhanced by loading the drugs into filomicelles. Self-

assembled from degradable di-block copolymers of PEG-PBCL, the aromatic polymer improves performance over other conventional aliphatic ones due to better loading of aromatic chemotherapeutics (such as Paclitaxel) in its core. Crucially, the flexibility of these filomicelles permit them to circulate longer *in vivo* compared to other spherical nano-carriers. Preliminary tests *in vivo* demonstrate sustained delivery for days as well as efficacy in shrinking tumors. Free drug injections of RA-Paclitaxel combination are able to shrink tumors, a feat not achieved by free Paclitaxel alone. These results highlight the irreversible synergy of killing cancerous cells while driving differentiation. Flexible ‘filomicelles’ circulate longer and lead to better accumulation in the tumors, increasing the efficacy of delivery, and hence the treatment.

COLL 116

Rational controlled morphology transitions in the self-assembled polystyrene-hydrophilic polyhedral oligomeric silsesquioxane (POSS) giant surfactants in solution

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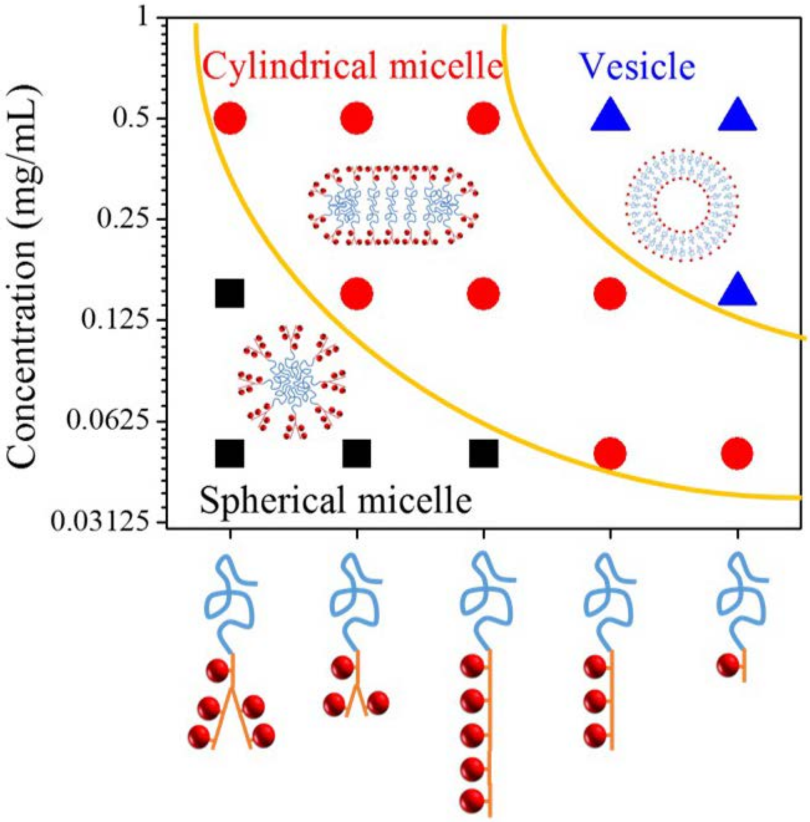
A series of polystyrene (PS)-polyhedral oligomeric silsesquioxane (POSS) based giant surfactants, with different number and topology of POSS groups, are synthesized through a new “click” chemistry. They are found to self-assemble into different supramolecular structures including vesicles, cylindrical and spherical micelles in H_2O/DMF mixed solvents. The self-assembled structures are confirmed by light scattering techniques and TEM. The transitions among different morphologies can be rationally controlled by the number and topology of the APOSSes, which the cross-section areas play an important role. Moreover, the giant surfactant concentration also has a significant effect on the different morphologies due to the change of the deprotonation degree of the carboxylic acid groups on APOSS. A phase transition diagram can be obtained by summarizing all the experimental results, which have a potential to predict the morphologies of the giant surfactants in similar conditions. It provides a feasible way of assembling these novel hybrid materials to desired functional structures in many fields.



COLL 117

Functionalized microparticles through PEG hydrogel encapsulation of nanoparticles: A suitable vehicle for passively targeted lung delivery

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Microparticles have attracted broad interest as a vehicle for many diagnostic and therapeutic agents treating a wide range of disease conditions. However, preparing microparticles of the desired size and with a general chemistry allowing for the encapsulation or controlled release of multiple agents remains a challenge. We have developed emulsion-polymerized microparticle composites consisting of a poly(ethylene glycol) (PEG) matrix encapsulating functional nanoparticles. The PEG matrix is polymerized through a Michael addition between aqueous phase diacrylate and trithiol PEG macromers in a water/oil emulsion, and functional nanoparticles may be therapeutic agent releasing or imaging agent bearing nanoparticles dispersed in the PEG macromer aqueous phase. Nanoparticles used here are composed of a hydrophobic core stabilized by amphiphilic block copolymers prepared by the Flash NanoPrecipitation process. Microparticle diameter and polydispersity can be controlled primarily by the viscosity ratio of the emulsion phases and the applied shear rate during

emulsification in a Couette cell, while microparticle functionality is due to the encapsulated nanoparticle species. This decouples the microparticle polymerization and size control from the microparticle functionality. Such independently tunable microparticles are well suited candidates for intravenous lung-targeted drug delivery, as the microparticle size can be tuned to effect passive retention in the lung after injection. Camptothecin (CPT) releasing microparticles can act as lung-targeted sustained-release depots for the treatment of non-small cell lung cancer. CPT is a cytotoxic agent that generates dsDNA cleavage of replicating DNA, making this a potent drug against proliferating cells when dosed in a sustained manner within its (narrow) therapeutic index. The use of CPT-releasing microparticles can widen the therapeutic index by increasing the local concentration of drug in the lungs and decreasing systemic exposure and toxicity while providing a sustained release dose.

COLL 118

Characterization of amphiphilic copolymer micelles for drug delivery

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Amphiphilic copolymers with a polyethylene glycol (PEG) backbone and side chains of different molecular weight and hydrophobicity form spherical aggregates (micelles) in aqueous solution. These copolymer aggregates can be used as carriers of hydrophobic drugs and for imaging purposes. Certain types of aggregates are expected to be more suitable for incorporation of small hydrophobic molecules in their core and subsequent release. The aggregates adsorb very sparingly to hydrophilic, negatively charged surfaces because of their outer, PEG-containing region. Atomic force microscopy (AFM) in tapping mode in liquid was used to characterize the adsorbed aggregates to detect the presence of a hydrophobic core and monitor possible size changes with other molecules incorporated. A good correlation was found between the volume of individual adsorbed aggregates of different copolymers as determined with AFM and light scattering data on the corresponding aggregates in solution.

COLL 119

Factors influencing the release kinetics of hydrophilic compounds encapsulated in polymeric nanoparticles using inverted flash nanoprecipitation

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Biologics, such as peptide-based antibiotics, polypeptides, and protein therapeutics, have shown strong growth within the pharmaceutical industry in recent years.

Nanoparticles (NPs) have been commonly employed for small molecule drugs, but formulations of water-soluble biologics generally suffer from low loadings and poor encapsulation efficiencies. Recently, a novel process for the formulation of biologics, “inverted” Flash NanoPrecipitation, was introduced. The process, which achieves high loadings and encapsulation efficiencies, can be used for the production of NPs and microparticles (MPs). The technique is a modification of the Flash NanoPrecipitation (FNP) procedure for encapsulating hydrophobic molecules in block copolymer-stabilized NPs. The inverse process yields a crosslinked hydrophilic core surrounded by a hydrophobic polymer block. When producing NPs, a second FNP step applies an outer PEG coating. The nanoparticles produced by inverse FNP therefore consist of three distinct layers: a hydrophilic inner core, a hydrophobic layer, and an outer PEG corona.

Here, we describe the major features controlling release from NPs produced via this process. Fluorescently-tagged dextrans and maltodextrins of different molecular weights were used to characterize encapsulation efficiencies in both FNP steps as well as release trends over time. This sugar selection enabled variation of the encapsulant molecular weight while maintaining a consistent chemical nature and avoiding any confounding effects from charge interactions with the crosslinked polymer core. The encapsulant molecular weight and hydrophobic polymer block molecular weight were systematically evaluated using this system and were found to affect release kinetics.

COLL 120

Interface-engineered PEG-PCL delivery system for docetaxel controlled delivery

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Chemotherapeutic drugs used in the treatment of various forms of cancer generally lack selectivity between normal and malignant cells and consequently are associated with significant adverse effects, many life-threatening. Drug delivery systems (DDSs) can change the pharmacokinetics of these cytotoxic drugs, significantly improving their therapeutic index, can protect the encapsulated drugs against degradation, improve their bioavailability, and maintain the free drug concentration within the therapeutic window.

Amphiphilic block copolymers combining hydrophilic biocompatible polyethylene glycol (PEG) blocks with hydrophobic biodegradable blocks can spontaneously self-assemble in water generating robust supramolecular nanoaggregates that can be loaded with drugs for generating a controlled delivery system. The dense PEG brush on the surface of these nanosystems reduces the interaction with proteins and figurative elements of the blood, conferring “stealth” properties and thus increasing the circulation time of the delivery system.

We will present our recent efforts towards engineering the interface in conventional amphiphilic PEG-PCL diblock copolymers and its effect on dynamic stability, docetaxel

loading and release profile, towards the generation of a novel anticancer delivery system.

COLL 121

Monodisperse plasmonic metal nanocrystals with plasmon wavelengths tunable from ~700 nm to ~15 microns

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Plasmonics has been one of the hottest topics in the fields of nanomaterials and nanophotonics. Currently, preparation of metal nanocrystals resonant at visible frequencies has been extensively developed. Nanocrystals of high quality have largely boosted a variety of plasmon-enabled applications and devices. However plasmonics in near-infrared (NIR) and mid-infrared (MIR) regions is far less advanced, although it is particularly desired for the development of NIR and MIR light manipulation, bio-imaging, ultra-sensitive bio- and chemical sensing. One of the main challenges comes from difficulties in colloidal synthesis of metal nanocrystals with strong anisotropy and high uniformity.

We have demonstrated a method for producing Au nanobipyramids (NBPs) with number percentages approaching 100%. The plasmon wavelengths of Au NBPs are tunable from ~700 to ~1600 nm, covering the fiber-optic communication windows located at 1300 nm and 1550 nm, as well as the two biological transparency windows located in 650-950 nm (first NIR window) and 1000-1350 nm (second NIR window). These unique features of Au NBPs make them an ideal candidate for infrared light communication, photothermal therapy and bio-imaging. Furthermore, we have developed a method for the synthesis of highly uniform Ag nanorods (NRs) through Au NBP-directed Ag overgrowth. The plasmon wavelengths of the Ag NRs can be varied from ~1 to ~15 microns, covering the “fingerprints” of most molecular vibrations. We have observed surface enhanced C-H stretching signals of organic molecules based on these Ag NRs, which could be a new wet-chemistry platform for ultra-sensitive bio- and chemical sensing based on surface enhanced infrared absorption spectroscopy.

Plasmonic metal nanocrystals with plasmon wavelength tunable from ~700 nm to ~15 microns can be easily obtained with our colloidal synthesis method. Our research would help to expand the research and application of plasmonic metal nanocrystals from the visible region to the NIR and MIR regions.

COLL 122

Self-assembled cationic amphiphiles as antimicrobial peptides mimics with potent antimicrobial activity and high selectivity

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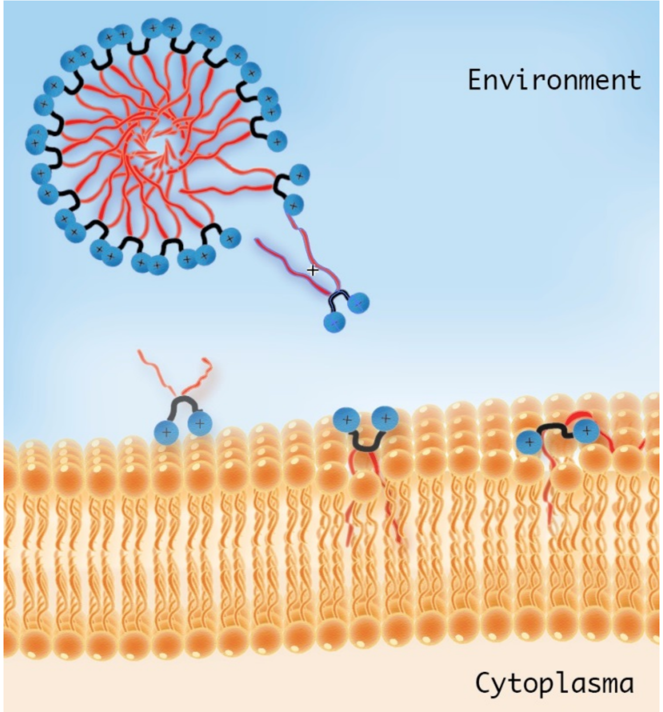
The rapid emergence of antibiotic-resistant bacteria has triggered extensive research in development of antibiotic alternatives. Inspired by the potent antimicrobial activity and high selectivity of naturally occurring antimicrobial peptides (AMPs), two series of cationic amphiphiles (CAms) were strategically designed with cationic ammonium moieties and non-polar domains segregated to opposite sides of the amphiphiles' backbone, known as a facially amphiphilic conformation. This presentation has been determined to be the main factor contributing to AMPs' unique biological profiles. The CAms self-assembled into spherical micelles above their respective critical micelle concentrations (CMCs) upon direct dissolution in water. Their antibacterial activity was then evaluated via a turbidity-based broth microdilution assay while the biocompatibility was determined in terms of hemolysis activity and cytotoxicity. Although it remains challenging for synthetic AMP mimics to obtain strong antimicrobial activity while maintaining high selectivity towards bacteria over mammalian cells, our CAms with optimized hydrophobicity exhibited potent activity against both Gram-positive and Gram-negative bacteria as well as displaying negligible hemolytic activity. In addition, we validated the membrane-disrupting mechanism of CAMs which is beneficial to reduce the tendency of resistance development in bacteria when used as treatment. In the end, an all-atom molecular dynamics simulation was applied to understand the CAm-membrane interaction on molecular level. This study highlights the promise of CAms as viable scaffolds for rationally designing the next generation of AMP mimics as effective antimicrobials to combat drug-resistant pathogens.



COLL 123

Porous metal aerogels as high efficiency alcohol oxidation electrocatalysts

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Noble metal nanoparticles (MNPs) have gained considerable attention due to their fascinating catalytic and plasmonic properties. These nanoparticles (NPs) have the potential to impact on several technologies, such as catalysts, sensors, and novel electrochemical devices. However, the application of NPs in the above technologies requires them to be assembled into functional nanostructures with useful and controllable physical properties. Recently, chemical oxidation of the surface ligands from colloidal Ag and Au/Ag NPs has been utilized to induce interparticle linkages and macroporous NP monoliths (hydrogels). Drying of the hydrogel under super critical condition yield porous nanostructure (aerogels) consisting entirely of metal colloids. Resultant aerogels exhibit direct NP interactions, wide range of porosity and high electrical conductivity that makes them promising for electrocatalysis. Herein, the extension of this technique to produce porous Ag/Pd/Au gel materials for application in ethanol oxidation reaction will be discussed. As-synthesized metal aerogels will be characterized by using powder X-ray diffractometry, UV-visible spectroscopy, electron microscopies, four point probe method, and surface area and porosimetry to evaluate the structure, morphology, surface, and optoelectronic properties. The influence of NP morphology and composition on electrocatalytic oxidation of ethanol will be systematically discussed in light of their application in fuel cells.

COLL 123

Porous metal aerogels as high efficiency alcohol oxidation electrocatalysts

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Noble metal nanoparticles (MNPs) have gained considerable attention due to their fascinating catalytic and plasmonic properties. These nanoparticles (NPs) have the potential to impact on several technologies, such as catalysts, sensors, and novel electrochemical devices. However, the application of NPs in the above technologies requires them to be assembled into functional nanostructures with useful and controllable physical properties. Recently, chemical oxidation of the surface ligands from colloidal Ag and Au/Ag NPs has been utilized to induce interparticle linkages and macroporous NP monoliths (hydrogels). Drying of the hydrogel under super critical condition yield porous nanostructure (aerogels) consisting entirely of metal colloids. Resultant aerogels exhibit direct NP interactions, wide range of porosity and high electrical conductivity that makes them promising for electrocatalysis. Herein, the extension of this technique to produce porous Ag/Pd/Au gel materials for application in ethanol oxidation reaction will be discussed. As-synthesized metal aerogels will be characterized by using powder X-ray diffractometry, UV-visible spectroscopy, electron microscopies, four point probe method, and surface area and porosimetry to evaluate the structure, morphology, surface, and optoelectronic properties. The influence of NP morphology and composition on electrocatalytic oxidation of ethanol will be systematically discussed in light of their application in fuel cells.

COLL 124 – Withdrawn.

COLL 125 – Withdrawn.

COLL 126

Graphene decorated with silver as a substrate for surface-enhanced Raman scattering detection of 2-thiouracil

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Graphene decorated with silver nanoparticles was synthesized and evaluated as a substrate with surface-enhanced Raman scattering (SERS) for 2-Thiouracil detection. The fabricated Ag/G was used as an efficient SERS substrate to detect the 2-Thiouracil (2-TU) molecules at a low detection limit of nM levels. The experimental and theoretical results indicate the chemical interaction between Ag/G and 2-TU substrate, which leads to significantly enhanced SERS bands of 2-TU at 789 cm^{-1}, 913 cm^{-1}, 957 cm^{-1}, 1368

cm^{-1}, and 1554 cm^{-1}, assigned to γ (C6-N3), δ (N3-C6-C8), (H-C7-C8-H) twist, v (C5-N4), and v (C5-N3), respectively. For the band at 815 cm^{-1}, the SERS signal exhibited a linear relationship with the concentration of 2-TU in the range of 1µM to 0.1µM and a detection limit (S/N = 3) was 10 nM.

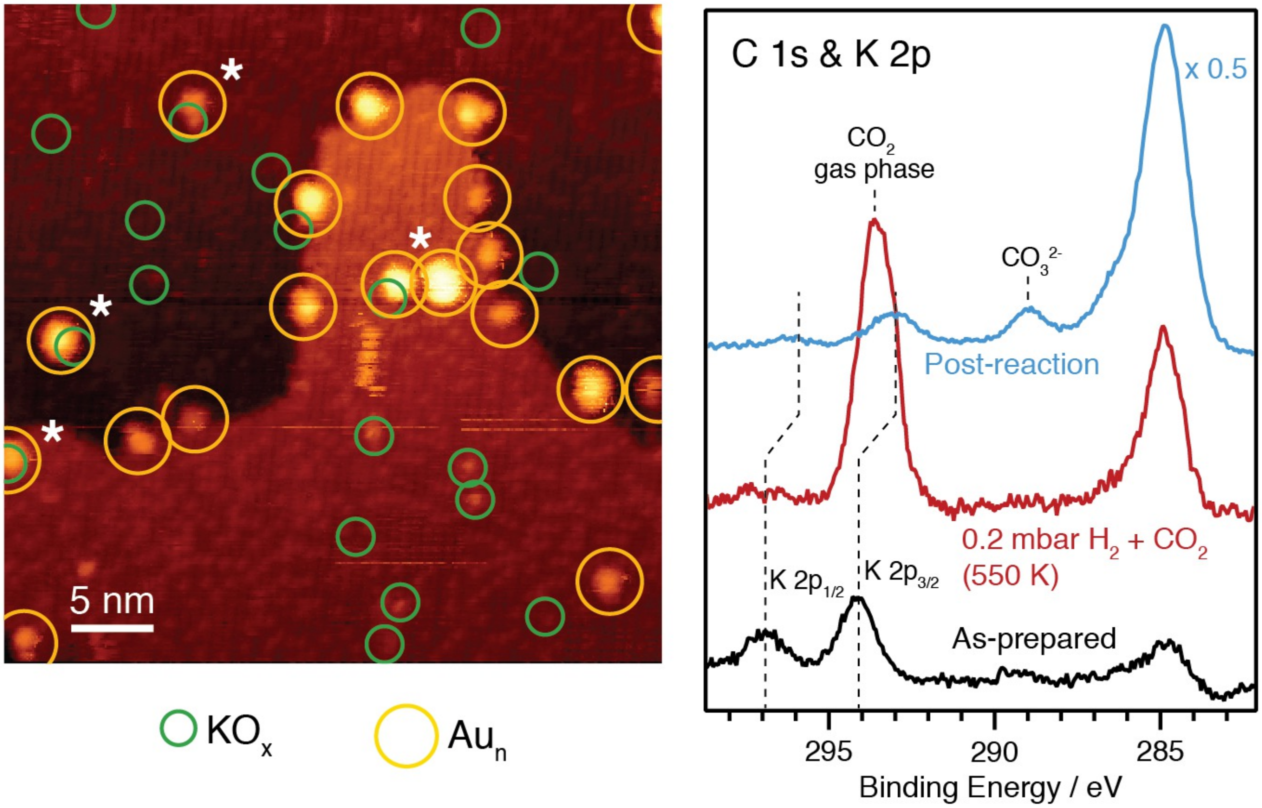
COLL 127 – Withdrawn.

COLL 128

Potassium promotion of a model Au/TiO$_2$ catalyst

David Grinter[1]*, dgrinter@bnl.gov, Si Luo*[1,2]*, Markus Soldemo*[3]*, Luca Piazza*[3]*, Jonas Weissenrieder*[3]*, Sanjaya D. Senanayake*[1]*, Dario J. Stacchiola*[1]*, Jose Rodriguez*[1,2]*.* (1) Chemistry, Brookhaven National Laboratory, Ridge, New York, United States (2) Chemistry, State University of New York at Stony Brook, Stony Brook, New York, United States (3) KTH Royal Institute of Technology, Stockholm, Sweden

The promotion effects of alkali metals, and potassium in particular, are of interest across a great number of catalyst systems. In our work we aim to understand the mechanisms behind these effects by systematically probing progressively more complex model systems using cutting edge experimental techniques (primarily STM and ambient pressure XPS). As potent catalysts for vital reactions including CO$_2$ hydrogenation and the water-gas-shift, Au and Cu nanoparticles supported on TiO$_2$ have attracted much attention in the past. Our studies have probed the enhanced activity of small gold particles in the presence of a low (< 1%) concentration of potassium on TiO$_2$(110) in UHV as well as under reaction conditions for CO$_2$ hydrogenation, an important synthesis route for methanol.



STM image (40 x 40 nm^2) and AP-XPS data (C 1s and K 2p) for a model potassium promoted Au/TiO$_2$ catalyst.

COLL 129

Multipod nickel nanostructures: Synthesis, characterization and applications

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With superior catalytic and mechanical properties, high saturation magnetization, and metallic character, nickel nanoparticles have applications in catalysts and electromagnetic interference shielding (EMI) composite materials. Multipod nickel nanostructures in particular provide a large surface area and geometries suitable for improved EMI shielding and catalysis. Such nanostructures for metallic nickel are uncommon in current literature. A fast, controlled and scalable route for the synthesis of such structures using microwave-assisted heating is presented. Insight into the formation and growth of the nickel multipods is provided using techniques including transmission electron microscopy and x-ray diffraction. Dielectric and magnetic properties of the materials is shown as part of their characterization.

COLL 130

Structure-function relationships for chemical warfare agent uptake into polyurethane films

***Tyler G. Grissom**, grissomt@vt.edu, Justin M. Sirrine, Timothy E. Long, Alan Esker, John R. Morris.* Chemistry, Virginia Tech, Christiansburg, Virginia, United States

Uptake of chemical warfare agents (CWAs) by polymeric coatings heightens the exposure risk to military and civilian personnel. However, a fundamental understanding of the absorption behavior of various CWAs into polymeric coatings is limited. We have employed a quartz crystal microbalance method coupled with a temperature-controlled gas saturator cell to deduce the volume fraction of sulfur mustard (HD), $C_4H_8Cl_2S$, simulants in militarily relevant polyurethane films. Quantification of HD simulant uptake in polyurethane coatings yields molecular-level insight into how specific functional groups in HD affect uptake. Segmented polyurethane was prepared from 2,000 g/mol poly(tetramethylene oxide) (PTMO), hydrogenated methylene diphenyl diisocyanate (HMDI), and 1,4-butanediol (BDO) to provide a model coating with 43 wt% hard segments. Flory-Huggins polymer solution theory yielded activity coefficients and interaction parameters that have been correlated to show how HD-simulant structure and functionality affect uptake. Importantly, we find that the presence of sulfur or chlorine atoms in the simulant molecules enhances uptake over hexane by more than a factor of five, which predicts extensive uptake of the actual CWA in analogous systems.

COLL 131

Covalent attachment of C_{60} Buckminster fullerenes on carbon-free Si(111) by wet chemistry

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The passivation or functionalization of non-oxidized silicon surfaces leading to the formation of surfaces and interfaces based on Si−N bonds have received substantial attention in recent years. For example, chemical reactivity of the amine-functionalized silicon surfaces could be used as a starting point for further reaction with large molecules, such as fullerene C_{60}, that can serve as model systems for more complex molecules and provide the roadmap for nanomaterials design. In this work, we propose an efficient wet chemistry method to covalently attach the buckminster fullerenes C_{60} to silicon surfaces via a monolayer of diamine functionality obtained by reacting hydrazine with Cl-terminated Si(111). The chemical nature and surface topography of the resulting C_{60}-modified Si(111) surfaces are investigated by X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and atomic-force microscopy (AFM). Density functional theory (DFT) calculations are performed to predict

core-level energies of surface species formed, which are compared with the experimental results, and to propose the possible mechanism of surface reactions.

COLL 132

Synthesis of CdSe QDs with different thiol-ligands, silica coating, and viability assessment on of COLO-205 and TK6 cells

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We report the synthesis and characterization of CdSe QDs, capped with four different thiol-ligands, in an aqueous medium, their internalization and biocompatibility with COLO-205 human colorectal adenocarcinoma and TK6 human spleen lymphoblasts. Furthermore, we report the silica encapsulation via ligand exchange and stability studies of the mentioned QDs. The thiol-ligands used for capping and stabilization were glutathione (GSH), thioglycolic acid (TGA), 3-mercaptopropionic acid (MPA), and L-Cysteine (L-Cys). Properties of the synthetized QDs were characterized with UV-Vis spectroscopy, XRD, FTIR and TEM. Stability of the encapsulated QDs was assessed by Z-potential analysis using DLS. To study the ligand effect on QDs biocompatibility, both normal and cancer cells were exposed to each synthetized QDs and viability was evaluated via Trypan Blue exclusion method. To further study the biocompatibility, their interaction with cells, and evaluate their bio-imaging potential, we performed measurements of intracellular QD uptake by cells and bacteria, monitored by confocal microscopy. Characterization results indicate that the non-encapsulated capped/QDs (bare-QDs) were successfully formed, exhibiting an improved optical response. FTIR spectrum analysis confirmed the ligand exchange of the bare-QDs, which allowed silica encapsulation of the QDs with good stability, determined by Z-potential analysis. Silica clusters were observed with TEM. Viability studies of the bare-QDs indicate that COLO-205 and TK6 cells can tolerate the freshly prepared QDs with high viability values after exposure. Intracellular uptake imaging with confocal microscopy showed that synthetized QDs emit light efficiently, even after penetrating the treated cells. We also have recently detected cellular internalization of CdSe QDs and relatively measured their fluorescence intensity within a cell system using a flow cytometry. Cell population analysis shows that around 25% of cells internalize the QDs, increasing cell fluorescence by up to 1000 fold. The synthetized QDs have potential for bio-imaging studies with minimal effects. Future and ongoing work includes viability assessment of silica encapsulated QDs and establishing a relationship between cellular uptake over time and used concentrations of the experimental QDs, in order to determine if QDs uptake is time or dose-dependent.

COLL 133

Surface properties of carboxylic acid terminated layer developed by electrochemical and wet chemical approaches

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Successfully immobilizing and patterning protein molecules on the designated places on a surface is critical in the development of high- performance biosensors with better selectivity and sensitivity. To fabricate a biosensor, the recognition layers or arrays are firstly required to be immobilized onto the surface. The major challenge to significantly improve the sensitivity of biosensors is to develop an effective method which precisely and easily immobilizes the recognition molecules onto a specific place on a surface while retaining their native biological activities. The activity of protein molecules on surfaces could only be improved with the consideration of protein orientation, protein-protein distance, and the protein's adsorption sites because they all impact their biological activities on surfaces. So, the investigation of surfaces where protein molecules mounted on is paramount. In our group, the carboxylic acid terminated patterns will be firstly fabricated on the surfaces through electrochemical and wet chemical methods. OTSpd denotes the carboxylic acid terminated pattern from the electrochemical method and OTSpd-UTSox means the one from the wet chemical method. When the negatively charged carboxylic acid terminated surface is in contact with the positively charged protein molecules in the buffer solution, protein molecules could be selectively absorbed on the pattern surfaces through coulombic forces. It has been proven that both OTSpd and OTSpd-UTSox chemical patterns could successfully immobilize lysozyme molecules on surfaces. However, because of the different fabricated mechanism, OTSpd and OTSpd-UTSox surfaces need to be further investigated at the molecular level for the understanding of bound protein activities on the surface. Here, Atomic Force Microscopy (AFM), Kevin Probe Force Microscopy (KPFM) and Fluorescence Microscopy have been used in our research lab to measure the friction force, energy dissipation, surface potential, and fluorescence signal on different pattern surfaces. It has been proven that OTSpd-UTSox surface has higher charge density and also more homogeneous than OTSpd surface. This information will work as a guidance to understand the protein activity on each pattern surface.

COLL 134

Investigation of the local environment of functional end-groups on polyethylene glycol (PEG) brushes

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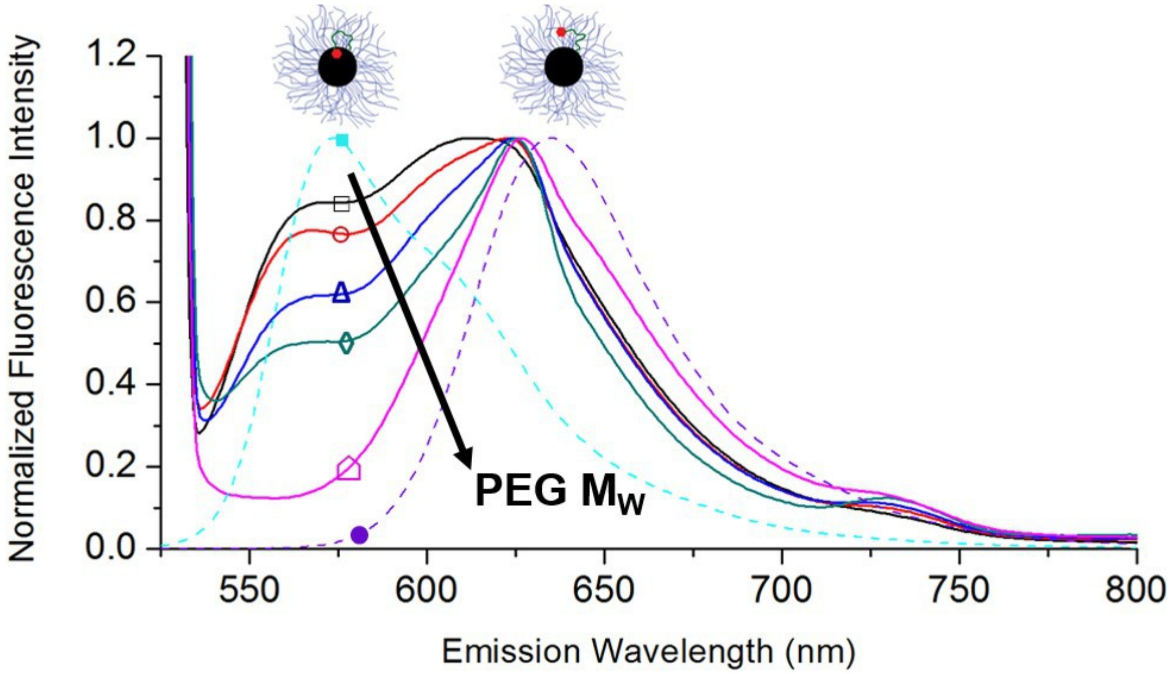
Targeted nanoparticles often require conjugating targeting ligands to polyethylene glycol (PEG) chains of a nanoparticle's dense protecting corona. "Click" chemistries are commonly employed for their bioorthogonality, with strain-promoted azide-alkyne cycloadditions (SPAAC) increasingly chosen to avoid cytotoxic copper catalysts. However, conjugation becomes compromised if reactive PEG chain ends cannot encounter their reaction counterparts. We use fluorescence to probe the location of Nile Red, methylpyrene, and butylpyrene – dyes with comparable hydrophobicities to SPAAC alkynes (logPs: 3.2-5.7) – tethered to PEG chains on 100 nm NPs. Using fluorescence peak shifts, we find that Nile Red resides 43% of the time in the 5k PEG corona and 57% at the more hydrophobic nanoparticle core. Increasing the PEG MW to 67k doubles the corona dye fraction to 86% (14% core). More hydrophobic methylpyrene and butylpyrene, monitored with I1/I3 ratios, reside 1% in the corona (99% core). We then compared these fluorescence results to the conjugation yields of functional end-groups of varying hydrophobicities – from hydrophilic amines and carboxylic acids to the very hydrophobic strained cycloalkynes – with ligands of increasing size to determine whether investigating the local environments of similarly hydrophobic dyes accurately depicts the location of functional end-groups. These results explain difficulties with using SPAAC reactions for conjugating large ligands to nanoparticles with PEG coronae.



Normalized emission spectra of 0.1 wt % NR-tethered NPs synthesized with 1.8k PS and PS−PEG copolymer stabilizer of 3.6k PS MW and PEG MWs of 5.5k (black open square), 16.6k (red open circle), 25k (blue open triangle), 36k (green open diamond), and 67k (pink open pentagon). The dotted lines show comparison normalized spectra for NR in toluene (light blue closed square) and ethanol (purple closed circle), representing the core and corona NP environments. Increasing the PS−PEG PEG MW increases the ratio of dye in the corona vs the core.

COLL 135

Thermodynamics of analyte tails in DNA and morpholino surface hybridization

Ursula Koniges, *koniges@gmail.com, Rastislav Levicky.* Chemical & Biomolecular Engineering, New York University, Brooklyn, New York, United States

Hybridization of in-solution nucleic acid targets to surface-immobilized probes is a common mechanism employed in genetic analysis methods, for example DNA microarrays. In such applications, in-solution targets can be imperfect length matches to surface probes, with the resulting possibility of nucleic acid tails extending toward the surface, toward solution, or with overhangs of both orientations. We report the impact of surface- and solution-oriented tails on hybridization thermodynamics at a surface, and compare these results to a perfectly size-matched target and to solution hybridization thermodynamics. Several different probe coverages and solution ionic strengths are investigated. In addition to a DNA probe, a probe comprised of an uncharged DNA analogue, morpholino, is used to investigate the electrostatic contribution to the tail-orientation dependent biases. The reported results indicate that a surface-oriented tail markedly increases the hybridization energy penalty, whereas a solution-oriented tail has a significantly lower energy penalty effect. These results also help explain observations from a comparative study of the performance of DNA and morpholino microarrays.

COLL 135

Thermodynamics of analyte tails in DNA and morpholino surface hybridization

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Hybridization of in-solution nucleic acid targets to surface-immobilized probes is a common mechanism employed in genetic analysis methods, for example DNA microarrays. In such applications, in-solution targets can be imperfect length matches to surface probes, with the resulting possibility of nucleic acid tails extending toward the surface, toward solution, or with overhangs of both orientations. We report the impact of surface- and solution-oriented tails on hybridization thermodynamics at a surface, and compare these results to a perfectly size-matched target and to solution hybridization thermodynamics. Several different probe coverages and solution ionic strengths are investigated. In addition to a DNA probe, a probe comprised of an uncharged DNA analogue, morpholino, is used to investigate the electrostatic contribution to the tail-orientation dependent biases. The reported results indicate that a surface-oriented tail markedly increases the hybridization energy penalty, whereas a solution-oriented tail has a significantly lower energy penalty effect. These results also help explain observations from a comparative study of the performance of DNA and morpholino microarrays.

COLL 136

Nano-imprinted SERS-based sensors for the detection of pathogenic bacteria

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The rapid and sensitive detection of biological pathogens in settings lacking laboratory equipment and trained personnel could significantly decrease the onset of foodborne illnesses. Conventional pathogen detection and identification methods are typically time-consuming, costly, and require technical expertise. Therefore, there is an urgent demand for a pathogen detection method that can deliver rapid analysis with a detection limit in the 1 to 100 colony forming unit (CFU)/mL range. One promising method, surface-enhanced Raman spectroscopy (SERS), harnesses the unique properties of metallic nanostructures and enhances the Raman signal on the order of 10^7 to 10^8. Although SERS sensors for biological pathogens have demonstrated high sensitivities and low detection limits, there is a need to transition the research into scalable technologies that can be mass produced. One such technique, “nanoimprinting”, allows for control over the sensor topography and nanostructure spacing through the careful selection of a pre-fabricated template. Nano-imprinted sensors were fabricated by expanding on our previous work in which NIR femtosecond laser pulses were used to create repeating silica “nanospikes” that were then decorated with silver nanoparticles. These sensors offered a significantly low detection limit using rhodamine 6G (R6G) and preliminary results demonstrated that bacteria detection is feasible. The nanospike topography was copied by casting the surface onto a polydimethylsiloxane “mother mold” that was used (via thermal contact) to imprint the original repeating nanostructure onto thin layers of commercially available polymers, for example, poly(methylmethacrylate) and polystyrene. The nanostructured polymer was then decorated with noble metal nanoparticles resulting in a scalable, low-cost sensor that can be tailored or modified to capture a specific analyte. Preliminary testing using R6G confirmed that the sensors effectively enhanced the Raman signal. Experimental details—along with results obtained using the substrates to detect common biological pathogens—will be presented. The potential development of disposable, low-cost sensors that can detect foodborne pathogens in a variety of relevant scenarios will also be discussed.

COLL 137

Impact of amphiphilic macromolecules' degree of unsaturation and hydrophobe conformation on large unilamellar liposome characteristics

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Liposomes have become increasingly common in the delivery of bioactive agents due to their ability to encapsulate hydrophobic and hydrophilic drugs with excellent biocompatibility. While commercial liposome formulations improve bioavailability of otherwise quickly eliminated or insoluble drugs, tailoring formulation properties for specific uses has become the forefront of liposome research. Many groups focus on triggered release from composite systems derived from one or several lipid types, stabilizing molecules such as cholesterol and poly(ethylene glycol)- (PEG-) lipids, and novel additives. Here, we report the design, synthesis, and characterization of two series of amphiphilic macromolecules (AMs), consisting of acylated polyol backbones conjugated to PEG that can serve as the sole additives to unilamellar vesicles. The physicochemical properties of AMs, including unsaturation and hydrophobe conformation, have profound impacts on liposome stability. The impact of chemical structures on the rate of hydrophilic drug release is further investigated to demonstrate how AMs can be utilized to fine tune the properties of liposomal formulations for the desired application. Collectively, AMs are demonstrated to be a novel technology with the potential to simultaneously stabilize and dictate the release profile of commonly used bulk lipid systems.

COLL 138

Effect of hydrophobic alkyl silane self-assembled monolayers on barnacle adhesion

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The purpose of this research study is to show the effect of hydrophobicity on barnacle glue adhesion. There is a great interest in developing non-biocidal surface coatings to reduce biofouling on marine structures such as ships and piers. Biocides are effective at reducing barnacle adhesion but are toxic to marine life because the coatings release compounds such as ammonium salts, silver,copper or antibiotics. They can be so detrimental to the local environment that many governments have made them illegal. The momentum is to develop an environmentally friendly antifouling coating.

Our approach was to fabricate hydrophobic surfaces of various topographies and study how the wettability affected adult barnacle adhesion. Self-assembled monolayers (SAMs) were made from alkyl silanes with methyl and perfluoro terminal groups to

minimize the surface energy. Contact angles were measured to characterize each substrate as hydrophobic or superhydrophobic. Then each type of substrate underwent two tests. The first test involved quantifying the adhesion of barnacle glue to the surface after immersing in water for one week. The second test was a barnacle reattachment assay where barnacles were added to the substrates and submerged in water for one week. Barnacles were removed using a force gauge. All barnacle slides were later tested for residue proteins using Coomassie G250 protein stain. Slides were scanned and remaining protein was quantified by measuring pixel density with ImageJ software.

There were mixed results in the comparison of data from these experiments indicating that contact angle alone is not enough to reduce the adhesion of barnacles to glass surfaces. While fluorinated coatings had the lowest amount of residue protein, the amount of remaining barnacle glue did not necessarily correlate with a higher contact angle. It seems more likely that the coating morphology had a stronger effect at reducing barnacle adhesion. The presentation will also discuss approaches to creating nanostructured coatings and how it has the potential to be more effective at reducing barnacle adhesion.

COLL 139

Nonlinear multimodal optical live cells imaging using DNA-mediated plasmon-coupled gold nanoprism assembly

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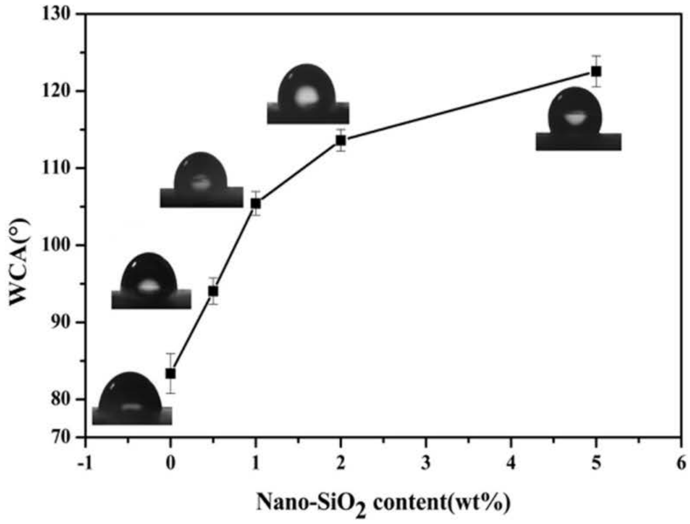
One of the most emerging nonlinear optical imaging (NLO) methods for the imaging of different biological systems is multiphoton excitation microscopy techniques, due to its deep penetration ability in to living cells and tissues. However, the nonlinear properties of nanomaterials can be tuned by properly designing nano assemblies. These are also responsible for nano antenna effects even in presence of biological materials. Driven by the need of deep tissue imaging using multimodal NLO probe, here we have shown the design optical nano antennas using DNA mediated gold nanoprisms assembly to enhance multiphoton imaging capabilities in second biological window. Our experimental data also signify the unique way to enhance two-photon fluorescence (TPF) as well as second harmonic generation (SHG) by a number of magnitudes by nanoprism assemblies. Theoretical modelling using FDTD simulations designate that the experimental enhancement of TPF and SHG are due to the electric field enhancement and quadrupole contribution of nano assemblies. Antibody conjugated assembly of nanoprisms are highly capable of exhibiting selective and bright multimodal TPF and SHG imaging of human Hep G2 liver cancer cells using 1100 nm excitation.

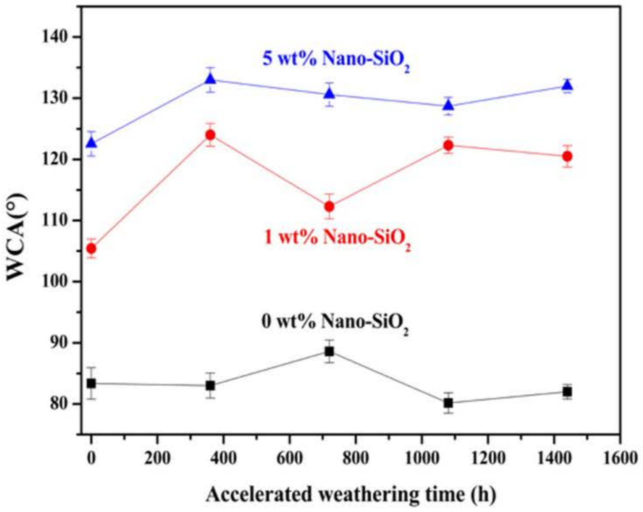
COLL 140

Durability of hydrophobic nanocomposite coatings on cement substrates

***Jing Feng**, fengjing@mail.crsri.cn, **Chengjing Xiao**, xiaocj@mail.crsri.cn, **Lingmin Liao**, stone142@163.com, Yuanyi Wang.* Materials and Structural Department, Changjiang River Scientific Research Institute, Wuhan, China

The hydrophobic/superhydrophobic organic materials have been wildly used to protect various substrates from weathering, contamination, corrosion and several other undesirable effects in outdoor and extreme conditions. In particular, the fluorine-containing polymers are of interest for anti-corrosion, anti-fouling, self-cleaning and anti-smudge application. However, they are of limited use in the conservation of concrete and other cementitious substrates due to a lack of durability. In our present work, the ambient-curable fluorocarbon/SiO_2 nanocomposite coatings were prepared on cement substrates, followed by using the 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PTES) to chemically modify the surface. The surface wettability, morphology, mechanical properties, and artificial weatherability were thoroughly investigated, using contact angle analysis, SEM, pull-off test, tensile test, and UV/condensation accelerated weathering measurements, respectively. Results indicated that the SiO_2 nanoparticles played a positive role in improving the hydrophobic character of surface, and the water contact angle (WCA) increased with particle contents. While the presence of nano-SiO_2 showed no significant effects on the adhesion strength. In addition, the nanocomposite coatings exhibited good water resistance (water absorption less than 0.5%), surface wettability (WCA>110°) and interfacial bond durability (>2.5MPa) under UV/condensation conditions. Even after 1440h of weathering, their WCA values were still higher than the original surfaces, at the same time, their adhesion strength increased slightly. Such results were likely to be interpreted by the FT-IR, SEM and tensile tests, which suggested that the cross-linked and more compacted structures formed at the interface of coating and cement when exposed to the UV-condensation environment.





The varation of the WCA as a function of nano-SiO_2 contents and accelerated weathering time

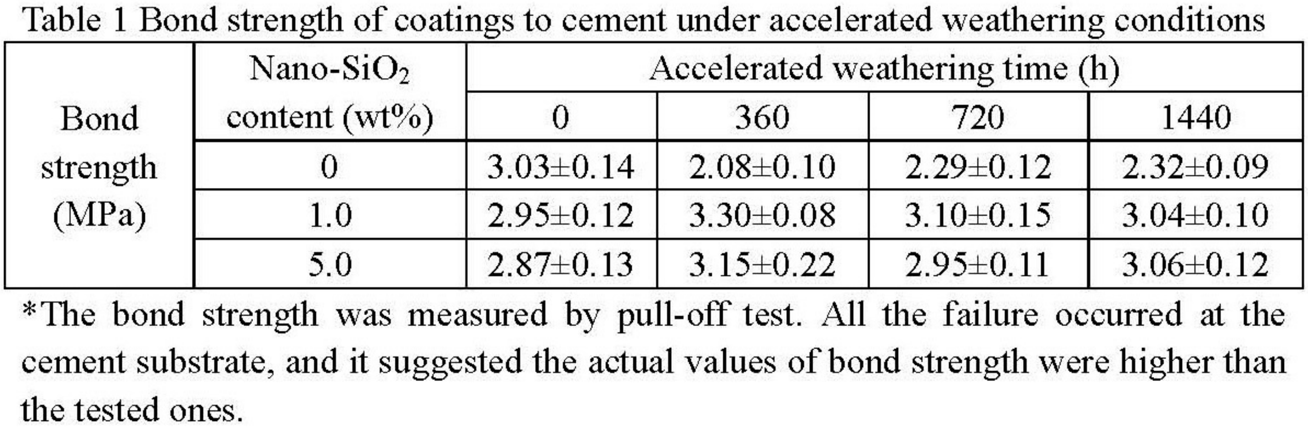


Table 1 Bond strength of coatings to cement under accelerated weathering conditions

	Nano-SiO_2 content (wt%)	Accelerated weathering time (h)			
		0	360	720	1440
Bond strength (MPa)	0	3.03±0.14	2.08±0.10	2.29±0.12	2.32±0.09
	1.0	2.95±0.12	3.30±0.08	3.10±0.15	3.04±0.10
	5.0	2.87±0.13	3.15±0.22	2.95±0.11	3.06±0.12

*The bond strength was measured by pull-off test. All the failure occurred at the cement substrate, and it suggested the actual values of bond strength were higher than the tested ones.

COLL 141

Nanostructured microparticles for human neural stem cell engineering

***Geunwoo Jin**, tue94752@temple.edu, Won H. Suh.* Bioengineering, Temple University, Philadelphia, Pennsylvania, United States

Engineered neural stem cells (NSCs), in recent years, have shown therapeutic potentials in achieving functional recovery of nervous system dysfunctions (e.g., decreased cognitive functions) in animal models that are associated with neurological diseases such as Alzheimer’s disease (AD) and Parkinson’s disease (PD). In this presentation, we will provide a new platform of nanostructured carbon-based microparticles that can be utilized to influence (alter) the differentiation pathways of adult stem cells and transform them into functional neurons. Ultrasonic spray pyrolysis (USP) coupled with wet-chemical etching methodologies were utilized to create the porous particles. We will show that the as-prepared particles can incorporate small molecules and peptides. The biological characterization details from multiple neural stem cell differentiation experiments and (accompanying) live-cell microscopy results (with and without the particles) will be presented. ReNcell VM (Millipore, Inc.) cells were utilized as the stem cell source. Key characterization methods will include microscopy, immunocytochemistry, and RT-qPCR.

COLL 142

Effect of inorganic nanostructured materials on neurogenesis

***Yanshuang Chen**, chenyanshuang03@126.com, Won H. Suh.* Bioengineering, Temple University, Philadelphia, Pennsylvania, United States

Damage and/or loss of functional neurons can lead to detrimental cognitive and paralyzing effects in humans. Prime examples of such negative situations are well documented in Parkinson's and Alzheimer's disease patients. In recent years, the utilization of neural stem cells and their derivation into neurons have been the focus of many research endeavors. The main reason is because neural stem cells are multi-potent and can differentiate into neurons, astrocytes, and oligodendrocytes. The research that will be presented involves the potential use of inorganic nanostructured materials to efficiently deliver bioactive molecules (i.e., retinoic acid, kinase inhibitors) to cells that can modulate the differentiation potential of certain cells into neurons. Specifically, PC12 (derived from rat pheochromocytoma) cells, as a neural model, was treated with select nanostructured materials with and without neuron inducers (molecules and ions) and the results were analyzed via biochemical assays and live-cell fluorescence microscopy. The presentation will include an in depth look into the cytocompatibility of the tested nanostructured materials that include silicon dioxide, titanium oxide, and carbon.

COLL 143

Gold nanoparticle functionalization for the generation of drug and gene delivery systems

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Gold nanoparticles gained tremendous momentum recently due to their biocompatibility, density, and special physicochemical, optical and surface properties. Towards our goal to evaluate the impact of the physicochemical parameters of drug and gene delivery systems on the cell uptake, we designed a model system comprising of gold nanoparticles decorated with different neutral or positively charged ligands. Our preliminary results towards ligand design and synthesis, as well as nanoparticle synthesis, functionalization will be presented, together with their interaction with cells in vitro.

COLL 144

Photogeneration of silver nanoparticles in stereolithography resin via 3D printing technique

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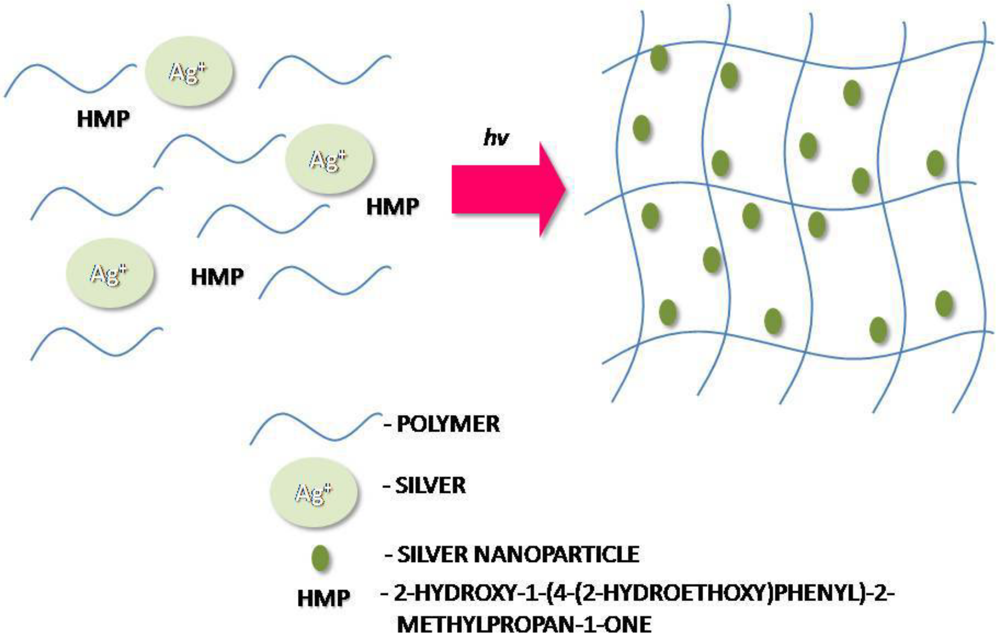
The synthesis route to reduce silver cations (Ag^+) to silver nanoparticles (AgNP) simultaneous with the photopolymerization of stereolithography (SL) resin to form a nanocomposite using 3D printing technique is explored and presented. With standard, commercially available stereolithography resin, the study further investigates whether the generated AgNP can be tuned in order to obtain the optimal condition and effect to the thermo-mechanical properties of the SL resin. Together with 2-hydroxy-1-(4-(2-hydroxyethoxy)phenyl)-2-methylpropan-1-one (HMP) and with the neat SLA resin as a baseline, a design of experiments is conducted to determine the best combination. Characterization of AgNP is performed using UV-Vis and TEM. The defined optimal settings are used to produce 3D-printed specimens that will be tested for thermo-mechanical property vis-a-vis the neat SL resin. The antimicrobial property is also tested to check whether the presence of AgNP has achieved a significant amount. The positive result of this study shall provide an avenue of a new way of developing a product for biomedical use as well as providing further rapid prototyping option to manufacturing research and development. The peculiar capability of 3D Printing technologies enables new opportunities for high customization, significant improvement in product performance, and lower overall manufacturing cost.



COLL 145

Microwave assisted synthesis of tungsten oxide nanoparticles using an ionic liquid

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Nanostructured tungsten oxide is an interesting material system because of its multi-functionality. It is a highly promising candidate for gas sensing, antimicrobial activity,

inactivation of toxic chemicals, serving as anodic material in dye sensitized solar cells, and electrochromic applications. Its unique optical properties that extend over a wide wavelength region make possible applications that are difficult to realize with other metal oxides. Liquid phase synthesis is a most promising synthetic approach for the large scale synthesis of nano tungsten oxide. However, typically, the hydrothermal synthesis methods involving nucleation and growth processes are inefficient due to the time required for synthesis and low selectivity as a result of undesired side reactions. Further, the addition of surfactants and/or polymers are often used empirically to manipulate the nucleation, growth and passivation of the nanoparticles. In this work, we have carried out microwave synthesis for producing tungsten oxide nanoparticles by taking advantage of the controls offered by microwave heating over conventional heating methods. We have also explored the use of an ionic liquid (1-Butyl-3-methylimidazolium tetrafluoroborate, $BMIMBF_4$) which acts as the medium, reducing agent, surfactant or passivating agent in influencing the nanoparticle formation process. For comparison, we have also carried out the synthesis in aqueous medium and also in ethylene glycol. Following microwave synthesis, the nanoparticles were sonicated and centrifuged to reduce agglomeration and then calcined to remove all organics. The nanomaterial properties were characterized to determine the chemical composition and morphology via XRD, SEM, and IR. The results suggest that crystallized WO_3 nanoparticles were synthesized. Further, the ionic liquid proved to be structure directing agent, stabilizer, capping agent, and also provided some protection against agglomeration. The dependence of nanomaterial properties on the key features of microwave synthesis, namely power input and time of exposure to microwave radiation and also the nature of the synthesis medium will be described in this presentation.

COLL 146

Interaction of hydrogen with Au under optical plasmonic excitation

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Hot electrons resulting from the decay of localized surface plasmons in metallic nanoparticles can participate in chemical reactions. One such example is the hot electron induced dissociation of hydrogen on Au nanoparticles under optical excitation. This optical hot electron induced dissociation capability may be leveraged for developing plasmonic H_2 sensors based on changes in spectral properties of the

localized surface plasmon resonance associated with thin films of Au nanoparticles. The main hypothesis for this type of application is that the formation of a metastable gold hydride layer following the H_2 dissociation event leads to a change in the dielectric constant of the Au nanostructures. In this work, we combine theoretical results derived from Density Functional Theory (DFT) with experimental data measured using *in-situ* spectroscopic ellipsometry to provide support for the proposed mechanism. In all, this work sheds some light on the fundamental optical changes induced by the interaction of Au with atomic hydrogen.

COLL 147

Synthesis and photophysical characterization of ultra-small $Ge_{1-x}Sn_x$ quantum dots

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Earth abundant Group IV elements have low toxicity making them ideal components for future commercialization in optoelectronic devices. Nonetheless, Si and Ge exhibit indirect band structures, which make their interaction with light much less efficient than many other direct bandgap semiconductors. Alloying Ge with elemental Sn has been shown to improve the light-mater interactions based on composition; however, the addition of Sn leads to low energy deep infra-red bandgaps. To address this issue, we have recently synthesized ultra-small (1-3 nm) Ge_xSn_{1-x} nanocrystals with strong quantum confinement effects that result in tunable visible to near infrared absorption and emission. Herein we report the physical and advanced spectroscopic characterization of $Ge_{1-x}Sn_x$ quantum dots along with theoretical calculations to support the findings. Orange-red luminescence is reported with composition dependent red-shifting and temperature dependent lifetimes.

COLL 148

Rhodanine based polymers as structure directing agent: A study of chemical and morphological evolution

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There have been reports that oxidative polymerization of rhodanine (Rd) can be accomplished in the presence of silver complexes in ethanol. It was shown that

polyrhodanine was incubated with silver salts to prepare silver-rhodanine “ensemble” for biological applications because of the antibacterial properties of silver and the antiviral properties of polyrhodanine.
In this presentation, we endeavor to investigate the catalytic conversion of rhodanine into polyrhodanine in various solvent systems under various conditions. We will present a systematic study of polyrhodanine formation and its role and evolution of various morphologies during the formation process. To our surprise, polyrhodanine undergoes various morphological transitions before attaining the morphology of micron-sized rods. We will represent preliminary investigation of mechanistic details as they pertain to such a reduction process. In addition, we will present a comparative study the ability of noble metal salts to induce the polymerization of polyrhodanine.

COLL 149

Using nano perovskites to detect organohalides

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Cesium lead halide ($CsPbX_3$) perovskites have bright tunable photoluminescence (PL) when prepared at the nanoscale. In addition to size and composition dependent PL, these nanomaterials also demonstrate rapid ion exchange, which provides for further PL tuning. In this presentation we explore this phenomenon by reacting $CsPbX_3$ with a number of different alkylammonium based salts, and classify PL response to anion types. The synthesized perovskites were characterized by TEM and XRD, and colorimetric changes were followed by UV-vis and fluorescence spectroscopy. We demonstrate that nano perovskites can be used as novel colorimetric indicators of organohalides in solution. The detection limits of this approach will be described, as will the novel use of nano perovskites to monitor an organohalide based elimination reaction with great kinetic accuracy.

COLL 150

Single trigger, dual responsive nanoparticles for sequential drug release

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Nanoparticles are attractive carrier systems due their ability to deliver therapeutic drug molecules in an image-guided approach which enables monitoring the accumulation and activation of drug molecules at the pathological site. Here we present a novel nanoparticle formulation, with specialized linker moieties, which allows for a single trigger molecule to release multiple payloads at different time points with a slow or fast unloading kinetics. This allows for a highly controllable system where small and large therapeutic molecules may be released at the diseased tissues for a possible combinational therapy. The fast release of therapeutic RNA molecules makes the cancer cells more vulnerable to chemodrugs which are released from nanoparticle surface slowly at a later time point with the same triggering molecule.

COLL 151

Characterization of functional nanocomposites of dendrons and gold nanoparticles

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Dendrimers (multi branched) and dendrons (individual branched) are a class of macromolecules with extensively branched 3D structure, and their formation of nanocomposite with metal nanoparticles offer the ability to achieve a high degree of surface functionality and versatility with a controllable balance of electrical conductivity and molecular interaction as sensing interfaces. This presentation describes recent results of an investigation of nanocomposites derived from thiol-functionalized triazole linked tri(ethylene glycol) dendrons and molecularly-functionalized gold nanoparticles, and their electrical and optical properties. The nanocomposites are prepared by exchange reaction of the dendrons with monolayer-capped gold nanoparticles, forming small aggregates dispersible in aqueous solutions or thin films with crossing-linked network structures. Results from measurements of the changes in surface plasmon resonance band and electrical properties will be discussed, focusing on interparticle interactions under different solvents or vapor molecules, along with implications to the design of a wide range of nanocomposites from dendrons of different generations as sensing interfaces.

COLL 152

First-principle study of the initial steps of methane dissociation on α-Fe_2O_3 (0001) and Fe_3O_4 (111) surfaces in chemical looping process

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Chemical Looping Combustion (CLC) has drawn much attention in the past few years for near 100% of the fuel carbon captured as CO_2 with the use of transition metal oxide surfaces as the oxygen carrier. However, theoretical studies focusing on reaction mechanism in the molecular level are extremely lacked to characterize the reaction process and geometry in details. Here we present a first-principle study using Density Functional Theory (DFT) to simulate the energy change and dissociation configurations

in the initial steps of methane CH_4 molecule on iron oxides surfaces, namely α-Fe_2O_3 (0001) and Fe_3O_4 (111) surfaces. Both of the homolytic and heterolytic CH_4 dissociation pathways were considered for the resulted CH_3 and H groups. For iron oxides surfaces, both Fe- and O-terminated configurations were included in the discussion since they were predicted as the most stable surface domains in previous theoretical and experimental studies. As a strongly correlated material, iron oxides were treated with Hubbard U correction, known as DFT + U method. The U^{d+p} was chosen because it can give more balanced corrections to both of the Fe-*d* and O-*p* orbitals. Optimized reaction configurations of the products showed that the CH_4 dissociation on both hematite and magnetite favors homolytic pathway where both CH_3 and H groups adsorbed on surface O-site, and that O-terminated surface is more preferred in the reaction than Fe-terminated surface in both of the iron oxide surfaces. Temperature factor was also included in the energy calculations.

COLL 153

Ab initio approach for the study of incongruent NMC metal dissolution in aqueous environment

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Lithium based transition metal oxides such as $LiCoO_2$ and nickel manganese cobalt oxide (NMC) are widely adopted as cathode materials in various electronic products. The rapid and large-scale commercialization of such materials is increasingly bringing detrimental impacts on our environment during the manufacture, usage and, disposal of these materials. Experimental work has shown that the mechanism affecting biologic systems varies among materials. For example, $LiCoO_2$ tends to uptake phosphate ions (nutrition of most biologic species), resulting in the nutrition shortage in the biological environment, while the dissolution of NMC in aqueous media has turned NMC into a toxic object. However, the experimental techniques are limited to gain molecular level understandings of these mechanisms. Here we use density functional theory (DFT) and thermodynamics to investigate the fundamentals of NMC metal dissolution and use free energy ($\triangle G$) to reveal the incongruent dissolution tendency among nickel, manganese, and cobalt. We found that the *ab initio* $\triangle G$ better explain the nickel dominated dissolution of NMC as compared to the metal vacancy formation energy. Also, levels of the metal dissolution tendency were observed upon delithiation states. The computational results corresponds well with the experimental counterpart. Insights into the second TM metal release is also investigated to compensate the experimental limitations. By calculating the $\triangle G$ of NMC with different ratios, promising candidates for environmental benign cathode materials can be found and to suggest future experiment work. Our work helps the redesign of potential cathode materials that meets both battery performance and environmental friendly purposes.

COLL 154

Graphene oxide: Metal nanoparticle system for dual sensing applications

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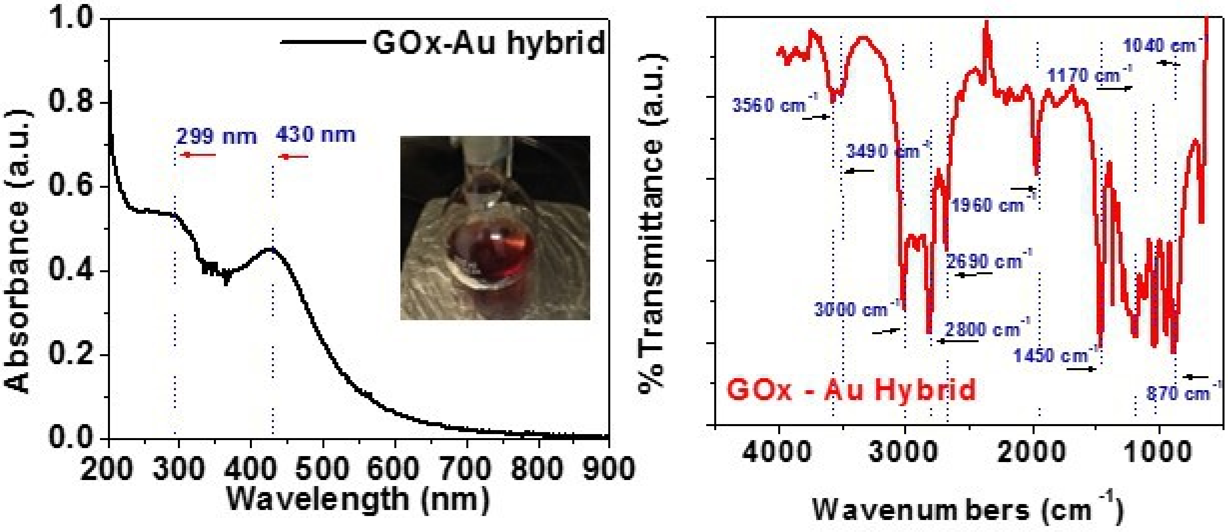
Research regarding the applications of graphene and metal doped graphene oxide hybrids is relevant for scientific discovery, developments in environmental monitoring of toxic substances, and in industry for use as sensors, batteries, solar cells, capacitors, catalysts and nanogenerators. A hybrid sensor possesses the advantages of using inexpensive and durable graphene oxide (GOx) while offsetting the cost of utilizing the sensitive, reliable sensing capabilities of gold or silver nanomaterials. For use as an electrochemical and optical sensor, the optical and electrochemical properties of GOx, reduced graphene oxide (r-GOx), and graphene oxide- gold/silver nanomaterial hybrids (GOx-M) must be understood in order the examine the materials' sensing capabilities. The energy and electron transfer properties of molecule-like monolayer protected gold clusters (Au MPCs) are being studied in order to understand the fundamental chemistry of these molecule-nanohybrid systems which have potential applications in sensors as well as catalysis. The purpose of this project is to determine the sensing capabilities of graphene oxide and compare this with graphene oxide – metal nanoparticle composites for pesticides. The first phase of this study involves the synthesis as well as characterization and analysis of graphene oxide generated by means of a modified Hummers method followed by the addition of metal nanoparticles to the surface. Synthesis strategies and characterization using UV-Vis, IR, fluorescence and electrochemical studies will be presented.



UV-Vis and IR charactarization of GOx-AuNP hybrid

COLL 155

Graphene quantum dots conjugated magnetic nanoplatform for efficient capture and two photon imaging of rare tumor cells

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Liver cancer is the one of the leading causes of cancer-related deaths in many developed countries. During the last few years, several clinical studies have demonstrated that circulating tumor cells (CTCs) can be used as a marker for understanding metastatic development, a key factor in increasing the overall survival rate for liver cancer. CTCs are extremely rare malignant cells; in blood containing billions of red blood cells for liver cancer a patient, until now, capturing and accurately identifying CTCs has been highly challenging.

Graphene quantum dots (GQDs) possesses a number of desirable properties. They are nanoscale in size with high specific surface area, have a high intrinsic NIR absorbance, and a large two photon absorption cross-section. Because they are biocompatible with low toxicity and are not prone to photo bleaching, they have been widely used as fluorescent bio-probes. Herein, we reports the development of GQD-conjugated, high-luminescence magnetic nanoplatform for the selective separation and diagnosis of Glypican-3 (GPC3)-expressed Hep G2 liver CTCs from infected blood. Experimental data show that by attaching an antiGPC3-antibody to the nanoplatform, Hep G2 hepatocellular CTCs can be selectively separated from infected blood at concentrations as low as 10 tumor cells/mL of blood in a 15 mL sample. Because of an extremely high two-photon absorption cross section (40530 GM), these modified nanostructures can be used as a two-photon luminescence platform for selective and high intensity imaging of Hep G2 tumor cells in a biological transparency window using 960 nm light. Experimental results of non-targeted GPC3(−) and SK-BR-3 breast cancer cells show that multifunctional-nanoplatform-based cell separation, followed by two-photon imaging, is highly selective for Hep G2 hepatocellular carcinoma tumor cells.

COLL 156

Single molecule electronics: Fabricating an on/off electromechanical single molecule conductance switch

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The use of single molecules as electronic components enables one to minimize the size of electronics to design cheaper, faster and smaller transistors, rectifiers, wires and microprocessors. One possible application of single molecule devices is as switches or sensors. Candidate molecules should exist in two or more states that could be interconverted by external stimuli, e.g. pH, potential, photons, etc. Molecules that can exhibit high and low conductive states may have critical roles in information storage. We have studied an electromechanical single molecule conductance switch that transits between ON and OFF states controlled by the electrode potential in an electrochemical environment. Among a wide range of attractive molecules, benzene derivatives are promising candidates due to controllable formation of molecular junctions with desired geometry.[1] At positive potentials, adsorption of the molecules on the electrode surface allows low conductivity junctions to form via anchoring groups. At negative potentials, direct contact between the π -system of the molecule and the gold electrodes results in higher conductivity junctions. Thus, conductance switching could be observed as a function of potential.

COLL 157

Probing hydrogen evolution using electrochemical optical readout measurements

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Plasmonic nanomaterials have the potential to compete with and/or complement conventional semiconductor-based nanomaterials for solar production of hydrogen because of their tunable absorption of the visible region of the solar spectrum. Considerable interest has been generated for designing different shape and size plasmonic nanomaterials for efficiently harvesting of solar energy to produce hydrogen. However, most studies are limited to studying hydrogen production on ensembles of nanoparticles so the effects of nanoparticle heterogeneity are hidden. We are developing strategies to investigate hydrogen production on the scale of single nanoparticles using electrochemical optical readout measurements based on pH-dependent fluorescence probes.

COLL 158

Preferential Cu diffusion to the ends of AuCu alloy nanorod during galvanic replacement reaction

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In galvanic replacement reaction between metal alloy nanoparticles and metal salts, along with concentration of metal salts, factors such as distribution of elements significantly affect the reaction mechanism, and thus the optical and catalytic properties of the products. This study investigates how alloy $AuCu_3$ nanorods follows different reaction pathways by varying Au precursor concentration during galvanic replacement.

While asymmetric diffusion of the Cu to one of the ends leads to hollow rods at low Au precursor concentrations, symmetric Cu diffusion leads to peanut shaped structures followed by breakage of rod in the center when high concentration of Au precursor was used. In-situ dark field scattering studies were also performed to study the interesting optical properties during these morphological transformations. The change in conductive junction during structural evolution was found to largely influence the optical properties. Also, the hollow Au-Cu NRs were demonstrated as excellent catalysts for *p*-nitrophenol reduction with a k_{app}/ m^2 value of 205.

COLL 159

Tunable size and shape control synthesis of crystalline and amorphous tin phosphide nanoparticles

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Tin phosphides as a class of materials that gained significant interest in catalysis, Li and Na ion batteries, and thermoelectric applications. Tin phosphide exists in four different stoichiometries such as Sn_4P_3, Sn_3P_4, SnP, and SnP_3. Several synthetic methods were reported to produce tin phosphides, especially for $Sn_4P_{3,}$ and none of them could afford in controlling the size and crystal phase, subsequently resulted in the formation of bulk. The challenge remained same in pursuit of nanoscale synthesis. Owing to lack of proper synthetic methodologies, the physicochemical properties of tin phosphides have poorly understood to date. The essence of developing a unique synthetic protocol to produce nanoscale tin phosphide has been achieved through colloidal synthesis. We have produced tin phosphide nanoparticles (NPs) for the first time with control over size, morphology, and crystal pahse. Out of four stable stoichiometries, we have developed a synthetic strategy for three different phases of tin phosphides including rhombohedral Sn_4P_3, hexagonal SnP, and amorphous $Sn_3P_{4.}$ Herein we report the synthetic parameters such as temperature, choice of precursor and their ratio, and additional coordinating solvents that are critical in obtaining the amorphous and crystalline phases, size and morphology of NPs in view of their application in photocatalysis.

COLL 160

Smart metallic coating based on nanocontainers for improving the corrosion resistance of magnesium alloys

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The design of coating structure is important for improving the anticorrosion ability of magnesium alloys. This presentation reports the results of an investigation of the design and preparation of a new smart metallic coating from an electroless nickel plating bath which contains nanocontainers (NCs) that are modified with pH-response nanovalves. The NCs were derived from hollow mesoporous silica spheres and loaded with inorganic corrosion inhibitor (fluoride ions) which could release and bond with the oxidation state of magnesium when corrosion process happens. The combination of fluoride and magnesium results in the formation of MgF_2 deposit as an inhibitive component at the interface between the substrate and the corrosion medium. This coating self-detects the local active corrosion processes on the damage area of the metal based on the local pH change as a result of the formation of hydroxide ions in active cathodic zones and the oxidation of the magnesium or aluminum at anodic sites. Releasing behavior of fluoride from the NCs at different pHs, and the durability of the corrosion resistance from immersion test and electrochemical impedance spectroscopic characterizations will be discussed. These findings provide new insights into the design and preparation of high-capacity anticorrosion metallic coatings based on nanotechnology.

COLL 161

Insights into the molecular and electronic structure of supported catalyst and catalytic supports by sum frequency spectroscopy

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The surface specific study of catalytic interfaces is an area of interest for scientists across various disciplines. We make use of the interfacial selectivity and sensitivity of sum frequency generation vibrational spectroscopy (SFG-VS) to obtain structural information for model catalytic surfaces. We examine the vibrational signatures of a supported Jacobsen's catalyst in the methyl, carbonyl, and fingerprint region. We report the oxomanganese stretching mode as direct probe for the oxidized organometallic catalyst anchored to the surface as this species is catalytically active and serves as an expoxidation facilitator. We demonstrate how SFG-VS can be used to provide orientational information as well as catalytic information directly at the surface of the support. We also present doubly-resonant sum frequency generation (DR-SFG) measurements where a tunable visible upconverting laser is scanned in the VIS-IR sum frequency measurements for a series of fullerene/substrate interfaces using both insulating and conducting surfaces. We present the qualitative and quantitative trends across the visible range used and provide high quality and comprehensive fullerene SFG spectra with direct insights into the vibronic structure of these carbon based supports.

COLL 162

Structural evolution of hollow Pt-Ag nanocrystals for the methanol oxidation reaction with enhanced activity and durability

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The control of the structure and surface composition change of hollow bimetallic nanocatalysts can effectively tune their catalytic properties. Here we demonstrate an unconventional strategy to synthesize hollow structured Pt-Ag nanocrystals for enhancement electrocatalytic property of methanol oxidation reaction. Shortly after the injection of Ag precursors, an intermediate of $Pt_{17}Ag_{83}$ alloying nanocrystals formed. Then the continued deposition of Pt on the surface of the intermediates induced Ag atoms to segregate and form Ag@Pt core-shell NPs. The structure finally evolved hollow structures by a thermodynamic controllable process. The hollow Pt-Ag nanocatalysts exhibited excellent catalytic activity and durability for methanol oxidation and *p*-nitrophenol reduction. The concept of forming hollow nanocrystals different from traditional method can be used toward the design and synthesis of other hollow nanostructures.

COLL 163

Sol-gel assembly of Au/Ag alloy nanoparticles into aerogels for application in surface enhanced Raman scattering

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The development of diagnostic tools for biomedical applications has been a great interest in science, engineering, and nano-medicine. Noble metal nanoparticles (MNPs) such as Au and Ag, have gained considerable attention in these technologies due to their fascinating physical properties. One such tool is surface enhance Raman spectroscopy (SERS) that has been developed as an analytical tool to probe molecular vibrations in the close proximity of metal nanostructures. The strong electromagnetic fields generated in the vicinity of the Au and Ag NPs are reported to enhance the Raman signal as much as 10^{10} fold, potentially enabling detection at the single molecular level. Although high SERS effects are reported with different arrays and low dimensional aggregates of Ag and Au nanostructures, uniform and reproducible SERS substrates are yet to be developed for practical applications. We have recently investigated the cross-linking of Au/Ag and Ag NPs into high surface area, highly porous, plasmonic nanostructures (aerogels) for identification of chronic biomolecules. The resultant metal aerogels exhibit interconnected network of micropores (< 2 nm) and mesopores (2- 50 nm) providing a facile conduit for molecular transport and narrow interparticle gaps between plasmonic NPs are resulting in significant SERS effects. Herein, the influence of gel morphology on identification of selected lipid biomolecules will be presented. As-formed metal aerogels were characterized by using powder X-ray diffractometry, UV-visible spectroscopy, scanning electron microscopy, transmission electron microscopy, surface area and porosimetry to evaluate their structure, optoelectronic, morphological, and surface properties. The influence of high surface area, nanoscale porosity, and NP morphology on SERS effects will be discussed.

COLL 164

Synthesis and characterization of size, composition and shape controlled ternary nanoparticles and electrocatalytic properties

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The ability to control the size, composition and shape of alloy nanoparticles is important to tune the catalytic and electrocatalytic properties for many energy conversion related reactions. This presentation describes recent results of a systematic investigation of the control parameters in a one-step synthesis of ternary nanoparticles with controlled size, composition and shape, focusing on PtNiCo nanoparticles. The nanoparticles are analyzed using several techniques, including inductively coupled plasma – optical emission spectroscopy, transmission electron microscopy, elemental mapping, and synchrotron high-energy x-ray diffraction coupled to atomic pair distribution function analysis. The results reveal highly-monodispersed ternary alloy nanoparticles with controlled composition and shape. The correlation between the size, composition and shape of the nanoparticles and the synthesis control parameters will be discussed. Results from testing the electrocatalytic activity of the nanoparticles for oxygen reduction reaction will also be discussed, focusing on determining the differences of electrocatalytic properties between nanospheres and nanocubes, which shine some light on the design and preparation of nanoalloy catalysts.

COLL 165

Photonic encryption of inverse opals with combinatorial codes for security applications

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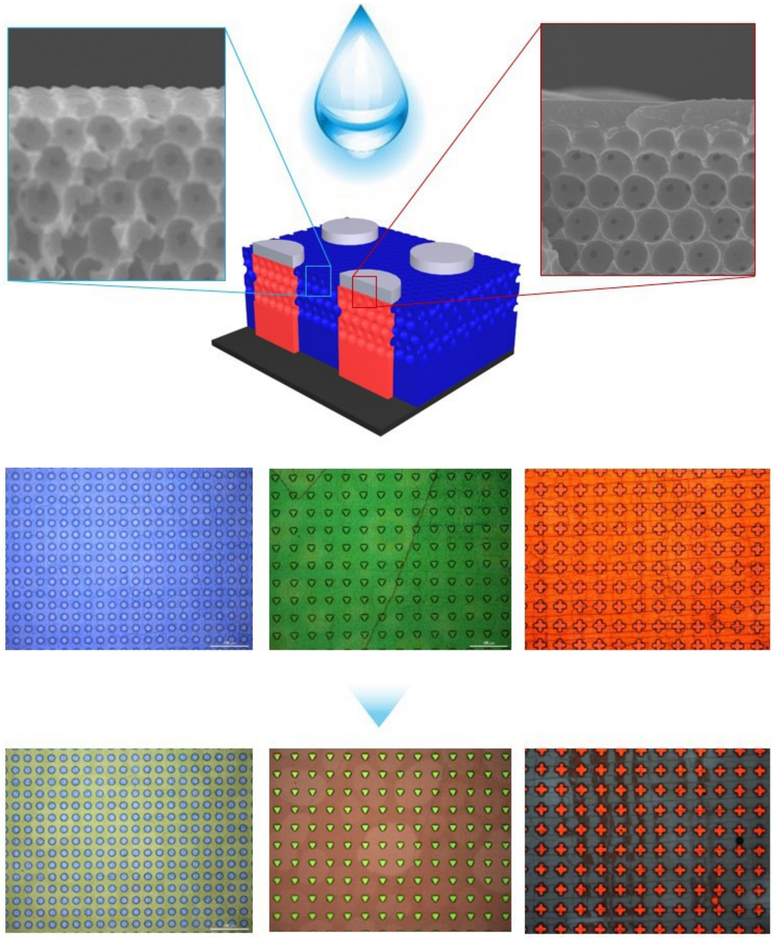
Self-assembly of monodisperse colloidal nanoparticles into regular structures have attracted a great deal of interest due to unique photonic property and various potential applications. Colloidal crystals whose spatial periodicity is comparable to half the wavelength do not allow propagation of the selected wavelength of light, thereby displaying pronounced reflection colors. The colors are iridescent and never fade as long as the structures persist, unlike chemical pigments or dyes. Such unique photonic properties of colloidal crystals render them appealing for security materials. However, micropatterning and encryption technology to achieve advanced functionality in security applications still remains an important challenge. In this work, we report a simple method to encrypt polymeric inverse opals with a combinatorial code of micropatterend graphic and unique spectrum. To accomplish this, we prepared micropattern of photoresist on the top surface of hydrophobic inverse opal by photolithography, which served as a shadow mask for directional reactive ion etching with oxygen gas. The selective infiltration provides unique spectral code with two peaks composed of the original and the shifted, where position of the shifted peak is determined by refractive index of the aqueous solution. Therefore, the decoded inverse opals deliver unique combinatorial code which is revealed only when aqueous solution agreed in advance is used for decoding. In addition, the photonic structures are chemically stable, maintaining the invariant combinatorial codes for many cycles of uses and a long storage period. Moreover, the inverse opal film can be released from substrate to be freestanding, which can be further transferred into any surfaces for anti-counterfeiting purpose. This photonic encryption material will provide new opportunity in a wide range of security applications.



COLL 166

Reductive grafting of gold-aryl layer from sterically demanding diazonium gold(III) salts

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Grafted aryl layer on the in situ electrochemically reduced gold surface from [Br-4-$C_6H_4N{\equiv}N$]$AuCl_4$ salt is robust and compact. Based on the open circuit potential experiments, grafting following our procedure is more efficient than grafting of [Br-4-$C_6H_4N{\equiv}N$]BF_4 on gold electrode surface; this follows the open-circuit potential order EOCP (in situ reduced gold) < EOCP (gold electrode). The formation of the grafted gold-aryl layer can be easily detected through the disappearance of the reduction peak after the first cycle, ferrocene electron transfer suppression, and sharp decrease in the current in the first few seconds in the chronoamperometry experiments instead of a decrease ensuing Cottrell law. In the sterically demanding diazonium salt [4-Br-2,6-Me_2-

$C_6H_2N{\equiv}N]AuCl_4$, the current of the reduction peak remains nearly constant after 20 cycles repetitive scan. The grafted layer was characterized using XPS, SEM, XRD and contact angle measurements.

COLL 167

Plasmon-assisted photocatalytic reactions on nanocrystal surfaces

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The visible-light extinction of noble metal nanoparticles surpasses those of semiconductor and molecular dyes by several orders of magnitude. At present, this phenomenon is widely used for enhancing Raman scattering in bio-sensing applications, meanwhile, the attempts of utilizing the plasmon energy for the generation of excitons in photocatalytic systems have been less successful. To explore this issue, our study focuses on understanding the key factors that prevent an efficient exciton-plasmon energy exchange in composite nanocrystals consisting of several interfaced inorganic domains. These will include a Au nanoparticle featuring a plasmon resonance in the visible range ($\lambda \approx 550$ nm), an insulating semiconductor shell (e.g. ZnS) designed to prevent the backwards transfer of photoinduced charges into Au, an acceptor shell (e.g. CdSe) with the band gap energy red-shifted from the plasmon resonance ($\lambda \approx 600$ nm), and a catalyst nanoparticle (e.g small-diameter Pt). In this geometry, Au plasmons will decay by transferring some of the energy to band gap excitations of the Acceptor (CdSe). The resulting electron-holes pairs will then be forced to dissociate across the Acceptor/Catalyst interface. The validity of the reported scheme is illustrated in this work by converting a significant portion of the plasmon energy towards the reduction of methyl viologen.

COLL 168

Exfoliated montmorillonite nanocomposites by catechol conjugated polymer for antifouling and photothermal antibacterial effect

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We have been prepared exfoliated montmorillonite (MMT) for photothermal antibacterial and antifouling effect. A near infrared (NIR) active hyper-thermal (IR825) antibacterial nanocomposites constructed using catechol conjugated polyvinylpyrrolidione with sultones groups through ionic exchange reactions in MMT sheets. Studying this nanocomposite revealed a sharp increase in photothermal heat as a function of irradiation time. Another agent was incorporated in MMT layer as antifouling capability

catechol and sultones quaternized polymer. The dispersibility of MMT has been improved by ion exchange reaction between MMT and functionalized polymer consisting of catechol moiety for adhesive property between the interlayer of and MMT by catechol, and the zwitterionic structure for the interval between the silicate layers of MMT by different ratio of polymer-to-MMT was easy to enlarge and exfoliate the clay layers. The layered MMT structure is promising for optimizing the required thermal stability to increase the photothermal heat. The remaining catechol moiety in exfoliated MMT allowed easy access to surface coating confirmed by several experiments which is contact angle, XPS measurement and antifouling effect and photothermal antibacterial effect. Our study suggest new design for photothermal and antifouling tags based stable thermal of MMT nanocomposites.

COLL 169

Anion mediated end-shape control in seed-mediated growth of gold nanorods

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End-shape-controlled gold nanorods (GNRs) were synthesized at room-temperature by a seeded-growth method, in which hexadecyltrimethylammonium bromide (CTAB) was used as a stabilizer and capping agent. The average dimension of the GNRs was 46 nm in length and 15 nm in diameter, which corresponds to aspect ratio of c.a. 3.0. Then, their both ends were further grown at the presence of silver precursor (AgNO3), resulting in formation of arrow-head GNRs. By tuning the amount of the silver precursor, the end-shape of the GNRs was changed to dumbbell like shape. Moreover, the growth rate of gold could be controlled by tuning the amount of hydrochloric acid (HCl). While arrow-headed GNRs having sharp edges were produced without HCl, the GNRs having dog-bone like or round-head shape at both ends were obtained with HCl.

COLL 170

Localization of electrochemical events on the surface of plasmonic nanoelectrodes

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The use of plasmonic materials as nanoelectrodes relies on the fundamental understanding of what is happening at the nanoscale level. Fluorescence is used as an optical readout of redox chemistry to follow electrochemical events on the surface of plasmonic nanoparticle electrodes. By using a fluorescent probe that alternates between an emissive and non-emissive state based on its oxidation state, the electrochemical activity of the probe along the surface of nanoelectrodes is studied. Moreover, comparing the properties of the fluorescence reporter in its native state

versus covalently tethered to the plasmonic nanoelectrode provides insight into the mechanistic properties of the molecule and its behavior in the nanoscale regime.

COLL 171

Triplet-state mediated super-resolution imaging of fluorescently-labeled gold nanorods

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We use a super-resolution technique, specifically ground state depletion with individual molecule return (GSDIM), to map the location of fluorescently-labeled-double-stranded DNA which are bound to the surface of gold nanorods. Our goals include developing an optical technique which can reconstruct the size, shape, and orientation of the gold nanorod substrates, as well as providing information about how ligands bind to the surface of gold nanoparticles. The ultimate objective of this project is to investigate and understand the heterogeneity of ligand attachment at the single particle, single molecule level, a regime that cannot be obtained through traditional, ensemble-averaged measurements.

COLL 172

Sequestration of methylene blue into polyelectrolyte coacervates

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Complex coacervation of oppositely charged polyelectrolytes can act as a driving force to separate solutes into either the polymer-rich phase or water-rich phase based on relative affinities between the solutes and polyelectrolytes, which therefore can be used as an efficient and non-energy-intensive manner to remove dilute contaminants from large volumes of water. We present here the sequestration of a cationic aromatic, water soluble dye, methylene blue (MB), into polyelectrolyte coacervates formed with branched polyethylene imine (BPEI) and one of three different anions, either sulfonated polystyrene (SPS), poly(acrylic acid) (PAA) or poly(vinyl sulfonic acid) (PVS). In both BPEI-PAA and BPEI-PVS coacervate system, MB can interact with PAA electrostatically to realize the sequestration of MB into coacervates. While in BPEI-SPS system, both electrostatic and π-π interaction contribute to the sequestration of MB into coacervates, leading to a significantly higher sequestration capacity over a large range of dye concentrations compared to BPEI-PAA and BPEI-PVS coacervate system. The red shift in UV-vis maximum absorbance wavelength (λmax) of MB in aqueous solution and coacervate with the presence of SPS demonstrates the formation of π-π interaction between MB and SPS in both solution and coacervate state. Additionally, the inverse of zeta potential of BEPI-SPS coacervates from negative to positive with an increasing concentration of MB indicating the existence of π-π interaction between MB and SPS.

COLL 173

Effects of cations on the structure and vibrational dynamics of mineral/water interfaces

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Interfacial water plays a role in many systems such as protein folding, heterogeneous catalysis, geochemical systems, and nanoparticle synthesis. The structure and dynamics of interfacial water are highly sensitive to the local electric fields. Furthermore, ions can play an important role in the interfacial environment. Ions can screen interfacial electric fields determining the distance over which water molecules are oriented with respect to the surface. Additionally, ions have been shown to affect the solvent organization in a manner that depends strongly on surface charge.

Using steady state and time-resolved vibrational sum-frequency generation (vSFG) spectroscopy we investigated interfacial water species and their relaxation dynamics when exposed to singly and multivalent cations. Cation identity has an effect on vSFG spectral response, and the vibrational dynamics, presumably reflecting differences in the organization of water at the interface consistent with recent classical MD simulations.

COLL 174

Design and analysis of parallel-oriented multilayer organic thin films

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Effective charge transport in organic semiconductor films is an important property for device efficiency, and is strongly related to the degree of ordering in the organic film. However, many polyaromatic molecules used in these films (*e.g.*, pentacene) crystallize in a sub-optimal packing arrangement (*e.g.*, herringbone), hindering charge transport through the film. In this collaborative study, we have developed tris(*N*-phenyltriazole) (TPT) with a bi-functional structure strategy: donor/acceptor regions are designed in the molecule to direct complementary π-π stacking and peripheral phenyl groups are designed for electron energy level alignment for facile charge transport. The result, as shown by molecular-resolution scanning probe microscopy studies, is films with highly-organized crystalline domains in a co-facial, parallel displaced stacking arrangement. This intermolecular interaction directs stacking of the π faces of energy-aligned phenyl groups throughout the film to create pathways for efficient charge transport. We have

studied TPT films thicker than 20 monolayers and found that the structure remains consistent throughout the layers. Excellent charge transport is indicated by STM characterization as well as by device conductivity characterization, showing conductivity values that compare well with other organic materials, such as pentacene. We further investigated the nature of the stacking and charge transport by functionalization of the TPT to alter the π-electron distribution of the molecule, which allowed us to gain a better understanding of how changing the π-π donor/acceptor strength affects stacking as well as charge transport.

COLL 175

Catalytic degradation of organophosphate esters using gold nanoparticles, supported copper(II) bipyridine complexes and plasmonics

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Gold surfaces modified with Cu(II) complexes were used for the catalytic hydrolysis of phosphate esters under low-power laser irradiation. Using Michaelis-Menten formalism to determine rate constants, citrate stabilized gold nanoparticles catalyzed the hydrolysis of methyl parathion (MeP) with $k_{\mathrm{cat}} = 1.8 \pm 0.2 \times 10^{-4}\ \mathrm{s}^{-1}$ at pH 8.1. Additionally, the AuNP supported copper(II) complex Cu[(*N*-(6-mercaptohexyl)-2,2'-bipyridinyl-5-carboxamide)]Cl_2 (**1**) enhanced the activity of MeP by 90-fold ($k_{cat} = 1.2 \pm 0.3 \times 10^{-5}\ \mathrm{s}^{-1}$) compared to the unsupported Cu(II) bipyridine complex. Laser irradiation (300 mW, 532 nm) of **1**/AuNP resulted in a 12-fold enhancement for MeP hydrolysis ($k_{\mathrm{cat}} = 4.3 \pm 2 \times 10^{-4}$) and a 1000-fold enhancement for BNPP hydrolysis ($k_{\mathrm{cat}} = 1.3 \pm 0.06 \times 10^{-4}$). The ability to influence homogeneous catalytic reactions using plasmonics is an important step towards the development of improved catalysts.

COLL 176

Oxidation behavior of stainless core/alloy nanoparticles

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In this presentation we describe the oxidation behavior of core/alloy nanoparticles with stainless interfaces. The oxidation behavior of Fe-Cr-Ni nanoparticles (NPs) was studied by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and salt-spray analysis. Zerovalent Cr & Ni precursors were thermally decomposed and deposited on the pre-synthesized α-Fe cores. Composition of shell layer was decided by

changing the shell deposition routes. Fe/Cr_XNi_{1-x} NPs showed highest resistance towards oxidation. The results were considered in relation to metal alloying rates and oxidative diffusion kinetics as described by Cabrera Mott Theory (CMT). The findings indicate that the NP composition can be tailored in order to control diffusion rates and oxide thickness at the nano-interface, leading to varied oxidation behavior. We thank the NSF for supporting this project (DMR-1410569).

COLL 177

Magnetite containing zeolites: Enhanced catalyst stability via modification

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Methanol-to-hydrocarbon (MTH) or methanol-to-gasoline (MTG) reactions receive considerable attention as scientists and society are moving towards renewable sources of both chemicals and fuels. Zeolite ZSM-5 is a well-known catalyst of MTH or MTG transformations, yet two significant issues inhibit its applications: a comparatively low yield of valuable hydrocarbons and deactivation by coke formation. We developed ZSM-5 catalysts containing magnetite nanoparticles which allowed for a higher yield of C_5-C_8 and C_9-C_{11} hydrocarbons. However, the stability of these catalysts on stream or in repeat catalytic cycles was still mediocre. In this presentation we explore doping of Fe_3O_4-ZSM-5 with various amounts of Ni and Ca species to enhance the catalyst stability. We determined that modification of Fe_3O_4-ZSM-5 with 10 wt.% of Ni species leads to a significant stability enhancement as well as higher yields of the desired hydrocarbons, while 1 wt.% of Ni is clearly insufficient to alter the catalyst behavior. We also found that calcination of the above catalysts at 350 °C before or after Ni addition significantly influences the catalyst properties. A possibility of a combination of the enhanced catalytic performance with magnetic fixation in a tubular reactor or a microreactor in the external magnetic field makes them promising for advanced industrial applications.

COLL 178

Growing patterned 2D monolayers into 3D: STM and MALDI studies of monolayer reactions

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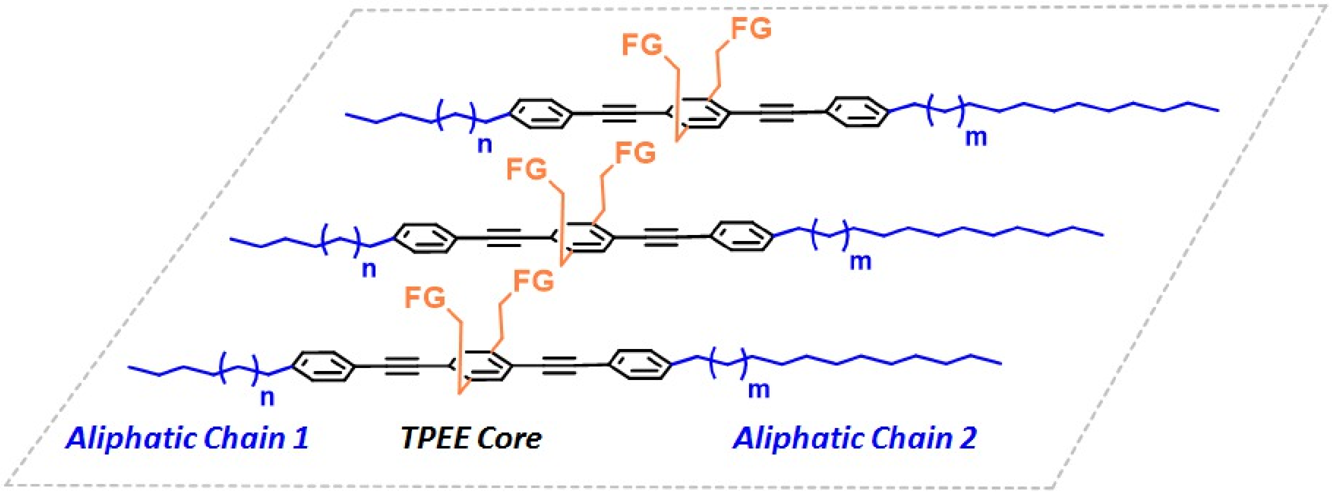
There is interest in preparing materials that provide precise, nanometer scale control of composition and structure over macroscopic distances. Such nanostructured materials find increasing application, for example, in photovoltaic materials. Monolayer (ML) self-assembly provides ready access to crystalline, 2D arrays with nano-scale features. Self-assembly of shape-complementary building blocks can yield complex architectures (i.e. supramolecular MLs) exhibiting composition and reactivity periodicity over extended distances. We are developing these surface supported, compositionally patterned MLs as templates for growing compositionally patterned, 3D materials. We have designed and synthesized a series of triphenyleneethynylene (TPEE) molecules that bear long aliphatic chains for patterned self-assembly (on graphite), and that present various reactive groups at the ML-solution interface for polymerization and template applications. The TPEE MLs present columns of reactive surface functionalities, ~ 1 nm wide, with nearest columns possibly spaced by distances of 5 - 20 nm. ML columns presenting hydroxyl or ketone groups react with solution reagents to form ester or oxime linkages at the interface. Efforts to grow compositionally patterned second layers are ongoing. Scanning Tunneling Microscopy (STM) and [Matrix Assisted] Laser Desorption/Ionization - Mass Spectrometry ([MA]LDI-MS) are used to directly characterize ML self-assembly on graphite and surface reactions.



TPEE Self-Assembly on Surface with Off-Surface Functional Groups

COLL 179

Green synthesis of iron(0) nanochains-polymer composites and their colloidal self-assembly

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With size-dependent optical, electronic, magnetic, and chemical properties, many investigations on the preparation of metal nanoparticles have already been performed and utilized in heterogeneous catalysis, magnetic sensors, and magnetic storage media, and power-transformer cores. To be applicable for variety of such applications, there is a critical need to chemical control over the particle size and morphology.
Over the last few years, various synthetic methods have been developed to produce iron nanoparticles, modify the nanoparticle surface properties, and enhance their optical response. The most widely used green synthesis is the borohydrate reduction of Fe(II) or Fe(III) ions in aqueous media. However, expanding this method towards controlling the particle size and morphology has been still limited in literature. Here we describe an extensive study of preparing iron nanoparticles and nanochains using borohydride reduction and in-situ incorporation of iron nanoparticles to variety of polymeric materials to make iron-polymer nanocomposites. The study describes here not only discusses the synthesis of variety of iron nanostructures with controlled morphologies, but also focuses their colloidal self-assembly on conductive substrates for magnetic storage devices.

COLL 180

Increased purity of surfactant-templated silica nanotubes through understanding of nanotube fragmentation into hollow nanospheres under stirring

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Synthesis of silica nanotubes was conducted via surfactant templating method using Pluronic triblock-opolymer surfactant, F127, composed of poly(ethylene oxide) outer blocks and a poly(propylene oxide) center block (PEO106-PPO70-PEO106) in the presence of excess amount of hydrocarbon swelling agent (toluene) at 11°C. Under previously identified conditions, the purity of the nanotube product was compromised by the nanosphere contamination. Here, it is demonstrated that the stirring speed has an effect on the presence of the spherical contamination: the higher the stirring rate, the higher the levels of contamination, as seen by transmission electron microscopy (TEM). The contamination with nanospheres was minimized at lower stirring rate. This finding demonstrates that the silica nanotube product forms when the synthesis is carried out at quite low stirring rates. Moreover, it is clear that the stirring, and thus presumably the shearing force, facilitates the nanotube fragmentation into hollow nanospheres. Eventually at a high stirring rate, only nanospheres were observed.

COLL 181

Control of exciton and trion dynamics in a molybdenum disulfide monolayer with interfacial dielectrics

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Molybdenum disulfide monolayer is a two-dimensional nanomaterial with properties that differ from the bulk. For instance, the optical properties of the monolayer material are largely determined by quantum confinement: direct band gap for the monolayer versus indirect band gap in the bulk, many-body effects, environmental effects due to higher surface-to-volume ratio. The direct band gap nature of molybdenum disulfide monolayer leads to photoluminescence quantum yields approaching unity. This effect makes molybdenum disulfide an attractive material for optoelectronic applications.
Molybdenum disulfide monolayers emit light from A and B excitons, as well as from A^- trion states. Photoluminescence in the monolayer material is influenced by screening by the surrounding dielectric environment. High quality large area monolayer samples were grown on sapphire substrates by chemical vapor deposition.
Monolayer quality was assessed by Raman microscopy. To study the effect of dielectric screening, samples were immersed in several organic solvents and the optical properties were investigated. The kinetics of photo- excited species were studied using time-resolved photoluminescence, and ultrafast transient absorption spectroscopies. It was shown that the dielectric environment strongly influences the population ratios of excited species as well as their relaxation dynamics. Experimental results are in good agreement with theory.

COLL 182

Spontaneous aggregate formation by poly(ethylene glycol)-containing zwitterionic amphiphiles at room temperature: A fluorescence, microscopy, and calorimetric investigation

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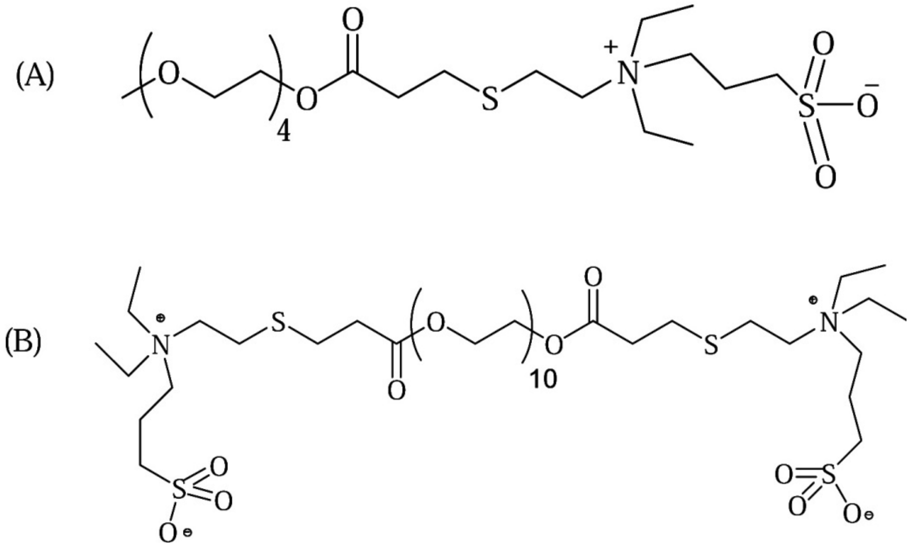
Two novel poly(ethylene glycol) (PEG) based zwitterionic amphiphiles, one is single-headed and the other is bola, were developed and characterized. The interesting fact is that PEG chain acts here as the hydrophobic backbone for both the amphiphiles. The interfacial properties and the solution behavior of the amphiphiles were thoroughly studied in aqueous buffer (pH 7.0). Despite having so called polar backbone, the amphiphiles were found to self assemble to form aggregates above a relatively low critical aggregation concentration (*cac*) at room temperature. The self-assembly formation was studied in aqueous solution by steady-state fluorescence probe techniques. The spontaneity of the aggregate formation was again confirmed by measuring the thermodynamic parameters using isothermal titration calorimeter. The thermodynamic parameters clearly suggest that the hydrophobic interaction among the PEG chains is the main driving force for aggregate formation. Spontaneous aggregate formation was again confirmed by dynamic light scattering and microscopic technique. The aggregates were observed to be fairly stable with respect to increase of surfactant concentration, solution pH, aging time and temperature.



Chemical structures of (A) single-headed amphiphile and, (B) bolaamphiphle.

COLL 183

Graphene oxide resin design for stereolithography

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Current stereolithography (SLA) resins are difficult to handle due to dispersion instability. There is always a need to mix the resin thoroughly prior to use and, in some instances, sonication is needed to yield better print quality. Moreover, printed parts often have poor mechanical properties and are prone to shrinkage, which limits their use to rapid prototyping. This study aims to incorporate functionalized graphene oxide (GO) into commercially available SLA resin to prevent shrinkage, improve mechanical property, and control resin viscosity for better handling and print quality. In the long run, this study will help convert the SLA process from rapid prototyping to rapid manufacturing.

GO is synthesized using modified Hummer’s method and functionalized with two different polymers: one that would improve GO-resin interaction to address shrinkage and enhance mechanical property and another polymer to control viscosity for better processability. Successful grafting of these polymers onto GO sheets is shown using Raman, UV-Vis, and Fourier Transform Infrared (FTIR) spectroscopy. Rheological measurements, stability test, tensile test, and scanning electron microscopy (SEM) are also performed to assess printing performance of the resin after GO functionalization.

COLL 184

Patterned crystallization on unpatterned substrates

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Many members of the large family of 1,3-bis(X-phenyl)ureas (PUs) crystallize in C(4)R12(6) motifs formed from intermolecular hydrogen bonding between urea amide and carbonyl groups. Needle-like morphologies are frequently exhibited in these systems. Previous work in our laboratory has shown that improved crystal quality and/or polymorph control can be accomplished by heterogeneous nucleation on functionalized siloxane-glass substrates. Slow evaporation crystallization of several PUs on siloxane substrates revealed unusual circular arrays of crystals under some solvent conditions. Fast drop-cast crystallization onto siloxane substrates resulted in the formation of fibers with similar curvature from the same select solvents. These observations suggest that the substrates stabilize fast growing and flexible 1-dimensional aggregates of PU molecules, which eventually thicken and fracture. This same growth mechanism has been observed in other molecular crystal systems.

COLL 185

Hybrid organic/inorganic TiO_2 composites for enhanced UV shielding and antioxidant properties

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Multifunctional TiO_2 composites were prepared by hybridization of inorganic TiO_2 using organic skin lightening materials with antioxidant properties such as phenylethyl resorcinol and alpha-bisabolol. Homogeneous TiO_2 microspheres, as supporting materials in the composites were synthesized through surfactant-assisted sol-gel method. Prior to the functionalization, carboxylation treatment using monochloroacetic acid was performed to introduce carboxyl chemical binders on the surface of TiO_2 substrate. The hybrid TiO_2 composites could be obtained through condensation esterification between carboxyl groups present on the TiO_2 surface and hydroxyl groups of skin lightening materials. The obtained composites demonstrated enhanced UV light adsorption ability in UVA region due to the presence of chemical bridges formed

between TiO_2 and skin lightening materials, which succcessfully tuned the bandgap of TiO_2. The antioxidant properties of functionalized TiO_2 composites were examined by scavenging activities of ABTS and DPPH free radicals. Both functionalized microspheres exhibited scavenging abitlity towards ABTS and DPPH free radicals. Our studies revealed that the surface modification of TiO_2 with phenylethyl resorcinol and alpha-bisabolol successfully suppress the generation of reactive free radicals and able to protect human skin from oxidative damage caused by harmful UV rays.

COLL 186

Synthesis of dibranched semifluorinated polymers for fluorous nanoemulsion-based drug delivery

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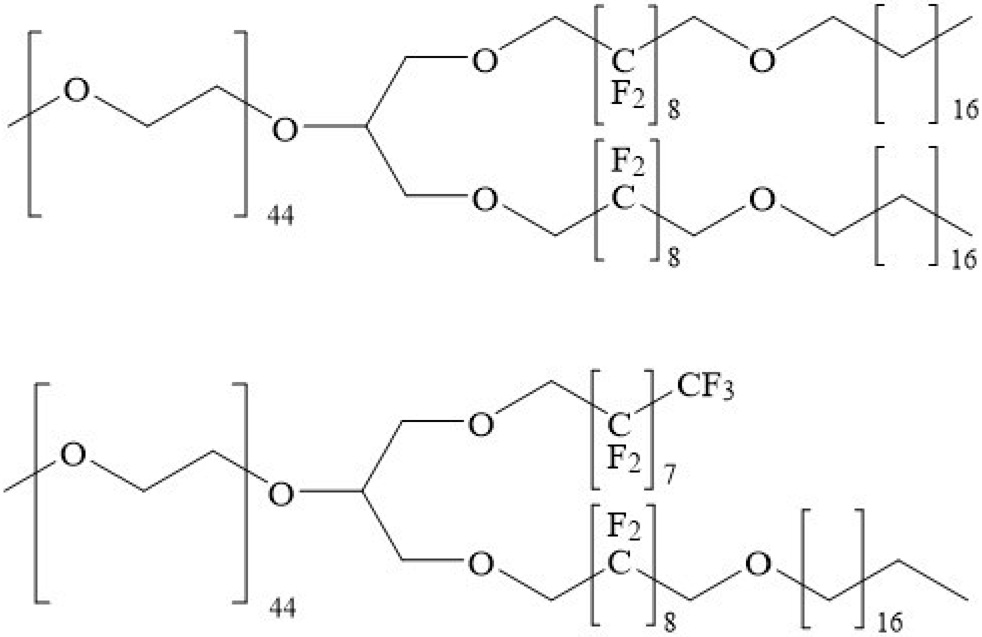
The introduction of fluorine atoms in an organic molecule considerably changes the properties of that compound. Fluorocarbons are more hydrophobic than hydrocarbons, resulting in their ability to form a fluorous phase, which is phase-separated from both hydrophilic and lipophilic phases. The introduction of fluorocarbons in organic molecules thus results in amphiphilic character that can lead to self-assembly into stable, well-organized semifluorinated colloids. These nanoaggregates can be used in a variety of applications, nanoemulsions being one of the most promising. Nanoemulsions are composed of a hydrophobic-oil nanodroplet core in which the hydrophobic drug is loaded. An amphiphilic polymer is then used to stabilize the emulsion in aqueous solution. Fluorous nanoemulsions, stabilized by semifluorinated block copolymers, are particularly promising for controlled drug delivery.

In order to investigate the drug release profile of fluorous nanoemulsions, two triphilic and dibranched semifluorinated polymers were synthesized. In both polymers, the hydrophilic unit is composed of poly(ethylene glycol) (PEG) that ensures water solubility and biocompatibility. The lipophilic block is a linear alkyl chain composed of eighteen carbon atoms. In one of the two synthesized polymers, the fluorous block comprises eight CF_2-residues and is placed between the hydrophilic and lipophilic blocks in both branches. The placement of the fluorous shell in an intermediate position between the PEG and the hydrophobic moiety shields the internal drug-containing oil droplet and allows controlled drug delivery. The second synthesized polymer is characterized by one shorter branch, composed of only the fluorous block. This design, when compared to that of the first polymer, allows the assessment of the relative importance of both the hydrophobic and fluorous blocks in the delivery properties of the corresponding nanoemulsions. Thus, we have investigated how varying the size and structure of semifluorinated polymers affects the formation and stability of nanoemulsions as well as the rate of drug release.



Scheme 1: Chemical structures of the synthesized, dibranched semifluorinated polymers

COLL 187

Polymorph selection by vapor phase deposition on functionalized substrates

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Many organic molecules crystallize as concomitant mixtures of polymorphs from conventional slow evaporation methods. Polymorph selection can often be achieved through heterogeneous nucleation on templates, though the role of solvent at the crystal/template interfaces is not well understood. The model compound diphenylurea (PU) crystallizes from various solvents as a concomitant mixture of α and β polymorphs. Herein we examine the vapor phase deposition of PU thin films directly onto siloxane–glass monolayer substrates with various terminal functionalities. Polymorph selection and a range of interesting crystal morphologies are observed. Comparison of the crystalline material deposited on siloxanes under vapor phase (solvent-free) and solution evaporation conditions provides some insight on the role of solvent at the crystal/template interface.

COLL 188

Understanding wax microprinting on new substrates

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Robust and cost effective microfluidic paper based devices have always been a dream for point of care diagnostics. Fabrication of such devices by wax printing has recently become popular, mostly using cellulose based filter papers. Here, we report the surface study of printed wax micropatterns on new substrates, i.e. regular printing paper (A4), premium photo paper (PPP), and modified polyethylene terephthalate (*m*PET). The micropatterns (lines and channels) of different sizes were studied under optical microscope and scanning electron microscope to measure the widths in x-y plane and thicknesses in z-axis, respectively. Measured widths of the micropatterns were compared with the printed widths using M/P ratios. When the patterns were printed from 10 µm to 120 µm, M/P ratio decreased from 4 to 1 for the 'channels' and 14 to 2 for the 'lines' revealing that the lowest consistent printing widths were 120 µm for the 'channels' and 240 µm for 'lines'. Printing in vertical fashion produces the micropatterns with smoother boundaries than horizontal fashion. Moreover, printing in horizontal fashion increases M/P ratio for the 'lines' while decreases for the 'channels'. Fidelity of the wax micropatterns were also evaluated by heating at different temperatures. Such as, after heating at 120 °C, PPP and *m*PET showed no significant difference in M/P ratio while this ratio was dramatically increased for A4 substrate from 2 to 6. Thickness of wax at different temperatures was also measured on these substrates, i.e. thickness of wax on *m*PET, PPP and A4 substrates at 25 °C were 30.06 µm ± 1.12 (*m*PET), 34.23 µm ± 2.05 (PPP), and 29.96 µm ± 3.84 (A4), which reduced to 15.86 µm ± 2.08, 20.50 µm ± 1.76 and 6.25 µm ± 1.86 at 120 °C respectively. Then, interdigitated electrodes (IDE) were patterned on PPP using combination of inkjet printing and wax printing followed by electrochemical characterization. The electrochemical response of IDE was comparable to commercially available screen printed electrodes. This study suggests that both PPP and *m*PET substrates can be used in future to fabricate robust multilayered wax printed devices in combination with inkjet printing.

COLL 189

Transferrin modified vitamin E: Conjugated lipidic mixed micellar system as nanocarrier for the delivery of curcumin in cancer

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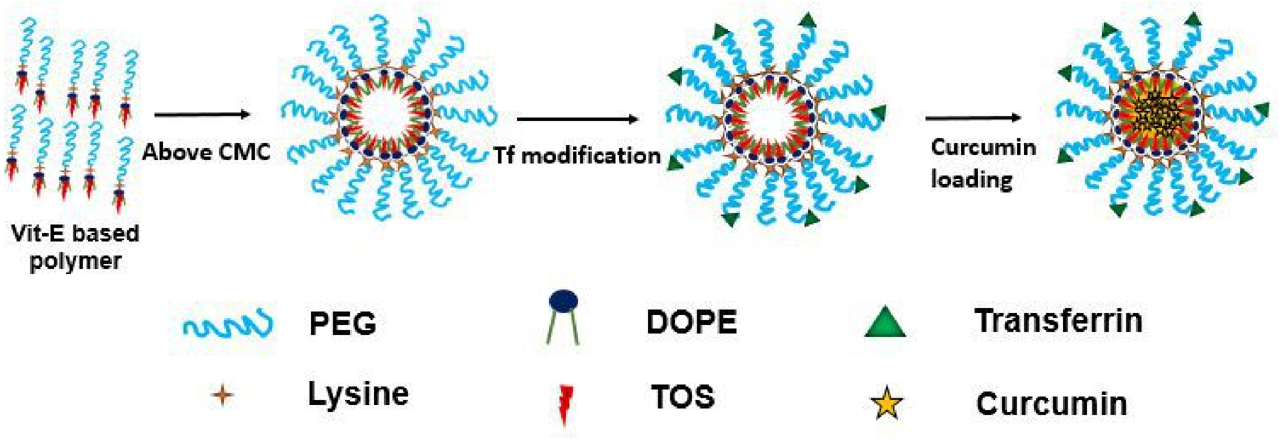
Micelles are self-assembled colloidal particles with the size in nanometer range, in which many small hydrophobic molecules self-assemble spontaneously. Transferrin receptor is a cell membrane-associated glycoprotein on the surface of the cells. The transferrin receptor expression on cancer cells can be up to 100-fold higher than the average expression in normal cells owing to their rapid proliferation rate and iron

demand, thereby transferrin has been explored as a targeting ligand for nanocarriers to deliver therapeutic agent into cancer cells.

In the present study, we have developed a Vit-E conjugated lipid-based co-polymer by conjugating two hydrophobic moieties, phosphatidylethanolamine (PE) and α-tocopherol with poly (ethylene glycol) via an amino acid linkage as shown in Figure 1. The synthesized polymers were characterized by IR and H1 NMR spectroscopy. Further it was modified with transferrin for active targeting to tumor tissue. The micelles size and surface charge size were measured by Zetasizer. Transferrin modified Vit-E/PEG-5k conjugated polymeric micelles (VPM) and unmodified VPM showed mean hydrodynamic diameter of 114.2±1.82 nm and 110.8±1.82 nm respectively. Therefore curcumin was loaded as a model hydrophobic drug and evaluated for drug loading, stability, in vitro release. Cellular uptake study indicated that the Tf-VPM were taken up by cancer cells with higher efficacy compared to VPM. The therapeutic efficacy of the newly developed curcumin loaded mixed micellar system will be assessed in vitro in various cancer cell lines and in vivo by using cancer cell xenograft mouse model.



COLL 190

Preparation of antimicrobial polymers from poly(ethylene-co-acrylic acid) (PEAA) grafted with aliphatic quaternary ammonium salts

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Aliphatic quaternary ammonium salt (QAS) was synthesized by quaternarization of dimethylaminoethanol (DMAE) with 1-chlorododecane. The antibacterial QAS was grafted onto poly(ethylene-co-acrylic acid) (PEAA) copolymer via Steglich esterification using N,N'-dicyclohexylcarbodiimide (DCC) as a catalyst. The effect of reaction temperature on the extent of grafting was investigated by determining the degree of esterification. All the QAS-modified polymers showed significant antibacterial activity against gram-positive bacteria *Staphyloccus aureus* and gram-negative bacteria

Escherichia coli. The modified polymers exhibited the highest antibacterial activity at 135 ^{o}C, while QAS had a lower antibacterial activity. It showed that grafted polymers performed higher antimicrobial activity than the QAS at high temperature, whereas their degradation rate were accelerated as the temperature increased. The results indicated that synthesized polymers using QAS were effective for inhibiting the growth of microorganisms with their hydrophobic chains bonded to PEAA polymers.

COLL 191

Photoinduced spiropyran/merocyanine isomerization at the air/water interface probed by second harmonic generation

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Photoinduced isomerization between spiropyran and merocyanine at the air/water interface was investigated with second harmonic generation (SHG). We demonstrated that spiropyran and merocyanine could be converted into each other reversibly by the 780 nm laser through two-photon processes. Dependence of the reaction rates on the incident laser power revealed that steric hindrance effects and excitonic coupling played important roles in the photoinduced isomerization process. This work provides in-depth understanding of the photoinduced reaction kinetics at the interface, which plays a key role in optical thin-film materials.

COLL 192

Dynamic two-dimensional host-guest architectures at the liquid-graphite interface

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Self-assembly of highly-ordered two-dimensional organic materials at surfaces is being explored as a route to develop the next generation of semiconductors, photovoltaics, sensors, and catalysts. A key opportunity with organic architectures that remains underdeveloped at this point is the design of dynamic and responsive systems. As a recent example, aryl-triazole oligomers exhibit responsive behavior to chemical and electronic stimuli in switching between two supramolecular architectures at the liquid-graphite interface (*ACS Nano* **8**, 10858, 2014). Through chemical functionalization, self-assembly was controlled by tuning supramolecular interactions of the oligomers that respond to host-guest complex formation with anions. Here, we present new studies

using a larger set of macrocycles that are designed for dynamic host-guest complexation to induce molecular switching at the interface between an organic solution and a graphite surface. Heteroaryleneethynylene-based macrocycles form well-defined architectures at the liquid-graphite interface. We have found two distinct supramolecular packing structures depending on the functionalization of the periphery with either alkyl or ethylene glycol chains. The molecules are designed to incorporate small aromatic guests and exhibit co-crystallization structures. We present new scanning tunneling microscopy analysis of different variations of this system and its host-guest behavior. Functionalizing the macrocycles may enable new directions in host-guest interactions at surfaces and dynamic responsive materials.

COLL 193

Supercritical fluid CO_2 deposition of compositional tailored SiO_2-TiO_2 thin films

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Silicon dioxide (SiO_2) films can be produced by hydrolysis of metal alkoxide precursors using tetraethylorthosilicate (TEOS) in the presence of an acid catalyst in supercritical fluid carbon dioxide (sc-CO_2). When titanium alkoxide precursors, such as titanium ethoxide (TEO), or titanium isopropoxide (TIPP) is mixed with TEOS, the reflective index and dielectric constant (*k* value) of the film can be changed. In this study, compositional tailored SiO_2 – TiO_2 thin films are made by varying TEOS/TIIP molar ratios in the mixture of the precursors in sc-CO_2. The thin films produced are investigated by attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR), and X-ray diffraction (XRD). With increasing TEOS content, the structure of the films in XRD show more amorphous-like, while in TIPP rich film, the films show crystalline-like structure. The cross sections of the films before and after annealing show the thickness changes. Scanning electron microscope (SEM) and energy disperse spectroscopy (EDS) measurements are also performed.

COLL 194

Investigating the contribution of steric effects for the preferential organization of methacrylate monomers at air-liquid interface using sum frequency generation spectroscopy

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Investigation of variations in monomer conformational change due to the presence of bulky substituent groups is important as it provides insight into the relations between surface structure and properties of monomers and polymers. The surface properties of

polymers are of interest because they are used as adhesives and as lubricant coatings. Since the monomer units are the building blocks of polymers, investigating functionalized monomers will lead to the understanding of how their surface properties affect the polymer surfaces. In this project, interfacial molecular structures of bulky functionalized methacrylate based monomers are characterized with femtosecond sum frequency generation spectroscopy (FSFGS) at the air-liquid interface. The ethyl group of methacrylate monomer was substituted with a methoxy group ($-OCH_3$), an isopropoxy group ($-OCH(CH_3)_2$), a tertbutoxy group ($-OC(CH_3)_3$), a phenoxy group (-OPh), and a methyl substituted phenoxy group ($-OPh-CH_3$). The α-methyl group has preferential surface ordering at the air-liquid interface for all monomer units. Alkene-methylene group positioned at 3000 cm^{-1} was not observed for 2-Isopropoxyethyl methacrylate monomer SFG spectrum. These observations suggest that the bulkiness of the substituted groups affects the conformation of the molecule at the interface.

COLL 195

Supramolecular nanotubes by anticancer drug assembly

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Over the past two decades, nanotubes (e.g. carbon nanotubes, peptide nanotubes, DNA nanotubes, and protein nanotubes) have attracted extensive interest in biological applications due to their unique physiochemical properties. We report here a new platform of supramolecular nanotubes that are formed by self-assembly of rationally designed prodrugs. We have synthesized a great diversity of prodrugs of different surface chemistries and functionalities (e.g. cationic, anionic, non-ionic, and tumor-targeting ligands) that are capable of associating in aqueous solutions into a tubular morphology, with a width of approximately 10 nm and lengths on the scale of several micrometers. We further demonstrated that other functional molecules such as imaging agents and small molecule drugs can be easily incorporated into these nanotubes through passive diffusion without altering their morphology, affording a facile yet effective means to dope in a variety of different functionalities. Our *in vitro* results revealed that these drug-containing nanotubes exhibited sustainable drug release in the presence of glutathione, a cancer-relevant reducing agent, and showed great efficacy against two cancer cell lines (U87 MG and MCF-7). We believe that this versatile soft nanotube platform has a remarkable potential in cancer treatment and diagnosis.

COLL 196

Ferromagnetism in undoped ZnO nanostructures synthesized by solution plasma process

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Ferromagnetism in undoped metal oxide nanostructures provides a precious platform for realizing advanced nanoelectronic and spintronic applications. Such ferromagnetism is dependent on various factors. In this work, we report the ferromagnetism of undoped ZnO nanostructures for different discharge times from 10 to 40 min by employing solution plasma process, which has a great benefit for the synthesis of nanostructures due to relatively facile and cost-effective method. Through crystallographic and morphological characterization, we reveal how crystallite size and morphological change affect the magnetic properties of ZnO nanostructures. Moreover, ZnO nanostructures discharged for 30 min show the strongest ferromagnetic behavior, which could be explained by the combined effect of more oxygen vacancies and larger surface to volume ratio. Our work paves the way for attempts to develop the ferromagnetism of metal oxide nanostructures for applications in nanoelectronics and spintronics.

COLL 197

Synthesis and characterization of epirubicin-loaded magnetically responsive nanoassembly to probe its in vitro antitumor potential under AC-magnetic field

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In our present work, we designed an iron based, $CoFe_2O_4$ magnetic core functionalized with sebacic acid (SA) to serve as a magnetic nanovector (MNV) for anticancer drug, Epirubicin. An alternating current magnetic field (1000 Oe) was externally applied on Epirubicin loaded MNV to trigger drug release (85 %). SA capping effects on surface of cobalt iron oxide nanoparticles, $CoFe_2O_4$ was investigated by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and X-ray diffraction (XRD). SA activated ferrite NPs sustain more colloidal stability, a narrow hydrodynamic particle size distribution (±60 nm) and show surface transition of cobalt iron oxide nanoparticles (CIONPs) from hydrophobic to hydrophilic as demonstrated by dynamic light scattering (DLS) and contact angle (CA) measurements, whereby CA decreases from 106° to 39° for uncapped and capped NPs respectively. Vibrating sample magnetometer (VSM) studies demonstrates high saturation magnetization (Ms) of SA coated (76.04 emu/g) than native CIONPs (78.64 emu/g) is promoting its magnetic mediated biomedical applications. Scanning electron microscope (SEM) and atomic force microscopy (AFM) investigation demonstrates the oval shape morphology of SA coated CIONPs

(CIONPs@SA) with average size of 40 nm. These SA activated CIONPs exhibit very low cytotoxicity upto 2.0 mg/mL against CHO and Huh7 cancer cell line. While, Epirubicin loaded magnetic nanovector effectively reduce the cell viability (56%) of Huh 7, validating the potential of MNV for tumor imaging and targeted (site specific) epirubicin delivery.

COLL 198 – Withdrawn.

COLL 199

Size-selective synthesis of CdS nanoparticles in room-temperature ionic liquids with water

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Room-temperature ionic liquids (ILs) are organic salts composed only of anions and cations with melting point in the vicinity of room temperature. ILs have many attractive physicochemical properties such as negligible vapor pressure and unique miscibility with organic solvent and water. It is believed that their unique properties result from their heterogeneous solution structure and they have been recognized to be an excellent media. We have found that CdS nanoparticles were size-selectivelysynthesized in hydrophilic ionic liquid (Tri-buthlymethyl phosphonium- Dimethylphosphate: TBMP-DMP) with various water contents. Our results show that the size-selective synthesis of CdS NPs would result from heterogeneous solution structure of IL containing water. Therefore, we compared optical behavior between ILs and AOT reverse micellar solution which is known as a typical microheterogeneous solution. Our results show that these optical behavior depending on water content in both solutions were very similar, suggesting that a reversed micellar like structure may be formed in the IL with water and nanoparticles were synthesized in “water pool” formed in the IL.

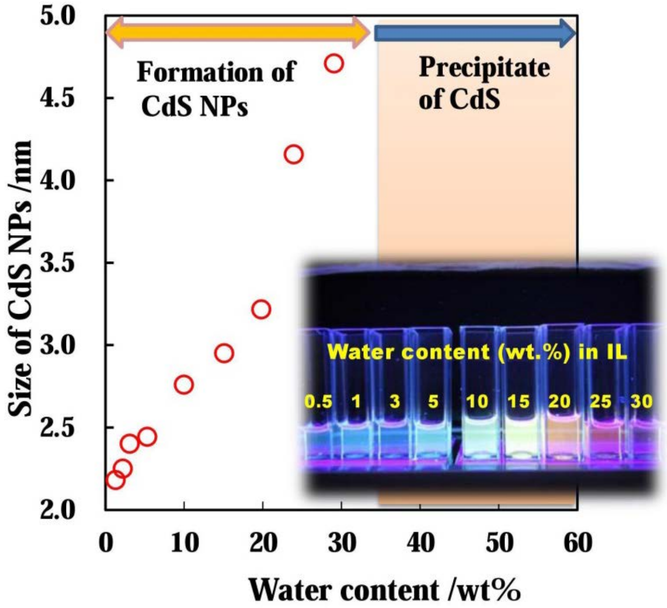

Fig.1 Size-dependence of CdS NPs on water contents.

COLL 200

Monodisperse-gold-nanobipyramid-supported bimetallic nanostructures for sensing and photocatalysis

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Plasmonic nanostructures with high purity, uniform size, narrow plasmon linewidth, large electric field enhancement and wavelength tunability are strongly desired. Among all metal nanocrystals, Au nanobipyramids (NBPs) have extraordinary properties, which make them favorable for numerous applications including biotechnology, plasmon-enhanced spectroscopy, optics, and solar energy harvesting. However, the plasmonic properties of Au nanocrystals are inferior to those of Ag ones, and Au nanoparticles are less catalytically active than Pt and Pd nanoparticles. To combine the excellent properties of Au NBPs with the advantages of other metals, we have successfully synthesized Au NBP-supported bimetallic nanostructures, which possess superior and/or new physical/chemical properties that are not provided by their monometallic counterparts.

We have developed a facile route to the synthesis of Au/Ag bimetallic nanostructures through Ag overgrowth on monodispersed Au NBPs. The resultant Au/Ag bimetallic nanostructures allow for combining the chemical stability of Au with the specific properties of Ag for high-performance sulfide sensing. The very low detection limit for sulfide ions has been achieved at the ensemble level. The unique properties of Au

NBPs make the Au/Ag bimetallic nanostructures an outstanding candidate in the development of ultrasensitive plasmonic sensors as well as other plasmon-enhanced technological applications. Furthermore, anisotropic Au NBP/Pd bimetallic nanostructures with position-dependent Pd deposition have been prepared for the exploration of the relationship between the electric field enhancement and plasmon-enhanced catalytic activity. Suzuki coupling reaction was chosen as a model reaction to compare the photocatalytic performances of the different anisotropic Au/Pd bimetallic nanostructures.

Our research provides useful guidelines for designing bimetallic nanostructures composed of two metals with different properties for various plasmon-based applications in optics, photonics, magnetics, biomedicine and chemistry.

COLL 201

Coacervation-based model for intracellular organization in a crowded environment

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The cellular matrix is an extremely complex and incredibly well organized environment, utilizing both membranous and non-membranous compartments to localize activity. Some non-membranous compartments exhibit liquid-like behavior suggesting they have been formed by aqueous phase separation. Model systems that mimic the multi-phasic media of the cellular environment, while circumventing some of the biological complexity, are attractive for investigating cellular organization. Complex coacervation is a promising model for polyelectrolyte-rich non-membranous compartments within the cell, as it results in the formation of a dense polyelectrolyte-rich phase in a dilute supernatant phase. However, there are no cellular compartments composed of a dilute phase, and the cytoplasm is crowded with proteins, polyelectrolytes and other macromolecules. Current models based on coacervation lack crowding agents to account for this crowded environment. Here, the effects of crowding on complex coacervation were investigated using a variety of polyelectrolyte systems and crowding agents. First, the well-studied coacervate system composed of the polyelectrolytes poly(acrylic acid) and poly(allylamine) was examined in the presence of both neutral polymer crowders, e.g. poly(ethylene glycol) and dextran, and protein crowders, e.g. albumin. A bio-inspired coacervate system composed of polyuridylic acid/spermine was also investigated in the presence of the same range of crowding agents. A combination of optical microscopy and UV-vis spectroscopy was utilized to evaluate the effect of macromolecular crowding on coacervation, providing a system to model non-membranous intracellular compartments. A greater understanding of the physicochemical nature of intracellular organization will lead to the development of structurally accurate cell mimics, which will be used to further study both physical and biological activity.

COLL 202

Synthetic adhesives with catechol functionality: An integrated approach to mechanism elucidation

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Tremendous research interest has focused on the catechol group to enhance current adhesive technology with broad substrate and environmental suitability. Much of this work has led to the development of adhesive systems that exhibit reasonable promise after considerable multi-variable optimization (e.g. oxidant, filler content, co-monomer composition, process conditions). Our group has been exploring the incorporation of catechols into synthetic polymers in an attempt to understand the interactions with alumina substrates and to eventually extend the technology to tune interfacial interactions with high-performance adhesives. The project includes atomistic molecular dynamics simulations of the interface of alumina interacting with short oligomers of synthetic polymer, and exploring the impacts of sequence and environment on the free energy of the polymer-substrate interaction. Complementary to the modeling effort, the synthetic component involves the preparation of catechol monomers co-polymerized with aliphatic acrylates, leading to a library of materials with controlled T_g and backbone polarity. Finally, to develop structure-property relationships, interfacial studies have been explored using dopamine hybridized with amino-propyl alkoxy silane surface treatments combined with adhesive testing and surface spectroscopy. Taken together, these approaches have led to an improved understanding of the modes of catechol interaction and function, and provides new insight to the design of rational interfaces.

COLL 203

Performance of organic photovoltaic cells with nanocrystal ZnO thin film via low-temperature annealing process

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Zinc oxide (ZnO) nanocrystalline particles for organic photovoltaic cells (OPVs) were synthesized through modified sol-gel reaction with hydrothermal method. The effect of hydrothermal treatment on formation of ZnO nanocrystalline particle was investigated by XRD. When the amorphous phase ZnO is processed by hydrothermal reaction, the crystalline phase could be obtained. The thin layer of crystalline ZnO required lower annealing temperature compared to the thin layer of amorphous ZnO prepared as the buffer layer in OPVs. Besides that, efficiency of the OPVs fabricated as buffer layer with crystalline ZnO nanoparticles through hydrothermal treatment was higher than the amorphous ZnO nanoparticles. Comparable power conversion efficiency (PCE) could be achieved for 2.53% through crystalline ZnO buffer layer. The low annealing

temperature will be a great solution to resolve the problem associated with energy consumption credited to advantages such as low manufacturing costs, high productivity and applying to the flexible substrates.

COLL 204

Flow-induced shape changes in bioinspired vesicles

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The structural integrity of bioinspired particles such as red blood cells and bacteria under flow conditions is dependent upon their ability to adapt their shape. Our goal is to examine the role of the composition of bioinspired vesicles on their shape during their flow through in a channel. Via the Dissipative Particle Dynamics simulation technique, we apply laminar flow in a cylindrical channel and investigate the shape transition of a bio-inspired four-component lipid vesicle encompassing DPPC, DMPC, glycolipids and cholesterol, and a hairy vesicle composed of phospholipids and pegylated lipids. We vary the channel dimensions, flow rate and composition to study their impact on the shape of the cell-mimetic and hairy vesicles. We will also characterize the critical flow rate at which the vesicles are ruptured. Our results could be potentially used to accelerate the design of smart particles with the ability to adaptive their shape under diverse flow conditions.

COLL 205

Host-guest complexes for functionalization of metal-oxide nanostructured substrates

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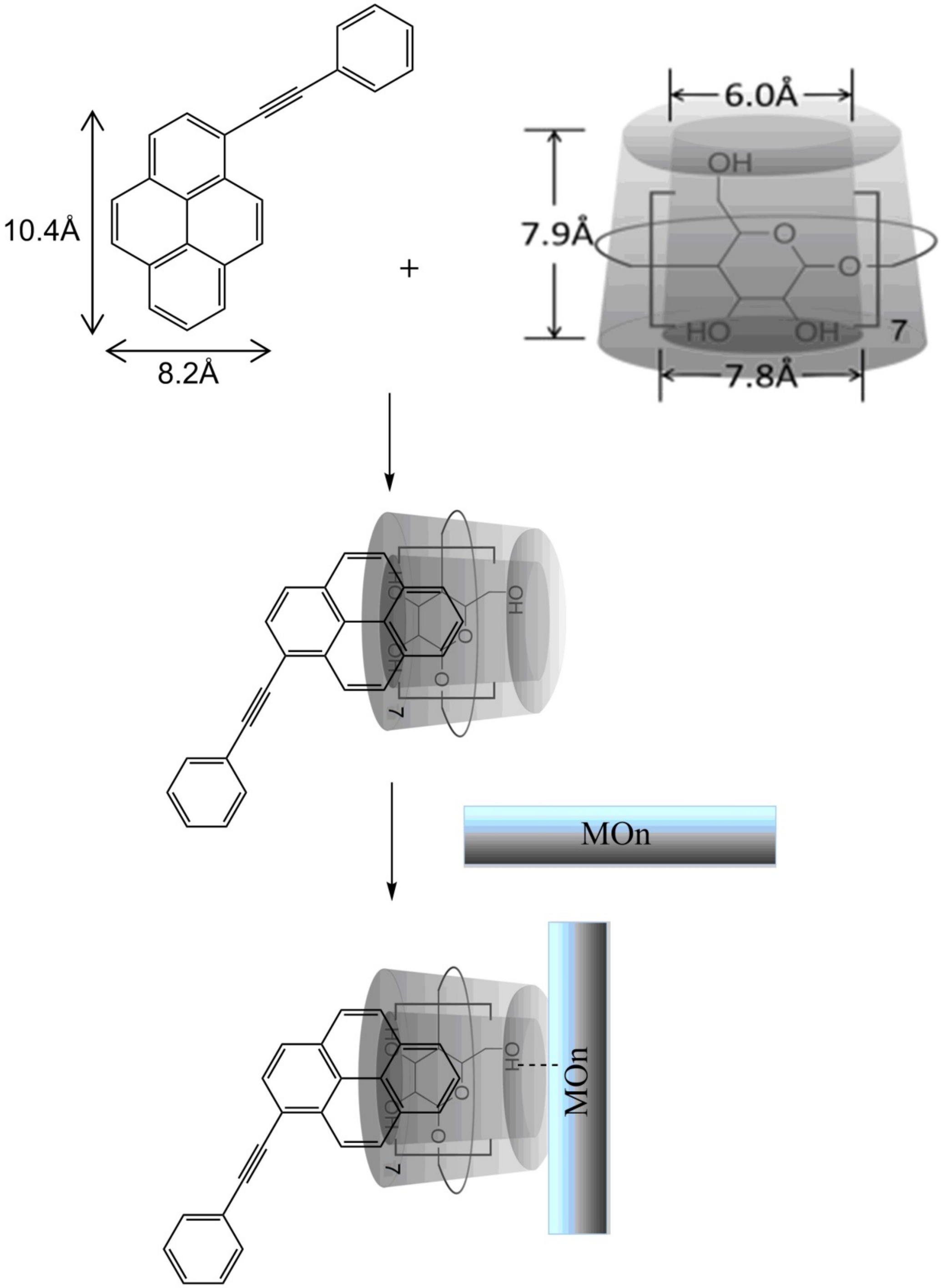
The photophysical properties of 1-phenylethynylpyrene (**Py2**), a chromophore without anchor group, and host-guest complex **Py2**@β-cyclodextrin (β-CD) were studied in aqueous solution and bound to ZrO_2, TiO_2 and ZnO films. β-CD encapsulated **Py2** to form a 1:1 host-guest complex and help guest molecules to bind to the films through the β-CD's –OH functional group. The formation of host-guest complex prevented the aggregation of **Py2** both in aqueous solution and on ZrO_2, TiO_2 and ZnO films.



Py2 and *β*-CD form host-guest complex and bind to MO_n films

COLL 206

Multifunctional Ag@SiO_2@Au hybrid nanostructures

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We report the synthesis of Ag@SiO_2@Au hybrid nanostructures. In a typical process, we prepare silica-coated Ag nanocubes (Ag@SiO_2) with an edge length of nanocubes at 40 nm and the thickness of silica shell at 10 nm. Next, we titrate $HAuCl_4$ into a suspension of Ag@SiO_2 in the presence of ascorbic acid (AA), poly (vinyl pyrrolidone) (PVP), and NaOH at room temperature. Because NaOH could effectively increase the pore size of silica, Au^{3+} and AA would diffuse across the silica shell to initiate two reactions: *i*) galvanic replacement reaction between Ag nanocubes and Au^{3+}; and *ii)* the reduction of Au^{3+} by AA. As a consequence, the Au atoms derived from both Ag and AA are deposited onto Ag nanocubes through heterogeneous growth, transforming Ag@SiO_2 nanocubes into Ag@SiO_2@Au hybrid nanostructures. Our TEM results reveal the details of structures that involve the decoration of Au nanoparticles (< 7 nm) on the surfaces Ag nanocubes, together with an outside layer of silica. The as-prepared hybrid nanostructures present excellent catalytic properties by efficiently converting 4-nitrophenol to 4-aminophenol due to the catalytic activity of Au nanoparticles. They also exhibit strong surface-enhanced Raman scattering (SERS) activity when they are functionalized with 4-nitrothiolphenol (4-NTP). The integrated catalytic and SERS properties would open up the possibility to *in-situ* SERS monitoring the catalytic reduction of 4-NTP by $NaBH_4$ when the molecules are bind to the Ag and Au surfaces but confined in the space of silica shell.

COLL 207

Synthesis, characterization, and application of a UCNPs/AuGNRs for simultaneous heating and measuring of temperature

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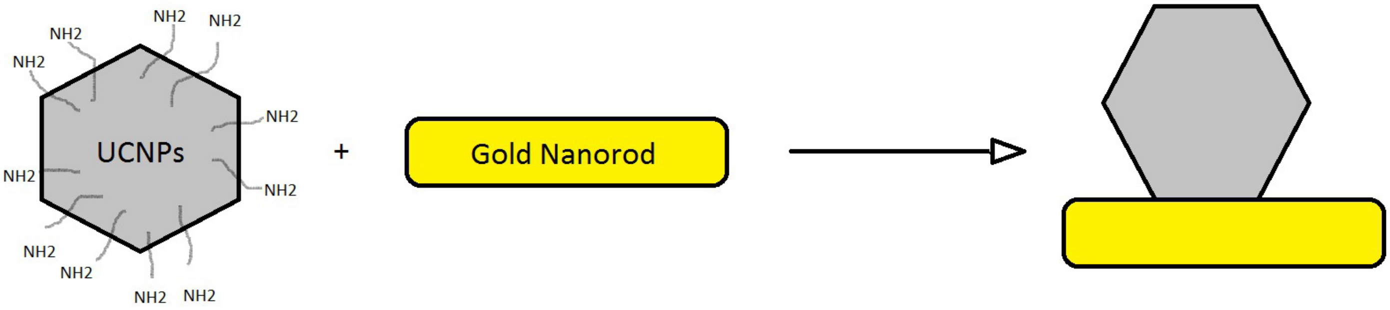
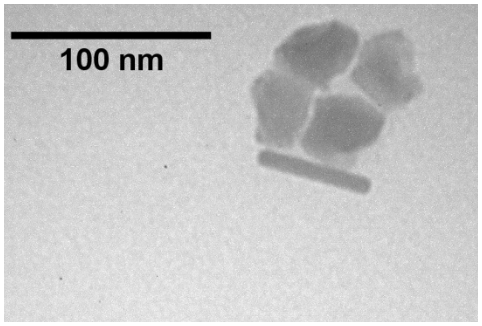
Over the past decade significant amount of attention has been directed toward development of nanomaterials capable of treatment of fatal diseases such as cancer. Amongst these nanomaterials, gold nanoparticles, spacially gold nanorods have been promising nanoparticles for both photothermal theraphy and drug delivery. Uncontrolled heating of gold nanorods however, lacks the precision, efficiency and applicability in both destruction of tumorous cells and release of the drugs. Hence, direct measurement of temperature in vitro and in vivo in order to obtain optimum laser intensity and temperature seems to be challenging. In this research, a gold nanorod coupled with upconverting nanoparticle can be a good candidate for simultaneous increase of temperature. Using an infrared laser (980 nm) the temperature of gold nanorod can be tuned and the temperature of the medium is measured by the emission of upconverting nanoparticles. The relative ratio of H and S bands, which are thermalized, is used to measure the temperature by means of Boltzmann equation. The result of this research can be used to further investigate the development of drug delivery techniques and treatment of cancer.





COLL 208

Structure of Zn-containing magnetic oxide nanoparticles: Fluorescence spectroscopy as a viable tool

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Zn-containing magnetite nanoparticles (NPs) stabilized by a thermally stable polymer, polyphenylquinoxaline, were shown to be efficient magnetically recoverable catalysts for the conversion of syngas to methanol. X-ray photoelectron spectroscopy (XPS) study showed that the highest activity of the catalyst was achieved when Zn species were intimately distributed within the magnetite NP without substitution of Fe^{2+} species. Here we demonstrate that the information on the Zn distribution within the Fe_3O_4 NPs can be obtained from studying fluorescent properties of these NPs. A significant decrease in the fluorescence emission intensity of Zn-containing Fe_3O_4 NPs compared to parent Fe_3O_4 NPs suggests that the Zn species quench the Fe_3O_4 emission through fluorescence resonance energy transfer. This distance dependent interaction allows for the determination of the Zn interactions with the magnetite surface and intercalation into the spinel magnetite structure. In addition, a series of Cr-doped Zn-containing Fe_3O_4 NPs were also synthesized whose scanning transmission electron microscopy (STEM)

energy dispersive spectroscopy (EDS) maps are shown in Figure 1. The investigation of their fluorescence properties showed a similar behavior.

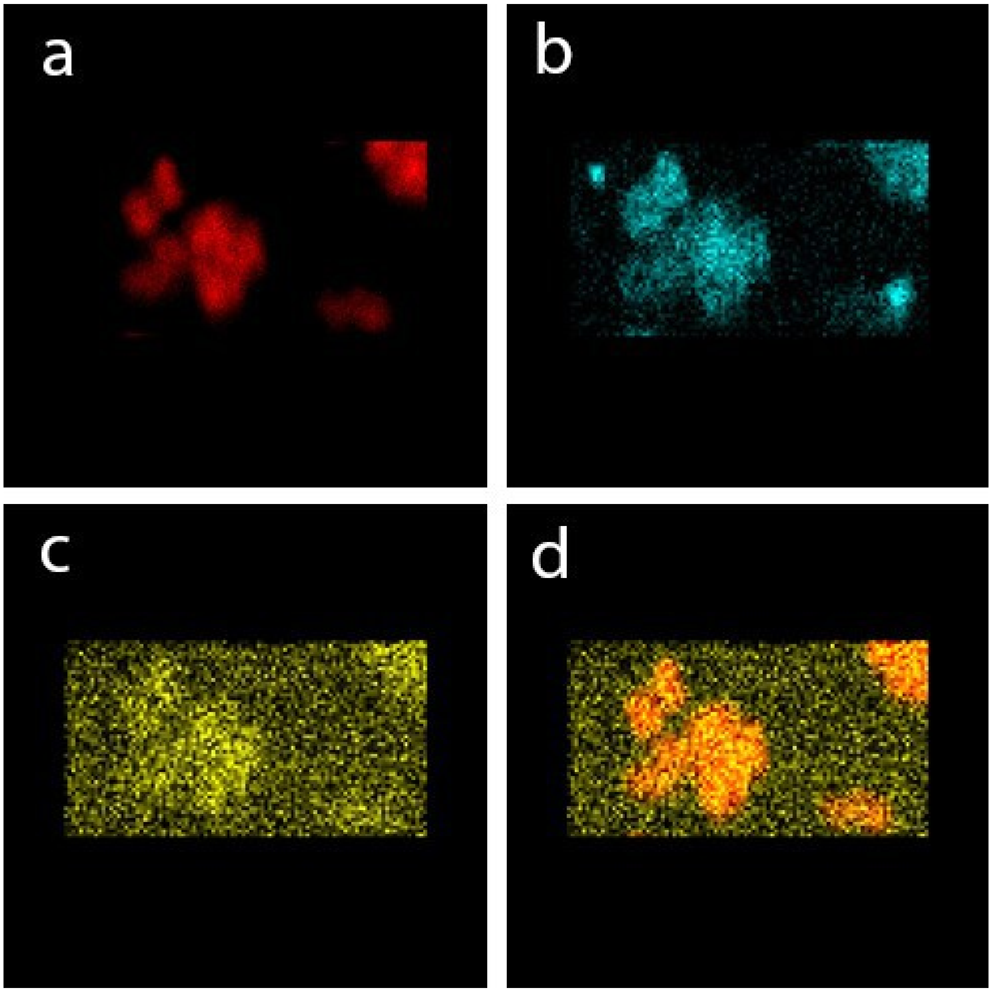

Figure 1. STEM EDS maps of Cr-doped Zn-containing magnetite NPs for Fe (a), Zn (b), Cr (c), and their superposition (d).

COLL 209

Functionalization of MgZnO nanorods toward highly selective and sensitive biosensors

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Surface functionalization of nanostructured metal oxide semiconductors such as ZnO and $Mg_xZn_{1-x}O$ (MZO), particularly nanorods and nanowires, is important for the development of biosensors and other devices. In particular, MZO is attracting increasing attention due to its improved resistance to acids and bases, compared to ZnO. The selectivity of MZO and ZnO based biosensors largely depends on the chemical properties and molecule immobilization methods at the surface. Our group has developed stepwise functionalization methods for MZO nanorods.

In this work we describe our most recent developments, including an unprecedented 2-D FTIR spectroscopic imaging method to study and monitor the surface functionalization. The binding between 11-azidoundecanoic acid and MZO nanorod films was studied by 2-D FTIR spectroscopic imaging leading to in-depth understanding of the binding process. The influence of solvent, concentration, binding time and morphology of nanorod film on binding performance, and the film stability were studied. Alkynated folic acid as the sensing molecule was immobilized afterward.

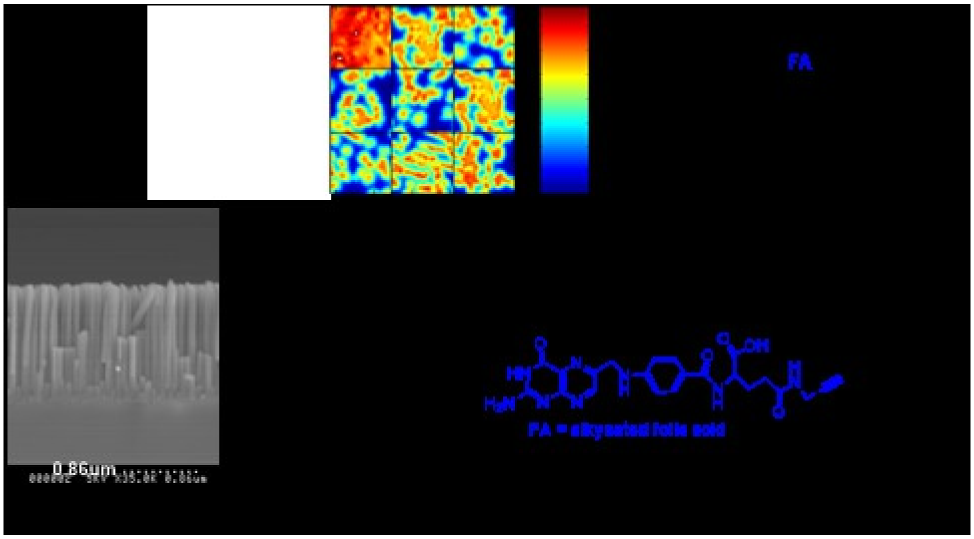

Fig. 1 Scheme of functionalization of MZO nanorod biosensors. *Inset:* FTIR microscopic image integrated at N_3 band (2212-2064 cm $^{-1}$) of nine different areas (200 um*200 um each) of the film after binding with 11-azidoundecanoic acid.

COLL 210

Polymer thin film characterization: Sum frequency generation spectroscopy, atomic-force microscopy and contact angle measurements

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In this project, functionalized methacrylate-based polymers are dissolved in various solvents and are spin-coated on a quartz substrate to create polymer thin films (PTFs). In addition, varying the annealing time and the volume of the polymer solutions will be tested in the preparation of polymer thin films. These PTFs will be characterized using sum frequency generation spectroscopy (SFG), atomic force microscopy (AFM) and contact angle measurements. The SFG spectroscopy chemically identifies the interfacial molecules and derives the molecular conformation on the PTFs. The AFM data presents the topography of the different thin films, which will help differentiate the surface roughness of each. It also measures the adhesion values, that is, the adhesion of a silicon-nitride tip to the PTF surface. Contact angle measurements yield data about the relative strength of the molecular interactions between the liquid and solid interfaces. On the other hand, surface tension measurements will be carried out to correlate the results to the surface free energy of the functionalized methacrylate-based monomers with spectroscopic results. This data will establish a deeper understanding of these PTFs and provide important data for the development of coating materials in the future.

COLL 211

Blue down-shifting phosphors for LED lighting using a Tm $^{3+}$-doped nanospinel

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Down-shifting phosphors, including nanophosphors, are routinely used in solid state lighting as the white light source excited by a blue light emitting diode (LED). Down-shifting LEDs are highly efficient compared to incandescent and fluorescent lighting due to high efficiency conversion of the near UV photon into red, green, and blue light. Here we present microwave synthesis of nanospinels doped with Thulium(III) to act as the blue phosphor. The population of Tm(III) *f*-levels is accomplished by energy transfer from a surface passivating group acting as a molecular photosensitizing antenna. Optical measurements of the nanospinel will be discussed including absorption, emission, lifetime, and transient absorption data. Ligand exchanges were completed in efforts to improve quantum efficiencies and the nanospinels were characterized by pXRD, TEM, EPR, and FT-IR.

COLL 212

Copper detection mediated by coupling molecular resonances and localized surface plasmon resonances

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The optical properties of noble metal nanoparticles have made them ideal candidates for a variety of applications including imaging, sensing, and catalysis. When these particles are excited with electromagnetic radiation, the electrons in the conductance band of noble metal nanoparticles oscillate at a specific frequency exhibiting a phenomena known as localized surface plasmon resonance (LSPR). Previous studies have reported that using a probe molecule that contains a resonance slightly longer in

wavelength than the LSPR of the substrate, spectroscopic shifts can be enhanced by a factor of 3 – 5 times. Herein, we demonstrate a sensitive assay that will detect copper in blood serum by coupling a dye to a nanoparticle surface using copper catalyzed click chemistry. These reactions are observed by monitoring the changes in LSPR frequency which demonstrates dye's molecular resonance coupling with the nanoparticles LSPR resulting in a shift of 5-6 nm in water to the infrared. Drying out the gold-nanoparticles substrates shows a larger shift of ~20 nm to the infrared, which can be detected by eye. Copper dependence is shown by modifying the concentration of copper available to mediate the click chemistry. Since the click chemistry is very specific to copper, it is expected that this assay will serve as a sensitive, selective, colorimetric assay for copper in complex biological solutions.

COLL 213

Application of different anisotropic particles prepared by seeded polymerization

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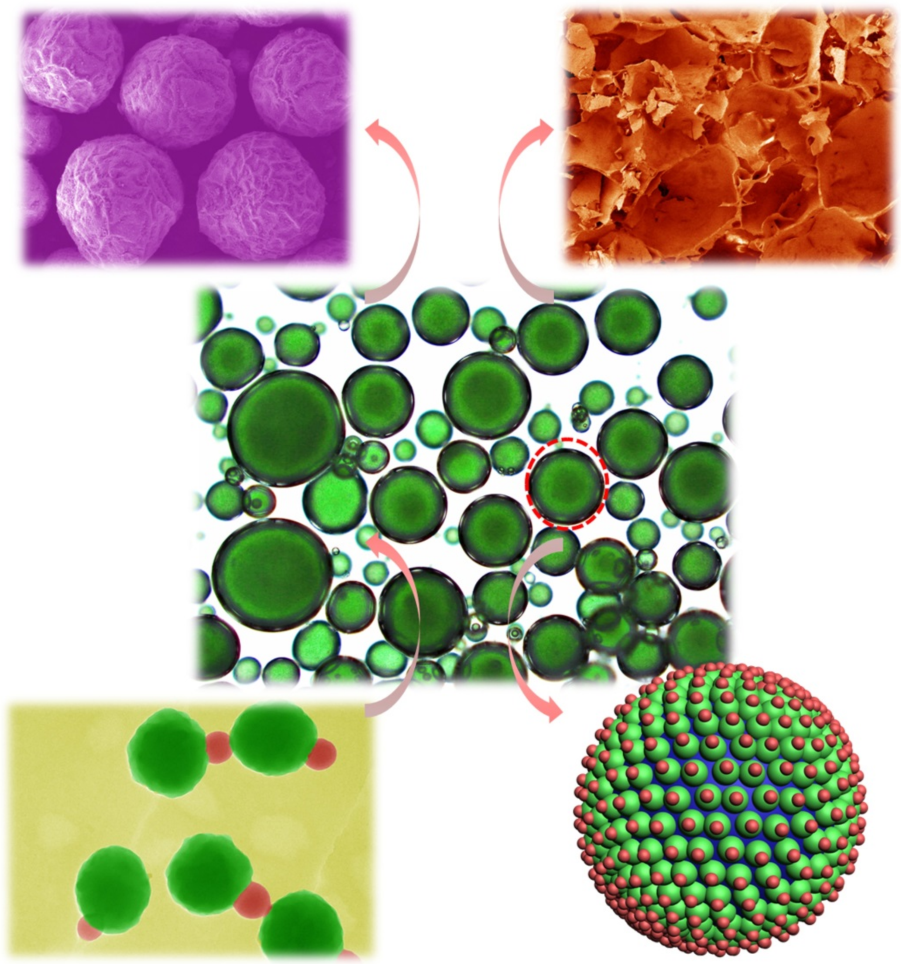
Anisotropic particles with morphological and/or compositional anisotropies (also termed Janus particles) have tremendous potential use in scientific research and frontier technology, such as biomedical applications, sensors, photonic crystals, optical devices, colloidal stabilizer and so on. To meet the need of different applications, various anisotropic particles with different sizes, nature and morphologies have been synthesized via seeded emulsion polymerization or seeded dispersion polymerization, sometimes as well combining with sol-gel method and the synthetic approach of inorganic nanoparticles by controlling the nature and the amount of the seeds, the nature and the amount of the second monomers, the type and the concentration of emulsifier or dispersant, the absorbed dose and dose rate, temperature and other factors. These various anisotropic particles can be used as solid surfactants to stabilize emulsions and further to fabricate hierarchical microspheres or porous materials. Meanwhile, some raspberry-like particles can be used to form transparent film with fire retardant properties or to build superhydrophobic surfaces with a high adhesive force to water, and thus to form superhydrophobic surface having antibacterial ability after being further decorated by Ag nanoparticles.



The amphiphilic snowman-like particles could be applied as solid surfactant to stabilize W/O emulsions, and then hierarchical microspheres or block polymers could be obtained after polymerization of the monomer phase.

COLL 214

Self-assembly of Janus dendritic ligands on nanocrystal surface

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The study of coordination behavior of ligands on nanoparticle surfaces are of critical importance to nanotechnology as it provides the key to understanding and engineering various properties such as solubility, optical, magnetic, electronic, and catalytic. To this end, the most commonly used ligands are limited to various commercially available alkyl containing molecules that have either acid, amine, phosphonate, or thiol surface binding groups.

To better understand how hydrophobic and hydrophilic ligands assemble and interact with one another on nanoparticle surfaces, we produced a series of Janus dendritic ligands containing both hydrophobic and hydrophilic moieties. The synthesis was designed with a strategy that combines both moieties at a late stage, giving us the flexibility to modify dendron end groups and surface anchoring functional groups independently, reducing the number of synthetic steps. The Janus dendritic ligands obtained were introduced on nanoparticle surfaces through solution phase ligand exchange, and the resulting dendron-nanoparticle hybrids were studied using various analytical techniques such as TEM, NMR, IR, DSC, and X-ray scattering (WAXS and SAXS).

The full synthetic strategy, nanoparticle functionalization methods, and self-assembly details will be discussed with a focus how hydrophobic and hydrophilic moieties interact with each other and direct higher order assembly in these nanoscale materials.

COLL 215

Solubilization of hydrophobic catalysts using nanoparticle hosts

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Catalysis in water is an important strategy for sustainable “green” chemistry. However, aqueous catalysis by organometallic catalysts is restricted due to solubility, activity, and stability issues of catalysts in water. Here, we report the solubilization of hydrophobic transition metal catalysts using hydrophobic pockets occurring in the monolayers of water-soluble gold nanoparticles (AuNPs). This nanoparticle platform solubilizes the catalyst and provides a protective environment. Grubbs, Cp*Ru(cod)Cl, palladium, and Wilkinson catalysts were encapsulated encapsulated into AuNPs and used for ring-opening metathesis polymerization (ROMP), allyl carbamate cleavage and hydrogenation of alkenes in water, respectively. This catalysis works in water, where it opens the potential for new green chemistry approaches and in living cells with potential applications in imaging and therapy.

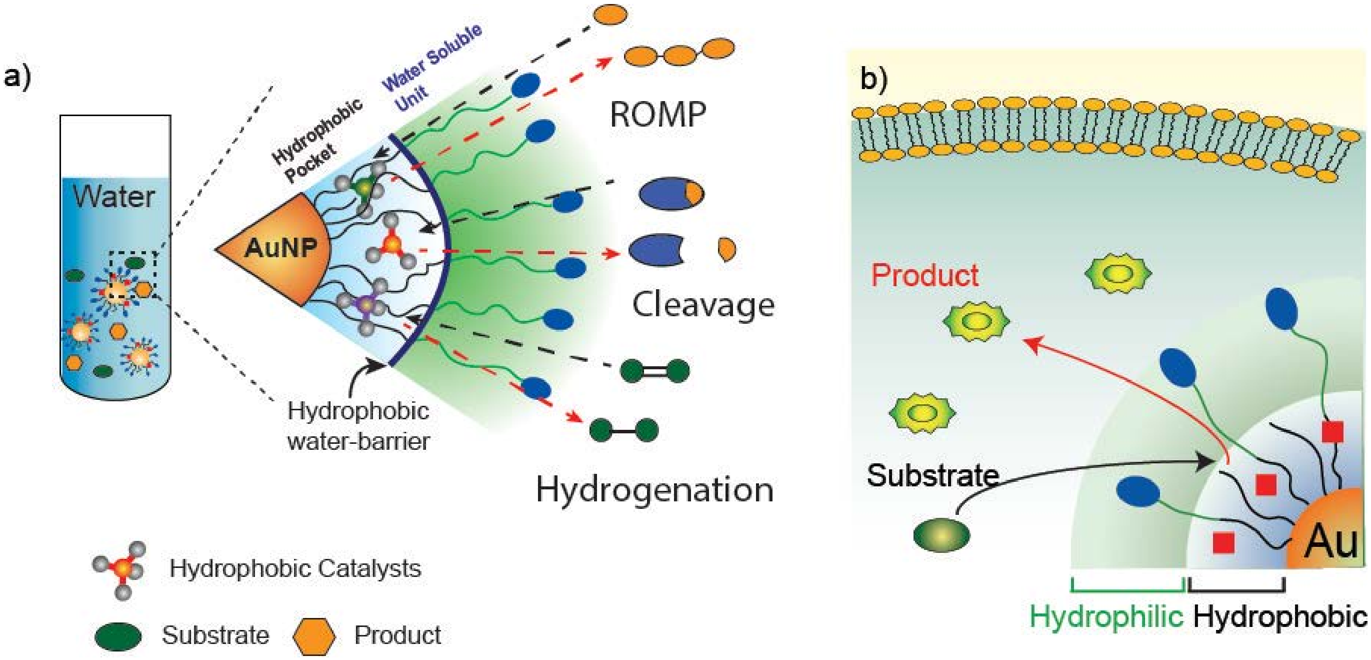

Figure1. Schematic illustrating catalytic reactions within NP monolayer (a) in water and (b) inside living cells.

COLL 216

Analytical method to fabricate reproducible SERS substrates

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The objective of this research study was to design an analytical method to fabricate reproducible surface enhanced Raman scattering (SERS) substrates using printable silver nanoparticle ink as the main component. Printable ink is used in the electronics industry as a low-cost alternative to make conductive paths as the particles can sinter at low temperatures. The ability to control the sintering process through a preheating treatment makes it an attractive way to make SERS substrates over conventional colloidal particles as well as its low-cost and high amplification factors. Central to making reproducible SERS substrates is understanding the relationship between heat and interparticle spacing. The optimal Raman signals occur at a point before nanoparticles coalesce and when many small spaces between the particles are present. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) systems were used to find the temperature at which the capping agent on the nanoparticle sublimates, thus allowing the nanoparticles to move closer together, forming aggregates. Scanning electron microscope (SEM) micrographs were collected and then analyzed using an elliptical approximation method on ImageJ to determine interparticle spacing. Rhodamine 6G was used as the analyte to assess the SERS amplification and reproducibility. The thermal pre-treatment allows for the formation of interparticle gaps

of the length scale of 10 nm or lower. The resulting Raman intensity increases when the heating method produces a greater abundance of smaller interparticle gaps. In addition to heating temperature, other variables have been observed in the ink preparation method including the effect of drop coating and spin coating samples. These experiments have been applied to two types of printable nanoparticle inks and TGA and DSC results show similar trends indicating the sublimation of the nanoparticle capping agent. Therefore it is expected that the fabrication method can be applied to multiple types of printable nanoparticle ink, making it a more useful method in producing SERS substrates. These results will be discussed to show how their importance in determining the optimal parameters for fabricating highly amplifying SERS substrates.

COLL 217

Ca^{2+} effects on the hydration and ordering of the sphingomyelin at air/water and air/aqueous interfaces studied by high-resolution broadband sum frequency vibrational spectroscopy

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Sphingomyelin（SM）is an important constituent of the mammalian cell membranes. It is well known that the structural variation and the interaction between SMs and Ca^{2+} cation in biological membranes play a significant role in the bio-membrane. In this report, the interaction of sphingomyelin with the divalent cation Ca^{2+} at the interface was investigated by High Resolution Sum Frequency Generation Spectroscopy (HR-SFG) in conjunction with surface pressure measurements. The results showed the present of Ca^{2+} causes a marked dehydration of the phosphate group in the liquid-condensed (LC) phase. In the presence of 2M Ca^{2+}, the PO_2^- symmetric stretch blue shifts from ~1090 to ~1130 cm^{-1}, suggesting that calcium binding results in phosphate dehydration. Ca^{2+}-concentration-dependent studies of the head group region revealed that, calcium ions cause a marked partially dehydration of the phosphate groups. Moreover, the conformation change of hydrocarbon chain has also been studied. The intensity of the CH_3 signal is sensitive to the orientation order of the acyl chains whereas the CH_2 signal intensity increases with increasing gauche defects and is therefore proportional to the conformational disorder in the chains. Overall, the results reveal that Ca^{2+} strongly interacts with the phosphate group of SMs monolayer. Such interactions can not only change the orientation of the PO_2^- group, but also change the interfacial SMs acyl chains conformation. These findings have shed light on possible mechanism behind membrane-related functions, which are unique to SMs and can be understood in relation to the molecular structure of SMs.

COLL 218

Design of a nanostructered lipid carrier intended to improve the treatment of tuberculosis

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Tuberculosis (TB) is the most prevalent and mortal worldwide infectious disease. The current treatment consists in a long-term multi-drug combination, being associated with noncompliance to therapy and appearance of several adverse-effects. Nanostructured lipid carriers (NLC) are a promising new biocompatible and biodegradable drug delivery vehicles wherein they can play the dual role of increase the drug's efficacy and decrease the drug's toxicity. In this work, NLC for the selective delivery of rifabutin (RFB) to alveolar macrophages (AMs) was designed. NLC were designed to exhibit both passive and active targeting strategies to be efficiently internalized by the AMs, traffic to the acidified phagosomes and phagolysosomes, and release bactericidal concentrations of the anti-tuberculosis drug intracellularly. NLC entrapping RFB were syntetized, characterized and further functionalized with mannose. Particles' size, zeta potential, morphology, drugs' % entrapping efficiency, drug release kinetics and macrophage uptake studies were evaluated. The mannose coating process was confirmed by FT-IR. Further, the cytotoxicity of the formulations was evaluated by MTT assay in A549, Calu-3 and Raw 264.7 cells. The size of NLC formulations was found to be in range of 200 nm and drugs entrapping efficiency was found to be above 80%. Moreover, the drug release was pH-sensitive, with a faster drug release at acidic pH than at neutral pH. In addition, high storage stability for the formulations is expected since they maintain the initial characteristics for 6 months. The results support that the developed NLC can be explored as a promising carrier for safer and efficient management of tuberculosis (TB) exploiting the pulmonary administration.

COLL 219

Preparation of temperature/pH sensitive bifunctional spherical polyelectrolyte brushes by photo-emulsion polymerization

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Spherical poly(2-(dimethylamino) ethyl methacrylate) (PDMAEMA) brushes (SPB) were synthesized on the surface of polystyrene latex particles by photo-emulsion polymerization. Dynamic light scattering results indicated that these SPB were both pH and temperature responsive. With these properties, they can be applied in the fields of controlled enzyme immobilization and protein separation.

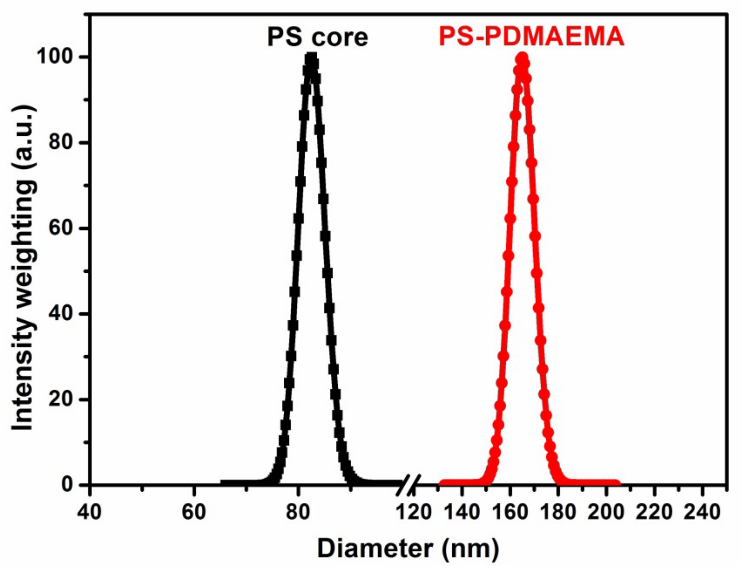

Figure 1. Size and size distribution of PS core and SPB with 50 wt% DMAEMA as determined by DLS.

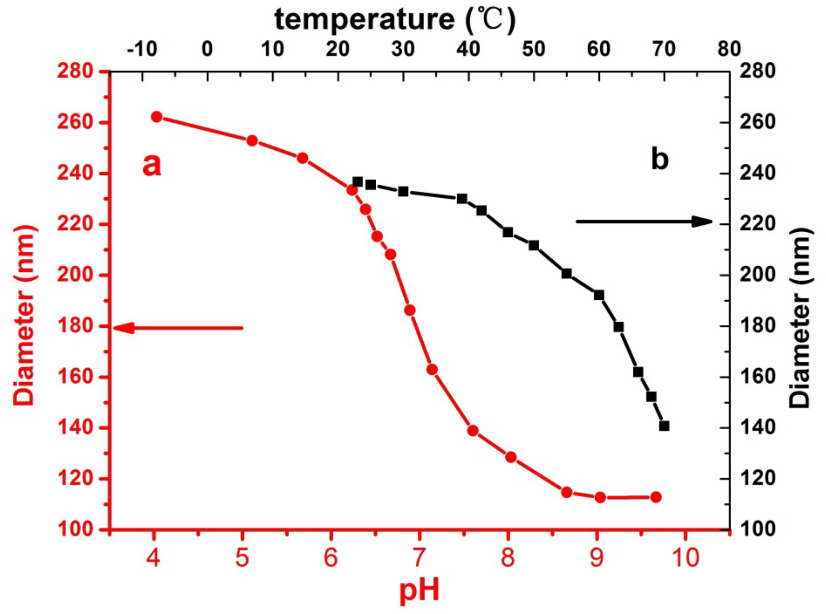

Figure 2. The hydrodynamic diameter of PDMAEMA SPB at different pH (a) and different temperatures (b).

COLL 220

Water absorptivity of polymeric materials obtained by LbL film approaches

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Layer by layer (LbL) deposition is a very versatile method to prepare very thin polyelectrolyte multilayer composite films by alternately depositing positively and negatively charged polyelectrolytes. During the deposition process, the polyelectrolyte self-assembles and self-organizes on an oppositely charged substrate via electrostatic or hydrogen bonding interactions. So it is possible to make a coating to any object by LbL films, or possible to include nanoparticles and other macromolecules of different shapes as far as the objects are properly charged.
In this study, some different kinds of materials such as porous inorganic micro-objects, nanoparticles, or microcapsules, were tried to be used as a component of the LbL process, or tried to be encapsulated by ionic polymers via LbL process. Used cationic polymers were poly(diallyldimethylammonium chloride), poly(allylamine hydrochloride), and poly(dimethylaminoethyl methacrylate). And used anionic polymers were polystyrenesulfonic acid sodium salt, sulfonated poly(phenylene oxide), poly(styrene-co-maleic acid sodium salt, and poly(methacrylic acid). Depending on the condition of LbL coating (or film formation), obtained multilayered materials were analyzed in terms of % swelling, water uptake, thermal properties, and mechanical properties.

COLL 221

Metastable colloid formation in mixtures of dimethylsulfoxide, water and hydrophobic naphthalenic compounds

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Dimethylsulfoxide (DMSO) is a polar aprotic solvent that is water soluble and known to dissolve a variety of hydrophobic compounds. It is commonly used in experimental biological systems as a cryoprotectant and a medium to deliver hydrophobic compounds through an aqueous milieu to the hydrophobic regions of proteins, membranes, and other hydrophobic environments. The unique properties of binary mixtures of DMSO and water have been well studied, and are still explored in the current literature. To our knowledge, ternary systems using DMSO/water/naphthalenic compounds have not been studied in depth. Our research focuses on using dilute DMSO solutions containing naphthalenic compounds (such as naphthalene, azidonaphthalene, and N-phenyl-1-naphthylamine (NPN)) and characterizing their behavior upon introduction into an aqueous environment. The concentrations used herein are similar to those being used to deliver azidonaphthalenes to the hydrophobic regions of enveloped viruses for the creation of novel inactivated virus vaccines. It was found that at very low mole fractions of DMSO, metastable colloids formed with spheres ~1 micron in size that avoid coalescence and are stable for several hours. For example, when NPN is added to water, micron-sized spheres form (see figure) that contain the NPN fluorophore. We are currently investigating this phenomenon using fluorescence

microscopy, infrared spectroscopy and fluorimetry to better understand what is happening on a molecular level and if the sphere size and stability can be tailored.

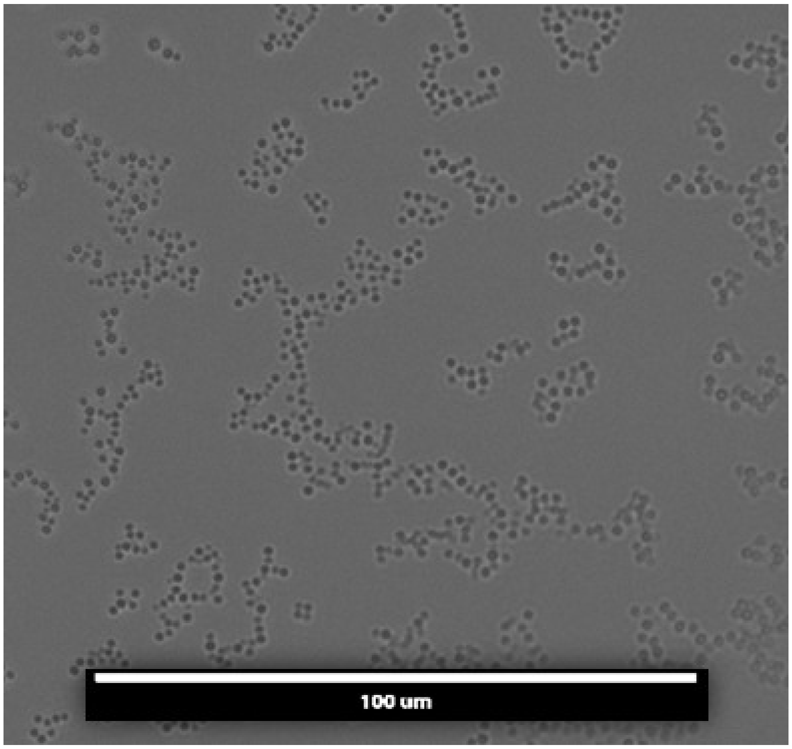

Figure 1: Micron-sized spheres are formed when NPN in DMSO is added to water. Shown is a bright-field image of the resulting metastable suspension.

COLL 222

Antimicrobial coating fabricated by protein films

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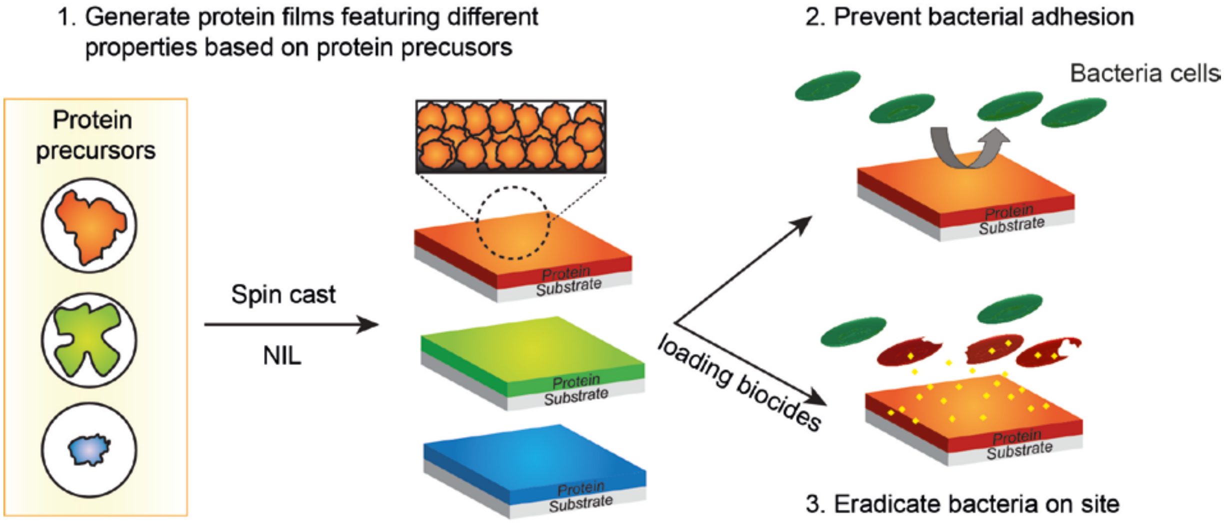
Antimicrobial films have been used for wound healing, medical devices and food industry. Here, we report a simple and eco-friendly strategy for generating protein film by nanoimprint lithography (NIL), serving as a scaffold for chlorination or a reservoir for drug loading. Protein-based films are inherently biocompatible and biodegradable. After NIL process, protein films were stable in aqueous solution, and resisted to bacteria adhesion. The diversity of amino acids on protein building blocks enables the post-functionalization and the control of payload release. After chlorinating by sodium dichloroisocyanurate or loading with antibiotics, the protein films showed antimicrobial

activity, inhibiting bacterial growth via the slow release of biocides. This strategy uses natural abundant biomaterials as precursors, requires no synthetic expertise, works under aqueous conditions, and is eligible for roll-to-roll processing, which is promising for large-scale antimicrobial coating fabrication.



Protein film fabricated through nanoimprint lithography (NIL) serves as a stable scaffold that prevents bacteria adhesion. After chlorination, these antifouling films can release biocides and eradicate bacteria.

COLL 223

Increasing information content in array-based cancer sensing using host-guest chemistry

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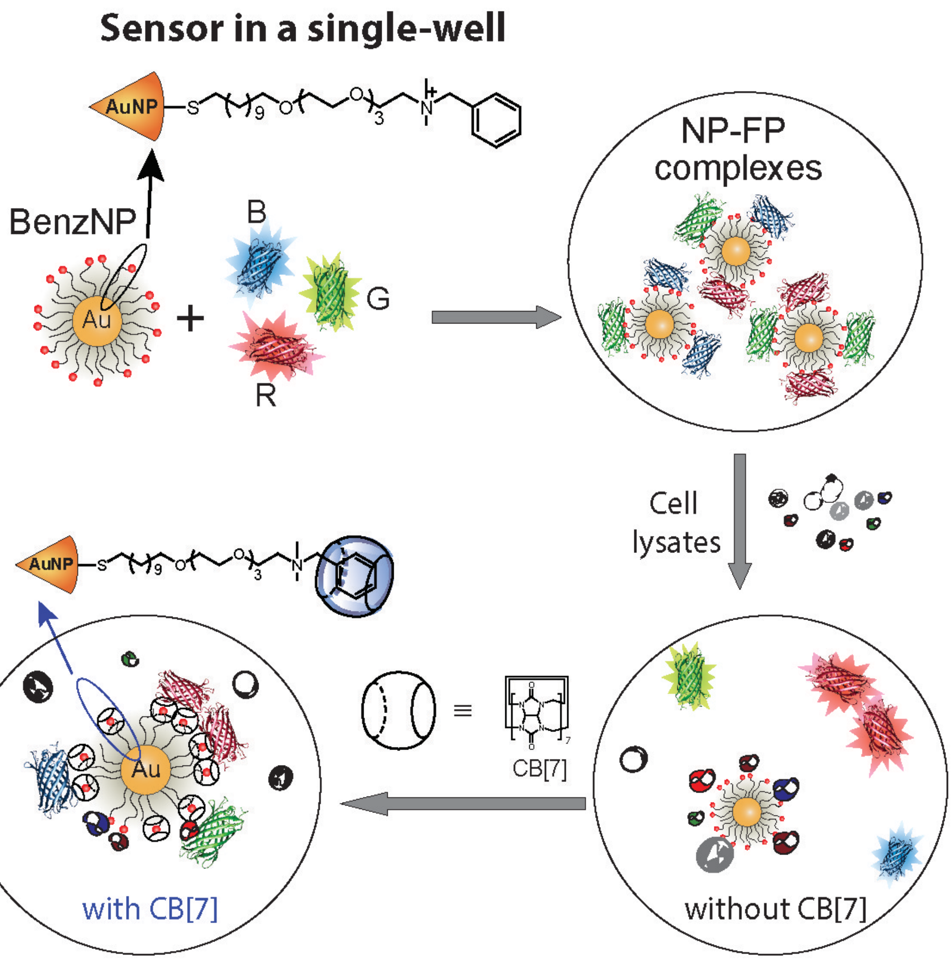
Rapid and sensitive method to discriminate between healthy, cancerous cells and their aggressiveness is critical for cancer diagnosis. Traditionally, biomarker-based approaches such as electrophoresis and mass spectrometry are used to determine cell state. Yet, these methods require prior knowledge of the cells, and are often not sensitive to subtle changes in proteomic signatures. Array-based ‘chemical nose’ sensing provides an alternative strategy to traditional approaches. This approach uses selective receptors to generate multiple output channels that are used to create patterns, similar to olfaction. These outputs serve as a global diagnostic pattern to profile cells of interest. The conventional array-based sensing protocols use spatially separated sensor units, each with their own recognition element to provide the outputs required for pattern generation. Recently, we introduced a multichannel sensor

employing a single nanoparticle recognition element with three different transducers to generate multichannel outputs in a single well configuration. This approach facilitates high-throughput screening platform for the discrimination of complex biosystem such as cells and tissues. Yet, this multichannel approach in a single well faces a challenge of sufficient non-interfering channels (e.g. fluorescent emission wavelengths) for effective pattern generation. Here, we report a nanosensor that doubles the existing channels from three to six by simple host-guest interaction between cucurbit[7]uril (CB[7]) and the cationic gold nanoparticle. Being able to increase the number of channels while maintaining the single-well configuration allow the nanosensor to successfully profile cancer cells based on their tumorigenic characteristics with minimal effort. The signatures of cell lysates required minimal sample quantity (200 ng), opening up new opportunities for cancer diagnostics use microbiopsy technology.


Sensor in a single-well
AuNP
S
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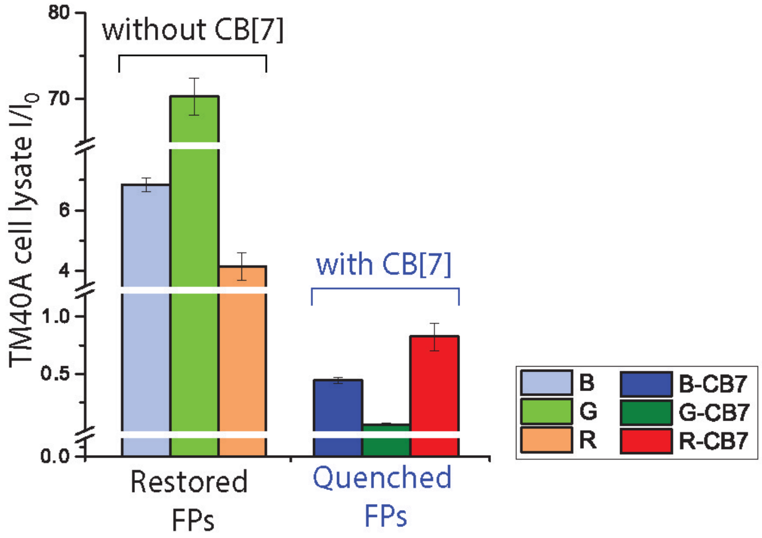
TM40A cell lysate I/I$_0$
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6
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B
G
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B-CB7
G-CB7
R-CB7

COLL 224

Kinetic modulation of nanoparticle embedded transition metal catalyst by tuning nanoparticle surface functionality

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Transition metal catalysts (TMCs) can catalyse a wide variety of chemical transformations, making them potential tools for catalysis in biological settings. We recently demonstrated that self-assembled monolayers on nanoparticles (NP) can be used to encapsulate TMCs, generating water-soluble “nanozymes”. These nanozymes feature catalysis reminiscent of enzymes, but can also catalyse a variety of bioorthogonal processes. We systematically investigated the role of surface structure in controlling the catalytic activity of nanozymes bearing different functional groups against a library of pro-fluorophore derivatives. It was found that the interactions between nanozymes and substrates were driven by steric hindrance and supramolecular interactions, affecting their V_{max}. Reaction kinetics at the catalytic sites were also controlled by varying the number of cleavable bonds of the profluorophore. We demonstrated that V_{max} reduces with increase in the number of cleavable bonds of the substrate. This fundamental study of nanozyme-substrate interactions provides the nanozymes with tunable catalysis reminiscent of their enzyme prototypes.

COLL 225

Array-based sensing using gold nanoparticle and fluorescent proteins for cancer diagnostics

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Biomarkers have been used widely for detecting cell stages and facilitating the discovery of novel therapeutics. This method, while proving powerful, is often limited by the knowledge of diseases and in-depth understanding of specific interactions between analytes and predetermined biomarkers. Array-based sensing approach offers a unique benefit of using selective interactions to detect global changes on cell surfaces. We form the array system by a gold nanoparticle complexed with three different fluorescent proteins, either individually or together in one channel. It has been used to differentiate cell types and states. For example, isogenic healthy, cancerous, and metastatic mammalian cell lines have been identified using this method. Recently our lab has also

used this approach to profile the mechanisms of various chemotherapeutic drugs. One of our current projects focuses on employing the unbiased array-based sensor on cancer stem cells (CSCs) with the goal of identifying novel therapeutic targets. CSCs are a subpopulation of cells in tumors that has the ability to self-renew and populate new tumors. They are resistant to conventional cancer treatment and are believed to be responsible for tumor reoccurrence and metastasis. Understanding of the phenotypic changes on CSCs in response to different stimuli has great implications in cancer therapies. Current work in the lab focuses on developing a sensor array system to rapidly profile CSCs.

COLL 226

Interaction studies of amphiphilic fluorophores with model cell membranes

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This work focuses on the fundamental studies on the interactions of novel amphiphilic fluorophores with model cell membranes. Lipid bilayer is the most fundamental structural unit of biological membranes. To understand how fluorophores translocate the lipid membranes, we have systematically varied the hydrophobic/hydrophilic balance of our fluorophores and examined their interactions with zwitterionic dipalmitoylphosphatidylcholine (DPPC), mixed zwitterionic/anionic dipalmitoylphosphatidylserine (DPPC/DPPS), DPPC/DPPS/Cholestrol liposomes as a function of charged lipid and fluorophore concentration. Differential scanning calorimetry (DSC) was used to examine the effect of fluorophore binding on lipid phase behavior, and changes in liposome structure were examined by cryogenic electron microscopy (cryo-EM).

COLL 227

Protein-based fibers containing gold nanoparticles as a platform for protease detection

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Techniques for the rapid and accurate detection of protease activity would be beneficial for diagnosing a number of diseases and medical issues, which include several forms of cancer and non-healing wounds. We have developed a platform for colorimetric and SPR based protease detection based upon a novel material that incorporates gold

nanoparticles into fibers of proteins. These fibers display an SPR peak that is red-shifted from the SPR for the nanoparticles suspended in solution. As the protease cleaves the protein bonds, the SPR of the nanoparticles blue shifts, observable by UV-Vis spectroscopy. In a separate experiment, the fibers are sequestered at the bottom of a cuvette. As the protease acts on the fibers, nanoparticles are released into solution, displaying a purple color. We discuss the protease kinetics for both scenarios and describe how using a combination of the SPR measurement with the colorimetric measurement can allow for the determination of protease presence as well as relative protease concentration.

COLL 228

Leaching kinetics of ion adsorption rare earths using low concentration of ammonium sulfate solution

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The leaching Kinetics of ion adsorbed rare earth (IARE) by low concentration of ammonium sulfate solution was investigated using column elution manner within a longer period. It was found that the leaching Kinetics curves plotting via time show a two stages linear relationship when leaching with low concentration of ammonium sulphate solution, indicating that the leaching process of IARE can be discribed by a successively two stage of inner diffusion controlled kinetics models. As the concentration of ammonium sulfate solution increased, the difference of the exchange rate constant between the two stages increases. The leaching rate for the first stage increased sharply, and that for the second stage increaseds first and then decreases. Combined with the leaching kinetics study results of samples with different particle size and re-adsorption rare earth, it is believed that the two stages of leaching processes are respectively corresponded to rare earth ions adsorbed on the clay surface and enterred into the inner layer of clay mineral particles, their proportion changes with the sample size, leaching agent concentration and the formation history of IARE. Increasing the leaching agent concentration, the share of rare earth ions on the surface which belongs to the first stage of leaching process increases.

COLL 229

Approaches in multivalent drug design for the diagnosis and therapy of autoimmune diseases

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Peptide based drugs frequently suffer from short half-lives after intravenous injection. There are several well known techniques to shield peptidic drugs against proteolytic processes, including PEGylation or introducing protective groups into the amino acid sequence. Unfortunately, these modifications often cause either total affinity loss or a reduction of drug potency. We recently demonstrated that adverse effects of PEGylation on the affinity of peptidic ligands to G-protein coupled receptors can be compensated by allowing them to bind multiple receptors simultaneously. Such a multivalent drug-receptor interaction was achieved by a covalent coupling of ligands to either nanoparticles or branched polyethylene glycols. Since we know, that neurokinin-1 receptors are involved in various autoimmune diseases and nociceptive processes, an efficient blockade of overexpressed receptors at the target site would be a promising strategy to relieve typical inflammatory symptoms. Especially peptide functionalized quantum dots, shielded by a PEG corona would be a powerful theranostic tool to investigate their action at sites of immune response.

This work addresses different chemical aspects, which should be taken into account for the design of peptidic multivalent binding neurokinin-1 receptor (NK_1R) ligands. On the basis of the commercially available peptidic NK_1R antagonist spantide I, we modified the N-terminal amino acid sequence to avoid an undesirable double PEGylation, which would result in cross-linking of branched polymer-drug conjugates and nanoparticle aggregation. In cell based binding studies, we confirmed, that different truncated peptide sequences are still active to neurokinin-1 receptors, although there is a loss of affinity and a loss of partial agonism. Based on this knowledge, we coupled these peptides either to branched 8armPEG20k or PEG-coated quantum dots to create multivalently acting antagonists. Compared to full-length spantide I, less quantum dot aggregation occurred during covalent ligand coupling. In addition the substantial hydrophobic nature of the truncated peptides could be compensated by PEGylation.

COLL 230

Dispersion of carbon nanotubes by dissolved humic acid: Chemical structures dependence

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Dissolved humic acid (DHA) was reported to be effective for suspending carbon nanotubes (CNTs) and thus altering their transport and risks. This process could widely occur in the environment because of the ubiquity of DHA and increasing application of CNTs. However, the dispersing mechanism of CNTs by DHA with different chemical structures is still unclear. Therefore, in this study, two humic acids were subjected to bleaching or hydrolysis to selectively remove the rigid, aromatic moieties or the flexible, aliphatic components, respectively. The adsorption of rigid, aromatic moieties-rich DHA on CNTs was lower than the flexible, aliphatic components-rich DHA, but the former had stronger ability for dispersing CNTs as identified by suspended amount and suspension stability. The adsorption of DHA with rigid structures resulted in stable suspension of CNTs due to stronger steric hindrance. However, the flexible, aliphatic components-rich DHA molecules conformed to the rigid CNTs better because of its flexible structures,

leading to stronger adsorption but weaker steric hindrance. This study emphasizes that the dispersion of CNTs by DHA is not only controlled by the apparent adsorption of DHA but also the chemical structures of DHA.

COLL 231

Immunomodulatory effects of gold nanoparticles in inflamed immune systems

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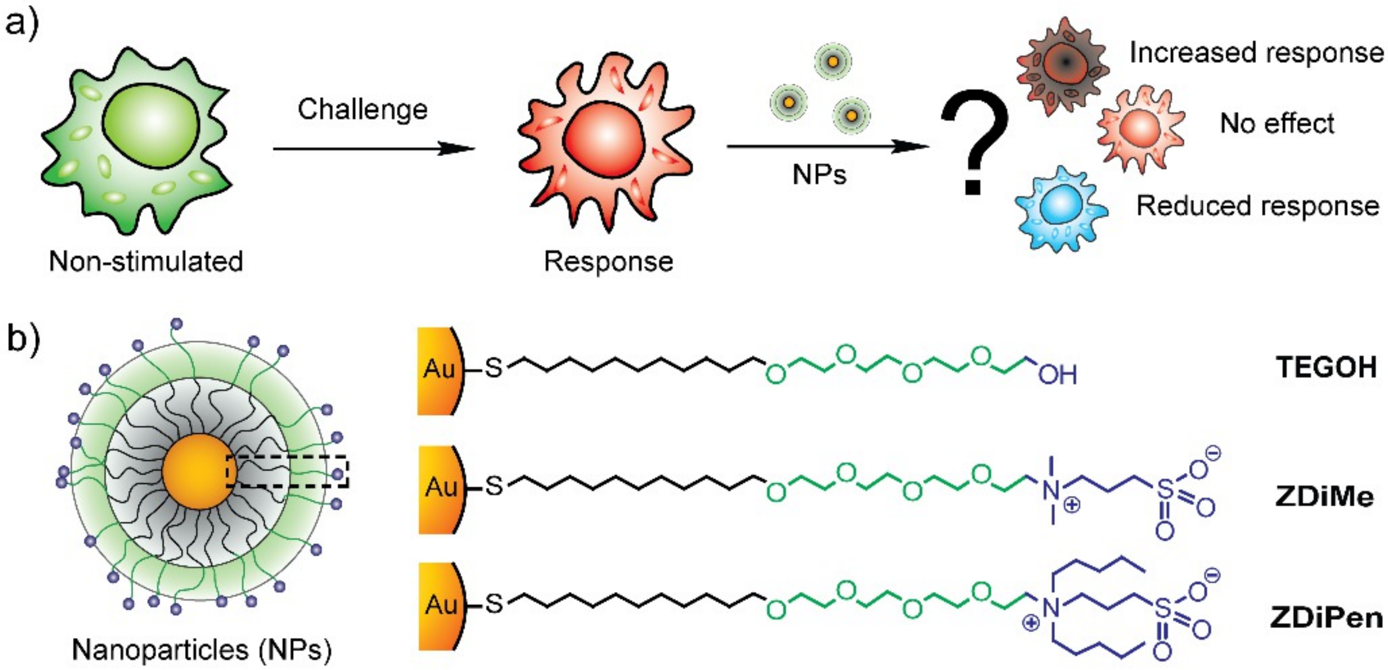
Nanoparticle (NP) surface chemistry plays a central role on the recognition of NPs and the response that is triggered by the immune system towards these materials. Multiple researchers have explored the relationship between NP surface chemistry and immune responses in unchallenged conditions. These studies, however, do no shed light on the behavior of these particles in inflamed subjects. We recently developed a series of uncharged NPs having specific surface functionality with variable hydrophobicity to directly study relationships between biological activity and NP surface chemistry. Using a lipopolysaccharide (LPS) immune-challenged mouse model, we demonstrate that hydrophobic zwitterionic functionalities dramatically boost inflammatory outcomes while hydrophilic zwitterionic structures generate minimal immunological responses.



COLL 232

Surface morphology of the grafted perfluorinated gold-organic film

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Perfluorinated organic film C_8F_{17}-4-C_6H_4- was successfully grafted on the in situ reduced gold by reductive grafting from the diazonium tetrachloroaurate(III) salt [C_8F_{17}-4-$C_6H_4N{\equiv}N$]$AuCl_4$. The highly irreversible broad reduction peak of 1.0 mM [C_8F_{17}-4-$C_6H_4N{\equiv}N$]$AuCl_4$ occurs at -0.08 V vs. Ag/AgCl in 0.1 M [Bu_4N]PF_6/CH_3CN at a glassy carbon working electrode. The surface morphology and evidence of the gold-organic film formation was investigated by attenuated total reflectance-infrared spectroscopy (ATR-IR), optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and atomic force microscopy (AFM). ATR-IR spectrum shows the $n_{C\text{-}F}$ stretching frequencies of the perfluorinated film at 1089 and 1230 cm^{-1} and the absence of the diazonium peak at 2305 cm^{-1}. OM, SEM, and AFM images show clusters or islands and isolated sub-micron deposits protruding less than one micron above the surface. EDS measurements showed the presence of gold in the thin film. Ferrocene/ferrocenium and $[Fe(CN)_6]^{3-/4-}$ electron-transfer experiments, sonication in organic solvents and water, and open circuit potential (OCP) experiments showed the efficient grafting and robustness of the grafted film.

COLL 233

Understanding interparticle interactions of nanoprobes based on bioconjugated gold-based nanoparticles

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Nanomaterials have found increasing applications in medical theranostics, which allow for the enhancement of rapid, sensitive, multiplexing, and point-of-care treatment and diagnosis. One important aspect of nanomaterials is the effective harnessing of the plasmonic coupling of nanoparticles, which is essential for the exploitation of unique optical properties of metal nanoparticles. This report describes recent findings of an investigation of bioconjugated gold-based nanoparticles for the detection of biomolecules, such as protein and DNA, focusing on understanding the creation of “hot spots” for enhancements in surface enhanced Raman scattering (SERS) and localized surface plasmon resonance (LSPR). Examples will include theoretical and experimental

analyses of SERS and LSPR characteristics in terms of the interparticle interactions for the nanoprobes in solutions. The theoretical modeling is aimed at developing a better understanding of the design and control parameters of the nanostructures and interactions for optimizing plasmonic coupling and spectroscopic enhancements in biomolecular recognition.

COLL 234

Tunable electron doping of transition metal dichalcogenides with superatom

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Complementary carrier doping of semiconducting materials in a controlled manner is vital for various electronic device applications. For atomically thin van der Waals materials, the electrical properties can be tuned by chemical functionalization of the surface. Here we present a new method to dope two-dimensional transition metal dichalcogenides (TMDCs) using molecular clusters. Atomically defined metal chalcogenide clusters act as nanoscale atoms that we call superatoms due to their ability to form solid state materials through charge transfer with electron acceptors such as C_{60} and the cubic iron oxide superatoms. For this study, we utilize an octahedral superatom $Co_6Se_8(PEt_3)_6$ as a dopant for MoS_2 and WSe_2. We chose this particular superatom because it is easy to prepare, is efficacious at electron transfer, and has potential to form an electron donating (*n*-type) surface dopant. By applying the superatom dopants, moderate *n*-type MoS_2 channel becomes heavily *n*-doped, and the transfer characteristics of WSe_2 changes from the *p*-type to the *n*-type transport behavior in the same gate voltage window. This electron doping of TMDC FET can be easily controlled by both the time the device is immersed in the superatom solution and the concentration of the dopant solution. As a demonstration of the utility of this method, we fabricate a *p-n* junction by spatially confining the area of the WSe_2 film that is doped. The lateral WSe_2 *p-n* junction is formed by preparing the hexagonal boron nitride (*h*-BN) mask and by superatom doping of the partially *h*-BN protected WSe_2 flake. Remarkably, the diode-like current rectification is observed at gate voltage ranging from 20 to 40 V, yielding a rectification ratio of three orders of magnitude at source-drain voltage 1.5 V. This chemical doping approach should be applicable to a variety of different TMDCs and superatoms.

COLL 235

NIH 3T3 cell spreading and viability on zein films may be facilitated by transglutaminase

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Zein is a biocompatible corn protein potentially useful in the development of biomaterials. In this study, the deposition of zein on oxygen plasma treated glass cover slips significantly enhanced cell spreading and viability. The mechanism for cellular response to zein coated surfaces was thought to involve the polyglutamine peptides in zein structure. We hypothesized that zein was a substrate for tissue transglutaminase (tTG), an extracellular enzyme involved in cell-surface interactions. SDS-PAGE results suggested an interaction between zein and tTG, where zein was the glutamine donor. Cross-linking between zein and tTG may be the first step in successful cell adhesion and spreading.

COLL 236

Synthesis of shaped palladium nanoparticles with bimetallic surfaces via selective surface passivation

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Ag-assisted syntheses have been used to great success in the production of gold nanoparticles with a variety of well-defined shapes, including high index structures. The mechanism behind this synthetic approach involves the selective passivation of specific surface facets through deposition of a sub-monolayer of Ag onto growing Au nanoparticles. Using new methods developed through expansion of this general approach, Pd nanoparticles with controlled shapes have been synthesized by incorporating small amounts of a second metal in combination with interactions from shape-directing anions. Due to their bimetallic surface composition and stepped facets, the synthesized nanoparticles have potential applications in the catalysis of selective oxidation and hydrogenation reactions.

COLL 237

Synthesis and surface active properties of novel hybrid type anionic surfactants having a short fluorocarbon and hydrocarbon chain

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Perfluorinated surfactants, especially perfluorooctanoic acid (PFOA) and its derivatives, are used in many industrial fields, although fluorocarbon is much more expensive than comparable hydrocarbon. However, fluorinated surfactants having long fluoro-carbon chain(≧8) are harmful to human health and the environment. In order to avoid these

problems, we investigated the novel hybrid type anionic fluorinated surfactants with a short fluorocarbon and hydrocarbon chain. Those were synthesized by the condensation reaction of fluoro-alcohol and alkyl glycidyl ether followed by sulfation with chlorosulfonic acid. The structure of products was characterized by H-NMR, IR and HR-MS. The surface active properties of newly synthesized anionic fluorinated surfactants were measured. The CMC of the final products were found to be 0.0012 to 0.0116 mmol/L and surface tension values was in the range of 13.84 to 20.16 mN/m.

COLL 238

Supracolloidal chains of linear assemblies of diblock copolymer micelles containing inorganic nanoparticles

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Self-organization of colloidal building blocks can create a variety of superstructures such as clusters, ribbons, and chains. In particular, directional attraction between colloidal particles with orthogonal repulsion to the attraction can produce a chain-like supracolloidal polymer. With diblock copolymer micelles, we can achieve the directional interaction between the micelles by manipulating the solvent of the micellar solution. In this presentation, we functionalized supracolloidal chains of diblock copolymer micelles by synthesizing plasmonic nanoparticles of silver and gold in the micellar building blocks. We first loaded the precursors of nanoparticles in the cores of diblock copolymer micelles, which were cross-linked, and then reduced them to nanoparticles within the micelles. Linear assemblies of these micelles containing nanoparticles were induced by manipulating the solvent polarity of solutions, which generated directional attraction between the micelles, resulting in nanoparticle-functionalized supracolloidal chains. We investigated plasmonic characteristics of supracolloidal chains containing silver and gold nanoparticles.

COLL 239

Formation of single crystalline colloidal structure in double-emulsion drops

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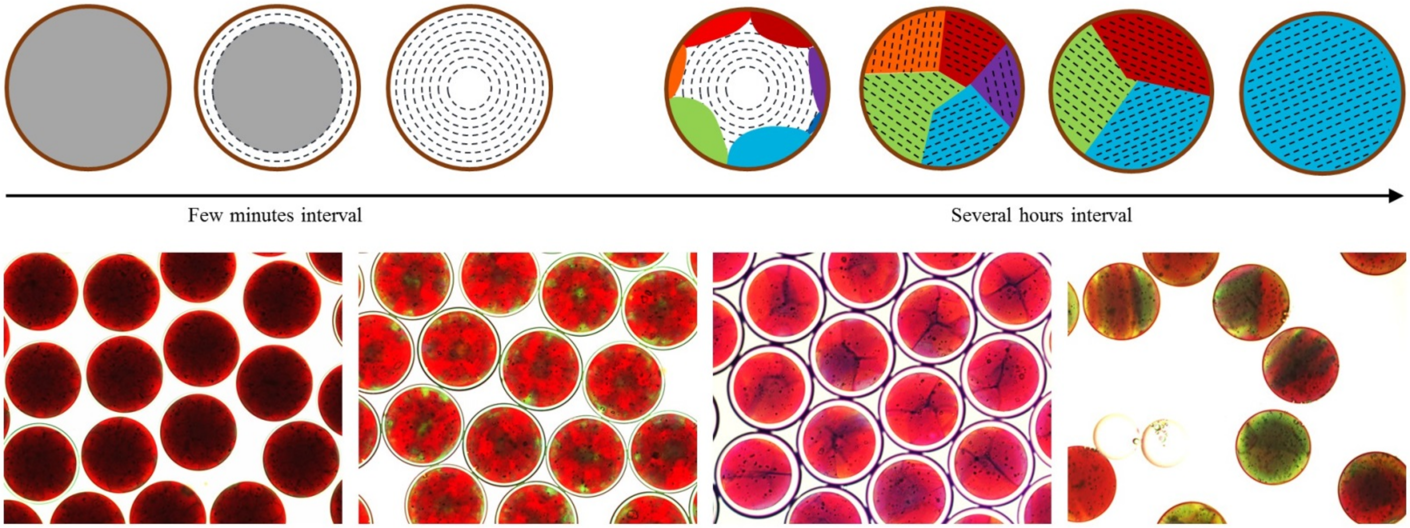
Colloidal crystals exhibit pronounced reflection colors through selective diffraction of light. Such unusual optical properties render the colloidal crystals promising for various photonic applications. In particular, the colloidal crystals in granule or capsule formats are appealing for pigments and injectable microsensors. Emulsion droplets have been used as template to create spherical assemblies of colloids. Within droplets, colloids form hexagonal array along spherical interface and face-centered cubic (fcc) crystals grow from the interface toward the center. However, the structures are polycrytalline and have high density of defects because fcc crystals are incompatible with spherical

geometry, which deteriorates the optical performance.
In this work, we report the evolution of charged colloids confined in droplets from polycrystalline structure to single fcc crystal. The single crystal is encapsulated in solid shell, which exhibit orientation-dependent vivid colors. With a capillary microfluidic device, double-emulsion drops are prepared, of which inner water is aqueous suspension of charged colloids and middle oil is elastomer precursor. The colloids in the inner drop are crystallized along the spherical interface within a few minutes, as reported previously; the crystal formation and growth are monitored by optical microscope as the crystals appear translucent whereas glasses are opaque. The colloidal crystals at this early state show uniform color appearance in reflection, confirming the crystal growth from the interface. In a time scale of hours, the fine polycrystals merge to form larger crystallites near the interface. The large crystallites further evolve to form only several crystallites with different orientations. Eventually, the crystallites are merged to form single fcc crystal with stacking faults; this is indirectly observed by optical microscope and further confirmed by confocal microscope. The crystal-laden microcapsules exhibit pronounced reflection colors from whole cross-section for certain orientations, of which wavelengths are consistent with Bragg diffraction from various fcc crystal planes.



Series of schematic and optical microscope images presenting crystal growth and merging

COLL 240

Gold nanorods as plasmonic sensors for particle-diffusion

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Plasmonic gold nanoparticles are widely used as sensor to detect surface coverage changes. If the interactions between a protein/particle (analyte) in solution and the nanoparticle surface (sensor) are negligible, the analyte diffuses through the sensor's sensing volume without attaching. The sensing volume of a gold nanoparticle is in the order of its own volume, i.e. in the attoliter regime. The diffusion of an analyte through the sensing volume results in a small fluctuation of the plasmon resonance wavelength. The measurement of these fluctuations require a combination of high time resolution and spectral precision, which we achieve with an optical dark-field spectroscopy setup, where the sensor is illuminated with a supercontinuum white-light laser. The scattered light of a single gold nanoparticle is detected by an electron multiplying charge-coupled device (EMCCD) coupled to a transmission spectrometer which allows a spectra read-out of 12,500 fps.

We test this technique successfully on small gold andpolystyrene nanoparticles as diffusors.We extract diffusion coefficients from our fluctuating plasmon resonance signal using a theoretical model that we developed and investigate the effects of diffusor-size, viscosity of the solution and diffusor-concentration. It was possible to show that the obtained diffusion coefficients follow the Stokes-Einstein equation. Comparing the results from our technique with those obtained by dynamic light scattering (DLS), we get insight intothe repulsive interaction between diffusorand sensor surface. Our novel technique is therefore an alternative method to DLS and FCS to obtain diffusion constants and offers a way to characterize repulsive surface-analyte interactions.

COLL 241

Study of tertiary diamine dative bonding and dissociation on semiconductor surface: Adsorption of triethylenediamine on Si(100)-2×1

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The functionalization of silicon surfaces with thin layers of organic materials is an important area of study of semiconductor materials, with current and potential applications in microelectronics, catalysis, and bio-sensing. Triethylenediamine (also known as 1,4-diazabicyclo[2.2.2]octane, or DABCO) contains two tertiary amine nitrogen atoms, of which one could donate lone electron pair to the surface to form a dative bond while the other may remain accessible for further modification. This structure can further be modified through reactions with this unbound nitrogen. We used infrared spectroscopy (MIR-FTIR), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) supported with density functional theory calculations (DFT) to study the reaction mechanism, including dative bonding possible dissociation and decomposition pathways on the Si(100)-2x1 surface.

COLL 242

Reactivity of polyoxometalates challenged with organophosphates and thioethers

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Factors that affect the decomposition of organophosphates and thioethers are investigated for the future development of applicable materials for air filtration media and self-decontamination. Solution based reactivity between polyoxometalates (POM) and various organic substrates are well documented within the literature; however, effective utilization of the hetero-metal substituted POMs in the absence of solvent is significantly less documented. Herein, a study was performed to monitor reactivity of POMs with various hetero-metal substitutions, including zirconium, against organophosphate and thioether contaminants in solution and heterogeneous conditions. A reproducible method for the decontamination of a liquid contaminant on a solid surface was developed and is described. Results from surface characterization and decontamination using IR spectroscopy, GC-MS, and microscopy are presented. Effects of POM morphology, hetero-metal selection on reaction rate and by-product generation from reactions with organic contaminant simulants are reported.

COLL 243

Surface modifications of poly(ethylenedioxythiophene) and polypyrrole nanoparticles and nanofibers

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Electrochemically grown poly(ethylenedioxythiophene) and polypyrrole thin films have been shown to react efficiently with thiols, permitting ready modification of film surface properties while leaving the bulk electronic properties largely unaffected. Water dispersible polypyrrole nanoparticles and nanofibers were synthesized in aqueous hydrochloric acid; poly(ethylenedioxythiophene) nanoparticles and nanofibers were prepared in aqueous camphorsulfonic acid. The resulting colloidal dispersions were purified and characterized by light scattering. The materials were spin coated onto appropriate substrates both before and after treatment with highly hydrophobic or hydrophilic thiols. Conductance measurements, contact angle analysis, electron and atomic force microsopy, and thermogravimetric analysis techniques were used to characterize the deposited films and potential applications of such materials will be discussed.

COLL 244

Surface modification of conducting polymer films using ATRP

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Electrically conducting polymers such as polypyrrole and polyaniline readily react with thiols to give materials with unique surface properties. Conducting polymer thin films were electrochemically grown on a quartz crystal microbalance (QCM) resonator and treated with a thiol terminated with an atom transfer radical polymerization (ATRP) initiator. Deoxygenated solvent containing a copper catalyst and monomers containing the polymerizable methacrylate moiety were circulated through the QCM cell and the ATRP growth from the surface was monitored by both the change in resonance frequency (mass increase) and resonance dissipation (viscoelasticity). The reaction kinetics were compared to a models system consisting of the same thiol assembled on gold and the resulting surfaces were characterized.

COLL 245

DNA functionalized quantum rods and their assembly into organized patterns on origami

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In this presentation we will describe the DNA-mediated self-assembly of CdSe/CdS quantum rods (QRs) onto DNA origami. We recently described a model system (Doane, et. al., *Nanoscale* 2015, 7, 2883) that aligned QRs in parallel fashion. In this presentation we describe recent results in the controlled spacing and orientation of the assembly, as well as the resulting optical response. Moreover, we will describe how co-functionalizing the QR interface with DNA and zwitterion monolayers improves hybridization efficiency and assembly yields.

COLL 246

Toward orthogonal plug and play protein immobilization on DNA based nanostructures

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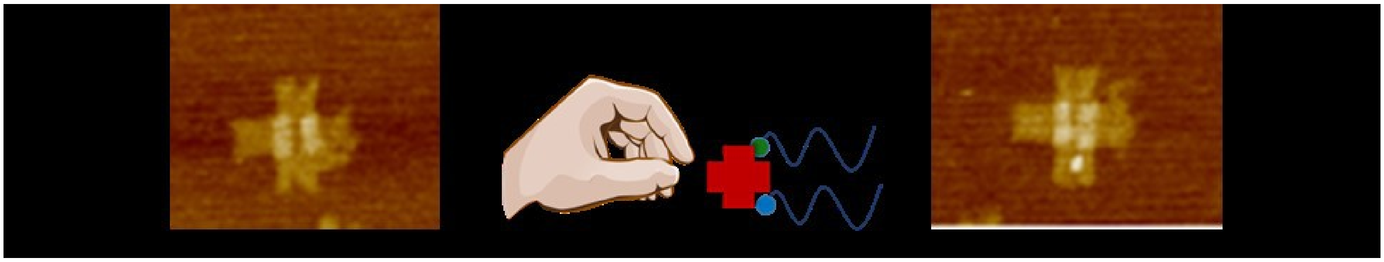
The standardization of parts and interfaces between parts can accelerate innovation by enabling rapid and diverse prototyping. The structural DNA community has developed and is still developing a wide variety of approaches for selectively binding macromolecules, including biomolecules, to DNA based architectures, including, for example, the use of biotin/streptavidin, his-tag/Nickel and click chemistry pairs.

Implementation of a modular approach has enabled independent optimization of functional components which can then be integrated into larger and/or more complex systems with minimal concerns for component compatibility. It is our belief that extending this modular approach to DNA based nanotechnology will expand the range of laboratories capable of participating in and contributing to the facile development of novel integrated systems. In the approach under development and described here, any protein of interest is generated with a standard purification motif (his-tag) and a standard linking motif (biotin). Unique localization is provided via attachment to an adaptor motif, composed of a streptavidin molecule individualized/specialized via biotinylated DNA “staple” molecules. A comparison of the efficiency of post assembly modification of a standard platform or chassis at room temperature and 45^0C suggests that insertion at temperatures compatible with maintaining protein function can be performed using this modular approach and may provide a pathway to high density protein positioning.



COLL 247

Catalytic behavior of polymeric alkene incorporated hybrid metal catalysts

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Synthesizing supramolecular nanoparticle embedded gels that encompass versatile functionalities is an area of great interest in both research and industrial fields because of their synthetic and catalytic applications. In this poster, we present the nanoparticle hybrid gel formation of various transition metals stabilized by polymethylhydrosiloxane (PMHS) and several different diene systems. In our preliminary results, we observed that cis-polybutadiene is a very good cross-linking agent for the production of a gel via a palladium nanoparticle catalyst than its other isomers. This prompted our exploration of other noble metals as catalysts for this gellification process; in addition, we sought to understand the effects on this system of different butadiene compounds, such as pinene. This led to the further exploration of diverse diene systems by the generation of novel diene incorporated metal catalysts. Via the utilization of different diene reagents, we sought to generate novel diene incorporated metal catalysts. The newly synthesized and novel hybrid gels were characterized via NMR, FTIR, TEM, and SEM and their catalytic properties and efficacy were assessed via various alcoholysis reactions. The

gels were once again analyzed via FTIR, TEM, and SEM to determine their structural integrity and overall composition.

COLL 248

Understanding low-temperature sintering and adhesion properties of metal nanoparticles printed sensor devices

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Metal nanoparticles provide a promising pathway for printing conductive devices on low-cost and scalable polymer or paper substrates towards flexible sensors and biosensors, but a key challenge is the ability to control the sintering process and adhesion properties without damaging the underlying substrates. In contrast to traditional thermal sintering process, this presentation describes recent results of an investigation of pulsed laser sintering and other sintering processes that can be performed under room temperature for the substrates, and adhesion properties as well. One example involves pulsed laser sintering of alloy nanoparticles on different substrates. Another example involves room-temperature sintering of commercial silver nanoparticles on different substrates. Understanding the adhesion properties is aided by theoretical simulation of particle-particle and particle-substrate interactions, which is discussed along with the implications for the design and preparation of different printable nanoparticle inks for printing on nanofibrous membrane paper consisting of layered cellulose nanofiber and cross-linked polyethylene glycol diacrylate structures. Results from testing of the sensor devices' sensing performance in detecting volatile organic compounds and mechanical strains will also be discussed, which are finding increasing applications in wearable electronics and sensors.

COLL 249

Substrates grafting: The effect of nanostructure morphology on catalytic activity

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Due to their unique catalytic activity, nanomaterials with novel architecture are sought after catalysts in organic synthesis [1]. Metal nanoparticle incorporated dendrimers are supramolecular nanostructures that have found applications in a variety of fields,

including catalysis. It has been shown that dendrimers are effective recoverable catalyst; however, there has been reports of diminished catalytic activity with increasing generation [2]. In an effort to generate a material with enhanced catalytic activity, we outline a new synthetic scheme for generation of dendrimer generated metal nanoparticles.

This presentation details comparative analysis between dendritic and other scaffolds. The production of these well-defined dendritic architectures was performed via a well-known hydrosilylation reaction. The generated material contained a triazine central core (2,4,6-triallyloxy-1,3,5 triazine , TAT) and 1,3,5,7 tetramethyltetracyclosiloxane (D_4^H) branches. For comparison, noble metal nanoparticles were also synthesized using D_4^H without TAT, which displayed unique morphologies. These nanoparticles were then isolated and immobilized onto cotton, glass, and charcoal. Both of these novel nanomaterials were examine for their catalytic activity in various organic syntheses. Furthermore, we detail the recoverability of the catalyst and their efficacy upon reuse in common organic synthesis. Transformations and catalytic assessments were confirmed via NMR, GC-MS, FTIR, TEM, SEM, and AFM.

COLL 250

Single-molecule investigations via DNA nanostructures: A cell adhesion study

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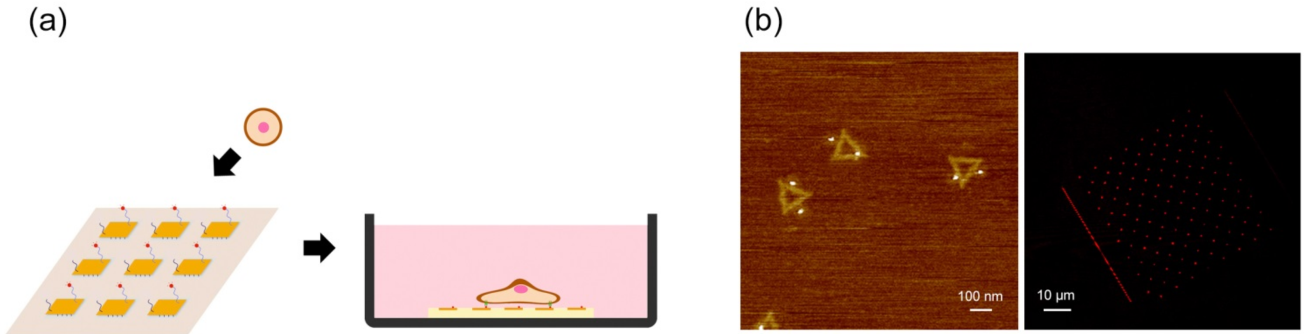
DNA assembles according to precise base-pairing rules. This allows for the construction of DNA nanostructures (DNA origami) in which DNA is folded into various shapes with a high degree of positional order allowing for complex arrangements to be obtained. In addition, DNA origami can be employed as scaffolds to pattern bioactive structures and nanostructures (e.g. Quantum Dots, CNTs etc.) at the scale of individual molecules. In order to take fully advantage of this approach we need to control the organization of DNA origami on surfaces into ordered array configurations. This in turn can allow for the fabrication of biochips for single-molecule investigations.

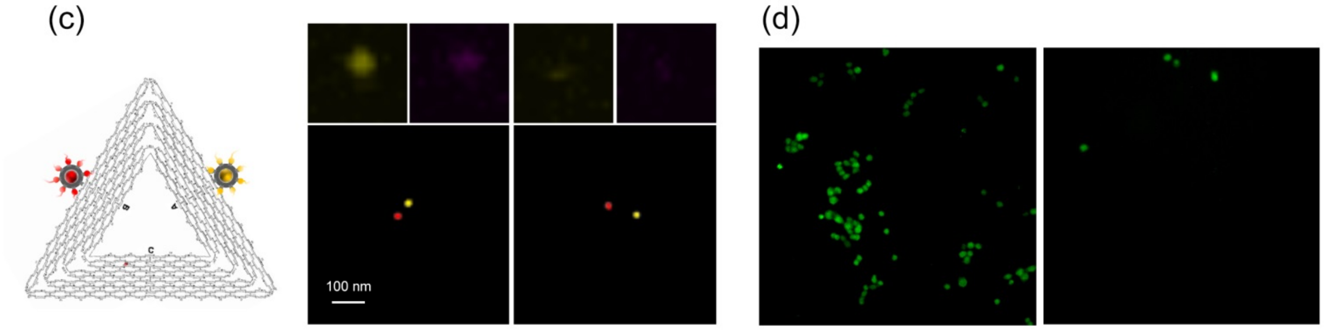
Combining our skills of nano-fabrication, DNA nanostructure engineering, and molecular-specific cancer targeting, we present a platform for in vitro cell-surface investigations with single-molecule resolution. DNA origami were organized into order arrays on surfaces, exhibiting individual integrin binding sites at specific nanoscale spacing (Fig. a, b). Spectral separation via Super-Resolution microscopy was employed to confirm the arrangement and geometric of single molecular modified DNA origami (Fig. c). We explored how the geometric organization of cancer-promoting αvβ6 integrin binding peptides affects cell adhesion and spreading (Fig. d). We will show that αvβ6 integrin binding peptides nanospacing affects spreading and direct cancer cell fate. This

approach can allow for improved intracellular signalling studies at the nanoscale, and for the development of novel cancer therapeutics platforms.



AFM image for Modified DNA origami

Fluorescence microscopy image for DNA origami arrays



Modified DNA origami

Super-Resolution image of spectral separation

Cell growth on modified DNA origami

Control

COLL 251

β-Galactosidase langmuir monolayer at air/subphase interface

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The interfacial properties of β-galactosidase were studied through surface chemistry and spectroscopic techniques. β-galactosidase interacted with X-gal to give the galactose as well as blue colored organic moiety. We investigated the β-galactosidase Langmuir monolayer in absence and presence of X-gal of varying concentration to the sodium chloride subphase. It was found that the limiting molecular area as well as the monolayer breaking point surface pressure kept on decreasing with the increasing amount of X-gal. In accordance to the data obtained from the isotherm it was also found that β-galactosidase forms a stable monolayer that does not aggregate at the air-subphase interface. The stability of the monolayer at the air-subphase interface was studied by using compression-decompression cycles with and without X-gal at varying concentration and different surface pressures. The infrared reflection-absorption spectroscopy (IRRAS) and Brewster angle microscopy (BAM) of β-galactosidase Langmuir monolayer was also investigated for pure and mixed β-galactosidase at the air-subphase (X-gal dissolved in limited amount of DMF and further diluted with 0.1 M NaCl solution). The objective of this article is to investigate the surface chemistry of β-galactosidase on air-subphase interface using Langmuir monolayer technique.

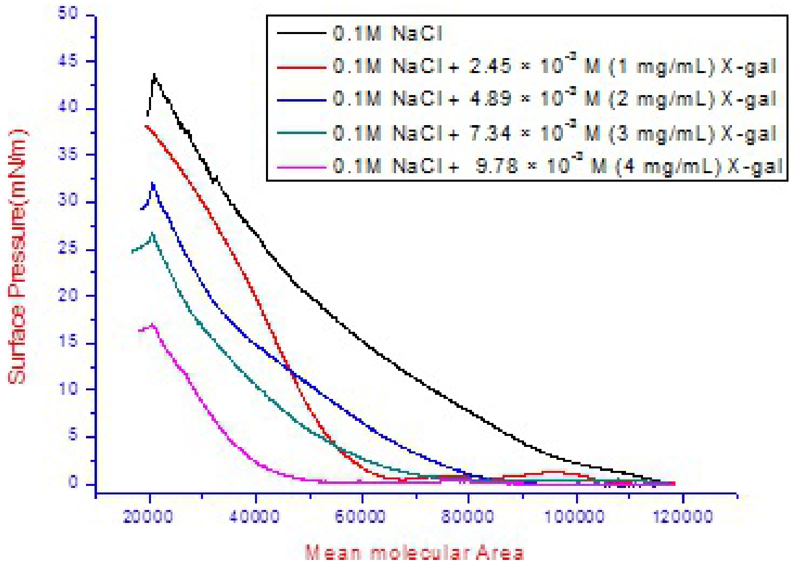

Figure: Surface pressure versus mean molecular area isotherms for 3.7×10^{-7} M β-Galactosidase spread on 0.1M NaCl and (2.45, 4.89, 7.34 and 9.78) × 10^{-3} M of X-gal

Sub-phase	Limiting Molecular Area (Å^2/molecule)	Collapse Surface Pressure (mN/m)
0.1M NaCl(only)	79,300	43
0.1M NaCl + 1mg/mL X-gal	58,200	38
0.1M NaCL+ 2mg/mL X-gal	52,200	33
0.1M NaCL+ 3mg/mL X-gal	44,050	28
0.1M NaCl + 4mg/mL X-gal	41,000	17

Table: Data showing limiting molecular area and collapse surface pressure for different subphases.

COLL 252

Synthesis and characterization of conductive reduced graphene oxide bi-layer films

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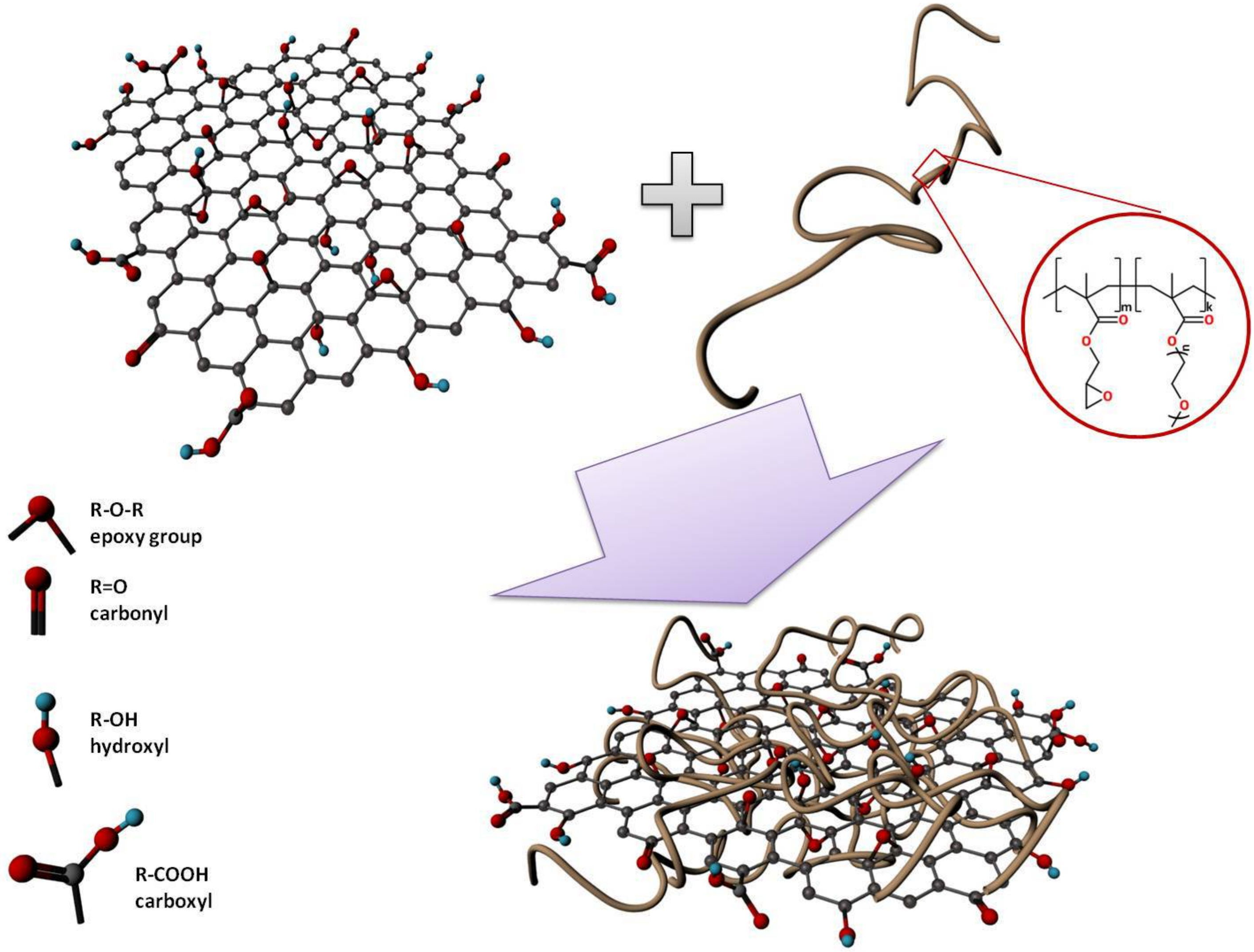
The major goal of the reported study is to develop highly conductive reduced graphene oxide (rGO) films, with suppressed intersheet resistance, understand their formation, and investigate their conductive properties upon thermal reduction. The bi-layer films are achieved based on the following: (i) casting GO sheets modified with poly(GMA-ran-OEGMA) [GMA: glycidyl methacrylate; OEGMA: oligo ethylene glycol methyl ether methacrylate] copolymer as a monolayer film, and (ii) incorporating a polymer interlayer (i.e., a polymer linker layer [PLL]) into the bi-layer GO structure. The attachment/anchoring of the copolymer to the surface of GO and formation of rGO films has been followed by AFM, TGA, FTIR and XPS.



COLL 253

Phase-resolved internal heterodyne high resolution sum frequency generation vibrational spectroscopy reveals chiral structures of biomolecules at interfaces

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Reliable determination of phases in molecular vibrations is fundamental in characterizing molecules at interfaces using sum frequency generation vibrational spectroscopy (SFG-VS). Here we present an approach that utilizes the azimuthal-angle phase dependence of the z-cut α-quartz crystal through the spectral interference between the SFG fields of the quartz surface, as the internal phase reference, and the adsorbed molecular layer. This straightforward method requires only an internal phase standard with a single measurement that is free of phase drifts. This method also provides unambiguous SFG spectral phase information on such surfaces. Here, the absolute phase of the molecular susceptibility tensors of the CH_3, CH_2, and chiral C–H groups in Langmuir–Blodgett (LB) molecular monolayers of lipid, cholesterols, and drop-cast peptide films are accurately determined. In particular, the phase-resolved SFG signals successfully probed the two distinct chiral N-H groups of the antiparallel β-sheets, as well as the detailed chiral Cα-H, amide I, amide II, and amide III spectral features. These results provides unique structural and conformational information of biomolecules at surfaces, and demonstrates it as one of the most promising tools for interrogating the detailed structure and interactions of complex bio-interfaces.

COLL 254

Effects of acidulated albumin on Cu^{2+}-mediated amyloid β-protein aggregation and cytotoxicity

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Alzheimer’s disease (AD), a prevalent neurodegenerative disease, is characterized by dysfunction of memory. The main histofpathological hallmark of AD is senile plaques formed by amyloid β-proteins (Aβ) in the hippocampus and cortex. In addition, elevated levels of metal ions in plaques, mainly Cu^{2+} and Zn^{2+}, indicate that they play a crucial role in Aβ aggregation in vivo. It has been proven that metal ions not only induce the generation of off-pathway Aβ aggregates but also lead to the formation of reactive oxygen species (ROS), which are harmful for nerve cells. Cerebral acidosis is another common complication of AD. Under mildly acidic conditions, Cu^{2+}-Aβ species have a higher tendency to generate neurotoxic aggregates. In this work, we fabricated acidulated human serum albumin (A-HSA) to mitigate Cu^{2+}-mediated $Aβ_{42}$ aggregation and cytotoxicity at pH 6.6. Extensive experiments showed that A-HSA could alter the

pathway of Cu^{2+}-mediated $A\beta_{42}$ aggregation and protect SH-SY5Y cells from cytotoxicity and oxidative damage induced by Cu^{2+}-$A\beta_{42}$ species. Noticeably, stopped-flow fluorescence analysis revealed that A-HSA changed the Cu^{2+}-$A\beta_{42}$ coordination mode from complex I to complex II on the millisecond timescale, which avoided the formation of aggregation-prone Cu^{2+}-$A\beta_{42}$ aggregates. Based on the findings, we proposed a mechanism of the modulation effect of A-HSA on inhibiting Cu^{2+}-mediated $A\beta_{42}$ aggregation and cytotoxicity under the mildly acidic condition.

COLL 255

Mechanistic studies of ZnS and CdS quantum wire growth via facile one-step approach

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Fabrications of high-quality semiconducting quantum wires (ZnS, CdS) with tunable diameters (6-10 nm) have been reported via a simple thermal decomposition of single-source precursors (diethyldithiocarbamate, DDTC) in oleylamine. In our recent studies, synthesis temperature (120-200 °C) can cause major variance in both wire morphologies and crystalline profiles. X-ray diffraction reveals emerging crystalline phases (originally wurtzite) during optimizations of synthesis conditions. Moreover, at varied synthetic temperature, evolutions of wire shapes and diameters also suggest intriguing growth mechanism in addition to solution-solid-solid (SSS) one. We thus employ X-ray absorption (EXAFS) and scattering (WAXS) techniques that *ex-situ* monitor the structural and morphological evolutions at each step of wire growth. In addition, electron microscopy (HRTEM) confirms an unusual ion transportation from catalyst tips that affect wire chemical compositions and lateral dimensions. We further examined syntheses below phase transition (180 °C) in cubic Ag_2S catalysts, suggesting alternative growth pathway beyond the superionic nature of the catalysts solely responsible for quality quantum wire growths.

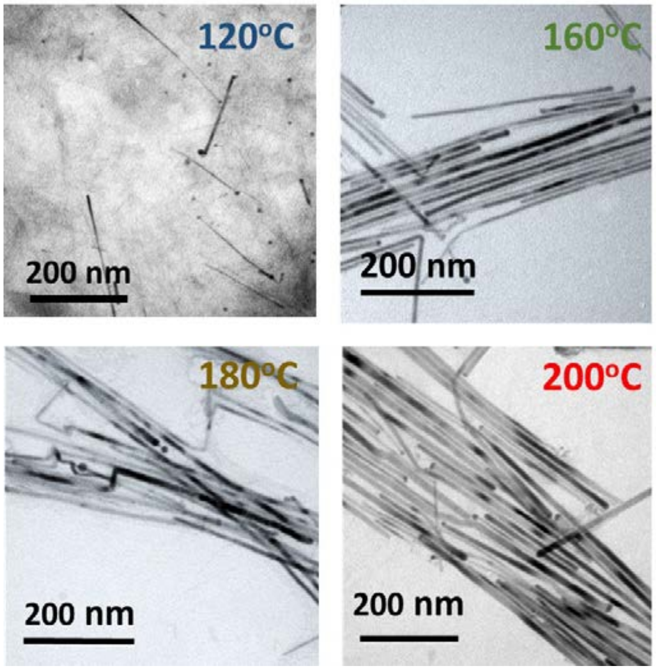

Figure 1. Representative TEM images of ZnS quantum wires synthesized at (a) 120 °C, (b) 160 °C, (c) 180 °C, (d) 200 °C in oleylamine solutions.

COLL 256

Development of thermometric titration to characterize catalyst supports: Advantages in process control and fundamental understandings of support

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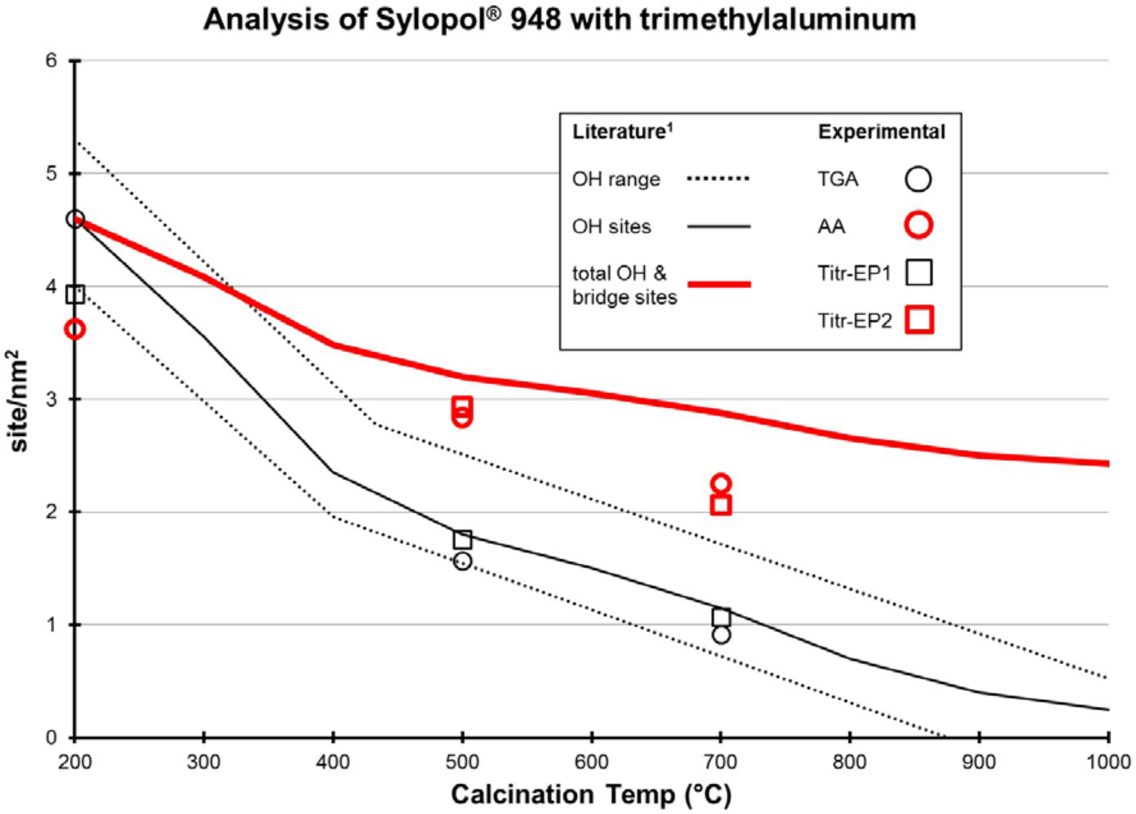
Much of the world's high-density polyethylene is produced in gas phase heterogeneous reactors. This production method relies on the Ziegler-Natta polymerization of ethylene on a high surface area silica catalyst support. These Ziegler-Natta polymerization centers are anchored to the silica at active sites on its surface, which consist of hydroxyl groups and strained siloxane bridges on the silica surface. In order to produce high-activity polyethylene catalysts on a large scale, the number of active sites on the surface of the silica (expressed as sites/nm^2) must be accurately known. Common methods used to determine this value have disadvantages including labor intensiveness, lack of precision, lack of accurately measuring accessible sites, inability to measure all available active sites, and/or lack of flexibility of the chemical reacting with the surface active sites. We are developing a thermometric titration method to overcome some of these issues. A thermometric titration involves titrating the silica with a reactive compound and using the exothermicity of the reaction as the observable to determine the end point (EP) of the titration. Proof-of-concept experiments show

thermometric titration of the silica agrees with literature values, atomic absorption (AA) analysis of the silica to quantitate the surface active chemical, and thermogravimetric analysis (TGA). Furthermore, the titration looks to have two end points which discern between the hydroxyl groups and strained siloxane bridges on the silica surface, allowing a more detailed study of the silica surface chemistry.



[1] Zhuravlev, L. T. The surface chemistry of amorphous silica. Zhuravlev model. *Colliods and Surfaces A: Physicochem. Eng. Aspects* **2000**, *173*, 1-38.

COLL 257

Transferrin modified PEGylated chitosan-cholesterol as self-assembled nanoaggregate for the delivery of curcumin in cancer

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The transferrin receptor expression on cancer cells can be up to 100-fold higher than the average expression in normal cells owing to their rapid proliferation rate and iron demand. Transferrin has been explored as a targeting ligand attached to the nanocarriers to deliver therapeutic and diagnostic agents as pay-load into the cancer cells due to their over expression. This approach takes the advantage of continuous recycling of the transferrin receptor from the surface to the endosomal compartment for efficient internalization of the nano carriers.

In the present study, we have developed a PEGylated chitosan conjugated cholesterol-based co-polymer (PCC) and modified the surface with transferrin by incorporating transferrin (Tf) in the self-assembled polymeric system for active tumor targeting. The synthesized polymers were characterized by IR, TGA and ^{1}H NMR spectroscopy. The size and surface charge of the nanoparticles were measured by zetasizer. A potent chemotherapeutic drug, curcumin was loaded and the loading efficiency, stability and *in vitro* release were determined. Cellular uptake study was evaluated on hepatocarcinoma cells by using flow cytometry, and visualized the cells under confocal microscope. Transferrin modified PEGylated Chitosan conjugated cholesterol nanoparticles (Tf-PCCs) and curcumin loaded Tf-PCC nanocarrier showed mean hydrodynamic diameter of 241.8±2.46 nm and 262.8±1.82 nm, respectively. Cellular uptake of curcumin indicated that the Tf-PCCs were taken up by cancer cells with higher efficacy compared to PCCs. The therapeutic efficacy of curcumin in the newly developed mixed micellar system will be assessed *in vitro* in various cancer cell lines by cytotoxicity assays and *in vivo* by using cancer cell xenograft mouse model.

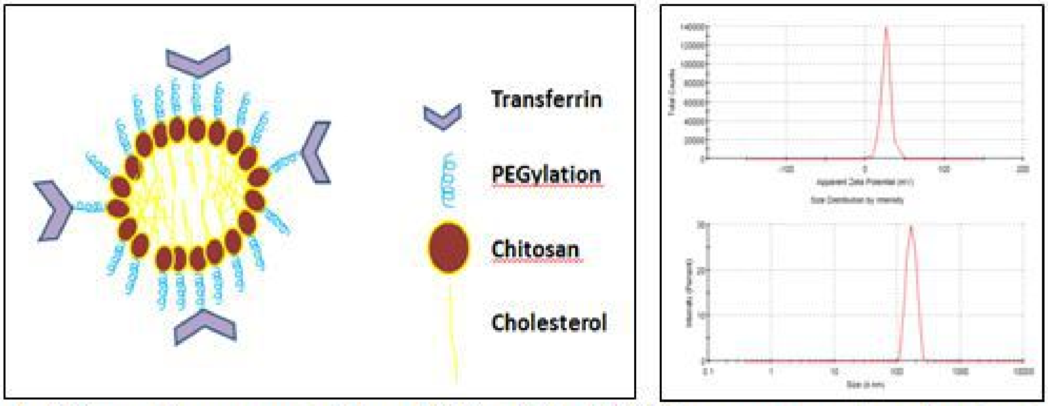

Figure 1. Schematic representation of Tf modified PCC nanoaggregate and zetapotential, hydrodynamic radius of chitosan based nanoaggregate

COLL 258

Comparison of sugar-based decyl glycoside surfactants from rhamnose, glucose, xylose and arabinose

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Glycoside surfactants have attractive properties as environmentally-friendly alternatives to existing surfactants derived from petrochemicals. They are biodegradable, less toxic and highly stable in extremes of temperature and ionic strength with usually better surfactant activities. These surfactants contain one or two sugar groups as a hydrophilic head group and an alkyl chain of different lengths, isomeric structure, and unsaturation as the hydrophobic tail group. Decyl glycosides are very effective compounds to change some interface properties such as surface tension, emulsification, wetting and foaming ability based on their structure. In this work, we have developed a high yield, scalable, low cost synthesis for decyl glycosides that allows exploration of the effect of different sugar headgroups on surfactant performance and properties. Decyl glycosides from rhamnose, glucose, xylose, and arabinose have been prepared and characterized using surface tensiometry to determine critical micelle concentration, dynamic light scattering to determine aggregation size, and fluorescence quenching spectroscopy to determine aggregation numbers. Results indicate that relatively small changes in sugar head group structure can strongly affect the surface activity and aggregation behavior of these compounds.

COLL 259

AuNBP@TiO_2 core-shell nanostructures for efficient NIR induced PDT

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Photodynamic therapy (PDT) is newly developed medical technique due to their mild and non-invasive therapeutic effect on cancer cell. The mechanism of PDT can be largely described by three points: i) photoexcitation of photosensitizer (PS) upon the irradiation, ii) the generation of reactive oxygen species (ROS) from PS in the target region and iii) consequent cellular toxicity. However, most of the available PSs are organic molecules which can be activated by visible light (400-700 nm) having limited penetration depth in tissue. Plasmonic nanostructures have attracted many attention due to their localized surface plasmon resonance (LSPR) property. LSPR occurs by the coupling of incident photons with the conduction electrons oscillating at the interface of metal and dielectric. The material, shape, size, and environments of nanostructures strongly affect the wavelength of the LSPR band. It has been reported that gold nanobipyramids (AuNBPs) with tailored shape can have LSPR band in the NIR range and they are expected to possess stronger local field and narrower spectral LSPR band than conventional gold nanorods (AuNRs).

TiO_2 semiconductor is well known as photosensitizer (PS) but this material has the large band gap of 3.0 or 3.2 eV, allowing for the absorption of only UV light. In this work, we synthesized highly uniform AuNBP@TiO_2 core-shell nanoparticles with tailored Au architecture. The amplified resonance field from Au core can excite TiO_2 shell. When the Au core absorbs NIR laser of 808 nm wavelength, surface plasmons are excited and the field is sufficiently energetic to be transferred to the conduction band of TiO_2 shell over the Schottky barrier. These hot electrons react with oxygen molecules in the medium to generate ROS. Additionally, the activity of our new configuration is compared with that of AuNR@TiO_2 core-shell nanoparticles. Thus, an advanced PDT agent active under NIR light is suggested based on tailored AuNP@TiO_2 core-shell nanomaterials.

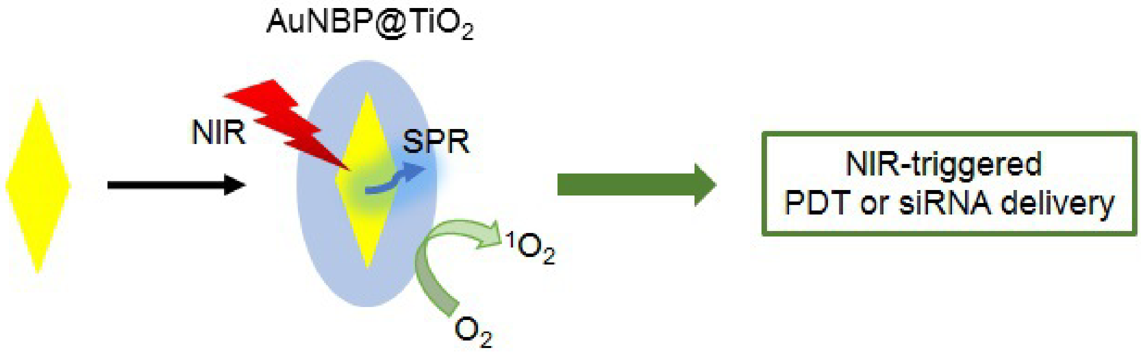

Figure 1. The Schematic diagram of AuNBP@TiO_2

COLL 260

Synthesis of water soluble MWCNTs by using amino acid

***Lu Hongwei**, luhw0801@sina.com, Liming Zou.* College of Materials Science and Engineering, DongHua University, Shanghai, China

A series of modify procedure have been taken to improve the poor dispersibility of multi-walled carbon nanotubes (MWCNTs) in water to broaden the application fields. MWCNTs were first purified by air and refluxed in hydrochloric acid solution. Then the as prepared purify MWCNTs were oxidized by $KMnO_4/H_2SO_4$ to get carboxy groups. Finally, Dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were used as catalysis, lysine were grafted to the surface of carboxylated MWCNTs by amidation reaction. Boehm titration showed that carboxy groups on the surface of oxidized MWCNTs reached 4.67mmol/L. Fourier Transform Infrared Spectroscopy (FT-IR) demonstrated that lysine were grafted to the surface of oxidized MWCNTs by amido bond. The grafted rate of lysine reached 62.50% implied by Elemental analysis (EA). UV-Vis spectrophotometry and direct visual inspection were used to investigated the dispersibility of lysine modified MWCNTs, the result showed that after modified by lysine, MWCNTs can be were dispersed in water for more than 3 month.

COLL 261

Construction of colloidosomes using food originated materials

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Colloidosomes are a kind of microcapsules, which are stabilized colloidal particles. At this present work, hollow colloidosomes are prepared on the templates of Pickering emulsions that are stabilized by zein/sodium caseinate (zein/SC) complexes.The emulsification capacity of zein/SC complexes is studied using oils with different polarities, including toluene, n-octane, octanol, hexane, sunflower oil and three non-volatile short-chain triglycerides (triacetin, tributyrin, and tripropinin). Results showed that Zein/SC complexes, having an average diameter of 167.9±5.2 nm, can be used to stabilize oils with low or middle polarities. In order to strengthen zein/SC colloidal particles on the interfaces of primary Pickering emulsions, layer-by-layer deposition of polyelectrolyte technique was applied. And a hollow colloidosome structure can be achieved by simply evaporating the volatile oil core. Both SEM images and fluorescence images (FITC labeled zein) indicated that the achieved colloidosomes were stabilized by spherical colloidal particles. Quartz crystal microbalance equipped with dissipation monitoring (QCM-D) is utilized to simulate the adsorption of polyelectrolytes. The result from QCM-D analysis showed that with an increase of absorbed layers, the adlayer on zein/SC surface displayed a viscoelastic property. According to the optical microscopic images, the obtained colloidosomes were sufficiently robust to survive the removal of the oil core, as well as multiple washing steps. Even in a completely dried state, the viscoelastic property of wall materials allowed the shell structure of the colloidosomes to stay intact, which was in accordance with the QCM-D analysis. For future applications, the colloidosomes strucutre provides an alternative method for the encapsulation and protection of bioactive nutrients, yeast or other probiotics against harsh environmental conditions for target delivery.

COLL 262

Micro-Raman study of 0D, 1D and 2D silver nanoparticles confined within interlayer spaces of titania nanotubes

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0D, 1D and 2D silver nanoparticles were successfully inserted within the interlayer spaces of titania nanotubes using a new synthesis method. The confinement not only constrained the size and shape of the nanoparticles, but also perturbed the surrounding titania layer. Micro-Raman spectroscopy technique was used to characterize the prepared materials and monitor changes introduced during subsequent treatment. A Raman band associated with the generation of reactive oxygen species on silver at elevated temperature, was observed in the samples even at room temperature and believed to be due to narrow confinement of the particles. Furthermore, inserting the nanoparticles between the titanate layers resulted in the formation of monoclinic phase from the original orthorhombic bulk titanate structure. UV and visible-light photocatalytic activities of these materials were measured for photo-oxidation of 2,4-dichlorophenol (DCP) molecules in water. The results showed substantial enhanced activity in relation of the nanoparticle geometry.

COLL 263

Hydrophilically patterned superhydrophobic cotton fabrics and their use in ink printing

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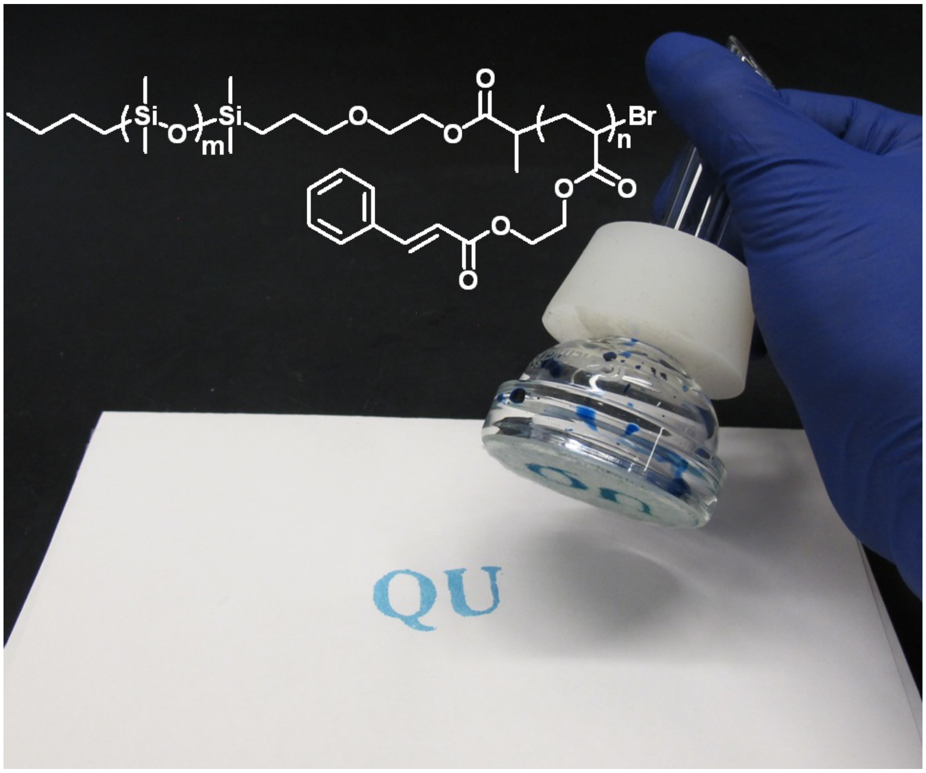
Fabric containing hydrophilic patterns in a hydrophobic background is useful as the scaffold for inexpensive microfluidic devices for facile medical diagnostic tests. Traditional batik painting also involves first building hydrophobic patterns into a cotton fabric and then dying selectively the hydrophilic regions with a dye. A traditional method for turning a region hydrophobic is to infuse wax there. This method is not necessarily economic in material use and does not yield patterns with high resolution. We report in this talk the coating of cotton fabric fibers with a monolayer of a diblock copolymer that possesses a photocrosslinkable anchoring block and a hydrophobic surface block. Photolyzing such a coated fabric sample under a mask crosslinks the anchoring block around the fibers in the unmasked regions. While the crosslinked copolymer is not removed by solvent extraction, polymer in the non-irradiated regions is readily removed, generating hydrophilic patterns among a superhydrophobic background. We will report on the polymer used for cotton fabric coating and photolithography as well as the characterization of the coated fabrics. We will also discuss the use of a patterned fabric in ink printing because a water-based ink is able to selectively permeate the hydrophilic regions only but not the superhydrophobic regions.



COLL 264

Synthesis and environmental studies of ZnSe/ZnS quantum dots

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The presentation describes the synthesis and characterization of luminescent ZnSe/ZnS quantum dots, and initial evaluation of their toxicity in a zebrafish model. ZnSe/ZnS quantum dots are particularly attractive because they are cadmium-free, and are made from earth abundant elements. The synthesis is similar to the synthesis of the most commonly used CdSe/ZnS quantum dots but their photophysical properties, particularly their chemical stability towards photo-oxidation, which leads to profound reduction in their emission quantum yield, needs to be improved. Our studies explore a number of strategies to improve the photostability of ZnSe/ZnS quantum dots including synthesis conditions, shell thickness and the use of dopants, molecular ligands, and polyelectrolyte coatings to improve chemical and photostability. It is anticipated that ZnSe/ZnS quantum dots will replace cadmium-containing quantum dots in a wide range of applications, which will result in significant environmental exposure. It is therefore important to study their interactions with biological systems and overall environmental

impact. Studies to validate the hypothesis that ZnSe/ZnS quantum dots are significantly less toxic than cadmium containing quantum dots are being conducted on a number of environmentally relevant organisms including nematodes, daphnia, shewanella, and zebrafish.

COLL 265

Binary co-patterned surfaces of a conducting polymer and gold particles via colloidal lithography

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Developing novel multi-component interfaces and hierarchical assemblies with high spatial control is an important strategy in nanoscale manufacturing of various sensors, functional coatings, electronic and plasmonic devices. In this work, a dual patterned surface composed of a conducting polymer and gold was fabricated by combining colloidal lithography and electrochemical deposition. The binary patterning protocol begins with the highly ordered formation of a hexagonally close-packed array of sacrificial colloidal microspheres on a conductive substrate. Interstitial spaces between the colloidal template expose electrochemically accessible areas of the electrode which are still capable of nucleating the electrochemical polymerization of conducting polymer such as a polycarbazole film. After electropolymerization, the sacrificial colloidal template can be dissolved and an inverse opal pattern is unveiled. The holes in the micropattern are made up of bare conductive substrate surface to which another material such as gold can be electrodeposited into. Through a potentiostatic method, the electrochemical reduction of Au^{3+} to Au^0 can be induced in these holes causing the accumulation of colloidal gold. The formation of polycarbazole-Au co-patterned surface has been extensively monitored using electrochemical quartz crystal microbalance (EC-QCM) and characterized using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and surface plasmon resonance spectroscopy (SPR). In addition, UV-Vis absorption studies revealed that the localized SPR peak of gold and polycarbazole polaronic peak are overlapping which can be a basis for future plasmonic applications. Lastly, the polycarbazole pattern can be selectively etched off thus leaving a highly patterned array of gold microparticles.

COLL 266

Aptamer functionalized ligand layers on SERS active colloidal nanocrystals

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Effectiveness Directorate, Wright-Patterson Air Force Base, Dayton, Ohio, United States

The functionalization of SERS active plasmonic nanocrystals by compact bio-recognition units such as functionalized aptamers can enable in situ readout of molecular recognition events and has promising potentials to allow biomolecular detections of unprecedented selectivity and accuracy. However, despite the prevalence of functionalized SERS active nanocrystal devices, the microstructure of aptamer functional layers on colloidal nanocrystals are poorly understood. To fill in this knowledge gap, we have studied the nanoscale surface morphology and chemical composition of aptamer functionalized ligand layers on noble metal nanocrystals. Experimental results regarding aptamer surface organization and their interaction with polymer surfactants will be presented. The effect of surface layer microstructure on the biological activity of aptamers are being researched and any potential discoveries concerning aptamer activity control will be discussed.

COLL 267

Detailed study on hydrothermal stability of mesoporous organosilicas prepared with block copolymer template and weak acidic conditions

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Periodic mesoporous organosilicas were prepared using 1,4-bis(triethoxysilyl)ethane (BTEE) in the presence of a poly(ethylene oxide)-*b*-poly(D,L-lactic acid-*co*-glycolic acid)-*b*- poly(ethylene oxide) triblock copolymer (PLGE) template under strong and weak acidic conditions. White powders were obtained even in the weak acidic conditions using iron chloride hexahydrate and its mixed acids. Small angle X-ray scattering (SAXS) and nitrogen adsorption isotherms showed highly ordered hexagonal (*p*6*mm*) mesostructure and high surface area around 1,000 m^2/g. Hydrothermal stability is a very important factor to use in various chemical industry. The powders were placed in sealed vials of 125 mL inside convection oven maintaining at 100 ^{o}C for 4 weeks. The hydrothermally treated samples were analyzed by every week up to 4 weeks using SAXS and nitrogen adsorption. Solid-state ^{29}Si CP-MAS NMR was also measured to observe the stability of siloxane bond up to 4 weeks for a hydrothermal treated sample. The results showed the organosilica samples showed quite effective to use as a catalyst or supporting material for 1 month.

COLL 268

Zinc bromide deliquescence and surface chemistry investigated by lab-based ambient pressure XPS

***Chris Arble**, carble@udel.edu, Sana Rani, John T. Newberg.* Chemistry & Bio-Chemistry, University of Delaware, Newark, Delaware, United States

Aqueous ionic interfaces are universally abundant and play a critical role in many physical, chemical, biological, environmental and technological processes. Ions at liquid interfaces experience an asymmetric environment that influences interfacial composition, orientation, dielectric forces and transport properties. Probing the electronic structures and interfacial concentrations of aqueous electrolytes is technologically very challenging. Herein we present results using ambient pressure X-ray photoelectron spectroscopy (APXPS) to examine zinc bromide, a salt utilized as an energy storage medium through the use of zinc-bromine flow batteries. APXPS was employed to study the solid-vapor and aqueous-vapor interfaces of zinc bromide salt under ambient water vapor conditions from ~10^{-7} % to 16 % relative humidity (RH). Zn, Br, and O spectral analyses show clear changes in widths, shifts and relative concentrations as zinc bromide changes phase from a solid salt to an aqueous solution (deliquescence) as a function of increasing RH. These results highlight the powerful utility of lab-based APXPS to probe changes in electronic structure and chemical composition of salts at solid-vapor and liquid-vapor interfaces.

COLL 269

Development of epoxy based multilayer nano-thin films using layer-by-layer technique

Saba Shabbir, Sadia Batool, ***Rohama Gill****, rohama_gill@hotmail.com, Anum Mahmood.* Department of Environmental Sciences, Fatima Jinnah Women University, Rawalpindi , Pakistan

Layer-by-Layer (LbL) technique has proved to be applicable for successful fabrication of multilayer thin films using a variety of materials. With synergistic combination of covalent and hydrogen bonding, bi and tri component composite multilayers of architectures PEI(CNER/PDMS)$_n$ and PEI(CNER/NH_2-MMT/PEI)$_n$ were built using two number average molecular weight (M_n) CNER - 870 and 1080. The film deposition parameters such as solvent, polymer concentration (i.e. 1.0,2.5,5.0,10,20,25,50,100 mg/mL), polymer ratio (1:2, 2:1,1:1) and dipping time (i.e.3,6,15,30,60 min.), dipping time ratio (1:2, 2:1,1:1) have been optimized to achieve a uniform growth of layers. The rationale behind selecting these components in multilayer thin films was, that CNER gives thermal, chemical resistance, mechanical stability, and brittleness to the architecture. However, clay can provide heat resistance and barrier properties while PDMS being an elastomeric soft and flexible component can overcome the inherent brittleness that is expected in epoxy based composite layers. The growth and thickness for each multilayer as a function of layer pair was monitored using UV-Vis spectrophotometer and ellipsometer. Atomic force microscopy and Field Emission Scanning Electron Microscopy (FE-SEM) were employed to study the homogeneity of deposited multilayers. Contact angle measurement showed that multilayers are hydrophilic and possess wetting properties as have angle ranges from 54-55° and 56-69° for clay and PDMS based thin films, respectively. The PDMS based multilayers have shown 60% oil adsorption from solution and adsorption desorption plateau was studied via UV-Vis spectrophotometer (Figure). In our previous study, oil adsorption

potential at low concentration of epoxy has already been studied. The prepared multilayer nanothin films are robust and can endure harsh environmental conditions of H_2SO_4, NaOH, NaCl and organic solvents.

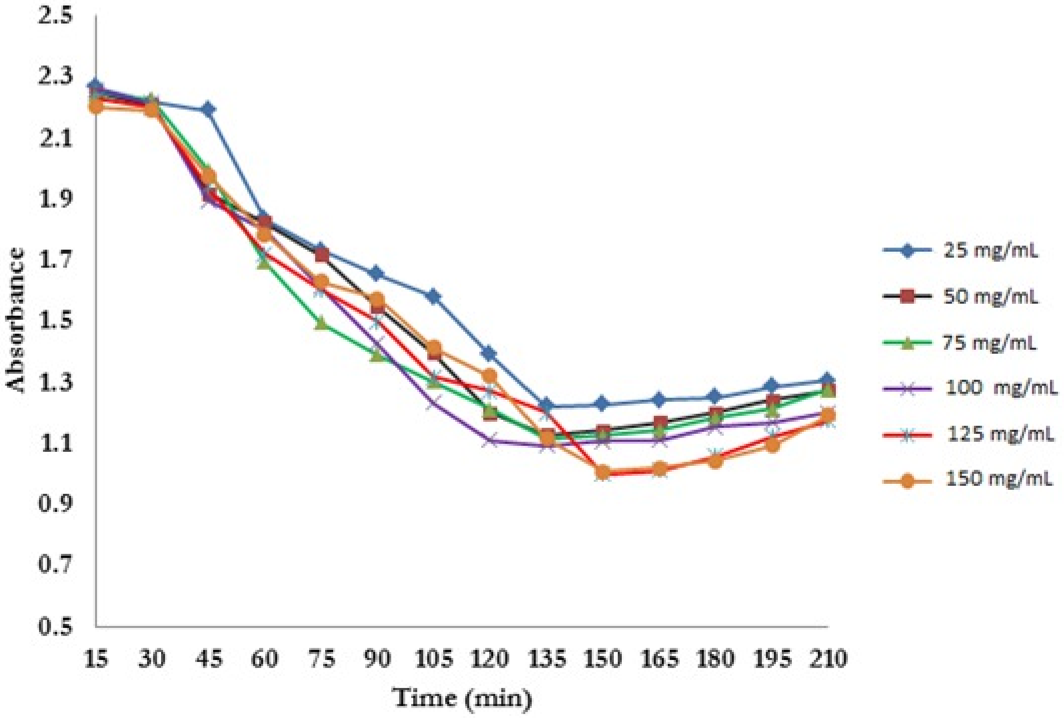


Figure: Absorbance of oil at λmax 232 nm depicting the oil adsorption potential of multilayer thin films prepared at different concentrations

COLL 270

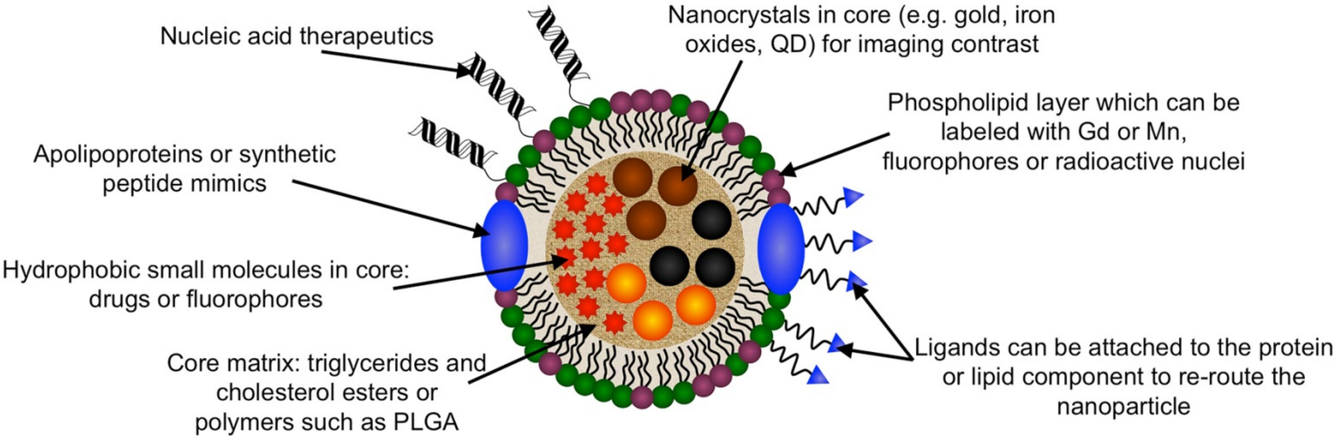
Lipoprotein and peroxidase-mimetic nanoparticles for imaging and therapeutic applications

***David Cormode**, davidcormode@gmail.com.* University of Pennsylvania, Philadelphia, Pennsylvania, United States

Nanoparticle delivery for contrast media and therapeutic materials is advantageous for the imaging and treatment of many diseases. Much work has focused on the development of synthetic nanoparticle platforms. However, nature offers numerous natural nanoparticles and agents that can inspire platforms for contrast agents and therapeutics. Such natural nanoparticles may have advantages such as biocompatiblility, biodegradability and lack of immunogenicity. In the first part of this talk we will focus on the adaption of lipoproteins for these purposes. We have formed hybrid nanoparticles from lipoproteins and gold nanoparticles to allow imaging of cardiovascular disease and cancer with computed tomography. Furthermore, we have loaded lipoproteins with drugs such as simvastatin to form a highly potent

cardiovascular disease treatment.

In the second part of the talk we will focus on the development of nanoparticle mimics of peroxidase. Iron oxide nanoparticles have been used in medicine for many years, mainly as MRI contrast agents or as therapeutics for iron deficiency. However, the biomedical applications of the catalytic activity of these nanoparticles are unexplored. Iron oxides readily catalyze the formation of hydroxyl radicals from hydrogen peroxide. We will discuss the application of these nanoparticles for the generation of light and as anti-biofilm agents for the treatment of oral diseases.



COLL 271

DNA controlled

Warren Chan, *warren.chan@utoronto.ca.* Institute of Biomedical Engineering, University of Toronto, Toronto, Ontario, Canada

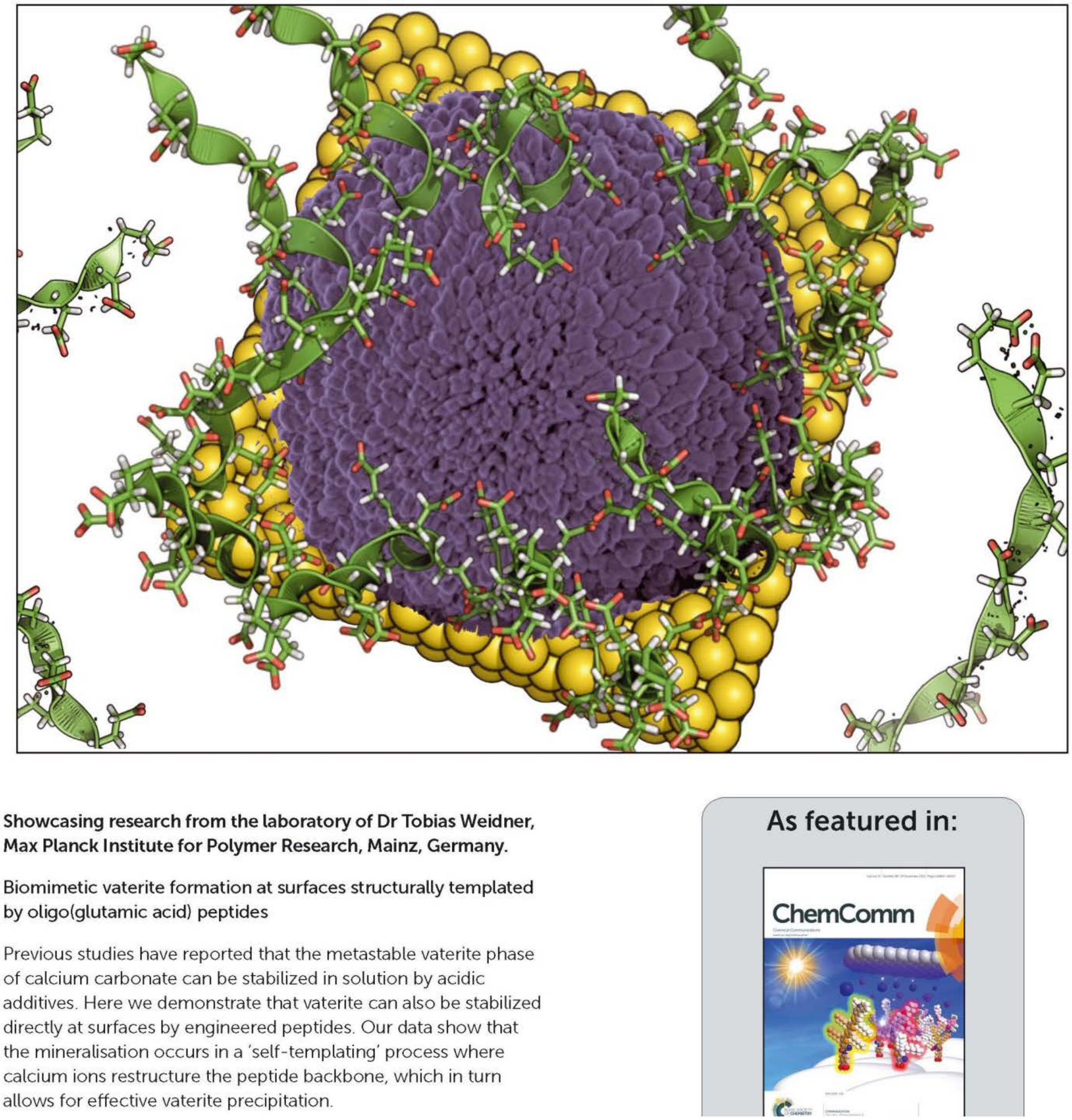
The design of nano-delivery systems requires the optimization of size, shape, and surface chemistry in order to optimally target solid tumours and for elimination from the body to minimize toxicity. In this presentation, I will discuss the use of DNA and gold nanoparticles as building blocks to engineer shape-changing, non-toxic nanosystems that can potentially target solid tumours. We characterized the physicochemical properties of these assembled nanosystems and their interactions with cells, their ability to target tumors in mice xenograft tumour models, and their elimination and toxicity. We further show how to design these assembled nanosystems to carry and deliver cancer therapeutics to the targeted site. These results suggest an intriguing trategy to mediate the nano-bio interactions and highlights new directions in the design of biodegradable and multifunctional nanomedicines.

COLL 272

Biomimetic vaterite formation at surfaces structurally templated by oligo(glutamic acid) peptides

Hao Lu[1]*, lu@mpip-mainz.mpg.de, Matthew A. Hood*[1,2]*, Sergio Mauri*[1]*, Joe E. Baio*[3]*, Mischa Bonn*[1]*, Rafael Muñoz-Espí*[1]*, Tobias Weidner*[1]*.* (1) Max Planck Institute for polymer research, Mainz, Germany (2) Max Planck Institute of Colloids and Interfaces, Potsdam, Germany (3) Oregon State University, School of Chemical, Biological, and Environmental Engineering, Corvallis, Oregon, United States

Nature uses proteins and peptides containing acidic residues to control the crystal structure of biological minerals. Calcium carbonate is important in nature, in particular for marine life and is found as a dominant component of marine sediments. Among its three most common anhydrous polymorphs – calcite, aragonite and vaterite – the latter is thermodynamically the least stable phase, and therefore occurs rarely as a geological mineral. Interestingly, the vaterite structure can be stabilized *in vitro* by biomolecules. Previous studies have focused on biogenic vaterite stabilization in solution state. Here we are, as the first, to demonstrate that vaterite can also be stabilized directly at surfaces – by engineered peptides. A thiol-terminated oligo(glutamic acid) sequence attached to gold surfaces served as a model system. Our data show that: instead of a static, 'one-way' process, the mineralization occurs in a 'self-templating' process where calcium ions restructure the peptide backbone and side chains into ordered states, which in turn allows for effective vaterite precipitation. This finding provides important information about the interfacial biomineralization of $CaCO_3$, and indicates a biomineralization pathway whereby template and precursor act together to trigger biomineralization. Such a mechanism is probably also relevant for other biogenic mineralization phenomena in general.



Showcasing research from the laboratory of Dr Tobias Weidner, Max Planck Institute for Polymer Research, Mainz, Germany.

Biomimetic vaterite formation at surfaces structurally templated by oligo(glutamic acid) peptides

Previous studies have reported that the metastable vaterite phase of calcium carbonate can be stabilized in solution by acidic additives. Here we demonstrate that vaterite can also be stabilized directly at surfaces by engineered peptides. Our data show that the mineralisation occurs in a 'self-templating' process where calcium ions restructure the peptide backbone, which in turn allows for effective vaterite precipitation.

As featured in:

COLL 273

Nanoparticle biointerfacing by cell membrane cloaking

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The emerging nanotechnology in biomedicine has sparked new hope for the treatment and diagnosis of various important human diseases. However, development of functional nanomaterials and nanodevices can be encumbered by unanticipated

material properties and biological events, which can negatively impact their effectiveness when introduced into complex, physiologically relevant systems. In this talk I will report on the preparation of a polymeric nanoparticle enclosed in the plasma membrane of natural human cells (e.g., RBCs, platelets, cancer cells, etc). The resulting nanoparticles are demonstrated to possess many surface functions of natural cells via studies of interactions with plasma proteins, cells, tissues, and microorganisms. Such multifaceted cell-mimicking properties can be attributed to the preservation of biomembrane on nanoparticle surfaces, which facilitates the display of intricate biochemistry that is difficult to replicate using conventional functionalization approaches. As the platform is entirely biocompatible and biodegradable, it can be applied toward a myriad of biomedical applications, where the vast implications of cell surface properties may benefit a variety of disease treatments.

COLL 274

Gold nanomaterials at the bio-nano interface

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Although gold cannot be regarded a biomaterial, its nanostructures have already found widespread use in a variety of biomedical applications owning to their unique properties, including bio-inertness, tunable photoluminescence, radioactivity (for Au-198 and Au-199), and strong scattering and absorption of light in the near-infrared region. Over the past decade, numerous methods have been developed for producing gold nanomaterials in the quality, quantity, and reproducibility required for a systematic study of their properties as a function of size, shape, or structure, and for the full exploration of their applications in biological studies and biomedicine. In this talk, I will briefly discuss some of the new developments, with a focus on the rational design and controlled synthesis of gold nanomaterials for optical imaging, drug delivery, and cancer theranostics.

COLL 275

Engineered nanoparticles for synergistic antimicrobial therapy

***Akash Gupta**[3], akash.umass@gmail.com, Neveen M. Saleh[3], Xiaoning Li[5], Arafeh Bigdeli[3], Krishnendu Saha[3], Ryan Landis[4], Morteza Mahmoudi[1], Vincent M. Rotello[2].* (1) Material Science and Engineering, EPFL, Swiss Federal Institute of Technology, Lusanne, Switzerland (2) Univ of Massachusetts, Amherst, Massachusetts, United States (3) Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States (4) Chemsitry, University of Massachusetts Amherst, Amherst, Massachusetts, United States

Bacterial infections cause 300 million cases of severe illness each year with thousands dying from infectious diseases. Antibiotic resistant bacteria further exponentiate one of

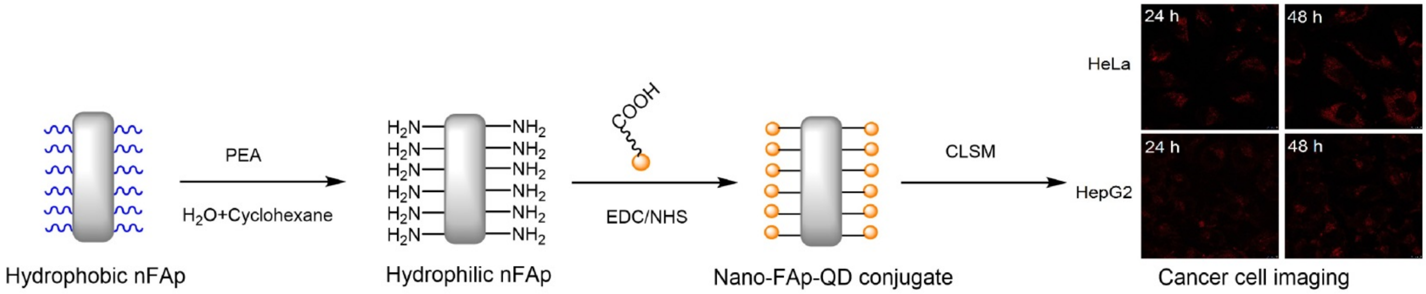
the greatest threats to human health. Nanoparticles have recently emerged as weapons in our antimicrobial arsenal to combat drug resistant bacteria. Here, we present functionalized gold nanoparticles (AuNPs) that exhibit broad spectrum activity against both Gram-negative and Gram-positive uropathogens. Interaction of NPs with bacterial strains could be regulated by tuning the functional groups on NP surface. NPs possessing highest antimicrobial activity were used in combination with antibiotics to exhibit synergistic effect on pathogenic strains. Synergy arising from the combination therapy was attributed to altered expression of outer membrane proteins which was validated by proteomic study. Fundamental study on the effect of AuNP functionality on bacterial surface can be instrumental to the development of novel antimicrobial therapies.

COLL 276

Low-toxic Mn-doped ZnSe@ZnS quantum dots conjugated with nano-hydroxyapatite for cell imaging

Zhou Ronghui[2], *zrh890720@sina.com, Xiandeng Hou*[1,2], *Lan Wu*[1], *Peng Wu*[1]. (1) Analytical & Testing Center , Sichuan University, Chengdu, China (2) College of Chemistry , Sichuan university, Chengdu , Sichuan, China

Quantum dots (QDs), especially non heavy metal-containing doped QDs, are appealing for fluorescent bio-imaging. However, since QDs are exogenous substances to biological environment, the biocompatibility of QDs is expected to be problematic in some cases. Herein, a biocompatible conjugate of Cd-free Mn-doped ZnSe@ZnS QDs and nano fluorine-doped hydroxyapatite (FAp, a well-known biocompatible material) was developed for cell imaging application. To construct the proposed conjugates, Cd-free highly luminescent Mn-doped ZnSe@ZnS QDs and monodispersed nano-FAp were first prepared in high-temperature organic media. For facilitating the conjugation, hydrophobic nano-FAp was made water-soluble via o-phosphoethanolamine (PEA) coating, which further provide conjugation sites for QDs anchoring. Cytotoxicity studies indicated the developed conjugate indeed possess good compatibility and low toxicity to cells. CLSM studies confirmed that the conjugates can be easily uptaken by cells and light up the microenvironment for at least 48 h, demonstrating the potential usefulness of this material in future biomedical research.



Schematic illustration of the modification procedure with PEA and the procedure for coupling the nano-FAp with MPA-capped QDs

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COLL 277

From nano to micro and back: Explore porphyrin supramolecular chemistry for cancer imaging and therapy

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Porphyrins are aromatic, organic, light-absorbing molecules that occur abundantly in nature, especially in the form of molecular self-assemblies. In 2011, we discovered ‘porphysomes’, the self-assembled porphyrin-lipid nanoparticles with intrinsic multimodal photonic properties. The high-density porphyrin packing in bilayers enables the absorption and conversion of light energy to heat with extremely high efficiency, making them ideal candidates for photothermal therapy and photoacoustic imaging. Upon nanostructure dissociation, fluorescence and photodynamic activity of porphyrin monomers are restored. In addition, metal ions can be directly incorporated into the porphyrin building blocks of the preformed porphysomes thus unlocking their potential for PET and MRI. By changing the way porphyrin-lipid assembles, we developed HDL-like porphyrin nanoparticles (<20nm), porphyrin microbubbles (~2um), giant porphyrin vesicle (~100um) and hybrid porphyrin-gold nanoparticles, expanding the purview of porphyrin nanophotonics. By mimicking light harvest systems in photosynthetic bacteria, we introduced high-ordered porphyrin aggregates into supramolecular assemblies, resulting unprecedented photonic properties (e.g., reversible photoacoustic nanosensors). Such optical properties are also responsible for our discovery of the ultrasound-induced microbubbles-to-nanoparticle conversion phenomenon, which may open the door to bypass the enhanced permeability and retention effect when delivering drugs to tumors. By closing the nano-micro-nano loop, the simple yet intrinsic multimodal nature of porphyrin self-assembly represents a new frontier in cancer imaging and therapy.

COLL 278

Controlling activity and selectivity of alkanethiolate-capped palladium nanoparticle catalysts: Effects of noncovalent ligand interactions and near-surface steric controls

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The systematic evaluation of metal nanoparticle catalysts functionalized with well-defined small organic ligands can potentially provide fundamental understandings on the influence of chemical environments near active sites. Our group previously reported the modified Brust synthesis using sodium S-alkylthiosulfates instead of alkanethiols could generate catalytically active Pd nanoparticles (PdNP) capped with a lower density of alkanethiolate ligands. These PdNP catalysts exhibited an excellent selectivity towards the isomerization of allylic alcohols to carbonyls in organic solvents. PdNP were also selective for the isomerization of terminal alkenes to internal alkenes rather than the hydrogenation. Herein, we report the synthesis and catalytic investigation of various PdNP capped with alkanethiolate ligands with linear alkyl, cyclic, or phenyl terminal groups and also PdNP capped with constitutional isomers of pentanethiolate ligands (with one or two methyl groups at different locations (α, β, or γ) from the surface-bound sulfur). These PdNP are characterized by thermogravimetric analysis (TGA), proton NMR, transmission electron microscopy (TEM), IR, and gas adsorption using the Brunauer-Emmett-Teller (BET) model. The catalysis studies on PdNP with different ligand structures (linear alkyl vs cyclohexyl vs phenyl) show that the chemical and structural composition of a monolayer surrounding the palladium nanoparticles greatly influences the overall activity and selectivity of nanoparticle catalysts for the hydrogenation, isomerization, and hydrogenolysis of allylic alcohols. The strong effect of non-covalent interactions between surface ligands and incoming substrates in the near-surface environment is observed. The investigation on the catalytic reactions of PdNP with constitutional isomers of pentanethiolate ligands also indicates that the steric interactions between the ligands on the metal surface and the alkene substrates influence the selectivity and reactivity of PdNP for the isomerization and hydrogenation of various terminal alkenes.

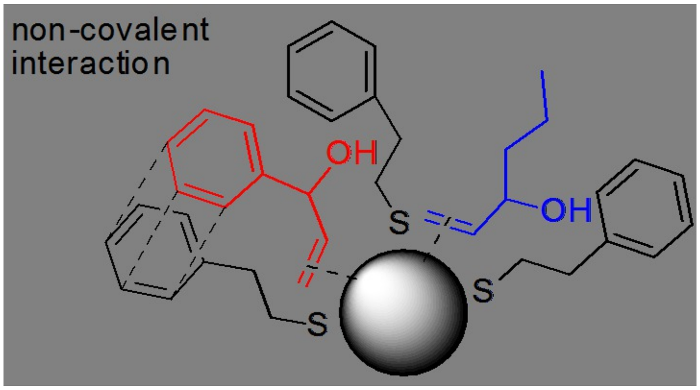

Figure 1. Surface ligand-substrate interactions on Pd nanoparticle catalyst

COLL 279

Semiconductor nanocrystals through the saturated ionic layer adsorption

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We demonstrate a general strategy for the synthesis of colloidal semiconductor nanocrystals (NCs) exhibiting the size dispersion below 5%. The present approach relies on the sequential deposition of fully saturated cationic and anionic monolayers onto small-diameter clusters, which leads to focusing of nanocrystal sizes with the increasing particle diameter. Each ionic layer is grown through a room-temperature colloidal atomic layer deposition (ALD) process that employs a two-solvent mixture to separate the precursor and nanocrystal phases. As a result, unreacted precursors can be removed after each deposition cycle, preventing the secondary nucleation. By using CdS NCs as a model system, we demonstrate that a narrow size dispersion can be achieved through a sequential growth of Cd^{2+} and S^{2-} layers onto starting CdS cluster “seeds”. Besides shape uniformity, the demonstrated methodology offers an excellent batch-to-batch reproducibility and an improved control over the nanocrystal surface stoichiometry. The present synthesis is amenable to other types of semiconductor nanocrystals and can potentially offer a viable alternative to traditional hot-injection strategies of the nanoparticle growth.

COLL 280

Structural and catalytic properties of silica-supported ruthenium nanocatalysts synthesized by a facile phase-transfer protocol

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Colloidal ruthenium (Ru) nanoparticles (NPs) with controlled morphology were synthesized by a facile phase-transfer protocol, using octadecylamine (ODA) as stabilizer. The as-synthesized Ru NPs were anchored to a mesoporous silica support (MSU-F) by sonication-assisted deposition, and activated by three different thermal treatments. The Ru NPs maintained a uniform morphology and good dispersion on the support during the thermal treatments. Thermal reduction at 350°C and Ar-protected calcination at 650°C completely removed the stabilizing ligand, and improved particle crystallinity. The supported Ru NPs showed promising catalytic performance for aqueous phase hydrogenation of the α-keto site of pyruvic acid, with the catalyst activated at 650°C giving the highest activity, presumably because of the higher density of surface active sites. Post-reaction characterizations suggest that the morphologies of the Ru NPs are maintained during hydrogenation, while the particles tend to migrate on the support framework.

COLL 281

Enhanced emission of nanocrystal solids featuring spatially extended excitons

***Mikhail Zamkov**, zamkovm@bgsu.edu.* BGSU, Bowling Green, Ohio, United States

Colloidal semiconductor nanocrystals show strong promise as next-generation light emitting materials. The emission characteristics of these nanoparticles in solid state devices, however, are often compromised due to strong coupling to the surrounding environment. Here, we demonstrate that the optical emission of nanocrystal films can be enhanced by employing a “spatially indirect” regime of exciton recombination, which favorably competes with non-radiative decay processes. Our study shows that solids of ZnSe/CdS NCs exhibiting type II carrier confinement support an intrinsically slower exciton diffusion to recombination centers than films composed of type I nanoparticles (CdSe/CdS). As a result, type II solids promote longer exciton lifetimes ultimately leading to a brighter emission. The slower propagation of excitons through type II solids is consistent with a reduced overlap between absorption and emission spectral profiles in these materials (larger Stokes shifts), which results in a decreased FRET rate. We expect that the improved emission of type II nanocrystal assemblies can avail the development of emerging NC light-emitting technologies.

COLL 282

Chemical reactivity of hydrous manganese oxide nanoparticles generated during permanganate use

***Alan T. Stone**, astone@jhu.edu, Xiaomeng Xia.* Environmental Engineering, Johns Hopkins University, Baltimore, Maryland, United States

Every year, one-third of U.S. water supply plants employ permanganate to oxidize inorganic water constituents such as Fe(II), Mn(II), and Cr(III), and organic water constituents such as taste and odor compounds, cyanobacterial toxins, pharmaceuticals, and personal care products. As permanganate is consumed, hydrous manganese oxide (HMO) nanoparticles are generated. HMOs are themselves oxidants, with patterns of reactivity quite unlike those of permanganate. With permanganate, precursor complex formation involves group transfer, e.g. nucleophile-electrophile reaction or 3+2 addition. With HMOs, precursor complex formation is an inherently surface chemical phenomenon. HMOs are strong cation exchange materials, and hence efficiently oxidize cationic substrates. With neutral and anionic Lewis Base-bearing substrates, the picture is presently less certain. Styrene, a potential water system contaminant, leaches from glues and cured-in-pipe coatings. Mandelic acid and benzaldehyde are intermediates in the oxidation of styrene. Benzoic acid is the ultimate oxidation product. For styrene and the oxidation intermediates and products just mentioned, six or more para-substituted forms are commercially available. Reactivity comparisons among them offer insight into precursor complex formation and subsequent reaction steps. Electronic effects are expected, but to our surprise hydration properties are important too. This is a reminder that substrate molecules lose waters of hydration during adsorption and that interfacial aspects of HMO reactivity are paramount.

COLL 283

Structures and behaviors of natural and synthetic phyllomanganates

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Manganese oxide minerals having layer structures, so-called phyllomanganates, are ubiquitous in aquatic and terrestrial environments, for example in soils, as coatings or varnishes, associated with mine runoff, in ocean crusts and nodules, etc. In many cases, they likely form as a result of biologically mediated reactions. The unusually high adsorption capacities and scavenging capabilities of phyllomanganates make their presence in soils and sediments a primary control on heavy metal and trace-element cycling and redox state; synthetic analogs of these phases are extensively studied for use as catalysts, cation-exchange agents, octahedral sieves, and battery materials. The most prevalent natural phyllomanganates, and most extensively studied synthetic phases, are those having the birnessite/buserite-like structure, and are constructed of sheets of Mn^{4+}/Mn^{3+}-O octahedra with ~7 Å (birnessite) or ~10 Å (buserite) basal spacing. The interlayer region is occupied by hydrated cations, e.g. Na^{+}, Ca^{2+}, Ba^{2+}, K^{+}, etc. Transformations between “hexagonal” and triclinic structure variations readily occur in response to changes in pH, redox conditions, etc. We have characterized the structures and behaviors of a wide range of natural and synthetic, and abiotic and biotic, phyllomanganates using time-resolved synchrotron powder XRD and Rietveld refinements, analytical SEM, XPS, and EXAFS/XANES and FTIR spectroscopies. These spectroscopic methods provide information about Mn oxidation state (XANES and XPS) and structural information for samples that typically are too poorly crystalline to yield useful powder diffraction patterns. Determination of actual Mn valence states, i.e. $Mn^{4+}:Mn^{3+}:Mn^{2+}$, in particular, is integral to establishing the stability of various phyllomanganates with respect to pH and in predicting their chemical reactivities. This study provides new insights into structural variations and complexities as functions of composition and formation environment.

COLL 284

Reactivity of oxide surfaces and trapping processes of uranium around mining sites

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There is a growing interest in uranium geochemistry and mineralogy at low temperature, in order to model uranium migration in the environment, in the perspective of remediation strategies on former mining sites and for monitoring present-day operations. We will review results concerning the trapping of uranium on opal internal surfaces in epithermal deposits as well as the complex interplay due to the formation of

inner sphere surface complexes bound to clays and Fe-oxides in a variety of mill tailings and granitic waste rocks located in various environments. By using complementary mineralogical, geochemical and spectroscopic approaches, these examples illustrate the diversity of the trapping processes under moderately oxidizing conditions, complementing the influence of redox reactions on U mobility. The growth of uranate nanoparticles enlarges the diversity of low temperature U phases. In addition, these environmentally relevant sites provide unique information on the timescale characteristic of uranium mobilization and migration/trapping.

COLL 285

Polycrystalline redox-active Fe(II)/Fe(III) layered double hydroxides: A comparison between natural minerals and synthetic analogs

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Green rusts are a family of redox-active Fe(II)/Fe(III) layered double hydroxides that are found at oxic/anoxic interfaces in nature. They are categorized based on their interlayer anion (carbonate and sulfate being the most common) and structure. Since their discovery in nature in hydromorphic soils in 1997, green rusts have been found in a growing variety of environments including groundwater and mine drainage. Due to their redox activity and nanoscale thickness, they are likely important drivers of iron cycling coupled to inorganic and organic contaminant cycling in those environments.

In this research, we show that both hexagonal platelets of natural green rust nanoparticles and their synthetic analogs can actually be complex polycrystalline phases, as opposed to coherent single crystals. We used dark-field transmission electron microscopy among other analytical TEM techniques to prove the existence of crystallites only a few nanometers in size, often surrounded by nanometer-sized regions of amorphous material. The natural green rusts were found in contaminated mine drainage at the former Ronneburg uranium mine in Germany, associated with metal contaminants such as Zn, Ni, and Cu. For comparison, sulfate green rusts were synthesized and also found to be polycrystalline, though different synthesis conditions produced different crystallite patterns. These patterns lend some clues to crystal growth, possibly due to oriented attachment. While pseudo-hexagonal platelets are the typical morphology of green rust found in the literature, we also successfully synthesized green rust nanorods. These results suggest that in addition to known characteristics of green rust that make it incredibly reactive (including a large surface area to volume ratio, large aspect ratio, and redox properties), these polycrystalline platelets can exhibit abundant defect sites and likely a rough surface topography. Carefully examining nanominerals

such as green rust on the nanoscale has important implications for reactions at biogeochemical interfaces in both natural and anthropogenic systems.

COLL 286

Coupled cycling of manganese and micronutrients in marine sediments

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The Mn oxides birnessite and todorokite are ubiquitous in oxic marine sediments and play a fundamental role in the biogeochemical cycling of micronutrient trace-metals in seawater. In the modern oceans, for example, birnessite provides the dominant sedimentary sink for the micronutrient Ni, where Ni concentration in seawater is coupled to an equilibrium reaction between dissolved Ni and birnessite in marine sediments. In the environment, authigenic Mn(III/IV) oxides are thought to form via the microbial oxidation of Mn(II), however, although todorokite is often found intimately associated with phyllomanganates in ferromanganese precipitates, it is widely regarded as a neo-formed phase, formed during the transformation of an authigenic phyllomanganate under diagenetic and mild hydrothermal conditions. In this regard, across significant areas of the seafloor, birnessite is a transient mineral phase. This is important because the long-term mobility and fate of dissolved micronutrients scavenged by birnessite will depend on how this phase transforms, and whether scavenged micronutrients are retained by neo-formed todorokite or released to sediment porewaters.

The presence of trace-metal impurities in authigenic phyllomanganates is traditionally believed to aid their recrystallization to todorokite, with the impurities eventually retained in the neo-formed mineral structure. Here, with combined experimental and natural sample work, we show that, in fact, Ni significantly retards the transformation of birnessite to todorokite under diagenetic and mild hydrothermal conditions, and is ultimately released from todorokite to porewaters during a late stage dissolution recrystallization process. The diagenesis of marine Mn oxides might therefore provide a significant benthic flux of micronutrients to seawater.

COLL 287

Mechanisms and kinetics of contaminant transformation by transition metal (hydr)oxides

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The influence of iron (Fe) and manganese (Mn) (hydr)oxides on contaminant transformation and fate is far greater then their environmental prevalence. Their high reactive surface area and their presence as grain and fracture coatings in contact with

groundwater enhance their reactivity. Additionally, Mn oxides are considered to be the strongest, naturally occurring oxidants and are capable of transforming a wide range of inorganic and organic substrates. Substrates affected by the presence of transition metal (hydr)oxides include toxic heavy metals and metalloids, such as arsenic and chromium, and numerous emerging organic contaminants, such as antibacterial agents and endocrine disruptors. Here we utilize traditional and *in situ*, quick-scanning X-ray absorption spectroscopy (XAS), and high resolution TEM in conjunction with wet chemical techniques to characterize the rates and mechanisms of As(III) and bisphenol A (BPA) oxidation by delta Mn(IV) oxide. We use similar techniques to examine the role of redox cycling in changing the reactivity of Fe (hydr)oxides with respect to common, redox active, inorganic contaminants. Our research demonstrates that an understanding of the rates, and mechanisms of contaminant transformation by transition metal oxides requires characterization of both the solid-phase and aqueous-phase products.

COLL 288

Geochemical processes controlling Mn(III) and vacancy concentrations in layered manganese oxides

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Layered manganese (Mn) oxides, such as birnessite, play an important role in metal sequestration and redox biogeochemistry in the environment due to its extraordinary adsorption and oxidation properties. The high reactivity of birnessite is largely controlled by the concentrations of Mn(III) and vacancy present in birnessite MnO_6 layers. Adsorption and electron transfer between Mn(II) and birnessite are among the geochemical processes that greatly affect Mn(III) and vacancy concentrations, hence birnessite structure and reactivity. In this study, we incubated Mn(II)-adsorbed δ-MnO_2 (an analogue to naturally occurring birnessite) under anaerobic conditions for 25 days and examined the effects of pH, Mn(II) concentration, coexisting cations and ionic strength on the Mn(II)-MnO_2 reactions using atomic pair distribution function (PDF) analysis and X-ray absorption spectroscopy (XAS). Results indicate that higher pH, Mn(II) concentration, ionic strength, and longer reaction time all promote Mn(III) formation and vacancy depletion. Triclinic birnessite phase was observed but transformed into an unknown mineral phase at the late reaction stage in the presence of Li^+, Na^+ or K^+ while triclinic birnessite was stabilized in the presence of Mg^{2+} or Ca^{2+}. The favorability for triclinic birnessite formation decreases in the order of $Na^+ > Li^+ > K^+ > Mg^{2+} > Ca^{2+}$. In contrast, Cu(II) strongly inhibits Mn(III) formation and vacancy depletion. The results provide insights into structural and reactivity variations of naturally-occurring birnessite and have important implications for understanding the dynamic interactions between Mn(II) and birnessite during oxidative birnessite precipitation and reductive dissolution.

COLL 289

Plasmonic nanocrystals with hot spots: Bio-chirality and heat generation

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The talk will discuss the optical and physical effects coming from electromagnetic hot spots in hybrid nanostructures incorporating plasmonic, semiconductor and molecular elements. Such plasmonic hot spots can be used to create strong circular dichroism of chiral bio-molecules and bio-assemblies, to generate hot plasmonic electrons and to efficiently induce local and collective heating via the photo-thermal effect in metal nanostructures.

COLL 290

Dynamics and heteregeneity of carbon dioxide adsorption and photoreduction uncovered from single-nanoparticle studies

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Most of the surface of a heteregenous catalyst is dormant; only a small fraction of nanostructures on the surface is catalytically active. In this talk, I will describe how we are employing surface enhanced Raman scattering (SERS) to identify catalytically active nanostructures from a heterogeneous dispersion. Time-lapse SERS imaging is being used to monitor the kinetics of CO_2 or carbonate adsorption and photoreduction on individual Ag/Cu composite nanoparticles in gas or liquid environments. In these bifunctional nanoparticles, the Ag component of the nanoparticle serves as the SERS substrate and Cu offers catalytic activity towards CO_2 photoreduction. From kinetic trajectories, different classses of nanoparticles will be cataloged: i) those with relatively weak adsorption of CO_2, which are not suitable as catalysts. ii) those which adsorb CO_2 permanently and are possibly poisoned and therefore are also not catalytically suitable, and iii) those that show the right characteristics of adsorption, followed by catalytic photoconversion to products like methanol. The origin of such heterogeneities in adsorption and photoreduction behavior are being traced to differences in nanoparticle structure or surface composition, from which structure/activity relationships will be established. This single-nanoparticle technique can be applied to the study of dynamics and heteregeneity in other interfacial and surface phenomena in materials science and molecular biology.

COLL 291

Boronic acid functionalized Ag nanorod arrays for glucose detection through surface enhanced Raman spectroscopy

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Glucose detection through surface enhanced Raman scattering (SERS) has recently attracted much interest due to its potential as a minimally-invasive and in vivo sensing technology. However, the application of SERS to glucose detection is greatly limited because of its small Raman scattering cross-section and low affinity with bare metal surfaces. In this study, an active SERS substrate composed of nearly aligned silver nanorods with uniform distribution was fabricated using high vacuum electron beam physical vapor deposition. A monolayer of 4-mercaptophenylboronic acid (MPBA) was self-assembled on the Ag nanorod surfaces, through the covalent interaction between its thio group and the Ag surface, thus resulting in a functional SERS substrate for glucose detection. The results from X-ray photoelectron spectroscopy and Raman spectroscopy clearly indicate that MPBA was successfully functionalized on the Ag nanorod surfaces. The specific binding of glucose with boronic acid motif in MPBA significantly affects the SERS signal of MPBA on Ag nanorods, which can be measured and correlated to glucose concentrations. Quantitative detection of glucose in a clinically relevant (0-20 mM) concentration range was successfully demonstrated. We found that both electromagnetic and chemical enhancement mechanisms are attributed to the enhanced SERS signals. These results provide new routes to the development of SERS-based glucose detection.

COLL 292

Large-scale full-wave simulation of SERS substrates through surface integral equation formulations and MLFMA

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Electromagnetic simulation tools play an important role in the fields of nanoplasmonics and surface-enhanced Raman spectroscopy (SERS), where breakthroughs are frequently slowed down by the limited power of these tools when addressing real-life problems. In this regard, the vast majority of simulations performed in the optical domain rely on volumetric solvers such as the discrete-dipole approximation (DDA), the finite-difference time-domain (FDTD) technique, or finite-elements methods (FEM). However, these approaches require a volumetric discretization of space, yielding a system of linear equations that, despite being usually sparse, involves a number of degrees of freedom N that scales proportionally to the volume, thus resulting in non-viable computational demands if realistic systems are to be solved. Boundary element methods (BEM), on the other hand, can efficiently tackle piecewise homogeneous

problems through the meshing of surfaces and interfaces, considerably shrinking the size of the linear system. In particular, the surface integral equation (SIE) method of moments (MoM), though giving rise to a dense full matrix, can efficiently be compressed with either algebraic or physics-based techniques. From these techniques, the multipolar plane-wave decomposition behind the multilevel fast multipole algorithm (MLFMA) is indeed the most groundbreaking, although its use is not yet widespread in optics. This work shows that MLFMA can be effectively used to solve the scattering problem of complex large-scale nanoparticle assemblies constituting usual SERS substrates. Concretely, we will use MLFMA to show how the SERS performance of plasmonic colloidal depositions is to a great extent determined by the distribution of the analyte molecules that attach to the nanoparticles' surface. We herein investigate this effect by considering a high-density monolayer of gold nanospheres (GNP's) and compare the SERS enhancement yielded by two different models of analyte distribution through MLFMA large-scale full-wave numerical simulations.

COLL 293

Metallic nanoshells with narrow size distribution as a new probe for cell imaging

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Metallic nanoshells are particles composed by a dielectric (silica) core and a thin metallic shell. When coated with Au or Ag, the optical extinction of nanoshells can be controlled by both the size of the core and the thickness of the metal layer. This control is related to the localized surface plasmon resonance (LSPR) is this type of nanostructures. In this work, we will introduce a facile method for the synthesis of nanoshell. This new synthetic methodology leads to a very narrow size distribution of the core (fabricated by reverse microemulsion), followed by a careful functionalization and controlled growth of the metal layer. The end result of this process was metallic nanoshells suspensions with average extinction response that closely match the optical characteristics of a single particle. By controlling relative core size and shell thickness, it was possible to tune the spectral profiles of the particles through visible and near infrared wavelengths. The narrow extinction of this system allowed the development of nanoshell-based probes capable of simultaneously target different biological markers on cancer cells. Hyperspectral dark field imaging clearly demonstrated the selectivity of these probes to selected targets at the cell membrane and nucleus, as shown in Figure 1.

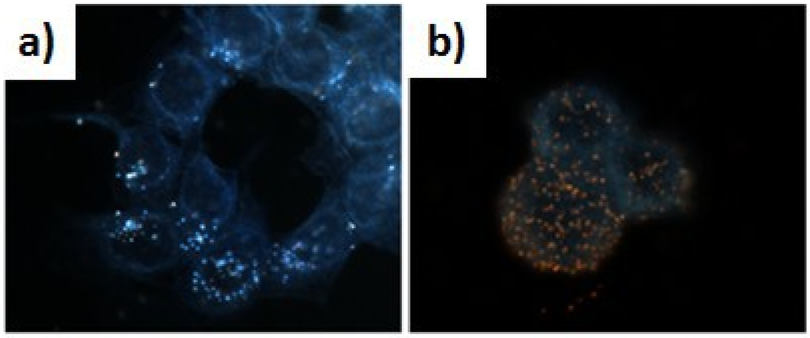

Figure 1. Dark field imaging of gold and silver nanoshells – varying core/shell ratios; probing the nucleus (a) and the membrane (b) of MCF-7 human breast cancer cells.

COLL 294

Determination of nanoparticle concentrations

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For understanding toxic effects of colloidal nanoparticles a correlation of such effects to the physicochemical properties of the nanoparticles is desirable. In order to compare different results an appropriate metrics for nanoparticles doses needs to be used. Different approaches for determining nanoparticle concentrations will be discussed. A comparison of mass versus particle number concentrations is given.

COLL 295

Composite surfaces with enhanced and tunable adhesion

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There has been significant interest in creating micro- and nano-structured surfaces that have adhesion that can be both strong and tunable. Much of the previous work has drawn inspiration from nature, such as the gecko, and developed surfaces consisting of fibrils with complex geometries to achieve the desired adhesion characteristics. While these bioinspired surfaces have been shown to have impressive adhesion characteristics, the complex geometries make difficult to manufacture in a scalable processes. Here, we present a different approach to realize strong and tunable adhesion through the use of surfaces comprised of arrays of cylindrical composite fibrils. The composite geometry alters the stress-state at the interface and leads to surfaces that have strong adhesion under normal loading and weak adhesion in shear. In this talk, the fabrication, experimental characterization, and mechanics modeling of surfaces consisting of composite pillars will be presented. The experimental

measurements and modeling demonstrate that these surfaces have both strong and tunable adhesion. Effects of material selection and scaling of the structures on performance will be discussed.

COLL 296

Adhesives for paper conservation: Physico-chemical properties and lifetime predictions

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Several hundred adhesives are used in the practice of conservation to repair and consolidate artifacts as well as to create archival housings. The specific adhesive or mixture of adhesives is chosen mostly on the basis of both experience and preferences of the conservator performing the intervention. Studies of adhesive properties have been mainly focused on determining the long-term stability in terms of color, pH and mechanical changes. However, because manufactures keep updating their adhesive formulations and because we wish to document the properties of the various adhesives used on artifacts, we have begun a study on the properties of currently used adhesives and their mixtures with the focus on adhesives used for archival holdings (i.e. book and paper collections). Products tested included natural (e.g. starches) and synthetic adhesives (e.g. cellulose derivatives, acrylics, poly vinyl acetates) and their various mixtures. Different preparation conditions were also tested to better reproduce the variability of methods conventionally used in conservation. Samples were extensively characterized using several techniques, such as rheometry, FT-IR spectroscopy, thermal analyses, mechanical tests (i.e. tensile strength, folding endurance, and tear resistance), colorimetry, optical and atomic force microscopy (AFM). Lifetime predictions were additionally evaluated on artificially aged samples. Through this study of adhesives, we aim to develop a database of the properties of adhesives used in conservation. The data may also be used by conservators as a tool to support their choice of adhesives.

COLL 297

NMR-based characterization of nanoparticle-polymer interactions

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Nanoparticles functionalized with amino groups have been reported to have enhanced biological response compared with non-functionalized nanoparticles, but the response

can vary significantly depending on the nanoparticle composition and the molecular structure of the surface layers. Diamond nanoparticles functionalized with small ligands and polymers are an ultra-stable platform for mechanistic studies of nanoparticle aggregation and toxicity. We are using NMR methods to investigate the structure and dynamics of molecular layers on diamond nanoparticles. Specific examples include (1) distinguishing between covalent vs. electrostatic bonding between ligands and nanoparticle surfaces and (2) distinguishing surface-bound polymers from free polymers. For example, ^{1}H NMR spectra of the free poly(allylamine hydrochloride) (PAH) ligand and the PAH terminated nanodiamond (NDPs) show distinct differences in line width that allow us to distinguish between free oligomers and polymers in solution, while for polymer-wrapped nanodiamond differences in line widths allow us to distinguish between the restricted motion of protons close to nanoparticle surface and flexible motion of protons further away from the nanoparticle surface. Diffusion-ordered NMR analysis shows a 10-fold decrease in diffusion coefficients in protons from PAH, establishing covalent grafting of PAH onto the nanoparticles. In this talk we will discuss these and other applications of NMR to probe nanoparticle-polymer interactions.

COLL 298

Nanotribology of a catechol-functionalized alkane with terminal chain branching

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A bio-inspired system was studied where the terminal chain branching found in fatty acids naturally present on hair and wool was combined with a catechol group as the hydrophilic moiety to mimic the adhesion strategies found in mussel proteins. Atomic force microscopy (AFM) was used to study the adhesion and nanoscopic friction of monolayers of a catechol-functionalized branched alkane, 4-[(18S)-18-methyleicosyl]benzene-1,2-diol, formed by Langmuir-Blodgett deposition on silicon oxide, mica, and polydimethylsiloxane (PDMS) substrates. Measurements were done in ambient air and in dry N_2 gas. In dry N_2, the friction of these monolayers was low and the adhesion was well described by van der Waals interactions. In ambient air, the adhesion and friction showed a stronger hysteresis and different friction responses at low and high loads. The results will be discussed in view of possible bonding to the substrate and lateral cross-linking in the monolayer.

COLL 299

Optimization of fiber-matrix adhesion and composite mechanical properties through formation of an engineered interphase

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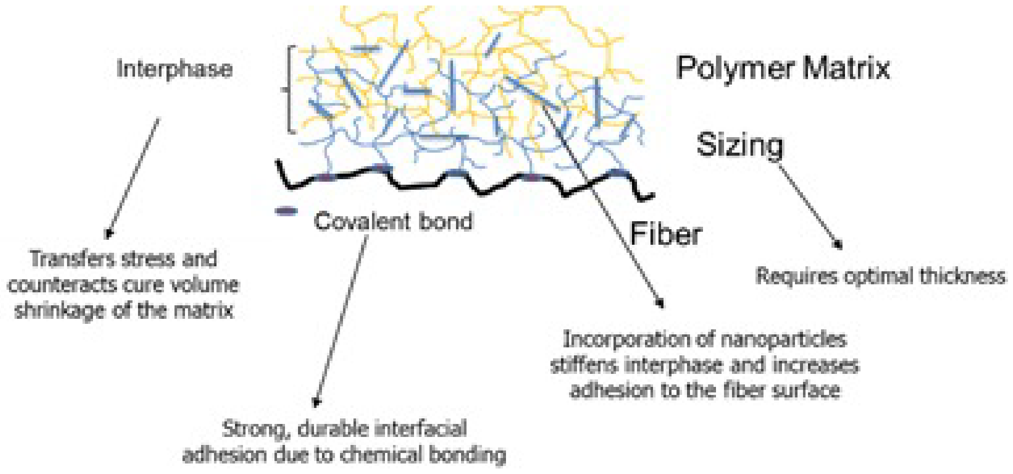
Although fiber reinforced composite materials are routinely used in numerous applications, in many systems, the fiber-matrix interphase is the limiting factor in optimal composite design and application. Carbon fiber reinforced vinyl ester composites offer many potential benefits such as ambient pressure cure, low moisture absorption, and low viscosity resin transfer molding processing. The fiber-matrix interphase that forms in these systems presents a challenge because of the low adhesion. A practical solution requires not only a higher level of adhesion combined with greater energy absorption equivalent to that attainable to a carbon fiber epoxy interphase, but one which is robust and can be implemented in a manufacturing environment.

This paper will present an approach based on formation of an ‘engineered interphase’ as a framework for optimizing any fiber-polymer combination. This example of ‘engineering’ the carbon fiber/vinyl ester interphase to increase interfacial adhesion is based on a combination of chemical/mechanical bonding, coating the carbon fiber with a compatible coating ‘sizing’, and incorporation of nanoparticles to optimize stress transfer. An important aspect of this approach is optimizing the thickness of the resulting interphase in order to have maximum beneficial effect on the fiber-matrix interphase mechanical properties. The in-situ optimized CF-VE matrix adhesion and interphase mechanical properties will be related to the composite laminate properties. Examples of the value of using this approach in other systems will also be presented. Ultimately, it should be understood that adhesion has multiple components which have to be simultaneously optimized.



An ‘Engineered Interphase’ offers advantages:

- **Chemical attachment to the surface**
- **Counteract residual shrinkage of matrix**
- **Improved Fiber-Matrix Adhesion**
- **Improved Composite Mechanical Properties**

COLL 300

Molecular structures of polymers at buried polymer/metal and polymer/polymer interfaces and their relations to adhesion

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Polymer interfacial properties such as adhesion are mediated by polymer interfacial molecular structures. It is difficult to probe molecular structures of polymer materials at buried interfaces in situ nondestructively. Traditionally, it is necessary to break the buried interface and study the two exposed surfaces. Here we demonstrated that sum frequency generation (SFG) vibrational spectroscopy is a powerful technique to study molecular structures of buried polymer/metal and polymer/polymer interfaces in situ. Such structures can be well correlated to adhesion strengths at the interfaces to under the adhesion mechanisms. We have extensively studied interfacial molecular structures and adhesion of model polymers, silicone adhesives, model epoxies, commercial epoxies, as well as underfills for microelectronics. The effects of plasma and hygrothermal treatments on polymer interfacial structures and adhesion have also been elucidated. In addition, interfacial molecular structures of polymer adhesives used in water and adhesive proteins have been investigated. A variety of interfacial processes such as interfacial ordering, interfacial diffusion, interfacial hydrogen bonding formation, and interfacial reaction were observed and their relations to polymer adhesion were revealed.

COLL 301

New approach for the evaluation of the effects of contaminants on surface sensitive processes

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The detrimental effects of a contaminant are determined by i. the amount of the contaminant in the environment, ii. the affinity of the contaminant for the critical surface, and iii. the compatibility (i.e. solubility) of the contaminant in the adhesive or coating. The most common approach for evaluating contaminant effects has been to evaluate the effect of a complex blend of multiple contaminants. Because this approach provides no information as to why a given contaminant is detrimental, it limits our ability to predict the effect of an untested contaminant. Developing an understanding of the relationship between contaminant structure and effect can lead to more intelligent design of surface preparation processes, more robust adhesive and coating formulations, and more reliable manufacturing processes. This paper discusses treating the effect of a complex contaminant mixture as a linear combination of the effects of its constituents. Using this approach, knowledge of the effects of a limited number of archetype compounds can be used to predict the effect of any new, untested contaminant based on the properties of its constituents.

COLL 302

Correlating surface chemistry to pressure sensitive adhesive performance

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Performance data (peel, tack, shear) are often used to assess how well a pressure sensitive adhesive (PSA) meets the desired performance for a given system. This performance is dependent on both the surface chemistry and roughness of the adhesive and substrate. PSAs are generally used on a very wide variety of surfaces. These substrate surfaces range from smooth to rough and vary in surface composition. Additionally the surface chemistry of the adhesive can have a profound effect on performance. In some cases the chemistry is designed to improve adhesion whereas in other cases the surface chemistry is unintended. Characterization of the chemistry and/or roughness of the substrate and adhesive using X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and a variety of microscopy techniques can identify key properties related to performance when analyzed in context to adhesion performance data. In this presentation the methods used to measure adhesion will be described as well as how an industrial analytical laboratory can advance development of adhesives.

COLL 303

Synthesis of complexes PEG-PLL with Se nano-core and Au nano-shell for fluorescence imaging and treatment of cancer

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Cancer has become the main factor of threat against the health of human being and is still very difficult to treat. However, many kinds of cancers could be cured if there were early detection and proper access to relevant prevention or medical help. Therefore, it is imperative to find an efficient method for cancer earlier diagnosis, effective prevention and treatment.

In recent years, amphiphilic block copolymers’s self-assembly behavior in the elective solvents has been attracting much attention. The block copolymers of different chemical compositions and structure can form some special structures in various solutions such as micelles, rods, vesicles and other different shapes. Block copolymers as important macromolecular material were widely applied in pharmaceutical field. Particularly, because the spherical polymeric micelles can significantly improve the effective utilization rate of drug and reduce the side effects, it has potential utility as a drug delivery system (DDS), imaging agent carrier and gene transfer, etc.

Selenium is one of the necessary trace elements for humans. It has many important biological functions such as antioxidant effect, immunity, growth-promoting, and others. Meanwhile, gold nanoclusters have unique properties such as strong fluorescence, non-toxic, water-soluble and good biocompatibility, which has broad prospects in biological imaging, sensing and others. On the basis of those described above, in this contribution

new nanomaterials Se@mPEG-PLL/Au has been synthesized and explored for cancer diagnosis and treatment. Our observations demonstrate that Se@mPEG-PLL/Au nanocomposites have relatively high transfection efficiency in HeLa and U87 cells, indicating the possibility to be utilized for cancer early diagnosis and auxiliary therapeutic treatment.

COLL 304

Tailoring the surface of gallium liquid metal alloys with phosphonic acids to enable their application in reconfigurable electronics

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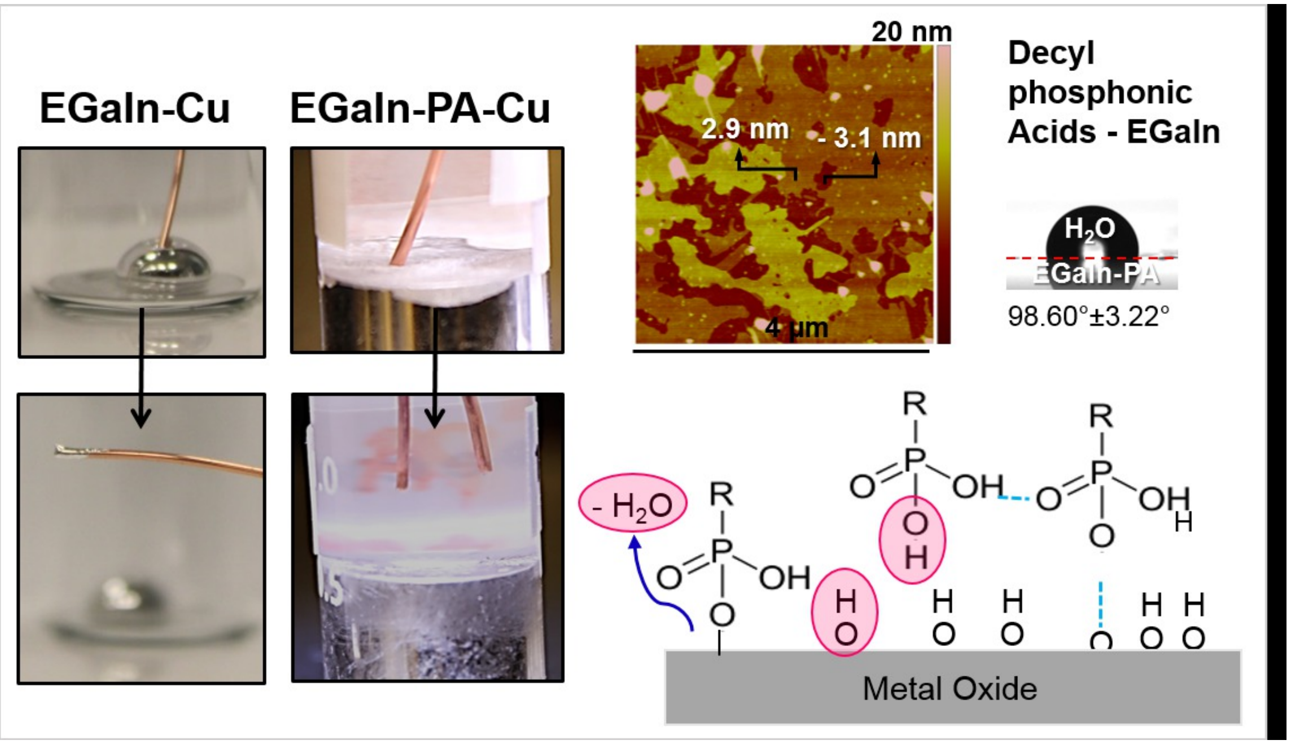
Conductive fluids are one of the key components of emerging technologies in reconfigurable electronics, such as tunable radio frequency antennas and electronic switches. Gallium liquid metal alloys (GaLMAs) are nontoxic alternatives to mercury promising a wide range of applications in flexible, conformal, and stretchable electronics. However, their reconfigurability in microfluidic systems is hindered by the instantaneous formation of a surface oxide layer at ambient environment. This solid oxide film sticks to most surfaces leaving unwanted metallic residues that can cause undesired electronic properties. Additionally, GaLMAs readily alloy with common electrode materials (Au, Ag, Cu) deterring their reversible contact. In this report, residue-free reversible flow of a binary alloy of gallium (eutectic gallium indium) is presented via tailoring the liquid metal surface by thin films of alkyl phosphonic acids. The organic film protects the surface oxide of GaLMA, enabling the liquid metal to flow through microchannels without sticking to the channel material. Furthermore, modification of the GaLMA/copper interface by alkyl phosphonic acids prevent alloy formation enabling reversible contact between the liquid metal and the copper electrode. Characterization of these interfaces by spectroscopy and microscopy provided insight into the mechanistic details of the interfacial interactions in these systems.



Alkyl phosphonic acids modify the surface chemistry of gallium liquid metal alloys

COLL 305 – Withdrawn.

COLL 306

Gold nanoparticle assembly via polymer single crystal

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Gold nanoparticles (AuNPs) have raised great interests due to their special properties and potential applications in many fields. In recent years, lots of efforts have been done to the assembly of AuNPs into varies of ordered structures such as AuNP wires and sheets so that more unique properties could be discovered and can be magnified to larger scale. In this work we report a method to assemble AuNPs into well defined, free standing frame structure using poly(ethylene oxide) (PEO) lamellar single crystal as the template. Here, PEO single crystals were employed as a template and PEO-P4VP block copolymer were used to form a precursor frame. AuNPs were then immoblized on the precursor frame and crosslinked simultaneously by P4VP block to give a free AuNP frame. By controlling the single crystal size and PEO-P4VP pattern, we are able to tune the size and width of the AuNP frame. We consider this approach to be an efficient way to assemble AuNPs and this methodology could be applied to other metal or semiconductor NPs.

COLL 307

On the edge of silver nanoparticles: Interface structure, equilibrium, and dynamic silver ion release

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Antimicrobial activity and environmental toxicity of silver nanoparticles (AgNP) is strongly linked to the oxidative release of silver ions. A thorough understanding of Ag ion release is thus highly relevant for environmental risk assessment, but may also improve product design. Unfortunately, Ag ion release remains poorly understood.
A key factor to understanding Ag ion release is the extraordinary oxidation state of Ag in the interface being between ionic and metallic. This fundamental property of Ag has been elucidated by analyzing the crystal structures of a specific class of Ag materials. Semi-metallic silver at the (111) faces of AgNP has a subvalency of +1/3 v.u., forming $\equiv Ag_3OH$ surface groups with a maximum site density of 4.7 nm^{-2}.
Subvalent silver at the AgNP surfaces can be released by oxidative dissolution, depending on the solution conditions such as the pH and silver ion concentration. This process of silver release leads to rearrangements of the surface structure. It is accompanied by an additional Ag ion release until a new equilibrium state is reached.
In the present study, the pH and time-dependent release of Ag ions by oxidative dissolution has been determined experimentally and combined with the new insights for developing a dynamic model that aims to predict the Ag ion release and equilibration as a function of particle size, solid-solution ratio, oxygen pressure, and pH. The model is able to describe the Ag ion release and equilibration for large range of pH values. The variation, due to the use of AgNP of different size will be discussed.

COLL 308

Role of trace amounts of iron in the photoinitiated growth of silver nanoparticles

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Aqueous solutions containing silver ions and organic acids have long been known to be photosensitive, with the products generally being silver aggregates of varying size and shape. We have found that the inherent sensitivity is in fact lower than expected and that trace amounts of species such as iron can play a dominant role in initiating the reactions. In the present work, we show that silver nanoparticles of well-defined size and shape readily form when solutions containing silver, citrate, and iron ions ($[Fe^{+3}]$ / $[Ag^{+}]$ < 0.001) are irradiated by light. Using UV-visible spectroscopy, nuclear magnetic resonance, dynamic light scattering, and scanning electron microscopy, we have carried out a detailed kinetic and mechanistic study, with an emphasis on the initial steps of growth. To the best of our knowledge, this is the first report of this photoinitiated synthetic route for producing nanoparticles directly from silver ions. The generality of the mechanism, including the effect of different ligands and metal ion initiators and the production of other types of nanoparticles, as well as its possible relevance to environmental processes will be discussed.

COLL 309

Tuning and enhancing the properties of quantum dots through the use of innovative organic ligand surface chemistries

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Photoluminescent semiconductor nanoparticles or quantum dots (QDs) have shown to be extremely useful in the fields of bioimaging, biosensing and as light emitting devices (LEDs). The maturation of QD synthesis over the past few decades allows for simple, reproducible production of QDs with bright, narrow, size-tunable emission and strong, broad absorption. This lends them towards the above applications, however, the advantageous properties often decrease significantly when transferred to aqueous biological environments.

The nature of a QD’s core architecture is not the only contribution to its photophysical properties. Their surface chemistries are pivotal to providing enhanced function. The organic ligands that passivate the surface of each QD can be exchanged and modified to impart unlimited functionalities, binding strategies, and increased stability. We will show how innovative ligand design can give QDs with various charge densities to allow for in depth membrane binding experiments on model lipid bilayers. We will also show how the use of cross-linking strategies can insulate QDs from the detrimental effects of photoxidation.

COLL 310

Deposition of metal nanoparticles on silica spheres using amphiphilic block copolymers in solutions

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We report here on the deposition of gold nanoparticles on silica spheres using poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) block copolymers in solutions. The deposition of gold nanoparticles on silica spheres using PEO-PPO block copolymers was achieved due to the interfacial activity afforded by amphiphilic characters of PEO-PPO block copolymers and the reducing function of PEO-PPO block copolymers for metal ions [Sakai et al., Langmuir, 2004; J. Colloid Interface Sci., 2012; Colloids Surf. A, 2015]. Furthermore, we found that the deposition of gold nanoparticles on silica spheres was tuned by temperature, polymer type, solvent type and solvent quality.

COLL 311

Strongly coupled binary nanocrystal superlattice films by liquid-air interface ligand exchange

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Binary nanocrystal superlattice films (BNSL) films are two-dimensional crystal structures of two kinds of nanocrystals, self-assembled with precise control of components and chemical composition. Lead chalcogenide (PbX) quantum dots (QDs) are ideal building blocks of BNSL films due to their high monodispersity and size tunability over a wide range. The coupling between neighboring QDs in a BNSL film may introduce efficient charge separation and directional charge transport, which make these films promising materials for efficient solar-to-electric conversion. However, the strong inter-particle coupling is inhibited by the long, insulating ligands, which come from the hot-injection synthesis of QDs.

In this research, we apply an easy and accessible method to replace the original long ligands with short ones while successfully preserving the long-range-order of BNSL films. These films are self-assembled from two sizes of PbSe QDs and form an $MgZn_2$ crystal structure. Generally, the short ligand solution is injected into the liquid subphase while the BNSL is floating on the surface. Ligand exchange happens when short ligands reach the liquid-film interface and substitute in for the long ones. The cracks, defects, and disorder introduced by solid state ligand exchange can be largely prevented by this method. The long-range-order crystal structure and short lattice constant are characterized and confirmed by grazing incidence small angle X-ray analysis (GISAXS). Then, near infrared transient absorption is applied to characterize the exciton transport within the $MgZn_2$ BNSL film after ligand exchange. Directional electron transport from the conduction band of the small particles to the relatively lower conduction band of the large ones is proven by comparing the bleaching band lifetime between the single and binary component nanocrystal superlattice films. This investigation demonstrates that liquid-air interface ligand exchange is an effective tool to prepare strongly coupled BNSL films, which are expected to have distinct optical and electric properties for deeper investigation.

COLL 312

Fabrication of polymer functionalized silica micro-particles by continuous method

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The flow reactor was used to graft polymer chains from the surface of silica micro-particles via reversible addition-fragmentation chain transfer (RAFT) polymerization. In order to modify the silica’s surface, new kind of silane-modified chain transfer agent (CTA) was synthesized. During the continuous flow process, modifying micro-particles with CTA and polymerization were finished step by step in a relatively short time without additional purification procedure. Block copolymer brushes can also be easily synthesized through this method. Compared with conventional batch method, TGA results showed this continuous method leaded to a higher grafting efficiency. GPC and NMR results of the cleaved polymer chains also indicated the same point and showed that a lower PDI of polymer brushes was gotten.

COLL 313

Generic synthesis of anisotropically-shaped metal chalcogenide nanostructures in gram scale

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Colloidal semiconductor nanoparticles have been the focus of much research in the last two decades, specifically investigating the effects of size, shape and composition on optoelectronic properties and fabricating efficient solid-state devices. In this context, one-dimensional structures (e.g., nanowires) and two dimensional structures (e.g., nanoplatelets) have shown tremendous promise in solar cell fabrication. To expedite the potential applications of these nanomaterials, their large-scale production is extremely critical. However, current high temperature synthetic methods failed to produce nanomaterials in large scale. Here we will present low temperature (<120 ^{0}C) syntheses of anisotropically-shaped metal chalcogenide nanostructures including CdSe, CdS, ZnSe, and ZnS nanowires and nanoplatelets in gram scale. We will also discuss the effects of surface ligand chemistry on their nucleation and growth processes.

COLL 314

Development of models and methodologies for characterizing nanomaterials in consumer products

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Nanomaterials are widely incorporated into consumer products for a variety of purposes such as the enhancement of mechanical strength, improvement of surface durability, and development of antimicrobial properties. As a result of their increased use, concerns have arisen regarding the environmental, health and safety with respect to nanoparticle release and accumulation. Researchers at NIST have worked extensively at developing the metrological tools to characterize these consumer products by (A) developing model systems of known composition and (B) employing these model systems to develop measurement methods for the detection/quantification of nanomaterials *in-situ* and upon release. Measurement methods involving surface characterization of nano-enabled materials are especially important for understanding the potential for nanoparticle release. This presentation will focus on the development of X-ray photoelectron spectroscopy (XPS) methodologies, a core surface chemical technique, for detection of multi-walled carbon nanotubes (MWCNT) within polymer composites by taking advantage of the different electrical properties of the starting materials. Application of XPS in both spectroscopy and imaging modes will be demonstrated as a viable approach for the qualitative detection of MWCNTs at a composite surface and assessment of the composite's dispersion properties, respectively. Preliminary work demonstrating a characterization approach to extract more quantitative XPS information will also be presented. Results using orthogonal techniques including SEM and Raman imaging will be presented to verify the results of this novel approach.

COLL 315

Quantum plasmonics and hot-carrier induced processes

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Plasmon resonances with their dramatically enhanced cross sections for light harvesting can serve as efficient generators of hot electrons and holes. Such hot carriers can be exploited in a wide range of photophysical and photochemical processes. The physical mechanism for plasmon-induced hot carrier generation is plasmon decay. Plasmons can decay either radiatively or non-radiatively. The branching ratio between these two decay channels can be controlled by tuning the radiance of the plasmon mode. Non-radiative plasmon decay is a quantum mechanical process in which one plasmon quantum is transferred to the conduction electrons of the nanostructure by excitation of an electron below the Fermi level into a state above the Fermi level but below the vacuum level. In my talk I will discuss the basic mechanism of plasmon-induced hot carrier formation, hot carrier relaxation, and how hot carriers can be exploited in a

variety of applications ranging from photodetection, photocatalysis, and to dope or induce phase changes in nearby media.

COLL 316

Visible light absorption by platinum nanocrystals mediated by nearfield dielectric scattering

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A strategy for enhancing visible light absorption and photocatalytic activity of small (diameters < 10 nm) platinum nanocrystals or Pt NCs is discussed. The idea is to decorate the Pt NCs around larger, spherical SiO_2 support nanoparticles and to make use of the size-tunable light scattering resonances of the SiO_2 nanoparticles to enhance the absorption of the Pt NCs. Both experiment and theory are used to demonstrate that such colloidally-prepared Pt NC systems are able of absorbing the scattered light at the nearfield of dielectric surface of the SiO_2 nanoparticles. Experiments further show that these systems drive photocatalytic redox reactions. This kind of light absorption by Pt NCs is conceptually different from the well-known surface plasmon resonance optical absorption of noble metal nanostructures and could open a promising, new doorway to utilize Pt NCs as visible light photon absorbers for solar energy conversion.

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COLL 317

Fundamental limitations to plasmonic hot-carrier solar cells

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Detailed balance between photon-absorption and energy loss constrains the efficiency of conventional solar cells to the Shockley-Queisser limit. However, if solar illumination can be absorbed over a wide spectrum by plasmonic structures, and the generated hot-carriers can be collected before relaxation, the efficiency of solar cells may be greatly

improved. In this presentation, I will discuss the opportunities and limitations for making plasmonic solar cells, here considering a design for hot-carrier solar cells in which a conventional semiconductor heterojunction is attached to a plasmonic medium such as arrays of gold nanoparticles. The underlying mechanisms and fundamental limitations of this cell are studied using a non-equilibrium Green's function method, and the numerical results indicate that this cell can significantly improve the absorption of solar radiation without reducing open-circuit voltage, as photons can be absorbed to produce mobile carriers in the semiconductor as long as they have energy larger than the Schottky barrier rather than above the bandgap. However, a significant fraction of the hot-carriers have energies below the Schottky barrier, which makes the cell suffer low internal quantum efficiency. Moreover, quantum efficiency is also limited by hot-carrier relaxation and metal-semiconductor coupling. The connection of these results to recent experiments is described, showing why plasmonic solar cells can have less than 1% efficiency.

COLL 318

Ultrafast charge separation in hybrid plasmonic and semiconductor colloidal nanoparticles

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In this talk I describe our recent efforts for understanding reversible ultrafast photoinduced charge separation in hybrid plasmonic nanostructres and highly reductive core-shell semiconductor nanoparticles. For plasmonic nanostructures, we have studies ultrafast charge separation in plasmonic core-shell structures with a gold core and an iron-iron oxide shell. Under ambient conditions, the iron shell is oxidized to produce iron oxide and a strong plasmon resonance, while in an oxygen free environment the plasmon is blue shifted and reduced in magnitude due to the damping effect of an iron metal shell. We show that in ambient conditions, we can reversibly use ultrafast photoexcitation of the Au core to inject electrons into the iron oxide shell, temporarily reducing the oxide shell to iron and damping the plasmon resonance. Since the process is quickly reversible, it is a reasonable approach to modulating the surface plasmon resonance of Au nanoparticles. I further describe our efforts to characterize ultrafast charge separation in ZnTe core and CdSe shell hybrid semiconductor colloidal nanoparticles. We characterize both the internal charge separation process between ZnTe and CdSe, as well as electron transfer to adsorbates on the surface of the colloids. ZnTe is highly reductive, making it an interesting target for photocatalytic processes. We show that in spite of the protective CdSe shell, the reductive power of ZnTe is largely preserved in these hybrid structures.

COLL 319

Generation of hot plasmonic electrons and heat in metal nanocrystals with hot spots

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The efficiency of generation of energetic plasmonic carriers in metal nanostructures strongly depends on the optical design and material composition. This study demonstrates the ability to generate large numbers of hot plasmonic carriers in specially-designed hybrid nanostructures. The hot-electron generation becomes especially efficient in plasmonic nanostructures with electromagnetic hot spots. The energy distribution of optically-excited plasmonic carriers is very different in metal nanocrystals with large and small sizes. For metal nanocrystals with smaller sizes (less than 30nm) or in nanostructures with hot spots, the excited state gets a large number of carriers with high energies. Nanostructures with a strong plasmonic enhancement generate unusually large numbers of energetic electrons, which can be observed using the ultra-fast spectroscopy, photo-currents and photo-chemistry. Along with the hot-electron generation in plasmonic nanocrystals, which is a quantum effect, electromagnetic radiation typically causes efficient heating in metal nanocrystals, which may also be concentrated in thermal hot spots [5]. The results obtained in this study can be used to design plasmonic hot-electron nanodevices for photo-catalysis, photo-detectors and solar-energy applications.

COLL 320

Plasmonic enhancement of the photovoltaic effect in semiconductor nanocrystals

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Metal nanoparticles represent a unique class of materials with remarkable light-extinction properties which can be potentially applied in photovoltaic systems. In this work, we observe an enhanced exciton generation in CdSe and PbS nanocrystals coupled to small Au nanoparticles (5-10 nm in diameter). To examine the influence of plasmon field enhancement on exciton production in semiconductor nanocrystals, the two types of nanoparticles were encapsulated in the CdS matrix. The plasmon to exciton energy transfer was detected using photoexcitation experiments which show the enhancement of the quantum dot photoluminescence during the selective excitation of the plasmon resonance band of the Au nanocrystals. Therefore, the demonstrated scheme for harvesting the NF radiation of metal nanoparticles presents an excellent opportunity for extracting the evanescent emission of surface plasmons that can find practical applications in photovoltaic or photocatalytic technologies.

COLL 321

Teaching old antibiotics new tricks: Novel multifunctional conjugates to fight bacterial resistance

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Antibiotics have radically altered the landscape of human health by reducing illness and death due to infectious disease since the emergence of their widespread use in the mid-1900s. However, for almost as long as antibiotics have been known, pathogen evolution of resistance to antibiotics has followed. Each year antibiotic resistant infections result in at least two million sick patients and 23,000 deaths, $20 billion in excess health care costs and an additional $35 billion in lost productivity.

There has been a large body of work on killing bacteria *via* various mechanisms that target critical functions (membrane disruption, inhibition of cell wall synthesis, etc), with most antibiotics targeting a single critical function. In an effort to overcome bacterial resistance to antibiotics, multi-drug strategies (antibiotic cocktails) have been employed. While the multi-drug approach has been effective for some diseases, bacteria have also evolved multi-drug resistance. Indeed, multi-drug resistant bacterial infections are a serious problem worldwide. Unresolved, these infections can spread to distant sites in the body.

To overcome bacterial resistance, we engineered a new multifunctional antibiotic (Pentobra) that combines membrane activity of a cell-penetrating peptide with antimicrobial activity of a common aminoglycoside (tobramycin). Pentobra displays two synergistic functions into a single molecule, which makes it difficult to develop resistance against. This weaponized molecule induced membrane destabilization resulting in a strong bactericidal effect against persister cells (*E. coli* and *S. aureus* persisters), and also against *P. acnes* clinical isolates. Pentobra is effective at low concentrations (no colonies visible), while tobramycin alone is largely ineffective. Moreover, Pentobra remains non-cytotoxic to eukaryotes. These results show that equipping aminoglycosides with membrane activity is a promising approach to eradicate pathogenic organisms that are recalcitrant to existing therapies. This approach can be expanded to other antibiotics, and can inform future therapeutics for infectious disease.

COLL 322

Amphiphilic ligand-coated gold nanoparticles as drug carriers, membrane fusogenic agents, and cell-penetrating particles

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We synthesized gold nanoparticles soluble in physiologic solutions via an amphiphilic sulfonate-terminated alkanethiol organic ligand shell. The capacity of the organic ligand shell to accommodate guest molecules and reorganize in response to the local environment endows these particles with a variety of properties of interest for biomedical applications. For particles with organic ligands of at least 10 carbons and a

total outer diameter comparable to phosphatidylcholine lipid membranes, we found that these particles can embed within and penetrate both model lipid bilayers and the membranes of live cells, without inducing permanent membrane rupture. Across a narrow range of particle diameters and ligand compositions, these particles exhibit other striking interactions with lipid bilayers, exhibiting membrane fusogenic properties and intra-membrane aggregation behavior. In addition, the organic ligand shell can efficiently sequester hydrophobic drugs for delivery into cells. *In vivo*, we find that the biodistribution of these particles is significantly influenced by the composition of the organic ligand shell, and we demonstrate a dendritic cell-tropic particle composition that can be used to dramatically enhance the potency of peptide vaccines. Together these diverse properties suggest a variety of potential uses for ligand-coated gold nanoparticles in nanomedicine.

COLL 323

De novo designed peptide for solution assembly into predetermined 2-D nanomaterials

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In this work, nanostructured, two-dimensional peptide nanomaterials were designed with desired morphology with subsequent computation of peptide sequences that can undergo self-assembly into the desired nanostructure. Specifically, two-dimensional nanoplatelets were formed with a 4-fold lattice symmetry all through facile solution assembly using de novo designed peptide sequences. As confirmed by circular dichrosim and analytical ultra-centrifuge, the peptides maintain a designed, intrinsic alpha-helical secondary structure in solution, bundling into coiled-coil homotetramer building blocks. The exterior sites of these coiled-coil tetramers are computationally calculated to install certain directional inter-tetramer interactions allowing themselves to further organize into a 2-D lattice structure with predetermined P422 symmetry in 2-D. Through examining the nanostructure using transmission electron microscopy, small-angle X-ray scattering and atomic force microscopy, these tetramer bundles were found to assemble into a 4-fold lattice structure but with much larger lattice parameters than the predicted symmetry as well as a pronounced third dimension of assembly. The experimentally observed larger lattice structure is consistent with P4 symmetry compared to the originally designed P422 symmetry. Although assembly goes predominately in 2-D mainly prodcuing plate-like assemblies, efforts such as N-termini acetylation and control of assembly conditions were made in an attempt to reduce the plate stacking. The overall morphology characterization of these peptide-assemblies will be discussed as well as the control of final nanomaterial morphology through control of assembly solution conditions; here we investigated assembling temperature, solution pH and solution aging time. Furthermore, a reserved histidine residue within the sequence forming the coiled-coil bundle serves as a metal ion binding site with different transition metal ions.

COLL 324

New materials for medical applications

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Over the past decades, new synthetic techniques have been developed for the synthesis of materials will well defined structures and functions. These materials are

now finding their way into new medical applications. A number of new materials for use in the treatment or improvement in a variety of medical applications are being prepared at tested.

COLL 325

Engineering nanoparticles to stop internal bleeding

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Young people between 5 and 44 are most likely to die from a trauma, and the primary cause of death will be bleeding out. We have a range of technologies to control external bleeding, but there is a dearth of technologies for internal bleeding.

Following injury, platelets become activated at the injury site. We have designed nanoparticles that are administered intravenously that bind with activated platelets to help form platelet plugs more rapidly. We have investigated the behavior of these particles in an number of in vitro systems to understand their behavior. We have also tested these particles in a number of models of trauma. The particles lead to a reduction in bleeding in a number of models of trauma including models of brain and spinal cord injury, and these particles lead to increased survival.

This work is not without challenges. One of the goals is to be able to use these particles in places where there are extreme temperatures and storage is challenging. We have engineering a variant of the hemostatic nanoparticles that is stable up to 50 C. A second challenge is that the intravenous administration of nanoparticles triggers complement activation as has been seen in a wide range of nanoparticle technologies from DOXIL to imaging agents. The solution is generally to administer the particles very slowly to modulate the physiological responses to complement activation, but that is not an option when one is bleeding out, so we have had to develop variants that reduce complement activation and the accompanying complications.

Ultimately, we hope that this work provides insight and, potentially, a new approach to dealing with internal bleeding.

COLL 326

Metalloporphyrin lipid nanoparticles as multimodality imaging contrast agents and photothermal sensitizers in a patient-derived orthotopic pancreas xenograft cancer model

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Porphysomes are porphyrin-lipid nanoparticles that pack ~80,000 covalently-attached porphyrin molecules in to a single 120 nm liposome-like particle comprised of biomimetic materials. They are investigated herein as theranostic agents for addressing unmet needs in cancer diagnosis and therapy.

The imaging modalities for which porphysomes generate contrast are determined by the chelation state of the porphyrin-lipid ring. Protocols for manganese and indium chelation are developed, and the fluorescence, MR, and SPECT image contrast generated respectively are investigated *in vivo* using a clinically-relevant patient-derived orthotopic xenograft pancreas tumor mouse model. Porphysomes are also effective photosensitizers for enhancing photothermal therapy (PTT) in the pancreatic cancer model as evaluated using IR thermal imaging and histological analyses of light irradiated tissues.

Porphysomes are robust, biocompatible “one-for-all” theranostic agents that are successfully developed for simultaneous multimodality image contrast and PTT sensitization to address an acute challenge in cancer therapy.

COLL 327

Thermo-sensitive diblock elastin-like polypeptides (ELPs) grafted onto iron oxide nanoparticles reveal transient thermal gradients

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Magnetic hyperthermia (MH) is envisioned to become a powerful therapeutic method by oncologists to fight against incurable cancers such as glioblastoma. Development of appropriate biocompatible coatings is critical for clinical translation of MH-agents.
With this aim, we have studied the grafting of diblock recombinant elastin-like polypeptides (ELPs) onto superparamagnetic iron oxide NPs. Diblock ELPs were designed with a thermosensitive (VPGVG)-containing block undergoing deswelling transition at a critical temperature and a hydrophilic (VPG^{A}/$_{G}$G)-based block to provide steric repulsion. In a precedent work, we have shown that these diblock ELPs form well defined micelles above their critical micelle temperature (CMT) and evidenced a gradual compaction of their core with increasing temperature.
In the present work, magnetic cores of superior magnetic heating efficiency were prepared by the DEG-NMDEA route introduced by Caruntu *et al.* and functionalized by mixed brushes of ELP and PEO chains by a convergent strategy using a heterobifunctional cross-linker, with phosphonate and maleimide reactive end groups, resulting into core-shell magnetic NPs with high specific absorption rate (SAR) under

alternating magnetic fields, significant temperature-size response and good colloidal stability in biological buffers. *In situ* dynamic light back-scattering during MH indicated that diblock ELP-grafted onto iron oxide NPs exhibit fast size changes versus the applied field strength profile. At longer times (*i.e.,* at thermal equilibrium), the ELP brush thickness well correlates with the macroscopic temperature measured by fiber optic thermometry. However, DLS measurements interestingly revealed a transient temperature gap in the range 10-50°C between the macroscopic and the local temperature for several minutes during MH. These results open new avenue towards the understanding of the cellular toxicity under radiofrequency magnetic field, a phenomenon sometimes referred to as “cold” or “intra-lysosome” hyperthermia.

COLL 328

Creation of biomimetic environments to study aortic valve pathobiology

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Background: Calcific aortic valve disease (CAVD) is the most prevalent aortic valve disorder, although its etiology remains unclear. We sought to create engineered environments that mimic various stages of CAVD in order to elucidate the sequence of events in disease progression. Specifically, we have designed complementary bottom-up and top-down approaches to produce scaffold environments that are reminiscent of the glycosaminoglycan (GAG)-enriched valve in early CAVD and disrupted collagen microarchitecture in late CAVD.

Methods and Results: Gels composed of photocrosslinkable gelatin, hyaluronic acid, and chondroitin sulfate were synthesized to mimic early CAVD. The total GAG concentrations were selected to match the ratios of collagen:GAGs in native healthy (0.2mg/ml) and diseased (1mg/ml) leaflets. Meanwhile, photocrosslinkable gelatin/collagen scaffolds were created via multi-photon excited fabrication and tailored to mimic the disrupted fibrillar microarchitecture found in later-stage CAVD. Increasing GAG content had no effect on the phenotype of activated valvular interstitial cells (aVICs), but was able to differentiate quiescent VICs (qVICs) into a myofibroblastic phenotype. GAG enrichment also did not affect the secretion of angiogenic factors by aVICs, but an increase in cytokine secretion was exhibited by qVICs in GAG-rich environments. Both the GAG amount and identity influenced the deposition of oxidized lipids onto the scaffold, which, in turn, affected ECM production, proliferation, and growth factor secretion by the VICs.

Conclusions: We have created novel scaffold environments to mimic the ECM disarray seen at multiple stages of CAVD. Our results thus far suggest that GAG enrichment precedes VIC activation in the initiation of CAVD and may fuel both oxidized lipid deposition and angiogenesis in the valve. Ongoing studies concentrate on assessment of late-stage CAVD scaffolds and top-down ECM enrichment approaches. These

platforms can help us better understand the sequence of events in the pathogenesis of CAVD and identify potential targets for treatment.

COLL 329

Single electron device as an electrochemical sensor and biosensor

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The conductance of nanoparticles modulates significantly on (local) charging by a single electron making them attractive for use in highly sensitive sensing devices. However, devices made from a single nanoparticle or arrays of nanoparticles have to be cooled to cryogenic temperatures to obtain the single-electron effect. Recently, we demonstrated the single-electron effect at room temperature in a monolayer (array) of one-dimensional “necklaces” of 10 nm Au particles. The array can be patterned down to a long single-file string of nanoparticles. The necklace array network architecture is a metamaterial where the band gap can be tuned from 0 to up to ~6 V at room temperature by regulating the array’s overall shape. The high conductance band gap of over 1 V at room temperature allowed a highly sensitive electrochemical field-effect transistor (eFET) to be fabricated that operates in salt solutions. Biofunctional activities were monitored in real time by interfacing the eFET to living cells. In one application, the infection of a single virus on an algal cell immobilized on an eFET was measured in real time. In another application, the membrane potential modulation during photosynthesis was measured in real time as a function of the carbon source in the solution. The single-electron effect in a necklace array in air, the eFET performance, and the application as a cell-based biosensor will be presented.

COLL 330

Ultrasensitive programmable multiplexed detection using hybridization chain reaction coupled to nanoparticles

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In this study, we have coupled the DNA polymerization capability of hybridization chain reaction (HCR) with the plasmonic properties of gold nanoparticles to develop a highly sensitive, reprogrammable and multiplexed detection. We have used this approach for

visual and spectroscopic detection of low copies of three different miRNAs linked to cancer progression; four different oligonucleotides specific to subtypes an infectious disease and two environmentally important metal ions for monitoring water and soil contamination. We have shown that as little as 20 femtomole of each miRNA can be detected visually without using any analytical instrument. The detection can be performed individually or simultaneously in seven different combinations. On the other hand, the oligonucleotides specific to four subtypes an infectious disease can be detected in liquid biopsy mimics (whole blood and urine) in sixteen different combinations using a single gold nanoparticle template. The results demonstrated that our system is extremely sensitive and selective to specific subtype generating no false-positive or false-negative output. Finally this approach was adapted for detection environmentally important heavy metal ions. As low as 10 pMs of two different metal ions were detected visually in water and soil samples.

COLL 331

Regenerative biomimetic nanostructures for portable biosensing devices

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There is an increasing interest for developing nanostructured materials and interfaces with controllable interfacial properties and functionality for integration in portable sensing devices. This presentation will discuss processing, characterization and reactivity of a new type of biomimetic nanostructures with regenerative properties based on cerium oxide nanoparticles, mixed and doped congeners, for the development of portable biosensors. These materials have tunable redox activity, optical and catalytic properties and can be used to amplify signals in chemical and biological detection schemes involving biomolecules such as enzymes and aptamers. The resulting hybrid nanostructures integrate biorecognition, signal amplification and detection capabilities and can function as all-in-one biosensing devices. The sensors have been interfaced with portable databases and user-friendly signal transduction methods, and have demonstrated excellent field detection capabilities. Unique features are 1) the built-in detection mechanism with all the sensing components deposited onto a solid platform (paper, plastic, etc), and 2) the ability to mass produce them by printing. Through careful engineering design of eco-friendly inks of characteristic viscosity and composition it is possible to maintain both the functional nanoscale properties and bioactivity of these materials by printing. Recent work focusing on the development of nanoparticle-based colorimetric tests and printed enzyme-based paper sensors for point-of-care diagnosis, food monitoring and personal exposure assessment will be discussed, with examples of applications.

COLL 332

Protein-targeted corona phase molecular recognition

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Corona phase molecular recognition (CoPhMoRe) uses a heteropolymer adsorbed onto and templated by a nanoparticle surface to recognize a specific target analyte. This method has not yet been extended to macromolecular analytes, including proteins. Herein we develop a variant of a CoPhMoRe screening procedure of single-walled carbon nanotubes (SWCNT) and use it against a panel of human blood proteins, revealing a specific corona phase that recognizes fibrinogen with high selectivity. In response to fibrinogen binding, SWCNT fluorescence decreases by >80% at saturation. Sequential binding of the three fibrinogen nodules is suggested by selective fluorescence quenching by isolated sub-domains and validated by the quenching kinetics. The fibrinogen recognition also occurs in serum environment, at the clinically relevant fibrinogen concentrations in the human blood. These results open new avenues for synthetic, non-biological antibody analogues that recognize biological macromolecules, and hold great promise for medical and clinical applications.

COLL 333

GCIS electronic and physical changes to soft material surfaces

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Gas cluster ion sputtering (GCIS) has been used to modify samples without leaving behind a significant amount of damaged material, allowing for depth profiling and sample cleaning to remove the effects of ambient contamination. Polyaniline is an important material to understand due to its natural conductivity, allowing for many applications such as a solar cells, antistatic and corrosion-resistant coatings, and superconductors. The cleaning process did not change the chemical composition of the thin film polymer sample but did appear to change the morphology of the sample. Alongside the physical changes that GCIS causes we present the effects that GCIS has on the electronic band structure of conductive polymers. The band structure of a material determines how it will interact at its interface; chemically, electronically, and with light. The soft sputtering standard Irganox 1010 has been used to study topological effects of GCIS with atomic force microscopy (AFM) and scanning tunneling microscopy (STM), while chemical changes were monitored with X-ray Photoelectron Spectroscopy (XPS).

COLL 334

Multifunctional nanohybrids for single-molecule investigations

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We present a universal approach for the generation of multifunctional nanomaterials that employ molecular building blocks assembled on carbon nanotube (CNT) electrodes. We will demonstrate single-molecule control in the formation of nanohybrids via the in-solution assembly of classes of molecular materials (organic, inorganic and biological with promising attributes) to DNA-wrapped CNTs.

We have linked in solution metallic single-walled CNTs (SWCNTs) with different conjugated molecular wires. The so formed CNT-based molecular junctions were interfaced to macroscopic electrodes, and Conductive Atomic Force Microscopy measurements were performed at different locations along the junctions (fig 1). This allowed us to measure the molecular conductance of a series of oligophenyls, highlighting the potential of an all-carbon based approach for solution-processable molecular electronics. Additionally, we will show how via a similar approach it is possible to produce organic-inorganic heterostructures consisting of single Quantum Dots (QDs) univocally linked at the terminal ends of individual CNTs (fig 2). Photophysical investigations at the single nanohybrid level showed a significant electronic coupling at the organic-inorganic interface. Studies in this context are critical in the design of novel light harvesting assemblies.

Finally, we will demonstrate the assembly of single electron transfer proteins on individual CNTs, paving the way to selective electrical addressability of proteins via the use of carbon nanoelectrodes. We believe that the knowledge developed makes a significant contribution towards the facile fabrication of nanohybrid materials for single-molecule investigations in a variety of research fields.

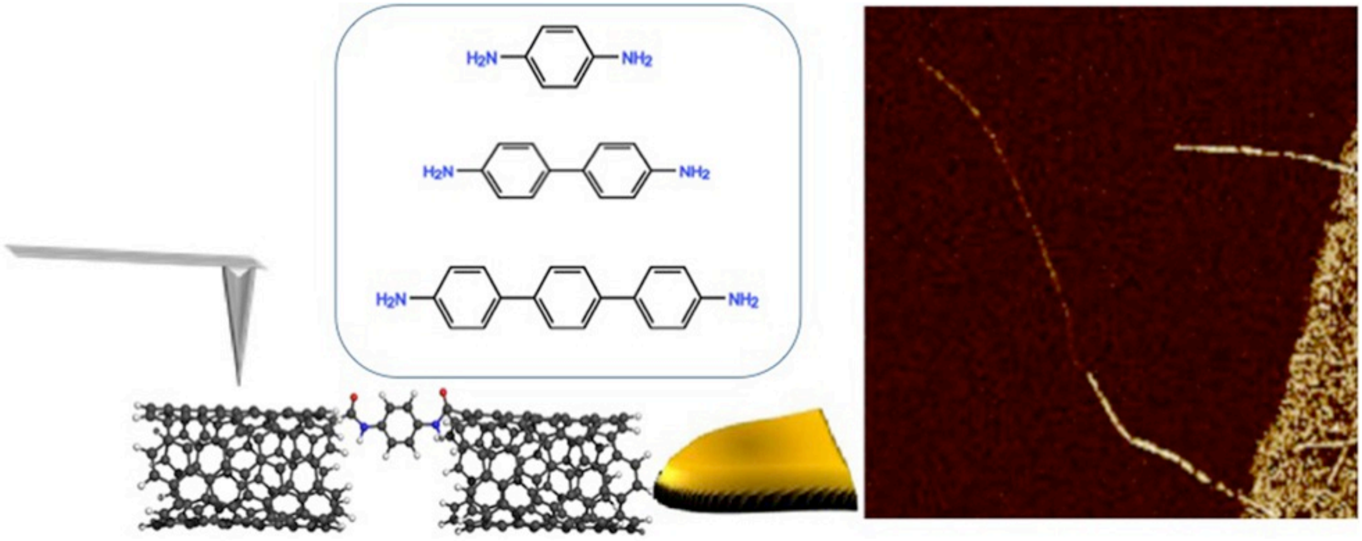

Figure 1

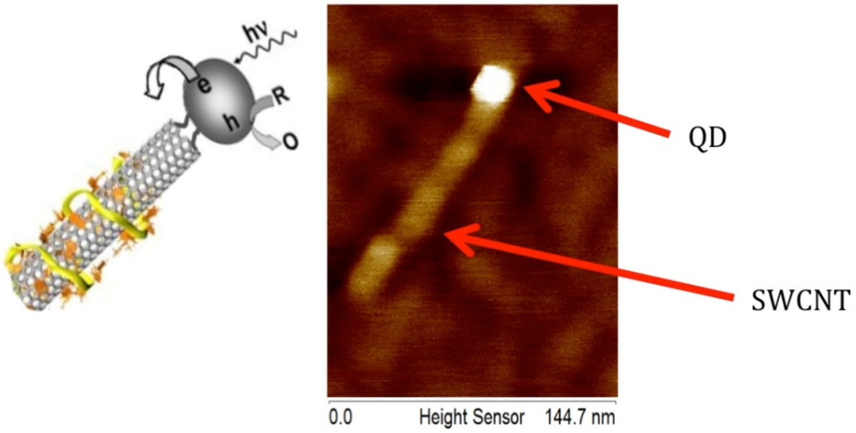

Figure 2

COLL 335

Microwave-assisted ultrafast and facile synthesis of fluorescent carbon nanoparticles from single precursor and the application for selective detection of picric acid

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An ultrafast and facile method for the preparation of fluorescent nitrogen-doped carbon nanoparticles (CNPs) has been developed from a single precursor (ammonium citrate dibasic serving as both carbon and nitrogen sources) using cheap home-use microwave oven. The obtained CNPs showed strong blue fluorescence with a quantum yield of ~ 20% and displayed excitation-independent fluorescence behavior. The effects of preparation conditions on fluorescence behavior of CNPs were systematically investigated, while the as-prepared CNPs were thoroughly characterized using various advanced techniques. The mechanism of nanoparticle formation was also discussed and proposed. Furthermore, explosive picric acid (PA) could quench the fluorescence signal of CNPs significantly and selectively, while other nitroaromatic explosives have insignificant effect on its fluorescence intensity. The excellent sensing performance to picric acid could be attributed to the synergistic effect of its low molecular orbitals, the presence of fluorescence resonance energy transfer as well as acid-base interactions between picric acid and fluorescent CNPs. These findings here suggest a simple way to prepare highly fluorescent CNPs, which holds great promise in the development of sensitive and selective sensors for PA detection.

COLL 336

Density functional theory modeling of ferrihydrite nanoparticle adsorption behavior

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Ferrihydrite is a critical substrate for adsorption of oxyanion species in the environment. The nanoparticulate nature of ferrihydrite is inherent to its formation, and hence it has been called a “nano-mineral”. The nano-scale size and unusual composition of ferrihydrite has made structural determination of this phase problematic. Michel et al. have proposed an atomic structure for ferrihydrite, but this model has been controversial. Recent work has shown that the Michel et al. model structure may be reasonably accurate despite some deficiencies. An alternative model has been proposed by Manceau.

This work utilizes density functional theory (DFT) calculations to model both the structure of ferrihydrite nanoparticles based on the Michel et al. model as refined in Hiemstra and the modified akdalaite model of Manceau. Adsorption energies of carbonate, phosphate, sulfate, chromate, arsenite and arsenate are calculated. Periodic projector-augmented planewave calculations were performed with the Vienna Ab-initio

Simulation Package (VASP[10]) on an approximately 1.7 nm diameter Michel nanoparticle ($Fe_{38}O_{112}H_{110}$) and on a 2 nm Manceau nanoparticle ($Fe_{38}O_{95}H_{76}$). After energy minimization of the surface H and O atoms. The model will be used to assess the possible configurations of adsorbed oxyanions on the model nanoparticles.

COLL 337

Redox reactions at transition metal complexes as models for mixed metal-oxides: A DFT study

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The calculated thermochemistry of redox reactions at reducible oxides obtained in DFT calculations varies strongly with the exchange-correlation (XC) approximation used. We probed the reaction profiles of reduction reactions on transition metal model complexes for 12 popular density functionals. We assessed the accuracy achievable for reactions, typically carried out over mixed metal oxides, namely hydrogenation, epoxidation, and oxidative dehydrogenation at model hydroxyl complexes of V, W, and Bi. These reactions form important building blocks when converting alkanes to more complex molecules that are the ultimate goal of catalysis over mixed metal oxides.
To this end, we calculated accurate CCSD(T) energies for comparison. The DFT functionals used show rather large deviations of up to 100 kJ mol^{-1} that vary with the fraction of exact exchange, EEX, of the XC approximation. In general, the best performance was found for functionals with a moderate percentage of EEX, between 20 and 30 %. Not unexpectedly, only reaction steps implying a reduction of the metal center were found to be particularly problematic at the DFT level.

COLL 338

Competition between adsorption and solid formation mechanisms: As(V) adsorption on goethite in the presence of Pb(II)

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Arsenate mobility in oxic environments is largely controlled by its adsorption to iron (hydr)oxides, but precipitation as heavy metal arsenates represents a potentially significant competing mechanism in view of their considerable insolubility. Predicting As geochemical behavior in heterogeneous contaminated systems where various simultaneous equilibria are taking place may be achieved in a thermodynamically sound

manner by coupling adsorption and solid-aqueous equilibria, provided that accurate equilibrium constants are employed.

In this work, the influence of adsorption and precipitation processes on As(V) mobility was investigated and modeled in synthetic systems of Pb(II) and goethite [Pb(II)-As(V)-OH Log K_{sp}=-76]. The variables investigated were: total As/Fe and As/Pb ratios, goethite particle size, pH, and inclusion of chloride and sulfate ions. A bottom-up approach is adopted here to gradually approximate the geochemical complexity of real contaminated scenarios. A unified surface complexation model for goethites of different particle sizes was used, which accounts for differences in their reactivity, and was coupled with a thermodynamic speciation model for aqueous and solid-phase equilibria.

The geochemical conditions found that favor As(V) precipitation as Pb(II) arsenate were high As/Fe, low As/Pb, goethites of small particle size, and especially the presence of chloride, and low sulfate concentrations (at low pH). The opposite conditions favor As(V) adsorption to goethite. Surprisingly, precipitation processes are more prevalent than expected and are favored from relatively low As/Fe in the presence of chloride, or with small particle sized goethites. Particularly interesting is the fact that goethite surface site saturation with As(V) occurs at five times higher As(V) concentrations in the presence of Pb(II) than in its absence; also, despite the fact that the goethite of smallest particle size adsorbs a higher concentration of As(V) than the larger-sized goethite when normalized by goethite mass, As(V) adsorption on the latter is not affected by the presence of Pb(II) (under nitrate electrolyte), whereas adsorption is decreased only in the smaller goethite. In the presence of low Cl^- concentrations, adsorption on both goethites is considerably decreased in favor of Pb(II)-As(V)-Cl precipitation (Log K_{sp}=-84). Lower pH values in the presence of high sulfate concentrations promote As(V) both adsorbing AND entering into solution.

COLL 339

Adsorption properties of *n*-alkanes on MgO, h-boron nitride, and graphite for selective separation: Neutron scattering, thermodynamics, and modeling studies

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Molecular adsorption on solid surfaces is of fundamental and practical importance. Both the symmetry and composition of the adsorbing surface play a significant role in determining the relative importance of the molecule-molecule (MM) versus molecule-substrate (MS) interactions. The petroleum industry has a substantial interest in improving selective separation efficiency for various hydrocarbons (linear, branched, and cyclic). Furthermore, monolayer adsorption can be used to investigate two-dimensional phase transitions and behavior that has no analogue in three-dimensions. Ultimately, these studies aim to provide fundamental information concerning selective alkane surface adsorption that may be applicable to adsorption on more complex materials such as metal organic framework and zeolites.

Nanometer scale magnesium oxide (MgO) with its simple cubic structure and essentially single facet exposure of the (100) surface is a prototypical material to study the interaction of alkanes adsorption. By combining thermodynamic, structural, and neutron scattering studies of diffusion a multifaceted effort has been aimed at developing a microscopic understanding of the molecule surface interaction contribution to competitive adsorption and selectivity. This study is the final chapter of a larger effort to characterize the first ten *n*-alkanes with the (100) surface of MgO. In addition, we will present the results of thermodynamic, computer modeling, neutron spectroscopy, and synchrotron x-ray diffraction studies in order to illustrate the physisorption of small linear and cyclic alkanes on MgO. For comparison, we will present additional work on hexagonal boron nitride and graphite to illustrate how a change in composition and symmetry can change the interaction potential. We aim to expand this work to competitive adsorption of linear alkanes on these surfaces in an effort to describe the process of gas separation.

COLL 340

Density-functional studies of hydrogen and organic peroxide adsorption and dissociation on MoO_3(100) and $H_{0.33}MoO_3$(100) surfaces

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Hydrogen peroxide (H_2O_2) adsorption and dissociation mechanisms on MoO_3(100) and $H_{0.33}MoO_3$(100) surfaces were studied by means of density-functional computations. Mechanisms were examined on both fixed and relaxed clusters. On both fixed and relaxed molybdenum oxide clusters, H_2O_2 adsorbs molecularly and does not dissociate. However, on the surface of both the fixed and relaxed molybdenum hydrogen bronze ($H_{0.33}MoO_3$) clusters, H_2O_2 can dissociate through a pathway involving either H-O or O-O bond cleavage. The barrier for direct H-OOH dissociation is 39.9 kJ/mol, leading to an adsorbed H atom and a HOO group. The dissociation of the O-O bond leads to the most energetically stable products, two OH species bound to the surface molybdenum atoms with the relative adsorption energy - 430.4 kJ/mol. The mechanism on the relaxed cluster is slightly more complex due to additional stability of the molecularly adsorbed structure and ability to form a geminal intermediate not found on the fixed cluster. On both the relaxed and fixed clusters, hydrogen cleavage is kinetically favored. Computations have started on methyl and dimethyl peroxides. In both cases, the chemical reaction on the molybdenum hydrogen bronze surface is made possible by the increased electron density at the surface with respect to the oxide due to the contribution from the HOMO orbital

COLL 341

Sorption of metals by nanocrystalline zinc oxide

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Unusual reactivity of metal oxides is often encountered at the nanoscale and these phenomena are often used for water purification and materials synthesis. We recently discovered that nanometric zinc oxide derived from a low temperature route reacts with aqueous cobalt and copper via what can be termed an ion-exchange process whereby zinc ions are released into solution and the other metal ions form a metal oxide shell on the nanoparticles. For example, immersion of nanocrystalline zinc oxide in a 1000 ppm solution of Cu^{2+} causes the solid to become blue as approximately 10% of the zinc ions are replaced by copper ions. The influence of particle size and the degree of aggregation of the zinc oxide nanoparticles was investigated. The use of these reactions in purification of water, zinc ores, and catalyst preparation will be discussed

COLL 342

Synthesis and characterization of mixed metal oxide clusters as precursors for solid state materials

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Metal hydrolysis in aqueous solutions result in the formation of soluble molecular clusters that can reach sizes within the nanoscale regime. These clusters are involved in additional condensation and agregation reactions to typically form amorphous or poorly crystalline materials that can then be utilized for the formation of solid state oxides. There is limited understanding of these processes, particularly for mixed metal oxide materials. In this presentation, we will present the synthesis and characterization of mixed metal clusters and related solution phases. In addition, we will discuss the impact of small organic molecules on the metal hydrolysis, overall topological features of the clusters, and resulting solid state material.

COLL 343

Fatty acids decompose during high temperature synthesis of oxide nanocrystals

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The most uniform metal/mixed metal oxide nanocrystals can be prepared through the thermal decomposition of metal salts in non-polar solvents; these reactions occur at

high temperatures, generally greater than 300 °C. They are notable for the very narrow diameter distributions of the resulting particles. This is due in part to a surprising lack of Ostwald ripening at long reaction times. The mechanism leading to the preservation of monodispersity after depletion of monomers is still not understood. Using iron oxide as a model, we report for the first time that under high temperature, the fatty acid surfactant thermally decomposes during the particle nucleation and growth. This decomposition is catalyzed by the iron oxide surfaces leading to a disproportionation reaction that releases carbon dioxide (CO_2) and carbon monoxide (CO). CO has a substantial impact on the surface of nanoparticles, generating reduced forms of iron oxide that subsequently catalyze the disproportionation of other CO molecules. This process results in a graphitic carbon deposit on the surface of nanoparticles that inhibits further growth and prevents Ostwald ripening. These observations offer insights both into the nanocrystal formation and growth mechanisms in these widely used method as well as the potential for metal oxide surfaces to catalyze formation of CO.

COLL 344

Vertically grown nanowire crystals of dibenzotetrathienocoronene (DBTTC) on large-area graphene

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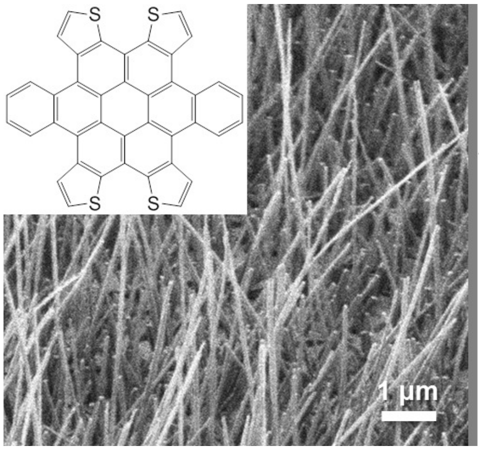
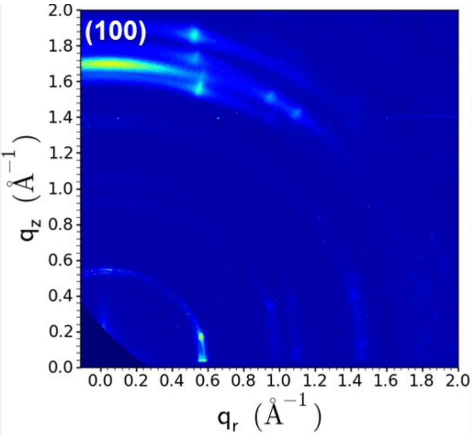
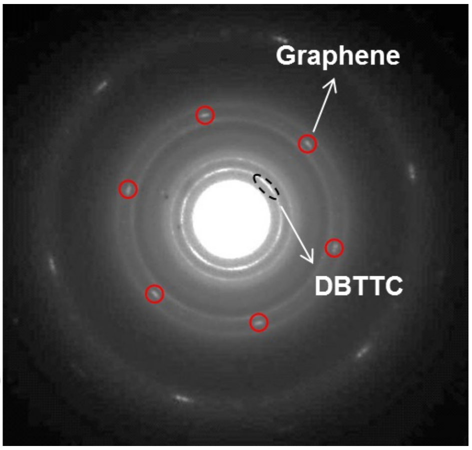
In this study we demonstrate controlled growth of vertical organic crystal nanowires on single layer graphene. We probe the microsctSurcture and morphology of dibenzotetrathienocoronene (DBTTC) nanowires epitaxially grown on graphene using Scanning Electron Microscopy (SEM), high-resolution transition electron microscopy (TEM), and Grazing Incidence X-ray Diffraction (GIXD). GIXD analysis shows strong π-π interaction between DBTTC and graphene, which results in vertical nanowire growth of DBTTC crystals, and selected area electron diffraction (SAED) pattern proves growth epitaxy of DBTTC on graphene. We show that the size, density and height of the nanowires can be tuned via growth conditions, thereby opening new avenues of exploration for 3-dimensional nanostructured architectures for organic electronics.







COLL 345

Optical properties of hedgehog particles

***Nicholas Kotov**, kotov@umich.edu.* University of Michigan, Ann Arbor, Michigan, United States

Hedgehog particles contain microscale particles as a core and metal oxide nanowires. Besides abilitie to disperse in both aqueous and organic media and defy "like disolves like" rule, recent studies demostrated that they display unusual optical properties. The scattering and other data including SERS will be presented and discussed.

COLL 346

Optical diagnosis in complex media

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Plasmonic nanostructures present unique optical properties due to the generation of strong electric fields caused by the excitation of the localized surface plasmon resonances (LSPRs). One of the main applications of such LSPRs are the so-called surface enhanced spectroscopies, mainly the surface enhanced Raman scattering (SERS) and metal enhanced fluorescence (MEF). These spectroscopies have potential for the detection of single molecules under the natural environmental conditions of the analyte and thus, present a broad potential application in different (bio)fields including medicine, the development of new diagnostic tools, multiplex detection and bioimaging and high-throughput screening[6] applications for drug discovery. Herein we will discuss about the the use of millifluidic devices and intelligent strips combined with plasmonic particles and light for the high-throughput screening, multiplex identification, quantification, profiling and/or counting of parameters such as cells, microorganism, proteins or nucleic acids in biological samples. Further, requirements of modern

medicine will be also devated.

COLL 347 – Withdrawn.

COLL 348

De-bondable adhesives based on selective depolymerization

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This presentation will describe strategies for de-bonding adhesives at room temperature in response to specific applied signals. The adhesives are made using polymers that depolymerize continuously, completely, and cleanly from head to tail when triggered by an applied stimulus. The polymers can be tuned to respond to different stimuli, and the rate of switching from bonding to de-bonding can be adjusted for various applications. Select polymers, adhesives, and proof-of-concept applications will be presented, along with a discussion of the design principles that we use to guide our development of this new class of adhesives.

COLL 349

Modulating wet adhesion of polyelectrolyte multilayers and coacervates with metal ions

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Polyelectrolyte coacervates have long been shown to be useful materials for wet adhesion, the most famous example of which being the glue created by the sandcastle worm. Here, we study the wet adhesive properties of both polyelectrolyte complexes as well as polyelectrolyte multilayers (fabricated by the layer-by-layer process). These materials are made using commercially available polymers, including biomacromolecules. Although much of our work is done with polyethylene imine and polyacrylic acid, polysaccharides can be used as a base for the polyelectrolyte wet adhesive as well. They can be used to adhere to a wide range of surfaces; polymer, metal, glass, etc. We show that these materials are suitable for wet environments such as adhering two pieces of liver tissue together. Furthermore, we show that it is possible to change the amount of adhesion created by these materials by adding various metal ions. That is, by wetting the material with salt solutions containing different metal ions it is possible to either increase or decrease the maximum adhesive force, defined by the value of a peel test. Transition metals first enhance the wet adhesive properties, then actually stiffen the polyelectrolyte material, causing it to fail much sooner. Alkali and alkaline earth metals on the other hand decrease the ability of the polyelectrolyte

material to act as a wet adhesive. This study provides insight into the way that metal ions interact with polyelectrolyte complexes and multilayers.

COLL 350

Surface treatment to enhance adhesion of polyolefin to woven fabric

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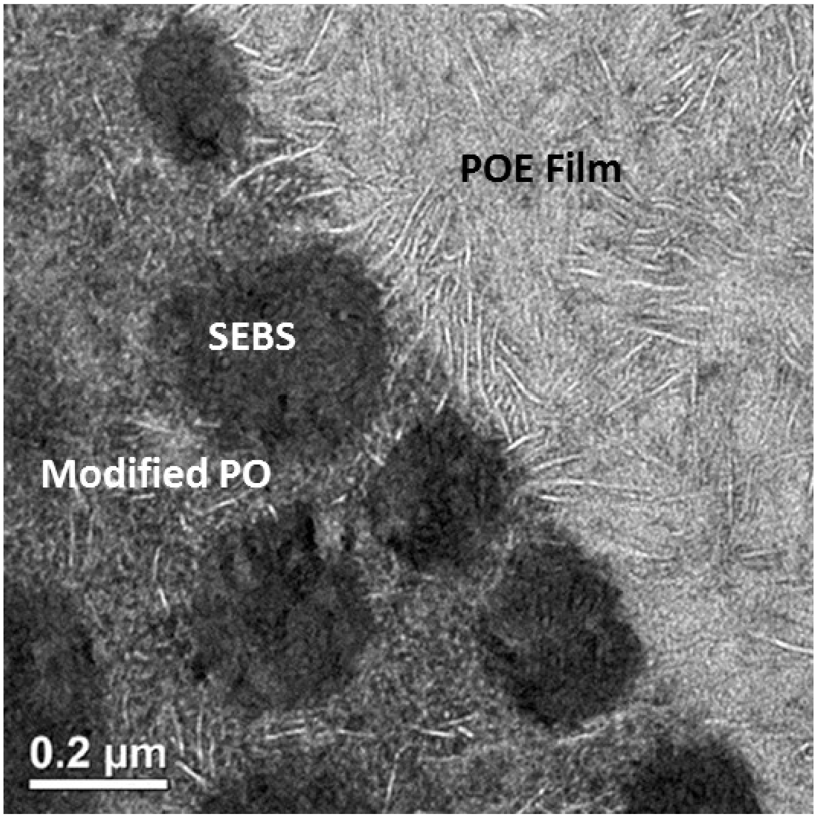
Polymer-film coated fabrics can be used in many applications requiring durability and extended outdoor exposures including tarps, awnings, tents, inflatable water craft and roofing. The use of polyolefins in many applications is advantageous because of 1) weight reduction vs. chlorinated elastomers 2) flexibility over an extended temperature range (-40 °C to 80 °C) 3) UV resistance, weather-ability and fire retardancy through high filler loading and 4) facile processing on a variety of equipment. However, due to the low surface energy and lack of polar groups, polyolefin films have poor adhesion to other polar materials like polyurethane, polyethylene terephthalate (PET) or polyamide. Developing solutions to improve the adhesion of polyolefins to polar substrates is critical for balancing the adhesion performance, processability and handling flexibility in the final product. This paper discusses the development of surface treatments comprising functionalized polyolefin blends to increase the bonding strength of polyolefin films with PET fabrics. Modification of the PET fabric surface using polar functionalized polyolefins resulted in a surface with better interaction with polyolefin coatings. The treated PET surface showed improved adhesion with polyolefin films. The impact of many factors including the types of functional polymers, solvents and crosslinking agents on the adhesion performance were investigated. Results indicated that polymer blends of maleic anhydride modified polyolefins in combination with styrene-ethylene-butylene-styrene block copolymers showed a balanced performance of viscosity and adhesion. Infrared spectroscopy (IR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to study surface chemistry and morphology. The adhesion mechanism is discussed in this study.



TEM micrograph showing the interaction of a polyolefin film with the primer.

COLL 351

Bio-inspired nanoparticulate medical glues for minimally invasive tissue repair

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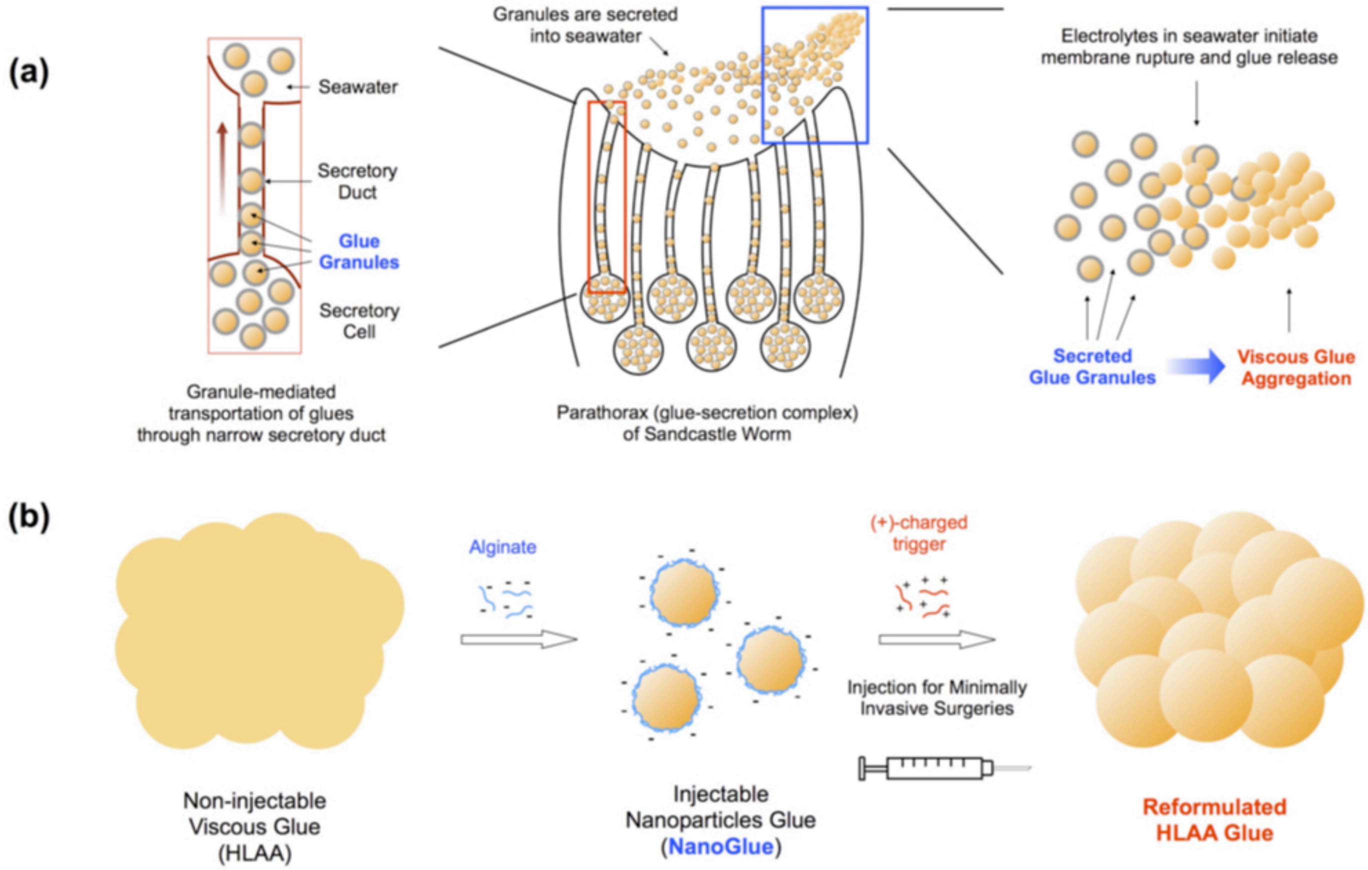
Methods to seal tissue leaks, attach devices, and to join tissues together during minimally invasive surgeries represents a significant challenge. Tissue adhesives and sealants used in clinic include fibrin sealants, cyanoacrylate-based glues, and protein/peptide-based glues, however their use in minimally invasive procedures is limited due to suboptimal usability/controllability by surgeons as they are generally applied in a low viscosity state, are hydrophilic and can dilute in blood or other fluids, and it is typically difficult to control their adhesive activation. In addition, the viscosity can present challenges when delivery is required through small-bore needles, especially, during procedures such as endoscopic and laparoscopic surgeries and surgeries on fragile tissues within confined space (e.g. ophthalmic applications). Inspired by the viscous glue secretion mechanism of the sandcastle worm (Phragmatopoma californica) using granule-packaged glues, we demonstrate a nano-encapsulated viscous poly(glycerol sebacate)-acrylate based glue that can easily be injected through small-bore needles for application during minimally invasive procedures (Figure 1). Negatively charged alginate was used to stabilize the nanoparticulate surface to significantly reduce its viscosity and to maximize injectability through small-bore needles. The nanoparticulate glues can be concentrated to ~30w/v% dispersions in water that remain localized following injection. With the trigger of a positively charged polymer (e.g., protamine), the nanoparticulate glues can quickly assemble into a viscous glue that exhibits rheological, mechanical and adhesive properties resembling the native poly(glycerol sebacate)-acrylate based glues. This platform should be useful to enable the delivery of viscous glues to augment or replace sutures and staples during minimally invasive procedures.



COLL 352

Stimuli-responsive reversible two-level adhesion from a structurally dynamic shape memory polymer

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A shape-memory adhesive has been prepared that exhibits two levels of reversible adhesion. The adhesive is a semi-crystalline crosslinked polymer that contains dynamic disulfide bonds. Melting of the crystalline regions via heat results in a drop in the modulus of the material that facilitates wetting onto and enhances surface contact of the substrate to form an adhesive bond. Exposure to higher heat or UV light results in dynamic exchange of the disulfide bonds which yields a further drop in the modulus/viscosity that improves surface wetting/contact and strengthens the adhesive bond. This improvement is shown to apply over a different substrates, contact forces and deformation modes. Furthermore, the adhesive acts as a thermal shape memory material and can be used to create joints that can reposition themselves upon application of heat.

COLL 353

Barrier adhesive for flexible packaging

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Barrier property is essential for many flexible packaging applications to protect products from oxygen and moisture. Thin foil, metalized plastic film, PVDC coated film and EVOH coextruded film are widely used to meet the flexible packaging industry’s need for long shelf life, such as dry food packaging, medical packaging, beverage packaging, etc.

A new adhesive technology has been developed, that functions as a laminating adhesive, but additionally provides barrier properties, and serves as a barrier layer in the total lamination structure. Basic chemistry, barrier mechanism, application conditions and barrier properties of this new barrier adhesive technology will be discussed in this presentation.

Advantages of barrier adhesives include, simplification of packaging structure, recyclability, improved flex resistance of metalized film, and chlorine and halogen-free chemicals that are polyester urethane based.

COLL 354

Rheological optimization in adhesive design

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The rheological criteria for a specific adhesive application are a reflection of both the bonding and debonding aspects of adhesion performance. Achieving intimate contact with the substrate during bonding is dictated by macroscopic flow and the surface energetics of the composition. The ultimate bond strength of the adhesive, however, is dictated by the resistance to debonding forces under end-use conditions including testing temperature and rate of deformation. The ability of the adhesive to dissipate energy, for example, plays a key role in transferring stress from the bond-line.

The work of Dahlquist in characterizing the rheological requirements for PSAs provided a fundamental basis for developing rheological parameters for other adhesive types. Class and Chu analyzed rubber/resin blends and provided rheological insights into PSA development. More recently rheological windows for radiation cured flexible laminating adhesives have also been reported.

Decidedly less information has been available on rheological correlations with performance of hot melts applied at elevated temperatures and especially those that contain crystalline modifiers (Figure 1). Evaluation of the rheological characteristics of numerous wax containing hot melts provides correlations for set time with G’. Multiple generations of hot melt technologies based on EVA, EnBA, m-PE, and EMA intended for the same application can be shown to conform to the same rheological requirements.

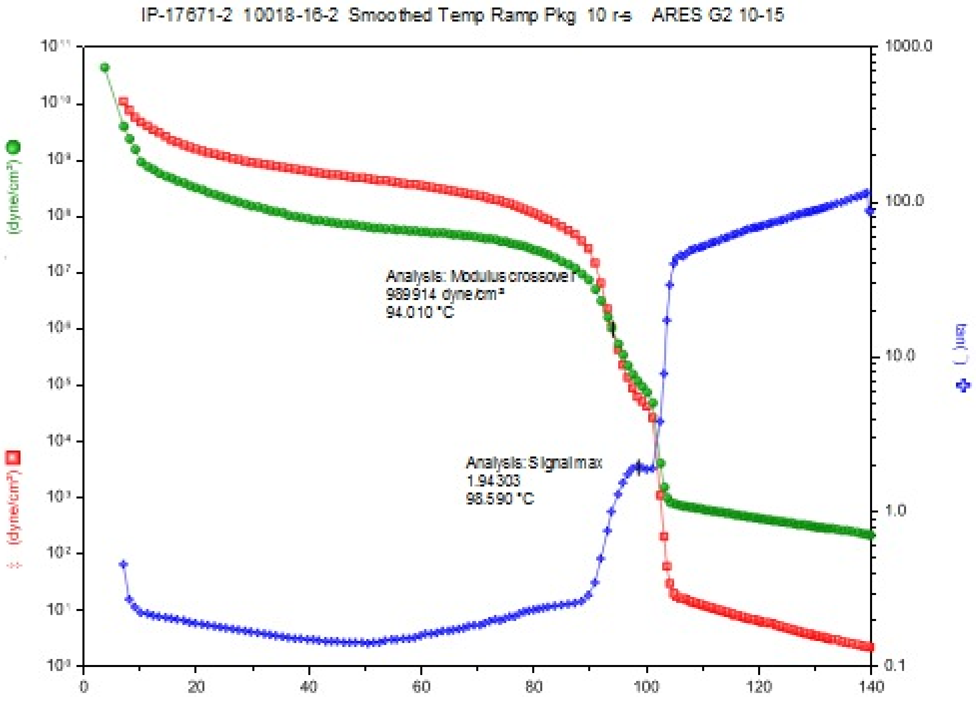

Figure 1. DMA of a fast setting (0.5 sec) packaging hot melt adhesive.

COLL 355

Novel borane complexes and borate salts for use as initiators in acrylic adhesives

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Novel borane complexes and borate salts were developed for use as initiators for acrylic adhesives, and surprisingly they also promote adhesion to low energy substrates such as polyethylene and polypropylene. The key for commercialization of these initiators is providing the appropriate shelf life while maintaining adequate initiation for curing of the adhesive system. The focus of this work was examining the shelf life and initiation of organoboron compounds in the acrylic adhesive system as a function of the molecular architecture of the organoboron curative. The two key molecular features which significantly affect stability are: 1) arrangement of the imidazolide bridged borate structure and 2) the chain length of the alkyl groups on the boron atom. The results show that excellent reactivity (initiation of polymerization) and shelf life stability can be attained with both trialkyl borane and tetra alkyl borate type initiators. The initial improvement can be attained by altering the structure of the organoboron compound. Typical results are shown in Figure 1.

The shelf life stability is also dependent on using the proper free radical trap and this work also show that hydroxyl amine and nitrile oxide compound perform superior to phenolic stabilizers.

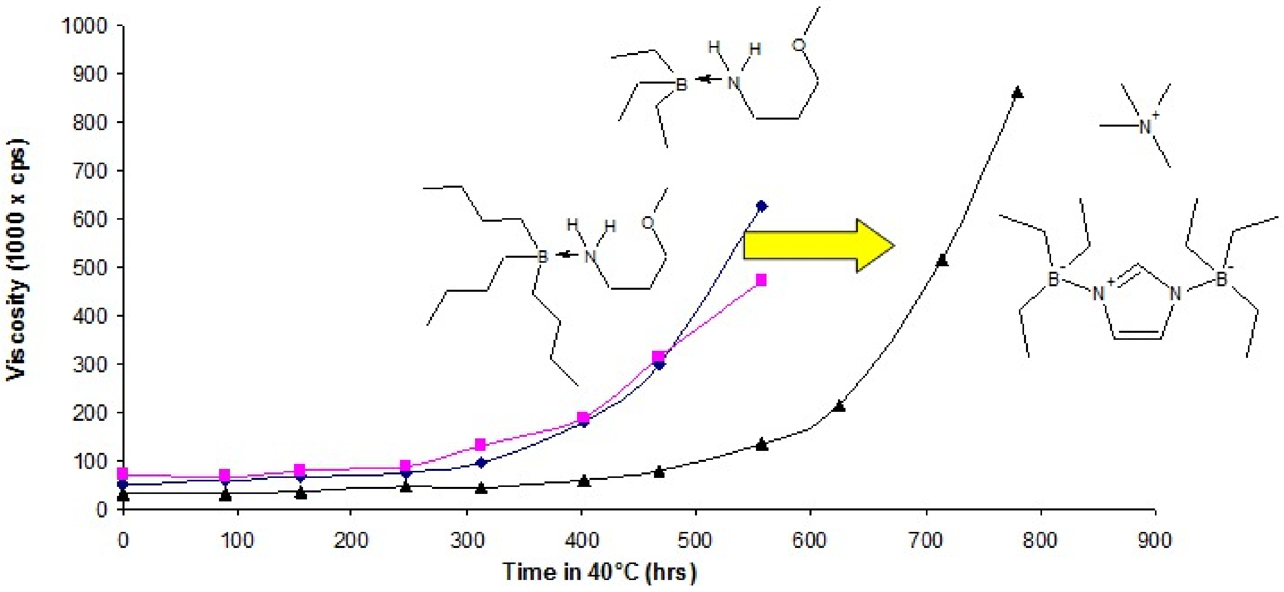

Figure 1. Structure Effect on Viscosity

COLL 356

Ultrafast dynamics at colloidal interfaces

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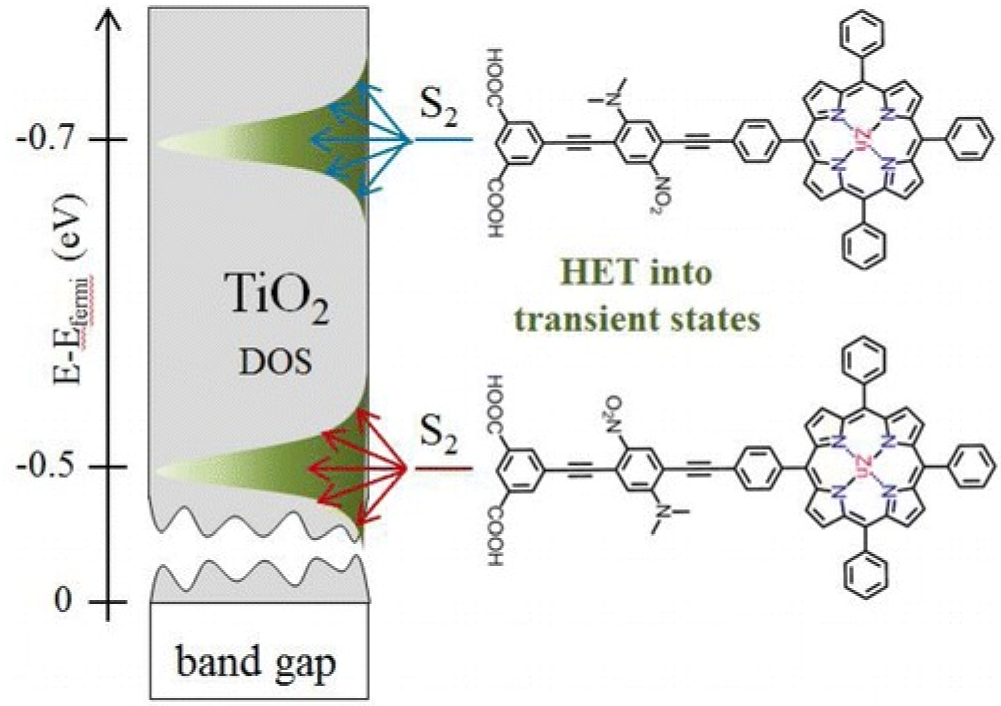
Electron transfer at colloidal interfaces is a critical process in surface catalysis, novel electronic applications and solar energy conversion. The fast kinetics (below 100 fs) and the inhomogeneous environment complicate identifying the parameters that dominate the reaction. We present ultrafast spectroscopic studies of electron transfer between molecular dyes and metal oxide colloids with well-defined variations in excess energy and dipole moment.

A series of three Zn(II) tetraphenylporphyrins (ZnTPP) with alternating dipole moment attached to TiO_2 colloidal films has been investigated. The influence of the dipole moment on the energy level alignment at the colloidal surface can be observed via UPS. Surprisingly, the ultrafast electron injection dynamics of the chromophores bound to the metal oxide semiconductor does not show the expected dipole dependence. These results are substantiated by measurements employing a different dye molecule with two distinct excited states.

The excited state dynamics of a phlorin macrocycle attached to TiO_2 colloids are compared after photoexcitation into the first and the second excited state. Electron transfer times for both states were very similar and around 50 fs. Surprisingly, the large difference in the density of acceptor states that are resonant with the respective donor level of the molecule does not significantly influence HET dynamics. These results indicate that electron transfer at colloidal interfaces involves only a subset of the surface projected density of state (DOS) that is present in the metal oxide conduction band. This complicates predictions of electron transfer efficiency based on steady state DOS calculations.



Electron transfer at colloidal interfaces is independent of the dipole moment at the interface.

COLL 357

Studying particle dynamics in the reentrant glass transition using colloidal suspensions

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We study the structure and dynamics of dense colloidal suspensions by using depletion forces as a way of controlling the inter particle attraction. The goal of these studies is to gain a better understand the reentrant glass transition. Confocal microscopy and particle tracking techniques allow us to determine particle trajectories in systems of varying attraction strengths. For a given volume fraction of colloidal particles we observe three qualitatively different states depending on the inter particle attraction strength. The behavior of the mean square displacement and long time diffusion constant show repulsive glassy systems at low attraction strength, statistically ergodic liquids at moderate attraction strengths, and attractive arrested systems with even more attraction. We use the non-gaussian parameter and a self overlap function to probe for heterogeneities in particle motion. Results indicate that the most heterogeneous dynamics occur at longer lag times in the arrested states than in the fluid states. Variance in the self overlap and in the spatial positions of mobile particles show that heterogeneous rearrangement events in attractive arrested systems are less frequently distributed spatially but occur over a larger range of length scales than the repulsive

glassy states. The length scale that maximizes four point susceptibility across a range of attraction strengths exhibits a reentrant glass behavior similar to that of the long time diffusion constant.

COLL 358

Computational models for nanoscale biofluid dynamics and colloid transport inspired by non-equilibrium thermodynamics

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Traditionally, the numerical computation of particle motion in a fluid is resolved through computational fluid dynamics (CFD). However, resolving the motion of nanoparticles pose additional challenges due to the coupling between the Brownian and hydrodynamic forces. Here, we focus on the Brownian motion of a nanoparticle coupled to adhesive interactions, and confining-wall-mediated hydrodynamic interactions. We discuss several techniques that are founded on the basis of combining CFD methods with the theory of non-equilibrium statistical mechanics in order to simultaneously conserve thermal equipartition and to show correct hydrodynamic correlations. These include (1) Accurate representation of nanoparticle dynamics: stochastic and hydrodynamic effects using fluctuating hydrodynamics (FHD) with Markovian noise; (2) Constructing a thermostat using fluctuating hydrodynamics with non-Markovian particle equation; (3) Memory function approach to coarse-graining with hydrodynamic interactions under confinement; (4) Generalized Langevin equations for bridging colloidal and molecular scale dissipation. Through the examples discussed, we also show a top-down multiscale progression of temporal dynamics from the colloidal scales to the molecular scales, and the associated fluctuations, hydrodynamic correlations. While the motivation and the examples discussed here pertain to nanoscale biofluid dynamics, the methodologies presented are rather general, and can be easily adopted to applications outside of biomedical engineering.

COLL 359

Vibrational properties of disordered colloidal suspensions with varying interparticle attraction strength

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We experimentally study vibrational properties of disordered colloidal suspensions as a function of the strength of the interparticle attraction. We probe the structural and dynamical changes in disordered colloidal glasses as the interparticle interaction evolves from nearly hard-sphere repulsive to attractive. This increase of the interparticle attraction is achieved through use of temperature-tunable surfactant micelle depletants. The depletion-driven entropic attraction between particles in suspension grows with increasing temperature. Increasing temperature changes particle interactions in a dense colloidal packing from repulsive (weakly attractive) to strongly attractive, and accompanying variations in structure and dynamics is investigated. We observed that particle dynamics decreased monotonically with increasing attraction strength, but for attraction strengths larger than $2k_BT$ particle dynamics are saturated, signifying the system reaching a point of maximal arrest. Therefore in 2D colloidal glasses the transition from the repulsive glass state to the attractive glass state occurs at an interparticle attraction strength of $2k_BT$.

COLL 360

Mass transfer in nanofluids

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The current work broadly covers two set ups-homogeneous and non-homogeneous. Homogeneous set refers to experiments done in Fluorescence Correlation Spectroscopy (FCS), where the nanofluid and dye are homogeneously mixed and observed. For the non-homogeneous set, diffusion experiments are set-up in a capillary with arrested bulk motion. The system used is Fluorescein-Na dye and alumina nanofluid (Size-13 nm). Effect of changing the dye concentration and alumina concentration was observed systematically.

The motion of the dye can be characterised by an apparent diffusivity or a characteristic initial velocity of the front. The Fluorescein-Na-alumina nanofluid system shows an increase in the apparent diffusivity of the dye with an increase in the alumina concentration up to 0.5% (w/w). An increase in apparent diffusivity and velocity was also observed for increasing dye concentration. FCS results show no enhancement for different nanoparticle concentration.

FCS observations can be explained by the theory of Brownian motion, which shows diffusivity is inversely proportional to viscosity. Here, change in viscosity are moderately less, hence no enhancement in diffusivity. In the non-homogeneous case, the motion of the dye front, and hence an apparent increase in the diffusivity can be explained by a diffusiophoretic motion of the colloidal nano-particles. Diffusiophoresis is the phenomenon causing the motion of colloidal particles in the direction of higher or lower concentration of the solute, when it is placed in non-uniform concentration of the solute

COLL 361

Rheology and microstructure of colloidal silica particle dispersions in ionic liquids

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Shear thickening dispersions of colloidal particles in ionic liquids are being developed for use to improve the ballistic, puncture and abrasion resistance of space suits and micrometeorite and orbital debris (MMOD) shielding for spacecraft. Ionic liquids are proposed as the solvent phase of STFs formulation for space application because of their stability over the broad range of temperatures and low volatility. However, this can be challenging because the high ionic strength of ionic liquids screens the electrostatic stabilizing forces that are typically important for dispersing particles in polar solvents. In our previous research (Gao *et al.* ACS Nano 2015), we created stable nanoparticle dispersions in the ionic liquid [C_4mim][BF_4] by inducing solvation layering, whereby a 5 nm layer or organized IL forms around the particle due to strong hydrogen bonding between anion $[BF4]^-$ and the fluorinated alcohol functionalized particle surface. However, in agreement with theory, the presence of this steric solvation layer prevented shear thickening by suppressing hydrocluster formation. To achieve a stable dispersion that also exhibits shear thickening, commercial silica particles with an alcohol-functionalized particle surface were dispersed in the ionic liquid [C_4mim][BF_4]. It was expected that the alcohol coating will exhibit weaker hydrogen bonding with the anion $[BF_4]^-$, leading to a thinner solvation layer that is still sufficient for dispersion, but enables hydrocluster formation at high shear rates. Dynamic light scattering (DLS), small angle neutron scattering (SANS) and rheology were employed to determine the solvation layer thickness and microstructure of dispersions. Analysis of SANS spectra across a broad range of particle concentrations was used to develop a quantitative model for the inter-particle interactions including the thickness of the solvation layer. The effects of temperature on microstructure and shear thinning and shear thickening rheology are investigated. Dispersions lose their stability and transit from stable dispersion to “soft” gel due to the loss of solvation layers thickness with increasing temperature. This work provides guidance on formulating colloidal dispersions in ionic liquids and may have implications for environmental and energy engineering as ionic liquids are candidates for remediation, separation, and recycling of nuclear waste.

COLL 362

Self-recognition of two rod-shaped macroions with different functional groups controlled by cation-π interaction

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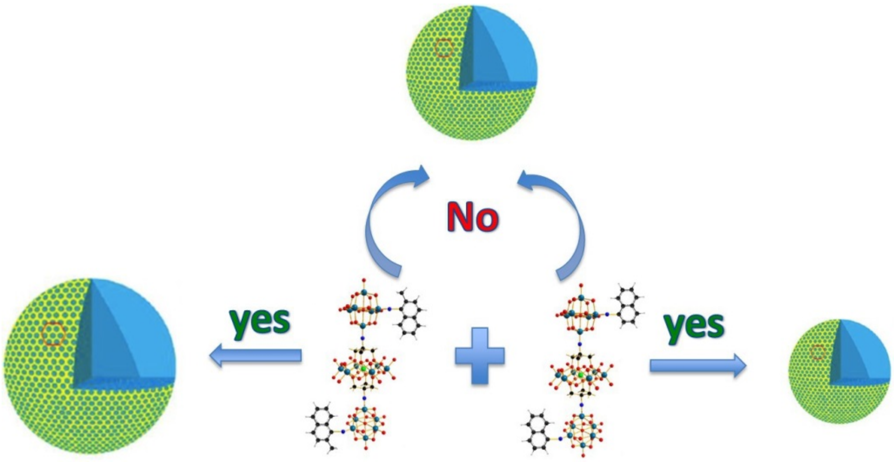
Two rod-shaped macroions, $[Bu_4N]_7[ArNMo_6O_{17}NC(OCH_2)_3MnMo_6O_{18}(OCH_2)CNMo_6O_{17}NAr]$ (Ar=naphthyl and 1-methylnaphthyl), with identical charge densities and morphologies except for slight difference of their functional groups were observed to self-assemble into vesicle-like structures in dilute solutions. Interestingly, instead of forming mixed spheres, the two highly similar macroions kept self-sorted and consequently self-assembled into individual supramolecular spheres with size of 30 nm and 55 nm, as confirmed by Laser Light Scattering (LLS) techniques. Control experiments reveal that the dominant driving force during their self-assembly processes is cation-π interaction rather than electrostatic interaction. This may be explained by the substantial enhancement of cation-π interaction, which contributes from the cooperativity of π-π environment on the surface of the self-assembled spheres. Although cation-π interaction is considered as a weaker force compared to electrostatic interaction, this work suggests that the delicate cation-π interaction might be significant in supramolecular assemblies, which leads to self-recognition phenomenon between two highly similar macroions.



Model of self-recognition process of two macroions in their mixed solutions.

COLL 363

Measuring weak interactions of individual colloids using near field light scattering

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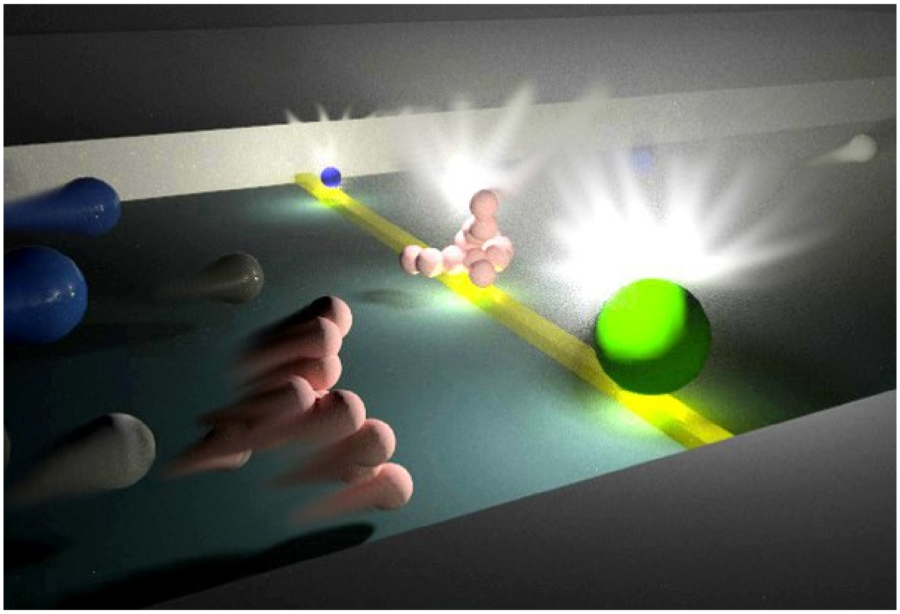
We present the market's latest particle analysis system. The NanoTweezer Surface uses cutting edge nanophotonics and microfluidics to analyze nanoscale particles in solution, chiefly characterizing their size and their surface properties, simply not possible with current instrumentation. The device uses near field optics to impart optical forces that drive the particles to interact against a reference surface, and by measuring the amount of light these particles scatter, the NanoTweezer Surface characterizes the interaction potential to infers the surface properties of the particle. Researchers are using our tool in nanomedicine and nanotoxicity to measure weak and non-ionic interactions such as those imparted when a particle is PEGylated, as well as assess ligand coverage during surface functionalization. The system allows researchers to better assess formulation stability, particle surface coverage and offers key new insights to make better colloidal systems. We will dive into the device physics as well as offer case studies.



COLL 364

Adsorption of asphaltene from non-equilibrium dispersions in heptane-toluene

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Fouling by asphaltene poses a serious problem for the petroleum industry. Asphaltene is the densest, most polar fraction of crude oil and is generally stable in liquid crude under the conditions present in the reservoir. Throughout the oil production process, crude oil experiences changing environmental conditions that can act to destabilise

asphaltene. Since equilibration or “aging” of asphaltene is a slow process, this means that asphaltene is often in a non-equilibrium state. Asphaltene exists as single molecules or as colloidal dispersions of nanoaggregates or clusters of nanoaggregates. The degree of aggregation increases with increasing destabilisation and when sufficiently destabilised a precipitate can form.

In this study a quartz crystal microbalance is used to monitor the adsorption of asphaltene from solutions in heptane-toluene before the onset of precipitation. It has been shown that the degree of aggregation and the adsorption behaviour can be altered by varying the ratio of heptane, an asphaltene precipitant, to toluene, an asphaltene solvent. Here we investigate the effect of asphaltene being in a non-equilibrium state on its surface adsorption. This is achieved by mixing heptane with asphaltene/toluene in a Y-junction immediately before it enters the quartz crystal microbalance. We hope that this fundamental study will give fresh insight that will help determine better strategies for dealing with asphaltene fouling.

COLL 365

Spontaneous fingering in colloidal suspensions

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Liposomes, also known as lipid vesicles, are composed of one or more lipid bilayers that encapsulate an aqueous volume and they are used in drug delivery systems. We present a simple device in which liposomes generate due to static phase interdiffusion (SPI). In this process, lipid-ethanol solution is contacted with aqueous environment and finger like patterns (similar to viscous fingering phenomena) are observed during the liposomes formation. Finger like patterns generally occur in an interface when a lower viscous or higher dense fluid is pushed through another miscible or immiscible fluid having higher viscous or lower dense one, and such phenomena are well described by the Saffman-Taylor instability theory. In the present study, we report an observation of a fingering like phenomena that occur when an aqueous suspension of liposomes is in contact with an aqueous media. Unlike in the well-defined viscous fingering case, the liposomes suspension is of a lower bulk density and higher viscosity as compared to the aqueous phase.

In addition, like lipid-ethanol and water system, similar patterns are also noticed in other type of systems, such as polystyrene-ethanol and water, polystyrene-methanol and water, and polystyrene-propanol and water. In all the aforementioned cases, suspension viscosity changes non-monotonically. Conversely, the case where solution viscosity decreases, such strings do not appear. For such evolved instability, it is hypothesized that there could be two possible reasons, i.e., viscosity gradient, and diffusiophoresis. The phenomena in which a colloid is driven due to presence of a non-uniform solute concentration, is known as diffusiophoresis. A good understanding of

such phenomena may have important consequences in the liposomes synthesis, and possibly to the enhancement of mass transport noticed in nanoparticle suspensions.

COLL 366

Colloidal stabilization of surfactant-free paraffin-in-water emulsions containing L-menthol by polar oil

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We report here on the colloidal stabilization of surfactant-free (SF-) paraffin-in-water (P/W) emulsions containing L-menthol (LM-P/W emulsion) by mixing of polar oil with paraffin. The SF-LM-P/W emulsion is not stable, in which turbidity of the SF-LM-P/W emulsion is not retained even for 3 days. On the other hand, the turbidity of the SF-LM-P/W emulsions remained unchanged even at 7 days after preparation when small amount of diethyl sebacate (DES) mixed with paraffin. Namely, the SF-LM-P/W emulsions are stabilized by DES. Mixing of glyceryl tri(2-ethylhexanoate) (GTE) with paraffin led to the colloidal stabilization of the SF-LM-P/W emulsions at higher content of GTE in paraffin. These findings provide better insight on the colloidal stabilization of oil-in-water (O/W) emulsions in the multi-component system.

COLL 367

Nanotechnology and photothermal treatment of cancer

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A short introduction about gold and silver nanoparticles and their plasmonic properties will be given. We then summarize the new properties of Gold when its size is reduced to the nanoscale. By conjugating small concentrations of gold nanoparticles to the nucleus membrane of cancer cells we were able to record the vibration (Raman) spectra of molecules in the cell near the gold nanoparticles in the different phases of its full cycle, or as the cell dies if given cancer drugs. This enabled us to follow the dynamics of drug delivery and measure the relative efficacy of different cancer drugs, using either Raman spectra method for detection. Finally, we were also able to show the efficacy of the photo-thermal therapy of cancer using gold nanorods in mice, cats and dogs. We recently have shown that this gentle method succeeded in treating a large breast cancer of a cat while still preserving its pregnancy and nursing functions.

COLL 368

Localized surface plasmon resonance (LSPR)-based magnetic rotational biosensing

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Localized surface plasmon resonance (LSPR) of metallic nanostructures has been extensively studied in the fields of drug delivery as well as biosensing due to the sensitivity to the external environments. Specifically, rod-shaped nanostructure is one of the sources utilized for sensing due to its anisotropic structures exhibiting two distinctive plasmonic bands. However, its sensitivity is quite limited that hinders fully utilization as biosensors. Here, we present a simple but effective method to enhance the figure of merit (FOM) for biosensing by inserting ferromagnetic segments into Au nanorods via electrochemical depositions. Under the rotating magnetic field, Au/Ni/Au multisegment nanorods rotate, sustaining their orientations due to the Brownian motion, which allows us to investigate the interaction between the biomaterials in fluids. Along with the observation of specific binding of biomolecules onto magnetic nanorods by LSPR shifts, we investigated shear-force induced behavior of nanorods under rotating magnetic field as a function of frequency. By using Fourier Transform (FT) method, we can simply transform the time domain to frequency domain, which leads to the enhanced FOM of the systems. We expect this study will contribute to the understanding of plasmonic/magnetic hybrid systems as well as the fundamentals of biosensing configuration.

COLL 369

Achieving high refractive index sensitivity with bimetallic nanocrystals

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Metallic nanocrystals (NCs) have tunable plasmonic properties that depend on their size, shape, composition, and local environment. However, investigation of bimetallic NCs for sensing applications has been limited due to difficulties in synthesizing structures with suitable optical properties. This challenge is being addressed with seed-mediated co-reduction as a route to architecturally controlled bimetallic NCs, including Au-Pd octopods with either Au or Pd interiors. Shown here, the RI sensitivity (RIS) of the octopodal Au-Pd NCs is enhanced by increasing either the internal or external atomic %Pd. In fact, to the best of our knowledge, these NCs display the highest ensemble RIS measurement to date for colloids with LSPR maximum band positions ≤ 900 nm in water. This effect is accounted for by the lower dielectric dispersion at the resonant wavelength. In identifying how internal and external composition affect the RIS of bimetallic NCs and provide chemical selectivity, new multifunctional platforms should be possible with less conventional plasmonic metals.

COLL 370

Controlled synthesis and growth mechanism of hollow gold nanospheres (HGNs) and their application in photothermal therapy (PTT) of cancer

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Hollow gold nanospheres (HGNs) exhibit unique optical and photothermal properties useful for many applications including photothermal therapy (PTT) of cancer. We have conducted extensive studies of the mechanism behind the growth of HGNs and determined the important role of oxygen in the reaction process using a number of spectroscopic techniques including X-ray spectroscopy. Based on the better understanding of the growth mechanism, we are able to control the synthesis of HGNs with well-defined size and shell thick, allowing surface plasmon resonance (SPR) at specific wavelength to be achieved, especially the highly desired near IR (NIR) region. In addition, we can control the surface morphology of the HGNs by varying surface ligand molecules. The synthesized HGNs have been used for *in vitro* studies of HGN-mediated PTT of oral squamous cell carcinoma (A431), with the primary goal to optimize the bioconjugation (protein vs peptide targeting ligands) and the HGNs (size and SPR) for best PTT performance.

COLL 371

Development of fluorescent core-shell nanoparticles for cell labelling

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The simultaneous discrimination of different types of cells in various biological fluids (blood, saliva, breast milk, etc…) is advantageous to detect infections, diseases and abnormalities in many fields such as food-processing or biopharmaceutical industries. The development of optical sensors elaborated in collaboration with Héma-Québec will allow sensitive and selective multiplex detection of cells in fluids and/or blood products by imaging and flow cytometry. These optical nanosensors are able to emit fluorescence and scatter light at very specific wavelengths since they are composed of a metallic core protected by a fluorescent silica shell. The metal core (Ag, Au or In) has two distinct roles: it allows the nanosensor to have a scattering signature and permits a coupling effect called Metal-Enhanced Fluorescence (MEF). Indeed, this core-shell architecture improves the excitation and the emissive rates as well as the photostability of common organic fluorophores. The identification of the different sensors in the same sample will be possible using their distinct scattering and fluorescence signatures. The synthesis of core-shell nanoparticles with different spectral properties, including through the use of Förster Resonance Energy Transfer (FRET), was developed. This non-

radiative energy transfer from a donor to an acceptor fluorophore allows a great variety of fluorescence signals since it is possible to modulate the proportions of the two emitters in the silica shell in order to change the intensity of the fluorescence spectrums. It also enables ratiometric normalization without increasing the complexity of the detection channels. A parametric study was done to understand the effect of the metal core on the FRET efficiency of these new nanosystems to demonstrate the potential applicability of this strategy. Different antibodies will be conjugated onto these nanosensors; examples will be given for the use of simultaneous detection of different cell populations.

COLL 372

Fluorescent core@shell hybrid particles for multi-elementary ionic detection

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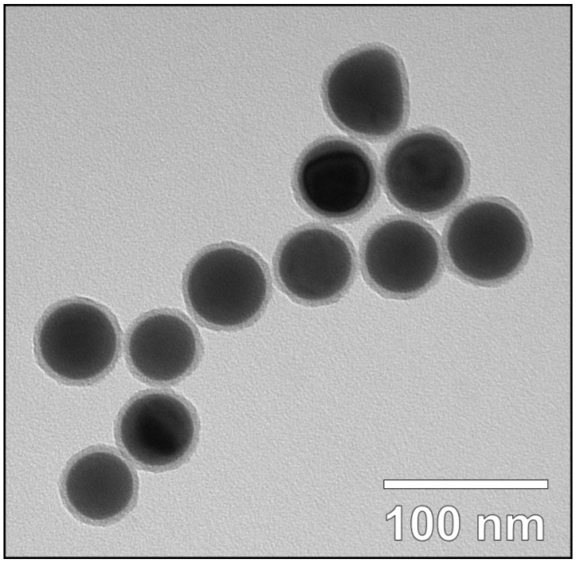
Biomedical studies of cell metabolism and signaling hinge on quick and precise detection methods for different molecules and ions of interest in physiological conditions. While fluorescence spectroscopy and microscopy apparatus are well implemented for these types of experiments, the intrinsic properties of organic fluorophores with regards to photostability, absorptive cross-section and brightness can be limiting for their long-term observations. Recently, many solutions have been developed to prevent these shortcomings, one of which being plasmonic core-shell particles incorporating fluorescent probes in their architecture. In this study, we have designed and applied such systems to measure variations in extracellular proton (pH), halide and metallic ion concentrations with fluorescence steady-state or time-resolved characterizations. Thorough optimization for the syntheses of metal cores (Ag, Au, In) and the condensation of multiple silica layers have allowed high tunability of analytical properties like sensitivity, ratiometric normalization, bimodal discrimination and response time. The applicability of our nanosensors was demonstrated both on colloidal suspensions and on planar microfluidic substrates, with diversified biological systems of reference such as neurons, cardiac fibroblasts, and *S. salivarius* biofilms.



Transmission electronic micrograph of In@SiO_2 nanoparticles for halide detection

COLL 373

Synthesis routes for the fabrication of plasmonic nanoparticle structures

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Utilizing plasmonic nanostructures promises advanced detection sensitivity. For the fabrication of SERS active materials several critical issues have to be taken into account. These address e.g. the availability of suitable plasmonic building blocks, their synthesis in reasonable amounts at low experimental affords and costs as well as questions regarding their performance for SERS investigations. The application of microwave assisted synthesis protocols provided a powerful tool to fabricate silver nanoparticle plasmonic substrates and allow for a fast, cheap and easy synthesis of larger amounts. Recent advances will be presented; in particular, the fabrication of SERS active silver nanoparticle films that can be applied by a simple microwave assisted synthesis approach. This approach can be adapted also to the functionalization of capillaries and potential applications in drug sensing will be discussed. Therefore, different systems have been investigated. Self-assembly as well as template guided assembly processes have been studied. These include e.g. polymer-Au nanoparticle hybrid structures. In this vain also the site-selective immobilization of Au nanoparticles into clusters on substrates is discussed to investigate the influence of interparticle and intercluster plasmon coupling. Therefore, an advanced chemical lithography technique was applied that is based on an Atomic Force Microscope tip mediated electro-oxidation process of a self-assembled monolayer of OTS. This permits the structuring of the

monolayer with chemically active sites, which provide dedicated binding sites for the immobilization of nanoparticles by self-assembly approaches.

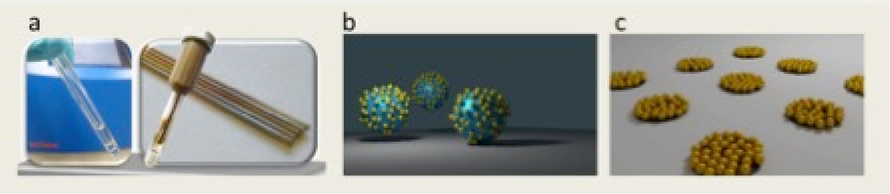

Figure 1: Overview of plasmonic nanoparticle systems for SERS applications. a) SERS active capillary systems can be efficiently fabricated by microwave-assisted synthesis protocols. b) Monodisperse PNIPAM-Au core-satellite nanoparticles stabilized by a silica shell can be used as building blocks for threedimensonal arrangements of plasmonic nanostructures. c) Electro-oxidatively structured monolayer for the fabrication of Au-cluster arrangements.

COLL 374

Bioengineered TRAIL-based therapies from cancer to fibrosis

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Tumor necrosis factor-related apoptosis reducing ligand (TRAIL) has been extensively studied in oncology. TRAIL selectively induces apoptosis in cancer cells by binding to its death receptors while sparing normal cells. However, the inherent short half-life and TRAIL resistance in primary cancers hampers its clinical development. We have developed a stable yet potent, bioengineered TRAIL and demonstrated its extended half-life in non-human primates. We recently discovered that systemically administered bioengineered TRAIL ameliorates liver cirrhosis, the advanced stage of fibrosis, in vivo by selectively eradicating activated myofibroblasts-like cells, the source cells that ultimately facilitate collagen deposition. Fibrosis is a debilitating chronic disease caused by hardening of connective tissues with no standard of care. In this talk, I will introduce how our research experience, at the crossroads of bioconjugation, drug delivery, and biology enabled the engineering of stable TRAIL-based therapies, the discovery of clinical targets for TRAIL in fibrosis towards clinical translation.

COLL 375

Molecular imaging, image-guided drug delivery, and theranostics

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After PhD work in organic chemistry with Prof. Murray Goodman at University of California at San Diego, I did post-doctoral research at Stanford University under the supervision of Prof. Xiaoyuan (Shawn) Chen. In 2008, I launched my independent

career at the University of Wisconsin - Madison and The Molecular Imaging and Nanotechnology Laboratory (http://mi.wisc.edu/) is mainly focused on three areas: 1) development of multimodality molecular imaging agents; 2) nanotechnology and its biomedical applications; and 3) molecular therapy of cancer.

In the Bioconjugate Chemistry Lecture Symposium at the 2016 Fall ACS Meeting which recognizes the exceptional achievement of Xiaoyuan (Shawn) Chen, my mentor, friend, and role model for the last 12 years and many more decades to come, I will present our recent work on molecular imaging and image-guided drug delivery in cancer and various cardiovascular diseases with peptides, proteins, and nanomaterials. The primary imaging techniques used in these studies are positron emission tomography (PET), photoacoustic tomography (PAT), optical imaging, and magnetic resonance imaging (MRI). Some of the major molecular targets that we focus on are CD105 (i.e. endoglin), VEGFR, CD146, c-Met, integrin $\alpha_v\beta_3$, among others. The nanomaterials that will be discussed in this presentation may include silica-based nanoparticles, nano-graphene oxide, micelles, iron oxide nanoparticles, 2-D nanomaterials, hybrid nanomaterials, among many others. Lastly, the emerging paradigm of intrinsically radiolabeled nanomaterials will be discussed as multi-modal PET/MRI, PET/PAT imaging agents, as well as for theranostic applications.

COLL 376

Surface modified ferritin nanocages for imaging and drug delivery

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Ferritin is a ubiquitous protein and a major component of human iron store. Each ferritin comprises of 24 subunits, including both heavy-chains and light-chains, and they constitute a cage-like structure, with an external diameter of ~12 nm and internal diameter of ~8 nm. Recombinant ferritins of relatively large quantities can be produced artificially. While apoferritin cages are very stable under physiological pH, they break down into subunits at pH 2-3 *in vitro*. Interestingly, the process is reversible: when the pH is adjusted back to neutral, the subunits reassemble into nanocages, and in an almost intact fashion. This provides a facile means to load small molecules or metal cations into the interior of ferritin cages. Meanwhile, the surface of ferritins can be modified by both chemistry and genetic methods. Functional molecules, such as peptide sequences, dye molecules, and single-chain variable fragments, can be easily imparted to the surface of ferritins. For instance, we have successfully loaded doxorubicin and $ZnF_{16}Pc$, a photosensitizer, into ferritins with high efficiency. We also showed that by imparting different targeting ligands to ferritin surface, cargos can be delivered to cancer cells, tumor endothelial cells, and cancer associated fibroblasts with high selectivity. Unlike artificial polymers, ferritins are not toxic, low immunogenic, and biodegradable. These features suggest ferritins as a powerful nanoplatform for constructing smart imaging and therapeutic formulations.

COLL 377

Application of click-chemistry bioconjugation methods in the imaging of cancer

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The use of Positron Emission Tomography (PET) for cancer imaging is a well-established and widely used molecular imaging modality both in clinical and research settings. PET offers the ability to quantitatively measure biological and receptor-based processes using a wide spectrum of specifically designed radiopharmaceuticals. The use of PET is expanding and the inclusion of longer-lived radiometal positron-emitters is broadening the application and appeal of this imaging modality.

This presentation will review the current state-of-the-art in non-standard PET nuclide application with an emphasis on the use of radiometals with peptide and antibody constructs. In addition, since the effective use of a radiometal nuclide often relies on their attachment to the targeting probe via a bifunctional chelator, this talk will focus on novel strategies for using “click” chemistry methodology for attachment of the radiometals to active biomolecules.

In addition, the development of pretargeting strategies based on an emergent type of click chemistry: the inverse electron demand [4+2] Diels-Alder cycloaddition between a tetrazine and a strained alkene dienophile will also be presented. This reaction is rapid, selective, and, most importantly, bioorthogonal, and thus presents a near ideal chemical system for in vivo chemistry. We have used this chemical technology to develop a modular strategy for the radiolabeling of antibodies, and, more recently, to create an effective and robust pretargeted PET imaging strategy for colorectal cancer.

COLL 378

Albumin based bioconjugates for diagnosis and precision therapy

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Albumin is the most abundant circulating protein in plasma and has recently emerged as a versatile protein carrier for drug targeting and for improving the pharmacokinetic profile of peptide or protein based drugs. Three drug delivery technologies related to albumin have been developed, which include the coupling of low-molecular weight drugs to exogenous or endogenous albumin, conjugating bioactive proteins by albumin fusion technology (AFT), and encapsulation of drugs into albumin nanoparticles. This lecture starts with a brief introduction of human serum albumin (HSA), and then summarizes the mainstream chemical strategies of developing HSA binding molecules for coupling with drug molecules. The recent use of Evans blue dye conjugates as molecular imaging probes and long-acting drug formulation will be highlighted. Moreover, the most important clinical applications of HSA-binding platforms will be discussed and the current challenges that need to be met for a bright future of HSA-binding will be specified.

COLL 379

Gold nanoparticle-enabled dynamic light scattering for chemical and biological target detection and analysis

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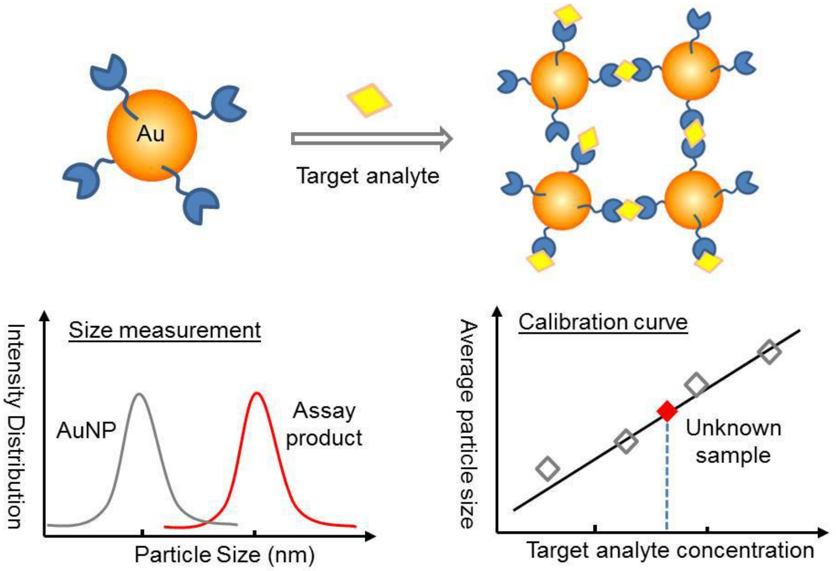
Dynamic light scattering (DLS) is an analytical technique used routinely to measure the hydrodynamic sizes of particles with diameters in the nanometer region. Gold nanoparticles are known for their exceptional light scattering properties. By combining the strong light scattering property of gold nanoparticle probes with the size measurement capability of DLS, a new technique named as D2Dx (from diameter to detections) for chemical and biological target detection and analysis was developed. Gold nanoparticles can be surface-modified with various chemical ligands, antibodies or other binding molecules to form gold nanoparticle probes. The binding of chemical or biological target analytes with their specific gold nanoparticle probes can lead to nanoparticle cluster formation, and subsequently, an average particle size increase of the assay solution. Such particle size increases can be measured by DLS, and correlated to the quantity of the target analytes. D2Dx is a single-step homogeneous solution assay, easy to perform, of low cost, and has excellent sensitivity and reproducibility. So far, this technique has been applied successfully for quantitative detection and analysis of a wide range of chemical and biological targets, including proteins, DNAs, viruses, carbohydrates, small chemicals, toxic metal ions, food and environmental toxins. In this talk, I will explain the principle of D2Dx, give an overview on the application potentials of this technique in biomedical research, food safety and environmental protection, and present our most recent results of using D2Dx for the detection of viruses and bacteria pathogens.



COLL 380

Electron transfer as a tool to create heterostructured nanoscale probes with robust, active, and enhanced sensing properties and functionality

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Sensing and diagnostics technologies using nanotechnology have advanced to the point where simple alloying and composition manipulation of the particles has been fully explored for tuning the sensing properties of the probes. In response, greater efforts are being made to create heterostructed nanoparticle probes, which involves nanoparticles with multiple components or structuring of the particles to achieve multiple functionalities, enhance particle stability or sensing activity. This class of particles includes core@shell, Janus, and other structured or assymetrical types of particles. In our own research, we have found that the plasmonic sensing properties of silver can be enhanced by coating gold nanopartices in a thin layer (within about 5 nm) of silver. This inverted structure unexpectedly leads to strong resistance to oxidation and chemical etching, resulting in sensing probes that are vastly superior to pure silver nanoparticles. The origin of the chemical stability enhancement was found to be an electron transfer phenomenon where gold initially withdraws electron density from silver sites, but ultiminately back donates electron density to silver. The research was furthered by extending the findings to new heterostructured systems including platinum coated by silver, which showed twice as much electronic enhancement as gold coated by silver. More recently we have applied the technology to silver coated by iron-cobalt coated by silver (double shell) nanoparticles, which are not only oxidation resistant, but possess a magnetically pure phase allowing these probes to be used for in-vivo studies of cellular organelles. This presentation will disscuss these findings as well as our recent studies on creating heterostructure nanoparticle probes using electron transfer as a means to

enhance particle stability and sensing properties. The results will focus on the material interfaces and the characterization of the heterostructured nanoparticles using powerful techniques such as scanning transmission electron microscopy with a high angle annular dark field detector, offering atomic resolution images and particle composition mapping with energy dispersive x-ray spectroscopy.

COLL 381

Using perovskite nanoparticles as spectrochemical probes for monitoring chemical reactions

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In this presentation we will describe the use of cesium lead halide $CsPbX_3$ (X= Cl, Br, I) perovskite nanoparticles (P-NPs) to colorimetrically detect ions in solution and monitor chemical reactions in real time. We recently described (Doane et. al., ACS Nano, 2016) that anion exchange between P-NPs and ions in solution results in a rapid colorimetric response. Photoluminescence (PL) changes of up to 160 nm are possible, allowing for detection to be visualized by eye. We have expanded this approach towards monitoring organic reactions involving organo-halides, and use the PL change to monitor reaction kinetics with great precision. We will also present recent results that show that the P-NPs can serve as halide reservoirs in a pseudo-Finkelstein reaction, and will expand on possible sensing and assaying targets.

COLL 382

Environmental egg tempera binding medium degradation analyzed by XPS and TOF-SIMS utilizing GCIS

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Binding medium degradation involves complex chemistries that occur at the surface interface of a paint layer that propagate inwards toward the bulk material, providing the basis for mechanical effects due to binding medium failure. Prior research has indicated two major correlations to the severity of binding medium degradation; i) depletion of long-chain fatty acid components within a paint layer, and ii) alteration of the amino acid composition of proteinaceous materials. In this study the effects of artificial aging (heat, humidity, and UV exposure) on thin films of egg tempera were observed through the use of x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). The newly available technology of gas cluster ionization sources (GCIS) allows for the ability to depth profile through soft materials with no beam-induced damage. By using the GCIS beam to depth profile through a degraded thin film, a 3-dimensional reconstruction that includes short-range (XPS) and long-range (TOF-SIMS) chemical information will fully characterize the chemical alteration undergone during environmental degradation. This information can then be used to produce multivariate models to quantify the severity of binding medium degradation observed in historical samples.

COLL 383

Effective electrocatalysts for oxygen reduction of by interfacial engineering

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Oxygen reduction reaction (ORR) represents a critical process at the cathodes of fuel cells and metal-air batteries. Because of its complex reaction pathways and sluggish electron transfer kinetics, effective catalysts are required to achieve sufficiently high current density that is needed for practical applications. In this presentation, we will highlight some recent progress in the design and engineering of functional nanomaterials for ORR electrocatalysis. For instance, when platinum nanoparticles were functionalized with aryl fragments by using diazonium salts as the precursors, we observed drastic enhancement of the ORR activity with increasing Hammett constants of the para-substituent groups, as a result of deliberate manipulation of the platinum electronic interactions with oxygen species. Similar enhancement was achieved when metal nanoparticles were deposited onto graphene quantum dots (GQD), where charge transfer from metal nanoparticles to GQD structural defects led to marked improvement of the ORR activity. Interestingly, the optimal defect concentration was found to increase with increasing oxygen affinity to the metal surfaces (e.g., Pt < Pd < Cu), consistent with the so-called volcano plot. In more recent studies, heteroatom-doped carbons have also been found to exhibit remarkable ORR activity, which is largely determined by the chemical nature of the dopants and effective electrochemical surface area. We developed an effective method based on thermally removable templates to prepare mesoporous nitrogen self-doped carbons that exhibited ORR activity even better than that of commercial Pt/C catalysts. Experimentally, FeOOH nanorods were formed during the oxidative polymerization of aniline by FeCl3. Pyrolysis at elevated temperatures led to the carbonization of the polymers, where the FeOOH nanorods served as the structural scaffolds to maintain the carbon skeletons and concurrently the thermal volatility resulted in the formation of abundant mesopores. Further improvement of the ORR performance was achieved by the incorporation of graphene nanosheets into the N-doped porous carbons, due to enhanced electrical conductivity within the catalyst layer.

COLL 384

Interface chemistry on metal nanocatalysts

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The interface structure on metal nanocatalysts plays a crucial role in determining their catalytic performances. However, currently there is lack of effective tools that allow us to characterize the interface structures of metal nanocatalysts at the molecular level. Such a situation prevents us from deeply understanding how the interface structure influences the catalytic performances of metal nanocatalysts. We report here our efforts towards decoding the complicated interfacial effects that promote metal nanoparticles' catalysis. Our main strategy is to create model metal nanocatalysts that make it possible to resolve the interfacial structure of interest using advanced characterization techniques, such as Sub-ångström-resolution aberration-corrected scanning transmission electron microscopy, X-ray absorption spectroscopy, X-ray single-crystal diffraction. We will discuss how the characterizations of interface structures can be simplified by the fabrication of the following four different types of model metal nanocatalysts: 1) monodisperse noble metal nanocrystals with sub-monolayer (hydr)oxide on their surface; 2) atomically dispersed metal catalysts on ultrathin metal oxide supports; 3) organic-capped ultrathin metal nanostructures; 4) atomically precise metal nanoclusters stabilized by monolayer organic ligands. The molecular understanding on how metal-metal oxide and metal-organic interfaces promote the catalytic activities and selectivities of metal nanocatalysts will be presented

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COLL 385

Hierarchical SAPO-34 zeolites by solid post-treatment for MTO reaction

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SAPO-34 suffers a lot from its short lifetime during methanol to olefin (MTO) process. Introduction of hierarchical porous into SAPO-34 zeolites crystal is an effective approach to enhance the catalytic performance. Post-treatment synthesis of hierarchically porous SAPO-34 zeolites is a promising and cost-effective method. However, the present post-treatment routes require water as the solvent, causing a lot of wastewater. Herein, we proposed a novel and green post-treatment method, which involves only parent SAPO-34 and the solid-state acid without solvent.
The as-synthesized hierarchically porous SAPO-34 catalysts exhibit superior catalytic performance in MTO reaction. Butterfly-shaped macropores appeared besides the inherent micropores after being treatment with solid-state acid treatment for 6 h at 100^{o}C (Fig. 1a,b&c). The catalyst lifetime of hierarchical SAPO-34 prolonged the original 350 minutes to 550 minutes with a methanol conversion of 99% and the selectivity to light olefins ($C_2^=$ -$C_4^=$, ~85%) remained unchanged.

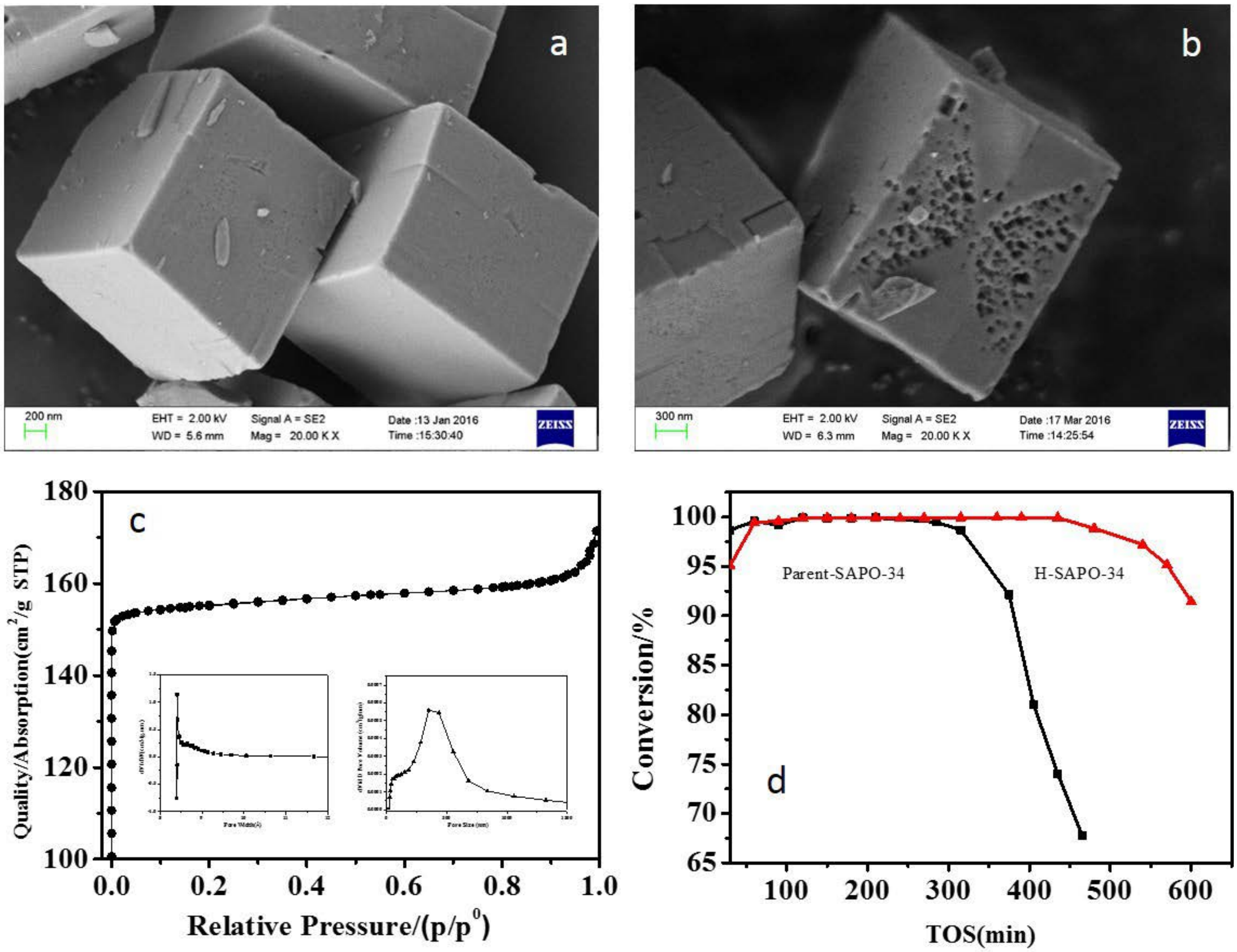

Fig. 1 (a) SEM images of parent SAPO-34; (b) SEM image of H-SAPO-34; (c) N_2 adsorption-desorption isotherm and pore size distribution of H-SAPO-34; (d) MTO catalytic properties of parent SAPO-34 and H-SAPO-34 (400^{o}C, 0.1 atm, GHSV of methanol=1.0 h^{-1}).

COLL 386

Importance of the Ti-Au interface for CO oxidation: A combined ambient pressure study over TiO_x/Au(111) inverse model catalysts

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We have attempted to elucidate the role of the Ti-Au interface in TiO_x/Au(111) “inverse” model catalysts during CO oxidation ($CO+1/2O_2 \rightarrow CO_2$), by studying the *in situ* surface chemistry as a function of TiO_x coverage on Au(111) using Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) and Reflection Absorption Infrared Spectroscopy (RAIRS). We deduced that as the coverage of TiO_x increases, the size of TiO_x nanostructures increase, while the relative Ti-Au interface decreases. Gas phase signature of reactants (CO and O_2), and products (CO_2) were clearly identified at 300 K, validating that the inverse catalyst is active for enhanced low temperature CO oxidation, while both bulk TiO_2 and Au(111), individually were inert. Stable surface intermediates including CO (ad) and CO_3^{2-}(ad) were identified under reaction conditions. The concentration of the surface bound $CO_{(ad)}$ and the $CO_3^{2-}{}_{(ad)}$ intermediates decreased with the Ti-Au interface, demonstrating a clear correlation for the presence of the Ti-Au interface and enhanced catalytic activity. The interface between TiO_x and Au likely increases the binding of $CO_{(ad)}$, while small TiO_x nanoparticles dissociate O-O bonds in O_2, and the production of the carbonate intermediates direct the pathway to CO_2 production. The TiO_x is completely oxidized (Ti^{4+}), while Au remains metallic (Au^0) during CO oxidation, suggesting that the TiO_x serves as the sole reservoir for active oxygen species (no O spillover to Au(111)) during the reaction. Our results validate that the perimeter sites between the Ti-Au interface in the *inverse* catalyst are likely comparative to Au-Ti perimeter sites in the conventional catalyst, Au/TiO_2.

COLL 387

Electrochemical redox of late transition metal perovskite oxides

***William Chueh**, wchueh@stanford.edu.* Stanford University, Stanford, California, United States

Transition-metal perovskite oxides are excellent oxygen ion conductors at elevated temperatures, and can undergo oxidation and reduction upon applying a thermal, concentration, or electrochemical driving force. The surface and bulk of these oxides serve as oxygen reservoirs, which has significant implications for their use as catalysts, electrocatalysts, and oxygen pseudo-capacitors. While the bulk properties of perovskites are relatively well understood, the surface redox properties are not. In this talk, I will present new understandings of the thermodynamics and kinetics of surface redox processes of late transition perovskites, particularly, doped LaFeO3-LaCoO3 solid-solution system. Using in-situ characterizations such as ambient pressure photoemission and absorption spectroscopies and well-defined atomically-flat surfaces, the surface redox processes are tracked as a function of electrochemical overpotentials and oxygen partial pressures.

COLL 388

Tailoring the properties of surfaces using thin films

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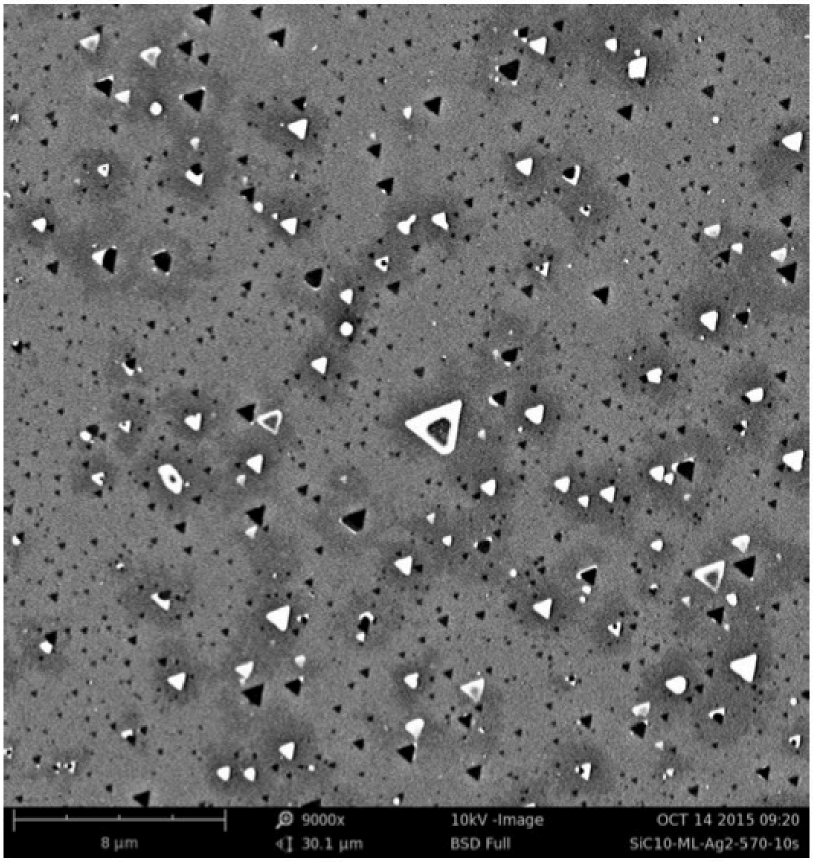
Ultrathin oxide and other nonconductive films such as carbides and nitrides can be grown by pulsed laser deposition. These films can dramatically change the electrical and chemical properties of the surface. In the case, of MgO/Ag/Mgo multilayers, we observed an increase in quantum efficiency and simultaneous decrease in work function with layer thickness in photocathodes. Photoemissive properties of cathodes are critical for electron beam applications such as photoinjectors for Free Electron Lasers (FEL) and Energy Recovery Linacs (ERL). An ideal photoemitter has a high quantum efficiency, low work function, low intrinsic emittance and long lifetime. It has been demonstrated here that emission properties may be systematically tailored by control of layer thickness in ultrathin multilayered structures. We have grown carbide/Ag/carbide multilayers to test the resilience of these films to temperature. We observed interesting diffusion patterns of the Ag and recrystalization of the carbide layer at temperatures below 700 C.



COLL 389

Atomic-scale imaging of water dissociation and OH diffusion on layered Co oxide materials

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Cobalt oxides are considered among the most promising materials as future earth-abundant catalysts for the oxygen evolution reaction (OER) in water splitting, with attractive properties in terms of stability, efficiency, abundance and low cost. In particular, oxy-hydroxide, β-CoOOH together with analogous compounds from Ni and Felayered have emerged as potential catalysts for OER, especially cobalt. It has been suggested through indirect evidence that the edges of the β-CoOOH layers may host the active sites for the OER, however, the precise nature and location of these sites has not been revealed hitherto. To understand the fundamental structure, composition and surface chemistry of these Co oxide based catalysts, we characterize here the surface of a model catalyst consisting of layered CoO_x nanoislands under ultra-high vacuum conditions by atom-resolved Scanning Tunneling Microscopy (STM) and X-Ray Photoelectron and Absorption Spectroscopies (XPS and XAS) together with density functional theory (DFT). The Au(111) surface is used as a growth template [1]. This allows for an atomic-scale investigation of the correlation between Co oxidation state and the adsorption of water, water dissociation and synergistic effects with the Au(111) substrate, as gold has been observed to strongly enhance the catalytic activity.
We find that the oxygen pressure has a profound effect on the CoO_x structure, accompanied by changes in the cobalt oxidation states. The structure at low pressure is a Co-O bilayer exposing the (111) plane with cobalt in the +2 oxidation state. However, this can be converted into an oxygen rich structure with cobalt in the +3 state,which bears strong resemblance to the β-CoOOH structure. Both structures exhibit a strong activity towards water dissociation at room temperature, leading to hydroxylation of up to 50% of the island basal plane oxygen atoms as observed in-situ by both dynamic STM movies recorded during H_2O dosing and by corresponding analysis of the hydroxyl component in the O1s core-level XPS spectrum. The reactivity towards water dissociation is measured as function of island edge concentration, revealing the island edges to host the most active sites. Detailed understanding of the reaction pathways of water dissociation observed in STM is provide by DFT which, importantly, reveals the assisting role of another water molecule during water dissociation and subsequent diffusion.

COLL 390

Physical and chemical design of catalysts for OER and CO2RR

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We report an updated picture of the use of multiple metals, and their homogeneous dispersion in oxy-hydroxides, to optimize the energetics of OER catalysts. We also

discuss a physical picture of electrochemical reduction of CO2 in nanostructured materials systems.

COLL 391

Catalytically active phase of methanol oxidation over Cu-based catalysts

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Different oxygen species, such as chemisorbed oxygen, subsurface oxygen, surface and bulk oxides, are typically present in the majority of “real-world” metal catalysts under reaction conditions. However, their role in catalysis is still very unclear and often leads to controversies regarding the nature of the catalytically active phases. Copper-based catalysts are well known to be active for various gas-surface catalytic reactions including the water–gas shift reaction, methanol synthesis and methanol oxidation, carbon monoxide oxidation, and fuel cell electrodes. Surface oxidation and the formation of Cu oxide overlayers are believed to play a critical role in copper catalysis. By employing a combination of complementary *in situ* tools ranging from atomically resolved scanning tunneling microscopy (STM) imaging to nanoscale structure and morphology information by low-energy electron microscopy (LEEM) to the overall surface chemistry provided by synchrotron-based ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) and coordinated density-functional (DFT) modeling, we provide new mechanistic understanding of the catalytic partial oxidation of methanol (POM) reaction catalyzed by Cu-based catalysts with controlled surface chemistry that changes sequentially from metallic copper, to oxygen chemisorbed surface (surface reconstruction), then to Cu_2O, and finally to CuO. The study leads to an improved understanding of a longstanding question regarding the nature of the catalytically active phase in Cu based catalysts in the POM reaction and identifes the critical chemistry factors that control the catalytic reaction.

COLL 392

Preparation and chemical reaction kinetics of tungsten bronze thin films and nanomaterials with and without a catalyst

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Microcrystalline tungsten bronze thin films were prepared using wet chemical techniques to reduce a tungsten oxide thin film that was prepared by thermal oxidation of a sputter deposited tungsten metal film on a quartz substrate. The crystallinity of these films was determined by X-ray diffraction and the surface was characterized by X-

Ray and Ultra-Violet Photoelectron spectroscopy. The total amount of hydrogen incorporated in the film was monitored using absorbance spectroscopy at 900 nm. The oxidation kinetics of the film and the hydrogenation of nitrobenzene in hexane were measured as a function of film thickness. A satisfactory fit of the resulting kinetics was obtained using a model that involves proton diffusion from the bulk of the film to the surface, followed by the reaction of the surface protons with the oxidants. Finally, the dependence of the reaction rates on the presence of catalytic amounts of first row transition metals on the surface of the film was explored. These nitrobenzene results on well defined surfaces are complemented by kinetic measurements of nanometric bronzes with hydrogen and organic peroxides.

COLL 393

Solid-state nuclear magnetic resonance to probe the interaction of nanomaterials with model and natural cell membranes

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The cell membrane is an important biointerface that can be targeted or crossed by natural or engineered molecules. To better understand the action mechanism of these molecules, it is thus essential to understand their interaction at a molecular level. Solid-state nuclear magnetic resonance (SS-NMR) spectroscopy is a valuable tool for this purpose as it allows monitoring changes in the organization and dynamics of the lipids in the membranes. Such experiments are usually carried out with membrane mimetics such as phospholipid bilayers, using ^{31}P SS-NMR to probe the polar region of the bilayer, or ^{2}H SS-NMR with deuterated lipids to study perturbations of the hydrophobic core. However, the complex composition of natural membranes has encouraged the development of challenging studies on intact cells to take into account all constituents. To do so, appropriate isotopic labeling of the cells must be carried out. In this presentation, we will illustrate how SS-NMR using model membranes *and* intact cells can bring complementary information on the antibacterial action of fullerenol nanoparticles. The interaction with model bacterial membranes made of DPPC (dipalmitoylphosphatidylcholine) and DPPG (dipalmitoylphosphatidylglycerol) will be compared to a study on intact *Escherichia coli* for which we have developed a ^{2}H-labeling protocol for the phospholipids. ^{31}P and ^{2}H SS-NMR showed a preferential affinity of fullerenol for the anionic DPPG in DPPC/DPPG bilayers, due to the polar hydroxyl moiety of this phospholipid at the bilayer surface. This was in agreement with the tighter packing of the lipids observed in the outer membrane of *E.coli* revealed by ^{2}H SS-NMR, induced by an interaction with the lipopolysaccharides. Model membranes are thus useful to scrutinize interactions with specific lipid components. Finally, we will present recent developments to study intact microalgae for environmental applications using high-resolution ^{13}C SS-NMR.

COLL 394

Role of local charge density in polycation-wrapped nanoparticle interactions with model cell membranes

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As part of a broad research effort in the NSF-funded Center for Chemical Innovation on Sustainable Nanotechnology, the goal of this work is to understand how nanoparticles interact with biologically relevant interfaces *in situ* at the molecular level. Understanding these interactions at the molecular level is important for predicting and controlling interactions of nanomaterials with living systems as well as designing environmentally sustainable nanomaterials. Using a multidisciplinary approach to study how nanoparticles interact with model cell membranes, we found that polycation-wrapped gold nanoparticles can disrupt the structure of supported lipid bilayers. We hypothesize that these polycation-wrapped nanoparticles deliver locally high concentrations of charge to the lipid bilayer, which allows the polycation-wrapped particle to remove lipids from the bilayer structure. We seek to understand the molecular level mechanism that drives these interactions. Using surface-specific nonlinear optical spectroscopies, namely second harmonic (SHG) and sum frequency generation (SFG), we investigate the interactions of polycation-wrapped nanoparticles and free polycations (without the nanoparticle present) with lipid bilayers. Specifically, SHG spectroscopy allows us to probe binding interactions and estimate the charge density associated with the adsorbate, while SFG spectroscopy allows us to investigate how the molecular structure and orientation of the lipids changes upon interaction with the adsorbate. Combining the determined surface charge density from second harmonic generation with measurements of attached mass from quartz crystal microbalance, we can estimate the number of charges associated with a polycation, or polycation-wrapped nanoparticle, attached to a lipid bilayer. These results provide experimental constraints for theoretical calculations on the same system, which yield atomistic views of the structures that are formed when certain polycations or polycation-wrapped nanoparticles interact with specific lipid membranes.

COLL 395

Peptoid-bicelles as surrogate cell membranes

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The study of membrane-affiliated interactions is significant to the understanding of cell function, detecting biomarkers to diagnose disease, and testing the efficiency of new therapeutic targets. The amphiphilic character of membrane proteins makes them difficult to work with due to low stability. Model membrane systems can be used to stabilize membrane protein structure and maintain native activity. The model membrane system of focus in this study are bicelles, disc-shaped lipid bilayers created by combining long- and short-chain phospholipid pairs. We have modified the chemistry at the edges and at the planar region of bicelles by incorporating peptoids, which are non-natural protein mimics. Peptoids are ideal for this application since a large diversity of side chains can be easily incorporated in a sequence-specific manner. In these preliminary studies two sequence of peptoids were designed to contain a lipophilic side chain at the C-terminus for interactions with the short and long-chain lipid tail groups for the edge and planar modification, respectively as well as thiol groups at the N-terminus for characterization. Peptoid-bicelles were imaged using transmission electron microscopy and size analysis was performed by dynamic light scattering. The presence of peptoids in the edges and planar regions of the bicelles was confirmed by attachment of gold nanoparticles to the thiol groups within the peptoid sequence. Our results show that the designed peptoids incorporate preferentially into the edges and planar regions of the bicelles, respectively as expected. Further studies will be performed to alter the diameter of the bicelles to allow for study of membrane proteins and complexes of various sizes.

COLL 396

Interplay at inorganic nanoparticle and zwitterioinic lipid bilayer interfaces

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Zwitterionic phosphocholine (PC) lipids are known for its anti-fouling property, yet it is adsorbed by all tested inorganic nanoparticles. This talk summarizes recent findings from our lab on this topic, with a focus on surface forces and adsorption mechanism. It is well-established that PC liposomes adsorb silica followed by membrane fusion with the surface. However, titania and other metal oxides only adsorb the liposome without fusion. These oxides adsorb PC liposomes via the lipid phosphate bonding, while the choline headgroup poses a steric effect. Citrate-capped AuNPs are adsorbed very strongly via van der Waals force, inducing a strong local gelation. The consequence of the gelation is a transient liposome leakage upon AuNP adsorption or desorption, and AuNP aggregation on the liposome surface. Finally, all the carbon-based nanomaterials (graphene oxides, carbon nanotubes and nanodiamond) are adsorbed by PC liposomes mainly via hydrogen bonding. These inorganic/lipid hybrid materials provide an interesting system for fundamental biointerface studies, and they are also useful for analytical and biomedical applications.

COLL 397

Influence of divalent cations on deformation and rupture of adsorbed lipid vesicles

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The fate of adsorbed lipid vesicles on solid supports depends on numerous experimental parameters and typically results in the formation of a supported lipid bilayer (SLB) or an adsorbed vesicle layer. One of the poorly understood questions relates to how divalent cations appear to promote SLB formation in some cases. The complexity arises from the multiple ways in which divalent cations affect vesicle-substrate and vesicle-vesicle interactions as well as vesicle properties. These interactions are reflected, e.g., in the degree of deformation of adsorbed vesicles (if they do not rupture). It is however experimentally challenging to measure the extent of vesicle deformation in real-time. Herein, we investigated the effect of divalent cations (Mg2+ , Ca2+, Sr2+) on the adsorption of zwitterionic 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) lipid vesicles onto silicon oxide- and titanium oxide-coated substrates. The vesicle adsorption process was tracked using the quartz crystal microbalance-dissipation (QCM-D) and localized surface plasmon resonance (LSPR) measurement techniques. On silicon oxide, vesicle adsorption led to SLB formation in all cases, while vesicles adsorbed but did not rupture on titanium oxide. It was identified that divalent cations promote increased deformation of adsorbed vesicles on both substrates and enhanced rupture on silicon oxide in the order Ca2+ > Mg2+ > Sr2+ . The multiple influences of divalent cations on different factors in the system are discussed, clarifying experimental observations on both substrates. Taken together, the findings in this work offer insight into how divalent cations modulate the interfacial science of supported membrane systems.

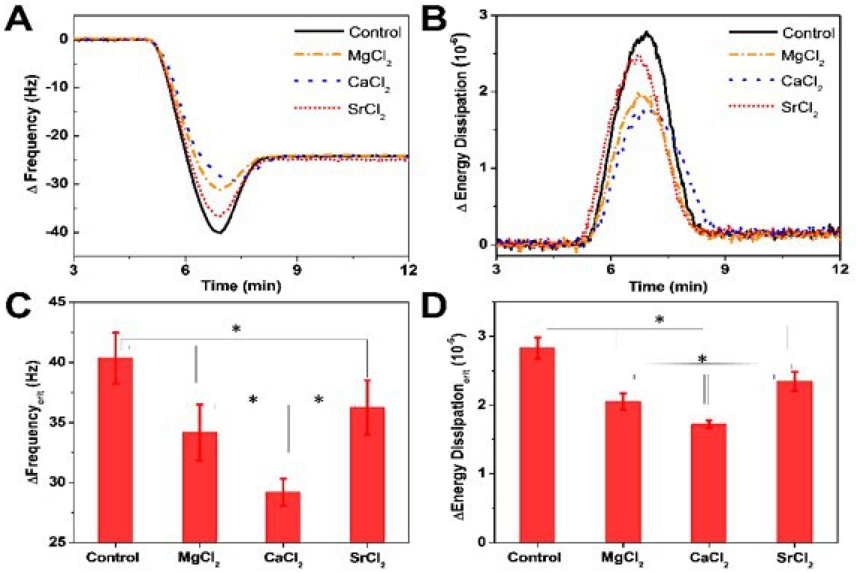

Figure 1. Effect of Divalent Cations on Vesicle Adsorption and Rupture on Silicon Oxide. QCM-D measurements were performed and vesicles were added at *t* = 5 min. **(A)** Δf shift and **(B)** ΔD shift as functions of time. Mean and standard deviation of **(C)** $|\Delta f_c|$ and **(D)** ΔD_c values (n = 4 measurements). The control experiment contained the same vesicle preparation and buffer conditions without divalent cations.

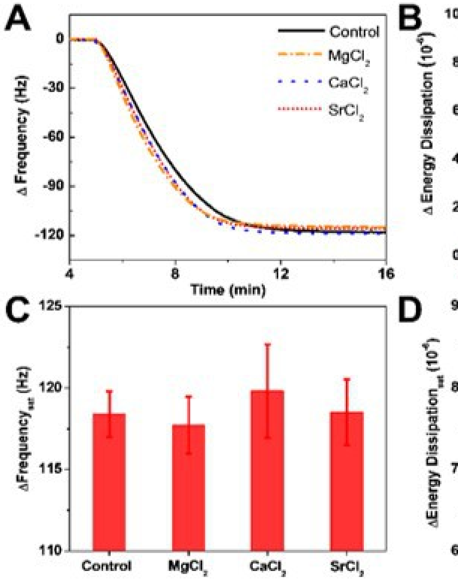

Figure 2. Effect of Divalent Cations on Vesicle
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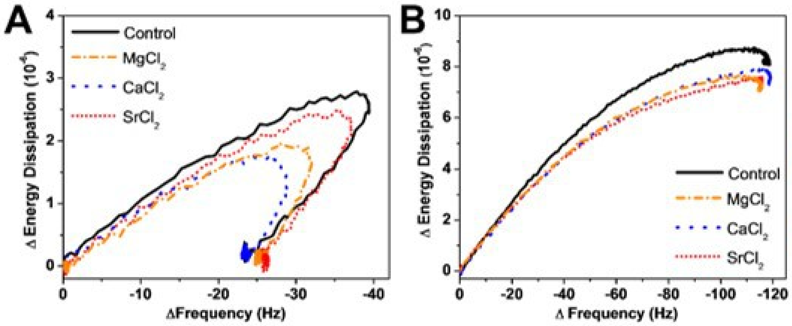

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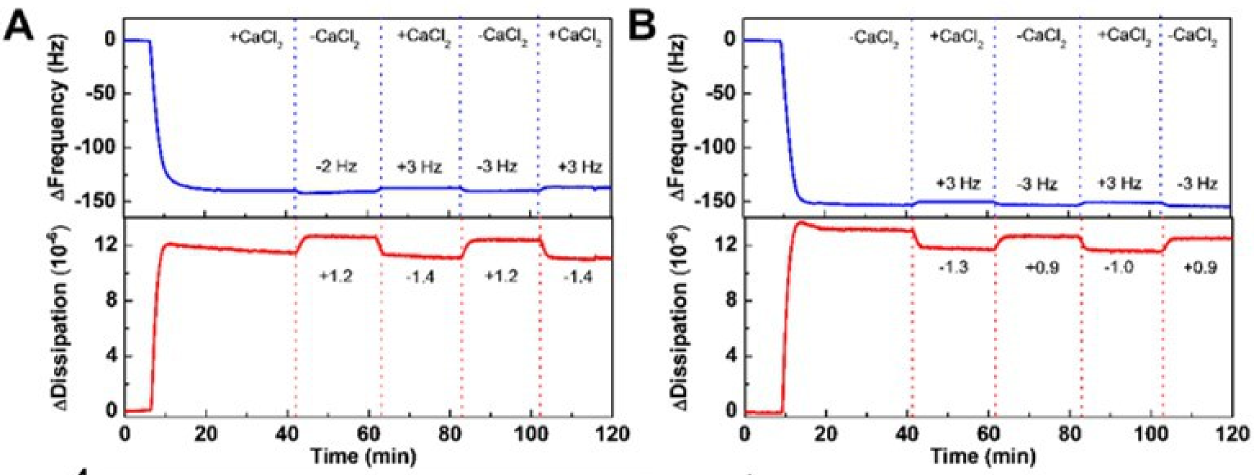

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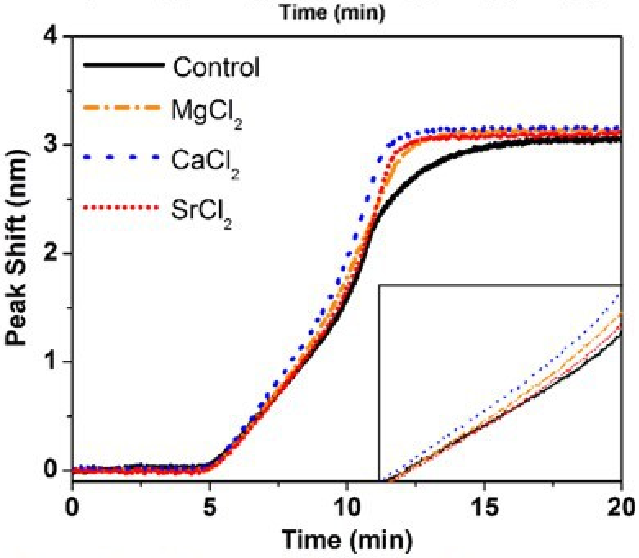

Figure 5. Influence of Divalent Cations on the Deformation of Adsorbed Vesicles on Silicon Oxide. LSPR measurements were performed and vesicles were added at t = 5 min. The time-resolved shift in the centroid position of the extinction wavelength is reported as a function of time.

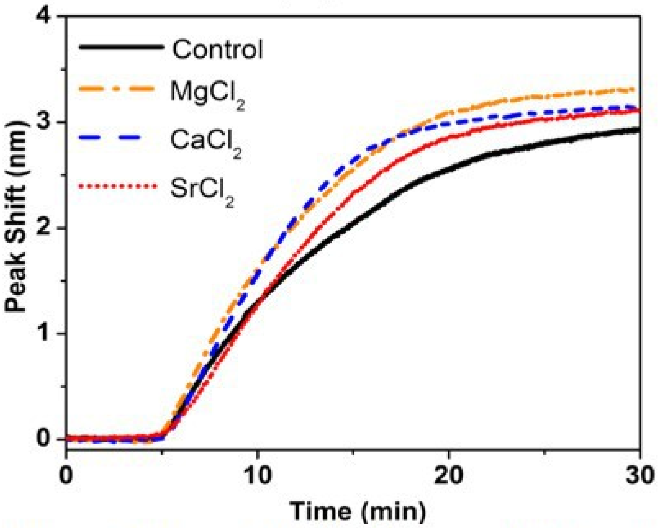

Figure 6. Influence of Divalent Cations on the Deformation of Adsorbed Vesicles on Titanium Oxide. LSPR measurements were performed and vesicles were added at t = 5 min. The time-resolved shift in the centroid position of the extinction wavelength is reported as a function of time.

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COLL 398

Nanoparticle-biomembrane interactions investigated by *in situ* surface nonlinear spectroscopy

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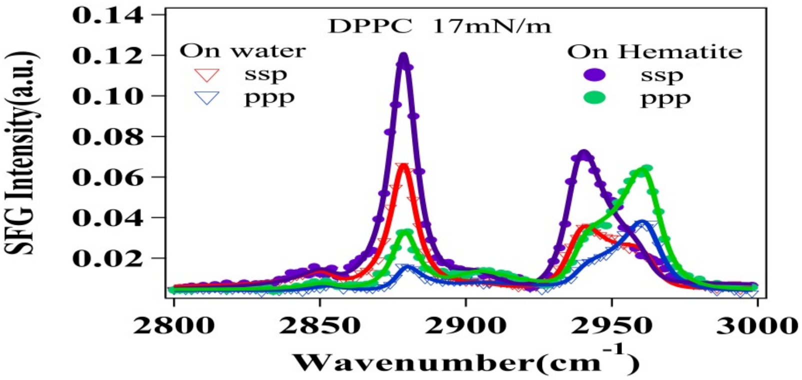
The interactions between nanoparticles and biological membranes play critical roles in the toxicity and biomedical functions of nanomaterials. However, there is still a lack of the molecular-level understandings of how the biological membrane structures respond to the nanoparticle attachments. In this presentation, we will demonstrate the recent progresses in the *in situ* characterization of nanoparticle-bimembrane interactions using

the sum frequency generation vibrational spectroscopy (SFG-VS), a surface-selective nonlinear optical probe with the submonolayer sensitivity. The molecular orientations and interfacial assembly structures of several typical phospholipid Langmuir monolayers influenced by the hematite nanoparticles will be discussed in detail. Assisted with the atomic force microscopy measurements, we discovered the hematite nanoparticles prefer to being attached to the loosely packed phospholipid domains at the air/water interface. The quantitative analysis of the polarization-dependent SFG-VS results revealed that with the presence of the nanoparticles at the lipid surfaces, the phospholipid assembly becomes much more tightly packed. These results clearly show that the sum frequency generation vibrational spectroscopy is fully capable of exploring the nanoparticle-biomembrane interactions in the aqueous environments.



COLL 399

Using total lipid extracts to construct a more realistic model membrane for better characterization of nanomaterial-cell interactions

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Artificial lipid membranes with tunable physicochemical properties are commonly used as model systems to study nanomaterial-cell interactions. Most of the studies used only one or a few phospholipid classes to construct the supported lipid bilayers (SLBs), which is a substantial simplification of the real mammalian/bacterial cell membrane.

To mimic the heterogeneous composition and complex nature of cell membrane more closely, total lipid extracts (TLEs) from *Escherichia. Coli* was used in this study. TLEs consist of a range of biological lipids: phosphatidylethanolamine (PE, ~57.5%), phosphatidylglycerol (PG, ~15.1%) and cardiolipin (CL, ~9.8%). To contrast with the TLEs, 1,2-dioleoyl-***sn***-glycero-3-phosphocholine (DOPC), a commonly used model phospholipid, was chosen as a simplified lipid bilayer composition.

We employed zinc sulfide (ZnS) as our model nanoparticles (NPs) which can be found naturally (e.g., sediment pore water) and anthropogenically (e.g., quantum dots in nanoelectronics). Cysteine, an important biological thiol was used to stabilize the ZnS NPs.

Quartz crystal microbalance with dissipation monitoring (QCM-D) was used to detect the formation of SLBs on silica sensor surfaces and the subsequent deposition of ZnS NPs. Typical QCM-D experiments involve passing solutions of NPs through a flow module that contains an electrode with phospholipid bilayers on silica substrate, and changes in resonance frequency are monitored as mass deposit onto the supported bilayers. Plots of frequency shift with respect to time serve as a fingerprinting tool to reveal the unique NP deposition dynamics. We observed that there were no intact lipid vesicles on the silica surfaces after the formation of SLBs using both TLEs and DOPC.

In addition to QCM-D, we are using surface-enhanced infrared spectroscopy (SEIRAS) as an in-situ tool to reveal the mechanisms of interactions between TLEs and ZnS NPs in real-time. By examining the SEIRAS spectra changes at infrared bands of interest, we are probing the role of specific functional groups as well as driving forces behind the interactions.

In summary, this study examines the feasibility of using TLEs as a more realistic model cell membrane system. When combined with QCM-D and SEIRAS, such studies may provide explanations of why some NPs are deposited to the model lipid membrane while others are not.

COLL 400

Development of a non-living model system for cell membranes to investigate cell injury by nanoparticle

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While our exposure to nanomaterials (NMs) has increased with advancements in nanotechnology, understanding harmful effects of such materials on humans is still wanting. The interactions between living cells and NMs that lead to adhesion and uptake of NMs and subsequent cell damage need elucidation. Here we have developed a novel non-living model system for cell membranes, which is suitable for studying interactions between living cells and NMs. In contrast to existing model systems for cell membranes –typically supported lipid bilayers– a soft hydrogel-based support for the lipid bilayer has been designed. The soft support architecture is robust and its mechanical behavior can be tuned to mimic that of living cells.

AFM indentation experiments show significant differences in the elastic modulus, adhesion forces and rupture forces of lipid bilayers with soft underlying supports compared to lipid bilayers on a hard substrate. The physiological relevance of the developed system is clear from AFM indentation studies, where the system undergoes

considerable deformation *before* and *after* bilayer rupture. This behavior is similar to that of real cells, in which deformation of cytoskeleton is dominant over that of the cell membrane, allowing cell membrane to bend and wrap NMs. Our current effort is to elucidate the physio-chemical and mechanical aspects of the interactions between NMs and this model system for cell membranes.

COLL 401

Curvature-undulation coupling as a basis for curvature sensing and generation in bilayer membranes at molecular and colloidal scales

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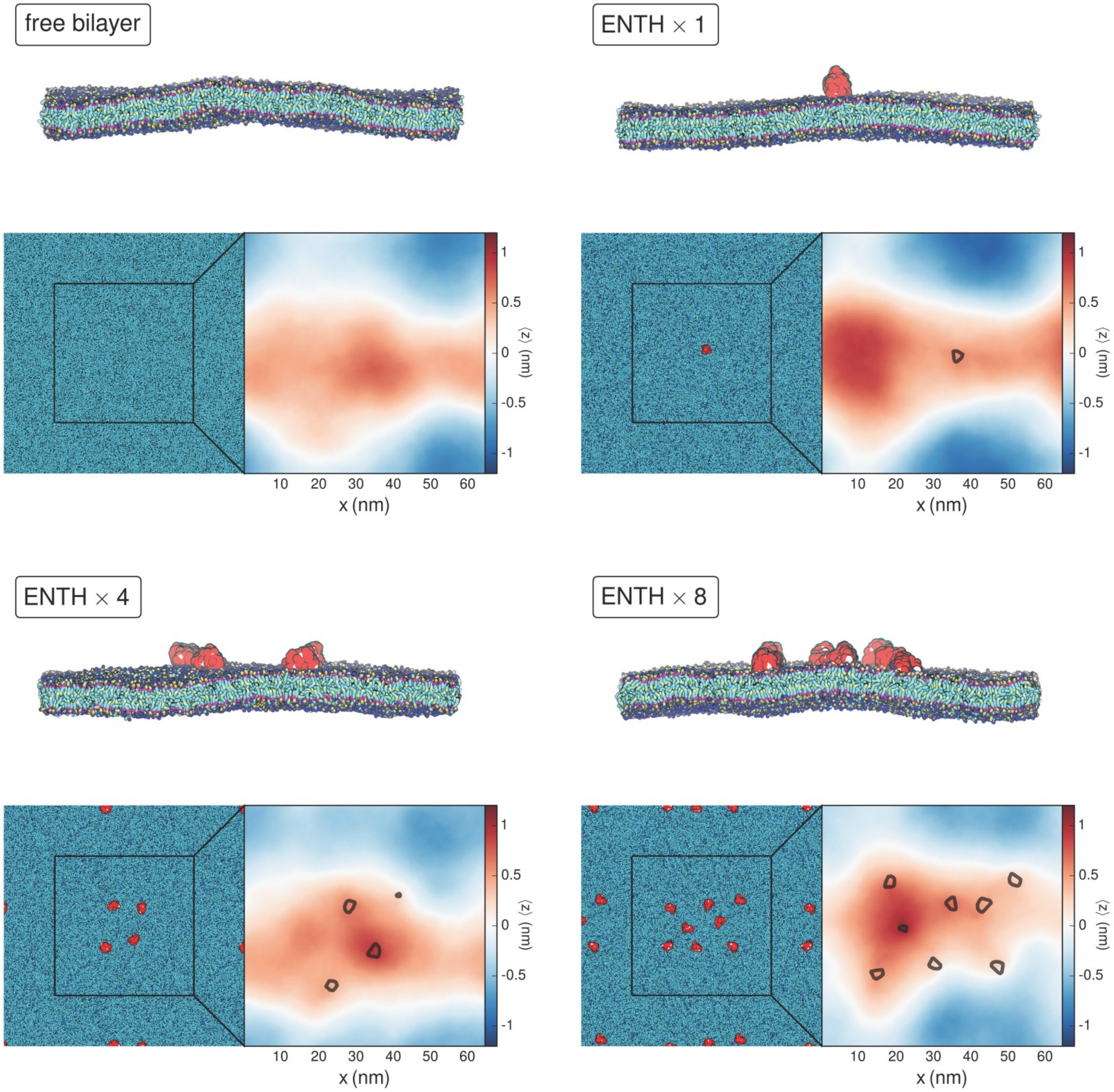
Most intracellular trafficking and many inter-cellular communications are orchestrated by curvature-driven or curvature associated cellular processes. Hence, understanding how proteins sculpt lipid bilayers is vital to our understanding of how cell membranes modulate cell signaling pathways and consequent cell fate. We present coarse-grained molecular dynamics simulations of the epsin (ENTH) domain interacting with a lipid bilayer and demonstrate a rigorous theoretical formalism and analysis method for computing the induced curvature field in varying concentrations of the protein in the dilute limit. Our theory is based on the description of the height-height undulation spectrum in the presence of a curvature field. We formulated an objective function to compare the acquired undulation spectrum from the simulations to that of the theory. We recover the curvature field parameters by minimizing the objective function even in the limit where the protein-induced membrane curvature is of the same order as the amplitude due to thermal undulations. The coupling between curvature and undulations leads to significant predictions: (1) under dilute conditions, the proteins can sense a site of spontaneous curvature at distances much larger than their size; (2) as the density of proteins increase the coupling focuses and stabilizes the curvature field to the site of the proteins We show that the curvature undulation coupling influences adhesion behavior at molecular as well as colloidal scales by investigating the interactions of functionalized nanocarriers with membranes.



Simulation snapshots showing a side profile, top view under periodic boundary conditions, and average height profile h(z) of a free bilayer along with either one, four, or eight ENTH domains (red). We omit water and counterions for clarity. The top view shows the size of the periodic simulation box (black square).

COLL 402

Defining single molecules forces required to activate cellular signaling using tension gauge tethers and nano yoyo

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Cell-cell and cell-matrix mechanical interactions through membrane receptors direct a wide range of cellular functions and orchestrate the development of multicellular organisms. To define the single molecular forces required to activate signaling through a ligand-receptor bond, we developed the Tension Gauge Tether (TGT) approach in which the ligand is immobilized to a surface through a rupturable tether before engaging with the receptor. TGT serves as an autonomous gauge to restrict the receptor-ligand tension. Using a range of tethers with tunable tension tolerances, we show that cells apply a universal tension of ~40 pN to single integrin-ligand bonds during initial adhesion. We found that less than 12 pN is required to activate Notch receptors. Next, we developed a novel low tension gauge tether (LTGT) platform that utilizes low unbinding force between single-stranded DNA (ssDNA) and ssDNA binding protein (SSB) (~4 pN dissociation force at 500 nm/s pulling rate). The ssDNA wraps around SSB and, upon application of force, unspools from SSB, much like the unspooling of a yoyo. One end of this nano yoyo is attached to the surface though SSB while the other end presents a ligand. A Notch receptor, upon binding to its ligand, is believed to undergo force-induced conformational changes required for activating downstream signaling. If the required force for such activation is larger than 4 pN, ssDNA will unspool from SSB and downstream signaling will not be activated. Using these LTGTs, in combination with reguilar TGTs , we demonstrate that Notch activation requires forces between 4-12 pN.

COLL 403

Spatio-temporal control of cell adhesion by nanoscale interactions of cell surface receptors

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During adhesion and spreading, cells form focal adhesions, micrometer-sized structures comprising transmembrane and intracellular protein clusters. Over the past two decades these structures have been extensively studied to elucidate their organization, assembly, and molecular composition, as well as to determine their functional role. Synthetic materials decorated with extracellular matrix molecules, are widely used to induce specific cellular responses dependent on cell adhesion. Nanotechnology provides tools to mimic and investigate such responses at single molecule resolution. This presentation focuses on cell interactions with nanostructured and chemically

functionalized surfaces presenting integrin-binding peptides and growth factors. Different aspects of cell adhesion and adhesion-mediated mechanotransduction induced by surface immobilization and spatial distribution of the ligands will be shown.

COLL 404

Observing single membrane proteins under mechanical tension

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More than one third of our genome encodes membrane proteins, which are essential gate keepers of cellular information. In spite of their importance in biological sciences, membrane proteins have been largely shunted aside in our efforts to understand their working mechanisms, in particular, in real time. I will talk about our recent efforts, where we endeavor to apply single-molecule magnetic tweezers to observe understand their molecular gymnastics. By pulling single membrane proteins with pN-scale force using magnetic tweezers, we are able to follow conformational changes of the membrane proteins at sub-nm resolution [1,2]. I also demonstrate this approach eventually leads to construction of the folding energy landscape of a-helical membrane proteins in a native bilayer environment [3]. This suggest a path toward understanding the structure and function relationship of membrane proteins at the single-molecule level.

COLL 405

Interrogation of spatial, temporal, and mechanical responses of cell signaling with single-cell perturbation nanomodules

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Spatial segregation, clustering, scaffolding, and compartmentalization of receptors as well as ligand-receptor interactions play critical means of controlling the molecular structures, and activities of receptors, and thus signaling of cells. In mechanical signaling that senses and responds to physical properties of extracellular environments, mechanical force resulting from cell-matrix and cell-cell interactions additionally serves as a key regulator of signaling. These spatial, molecular (*i.e.* ligand-receptor interaction), and mechanical cues often interplay either concurrently or consecutively in many mechanical signaling processes. This enables a vast diversity of signaling outcomes, orchestrating complex multicellular behaviors and functions in developmental, physiological, and pathological processes. Despite our increased

understanding of mechanical signaling via recent advances in imaging and force-sensing tools, much is still unknown about the interplay between spatial, molecular, and mechanical cues and how they are integrated to potentiate mechanical signaling. To address this unmet need, we developed single-cell perturbation modules based on nanoparticles capable of localizing, visualizing, and mechanically activating mechanosensitive membrane proteins at the single cell or molecule level. The key to this nanomodule is the ability to quantitatively deliver a specific spatial, biochemical, and mechanical cue to any desired location and at any given time. In this talk, I will discuss about design, fabrication, and utility of the nanoprobes as a perturbative tool. I will further discuss about applications of nanoprobe systems to dissect, interrogate, and understand the mechanisms underlying cell-cell communication processes via Notch and E-cadherin.

COLL 406 – Withdrawn.

COLL 407

Poly(styrene methyl methacrylate) microparticles: A mechanistic study of particle formation

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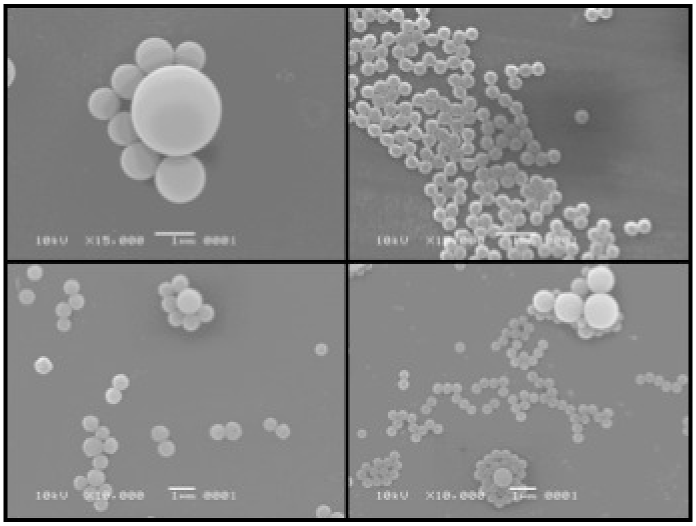
Polystyrene latex microspheres (PSLs) have been utilized as a seed material in particle image velocimetry (PIV), a measurement technique conducted in wind tunnels to measure flow velocity. PSLs are particularly useful for PIV measurements due to their uniform size and relatively low density, determined *a priori*, resulting in a shorter time period required to accurately reflect the airflow velocity (i.e. lag-time). Generation of ultra-low density PSLs would further reduce particle lag-time and extend the duration of particle airflow entrainment due to the reduced mass of the PSLs. In this work, a series of copoly(styrene methyl methacrylate) synthesis experiments were conducted to further elucidate the mechanism of copolymer microsphere formation via surfactant-free emulsion polymerization. This information was critical toward the development of ultra-low density PSLs. The resultant PSLs were characterized using various microscopic and spectroscopic techniques to determine the effects of particle composition and the effect of monomer addition time on particle size, morphology, and distribution. Through these studies, it was determined that PSLs generated from methyl methacrylate (MMA) only, having a higher solubility in water than styrene, were more reactive with the water-soluble initiator, potassium persulfate, relative to the styrene only case, resulting in formation of smaller particles. For mixed monomer compositions, where the styrene monomer was added at specific times after the initiation of MMA polymerization, it was

determined that an increase in solvated monomer concentration (i.e. the amount of monomer present in solution at the time of initiator addition) increased the number of particles formed. Delaying styrene addition maintained solvated monomer concentrations for longer reaction times resulting in extended stable particle growth.



COLL 408

Hollow, core-shell and ultra-low cross-linked microgels at fluid and solid interfaces

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We investigate the influence of the structure of microgels on their behavior at interfaces. In particular we study three different types of microgels: (i) core-shell microgels with a solid silica core surrounded by a cross-linked poly(*N*-isopropylacrylamide) polymer shell (with different cross-link densities); (ii) the corresponding hollow microgels where the core was dissolved; and (iii) ultra-low cross-linked PNIPAM microgels. The structure in solution was determined by means of neutron and light scattering. The structure of the microgels at interfaces was investigated by scanning force and electron microscopy. Compression isotherms of the microgel-laden oil-water interfaces were determined. They show that the removal of the core leads to an increase of the surface pressure at low compression and the same effect can be observed when the polymer crosslink density is decreased. Low cross-link density and a missing core thus facilitate spreading of the polymer chains at the interface and, at high compression, hinder the transition to close hexagonal packing. It is especially remarkable that a low cross-link density leads to a high compression modulus at low compression, while this behavior is reversed at high compression. This is related to an enhanced spreading of polymer chains at the

interface and thus high adsorption energy. These conclusions are fully supported by computer simulations, which show that the cross-link density of the polymer shell defines the degree of deformation at the interface. Additionally, the core restricts the spreading of polymer chains at the interface. These results illustrate the special behavior of soft microgels at liquid interfaces.

Virtanen, O.; Mouran, A.; Richtering, W. submitted

COLL 409

Modelling clay-polymer nanocomposites using a multiscale approach

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A nano-composite is defined as a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometres (nm); we have developed an advanced multiscale simulation system to predict the properties of polymer-clay nanocomposites based on their molecular structures and composition. These methods could have applications in modelling a wide range of materials and it is our aim to create a “virtual lab” to compute the properties of new soft materials based simply on knowledge of their chemical composition, molecular structure and processing conditions. Here we will present our findings from modelling chemically specific combinations of clay, polymers and organic surfactants. We use our multiscale methods and tools to take us from a parameter free quantum description to atomistic and coarse-grained simulations, ultimately leading to predictions of the materials properties of these nanocomposites. Our simulations approach realistic sizes of clay platelets (diameter 100 Å) at low clay volume fractions (5%). These systems exhibit property enhancements compared to the pristine polymer (elastic properties, gas permeation), but homogenous dispersion of the clay sheets is required.

Our multiscale approach provides us with predictions of the melt intercalation behaviour and final morphologies of organic-treated montorillonite clay – polyvinyl-alcohol and montorillonite clay – polyethylene-glycol systems. Many hitherto unobserved phenomena come into view as a result of this study, including the dynamical process of polymer intercalation and exfoliation into pristine and organo-treated clay tactoids and the ensuing aggregation of polymer-entangled tactoids into larger structures. We observe the role of surfactants and are able to elucidate how it facilitates polymer intercalation and ultimately clay sheet exfoliation, which is driven by attraction to the clay surfaces. We will also present our recent findings on the use of shear forces to separate aggregated tactoids.

From our multiscale simulations, we can compute various characteristics of these nanocomposites, including clay-layer spacings, out-of-plane clay sheet bending

energies, X-ray diffractograms and materials properties, which we relate to the system's final morphology.

COLL 410

Bio-compatible gel formation and its application in drug delivery studies

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The current study is focused on formation of bio-compatible gel by using cellulose nanocrystals (CNCs) and Closite-Na^+ (CNa^+) montmorillonite (MMT) clay by simple sonication process without any chemical modifications, primarily for drug delivery application. Three different weight ratios 1:1, 1:2 and 2:1 of CNCs to CNa^+ clay were taken for the gel formation. Polarized optical microscopy (POM), X-ray diffraction spectroscopy (XRD) and field emission scanning electron microscopy (FESEM) techniques were utilized for structural analysis of the gel. POM and FESEM studies confirmed the formation of cubic shape micro-nano complex structure in-between CNCs and CNa^+ clay for the weight ration 2:1 of CNCs to CNa^+ clay. Particle size analysis via light scattering technique showed that the distribution of particle diameter is in the range of 70 nm – 120 nm. Interaction between CNCs and CNa^+ clay due to their ion exchange capabilities was confirmed by Fourier transform infrared spectroscopy (FTIR). Thermal stability of the complex was analyzed by thermal gravimetric analysis. 5-Fluorouracil, which is an anti-cancer drug was loaded on the CNC-CNa^+ gel of weight ratio 2:1 and its release studies were carried out. UV–Vis spectroscopy analysis confirmed the drug loading on gel and the loading efficiency was around 30%. Drug release experiment was carried out in phosphate-buffered saline (PBS) medium, which gave satisfactory results. Thus the gel formed by simple sonication technique in this study by using CNCs and CNa^+ clay may be utilized in drug delivery area.

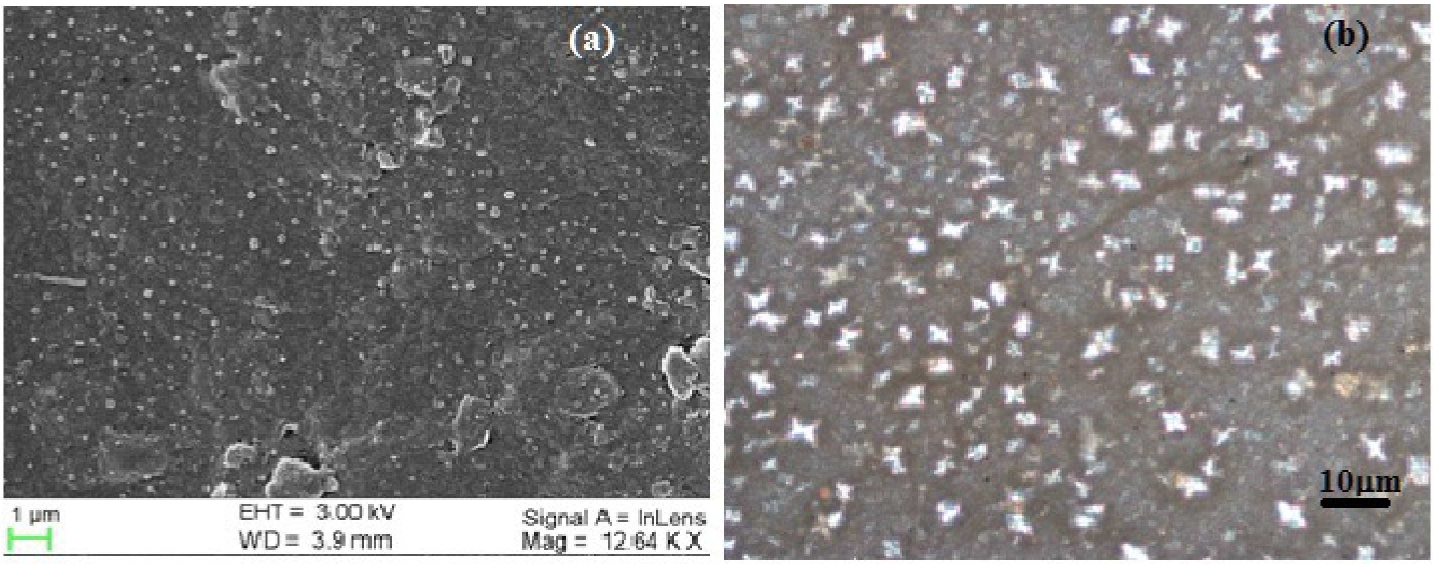

Figure 1: (a) FESEM and (b) POM images of themicro-nano complex cubic shaped CNC: CNa+ at weight ratio of 2:1

COLL 411

Morphology and response of mosaic polymer brushes

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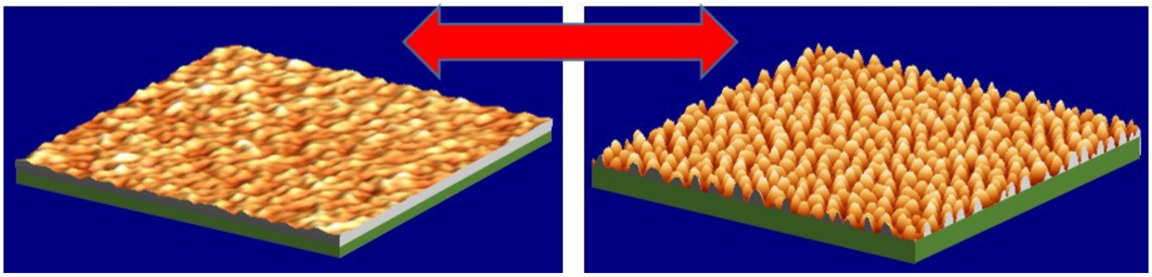
Mosaic polymer brush (MB) is an array of homogeneously distributed islands of densely grafted polymers, which lateral sizes and separation distances are comparable to the extended polymer chain length, i.e. 10 - 50 nm. Our approach to fabrication of MB utilizes the phenomenon of microphase separation in thin films of supramolecular assemblies of block copolymers (ABC). Selective attachment of one of the blocks of the ABC to the substrate surface results in the well-defined patches of tethered polymers with a high local grafting density. These MB exhibit variable morphologies in response to different stimuli such as solvent. In the relaxed state the islands spread over surface reaching the neighboring islands; the substrate is completely covered by the polymer. In the collapsed state the substantial fraction of the substrate surface is uncovered as the grafted polymer adopts island-like conformation. We will report on our recent findings in the mechanism of collapse and relaxation of dot-like and ridge-like MBs observed in binary solvents of different miscibility with the grafted polymer as well as thermal response. The experimental results obtained by the means of Atomic Force Microscopy and voltammetry are complemented by the coarse-grain and all-atomic molecular dynamic simulations of MBs.



Reversible response in morphology of MB: relaxed vs. collapsed state

COLL 412

Self-assembly of functionalized hexaphenylbenzenes

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In some examples, it will be shown that the properties of materials can be tuned by tailoring the molecular structure. In aqueous solution at low concentration, polycyclic aromatic compounds functionalized with polyethylene glycol (PEG) chains lead to bundles of fibers. The hydrogel fiber formation is verified by special analytical methods of cryogenic transmission electron microscopy, polarized and depolarized dynamic light scattering. The water content in the hydrogel fibers can be controlled by the substitution pattern of the amphiphile and by the length of the PEG chains. In aqueous solution at high concentration, physical hydrogels are formed. The hydrogels show an exceptionally strong dependence of the shear modulus on the concentration comparable to high molecular weight cellulose-based fibers. But in our case, a molecule with a relatively small molecular weight shows this extraordinarily mechanical behavior due to very strong intermolecular interactions.

In bulk a series of aromatics functionalized with PEG chains result in remarkable amphiphiles with supramolecular organization and suppressed dynamics. These materials are promising as electrolyte in Li-ion batteries.

Furthermore, the influence of amphiphilic aromatics on the properties of carbon nanomembranes is investigated. The thickness, chemical functionalization and appearance of nanopores can be adjusted dependent on the molecule.

In solution, in bulk and on the surface, geometry, size and amphiphilicity of the molecules are decisive parameters for the formation of defined structures.

COLL 413

Fluorescence lifetime spectroscopy studies to monitor the stability of luminescent semiconductor quantum dots-containing polymer films used in consumer electronics

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Historically, the photophysical properties of semiconductor quantum dots (QD) have been extensively studied in *controlled laboratory settings*. QD have exhibit broad absorbance, narrow emission peak widths, high molar absorptivities, and high quantum yields. In recent years QD core and core/shell nanoparticles have been incorporated in mass-produced consumer electronics including flat panel displays and touch screens. QD are even being proposed as potential absorbers and charge carriers in photovoltaic and other photoelectronic devices. Such wide scale applications of semiconductor QD raise significant concerns about their long-term chemical stability in *real world biological systems and the environment*. This presentation will focus on the stability of both core and core-shell QD under conditions that mimic various stages of production of some

consumer electronics. We primarily use time correlated single photon counting based fluorescence lifetime (FL) as our detection method. FL is particularly useful in monitoring the degradation state of QD as it is sensitive to the QD environment, concentration independent, and provides valuable insight about the QD crystalline quality when coupled with the standard spectroscopic characterization methods including UV-Vis spectrophotometry, steady state photoluminescence and transmission electron microscopy. This presentation will the focus on three areas: (1) stability of three types of QD cores in solvents with varying polarity, (2) the stability of the QD cores overcoated with varying shell thickness, (3) the stability of both core and core/shell QD incorporated in polymer films.

COLL 414

pH responses of dumbbell-shaped multilayer hydrogel capsules

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Shape and stimuli-sensitivity of micron-sized delivery carriers are considered as important factors for controlled and effective delivery of therapeutics. We present a novel type of dumbbell-shaped ultrathin hydrogel microcapsules which undergo large and rapid volume changes in response to solution pH. The novel dumbbell-shaped pH-sensitive poly(methacrylicacid) (PMAA) hydrogel capsules were fabricated via layer-by-layer technique by coating hydrogen-bonded PMAA/poly-(N-vinylpyrrolidone) (PMAA/PVPON) onto the dumbbell-shaped F_2O_3 inorganic templates followed by PMAA chemical crosslinking and core dissolution. The swelling behavior of the hydrogel capsules is controlled by the wall rigidity, which is regulated by the cross-link density and the number of PMAA layers deposited within the capsule shell. We found that rigid hydrogel capsules undergo isotropic volume changes when pH increases from 5 to 8. In contrast, the capsules with a less rigid structure experience preferential swelling at longitudinal direction at pH 8. We believe, this study on pH-swelling of dumbbell-shaped hydrogel capsules can open new prospects for developing novel hydrogel materials with predictable shape- and size-changing properties.

COLL 415

Methacrylate-based amphiphilic copolymers for the compatibilization of inorganic nanoparticles in polymer matrices

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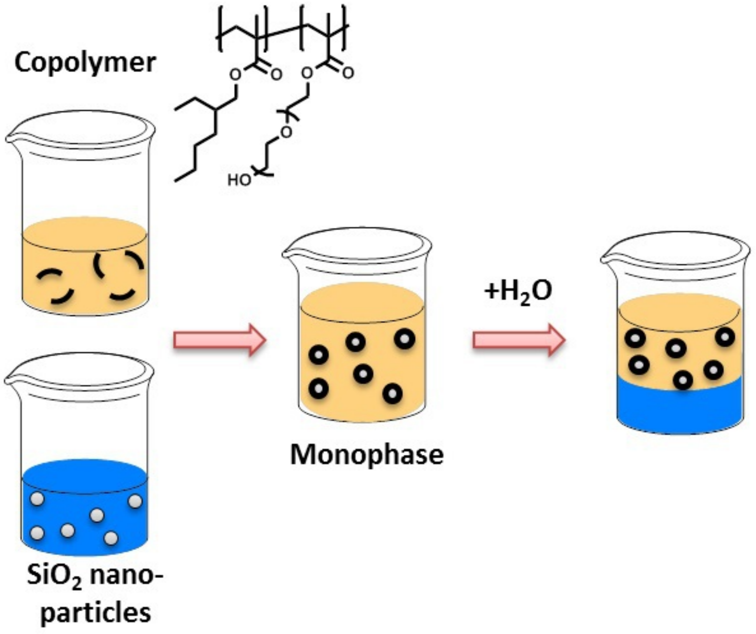
Through the incorporation of inorganic nanoparticles into polymeric matrices, materials with tunable properties can be achieved, such as enhanced mechanical stability, flame retardancy, scratch and UV resistance. However, the compatibilization of inorganic

materials in polymers is not a trivial task, and it is essential for the preparation of homogeneous nanocomposites for a compatibilizing agent to be used. In literature, several different methods have been described using small molecules and covalent attachment to the particles' surface, whereas our strategy utilizes multicomponent solvent mixtures for the non-covalent surface modification of inorganic particles via amphiphilic copolymers. These ternary mixutres use immiscible water/organic solvent blends and certain ratios of ethanol to make the nanoparticle coating possible. By this method, hydrophilic nanoparticles can be easily hydrophobized with different amphiphilic copolymers, depending on the application demands. Here, the binding process is studied by isothermal titration calorimetry, and the successful coating of particles is confirmed by dynamic light scattering and scanning electron microscopy. Changes in the mechanical performance of various nanocomposites is also studied by dynamic mechanical analysis.



COLL 416

Contact-initiated polymerization between complimentary-functionalized colloids and surfaces

Kristin M. Hutchins[2,1], *kmhutchi@illinois.edu, Nina Sekerak*[1], *Jeffrey Moore*[2,1]. (1) Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (2) Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States

Chemical reactions initiated *via* physical contact at the atomic level are ubiquitous in organic synthesis and catalysis, while reactions initiated through intentional and controlled macroscopic physical contact are less studied. Macroscopic control over reactivity may enable the design of novel self-healing materials, as well as temporal and spatial control of chemical transformations. Here, we demonstrate a macroscopic, spatially-controlled polymerization reaction initiated by contact between complimentary-functionalized co-initiators. We show that the reactivity is achieved using two systems. The first system utilizes a complementary-functionalized surface and polymer bead, and the second system uses polymer colloids that are similarly functionalized with complementary co-initiators (Figure 1). Our study will facilitate the design of new spatially-controlled dual catalytic and initiator systems, as well as unique self-healing motifs.

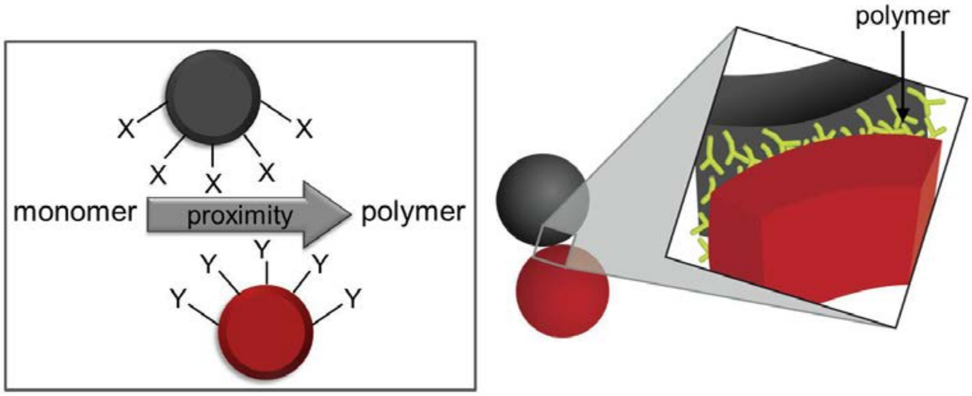


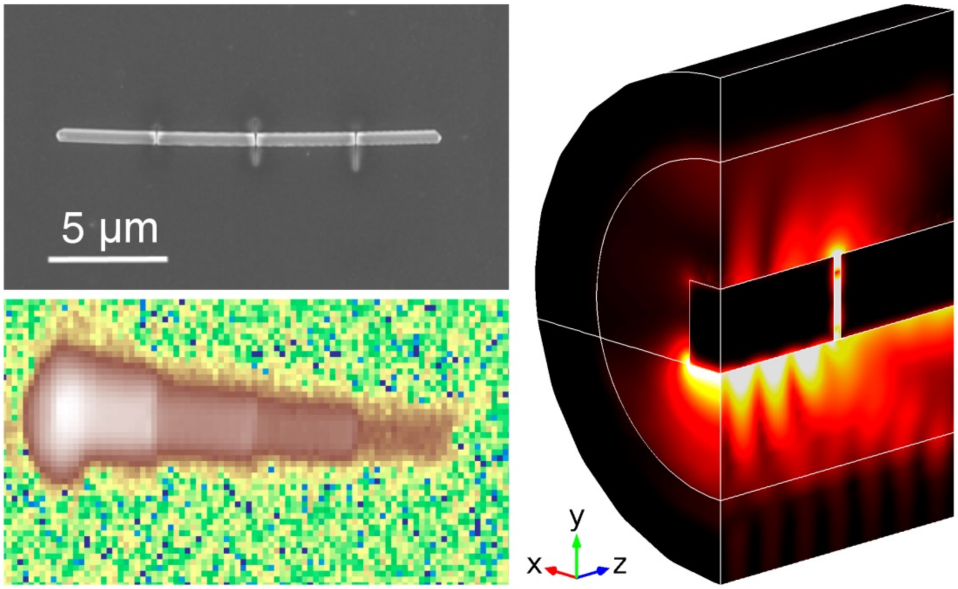
Figure 1. Contact-initiated polymerization reaction between complementary-functionalized polymer colloids (where X and Y are co-initiators).

COLL 417

Transient absorption studies of single plasmonic nanostructures

Gregory V. Hartland, *ghartlan@nd.edu, Paul Johns.* Department of Chemistry and Biochem., University of Notre Dame, Notre Dame, Indiana, United States

The ability to interrogate single molecules and particles has revolutionized optical imaging. In this talk I will present recent results from my laboratory where transient absorption microscopy has been used to study plasmons in single metal nanostructures. In these experiments propagating surface plasmon polaritons (SPPs) are launched in single metal nanowires, and their motion is monitored by recording transient absorption images of the nanowire. These measurements provide information about the propagation lengths of the SPP modes, and how they couple between nanostructures. In particular, measurements for nanowires with different sized cuts along the nanowire show that the SPP transmission probability increases as the cut width increases. This unexpected result is attributed to the excitation of localized surface plasmon modes associated with the cut at small cut sizes, which dissipate energy. This assignment was confirmed by finite element method calculations of the SPP losses as a function of cut width.



Scanning electron microscope image, transient absorption image, and field plots generated from finite element method calculations for a cut nanowire.

COLL 418

Plasmonic nanoparticles: From fundamental optical properties to applications

Stephan Link, *slink@rice.edu.* Dept of Chem, Rice University, Houston, Texas, United States

A surface plasmon in a metal nanoparticle is the coherent oscillation of the conduction band electrons leading to both absorption and scattering as well as strong local electromagnetic fields. These fundamental properties have been exploited in many different ways, including surface enhanced spectroscopy and sensing, photothermal cancer therapy, and color display generation. The performance of plasmonic nanoparticles for a desired application not only depends on the particle size and shape, but is tunable through nanoparticle interactions on different length scales that support near- and far-field coupling. Chemical synthesis and assembly of nanostructures are able to tailor plasmonic properties that are, however, typically broadened by ensemble averaging. Single particle spectroscopy together with correlated imaging is capable of removing heterogeneity in size, shape, and assembly geometry and furthermore allows one to separate absorption and scattering contributions. In this talk I will discuss our recent work on understanding the radiative, non-radiative, chiral, and mechanical properties of individual and coupled plasmonic nanostructures. In addition, I will present passive and active mechanisms for color generation and tuning using coupled plasmon resonances of gold and aluminum nanoparticles

COLL 419

Darkfield/hyperspectral structure of isolated and aggregated of silver nanowires

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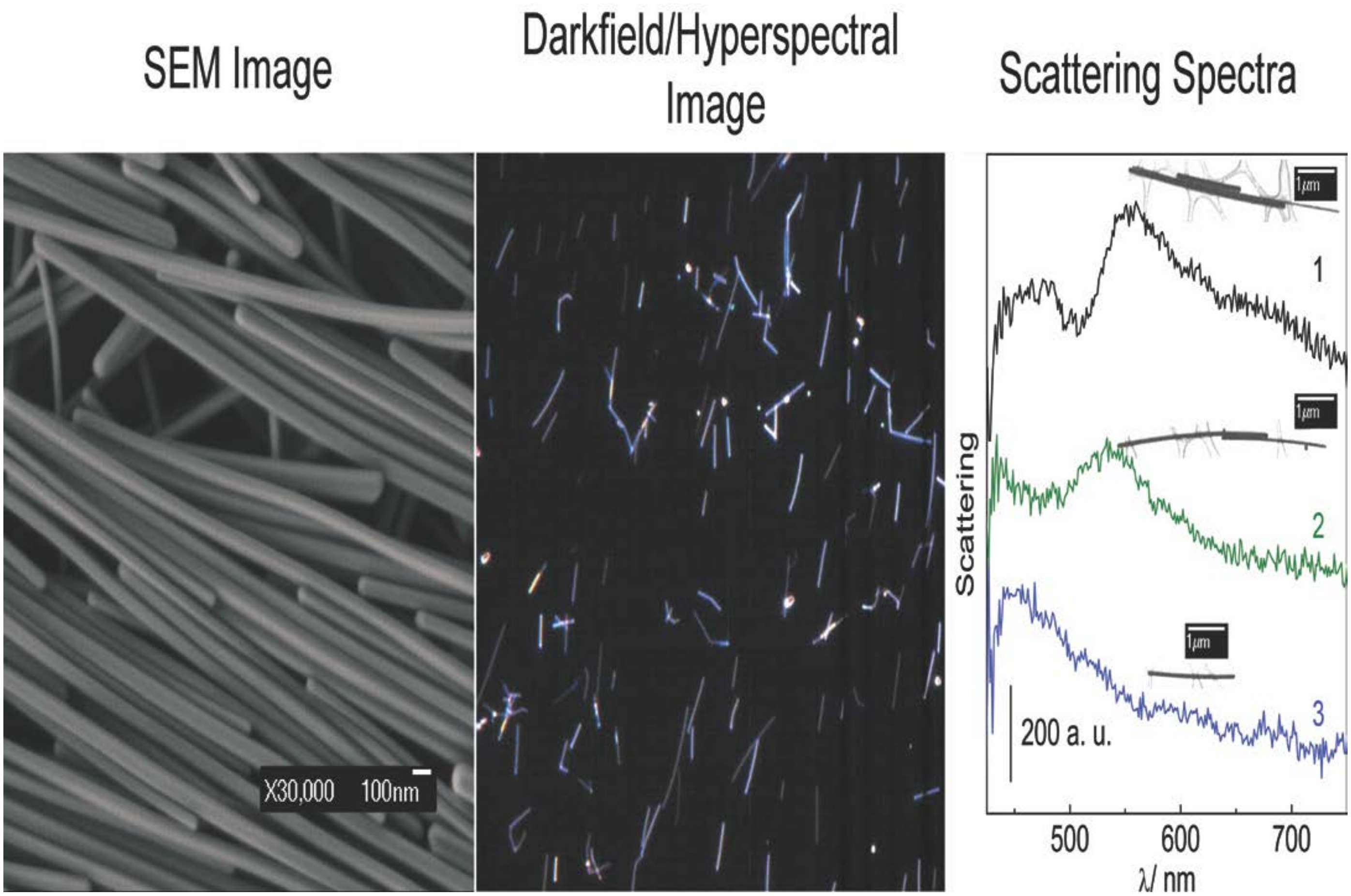
Surface plasmon resonance (SPR) is a very interesting phenomenon present on many metals, silver, gold and copper nanostructure being the most important ones (plasmonic metals). Their application are seen on many different areas in science, with a special feature in Raman spectroscopy due surface enhanced Raman scattering (SERS) effect. Although the extinction spectra of a nanostructure made by these plasmonic metals have been known for a long time, they are typically measured for a concentrate medium, and thus and average behavior is usually bserved, Such measurements do not show the singularity of each isolated particle or system of particles. However recent advances of darkfield/hyperspectral microscopy make such measurements possible. Utilizing darkfield/hyperspectral microscopy is possible analyze/detect plasmonic nanoparticles smaller than 20 nm, even though the resolution is limited to 100 nm.
In this work we show a study the electronic structure of silver nanowires isolated and aggregated forms, obtained by darkfield/hyperspectral microscopy. Silver nanowires with an average diameter of 100 nm were obtained by the Xia methodology, and were analyzed by dispersing in water and depositing on a transmission electron microscopy grid. Figure 1 shows the images obtained by darkfield/hyperspectral microscopy and the spectra of some representative areas.
The spectrum obtained from an isolated silver nanowire is very similar to the usual spectrum observed by UV-Vis spectroscopy (which represents and average).However, the spectra of aggregated of nanowires explicitly shows an interesting dependence on many factors, like the size of the aggregated and the region measured. In the regions were the aggregated are very close, plasmon coupling occurs, and can be observed by the generation of a new band with lower energy. The plasmon coupling has been observed and calculated for many other types of nanostructures (like nanospheres, nanorods, nanocubes, and others), but, to our knowledge, this is the first case were experimental and theoretical data are shown.



COLL 420

DNA nanotechnology for ultrasensitive visual detection of *Ebolavirus* subtypes

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With the enhanced health concern worldwide for infectious disease outbreaks, the need for molecular diagnostics that advance clinical care and public health has never been greater. In the present study, we have developed the chemistry for preparing a fully programmable multianalyte sensing platform which is capable of rapidly identifying and fully differentiating a set of pathogenic oligonucleotides. It allows one to rapidly detect nucleic acid targets with high sensitivity and excellent selectivity in both ideal and liquid biopsy samples; blood serum and urine. This approach relies on a new multiplexed version of the capture probe functionalized gold nanoparticles coupled with hybridization chain reaction (HCR) amplification strategy and offers new opportunities for studying visual detection of multiple biomarkers using a single nanoparticle template. Short single stranded oligos belonging to four different Ebolavirus subtypes were detected individually or simultaneously in 16 different combinations using a single nanoparticle

platform. Sensitivity results show that the visual detection limit was greatly improved, exhibiting a remarkable level of 200 attomole. To evaluate the selectivity of the system, sixteen tests were run with different combinations of the four target Ebolavirus subtype oligos and one control oligo. The results of 16 x 5 array tests showed that our system is extremely selective with no false-positive or false-negative. Finally, we were also able to identify and differentiate the content of the Ebolavirus in patent mimicked liquid biopsies including whole blood and urine samples with 8 different oligos cocktails composed of various, but unknown, targets. A strong agreement (around 95%) between the experimental results and the actual Ebolavirus compositions was observed. In conclusion, the results presented here validate the multiplexing and programmable capabilities of the HCR coupled AuNPs sensing platform and open new avenues for the multitarget detection of other pathogenic oligonucleotides including but not limited to DNA or RNA of Zika, and HIV etc.

COLL 421

Structure and plasmonic properties of single Au-Cu alloy nanorod during galvanic replacement reaction

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Galvanic replacement reaction is perform between $HAuCl_4$ and Au-Cu alloy nanorod templates. Detailed structural tranformation and composition of the nanorod during reaction is monitored with transmission electron microcopy and energy dispersive X-ray spectroscopy. At low $HAuCl_4$ concentration, the shape of the nanorod was maintained after the reaction. The solid Au-Cu rod became hollow and unusual diffusion of Cu atoms towards the end of the rods was observed. At high concentration of $HAuCl_4$, the shape of the nanorod changed dramatically during the reaction. The optical properties of the reaction intermediates are monitored at the single nanoparticle level and modeled by electrodynamics simulations.

COLL 422 – Withdrawn.

COLL 423

Probing nanoelectrochemistry with optical microscopy

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Nanoscale electrochemistry at the single particle, single molecule level can not only reveal behavior obscured by ensemble averaging, but can also provide insight into how electrode structure affects redox events. Probing electrochemical reactions at this level

is inherently challenging due to the small number of electrons transferred between a nanoparticle electrode and analyte molecule(s), which limits the use of conventional techniques such as voltammetry and amperometry that do not have the required sensitivity. Alternatively, optical microscopy is routinely employed for single particle and molecule investigations. Plasmonic nanoparticles are particularly attractive for electrode materials as they offer locally enhanced electromagnetic fields that enable detection of charge transfer reactions down to a single molecule. Additionally, tuning the size, shape, and composition of plasmonic nanoparticles leads to a broad range of electrode-analyte reactions that can be investigated at the nanoscale. We use optical microscopy (e.g. surface-enhanced Raman scattering, fluorescence, electrogenerated chemiluminescence) to probe electrochemical heterogeneity at plasmonic nanoparticle electrodes.

COLL 424

Diamond at the extremes

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From alkanes to diamond, sp^3-hybridized carbon enjoys a special place in chemistry. When coordinated into the 3-dimensional crystalline form of diamond, sp^3-carbon becomes a versatile material with many unusual chemical and physical properties. Diamond’s highly stable surfaces make it an outstanding electrode for “extreme electrochemistry,” able to facilitate electrochemical reactions lying far outside the stability limits of water. Diamond’s surface chemistry and high-lying conduction band conspire to make it an excellent solid-state electron emitter. When illuminated with ultraviolet light, diamond surfaces emit electrons directly into vacuum, water, or ambient-pressure gases. In water, this electron emission produces solvated electrons – the chemist’s perfect reducing agent – and other species that in turn initiate electrochemical reactions not feasible in conventional electrochemical or photoelectrochemical studies. Examples include the 1-electron reduction of CO_2 and reduction of H^+ to H (solvated hydrogen atom), a critical step in the aqueous-phase synthesis of NH_3 from N_2. Ultimately, diamond’s combination of bulk and surface properties lead to fascinating science with potential applications in biology, energy, and environmental science.

COLL 425

Rainbow-coloured Pickering emulsions: Behaviour of pigment particles at fluid interfaces

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Apart from a few examples like carbon black and titanium dioxide particles, very little exists in the literature on the behaviour of coloured pigment particles at liquid interfaces despite their use in many products and processes like paint and plastics. We describe the properties of a range of organic pigment particles in either bulk water or oil and their ability to stabilise emulsions of oil and water. The pigments chosen include one example of each primary colour of the rainbow (red, orange, yellow, green, blue, indigo and violet). We determine the surface energy of discs of the particles from appropriate contact angle measurements and measure their (low) solubility in water and oil by spectrophotometry. Emulsions of equal volumes of water and heptane can be stabilised by pigment particles, but the emulsion type depends on the surface energy of the pigments. By varying the particle concentration, we show that emulsions display limited coalescence behaviour. By varying the oil:water ratio, emulsions of certain pigments can be catastrophically phase inverted from one type to another, which could be significant in applications of these systems. We discover a correlation between the pigment surface energy and the propensity of the emulsion to phase invert. For those pigment-stabilised emulsions which do not phase invert, high internal phase emulsions remain stable to coalescence.

COLL 426

Assembly for nanofabrication in the magnetic recording industry

Ricardo Ruiz, *ricardo.ruiz@hgst.com.* HGST, Western Digital Corp. Brand, San Jose, California, United States

The beauty and uniformity of the periodic patterns formed by self-assembled block copolymers has inspired a wide landscape of visionary applications in nanofabrication ever since it was first demonstrated that block copolymer films could be used as sub-lithographic resolution masks about two decades ago. Commercial applications like those found in the magnetic recording and semiconductor industries, however, demand much more than just challenging dimensions below 10 nm. The journey towards insertion of self-assembly in the manufacturing of magnetic recording media has been one that spurred innovation in polymer science, chemistry, soft matter physics and nanofabrication alike. Breakthroughs in the field have included directed assembly with density multiplication, engineering of interfacial energies, finding or designing new block copolymers with suitable etch contrast, understanding thermal fluctuations and their role in line roughness, tailoring pattern transfer techniques and complementing the benefits of block copolymers with other powerful nanofabrication methods such as nanoimprint and double patterning. In this lecture, I will review about a decade’s worth of innovation in self-assembly and nanofabrication with a particular focus on contributions from the team at HGST towards applications in the magnetic recording industry.

COLL 427

Nano-enabled filters for point-of-use water treatment in developing countries: turning theory into practice

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3 billion people live on less than $2.50 per day. The limited resources at the "bottom of the pyramid" present special challenges in designing reliable water purification technologies. For example, high-performance membrane systems are completely effective at water purification, but their capital costs are too high for low income markets. Chlorine is cheap and effective, but despite decades of availability has limited acceptance due to off-tastes. To achieve universal access to clean water, more options are needed. We have developed an alternative, consisting of a paper-based filter laced with biocidal silver nanoparticles (AgNPs), combining physical filtration with chemical disinfection. The development of these AgNP papers has been presented at previous ACS meetings spanning the last decade. Protozoa and other larger parasites are removed by choosing an appropriate pore throat diameter, while biocidal silver is made affordable by the need for only part per thousand by mass of silver:paper due to the silver being deposited as nanoparticles on the paper fibers. The papers are paired with a filter holder that incorporates local water handling practices based on human-centered design principles. Findings from field work in Bangladesh, Ghana, Honduras, and South Africa using these AgNP filters point to the need for filter holder systems tailored for local populations to achieve correct and consistent filter use. Critically, it is not enough to select a paper with the necessary physical and chemical technical specifications to achieve disinfection, the filter holder design must also incorporate social factors to be desirable, affordable, and effective for the population where it is introduced.

COLL 428

New core-shell magnetic nanoparticles prepared by polydopamine chemistry mediated surface-initiated live radical polymerization for efficient uranium adsorption

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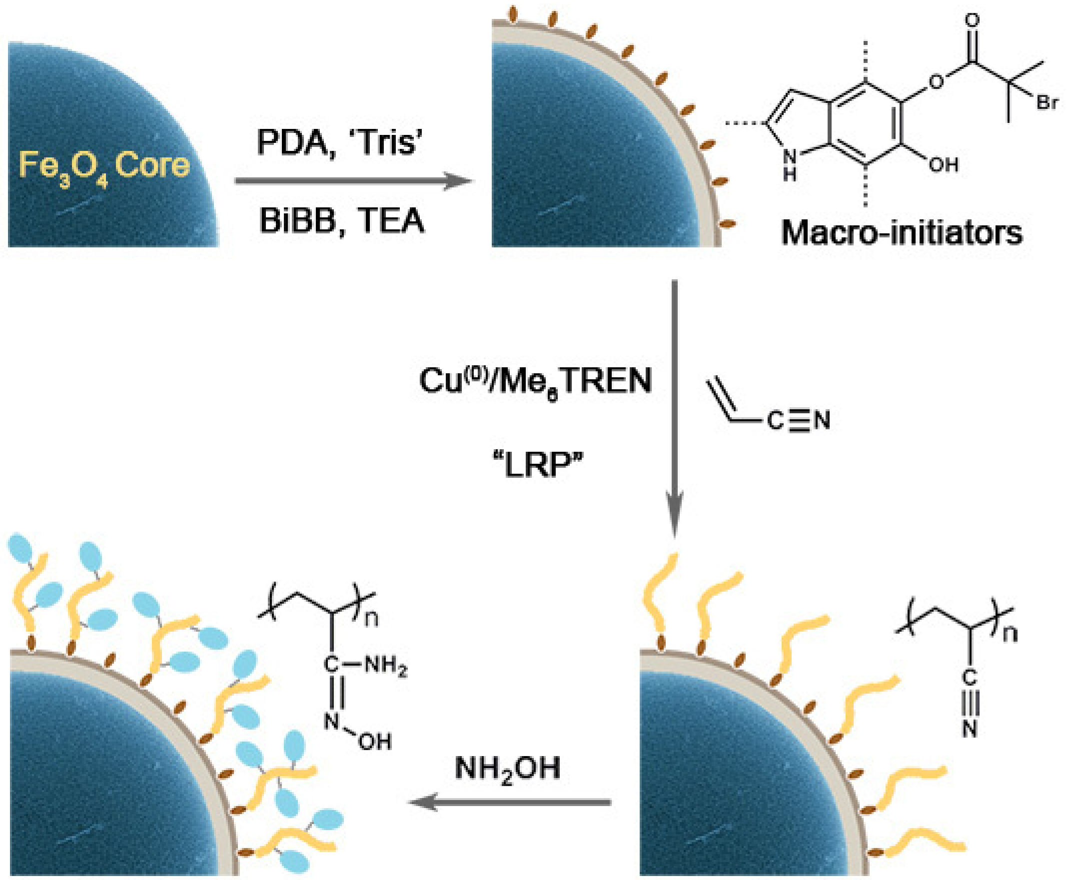
We report an effective and facile strategy by integrating surface-initiated live radical polymerization (LRP) with mussel-inspired polydopamine (PDA) chemistry for controlled building a new class of core-shell structured magnetic nanoparticles (MNPs) for efficient adsorption toward uranium in aqueous solutions. The strategy initially involved deposition of a PDA encapsulation layer by spontaneous self-polymerization on Fe_3O_4 core, which served as a safety shell and provided an enabling platform for anchoring of 2-bromoisobutyryl bromide (BiBB) to form macro-initiators. Dense polyacrylonitrile (PAN) brushes were then grown from the BiBB-attached PDA shell via LRP using $Cu^{(0)}$/Me_6TREN as catalytic/ligand system, followed by conversion to amidoxime (AO) functionalized polymer brushes. The core-shell Fe_3O_4@PDA@PAO MNPs exhibited favorable superparamagnetic characteristics and fast response within 6 s under applied magnetic field. Due to the strong binding ability of AO ligands, Fe_3O_4@PDA@PAO showed remarkable adsorption capacity (q_e=162.5 mg/g) toward uranyl ions at optimal pH condition. Study on the adsorption kinetics suggested that the adsorption process might conform to the pseudo-second-order model. We conclude that the Fe_3O_4@PDA@PAO MNPs are of potential for effective adsorption and magnetic separation of uranium from radioactive wastewater, and, the integrated synthetic strategy by combining LRP technique and PDA chemistry would bring more opportunities for versatile modification or surface functionalization of nanomaterials.



COLL 429

Preparation of silver nanoparticles on synthetic electrospun PAA nanofibers for antimicrobial applications

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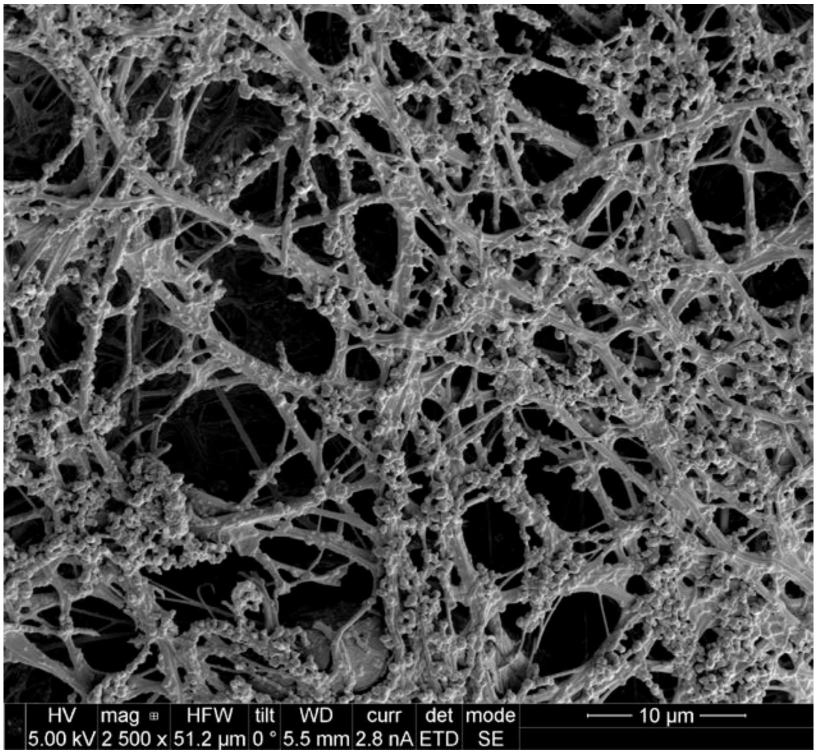
Controlling the size and shape of nanoparticle is an important challenge for recent studies in the citrate ion reduction of metal colloid synthesis. Because of small size of nanoparticles and the highly relative surface area for contact with the outer membrane of target cells, there is a demand for fabrication of even smaller sized nanoparticles. We

developed the water-stable silver containing polyacrylic acid (PAA) fibers, by thermally crosslinking PAA with ethylene glycol, neutralizing to the sodium carboxylate form (PAA-Na), and reducting to nano-silver nanopartilces to fabricate small silver-clusters on the fibers using citrate. This work was done through using an electrospinning processing characterized by scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS), and antimicrobial test. In the present work, we have reported a synthetic approach for the preparation of a PAA nanofiber network containing Ag nanoparticles, and investigated their antimicrobial applications. Our findings indicate that the silver containing nanofibers are capable of providing more activities than drugs against antifungal and antibacterial infections. Clinical translation of this and related polymer/silver systems are in progress.



SEM image on the surface of electrospun polyacrylic acic nanofibers contaiing silver

COLL 430

Versatile magnetically-active hybrid networks (MHNs): From crude oil remediation to Pickering emulsifiers

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This presentation will highlight our advances on nanoparticle-based systems that are capable of capturing crude oil from water, by the dual mechanisms of absorption and emulsification. It is well known that some nanoparticles have the capacity to sequester oil from water, and if the conditions are favorable, they can even form stable oil-in-water emulsions by Pickering stabilization. Nevertheless, once the nanoparticles have sequestered the oil either by absorption or emulsification, the separation of the loaded material from the water is a challenging task, and in many cases the limiting step. For this reason we have designed magnetically-active hybrid inorganic/organic composite materials capable of absorbing oil, and forming stable emulsions, known as magnetically-active hybrid networks (MHNs). The MHNs have been synthesized from the coupling of amine-functionalized iron oxide nanoparticles and pre-established shell crosslinked knedel-like (SCK) polymer nanoconstructs. Unique insights were determined, into fundamental aspects of the polymer chemistry involved during the preparation of these materials and the resulting structures and morphologies. Assessment of the ability of the MHNs to capture complex hydrocarbons, such as crude oil, determined a loading capacity in the range of 3.5 – 4.5 mg of oil sequestered per 1 mg of MHNs. The materials exhibit the capacity to recover *ca.* 90% of the oil sequestered, and thanks to their magnetic responsivity, can be re-utilized over multiple cycles of remediation without compromising the loading capacity. Additionally, the versatility of the MHNs was demonstrated by their ability to form stable Pickering emulsions upon mechanical stimulus. Two methods of emulsification, vortex and/or probe sonication were utilized to stabilize toluene-in-water and dodecane-in-water emulsions, in the presence of the MHNs. Moreover, the emulsions with the smallest droplet size and narrowest dispersity were obtained at a water-to-oil ratio of 3:1, and an MHN concentration of 1 mg/mL. The unique magnetic character of the MHNs yielded magnetically-active droplets that could be manipulated with an external magnetic field. This property has been explored to easily separate the emulsified oil phase from the water phase, and could be used in the extraction of hydrocarbons from oil sands, and the subsequent water purification necessary after the application of steam-assisted gravity drainage (SAGD) technology.

COLL 431

Combining the Polanyi-Dubinin-Manes framework with molecular models to predict adsorption isotherms of aqueous organic contaminants on activated carbons

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Activated carbon adsorption is a powerful technology for removing organic contaminants from water. Information about adsorption isotherms is important to select the most effective activated carbon for water treatment applications. Many activated carbons with different physical and chemical characteristics are manufactured, and only few isotherm data are available for the more than 100,000 chemical substances and mixtures that have been or are currently being produced. The Polanyi-Dubinin-Manes (PDM) model is based on two postulates: (1) adsorption is described as a (micro)pore filling process and (2) the volume occupied by the adsorbed compound is a temperature-independent function of the adsorption potential. To apply the PDM model to aqueous contaminants, the affinity of water and of the contaminant for the activated carbon surface needs to be known. The affinity coefficient for water was estimated from the adsorbent oxygen content. Affinity coefficients of individual adsorbates were estimated from adsorption isotherm data collected by the U.S. EPA for 62 neutral organic contaminants. These affinity coefficients were used to develop a poly-parameter QSPR that permits the estimation of a contaminant's affinity coefficient from molecular descriptors. The resulting poly-parameter QSPR provides a new framework for predicting the affinity of aqueous contaminants for the activated carbon surface. To illustrate the applicability of the developed model, single-solute adsorption isotherms were predicted for representative emerging contaminants on several activated carbons.

COLL 432

Understanding the role of colloidal particles in lead release to drinking water

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Lead service lines (LSLs) are a major source of lead in distributed drinking water, and high levels of iron are often observed along with elevated lead release. Unlined iron distribution mains have been linked specifically with elevated lead release from LSLs, and iron-rich colloidal particles—known to mobilize lead bound within soil matrices—may play a role in mobilizing lead from corrosion scale to the point of use via adsorption. Interactions between colloidal iron and lead were explored by characterizing residential point-of-use drinking water samples using size exclusion chromatography with UV and multi-element (ICP-MS) detection. At all sites with detectable levels of iron, colloidal iron and lead were highly correlated. As well, a substantial fraction of the two metals occurred in the size fraction 0.05 – 0.45 µm. Colloidal natural organic matter was correlated with both iron and lead, which may have implications for lead mobilization via adsorption—the presence of natural organic matter shifted the point of zero charge of synthesized iron oxide particles in the negative direction, increasing electrostatic attraction between cations and the oxide surface. The link between iron distribution mains and lead release from LSLs was further explored using a model distribution system dosed with an ortho-polyphosphate corrosion inhibitor. Lead release was greater from LSLs supplied by iron distribution mains, and the effect of an upstream source of iron was not diminished by increasing the concentration of ortho-polyphosphate. These findings were supported by observations via size exclusion chromatography—colloidal lead and iron were highly correlated in the presence of an upstream source of iron and uncorrelated otherwise. Phosphate may also influence lead mobilization via adsorption—the presence of ortho-polyphosphate shifted the zeta potential of synthesized iron oxide particles to more negative values as well. This work highlights the importance of iron—and of natural organic matter and phosphate—in controlling lead exposure via drinking water.

COLL 433

Column with magnetic activated carbon functionalized by amines for water purification

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Global fresh water demand increases by the increase in population. Thus, the demand on efficient technologies is in increase. On the other side, the disposal of waste rubbers is a problem. Thus, the negative-value solid waste to positive value material is a potential solution. Here, we modify the rubber-derived carbon by iron oxide and the obtained material was subjected to surface modification using polyethylenimine to produce a composite of AC-Fe-PEI. The efficiency of the amine functionalized material was tested for the removal of methyl red form aqueous solutions in batch and column systems. The results indicated high percentage removal and the breakthrough was observed in 150 min using 1 mM concentration of methyl red. The results indicated that the composite was better than the pristine carbon. Therefore, it is recommended to scale up the design and the materials.

COLL 434

Concentration of aqueous contaminants in water using polyelectrolyte complex coacervates

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Contaminants increasingly found in our water supplies include pharmaceuticals (hormones, antibiotics, SSRIs) and various compounds from cosmetic formulations. Unlike metal ions which have often been the focus of water treatment materials, these contaminant are not necessarily charged. They may contain aromaticity or hydrophobes and are not necesarily amenable to standard modes of water treatment. These contaminants are also often found in extremely low concentrations which are therefore difficult to treat. One possible treatment method may be to concentrate these contaminants into a polyelectrolyte complex coacervate, which is a polymer rich aqueous material that is created by mixing solutions of oppositely charged

polyelectrolytes. Polyelectrolytes have long been used to flocculate contaminants, but this mode of water treatment is slightly different. The idea is that during the liquid-liquid phase separation that happens the contaminant will selectively partition into the liquid polyelectrolyte phase based on differences in the environment between the polyelectrolyte and water rich phases. In this work, both electrostatic and hydrogen bonding interpolymer complexes were used to sequester various small molecules of interest into the polyelectrolyte complex coacervate phase. This includes using water soluble block copolymers with a hydrophobic segment to increase the hydrophobicity of the environment within the polyelectrolyte complex coacervate. Aromatic, water soluble dyes were used due to their ease of detection with UV-vis. We should that electrostatics, pi-pi interactions, as well as hydrophobic interactions.

COLL 435

Superhydrophobic oil and water separations

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The treatment of water for pollution control, produced water for oil and gas productions, and the treatment of municipal water required very efficient methods as well as economical methods for production and distribution. They rely on smart technologies as well as materials to enable high degrees of separation. In filters, high selectivity and filtration up to the nano level is imporant for purification, however, the sacrifice is in the throughput. Int this talk, We will focus on the use of superhydrophobic films and materials capable of oil-water separation technologies that are useful for clean-up of produced water as well as oil and gas applications. Superhydrophobic films can be prepared by utilizing the Cassie-Baxter phenomena and can be combined with the surface deposition method. By controlling the methods of deposition in micro-mesh size patterns, it is possible to control intrusion pressure and selectivity in wetting. We have investigated electrcally conducting polymers, polymer brushes, and cross-linked hybrid materials.

COLL 436

Superparamagnetic microspheres for selective binding and magnetic enrichment of palladium: synthesis, adsorptive behavior and mechanism study

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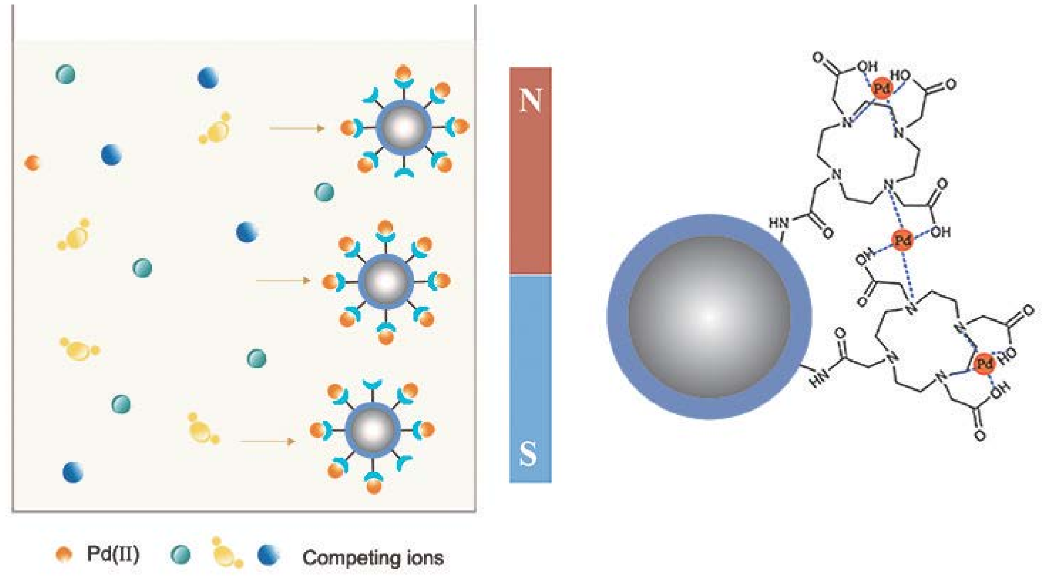
Development of economic and green technologies for effective recovery of palladium has attracted worldwide attention in recent years. Magnetic separation involving the use of functional magnetic nanoparticles (MNPs) with superparamagnetic characteristics

holds great promise in this respect. This study presents a novel class of core-shell structured superparamagnetic microspheres decorated with polyazamacrocyclic receptors, which show a highly-selective binding to Pd(II) in HNO_3 media. The superparamagnetic microspheres possess high saturation magnetization (53.8 emu/g) and high adsorption capacity (q_{max}≈105.3 μmol/g), affording an efficient enrichment and fast separation (within 13 seconds) of palladium under applied magnetic field. Adsorptive behavior was fully investigated combined with corresponding theoretical analysis by using kinetic equations and Langmuir/Freundlich isotherm models. Moreover, the coordination mechanism of the polyazamacrocyclic receptors to Pd(II) was carefully examined based on high resolution X-ray photoelectron spectroscopy (XPS). A suggested mechanism involving the synergistic effect of the cyclic amines and the carboxyl arms of the polyazamacrocyclic receptors was proposed to describe the coordination manner, while explaining the selectivity to Pd(II) in HNO_3 solutions. From a practical perspective, the Pd(II)-enriched microspheres could be readily regenerated for cycle use. We conclude that this kind of polyazamacrocyclic receptor decorated superparamagnetic microspheres is of potential for effective recovery of Pd(II) as well as other precious metals.



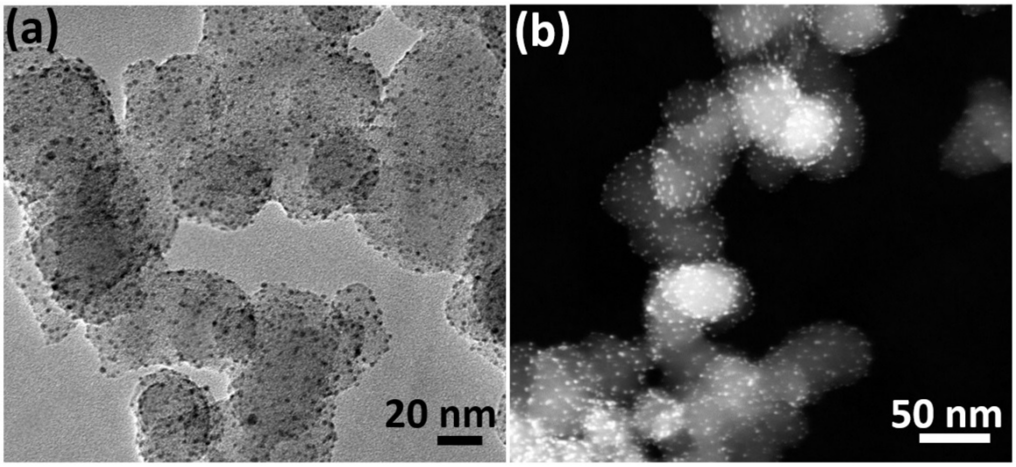
COLL 437

In situ growth of ultrafine and ligand-free noble metal nanoclusters on carbon supports through a "soft nitriding" method

*Ben Liu[2], Huiqin yao[2], Lei Jin[2], James Rusling[2], Steven L. Suib[1], **Jie He**[2], jie.he@uconn.edu.* (1) Univ of Connecticut, Storrs Mansfield, Connecticut, United States (2) Dept of Chemistry, University of Connecticut, Storrs, Connecticut, United States

Supported noble metal particles (*e.g.* Au, Pd and Pt) on high-surface-area supports are of great importance for many reactions in the field of heterogeneous catalysis. The

catalytic activities of noble metal particles are highly size-dependent as confirmed by numerous previous studies. In particular, ultrasmall noble metal nanocatalysts (UNMNs, < 2 nm), referred to nanoclusters with a few to hundreds of atoms, have received substantial attention recently, since they hold a high surface-to-volume ratio and a large proportion of surface (edge and corner particularly) atoms. However, all current synthetic approaches of noble metal nanocatalysts require excess surface ligands to prevent the overgrowth and stabilize the nanoclusters, due to the high surface energy. We present a robust and universal “soft” nitriding method to *in situ* grow ligand-free ultrafine noble metal nanocatalysts (UNMNs) (*e.g.* Au, Pd and Pt) onto carbon supports. Through a low-temperature urea-annealing pretreatment (300 ^{o}C), “soft” nitriding that enriches the nitrogen-containing species on the surface of carbon supports, can enhance the affinity of noble metal precursors and/or their nanocatalysts to carbon supports. We demonstrate that, sub 2 nm, ligand-free UNMNs grew *in situ* on 7 different types of nitrided carbons in the absence of any organic capping agents *via* chemical reduction or thermolysis. Ligand-free UNMNs supported on carbon were found to be electrocatalytically much more active for methanol oxidation, compared to their counterparts with surface capping agents and/or larger nanocrystals. Moreover, these ligand-free UNMNs supported on carbon showed superior activity and selectivity (>95%) in epoxidation of C=C bonds. Our method is expected to provide useful guidelines for the rational design and the manufacture of supported ligand-free UNMNs on a variety of supports; and additionally, to broaden their applications in energy conversion and electrochemical catalysis for energy storage.



COLL 438

Controllably fabrication of graphene and graphene-like materials with tailored structures for metal free catalytic applications

Mehulkumar Patel[1], *Keerthi Savaram*[1], *Feng Hu*[1], *Feixiang Luo*[2], *Flach Carol*[3], *Richard Mendelsohn*[1], *Eric L. Garfunkel*[2], *Michal Szostak*[1], ***Huixin He***[1], *huixinhe@rutgers.edu.* (1) Chemistry Department, Rutgers University-Newark, Harrison, New Jersey, United States (2) Department of Chemistry and Chemical Biology, Rutgers

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There is an ever-increasing interest in the development of new carbon-based materials as benign, abundant, and readily available metal free catalysts for chemical synthesis. Carbon based materials provide additional advantages as catalysts, due to the existence of colossal π structures, which promotes strong interactions with the reactants. More importantly, physicochemical and electronic properties, which in principle determine the catalytic properties of a material, can be tailored and fine-tuned by molecular engineering and/or heteroatomic doping. A plethora of reports have demonstrated that doping with heteroatoms into graphene matrices gives rise to enhanced performance in electrocatalytic oxygen reduction reaction (ORR), when compared to their undoped analogues. In addition, co-doping with several different heteroatoms showed further improvement in ORR performances. Compared to ORR, studies that use doped and/or co-doped carbon materials as catalysts for selective organic synthesis are in their early stages of development, although a great potential has already been demonstrated. Importantly, these carbo-catalysts merge the benefits of green synthesis with heterogeneous reaction conditions, which greatly simplifies work-up conditions and is particularly attractive from an industrial standpoint. However, there are only few reports demonstrating that carbon based materials match the efficiency of transition metal catalysts in synthetically useful reactions. There is no very much systematic study about how the electronic and geometrical structures, surface functionalities, therefore the interface properties of graphene based materials, determine their catalytic performance. In this talk, case studies will be presented to show our efforts along this line so that graphene with tailored structures can be designed and fabricated for different metal free catalytic applications.

COLL 439

Plasmonic enhanced energy transfer and charge separation at the interface between sensitizers and TiO_2 –encapsulated metallic nanoparticles

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We report two studies on the plasmonic effects on the enhancement in energy transfer and charge separation at the interface between sensitizers and TiO_2-encapsulated metallic nanoparticles. In the first study, the Au nanospheres are encapsulated at the nodes of a continuous nano-network formed by TiO_2 nanowires. Such Au@TiO_2 nano-network is deposited at the micro-gap between two micro-electrodes and on the photoanode of dye-sensitized solar cells (DSSCs). The plasmonic core exhibits clear enhancements in photoeletric conductitivity and photovoltaic performance compared with bare TiO_2 nano-networks, which correlate well with plasmonic-induced hot electrons. In the 2nd study, the plasmonic nanoparticles (PNPs) are conjugated with the natural extract light-harvesting complex II (LHCII) trimers in aqueous solutions and on LHCII-sensitized solar cells. Three types of PNPs with distinct surface plasmonic resonance are prepared, including gold nanospheres (AuNSs), silver nanospheres (AgNSs) and silver nanoplates (AgNPs). These PNPs are further coated with a 2-5 nm thick TiO_2 layer to form core-shell nanoparticles, denoted as AgNS@TiO_2, AuNS@TiO_2 and AgNP@TiO_2, respectively. Adsorption of LHCII on the PNPs to form LHCII-PNP hybrids demonstrates combined photon absorption in broader spectrum by LHCII and PNPs. More efficient charge separation is facilitated at the LHCII/TiO_2 interface as revealed by quenching of the steady-state fluorescence emission and reduction of the transient fluorescence lifetime of LHCII after adsorbing onto PNPs. Femtosecond transient absorption technique provides further conclusive proof for charge injection from excited LHCII into the conduction band of TiO_2 shell of the PNPs. The plasmonic effects are further demonstrated in the enhanced photovoltaic currents after incorporating small amounts of PNPs in LHCII-sensitized solar cells built on a novel 3D photoanode consisting of vertically aligned TiO_2 nanotree arrays. The photocurrent is clearly enhanced by all PNPs under illumination at the selected wavelength windows around Soret and Q bands of LHCII trimer, and the “dark region” between them. This study reveals that the core-shell PNPs can significantly enhance charge injection into TiO_2. Understanding of this plasmonic phenomenon may lead to more efficient photovoltaic devices.

COLL 440

Designing high-performance one-dimensional catalysts for small molecule reactions: Probing size-and composition-dependent electrocatalytic behavior in noble metal nanowires

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In recent years, we have expended significant effort in probing and understanding the use of one dimensional (1D) noble metal nanostructures for a number of small molecule reactions. In this talk, we highlight recent theoretical and experimental progress aimed at precisely deducing the nature of the complex interplay amongst size, chemical composition, and electrocatalytic performance in high-quality elemental, binary, and ternary 1D noble metal-based nanowire systems. In terms of these structural parameters, significant enhancements in both activity and durability of up to an order of magnitude can be achieved by rationally tuning both wire size and composition. The fundamental insights acquired are then utilized to discuss future and potentially new directions towards the continuous improvement and optimization of these 1D catalysts.

COLL 441 – Withdrawn.

COLL 442

Metal-organic coordination networks at surfaces to control single-site transition metal oxidation state

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Control of the chemical state and reactivity of metal centers on surfaces is a key challenge in developing higher selectivity in heterogeneous catalysts. Our collaboration has developed on-surface redox complexation for the formation of single-site transition metal centers to functionalize solid surfaces. We show that these inorganic complexes have well-defined oxidation states and precise, highly-ordered structures. Additionally, we demonstrate that by modifying the ligand to shift the LUMO energyposition, the oxidation state of the metal centers can be changed in a predictable way: vanadium is oxidized to V(II) by bis-*pyridinyl*-tetrazine (DPTZ) and to V(III) by the more nitrogen-rich bis-*pyrimidinyl*-tetrazine. We also address the chemical accessibility of the single-site metal centers by studying the interaction and reaction of gases with our metal-ligand systems. Preliminary results of CO_2 interaction with V-DPTZ indicate an oxidation state shift from +2 to +4 showing that these metal centers are available to reduce CO_2 react with gas species. These systems were studied using scanning tunneling microscopy, non-contact atomic force microscopy, and X-ray photoelectron spectroscopy. Control of single-site metal centers at surfaces allows for new insights into redox reactivity inorganic complexes at surfaces.

COLL 443

Colloidal sphere-patterned and electrosynthesized thin polythiophene arrays for molecularly imprinting polymer (MIP) sensing

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Nanostructured and electrochemically polymerized conducting polythiophene arrays have been employed in developing molecularly imprinted polymer (MIP) sensors for analyte detection and chiral differentiation. Incorporating nanopatterns into the thin MIP sensors increases the surface area of the film and exposes more binding sites for the analyte thus resulting to a more sensitive detection. In the presentation, the main pattern used is a hexagonally close-packed monolayer of colloidal polystyrene (PS) spheres, which was assembled on a conductive electrode. Then, a solution-phase pre-polymerization complex (PPC) composed of the conducting polymer precursor and analyte molecule is electropolymerized within the electrochemically accessible interstices of the PS honeycomb lattice. The colloidal pattern can be selectively etched to reveal an inverse opal polymer pattern. The analyte molecule can then be extracted in order to form specific recognition sites that have sizes, shapes and functional groups complementary to the imprinted analyte. As monitored by quartz crystal microbalance measurements, these nanopatterned surfaces demonstrate high binding activity towards the imprinted analyte and selectivity as compared to structurally-related analog molecules. The first part of the presentation will be focused on applying the patterned thin film sensor for aspartame detection. The resulting aspartame sensor demonstrated a linear sensing range from 12.5 to 200 μM and a limit of detection of 31 μM. Specifity towards the analyte have been demonstrated against other peptides have been investigated. In the second half of the presentation, the application of the patterned polythiophene array in differentiating a chiral compound (−)-norephedrine (1*R*, 2*S*) over its diastereomer (+)-norephedrine (1*S*, 2*S*) will be presented. The formation of the films used has been monitored using a combination of surface-sensitive techniques including electrochemical quartz crystal microbalance, atomic force microscopy and X-ray photoelectron spectroscopy.

COLL 444

Designing flexible laminated bionanocomposite and nanoshells

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I discuss recent results from our research group on designing soft and strong responsive polymer and biopolymer nanocomposite materials and structures at biological interfaces. Ultrathin silk fibroin proteins, cellulose nanocrystals, and star block copolymers are assembled in order to conduct surface modification and protection of

microparticles, cells and cell assemblies, assemble self-rolled arrays, and form responsive permeable but strong microcapsules. Biocompatible, compliant and permeable LbL shells are formed from silk fibroins, silk ionomers, and graphene oxides sheets and transferred onto various synthetic cores as well as yeast and bacterial cells. Organized multiplexed arrays of ink-jet printed silk templates have been utilized for cell encapsulation with high viability and long-term storage ability. Fexible laminated bionanocomposites from silk, cellulose nanocrystals, and graphene oxide components with interphase morphology possess high elastic modulus and toughness and conductive patterning capability.

COLL 445

Immune modulatory biomaterials for cell-based therapies

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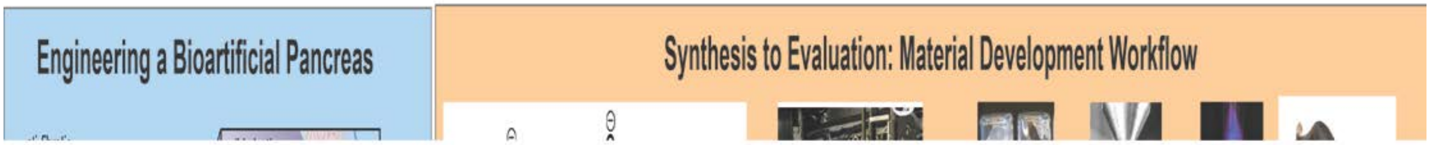
Immune cell recognition of implanted biomedical devices initiate a cascade of inflammatory events that result in collagenous encapsulation of implanted materials which leads to device failure. These adverse outcomes emphasize the critical need for biomaterials that do not elicit foreign body responses. One prime example for the use of this technology is with the development of a bioartificial pancreas for the treatment of patients suffering from diabetes. Immunoisolation of insulin producing cells with porous biomaterials provide an immune barrier that is a potentially viable treatment strategy for Type1 diabetic patients. However, clinical implementation has been challenging due to host immune responses to implanted materials. To address this challenge, we have focused our efforts on the development of improved biomaterials for the use in pancreatic islet cell transplantation.

To enable the discovery of novel superbiocompatible biomaterials we have developed a high throughput pipeline for the synthesis and evaluation of >1000 material formulations and prototype devices. Here, we describe combinatorial methods we have developed for covalent chemical modification and in vivo evaluation of alginate based hydrogels. Using these methods, we have created and screened the first large library of hydrogels, and identified leads that are able to resist foreign body reactions in both rodents and nonhuman primates. These formulations have been used to generate optimized porous alginate hydrogels fabricated with tuned geometries to enhance biocompatibility. We have identified a lead alginate derivative and capsule formulation geometry that shows minimal recognition by macrophages and other immune cells, and almost no visible fibrous deposition in rodents, and up to at least six months in nonhuman primates. Significantly, our lead formulation has enabled us to achieve the first long term glycemic correction of a diabetic, immune competent animal model with human embryonic stem-cell derived islet cells, encapsulated using our novel superbiocompatible, chemically modified alginate formulation.



COLL 446

Designing novel oriented ApoE nanoconstructs for enhanced interaction with the blood brain barrier

Luciana M. Herda, *luciana-maria.herda@cbni.ucd.ie, Delyan R. Hristov , Ester Polo, Kholoud Alnahdi, Daithi Garry, Diana Hudecz, Kenneth A. Dawson.* Centre for BioNano Interactions, University College Dublin, Dublin, Ireland

Random covalent conjugation of targeting moieties is currently the most common strategy to synthesise nanomaterials for biological applications. Two aspects play a key role in nanoparticle-cell predetermined receptor specific interaction, specifically favourable surface density and accessibility. However, often the actual surface landscape and functionality of these constructs is not well characterised. It is unlikely that current random grafting approaches can provide optimum presentation of relevant epitopes for receptor recognition and possibly subsequent endocytosis. Therefore, engineered protein fragments with tags, for site-specific grafting is considered preferable for optimising the biofunctionality of targeted constructs for *in vitro* applications.

In this work we investigate the change in biofunctionality of two engineered Cys-tagged apolipoprotein E (ApoE) with different orientation grafted onto silica nanoparticles and compare it to a randomly grafted ApoE control. Initially, an immuno-mapping platform, optimised in-house on a well-known model, is used as a quality checkpoint to quantitate surface accessibility of the receptor binding region. By using selective labelling and imaging, we were able to gain insight into the arrangement of available epitopes on the constructs surface. Subsequently, an *in vitro* blood-brain barrier model, developed in-house, is employed to study how controlling the bio-nano interface impacts biological behaviour.

COLL 447

Retinoid loaded filomicelles induce cell differentiation via sustained biomolecular signaling

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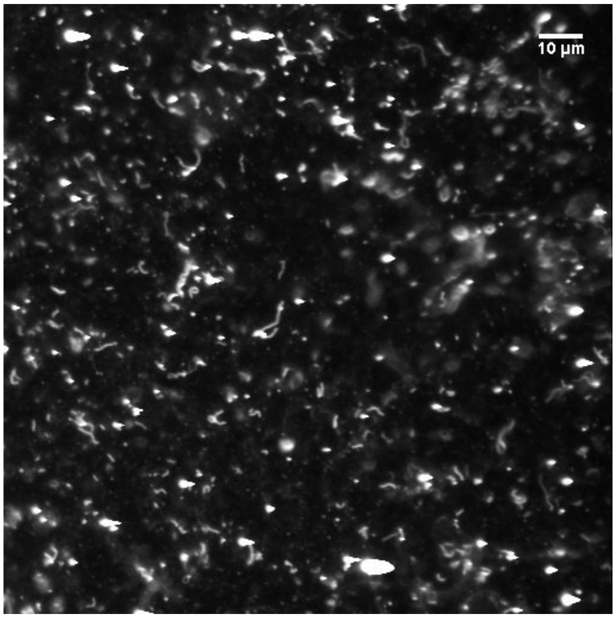
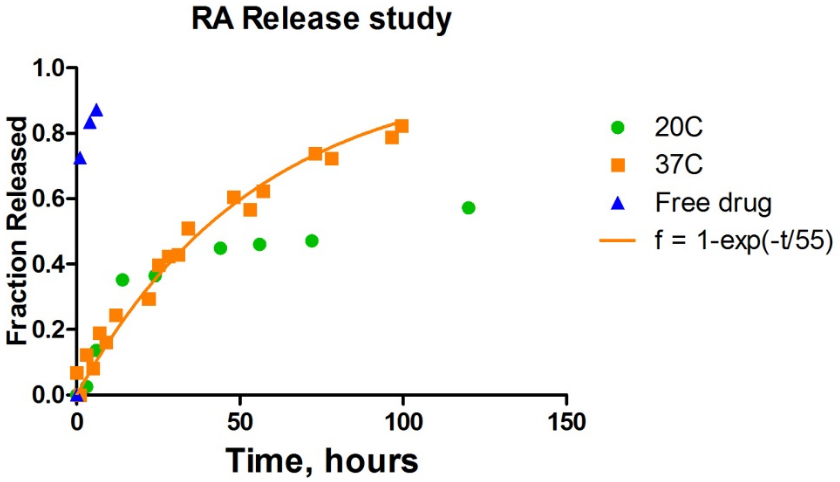
Bone marrow derived Mesenchymal Stem Cell (MSCs) are currently being explored for different regenerative therapies. For example, cell therapy involving MSC injection can help in healing bone fractures faster. The success of this therapy hinges on guiding the stem cells into the osteogenic lineage and biochemical cue can be a simple and effective means to achieve the same. A class of small molecules called Retinoids, which affect gene expression through the RAR and RXR receptor pathways have been linked to differentiation of stem cells and progenitor cells in different contexts. For example, MSCs grown in Matrigel grafts in mice, pretreated with free form of RAR antagonists (AGN or CD2665), have been shown to differentiate into osteogenic lineage and produce markers of bone. The resultant bone like mass however lacks spatial uniformity. Compared to the free drug which can be significantly lost via diffusion into surrounding space, filomicelle self-assembled from PEG-PCL copolymer can deliver the drug payload and provides a strong differentiation signal for almost a week. Filomicelles can load approximately twice the amount of drug that can be loaded in the equivalent mass of spherical assemblies. This allows a therapeutic concentration to be achieved more efficiently and uniformly.



Dye loaded filomicelles embedded within Matrigel



Retinoic acid drug release profile of PEG-PCL based filomicelles

COLL 448

ROS responsive polymers for drug and cell delivery in regenerative applications

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The Duvall Advanced Therapeutics Laboratory specializes in innovative design of smart polymer-based technologies for: (1) intracellular delivery of biological drugs such as peptides and nucleic acids, (2) proximity-activated targeting of drugs to sites of inflammation and matrix remodeling, and (3) long-term, “on-demand” drug release from localized depots. These delivery systems are designed to improve the therapeutic index of existing drugs and/or to serve as enabling technologies for manipulation of intracellular targets currently considered to be “undruggable”. To achieve optimal, finely-tuned properties for these varied biomedical applications, polymers are utilized that respond to one or more environmental stimuli including pH, matrix metalloproteinases, reactive oxygen species (ROS), and temperature. This talk will focus on the latest innovations from our lab on ROS responsive polymeric biomaterials. The two applications that will be discussed are development and application of (1) cell (ROS) degradable scaffolds for local delivery of siRNA nanoparticles to promote skin wound healing and (2) polymeric hydrogels with inherent antioxidant properties that can be harnessed for controlled drug release and encapsulation and delivery of cell therapies.

COLL 449

Novel strategies to modulate the inflammatory response to biomaterial

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Biomaterials implanted into the body immediately elicit an inflammatory response, mediated primarily by macrophages. Macrophages exist on a spectrum of phenotypes, with activities ranging from inflammatory to anti-inflammatory behavior. Biomaterial surface modification strategies designed to modulate macrophage behavior have major potential to mitigate the foreign body response or to promote tissue regeneration. This paper will present evidence that biomaterials that cause macrophages to first exhibit pro-inflammatory behavior (also known as M1 activation) followed by an anti-inflammatory phenotype (also known as M2) promote vascularization and integration, while biomaterials promoting one phenotype or the other suffer from the foreign body response. Using *in vitro* models of macrophage-biomaterial interactions, animal models, and clinical samples, we demonstrate how macrophage activation states dictate the success or failure of biomaterials. We will also present novel biomaterial surface modification strategies designed to cause rapid M1 activation and delayed M2 activation of infiltrating macrophages. Particular emphasis in our group is on surface modification strategies based on controlled affinity interactions between biotinylated proteins and avidin-based proteins. Finally, we will discuss new directions in immunomodulatory biomaterials design, including surface modification strategies to promote specific phenotypes of macrophages to enhance tissue formation (M2a) or remodeling (M2c). Ultimately, understanding and controlling the response of macrophages to implanted biomaterials represents a new and important area of biomaterials research.

COLL 450

Hydrogen-bonded multilayers of tannic acid as mediators of T-cell immunity

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Type 1 diabetes is an autoimmune-mediated disease resulting in the destruction of insulin-secreting pancreatic β-cells. Transplantation of insulin-producing islets is a viable treatment to restore euglycemia in Type 1 diabetics; however, the clinical application remains limited due to the use of toxic immunosuppressive therapies to prevent immune-mediated rejection. A nanothin polymer material with dual antioxidant and immunosuppressive properties capable of modulating both innate and adaptive immune responses crucial for transplantation outcome is presented. Through the use of hollow microparticle capsules composed of hydrogen-bonded multilayers of natural polyphenol (tannic acid (TA)) with poly(N-vinylpyrrolidone) (TA/PVPON) and with poly(N-vinylcaprolactam) (TA/PVCL), we demonstrate that autoantigen-stimulated diabetogenic $CD4^+$ T cells in the presence of TA/PVPON or TA/PVCL will secrete attenuated levels of pro-inflammatory cytokines, interferon (IFN)-γ and tumor necrosis factor (TNF)-α, and decreased synthesis of reactive oxygen and nitrogen species. These results provide evidence that TA-containing capsules are efficacious in immunomodulation, protect transplants, and prevent diabetogenic autoreactive T-cell responses. Transplantation with (TA/PVPON)- or (TA/PVCL)-coated pancreatic islets may decrease the risk of graft rejection due to attenuation of oxidative stress and IFN-γ, and restore euglycemia in Type 1 diabetics.

COLL 451

Silica-based surface modification of disposable gloves as bacteria repelling hygienic surfaces for healthcare environment

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Gloves made of materials such as latex, nitrile, and polyethylene are the most common types of barriers used to prevent cross-contamination and transmission of pathogenic bacteria in the healthcare industry. In this study, we report a surface modification approach involving “fluorinated silica nanoparticles” (FSNs) to improve the barrier properties of disposable glove surfaces. The bacterial antiadhesive (antifouling) properties of the modified gloves were evaluated with *Salmonella* Typhimurium LT2 and *Staphylococcus aureus* at bacterial concentrations of 8.6 to 9.0 log CFU/mL through the dip-inoculation approach. The ability of FSN-coated gloves to inhibit bacterial attachment is attributed to their nanotextured morphology and low surface energy, the synergistic combination of which leads to superhydrophobic surfaces. Superhydrophobicity translates into a reduced effective (real) contact between glove surfaces and water containing bacterial pathogens, decreasing the probability of bacteria to reach glove surfaces. Bacterial attachment to glove surfaces were enumerated by the pour plating method as well as direct counting via scanning electron microscopy. The bacterial populations of *S.* Typhimurium LT2 and *S. aureus* on FSN-coated latex, nitrile and polyethylene gloves was reduced by 1 to 2 log units (>97.7%) in comparison to bare gloves.

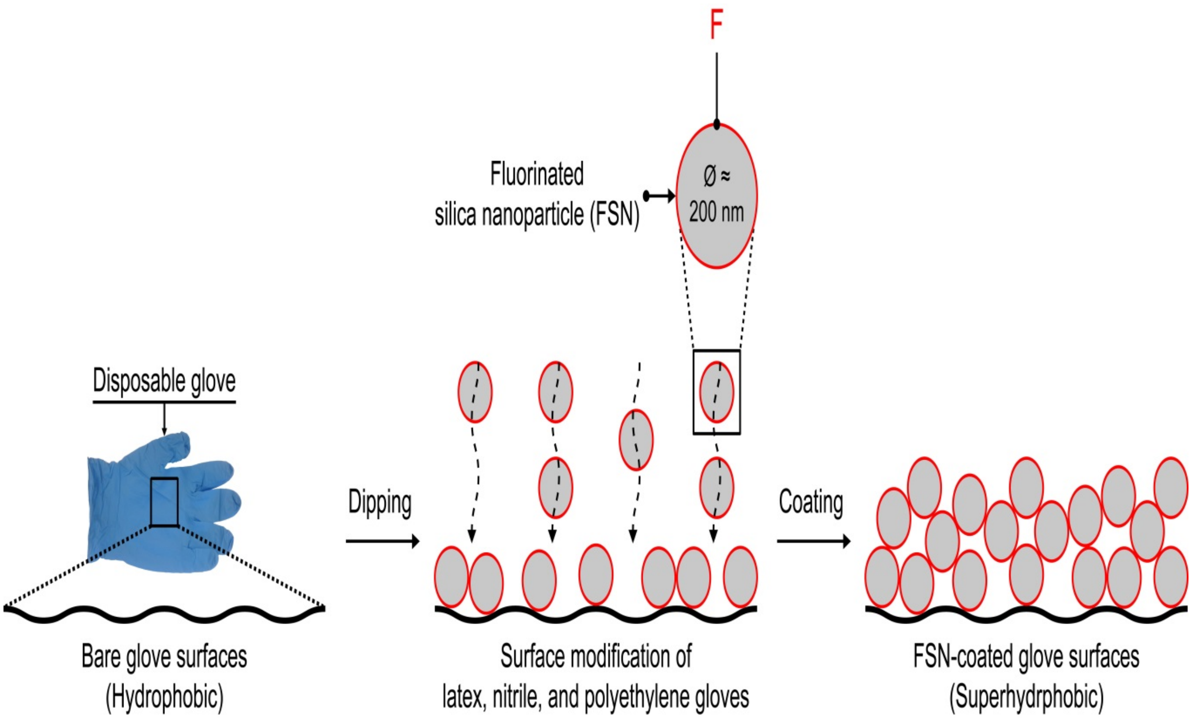

Fig. 1. Schematic illustration of surface modification of disposable gloves with “fluorinated silica nanoparticles” (FSNs) to achieve bacteria-repellent and antiadhesive (antifouling) properties.

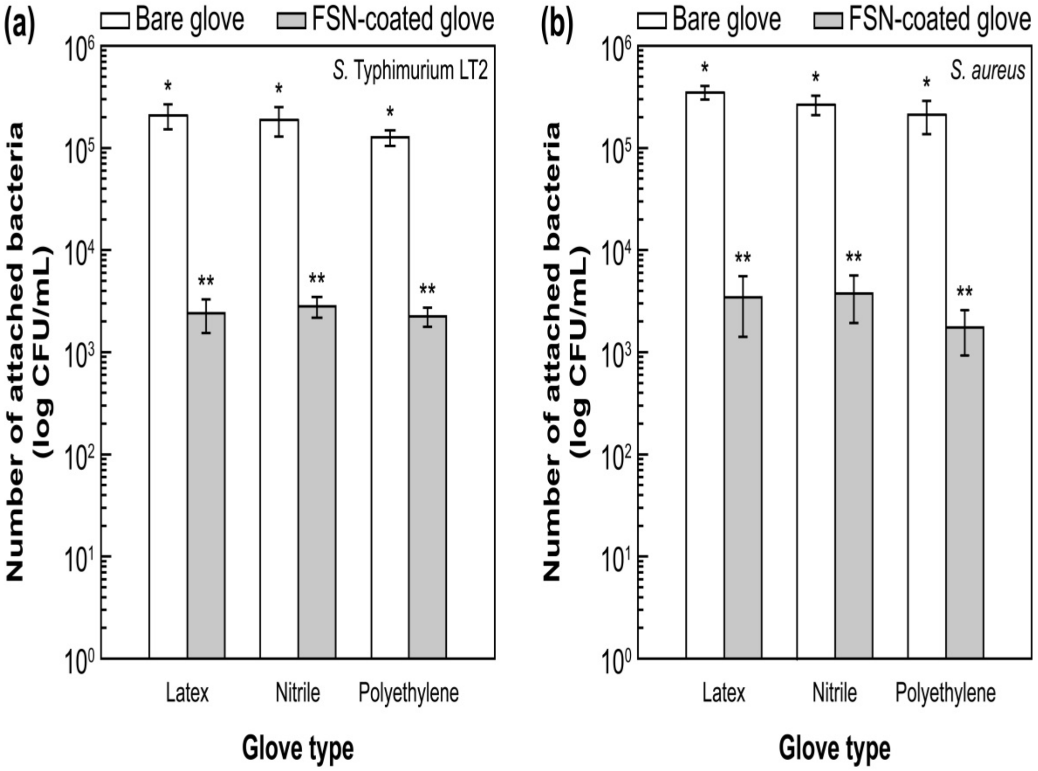

Fig. 2. The comparison of bacterial attachment to bare and FSN-coated gloves for (a) *S.* Typhimurium LT2 and (b) *S. aureus* upon 1 h exposure to bacteria.

COLL 452

Distinct mechanisms involved in fumed silica, graphene oxide, rare earth oxide, and multiwall carbon nanotube-induced membrane damage

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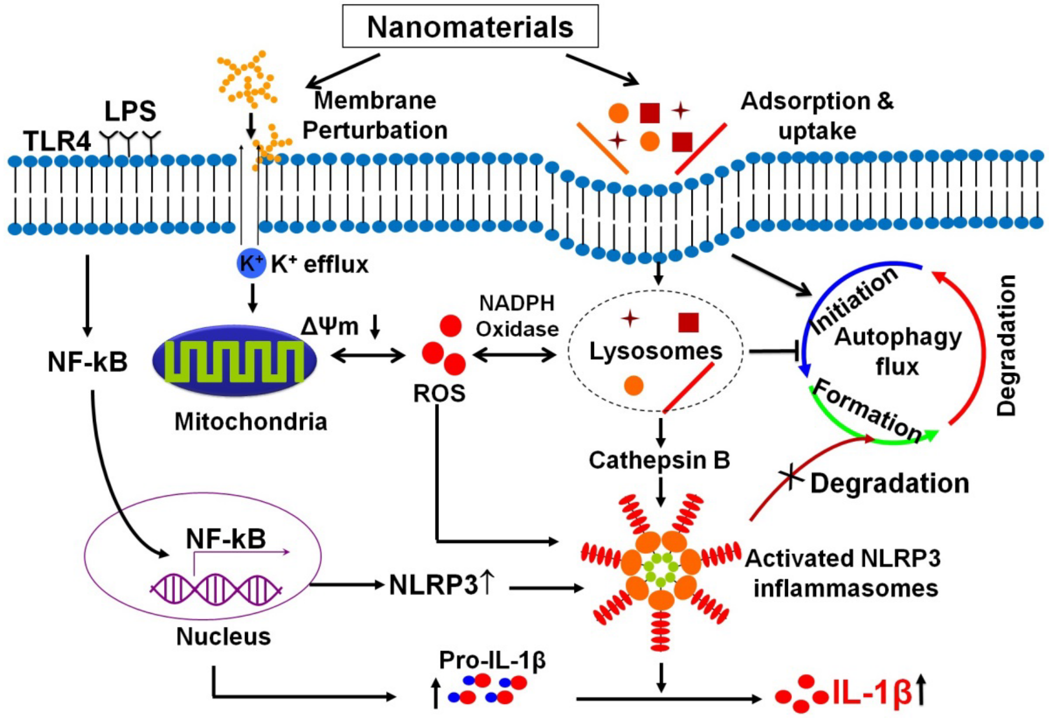
Interactions between engineered nanomaterials (ENMs) and membranes in cells play a major role in determining the toxicological outcomes. We recently found that there are distinct mechanisms involved in fumed silica, graphene oxide, and rare earth oxide-induced membrane damage, which lead to the cytotoxicity or NLRP3 inflammasome-dependent pro-inflammatory response. For fumed silica, the particles adsorb to the plasma membrane and the vicinal silanol groups and 3-member siloxane rings on fumed silica surface are highly reactive to generate hydroxyl radical that could compromise the integrity of plasma membrane, that lead to cytotoxicity, potassium efflux, NLRP3 inflammasome activation and pro-inflammatory cytokine, IL-1β, production; lung exposure to fumed silica can lead to IL-1β production and acute lung inflammation, supporting that similar interactions between fumed silica and cells also happen in vivo. Analogous to fumed silica, graphene oxides (GO) also induces membrane damage by lipid peroxidation, plasma membrane damage, and cell death. Different from fumed silica and GO, rare earth oxides (REOs) do not adsorb on the plasma membrane, instead, they are taken up inside the acidic lysosomal compartment of the cells via phagocytosis by macrophages. REO could strip phosphate groups off phospholipid to induce lysosomal membrane damage, which leads to lysosomal enzymes, and NLRP3 inflammasome activation. Similar to REOs, multiwall carbon nanotubes (MWCNTs) also elicit lysosomal membrane damage, IL-1β production, and lung fibrosis, however, the mechanism involves the highly reactive carbon surface of the tubes and surface coating with block copolymer Pluronic F108 abrogates the lysosomal damage and fibrogenic effect induced by MWCNTs. In summary, there are distinct mechanisms involved in ENM-induced membrane perturbation, and further work is needed to develop direct measurement methods for the material-membrane interactions and multi-scale modeling of the nano-bio interfaces.



COLL 453

Second harmonic generation spectroscopy for probing oxidized multiwalled carbon nanotubes at supported lipid bilayers

***Alicia McGeachy**[4], aliciamcgeachy@gmail.com, Laura L. Olenick[4], Julianne Troiano[3], Ronald Lankone[2], Eric Melby[7], Thomas Kuech[7], Eseohi Ehimaghe[3], Joel A. Pedersen[6], Howard Fairbrother[1], Franz Geiger[5].* (1) Johns Hopkins University, Baltimore, Maryland, United States (2) Dept of Chem Fairbrother Lab, Johns Hopkins University, Baltimore, Maryland, United States (3) Northwestern University, Evanston, Illinois, United States (4) Chemistry, Northwestern University, Evanston, Illinois, United States (5) Dept of Chem Tech KG G6, Northwestern University, Evanston, Illinois, United States (6) Univ of Wisconsin, Madison, Wisconsin, United States (7) Environmental Chemistry and Technology, University of Wisconsin - Madison, Madison, Wisconsin, United States

Motivated by the rising concerns regarding the potential biological and environmental implications of the widespread use of engineered nanoparticles in consumer products, we take a molecular approach to better understand, from a fundamental perspective, what factors contribute to nano-bio interactions. To this end, we have utilized two model systems: 1) supported lipid bilayers (SLBs) as an idealized model for cellular membranes and 2) oxidized multiwalled carbon nanotubes (O-MWCNTs) as a model for aged CNT-containing composite materials. Although the nano-bio interface is inherently difficult to access experimentally, valuable insight can be gleaned through the use of nonlinear optical techniques, namely second harmonic generation (SHG) and sum frequency generation (SFG) spectroscopies. As no “silver bullet” approach exists for investigating the molecular-level interactions occurring at the nano-bio interface, we

coupled quartz crystal microbalance with dissipation monitoring (QCM-D) with SHG and SFG spectroscopies. From this multi-technique approach we have determined that O-MWCNTs adsorb to SLBs formed from DMPC, DOPC, and 9:1 mixtures of DOPC and DOTAP at high ionic strength (100 mM NaCl) without disrupting the structural integrity of SLBs. From SHG adsorption studies, we have extracted apparent equilibrium constants and free energies of adsorption for O-MWCNTs interacting with SLBs formed from DMPC at 100 mM NaCl. Further, preliminary QCM-D studies suggest that O-MWCNTs with higher percent oxygen contents adsorb to SLBs formed from DMPC to a larger extent than tubes with lower oxygen contents. In addition to building a better understanding of nano-bio interactions, we aim to use this information to develop better design rules for these materials so as to minimize or abate negative biological outcomes that may arise from O-MWCNT introductions into the environment. Moreover, the results described here can be used as quantitative benchmarks for informing computational models that investigate interactions at the nano-bio interface.

COLL 454

Biopores inside synthetic membranes of giant unilamellar vesicles (GUVs) as model of cell membranes

***Martina Garni**, martina.garni@unibas.ch, Mihai Lomora, Tomaz Einfalt, Fabian Itel, Ionel A. Dinu, Wolfgang Meier, Cornelia Palivan.* Department of Chemistry, University of Basel, Basel, Switzerland

Cells represent the fundamental structural and functional biologic unit with an autonomy provided by compartmentalization, which is based on the boundary lipid membrane with embedded membrane proteins serving for the molecular transport and communication between the inter- and intra-cellular space. We introduced a biomimetic strategy to visualize transmembrane processes by insertion/reconstitution of biopores into flexible and fluid synthetic membranes of giant unilamellar vesicles (GUVs) with sizes in µm range similar to the size of living cells. Here, we present how such biopores and membrane proteins inserted in thick synthetic membranes (thickness at least 3-4 times higher than the size of the biomolecule) are functional, and allow diffusion of ions and molecules up to approximately 600 Da. As model biopores we selected gramicidin (2.5 nm in length), which served to engineer membranes selectively permeable to protons, Na^+ and K^+ ions, whilst ionomycin (1.5 nm in diameter) induced a selective permeability to Ca^{2+} ions. Successfully inserted outer membrane protein F (OmpF) allowed the diffusion of molecules up to 600 Da. A key parameter in inserting biopores/membrane proteins in synthetic membranes is the flexibility and fluidity of the membrane, able to adapt in the region of the biomolecule.

The insertion of biomolecules inside the membrane of GUVs serves for a rapid assessment of the biomolecule functionality via microscopy techniques. Our approach facilitates the control of specific catalytic reactions in confined spaces, selectively permeabilized to the substrates and products of the reaction: a deep insight of biological processes in real time can be obtained in this straightforward manner.

COLL 455

Membrane oxidation as a primary mechanism of antimicrobial activity of graphene oxide

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Graphene oxide possesses attracting properties for the design of novel antimicrobial surfaces due to its contact-based antimicrobial activity. Graphene-based antimicrobial materials have already found promising applications in multiple fields, from biofouling-resistant membranes in water treatment to antimicrobial fabrics and polymers for biomedical materials. However, the mechanisms of antimicrobial activity of graphene are still a matter of debate, which limits the efficient design of graphene-based antimicrobial applications. In this work, we demonstrate the importance of oxidative stress in the antimicrobial activity of graphene oxide surface coatings, and investigate how the physicochemical properties of graphene oxide sheets can be tuned to optimize their antimicrobial activity. For graphene oxide-coated surfaces, decreasing sheet size is found to increase bacterial inactivation. This size-dependent change in the antimicrobial activity of graphene oxide is related to changes in the material structure that increase its oxidative capacity. Using glutathione oxidation by graphene oxide and toxicity mitigation by antioxidant molecules, the size-dependent bactericidal effect of graphene oxide is shown to be primarily due to oxidative mechanisms. These findings shed light on the fundamental mechanisms of antimicrobial interactions of graphene oxide.

COLL 456

Influence of peripheral membrane proteins on nanoparticle interaction with model cell membranes

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The cytoplasmic membrane represents the frontier between cells and their external environment and serves as an initial point of contact between nanoparticles and

eukaryotic cells. Concerns about the interaction of engineered nanomaterials with biological systems in the environment have increased as their production and use has accelerated. We have employed supported lipid bilayers, widely used models of cell membranes, to systematically investigate the influence of specific membrane components on their interaction with nanoparticles. The cytoplasmic membrane can contain up to 70% protein on a mass basis, yet the influence of membrane proteins on the interaction with nanoparticles with biological membranes has received little study. As an initial step toward understanding the interaction of nanoparticles with protein-containing membranes, we have formed supported lipid bilayers incorporating model peripheral membrane proteins. We used quartz crystal microbalance with dissipation monitoring to study the interaction of gold nanoparticles bearing cationic, neutral, and anionic coatings with model membranes containing proteins. The results obtained with protein-containing bilayers contrast strongly with those obtained from pure phospholipid bilayers. For example, neutral and anionic nanoparticles that interact minimally with phospholipid-only bilayers, interact to a substantial extent with model membranes containing proteins. Furthermore, some nanoparticles appear to remove proteins from the membrane. These results highlight the importance of systematic investigation of membrane components in addition to phospholipids for understanding nanoparticle interactions at the nano-bio interface.

COLL 457

Supported lipid bilayers containing lipids with varying transition temperatures studied by vibrational sum frequency generation spectroscopy

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The nano-bio interface is becoming increasingly important as the amount and prevalence of engineered nanomaterials rise. A key question concerns the quantification of structural changes in lipid membranes once they are brought into contact with nanoparticles. Here, we use supported lipid bilayers (SLBs) as idealized model systems for cell membranes and discuss how to probe SLBs using the interface-specific nonlinear optical technique sum frequency generation (SFG) spectroscopy, as well as fluorescence microscopy, X-ray photoelectron spectroscopy, and quartz crystal microbalance with dissipation monitoring in the context of the nano-bio interface. Our combined study sheds light on how SFG responses produced in the C-H stretching region from symmetric SLBs under isothermal (T = 22±2°C) conditions co-vary with the transition temperatures of the lipids from which the SLB is formed. The specific lipids studied here are 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (18:1 Δ9-Cis, DOPC),1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (16:0-18:1, POPC), 1,2-dilauroyl-*sn*-

glycero-3-phosphocholine (12:0, DLPC), 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (14:0, DMPC), 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (16:0, DPPC), and 1,2-distearoyl-*sn*-glycero-3-phosphocholine (18:0, DSPC) in 100 mM NaCl, 10 mM Tris buffer, pH 7.4. We find that the intensity of the SFG signal at 2870 cm^{-1} (±15 cm^{-1}), which has been attributed by others to the methyl symmetric stretch arising from the lipid tail, co-varies positively with the transition temperature (T_m) of the lipid: when the lipid T_m is below (*resp*. above) the laboratory temperature, the intensity of the peak near 2870 cm^{-1} is low (*resp*. high). These results are consistent with temperature-dependent measurements reported by Liu and Conboy. The implications of our work for engineering environmentally safe nanomaterials are discussed.

COLL 458

Qualitative and quantitative analyses of the molecular-level interaction between memantine and model cell membranes

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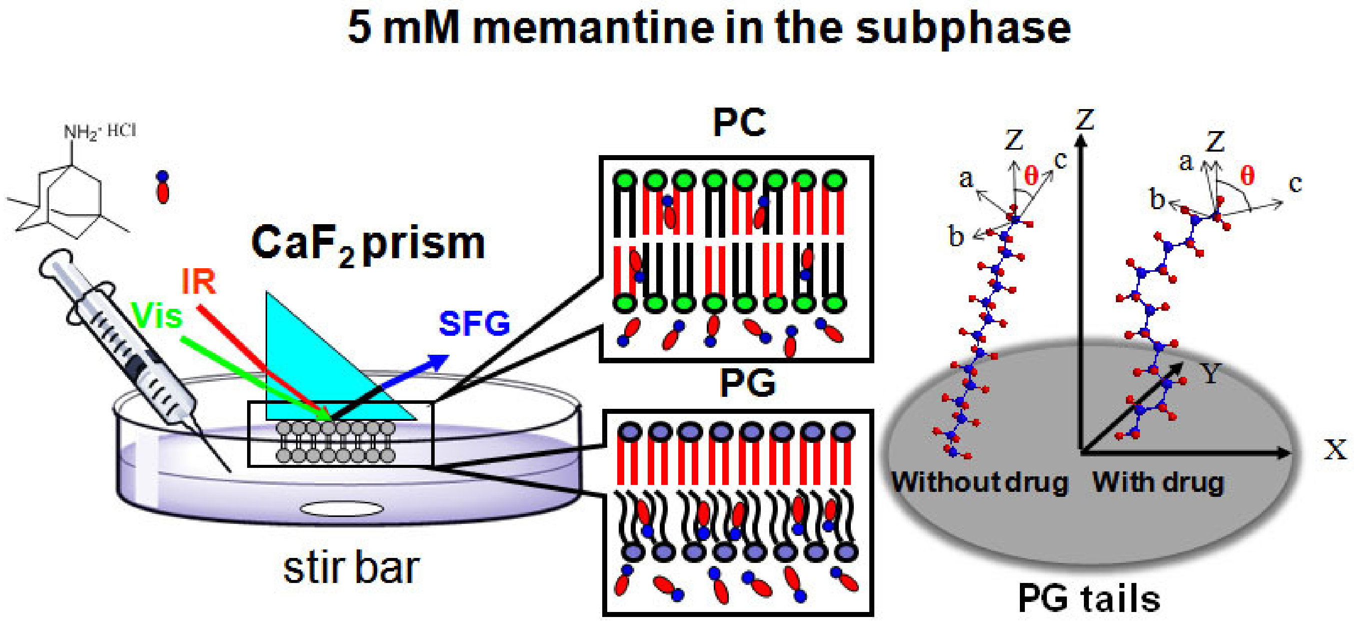
Sum frequency generation (SFG) vibrational spectroscopy was employed to study the interaction between memantine (a water-soluble drug for treating Alzheimer's disease) and lipid bilayers (including zwitterionic PC and negatively charged PG lipid bilayers) at the molecular level in real time and *in situ*. SFG results revealed that how the memantine affected these lipid bilayers in terms of the lipid dynamics, average tilt angle (θ), as well as angle distribution width (σ). It was found that memantine could adsorb onto the zwitterionic PC surface but did not affect the flip-flop rate of the PC bilayer even at the presence of 5.0 mM memantine, indicating the negligible interaction between memantine and PC bilayer. However, for the negatively charged PG bilayer, it was found that the outer PG leaflet could be significantly destroyed by memantine at a relatively low memantine concentration (1.0 mM), while the inner PG leaflet kept intact. Besides, the θ and σ of CD_3 groups in the outer PG lipid leaflet were calculated to be around 82.0°and 19.5°after adding 5 mM memantine, respectively, indicating that these CD_3 groups were prone to lie down at the membrane surface (versus the surface normal) with the addition of 5 mM memantine while nearly stand up without the addition of drug molecules. These monolayer- and molecular-level results could hardly be obtained by other techniques. To the best of our knowledge, this is the first experimental attempt to quantify the drug-induced orientational changes of lipid molecules within a lipid bilayer. The present work provided an in-depth understanding on the interaction between memantine and model cell membranes, which will potentially benefit the development of new drugs for neurodegenerative diseases involving drug–membrane interaction.



COLL 459

Impact of nanoscale lithium nickel manganese cobalt oxide (NMC) on the gram-positive and gram-negative bacteria

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Nickel manganese cobalt oxide (NMC) is a class of lithium intercalation compounds of emerging importance in nanoparticle form as cathode materials for lithium-ion batteries. To evaluate the potential environmental impact of release of this material in the environment, we synthesized NMC nanosheets and investigated their interaction with two bacerial strains: *Shewanella oneidensis* and *Bacillus subtilus*. Exposure to NMC significantly impaired bacterial population growth and respiration, dependent on the incongruent material dissolution and measurable release of all four metal constituents (Li, Mn, Co, and Ni) into solution. The largest impacts arose from Ni(II) and Co(II) species.

COLL 460 – Withdrawn.

COLL 461

Tracking plasmonic particle motion in optical tweezers and in living cells

Jochen Feldmann, *feldmann@lmu.de.* Physics, LMU Munich, Munich, Germany

I will review our work on tracking the motion of plasmonic particles in optical tweezers and within living cells. Using this so-called "nano-ear" technology we could analyze the flagellar rotation dynamics of an individual bacterium and analyze the local viscosity in the interior of a living cell. In addition, thermophoretic effects caused by the optothermal heating of plasmonic Janus-particles and possible applications for in-vivo force measurements will be presented and discussed.

COLL 462

Nanoconjugation and its impact on endosomal signaling: A case study of the epidermal growth factor receptor

***Bjoern M. Reinhard**, bmr@bu.edu.* Boston University, Boston, Massachusetts, United States

The interactions of nanoparticles (NPs) with cellular components forms the basis for novel NP-based approaches to control and manipulate cellular processes. One aspect of particular interest to our laboratory is the effect of epidermal growth factor (EGF) nanoconjugation on EGF receptor (EGFR) signaling. Endosomal EGFR signaling is subject to strict spatial control so that changes in the trafficking of the activated receptor due to conjugation of its ligand to a NP are expected to have profound consequences for the signaling outcome. To test this hypothesis, we investigated the trafficking of nanoconjugated EGF ligand i) through optical tracking studies in living cells and ii) through density fractionation of NP containing endosomes. These studies show that conjugation of EGF to nanoparticles impacts intracellular trafficking and that this perturbation is correlated with distinct changes of the signaling outcome. Most importantly, EGF-mediated apoptosis is observed at concentrations that are significantly lower than for the free ligand.

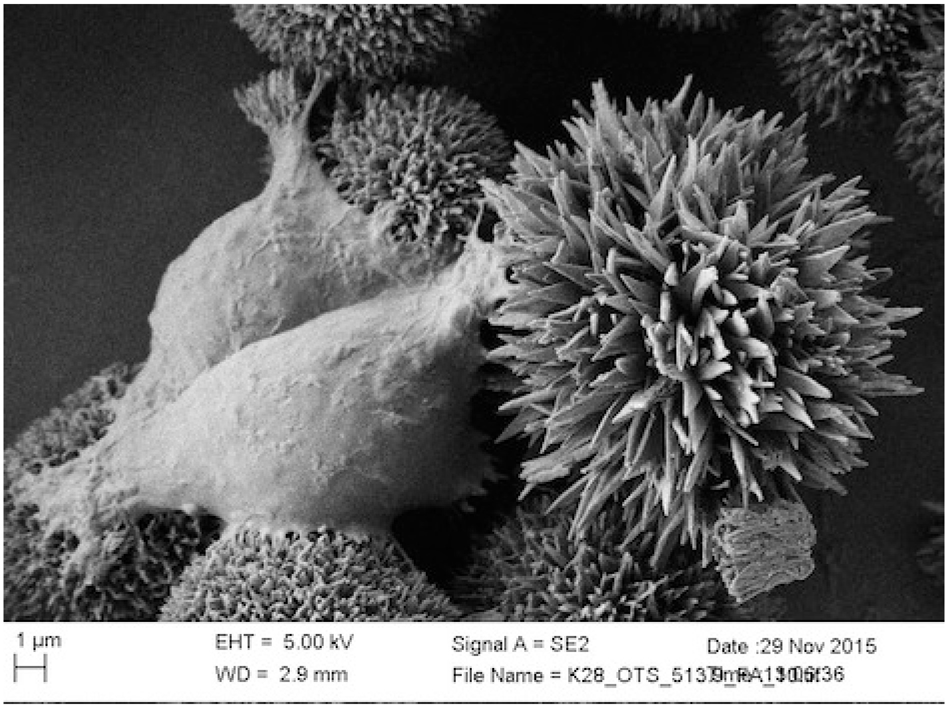
COLL 463

Cellular photostimulation with hydrogen-bonded organic semiconductor microcrystal interfaces

***Marie Jakesova**[1], marie.jakesova@jku.at, Monika Litvinukova[2], Mykhailo Sytnyk[3], Wolfgang Heiss[3], Rainer Schindl[2], Niyazi Serdar Sariciftci[1], Eric D. Glowacki[1].* (1) Physical Chemistry, Johannes Kepler University, Linz, Austria (2) Institute of Biophysics, Johannes Kepler University, Linz, Austria (3) iMEET, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

Successful bioelectronics should rely on an active material that is biocompatible and interfaces intimately with cells. We report on biocompatible hydrogen-bonded semiconductor nanostructured crystals for cellular photostimulation. The biomimetic hierarchical crystals show impressive affinity for cellular coupling and efficient stimulation. The close interface between the nanostructured crystals and cells was elucidated using electron microscopy. Light irradiation was found to elicit a reversible electrophysiological response, measured using patch-clamp microelectrochemistry, only in cells that grow in contact with the nanostructured crystals. The mechanism of action

was studied by investigating the effects of photoexcitation on specific ion channels. In total, three different types of ion channels and two types of cells were studied. We discuss the interplay between capacitive, faradaic, and thermal effects on cellular electrophysiology. Over the presented materials would be a potent candidate for cellular photostimulation, which is highly relevant to the new generation of wireless retinal implants.



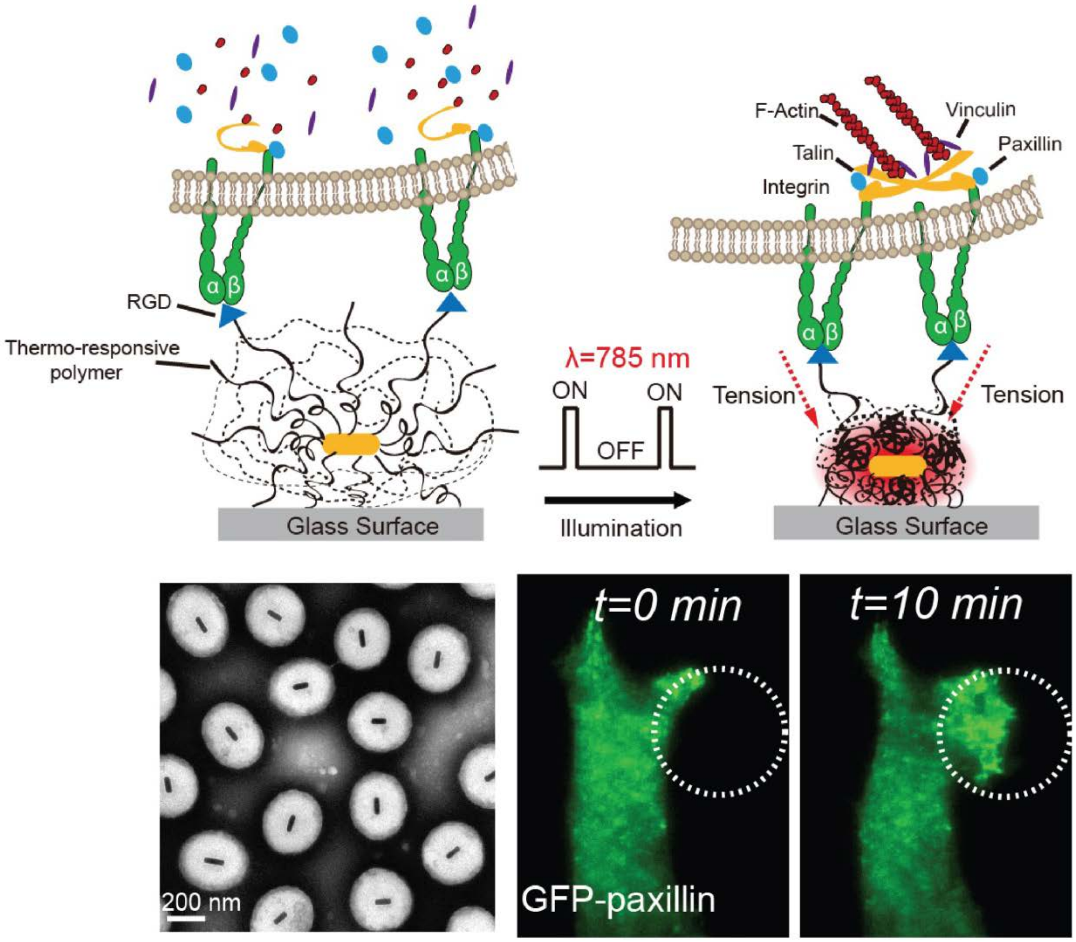
COLL 464

Gold-polymer core-shell nanoparticles as optically triggered mechanical actuators

Khalid Salaita, *k.salaita@emory.edu.* Chemistry, Emory University, Decatur, Georgia, United States

Optical approaches for the controlling biological systems are transforming the field of cell biology, as exemplified by caged or photoswitchable molecules and by optogenetic constructs. Similarly, methods to harness light for delivering precise physical inputs to biological systems could potentially transform the study of mechanotransduction (how forces are converted into biochemical signals). Toward this goal I will describe our efforts aimed at developing optomechanical actuator (OMA) nanoparticles to manipulate receptor mechanics with high spatiotemporal resolution using near-infrared illumination. Nanoparticles are comprised of a gold nanorod coated with a thermoresponsive polymer shell. Illumination leads to local heating, and particle collapse, thus delivering piconewton forces to specific cell surface receptors with high spatial (~micron scale)

and temporal resolution (msec timescales). Optomechanical actuator nanoparticles were used to exert forces through the integrin receptors, thus mechanically controlling focal adhesion formation, cell protrusion, and cell migration in living cells. This new approach to controlling mechanotransduction circuits allows for optically controlling cell migration without the use of genetic engineering.



COLL 465

Gold nanoparticle arrays for plasmon-enhanced single-molecule fluorescence in live bacteria

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Live-cell imaging elucidates subcellular dynamics, and single-molecule imaging extends the capabilities of fluorescence microscopy to the scale of tens of nanometers. To understand the physics of cellular processes on the molecular scale though, improved localization of single molecules is important. In this work, Moiré nanosphere lithography provides deposition masks to form gold nanoparticle arrays. The extracellular arrays act

as plasmonic antennas for enhancing the fluorescence of the red fluorescent protein PAmCherry in the membrane of the human pathogen *Vibrio cholerae*. Examining fusions of PAmCherry and the *V. cholerae* regulatory protein TcpP in the near field of the plasmonic arrays allows for higher precision localizations and longer single-molecule tracks. Nanoparticle arrays are characterized with correlated dark field scattering and scanning electron microscopy, and the plasmon-enhanced fluorescence is imaged with single-molecule localization microscopy.

COLL 466

Simultaneous cytosolic delivery of siRNA and chemotherapeutics for enhanced breast cancer therapy

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Using siRNA-mediated protein with small molecule drug treatments to target multiple cellular pathways can create more effective combination cancer therapies. Here, nanoparticle-stabilized capsules (NPSCs) consisting of an inner linoleic acid oil core, coated on the surface with positvely charged arginine functionalized gold nanoparticles, are used as a platform for co-delivery of survivin-targeted siRNA and tamoxifen for breast cancer therapy. The oil core of the NPSC allows the vehicle to enter cells through a non-endocytotic lipid-based mechanism, causing direct delivery of encapsulated cargo to the cytosol. This delivery mode contrasts traditional delivery vehicles that rely on endocytosis, which results in endosomal entrapment, and reducies the effective concentration of delivered agent that acts on the cell. The NPSC delivery mechanism maximizes the potency of delivered cargo by allowing delivered molecules to interact directly with cellular components necessary for biological effect. The modular nature of the NPSC system also allows for orthogonal loading of negatively charged cargoes and hydrophobic therapeutics, enabling simultaneous delivery of chemically distinct combinations. The utility of this co-delivery was demonstrated through NPSC co-delivery of tamoxifen and survivin-targeted siRNA into breast cancer cells, inducing cellular apoptosis by disabling pathways and resulting in enhanced death in breast cancer cells.

COLL 467

Rapid cytosolic delivery of protein coupled with nuclear trafficking signals using nanoparticle stabilized capsules

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Delivery of proteins into cells generally results in endosomal entrapment. As a result, the utility of protein delivery strategies is limited for both fundamental and therapeutic applications. We recently have developed a method for rapid cytosolic delivery of protein using nanoparticle stabilized capsules (NPSCs). NPSCs are stabilized by supramolecular guanidine-carboxylate interactions between the peptide HKRK-functionalized gold nanoparticles (HKRK-NPs) of the shell and the hydrophobic fatty acid (oil) components in the core. This method produces capsules that are capable of rapidly releasing active protein directly into cytosol. We have used this method to quantitatively monitor nuclear protein trafficking. For these studies we have used five different nuclear localization signals (NLS) attached to eGFP. Quantitative comparison of the nuclear accumulation of the five NLS-eGFPs from laser LSCM results has shown vastly different nuclear import efficiencies. The dynamics of the nuclear accumulation of the NLS-eGFP in the cell has been tracked through live cell microscopic imaging that reached equilibrium in as little as 6 minutes.

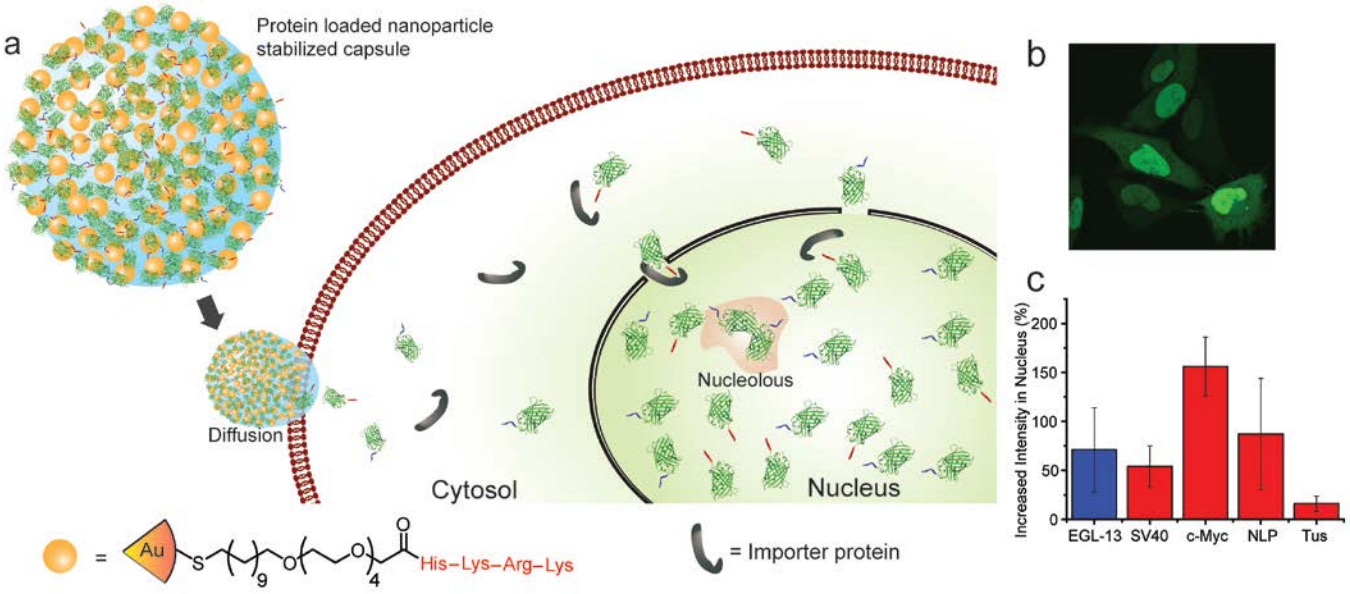

Fig.1. (a) Cytosolic delivery and nuclear accumulation of eGFP with NLSs using NPSCs. (b) LSCM image showing cellular distribution pattern of NLS-tagged eGFP. (c) Statistical analysis revealing nuclear importing efficiency (6 cells per group).

COLL 468

Multifunctional polymer nanoparticles: Combinatorial therapy for triple negative breast cancers

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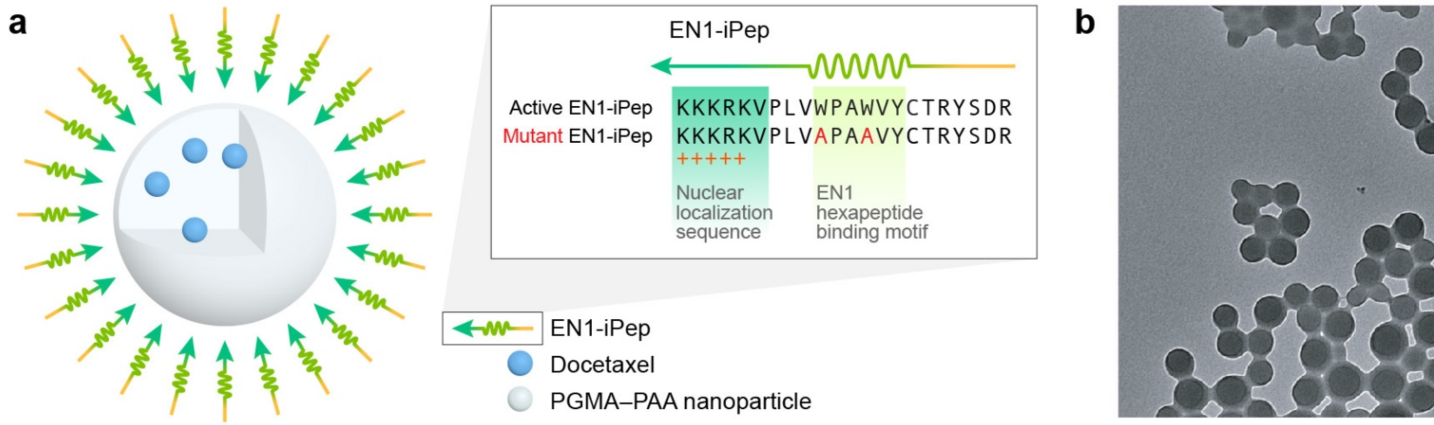
Triple negative breast cancers are associated with a particularly poor prognosis among the various breast cancer subtypes. There is currently no targeted therapy available, leaving chemotherapy as the only option, but in advanced disease, these tumours tend to acquire resistance against chemotherapeutic drugs. There is an urgent need to develop novel and more specific therapies to treat triple negative breast cancer tumours. Transcription factors (TFs) are proteins that bind and regulate many genes. The highly specific protein–protein interactions between transcription factors and their cofactors are required to cooperatively bind specific DNA sequences. However, it has been suggested that transcription factors may also play a role in cancer initiation, recurrence, and resistance. Triple negative breast cancers selectively overexpress Engrailed 1 (EN1), a transcription factor associated with chemotherapeutic resistance. We have developed nanoparticles capable of delivering both interference peptides (EN1-iPep) that disrupt EN1 binding and an anticancer drug (docetaxel) in an animal model of triple negative breast cancer. Our nanoparticle system consists of poly(glycidyl methacrylate) nanospheres, whose reactive epoxide side chains allow for functionalization of the nanoparticle surface. Nanoparticles were modified with poly(acrylic acid) to create an electrostatically favourable surface to facilitate binding of EN1-iPep. Nanoparticle targeting was achieved using the RGD peptide motif. We will present the rationale behind design of our EN1-iPep, preparation of the multifunctional nanoparticle platform, *in vitro* data showing synergy between docetaxel and EN1-iPep, and *in vivo* targeting and treatment. Our results demonstrate that these multifunctional nanoparticles, combining delivery of docetaxel and EN1-iPeps, are a promising therapy for triple negative breast cancers.



COLL 469

Development of biodegradable nanophotosensitizers through bioinspired route for photodynamic therapy applications

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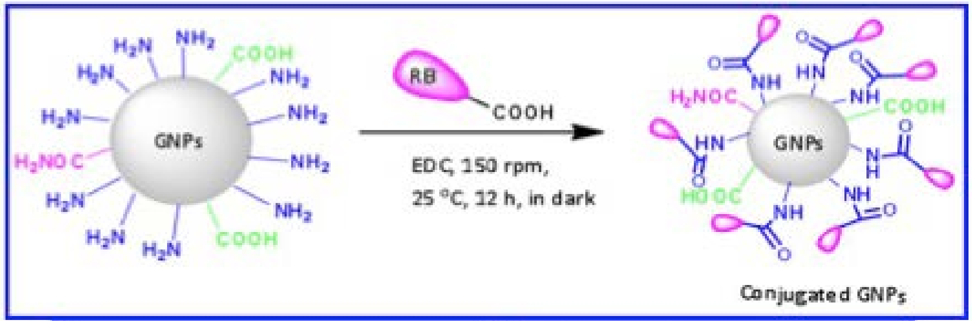
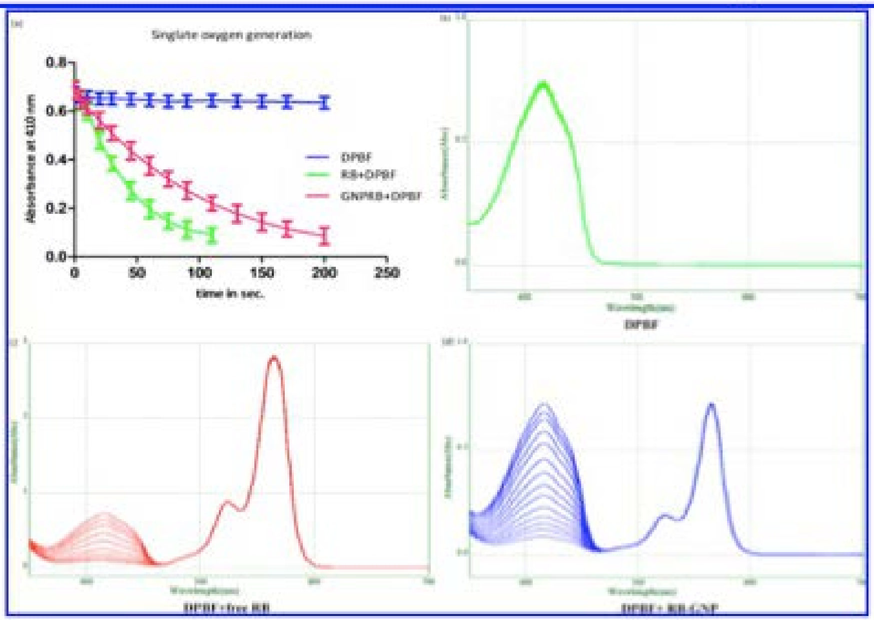
Photodynamic therapy (PDT) plays a vital role for the treatment of several diseases including cancer. Poor hydrophilicity is a major drawback of using photosensitizers in biological systems. Certain tumor grasping porphyrin based photosensitizers have the capability to fluoresce upon excited with light. Various conjugatable porphyrins were synthesized, characterized and finally conjugated on the surface of the nanoparticles. Prodrug model systems containing biodegradable materials (e.g gelatin nanoparticles) nanophotosensitizer (GNPs) conjugates were thus developed. The conjugation protocol upon optimization revealed high drug loading on GNPs. Furthermore, photophysical properties of the nanoconjugates were determined using a light source showing high value of singlet oxygen quantum yield. This model enzyme activatable controlled drug release system is valuable for further photodynamic therapy studies.





COLL 470

Ultrasensitive real-time imaging of cancer cells based on multi-functional nanoscale probes

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Early cancer diagnosis remains a critical strategy for reducing cancer mortality and improvement of the cure rate. Diagnosis and therapy in combination with nanotechnology may offer an alternative promising and overcome the difficulty. And the early diagnosis based on some smart nanoscale molecules and nanostructures could be crucial for a successful treatment of cancers.

This study has established some ultrasensitive and intelligently multi-functional nanoprobes for real-time tracking and analysis of disease related biomolecules/cells/tissues. Meanwhile, we have developed a new strategy for the fast and high sensitive recognition of the target biomolecules and cancer cells by combining the nanoscale macromolecules and functionalized nano-interface with the spectra-electrochemical study. Especially, the ultrasensitive in vivo bio-imaging of cancer cells and tumor tissues has been realized through in situ biosynthesized near-infrared fluorescence nanoclusters and magnetic nanoclusters, establishing creative methods for non-invasive molecular diagnosis and treatment of cancers.

COLL 471

Surfaces presenting α-phenyl mannoside derivatives enable formation of stable, high coverage, non-pathogenic *Escherichia coli* biofilms against pathogen colonization

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Prevention of pathogenic colonization on medical devices over a long period of time remains a great challenge, especially in a high nutrient environment that accelerates the production of biomass leading to biofouling of the device. Since biofouling and the subsequent pathogen colonization is eventually inevitable, a new strategy using non-pathogenic bacteria as living guards against pathogenic colonization on medical devices has attracted increasing interest. Key to the success of this strategy is to pre-establish a high coverage and stable biofilm of benign bacteria on the surface. Silicone elastomers are one of the most widely used materials in biomedical devices, such as urinary catheters, tracheostomy tubes, drainage tubes and gastro-intestinal feeding tubes. In this work, we modified silicone surfaces to promote formation of high coverage and stable biofilms by a non-pathogenic *Escherichia coli* strain 83972 with type 1 *fimbriae* (*fim*+) to interfere with the colonization of an aggressive biofilm forming, uropathogenic *Enterococcus faecalis*. Although it is well known that mannoside surfaces promote the initial adherence of *fim*+ *E. coli* through binding to the FimH receptor at the tip of the

type 1 *fimbriae*, it is not clear whether the fast initial adherence could lead to a high coverage and stable protective biofilm. To explore the role of mannoside ligands, we synthesized a series of alkyl and aryl mannosides varied in the structure and immobilized them on silicone surfaces pre-coated with a poly(amidoamine) (PAMAM) dendrimer. We found that stable and densely packed benign *E. coli* biofilms were formed on the surfaces presenting biphenyl mannoside with the highest initial adherence of *fim*+ *E. coli*. These non-pathogenic biofilms prevented the colonization of *E. faecalis* for 11 days at a high concentration (10^8 CFU mL^{-1}, 100,000 times above the diagnostic threshold for urinary tract infection) in the nutrient rich Lysogeny Broth (LB) media. The result shows a correlation among the initial adherence of *fim*+ *E. coli* 83972, the coverage and long-term stability of the resulting biofilms, as well as their efficiency for preventing the pathogen colonization.

COLL 472

Development of microcapsules with dual functionality - vector and antimicrobial protection

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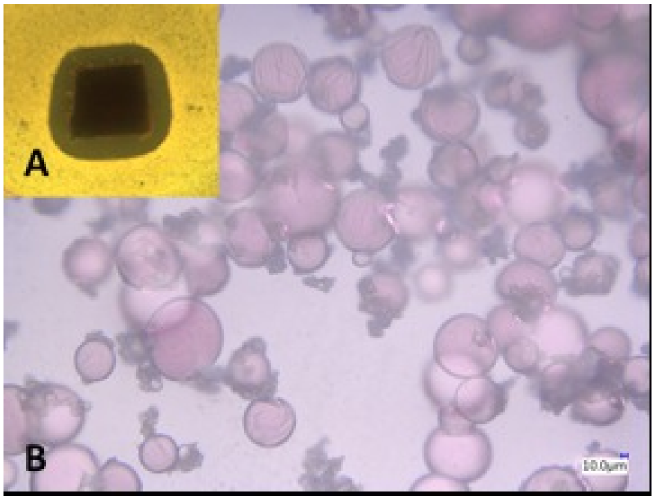
Insects and bacteria are not merely nuisances to the Warfighter, but threats. Vector-borne illness and bacterial infection can compromise the health and the effectiveness of the Soldier in the field, and therefore the ability to incorporate protection into a textile would be advantageous. Other technologies require repeated treatments of the textile by the Warfighter, which may be infeasible while in the field. The technology developed here would provide safe and reliable vector and antimicrobial protection to the Soldier using microencapsulation.

Microcapsules are formed using complex coacervation. An emulsion is formed using an anti-vector oil and the anionic surfactant, SDS, in a solution containing BSA. This solution is homogenized, generating SDS/BSA micelles that surround the anti-vector droplets. A commercially available antimicrobial polymer is then added to the solution under stirring conditions. The antimicrobial polymer is heavily aminated and cationic. It adsorbs onto the surface of the anionic micelles due to the electrostatic interaction between the two, and the microcapsules precipitate out of solution. Glutaraldehyde is then added to crosslink and stabilize the particles. The polymer contains no primary amines, thus the glutaraldehyde preferentially reacts with the BSA, preserving the antimicrobial activity of the microcapsules and leaving reactive groups on the surface for coupling to a textile. Particle formulation has been optimized for particle stability, loading capacity, and antimicrobial activity. The different formulations were characterized using DLS, microscopy, GC, and antimicrobial testing. Antimicrobial activity is demonstrated on a fabric swatch in the figure below (A) as well as microscopy of anti-vector (dyed red)-containing particles (B). Encapsulation of anti-vector oil was successful and antimicrobial activity is retained both in solution and when applied to a textile.



COLL 473

Biomedical applications of carbon dots: Interaction, drug delivery, and imaging

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Carbon dots (C-Dots) as novel carbon nanomaterials have recently attracted great attention due to their unique properties, excellent biocompatibility, and promising biomedical applications. Nontoxic water soluble C-Dots were prepared and characterized using chemical methods. C-Dots were incubated with human insulin and other peptides to study the effects on protein fibrillation, which is associated with some central nervous system (CNS) diseases such as Alzheimer's disease. It was found that they could inhibit peptides from forming fibrils. Therefore, they could be potentially used as a drug for CNS disease treatment. For this purpose, C-Dots were covalently conjugated to transferrin for crossing the blood brain barrier. To improve the anti-cancer drug efficiency and reduce the side effect, we also conjugated together C-Dots with transferrin and doxorubicin. Experiments showed that the conjugated system facilitated the cellular up-taking of doxorubicin by cancer cells. Strikingly, we also found that these C-Dots specifically bind to calcified bones with significant enhancement of fluorescence, demonstrating that they could offer a new *in vivo* method to detect and image bones by fluorescence. Another challenge in the bionanotechnology was to determine protein concentration in the protein-nanoparticle conjugates. For this purpose, we established a simple and nondestructive approach to quantify the protein concentration in the protein-C-Dots aqueous solution using circular dichroism spectroscopy.

COLL 474

Quantification of nanoparticle tumor delivery efficiency

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The concept of “targeting” nanoparticles into tumors for improved diagnosis and therapy of cancer is attractive but challenging. The premise of this concept is to specifically deliver imaging and/or therapeutic nanoparticles to the target (*i.e.*, the tumor) while minimizing off-target accumulation. The predominant belief in the nanotechnology community is that the rationale of nanoparticle tumor targeting is based on the enhanced permeability and retention (EPR) effect which was introduced by Maeda *et al.* in 1986. Recently, we quantified the nanoparticle tumor delivery efficiency, *i.e.*, the number of systemically administered nanoparticles that accumulate in the target tumor tissue by surveying manuscripts published from 2005 to 2015. Surprisingly, we found that only 0.7% of the injected nanoparticle dose actually interacts with the tumor (median value derived from 232 data sets). Our results suggest that only 7 out of 1,000 systemically administered nanoparticles reach the targeted tumor tissue. This presentation will explore the potential causes of the poor delivery efficiency from the perspective of the tumor biology and organs that compete for administered nanoparticles, followed by a discussion of the impact on the clinical translation of nanomedicines. The lack of translational progress is currently impeded by the inability to control the nanoparticle transport inside the body due to the complexity of these biological systems.

COLL 475

Polyamine/nucleotide coacervates strongly partition RNA to mimic early Earth protocells and modern cellular compartments

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Phase separation of aqueous solutions containing polyelectrolytes can lead to formation of dense, solute-rich liquid droplets referred to as coacervates surrounded by a dilute continuous phase of much larger volume. This type of liquid-liquid phase separation helps explain the appearance of polyelectrolyte-rich intracellular droplets in the cytoplasm and nucleoplasm of modern biological cells, and may also be relevant to non-membranous protocellular compartmentalization of nucleic acids on the early Earth. Here we describe complex coacervates formed upon mixing the polycation poly(allylamine) (PAH, 15 kDa) with the anionic nucleotides adenosine 5’ mono-, di-, and triphosphate (AMP, ADP, and ATP). Non-membranous droplet formation was observed over a wide range of pH values and $MgCl_2$ concentrations. The nucleotides themselves as well as Mg^{2+} and RNA oligonucleotides were all extremely concentrated within the droplets. For instance, nucleotides present at just 2.5 mM in bulk solution had concentrations greater than 1 M inside the coacervates droplets; a solution with a total Mg^{2+} concentration of 10 mM had 1-5 M Mg^{2+} in the droplets; and RNA random sequence (N_{54}) partitioned ~10,000-fold into these systems. These structures are thus rich in nucleotides, Mg^{2+}, and RNA, providing a system poised for the spontaneous generation of non-membranous droplets that occurs in cell cytoplasm. In addition, the compartmentalization of nucleotides at high concentrations could have facilitated their non-enzymatic polymerization to form oligonucleotides under prebiotic conditions in an RNA world, making coacervate droplets an appealing platform for exploring protocellular and cellular environments.

COLL 476

Sensitive detection of RNA viruses with the help of reverse transcription loop-mediated isothermal amplification, magnetic nanoparticles, and chemiluminescence

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RNA viruses, particularly, the highly pathogenic avian influenza (HPAI) virus, pose serious health concerns, and cause huge economic losses worldwide. Diagnostic tools for the early detection of these deadly RNA viruses are urgently needed to implement treatment and disease control strategies. Conventional reverse transcription polymerase chain reaction (RT-PCR)-based chemiluminescent (RT-PCR-CL) detection is frequently used for the diagnosis of viral infections. However, the requirements for expensive PCR machines and longer thermocycling times are significant drawbacks. In this study, we propose a method based on reverse transcription loop-mediated isothermal amplification (RT-LAMP) combined with chemiluminescence (CL) to detect H7N9 virus. The proposed method does not require any expensive instruments, and processing time is remarkably shortened compared to that of RT-PCR-CL. Since several factors including RT-LAMP temperature, probe concentration, hybridization temperature, and hybridization duration might affect the CL signal, each of these parameters was investigated and optimized. One thousand copies/mL of H7N9 RNA were detectable using the optimized RT-LAMP-CL method. The detection time was significantly reduced by using RT-LAMP, in comparison with conventional RT-PCR-CL. This technique holds great promise for viral detection and diagnosis, especially with regard to avian influenza virus.

COLL 477

Synthesis of multifunctional magneto/plasmonic liposomes for drug delivery applications

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Combining liposomes with different types of nanoparticles (magnetic, plasmonic) recently emerged as a very intriguing approach leading to the synthesis of multifunctional nanovesicles for drug delivery applications. The importance of such nanohybrids resides in their ability to interact with several external stimuli (NIR lasers and/or magnetic fields) thus being able to release the incorporated therapeutic agents in a very controllable and reproducible manner. Moreover, owing to their amphiphilic character, the liposomes can incorporate hydrophilic as well as hydrophobic molecules of interest. In this letter we report the successful synthesis and characterization of two classes of such multifunctional hybrid nanoobjects: plasmonic liposomes and magnetoliposomes. Two strategies have been developed for the creation of the two types of nanoobjects. Firstly, the plasmonic liposomal nanocarriers (PLiN) have been prepared by taking advantage of electrostatic interactions between small unilamelar cationic liposomes and negatively charged biocompatible gold nanoparticles synthesized using an original method developed in our laboratory. This allowed the synthesis of liposomes decorated on their outer surface with plasmonic nanoparticles. On the other hand a completely different strategy has been developed for the synthesis of magnetoliposomes (MLip). In this case the hydrophobic/hydrophylic interactions between small SPIONs and neutral phospholipids have been used for magnetoliposomes synthesis thus allowing the incorporation of hydrophobic SPIO nanoparticles into the liposomal lipid bilayer.

The two classes of liposomes have been analyzed by UV-Vis absorption spectroscopy, Photon Correlation Spectroscopy (PCS), Zeta Potential Measurements and Transmission Electron Microscopy (TEM). Their plasmonic properties have been evaluated using SERS for excitation wavelengths ranging from UV to NIR (325-830 nm). The hyperthermic properties of the nanohybrids, arising from their interaction with an external laser or a magnetic field, have been assessed for NIR lasers (785 nm) and external magnetic fields with intensities ranging between 5 and 60 kA/m and frequencies between 100-400 kHz. The toxicity of the nanohybrids have been assessed in-vitro on different cell lines using the standard MTT assay.

COLL 478

Plasmonic metal oxide nanocrystals

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Degenerately doped metal oxide semiconductors, like ITO, exhibit plasmonic resonance at near and mid-infrared wavelengths tunable by varying their composition. Nanocrystals of many such materials have now been synthesized and applications are emerging that leverage the responsiveness of their localized surface plasmon resonance (LSPR) to electronic charging and discharging. For example, we are developing a new class of electrochromic glass that can dynamically control heat loads and daylighting in buildings to save energy and enhance comfort of building occupants. Further applications of these novel plasmonic nanocrystals will hinge, in part, on their ability to concentrate infrared light into nanoscale volumes and to enhance electronic and vibrational state transitions via associated field enhancement effects. Through simulations, we have predicted high field enhancement factors exceeding 300x for faceted nanocrystals. Experimentally, we can assess the potential of plasmonic oxide nanocrystals for field enhancement by observing the homogeneous LSPR linewidth, which is inversely related to the dephasing time. We have sought to distinguish this *intrinsic* linewidth from the heterogeneous broadening that is always present for colloidal nanoparticles. Measuring LSPR spectra of individual nanocrystals by tip-enhanced synchrotron FTIR spectroscopy we find single nanocrystals can have linewidths less than half of the corresponding ensembles. Thus, the dephasing times are long and plasmonic oxide nanocrystals have great potential for diverse applications in energy. To minimize electronic scattering and maximize the potential for field enhancement, we can rationally engineer dopants. In particular, separating the dopant orbitals either physically or *electronically* from the conduction levels is shown to dramatically reduce LSPR linewidths. Finally, multi-modal LSPR are generated in anisotropic plasmonic nanocrystals, which has been a primary strategy for sculpting plasmonic hot spots around gold and silver nanoparticles. In semiconducting metal oxides, both shape and the underlying crystalline anisotropy collaborate to produce tunable multi-modal LSPR properties.

COLL 479

Phase, size, and composition dependent plasmonic properties of colloidal In_2O_3 nanocrystals

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Synthesis, properties, and applications of gold and silver nanostructures with tunable localized surface plasmon resonances (LSPRs) have been a subject of intense investigation over the past decade. The focus on these noble metal plasmonic nanomaterials stems from their facile synthesis, stability to oxidation, and the visible-range LSPR transitions. However, among other drawbacks, these nanostructures are also costly for large-scale applications and exhibit high optical losses. Consequently, doped transparent metal oxide nanocrystals have emerged as a new class of

unconventional plasmonic materials. In this talk I will present the results of our recent work on colloidal indium oxide-based plasmonic nanocrystals. Using size-structure correlation, indium tin oxide (ITO) nanocrystals were prepared in the stable bixbyite (*bcc*-ITO) and metastable corundum (*rh*-ITO) phase, revealing a dramatic difference in their optical and electrical properties. Unlike *rh*-ITO, *bcc*-ITO nanocrystals exhibit a strong LSPR absorption in the near-IR region due to the presence of free electrons, enabled by the presence of low activation energy donor states. Fundamental understanding of the electronic structure and phase-dependent plasmonic properties allowed us to design and prepare plasmonic In_2O_3-based nanocrystals tunable in the mid-IR region. Application of these colloidal mid-IR plasmonic nanocrystals will also be discussed.

COLL 480

Plasmonic metal sulfide nanocrystals

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Colloidal nanocrystals have been demonstrated as excellent building blocks for plasmonics, where light is propagated, manipulated, and confined by solid-state components that are smaller than the wavelength of light itself. Semiconductor nanocrystals possess free carrier densities that are tunable and could provide the foundation for active, on-demand plasmonic materials that operate in frequency ranges beyond those offered by metal nanoparticles. However, the use of semiconductor nanocrystals in plasmonics is limited by the ability to synthesize these nanomaterials with precise chemical and shape control. Here, I will present our work on the synthesis, assembly, and characterization of colloidal copper sulfide nanocrystals. I will present spectroscopic data for CuS nanodisks demonstrating localized surface plasmons in the near- to mid-infrared wavelengths. I will also discuss how CuS and related metal chalcogenide nanocrystals have the potential to exhibit extraordinary two-photon action cross-sections for bioimaging applications. Colloidal CuS nanocrystals also present a novel structure for nonlinear optical processes since there is no physicochemical interface between plasmonic and photoluminescent components.

COLL 481

Metal nanoparticles: from classical confinement to quantum confinement

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The optical properties of metal nanoparticles are of particular interest, as these properties reflect the intrinsic electronic structure and motion in response to light. While plasmonic nanoparticles have been extensively studied, their evolution with decreasing size to the quantum confinement regime remains elusive. This talk will discuss how the optical properties and electron motion evolve from the metallic to the insulating state with decreasing size. Using gold as a model system, atomically precise nanoparticles in the quantum size regime have been successfully synthesized, and more importantly, their atomic structures (metal core plus surface ligands) have been unequivocally determined by X-ray crystallography. The availability of such “perfect” nanoparticles provides unique opportunities for unveiling the mysterious aspects of nanoparticles, such as the emergence of the metallic state, the metal-ligand interfacial bonding, and the origin of stability, as well as new properties that are not observed in plasmonic nanoparticles.

COLL 482

Controlled synthesis of plasmonic noble metal nanoparticles

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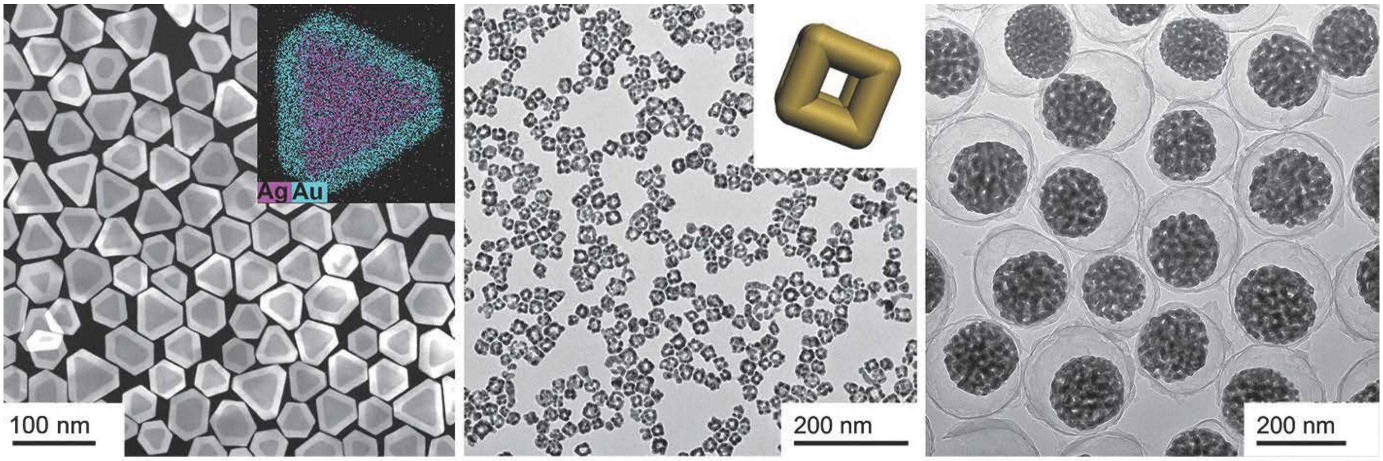
Plasmonic noble metal (Au, Ag) nanoparticles are widely applicable in surface-enhanced Raman spectroscopy (SERS) due to their outstanding optical properties. Controlled synthesis of the noble metal nanoparticles are of great significance for their enhanced activity in these applications.

Conventional wet-chemistry synthesis of plasmonic noble metal nanoparticles usually suffers from poor yield, reproducibility and scalability. Toward solving this problem, we proposed a coordination-based synthesis by introducing a proper ligand to reduce the reduction potential of the noble metal salt such that self-nucleation events are effectively suppressed. By this means, a series of plasmonic noble metal nanoparticles, such as Au and Ag nanospheres and triangular nanoplates, have been synthesized on a large scale in high yield from a one-pot seeded growth system, with their size well tunable and stoichiometrically predictable in a broad range of 10-200 nm or a few microns. On the other hand, with appropriate ligands, galvanic replacement can be prevented when Au is depositing onto various Ag nanoparticles, giving rise to an unconventional class of Ag@Au core/shell nanocrystals. These novel nanocrystals show excellent Ag-like plasmonic property and Au-like chemical stability, and thus are particularly useful in biosensing or SERS applications under many harsh conditions.

The SERS activity of plasmonic nanoparticles also relies on availability of high-density hotspots for enhanced sensitivity, which can be achieved by rational design of nanostructures with inherent nanogaps. To this end, we successfully synthesized Au nanoframes with inherent nanogaps of < 7 nm by templating of Au against non-metallic AgI nanoparticles. In another demonstration, the nanogap structures can be obtained by dealloying Au-Ag alloy nanocrystals, leading to highly porous Au-Ag colloids. The ultrasmall nanogaps represent the hotspots, and thus enable superior activity in SERS applications.

In summary, we report controlled synthesis of plasmonic noble metal nanoparticles and unique strategies for constructing unconventional nanostructures, which opens up new opportunities in achieving significantly enhanced activity in many SERS-based applications.



Ag@Au core/shell nanoplates Au nanoframes Porous Au-Ag nanospheres

COLL 483

Synthesis of various plasmonic nanoframes and their optical characterization

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Among the nanomaterials, plasmonic nanoparticles have been utilized in catalysis and biomedical application, since light-induced oscillation of electrons and/or local heating effectively reinforces their catalytic and therapeutic functions. Designing the morphology of plasmonic nanostructures is one of the mainstream research topics in that the geometric variations, such as sizes and shapes, determine their physical properties. Herein, we investigated the synthesis of nanoframes by using Au nanoparticles with the desired geometry as an in-situ template. Tactics for nanoframe synthesis involve the utilization of well-defined Au nanoparticle templates, site-selective growth of Pt nanoframe at the edges of Au nanoparticles, etching of inner Au, and regrowth of metal wrapping Pt ridges with the desired metal. We thoroughly studied the mechanism on each reaction step, and systematically characterized the intermediates. The synthetic method will open up a new door leading to other metal nanoframes with various shapes and compositions.

COLL 484

Organization of methacrylate monomers at hydrophilic and hydrophobic interfaces probed by sum frequency generation vibrational spectroscopy (SFGVS)

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Sum Frequency Generation vibrational spectroscopy (SFGVS) has been successfully used to selectively probe molecules at various interfaces. Investigation of the solid-liquid interface is important because it can provide useful molecular level insight of various environmental and industrial processes like corrosion, lubrication and oil refining. Before studying functional methacrylate-based polymer thin films/liquid interface, the interfacial interactions of these methacrylate monomers with with hydrophilic and hydrophobic interfaces was studied in a more controlled environment using a broadband SFG spectrometer with co-propagating beam geometry. The home-built sample cell with quartz window was used and SFG photons generated from the quartz/monomer interface was collected at ssp, ppp, pss and sps polarization combinations. The cleaned quartz surface will serve as the hydrophilic surface while the quartz window modified with deuterated octa-decyltrichlorosilane (d_{37-}OTS) self-assembled monolayer can represent a hydrophobic surface. The substituted ethyl group of the monomer was modified with various functional groups to obtain the average orientation and molecular conformation of specific functional groups and correlate the results with electronic and steric effects. Polarization mapping method was also applied to the system to obtain better resolved peaks of multi-functional small molecules.

COLL 485

Benzoic acid and its pH dependent penetration through interfaces

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As a commonly used food preservative, there is relatively little known about what is important for the penetration of benzoic acid into bacteria to have the desired bactericidal effect. It has been shown that there is a pH dependent effect of benzoic acid on bacteria that includes an acidification of the cytosol and penetration into the bacteria, but little has been shown of the chemistry behind this dependence. To explore the pH dependence of benzoic acid, various methods have been employed and compared including, reverse micelles to look at specific interactions at an interface, Langmuir monolayers to explore interactions of benzoic acid at a lipid interface, and bulk liquid membranes to explore passive diffusion. Through the comparison of these models it was possible to determine why the pH plays a valuable role in the bactericidal effect of benzoic acid along with specific interactions at a surfactant/lipid interface.

COLL 486

Designing responsive behavior in dynamic self-assemblies of small molecule systems at surfaces

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The study of responsive and dynamic molecular systems is of high interest both for better understanding natural systems and for the development of next-generation materials. In general, it can be difficult to predict supramolecular packing and self-assembly behavior in dynamic systems because of the delicate balance between various intermolecular interactions of varying strength and length scale. Our interdisciplinary team approaches this problem through a combination of innovative organic synthesis, molecular-level self-assembly characterization, and multiscale simulation. Here, we will present examples of molecular systems where we have tuned intermolecular interactions to explore different structural phases of assembly. Some of these exhibit dynamic behavior. We also show examples of how that dynamic behavior can be used to create a structural response to chemical and electronic stimuli.

COLL 487

Bilayer films for enhanced dehydration of solution-processed dielectric thin films

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Solution-processing offers the electronics industry a compelling route to lower cost and increased energy efficiency in the fabrication of thin-film transistors. Further, by using water as the solvent with nontoxic and Earth-abundant precursors, we enable a sustainable approach that is eminently scalable. We have previously shown the utility of solution-processed aluminum oxide phosphate (AlPO) dielectric thin films. One of the major challenges with solution-processed thin films is eliminating water. Further, the AlPO films readily sorb atmospheric water, thus a robust method to prevent rehydration is of paramount importance. This talk will describe a method of utilizing capping layers of hafnia and niobium oxide phosphate to eliminate water from the thin films, along with blocking the resorption of water by the dielectric layer.

COLL 488

Understanding the behavior of ionic liquids at carbonaceous surface

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Ionic liquids (ILs) are known to have remarkable properties including vanishingly low vapor-pressures, they are non-flammable, have wide thermal stability windows, and their physical and chemical properties are highly tunable, making them ideal for several applications including lubrication. Additionally, carbon based materials such as graphene, have been shown to be good solid-state lubricants. Graphene possesses impressive tribological properties including macroscale friction coefficients lower than bulk graphite, an impermeable and chemically inert basal plane, and the ability to operate as a solid-state lubricant. While the lubricating properties of ILs have been investigated on a variety of surfaces, little is known about the IL-carbon interface, and in particular, about the graphene-IL interface.
We have investigated the IL nanostructure on graphene and graphite (as the bulk reference for graphene). Normal force measurements reveal a layered structure on both interfaces. However, significant differences in layering are observed between graphene, graphite, and (physical and chemical) defects. We have further evaluated the friction response of ILs on carbon substrates. Our results suggest that ILs can behave differently at the interface of chemically similar carbon materials and we explain the underlying mechanisms. Our results lend to the fundamental understanding of ILs as designer lubricants and to graphite-IL and graphene-IL composite lubricant systems.

COLL 489

Overcompensation and kinetics: Examining polyelectrolyte diffusion in thin films

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Polyelectrolyte multilayers (PEMUs) are made by alternately depositing positively and negatively charged polyelectrolytes on a substrate. After few decades of investigating their properties and applications as coatings and membranes in fields such as electronics and medicine, it is now evident that the growth of these films is affected by many aspects of polyelectrolyte diffusion. To inspect these features, PEMUs prepared with sodium poly(4-styrenesulfonate) (PSSNa) and poly(diallyldimethylammonium) chloride (PDADMACl) were cycled between 2 M NaCl for 30 minutes and 10 mM PSS in 1 M NaCl for 5 minutes according to our previously published technique. The cycling homogenizes the films and compensates an extra amount of PDADMA inside the film with PSS eliminating the excess chloride counterions. The ion-free films are used as the starting platform for addition of PDADMA and PSS. Film thickness, polymer molecular weight and concentration, and salt concentration are modified to monitor their effect on the diffusion. The films were radiolabeled with iodide-125 and sodium-22 to measure indirectly the amounts of PSS and PDADMA added after soaking them in the polyelectrolyte solutions for a certain duration of time. It was found that both PDADMA and PSS have an overcompensation limit in these thin complex films which was independent of the varied conditions. Diffusion rates were calculated for each polyelectrolyte in different concentrations of salt and a universal equivalence plot was created. The latter can be used to alter or equalize the diffusion rates of each polyelectrolyte opening the door for calculated tailoring of polyelectrolyte multilayers growth.

COLL 490

Gold nanorings-enhanced singlet oxygen generation by using polyelectrolyte multilayers as nanoscale control in the near infrared

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We report the observation of gold nanorings (Au NRs)-enhanced singlet oxygen ($^1O_2$) generation in the Near Infrared (NIR) range and the significant changes in the presence of Au NRs with different localized surface plasmon resonance (LSPR) peaks and the distance between Au NRs and photosensitizer (PS). We elucidate the potential of layer-by-layer (LbL) assembly to understand the distance dependence nature of Au NRs-enhanced $^1O_2$ generation from Al(III) phthalocyanine chloride tetrasulfonic acid ($AlPcS_4$) conjugated on the Au NRs. The varied distance between $AlPcS_4$ and Au NR surface was controlled by constructing different numbers of alternate layers of poly(styrene sulfonate)(PSS) and poly(allylamine hydrochloride)(PAH). Numerical simulation using boundary element method (BEM) was used to calculate electric field enhancement of $AlPcS_4$-Au NR system. By modifying plasmon coupling parameters such as the LSPR wavelength of Au NRs and the spacing between $AlPcS_4$ and Au NRs, we can readily tune $^1O_2$ yields for applications in $^1O_2$-based clinical therapy.

COLL 491

Battery slurry microstructure as a function of formulation

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It is evident from literature that controlling battery slurry microstructure affects battery performance and lifetime. In the complicated mixing process combining active material, conductive additive, polymer binder and solvent, slurries can have fluid to gel-like viscoelastic properties. It is unclear what leads to the vastly different responses observed in these heterogeneous systems. The goal of this work is to determine and

analyze gelation in battery slurries as a function of molecular weight of the polymer binder, the size of the active material, and the conductive additive. One of the fundamental concepts that limit gelation is gravity, where the bond number determines whether the particles will settle in solution due to gravity or be suspended long enough to make a gel. For micron sized active material, we find that a gel is dependent on whether the amount of free nano-sized carbon conductive additive is larger than a critical concentration. Free carbon is defined as the carbon in a non-aggregated state. The critical fraction of free carbon is determined experimentally by varying concentration and measuring the rheological response. It was previously shown that dry mixing strongly impacts the amount of free carbon in the system. In practice a longer dry mixing time reduces the free carbon. Future work will connect slurry microstructure to battery performance as a function of dry mixing.

COLL 492

Potential mechanism describing color richness in squid *Doryteuthis pealeii* chromatophores

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Cephalopods are well known for their ability to camouflage to their surroundings within millisecond time scales. One important feature of this fast camouflaging process is the organization of their optical organs. For instance, the longfin inshore squid *Doryteuthis pealeii* contains organized layers with reflective iridophore organs located below the pigmented chromatophore organs, which can change their size to filter light. While it is known that chromatophores contain nanoscale granules that contribute to the range in visible color displayed along the *D. pealeii* dermal tissue, the contribution of pigments and proteins within the granules to bulk coloration remains largely unknown. We hypothesize that the chromatophore granules contain high refractive index biomolecules that contribute to the efficient collection and absorption of light within the dermal tissue. To test this hypothesis, we sought to define the complex refractive index for the soluble portions of the granule. We isolated and purified pigments and proteins extracted from the granules using both acidic and basic conditions. Real refractive indices of the soluble extracts were measured with an Abbe refractometer at 589 nm and 25 °C in triplicate using serial dilutions in both conditions. Our data suggests that even though the refractive index of the soluble biomolecules vary as a function of extraction procedure, they maintain values greater than 1.7, which is a unique feature for biological materials. This high refractive index suggests that light is refracted closer to the normal of the surface of the skin, elucidating a potential mechanism for the efficient collection and absorption of light within the dermal tissue.

COLL 493

Insight into MWCNTs- phosphonium ionic liquid nanofluids: Interaction and rheology study

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Carbon nanotubes (CNTs) have been used as additives to improve mechanical, thermal, electrical and tribological properties of the composites. However, CNTs have a strong tendency to aggregate because of their nanosize and high surface energy. CNTs can be chemically modified to achieve good dispersion in the matrix, but this can damage its structural properties. Therefore, their physical modification using surfactants is preferred. Ionic liquids, which are room temperature salts, form well dispersed matrix with CNTs because of cation-π or Vander Waals interactions between the two. In this study, solid-liquid interaction between MWCNTs and a phosphonium ionic liquid is investigated. Ionic liquid prevents CNT agglomeration when incorporated between the nanotubes. In this work, IL-CNT composite is characterized using DSC, Raman spectroscopy and TEM, to analyze the IL-CNT interface behavior. FTIR gives probable insight to the bond formation between IL and CNTs. Detailed information about microstructure of nanofluids is studied from the rheological properties of these composites at different concentrations. This interaction study is important for the future application of well dispersed CNT-IL additive system in tribology.

COLL 494

Tic-tac-toe binary lattices from interfacial self-assembly of branched and spherical nanocrystals

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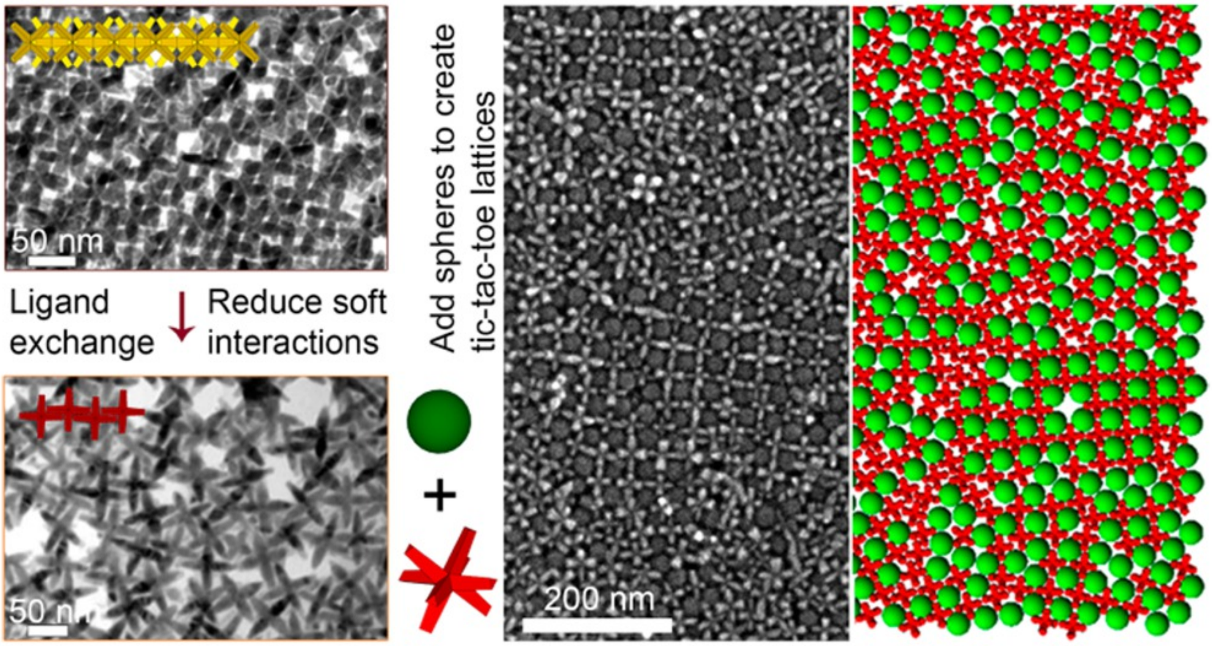
Binary self-assembly (BSA) of colloidal nanocrystals (NCs) has emerged as a smart way to obtain materials with unique properties, though a strict control of present interactions is needed for guiding the process. Control ligands coating or shape complementarity (SC) have been shown to be effective strategies to obtain ordered meso-crystals starting from simple particles. In our work we combine these approaches and apply them to a system formed by nano-spheres and multi-branched NCs (octapods), a class of colloids that demonstrated a wide ability to form ordered superstructures, but whose behavior in binary SA has never been investigated. Two sizes of octapods (aspect ratio $(L/D)_1 = 4$ and $(L/D)_2 = 7$) and spheres (radii $R_1 = 7 \pm 1$ nm and $R_2 = 12.5 \pm 0.9$ nm) have been employed. Because of the syntheses paths octapods present heterogeneous ligands, while spheres not. In order to homogenize octapods, ligand exchange was performed with 1-dodecanethiol. SAs were carried out following an established liquid interface technique. Ordered binary assemblies were found only when coupling ligand exchanged $(L/D)_1$ octapods with R_2 spheres. TEM projection of this ordered SA resemble tic-tac-toe game (Fig. 1, right), with a sphere

surrounded by four octapods. Not all the assembled membrane, though, is ordered: tic-tac-toe are immersed in a disordered matrix where the NCs interact randomly. A disordered mix of components was found using non-exchanged octapods, identifying surface interaction as a key player in SA. Single component experiments confirmed it: ligand exchange breaks the interlocked chains formed by as-synthesized $(L/D)_2$ NCs (Fig. 1, left) and enhance alignment in $(L/D)_1$. Reducing SC of NCs couples brought either toward phase segregation ($(L/D)_2$ with both kinds of spheres) or disordered domains ($(L/D)_1$ with R_1). In these cases ligand exchange did not affect the assembly. We thus demonstrated that ordered BSA can be obtained starting from strongly anisotropic components by carefully optimizing both entropic (SC) and enthalpic (ligand-mediated surface interaction) contributes.



COLL 495

Ion sorption, diffusion, and transport in polymer membranes

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Charged polymer membranes are widely used for water purification applications involving control of water and ion transport, such as reverse osmosis and electrodialysis. Efforts are also underway worldwide to harness separation properties of such materials for energy generation in related applications such as reverse electrodialysis and pressure retarded osmosis. Additional applications, such as energy recovery ventilation and capacitive deionization, rely on polymer membranes to control transport rates of water, ions, or both. Improving membranes for such processes would benefit from more complete fundamental understanding of the relation between membrane structure and ion sorption, diffusion and transport properties in both cation

and anion exchange membrane materials. Ion-exchange membranes often contain strongly acidic or basic functional groups that render the materials hydrophilic, but the presence of such charged groups also has a substantial impact on ion (and water) transport properties through the polymer.
We are exploring the influence of polymer backbone structure, charge density, and water content on ion transport properties. Results from some of these studies will be presented, focusing on transport of salt, primarily NaCl, through various neutral, positively charged and negatively charged membranes via concentration gradient driven transport (i.e., ion permeability) and electric field driven transport (i.e., ionic conductivity). One long-term goal is to develop and validate a common framework to interpret data from both electrically driven and concentration gradient driven mass transport in such polymers and to use it to establish structure/property relations leading to rational design of membranes with improved performance.
Ion sorption and permeability data were used to extract salt diffusion coefficients in charged membranes. Concentrations of both counter-ions and co-ions in the polymers were measured via desorption followed by ion chromatography or flame atomic absorption spectroscopy. Salt permeability, sorption and electrical conductivity data were combined to determine individual ion diffusion coefficients in neutral, cation exchange and anion exchange materials. The use of models to correlate and, in some cases, predict the experimental data is discussed.

COLL 496

Rapid and efficient separation of oil from oil-in-water emulsions using a Janus Cotton fabric

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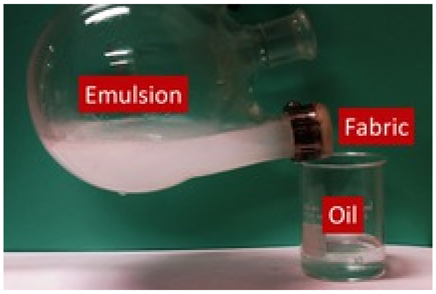
The fast and efficient separation of oil from oil-in-water emulsion is industrially important. Superhydrophobic filters with pore sizes reaching hundreds of micromaters have been used in the past to separate oil rapidly from simple oil/water mixtures that are created by shearing oil by mechanically shearing oil/water mixtures without using a surfactant. However, these filters cannot separate oil from surfactant-stabilized oil-in-water emulsion. The filters work for simple oil/water mixtures because oil droplets are not stable in this case and readily coalesce into a phase that fills the pores of the superhydrophobic filters. We further propose that the impregnating oil not only blocks water permeation but also serves as sites for additional oil deposition and also as the reservoirs fueling selective oil transport through the superhydrophobic filter. The filters do not work for surfactant-stabilized emulsions because the oil droplets in this case are too stable to aggregate into large droplets that would fill the filter pores and then permeate the filters.

We report in this talk a the design and preparation of novel bi-functional Janus cotton fabric that can separate oil from oil-in-water emulsions. This fabric is superhydrophobic

on one surface and polyamine-bearing on the other. When used as a filter, the polyamine-bearing side causes the micrometer-sized oil droplets to coalesce. The coalesced oil then fills fabric pores on the superhydrophobic side and selectively permeates it. Oil separation using this method is rapid and the separated oil is pure. Furthermore, the content of the model oil hexadecane (HD) in water after a separation can be reduced to less than 0.03 ± 0.03 vol%. These features suggest the practical potential of this technology.



COLL 497

Inorganic−organic thiol−ene coated mesh for oil/water separation

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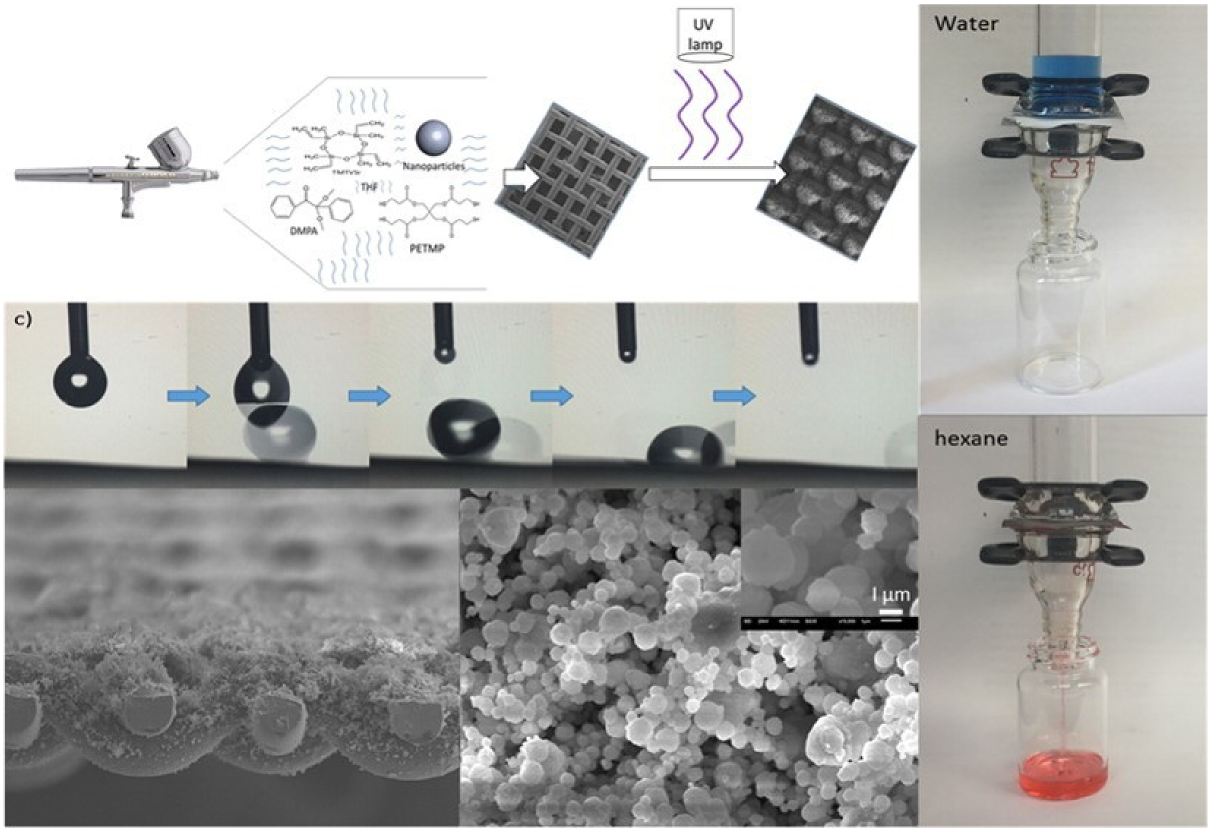
A highly efficient mesh for oil/water separation was fabricated by using a superhydrophobic and superoleophilic coating of thiol−ene hybrid, consisting of pentaerythritol tetra(3-mercaptopropionate) (PETMP), 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (TMTVSi), and hydrophobic fumed silica nanoparticles, via a simple two-step fabrication process. Spray deposition and UV curing photopolymerization were sequentially performed, during which solvent evaporation provides microscale roughness while nanoparticle aggregation forms nanoscale roughness. The hierarchical morphologies were stabilized after UV curing photopolymerization. High contact angle (>150°) and low roll-off angle (<5°) were achieved due to the multiscale roughness structure of the hierarchical morphologies. These coatings also have excellent chemical resistance, as well as temperature and pH stability, after curing.



COLL 498

Membrane distillation for desalination: Experimental studies with precipitating scaling salts

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Membrane distillation (MD) techniques employ hot brine on one side of a porous hydrophobic membrane whose pores remain gas-filled. Water vapor from the hot brine diffuses through the membrane pores to the other side for condensation. A variety of conditions can exist on the other side of the membrane leading to different techniques: Direct Contact Membrane Distillation (DCMD) when a cold distilled water is present; a cold condenser surface in Air Gap Membrane Distillation (AGMD); vacuum in Vacuum Membrane Distillation (VMD) etc. Although reverse osmosis is the method of choice for desalination, it cannot concentrate the brine very much due to osmotic pressure limitations. Further the scaling salts precipitate on the membrane surface at higher water recovery. There is an extraordinary interest in MD now since MD techniques do not suffer from osmotic pressure limitations. However scaling salt precipitation can be a serious problem. We have overcome these problems by employing porous hydrophobic hollow fiber membranes having highly porous plasma-polymerized fluorosilicone coating, crossflow of hot brine over these hollow fibers and spontaneously oscillating

environment. Successful concentration of seawater up to ~20% salt was demonstrated in larger scale.

The scaling behaviors of scaling salts such as $CaSO_4$ and $CaCO_3$ in small crossflow hollow fiber modules were studied extensively using supersaturated solutions having high SI values. The highly encouraging results will be summarized. The scaling behavior of polymeric solid hollow fiber-based heat exchangers potentially usable in DCMD processes was also experimentally evaluated.

If this technique is to be used to further concentrate the reverse osmosis desalination process concentrate, we should know how it behaves with antiscalants. Extensive scaling experiments with the addition of antiscalant were conducted to see the effects of concentration and different kinds of antiscalants on inhibiting scaling from deposits of $CaSO_4$ and $CaCO_3$. The parameters, induction period, calcium concentration, distillate conductivity and water vapor flux, were investigated. In addition the scaling behavior of polymeric solid hollow fiber heat exchangers potentially usable in such DCMD processes was experimentally evaluated.

We will also illustrate how our technique successfully handles produced water from a variety of sources at temperatures going up to 130^oC.

COLL 499

Nanofiltration membranes for the removal of organic pollutants from wastewater: A critical review of methods of preparation and fouling control

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The incidence of emerging or recently recognised pollutants in our water resources poses a major long term threat to ecosystem and human health. Wastewater effluents from municipal treatment plants, hospitals and chemical, pharmaceutical and agriculture (especially, raising of livestock) are the common sources of trace contaminants in the environment. These contaminants are present usually in the µg/L concentration range or less, which make them difficult to remove using traditional/ conventional wastewater treatment methods. Over the past decade, nanofiltration (NF) and reverse osmosis (RO) removal mechanisms have become more and more popular because of their ability to remove micro-pollutants. Most of the available commercial NF membranes are thin-film composite (TFC) membranes formed through Interfacial polymerization between two monomers and there has been intensive efforts, both industrial and academic, to improve the productivity and selectivity of TFC membranes. Along with that, nanofiltration membranes prepared through phase inversion method with nano-sized inorganic materials blended with polymers as well as membranes coated with hydrophobic/ hydrophilic layers have been extensively investigated. Despite the enormous applicability of nanofiltration in removing trace organic compounds from wastewater, two major problems still exist: fouling and concentration polarization. Researchers have suggested that an appropriate alteration of the membrane system might be the best possible approach in resisting membrane fouling and thereby improving performance. The main objective of the present study is to undertake a

critical review of methods of preparation of nanofiltration membranes for the removal of organic pollutants as well as fouling control during water treatment.

COLL 500

Novel polymer membrane chemistries for water treatment and reuse

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Wastewater is possibly the only sustainable, ever increasing, yet most ignored source of freshwater. Direct potable reuse of wastewater is often considered taboo, but growing pressures stemming from intense water shortage are forcing many regions to adopt innovative modes of recycle and reuse. Membrane filtration processes provide the scope of treating many types of wastewater to very high levels of purity. This presentation will review a few key innovations in membrane filtration materials that have vastly improved the performance and sustainability of membrane processes with respect to treatment of wastewaters. Improvements in both ceramic and polymeric membrane materials will be outlined. We will discuss how sol-gel processes for ceramics and phase inversion processes for polymeric membranes have led to remarkable membrane microstructures with unique separation and interfacial characteristics, including fouling resistance. The presentation will highlight one of the recent membrane material innovations we are currently working on, which takes a novel conducting polymer base and transforms it into a scaffold for templating membranes with unique characteristics. In closing, it will be emphasized how strides have been made to make membranes more energy efficient and fouling tolerant to enable reliable, economical, and sustainable water reuse.

COLL 501

Enhancing solar harvest of interfacial solar membrane for water purification

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The rapid growth of population, global warming, and the environmental pollution cause the freshwater scarcity be an increasing serious global challenge. To sufficiently convert the solar energy to heat and achieve a high water evaporation rate with low energy input and carbon emission, we engineer and design the hybrid interfacial solar membranes which are superior to the current state of art, including high solar energy harvest efficiency, mechanical and chemical robustness, effectively photothermal conversion, and thermal transfer to water, in order to increase the water evaporation rate. A hybrid coating, plasmonic particle-embedded polypyrrole thin film coating, was

developed to enhance the solar energy harvest efficiency. Polypyrrole has selected due to its broad spectrum absorption (Fig. 1), high photothermal conversion efficiency, outstanding stability, economically inexpensive, as well as good biocompatibility and low long-term cytotoxicity. Moreover, the fabrication technology is environmental friendly and allows polypyrrole thin film to tightly coat on a variety of substrates regardless of curvature, such as glass, nonconductive flexible polypropylene, and conductive stainless steel mesh. After coating polypyrrole thin film on polypropylene mesh, water evaporation conversion efficiency raise to 72%, which is much higher than that of commercialized solar stills with typical efficiencies of 24%-45%. Importantly, the polypyrrole thin film remains good adhesion under continuously flow and seawater salinity. Based on such human and environmental friendly polypyrrole system, we seeks to understand and engineer this hybrid (plasmonic nanomaterial/polypyrrole) thin film coating to trap the light (solar energy) coating in order to sufficiently harvest the solar energy and increase water evaporation conversion efficiency.

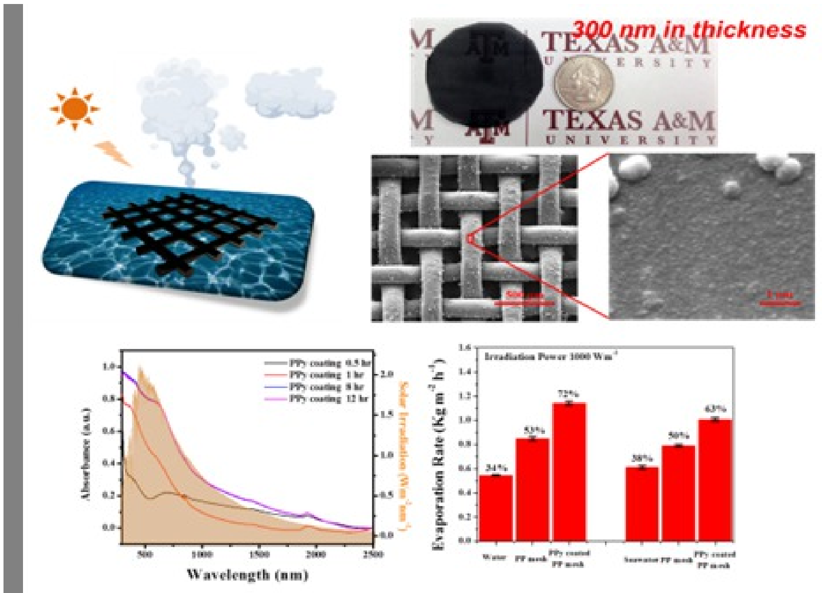

Fig. 1 Interfacial solar membrane for water desalination. Illustration shows how water evaporates. The absorption spectra of coating material matches spectra of sunlight. The evaporation efficiency achieves 72% with 300 nm thin coatings.

COLL 502

Scalable fabrication of underwater superoleophobic membranes from polymer-grafted silica nanoparticles for oil/water separation

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Scarcity of fresh water has become a global crisis. Each year, oil spills and inappropriate wastewater disposal generate billions of gallons of water polluted by hydrocarbons further aggravate the problem. There have been significant efforts to create membranes for oil/water separation. Nevertheless, they often have low permeability and are not scalable. Therefore, there is an urgent need to develop a robust method to fabricate oil/water separation membranes with desired wettability and anti-fouling properties in a scalable and economical fashion. Here, we synthesized chain-like silica nanoparticles of different chain length, followed by grafting of poly(acrylic acid). The particles then were deposited onto different solid and membrane substrates (over 1800 mm^2 of the area with less 100 μL of the dispersion) through spraying coating and flow-directed assembly methods. Scanning electron microscopy showed that the nanoparticles assembled into fractal-like thin films with nanoporosity, which could be tuned by particles' length distributions and coating parameters (concentration, speed, etc.). The resulted coating showed underwater superoleophobicity (contact angles of hexadecane and dichloroethane in water > 160^o) with low oil contact angle hysteresis in water. Even after the surface was wetted by oil in air, the underwater superoleophocity could be fully recovered in water (pH > 7), due to the unique morphology of the particles and enhanced water affinity of ionized polymer brushes on the particles. Finally, the coated membrane were used to separate oil/water mixture as well as surfactant-stabilized emulsion. Our approach demonstrated here is facile yet effective to fabricate oil/water separation membranes with controlled surface chemistry and morphology. More importantly, it is highly compatible with industrial settings for scalable manufacturing.

COLL 503

Inverse opal-templated multiscale architectured membranes with tunable separation properties

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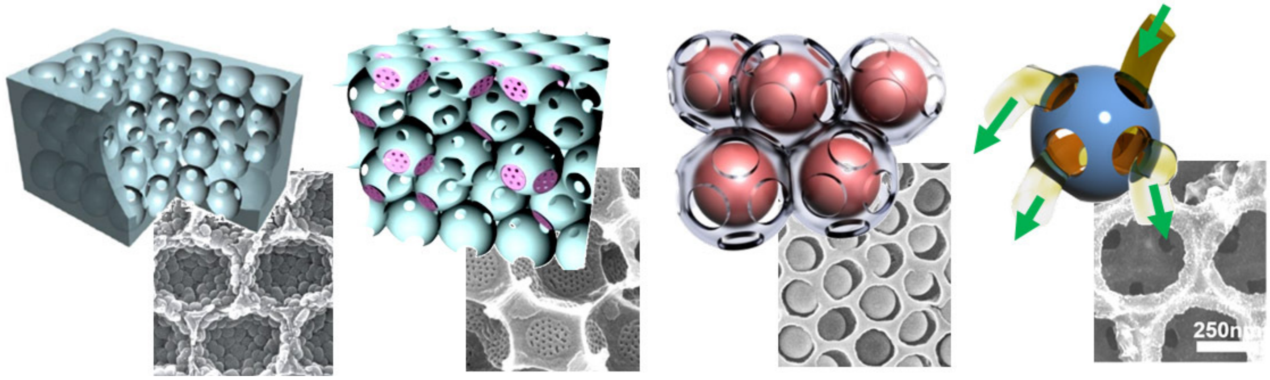
Membrane has been used from time immemorial to purify water. Advances made in membrane technology for more than a century have to do with either enhancing separation efficiency of the membrane or improving the permeation flux. Enhancing the separation efficiency, however, inevitably led to reducing the permeation flux, and improving the permeation flux resulted in a loss in the separation efficiency. This inherently built-in dilemma has to be dislodged for the filtration membrane to fully reach its potential. In this presentation, we suggest multiscale porous membranes that allow for high permeation flux without sacrificing separation efficiency. In order to create the multiscale architectured membranes, primary structure is first prepared by assembling closely packed colloidal particles, filling the gaps with a suitable material, and dissolving out the particles to form inverse opal structure. Then, secondary nanostructures are

incorporated inside the structured template to elaborately tune the pore size, tortuosity, and interfacial properties. Embedded nanostructures can be created by layer-by-layer assembly of polyelectrolyte multilayers, microphase separation of block copolymers, or self-assembly of another colloidal particles, etc. Finally, the constructed multiscale architectures are utilized for water-treatment applications, such as ultrafiltration of nanoparticles or nanofiltration of metallic ions. Due to the perfectly ordered characteristics of the multiscale architecture, it offers advantages of reduced tortuosity as well as pore size uniformity, resulting in high permeability and selectivity simultaneously.



COLL 504

Bimetallic Ru-Pt and Pt-Co fuel cell catalysts prepared by strong electrostatic adsorption and electroless deposition

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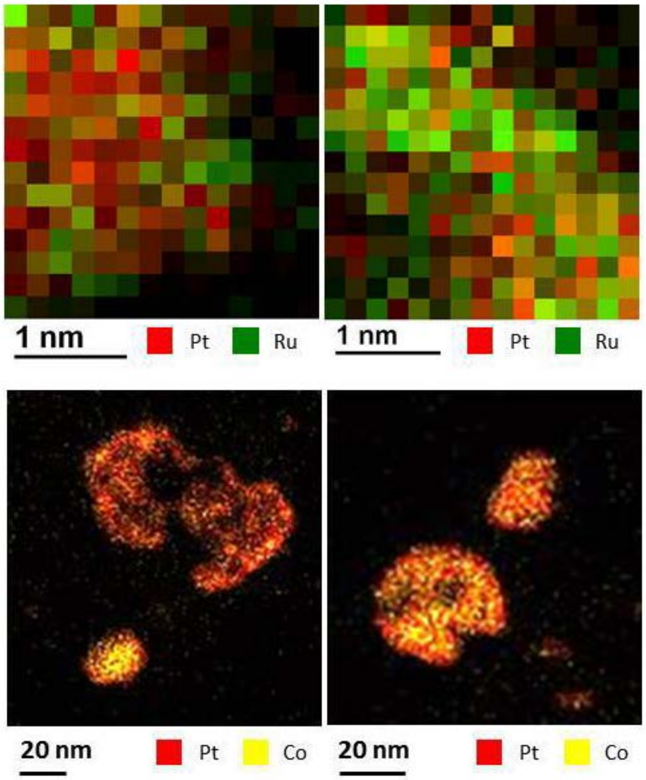
The methods of Strong Electrostatic Adsorption (SEA), and its incipient wetness analog, Charge Enhanced Dry Impregnation (CEDI), have been shown to yield supported metal nanoparticle catalysts with high dispersion and narrow size distribution. Catalysts prepared by SEA and CEDI therefore are desirable as seeds for addition of secondary metal using Electroless Deposition (ED), as the prepared bimetallic catalysts should be of similar dispersion as the base catalyst. This study demonstrated the use of these methods to prepare two series of carbon supported bimetallic catalysts containing Pt which were then characterized and evaluated with cyclic voltammetry. The first system used Pt as the base metal, prepared by SEA on XC72R carbon, with Ru as the secondary metal added by ED (Pt@Ru/C). The second system used Co as base metal, prepared by a modified CEDI method on Carbon Black, with Pt added by ED (Co@Pt/C).

Using XRD, HAADF-STEM, and XEDS characterization, the Pt@Ru/C catalysts did not have alloying of the component metals and that the catalysts have bimetallic surface composition. The resulting Co@Pt/C catalysts had particles with irregular morphology that were larger than the seed Co particles. These were determined to have thin alloyed Pt-Co phases and domains of pure Pt. Evaluation of these catalysts showed higher mass activities, with respect to platinum content, compared to commercially available monometallic and bimetallic catalysts. This enhancement in performance is associated with the electronic interaction between Pt and Ru on the catalyst surface and lattice contraction for Pt-Co alloys.



XEDS maps of the Pt@Ru/C (top panels) and Pt-Co/C (bottom panels) prepared by ED and SEA/CEDI.

COLL 505

Synthesis and electrochemical study of palladium based nanomaterials

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Energy production and storage are crucial toward the development of sustainable and renewable energy alternatives to fossil fuels. Hydrogen fuel cells are promising solutions for the efficient and clean supply of electricity; however, hydrogen storage remains one of the most challenging prerequisites to overcome toward the realization of

a hydrogen based economy. Palladium is well known for its remarkable capacity for hydrogen absorption/adsorption, and is broadly used as a primary catalyst for the low temperature reduction of automobile pollutants, hydrogenation reactions, hydrogen purification, petroleum cracking, and a wide range of electrochemical applications Recently, our research group has synthesized a number of different Pd based nanomaterials for green chemistry applications.

In this presentation, various methods for the synthesis of Pd based nanomaterials, as well as the impacts of their dimensions, morphologies and compositions toward various electrochemical applications are presented and compared. Various nanomaterials, including activated carbon materials modified with Pd based nanoparticles, Cd@Pd core/shell nanostructures, and Pd/graphene nanocomposites were synthesized and examined for hydrogen sorption and storage. Our studies indicated that synergistic effects between the Pd nanoparticles and carbon substrates drastically increased the capacity for hydrogen storage. In addition, five Pd-based nanoporous catalysts (Pd, PdCd, PdPb, PdIr, and PdPt) with controlled compositions were prepared and investigated for their electrocatalytic activities in the oxidation of formic acid, showing that a second incorporated metal strongly affected the activity and stability of the Pd-based nanomaterials.

COLL 506

Nanoparticle-structured interfaces in catalysis and sensing

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Understanding surface and interfacial chemistry of materials at the nanoscale dimension is essential for harnessing their catalytic and sensing properties. This presentation will discuss some of the recent findings in preparation of metal, alloy and core-shell nanoparticles and assemblies as catalytic and sensing interfaces. Selected examples will highlight the importance of nanostructural tuning in terms of size, composition, shape and interparticle properties. While alloying noble metals with non-noble metals in the form of nanoalloys is valuable for the design of low-cost, active and robust catalysts, fundamental understanding of the atomic-scale structural evolution at the reaction interface is a key to achieving the catalytic or electrocatalytic properties by design. While assembling nanoparticles by molecular or biomolecular linkers into ensembles or continuous thin films is significant for creating multifunctional properties for chemical sensing or medical diagnostics, understanding of the interparticle interactions at the sensing interface is critical for effectively exploiting the magnetic, electrical, and spectroscopic properties for enhanced sensing or biosensing performance. Recent insights into these fundamental aspects will be discussed.

COLL 507

Porous binary composite catalysts for CO oxidation and water-gas shift reaction

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Binary composites of metals and metal oxides (or metal oxide/metal oxide) are heavily utilized in catalysis due to the creation of dynamic interfaces which facilitate many reactions for the production of chemical commodities and advanced energy applications. High purity hydrogen production is a key process to enable fuel cell catalysis or hydrogenation reactions, which find utilization in energy and food sectors respectively. In sourcing hydrogen from petrochemical or biomass sources, carbon monoxide is generated as an impurity which can poison catalysts or deactivate fuel cells. Its removal by the water-gas shift (WGS) and preferential oxidation (PrOX) can reduce CO concentrations to >10 ppm. Catalysts for the process usually incorporate a metal supported on a reducible metal oxide, where the metal activates CO and the metal oxide gives up lattice O to oxidize CO, desorbing CO_2. In the work presented we investigate a series of derivative materials from the University of Connecticut (UCT) Mesoporous Materials family in performing these reactions, composed of Nickel/Nickel Oxide on Ceria nanomaterials. These active catalysts have favorable porosity, crystallinity, and interfacial sites to facilitate both reactions to enable high-purity hydrogen production. *In-Situ* Raman microscopy and X-Ray Diffraction reveals dynamic changes in the catalysts due to the formation of oxygen vacancies and Ce^{3+} centers. The exercising of synthetic control provided by the inverse micelle method results in well-structured nanoparticle aggregates with a high dispersion of nickel over the ceria surface, providing a wealth of interfacial sites which we propose are the active sites for the reaction.

COLL 508

Design of highly-controlled layered films of nanoparticles through copper-catalyzed click chemistry

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A high level of precision and control over the architecture of nanostructures is a requirement for many fields, such as catalysis. This level of precision is achieved in molecular layer deposition (MLD) but the sub-nanometer scale of these methods means that the formation of micron-scale features can be time-consuming and costly. Layer-by-layer (LbL) deposition methods provide a means to achieving this scale quickly, but the features formed are not as well-controlled or stably-attached to the surface as their MLD counterparts. A method combining the scalability of LbL and precision of MLD is

presented, that takes advantage of the copper(I)-catalyzed “click” reaction between terminal azide and alkyne functional groups to form the stable triazole ring. Nanoparticles are functionalized with alkyne and azide moieties and are added in a layer-by-layer fashion to an azide-functionalized gold substrate. Scanning electron microscopy (SEM) and atomic force microscopy are used to confirm that each nanoparticle layer consists of a *single* layer, allowing for covalent binding of each particle. SEM also confirms that the nanoparticle layers exhibit exceptionally high surface coverage. Density functional theory calculations focused on the copper(I) intermediate provide a possible explanation for the high coverage achieved by this method. The formation of the triazole ring through the “click” reaction is confirmed by infrared spectroscopy and X-ray photoelectron spectroscopy. This high coverage, precise control over layer height, and covalent stability of this nanoparticle layer deposition method allows for a greater level of control over the structures formed by traditional LbL techniques. Further control of nanoparticle placement is being investigated.

COLL 509

Supported gold nanoparticles for sensing and photothermal applications

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A considerable amount of research has been devoted to studying the unique and tunable behavior of nanoparticles and to identifying novel applications for these properties. Noble metal nanoparticles, especially gold nanoparticles, have received much of this attention due to the exhibition of localized surface plasmon resonances (LSPRs). This presentation will highlight our recent advances used to grow nanoparticle deposits on a variety of supports and evaluate them for sensing and photothermal applications. The materials of interest in this talk are composed of gold nanoparticles deposited on ‘active’ or ‘inert’ solid supports. The ‘active’ supports, in the forms of iron oxide or monosodium titanates nanostructures, or the ‘inert’ solid supports, in the form of stainless steel, provide a unique platform for creation of highly active nanostructures. It was found out that, surface topography plays an important role during the nanoparticle’s growth. The presence of valleys, steps and crevices present on the supports are important features for nanoparticle’s deposition. The interactions between substrate chemistry, surface type, surface roughness, solution chemistry, and nanomaterial morphology are key components for the deposition process and will be described in detail. Their sensing- via surface enhanced Raman spectroscopy (SERS) and photothermal applications will be discussed during this talk.

COLL 510

Porous biocompatible polymer nanocapsules with nanometer-thin walls: applications in sensing & catalysis

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Using self-assembled scaffolds to template the synthesis of organic nanostructures is an attractive way to create materials with new shapes and properties. Vesicle-templates polymer nanocapsules, prepared by directed assembly within bilayers scaffolds, can retain medium-sized molecules such as pH-sensitive indicator dyes, catalysts, imaging agents and provide uninhibited access for small molecules to the capsule interior. Entrapment of large and medium sized molecules in porous nanocapsules can lead to new functional nanodevices, such as nanoreactors, sensors, or imaging systems. Porous polymeric nanocapsules with nanometer-thin walls offer a promising platform for cellular delivery of therapeutic or diagnostic agents. The entrapment of homogeneous catalysts in hollow porous nanocapsules will combine high efficiency of reactions in the native homogeneous and nearly homogeneous phase with the ease of separation of catalysts from products typical for heterogeneous systems.

COLL 511

Fine control of cell adhesion and morphology with polyelectrolyte multilayers

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The adhesion, phenotype, differentiation and proliferation of cells depend acutely on various physical and chemical cues. Surface charge, charge density and ligand density are examples of chemical cues, while substrate (visco)elasticity is an example of a mechanical variable which is thought to control cell fate. Producing surfaces with defined composition, charge and mechanical properties is thus a major issue in understanding cell fate. Thin films of polyelectrolyte complex made by the layer-by-layer, or multilayer, approach offer highly reproducible surfaces. Using these films we have produced a variety of cell behaviors including the following:

1. Cell and protein non-adhesive (antifouling) surfaces using zwitterionic copolymers and zwitterion-like bulk compositions.
2. Cytotoxic coatings with high positive charge density.
3. Adhesive compositions which promote attachment and proliferation.
4. Multilayers which lead to the formation of cell clusters including stem cell clusters.

Fundamental understanding of why a particular multilayer surface gives a particular cell response will be highlighted in this talk.

COLL 512

Controlling nanostructure within hydrogels for directing cell-matrix interactions

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Hydrogel-based biomaterials increasingly are used as extracellular matrix (ECM) mimics for cell culture and regenerative medicine applications. Synthetic hydrogels have been designed to afford precise control of mechanical and biochemical properties for directing cell function and fate. However, these materials often are homogeneous on the nanoscale unlike the hierarchically structured native ECM. To address this, we have synthesized self-assembling peptides decorated with reactive groups for incorporation within hydrogels formed by light-mediated thiol–ene click chemistry. Specifically, collagen mimetic peptides (CMPs) based on variants of Proline-Hydroxyproline-Glycine repeats [$(POG)_n$] have been functionalized with alkenes. These multifunctional CMPs assembly to form fibrils (~10-250 nm wide, TEM and AFM) and physical gels (G~100 Pa, rheometry). Pendant groups on these multifunctional CMPs have been reacted with various thiols (e.g., thiol-functionalized peptides, PEG) by photoinitiated, radically-mediated thiol–ene reaction. These synthetic matrices have been photopatterned with various biochemcial cues and are being utilized for controlled cell culture to probe the role of microenvironment structure, mechanics, and chemistry in directing specific cellular functions and fates of wound-healing fibroblasts and stem cells. More broadly, this approach is promising for controlling the nanostructure and topography of well-defined hydrogels for various biological applications.

COLL 513

Tailoring of polyelectrolyte multilayer surface properties and growth factor release

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The effect of solution pH during layer-by-layer buildup of polyelectrolyte multilayer (PEM) coatings on properties relevant to in vitro and in vivo cell function was investigated. In one example, bone morphogenetic protein 2 (BMP-2), a potent osteoconductive growth factor, was adsorbed onto the surface of anodized titanium, and PEM coatings were built on top of the BMP-2. High levels of BMP-2 released over several months were achieved. Three different diffusion regimes could be determined from the release profiles: an initial burst release, a sustained release regime and a depletion regime. BMP-2 was shown to maintain bioactivity after release from a PEM and the presence of a PEM was shown to preserve BMP-2 structure. In another example, basic fibroblast growth factor (FGF-2)-eluting PEMs were prepared on a range of cell culture surfaces. No visible change was observed in surface roughness as the assembly pH was varied, whereas the surface energy decreased for samples prepared at more basic pH.

COLL 514

Peptide-conjugated hydrogel cubes with pH/redox-sensitivity for anti-cancer drug delivery

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“Stimuli-responsive” hydrogels have been receiving well deserved attention because of their potential to optimize cancer therapy and achieve both targeting and on-demand drug release. Herein, we report on a novel type of hydrogel particles of controlled shape with conjugated hepsin-targeting peptides for breast/prostate cancer treatment. The cubical poly(methacrylic acid) (PMAA) multilayer networks with disulfide links are obtained by crosslinking PMAA with cystamine within hydrogen-bonded multilayers of PMAA/poly(vinylpyrrolidone) (PMAA/PVPON) on sacrificial mesoporous templates. These cubical mesoporous hydrogels exhibit pH- and redox-sensitivity and selective affinity to hepsin-overexpressing cancer cells. The successful FITC-IPLVVPL peptide conjugation to the hydrogels was confirmed by confocal microscopy and scanning electron microscopy. The binding of the peptide-hydrogel particles to hepsin-positive MCF-7 cancer cells was verified by flow cytometry and confocal microscopy. The stability of doxorubicin (DOX)-loaded hydrogels in serum-containing cell culture media was investigated. Cell viability assays demonstrate that the peptide-decorated PMAA hydrogel particles can inhibit the cancer cell growth by successful transportation of DOX into cell nuclei. The integration of an active targeting moiety, pH-sensitivity and redox-triggered degradation into shaped polymeric networks can be a new platform in controlled therapeutics delivery.

COLL 515

Self-defensive antibacterial polymer coatings

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Bacterial colonization of medical devices and implants is a significant unsolved problem. However, antimicrobial protection of biomedical devices have proven to be an extremely challenging task, mostly due to depletion of antimicrobial activity of the coatings over time, accumulation of bacterial debris near surfaces, and/or development of bacterial resistance to treatment. Here, we describe two strategies to develop ultrathin antibacterial polymer coatings which can be assembled at a variety of surfaces using the layer-by-layer (LbL) technique. The first one includes constructing polymer matrices capable of hosting, protecting and delivering antibiofilm agents in response to bacterial infection. The coatings combine several advantageous features, whose synergistic action results in its outstanding performance. These features include high loading

capacity to antimicrobial agents (AmAs), non-leaching nature of the coating, biocompatibility, and its unique capability to release AmAs only where and when needed. Specifically, the coatings do not release antibiotics in PBS at pH 7.4 in the absence of bacteria, but release increased amounts of antibacterial agents when pH is lowered locally from 7.4 to 5.5 in the presence of pH-lowering bacteria, such as *Staphylococcus epidermidis*, *Staphylococcus aureus* and *Escherichia Coli*. The second type of LbL antibacterial coatings does not contain antibiotics and kills bacteria through pH-triggered hydrophobicity. Importantly, all types of coatings were nontoxic toward murine osteoblast cells, supporting cell attachment and proliferation. We believe that these coatings present a promising way to provide antibacterial protection of surfaces, and might be especially useful for preventing bacterial colonization of orthopedic implants.

COLL 516 – Withdrawn.

COLL 517

Bioactive carbohydrate surfaces and microarrays for fimbriae-mediated bacterial adhesion

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The comprehensive study of the roles played by glycans in biology has inspired the development of a variety of carbohydrate-based tools, including microarrays and biosensors. In this study, bioactive mannose surfaces and microarrays immobilized on solid substrates, which have well conserved bioaffinity to bacterial adhesion, were developed using a facile chemical strategy. Carboxyl-terminated poly(ethylene glycol) thiol or its mixture with poly(ethylene glycol) methyl ether thiol was assembled on gold substrates, followed by covalently conjugating with mannose derivative. Microarrays of mannose derivative were also constructed using a printing method. The recognition affinity of the bioactive surfaces or arrays towards fimbriated *Escherichia coli (E. coli)* were evaluated using genetically engineered *E. coli* cells. The anchored mannose derivative were capable of binding fimbriated *E. coli* with a high surface coverage. Interestingly, domains of bacteria were found on the bioactive surfaces modulated with poly(ethylene glycol) methyl ether thiol, due to formation of small, packed domains of mannose on surfaces. In addition, the microarrays of mannose derivative showed highly site-specific binding to *E. coli*. Similar strategies have also been employed for developing mannose surfaces and microarrays on microscope slides. Disruption of the bacterial adsorption on the bioactive surfaces will be demonstrated by applying a solution of FimH inhibitor.

COLL 518

Robust protein films fabricated via nanoimprint lithography: A versatile approach for constructing functional biomaterials

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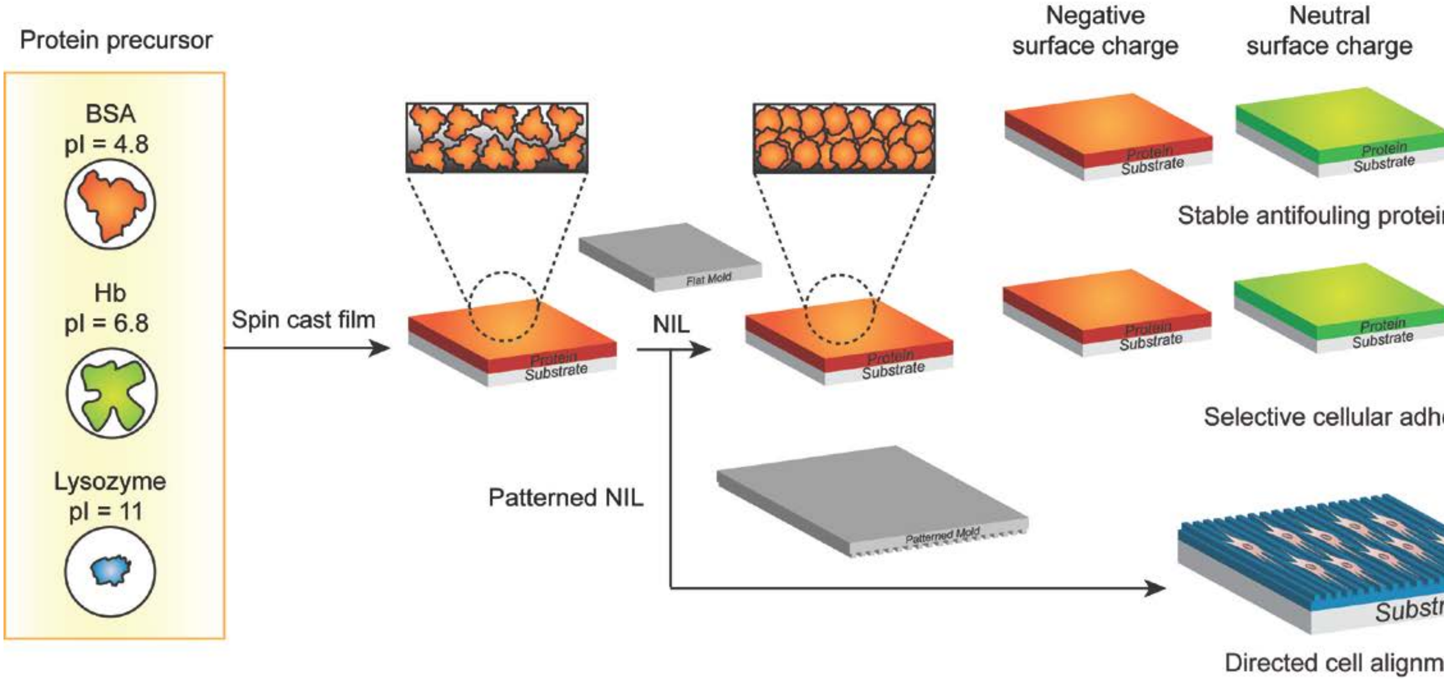
Proteins provide versatile and sustainable precursors for functional materials. Current approaches for generating stable protein films require either naturally self-assembling proteins or the use of additional crosslinking reagents. We report here a general strategy for generating robust protein films using nanoimprint lithography. This approach provides control of the surface properties of the fabricated films through either the protein diversity or the choice of imprinting conditions. This control is demonstrated through the generation of films featuring vastly differing biological properties, including biodegradability, surface charge, antifouling and cytophilicity. This strategy is generalizable to essentially all proteins, providing access to useful biomaterials, and more broadly to the creation of eco-friendly materials.



Different charged protein films fabricated via nanoimprint lithography (NIL) are used for controlling cell adhesion. The features generated by molds or inkjet printer using different protein precursors can be used for directing cellular behaviors.

COLL 519

Biofouling of receptor-doped polymeric electrochemical sensing membranes

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When continuously exposed to biological samples, conventional polymeric-membrane ion-selective electrodes (ISEs) exhibit a breakdown of selectivity and response. To address this, extensive washing procedures and frequent recalibrations are needed for many clinical and biological applications. Initial work with fluorous membranes shows both improvements in selectivity and gives sensors with lower limits of detection than in case of sensors with conventional membranes. Moreover, experiments with fluorous pH-selective membranes have shown that long term exposure to serum has no effect on the electrode selectivity. However, stirred serum solutions cause a transient drift of the sensor response. To explore this effect systematically, we developed a potentiometric test. For comparison, conventional polymeric membranes and fluorous membranes were exposed to solutions that were stirred intermittently. Both types of membranes exhibited a response to stirring when exposed to diluted equine blood serum but not when exposed to non-biological electrolyte solutions. The transient potentiometric response is determined by the hydrophobicity of the ionic sites that are part of the sensor membranes; a lower hydrophobicity causes a larger effect of stirring on the EMF. For the fluorous electrodes, synthesis of a more hydrophobic ionic site and its use along with fluorophilic H^+ ionophores successfully reduced the effect of sample stirring on the emf. A theoretical model is consistent with these experimental findings.

COLL 520

Examining the interactions between graphene oxide and model biological membranes through confocal microscopy

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A good understanding of how nanomaterials interact with biological systems not only ensures the safe design and production of nanomaterials, but also enables various nano-based biomedical applications. Graphene oxide (GO) is an atom-thick carbon lattice with oxygenated functional groups on the peripheral and the basal plane. Since GO is colloidally stable in aqueous solutions, it has attracted tremendous interest in applications such as water filtration, drug delivery, and bio-sensing. Using giant unilamellar vesicles (GUVs, diameters in the range of 10 to 40 mm) as model biological

membranes, this study aims at elucidating the mechanisms for the toxicity of GO to biological cells through the observation of the interactions of GO with GUVs through confocal laser scanning microscopy (CLSM). We constructed a custom-made flow chamber to enable real-time monitoring of physical changes of GUVs upon exposure to GO suspensions using the fluorescence staining approach reported by Li and Malmstadt, Soft Matter, 2013. Our preliminary results showed that some of the deposited GUVs underwent disruption upon exposure to GO under physiological conditions. Separate experiments were conducted to demonstrate that under such conditions, GO underwent considerable adhesion to the lipid bilayers, implying that the rupture of GUVs may be triggered by the attachment of GO. Additional experiments will be conducted at different pH and ionic strength conditions to elucidate the effects of solution chemistry on GO-GUV interactions.

COLL 521

Retinal cell labeling using hybrid lipid-coated gold nanorods

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Cell transplantation is a promising prospective therapy for retinal degenerative diseases and is currently being investigated in multiple clinical trials as a neuroprotective strategy to treat geographic atrophy, the advanced form of dry Age-related Macular Degeneration (AMD). In rodent models of retinal degeneration cell transplantation has been shown to rescue rod and cone photoreceptors, preserve electrophysiological responses of the retina and in visual pathways of the brain, and perhaps most clinically relevant, preserve eyesight. Characterization of cell based therapies rely on specific information regarding cell survival, migration, and integration in the host that is primarily derived from post-mortem histological assessments. However, the serial nature of this method requires large numbers of animals for these studies at multiple time points since there is currently no method for evaluating efficacious cell-based therapies longitudinally in vivo. Consequently, there is a critical need for the development of technology that would enable us to understand the consequence of transplanting cells into the host retinal tissue as well as visually track transplanted cells survival and migration in vivo. Without this technology improvement and development of cell-based therapies will continue to be significantly hindered. Here we report the use of hybrid lipid-coated gold nanorods as retinal cell-labeling agents that can also act as contrast agents for in vivo imaging technologies such as optical coherence tomography (OCT). The surface architecture of the gold nanorods can be modified to improve their stability and enhance cellular internalization in retinal pigment cells as visualized by fluorescence confocal microscopy. The approach used to synthesize the hybrid lipid-coated gold nanorods is simple and can be used to produce a library of tailored nanoparticles of varying composition, shape, optical and electronic properties, and surface ligands. When combined with optical imaging technologies, these cell-labeling contrast agents can be

used by researchers to assess the distribution, survival, migration, and differentiation of transplanted cells as well as track their location and rate of integration into the host retina in vivo.

COLL 522

In situ characterization of the nanoparticle biomolecular corona

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The interaction of nanoparticles with the biological environment results in the formation of a biomolecular corona, which substantially modifies the nanoparticle pristine surface properties. This complex multilayer of biomolecules ultimately mediate the interactions of nanoparticles with cells and organisms but the exact mechanisms that govern these interactions are still not completely understood. Several methods to characterize the corona have now been established. All these approaches require the isolation of the nanoparticle-biomolecular corona complex from the biological environment and the subsequent characterization in different media, typically PBS buffer or water, often accomplished through more or less harsh treatments that can further modify the nanoparticle bio-interface. While it can be certainly hypothesized that the exposure of certain protein domains on the nanoparticle corona can trigger specific cellular recognition pathways, the environment in which the biological recognition occurs plays a key role in the recognition event itself and has to be taken into account. In order to deeply understand the influence of the biomolecular corona on the interactions between nanoparticles and biological machinery, it is therefore imperative to seek for methodologies that enable to acquire molecular information in a realistic biological scenario.

Here, we present a new approach, based on flow cytometry, for the characterization of the nanoparticle biomolecular corona in relevant biological conditions, i.e. in presence of complex media, such as human plasma and human serum. We demonstrate that even a common flow cytometer, in combination with fluorescent immunoprobes, can be easily utilized to perform epitope mapping of biologically relevant sequences of the biomolecular corona of nanoparticles, both in conventional media and *in situ* in a more realistic biological environment, providing new insights on the microscopic properties of the corona for a deeper level of understanding of cells-nanoparticles interactions.

COLL 523

Single cell analysis uncovers unique cellular responses to distinct nanoparticle properties

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Distinct physical and chemical properties of engineered nanoparticles (NPs) engage and activate distinct proteins and cellular pathways that, in turn, govern the cellular response and ultimately the impact on human health. The relationships between NP properties and these key cellular processes and response are far from being understood. This knowledge gap is largely due to experimental challenges that NPs present, including the difficulty to achieve uniform NP distribution over the exposed cells. The distribution typically spans 2-3 orders of magnitudes, indicating that some cells are “overloaded” with hundreds or even thousands of NPs while other cells are loaded with only few or no NPs. Yet responses, such as regulation of gene expression or pathways, have been measured exclusively in the population as a whole. This approach identifies averaged, often most common or generic processes, while leaving other critical processes undetected due to the dilution of signals across many cells, each caries a different number of NPs. As a result, it is unclear whether population studies identify only generic, emergency state responses in a subset of “overloaded” cells, and whether responses unique to the properties of the NPs at lower loads, where many cells might carry not even one NP, are diluted and missed altogether. To answer these questions, we exposed alveolar epithelial cells to aminated or carboxylated quantum dots (QDs), and sorted out individual cells by their QD load for single-cell RNA-Seq analysis. We found that cells can respond to the same QD type with different strategies, which showed a coherency within a QD type. These multiple response patterns were mainly observed in cells carrying lower QD loads. In contrast, cells carrying higher loads responded more uniformly within and across QD types, with strong downregulation of multiple functions. A common thread in single cell responses to aminated QDs at lower loads was a robust upregulation of stress responses, while responses unique to carboxylated QDs at lower loads showed activation of DNA repair mechanisms. These observations reflect a greater capacity for activating mechanisms that might help to manage adverse effects at lower QD loads, versus reverting to a general shutdown of key processes at higher loads.

COLL 524

Cascade reactions in confined spaces at the nanoscale for replacing part of an impaired metabolic pathway

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Pentose phosphate pathway (PPP) and glycolysis (G) are two parallel and major metabolic pathways for the formation of nicotinamide adenine dinucleotide phosphate (NADPH), and energy storage. Various significant biological reactions involve NADPH as reducing agent, being an excellent source of electrons for anabolic synthesis of fatty acids, lipids and DNA, important in cellular antioxidation systems, or as substrate for NADPH oxidase that plays key roles in pathological processes by generating reactive oxygen species (ROS) – used by the immune system to combat infections. Human

disorders caused by defects in enzymes, such as phosphoglucomutase, glucose-6-phosphate dehydrogenase, or glucose-6-phosphatase, are harmful to the body inducing for example glycogen storage diseases, manifested by hypoglycemia, glycogen deposition in the liver, growth retardation, hyperuricemia and gout. An elegant manner to replace part of an impaired metabolic pathway is to use nanotechnological systems, which combine active compounds with synthetic compartments to generate nanoreactors and artificial organelles. Encapsulation of enzymes in polymeric nanocompartments simultaneously protects them from proteolytic attack and allows them to act "*in situ*". NADPH and 6-phospho-D-glucono-1,5-lactone are produced "*in situ*" by involving two enzymes: phosphoglucomutase and glucose-6-phosphate dehydrogenase. They will be co-encapsulated in the same polymersome and the products will be released once the optimum conditions are met. This represents a novel strategy, to fix part of a deficient metabolic pathway, as a potential treatment for specific PPP and G disorders, induced by enzyme deficiencies.

COLL 525

Structural elucidation and multi-functionalization of cell membrane-coated nanoparticles

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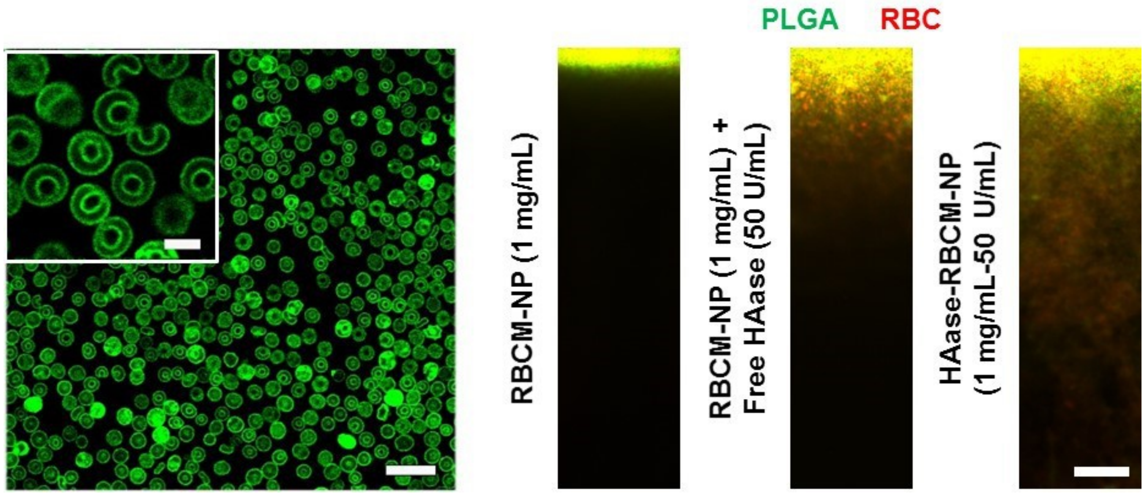
Cell membrane-coated nanoparticles (CM-NPs) are a novel class of materials and are superior to synthetic nanomaterials in some aspects because their surfaces preserve the natural structures of cell membranes. We have previously developed a unique approach to chemically modify membranes of live cells using a bifunctional linker, succinimidyl-[(N-maleimidopropionamido)-polyethyleneglycol] ester. This approach was first used to study the membrane orientation of CM-NPs by anchoring a 6-FAM ssDNA probe on live cells to mark the outer leaflet of bilayer membranes. Then, a BHQ1 ssDNA quencher with a complementary sequence was used to quench the 6-FAM exposed to the outside of CM-NPs, which were made of 6-FAM ssDNA-modified membranes, via fluorescence resonance energy transfer between 6-FAM and BHQ1. The fluorescence intensities of particle solutions before and after the addition of ssDNA quencher were measured to quantitatively determine the fraction of CM-NPs with a correct outside-out (also called right-side-out) membrane orientation. It was shown that 84% of red blood cell membrane-coated nanoparticles (RBCM-NPs) maintained a correct orientation. Based on the same membrane engineering approach, a facile strategy has also been established to fabricate multifunctional CM-NPs, providing CM-NPs functionalities beyond the natural function of cell membranes. As a proof of concept, we conjugated hyaluronidase (HAase) on RBC membranes that were fabricated into RBCM-NPs. The conjugated HAase assisted NP diffusion more efficiently than free HAase in matrix-mimicking gels, and the modification did not reduce the ultra-long blood circulation time of RBCM-NPs in mice.



Hyaluronidase (HAase)-functionalized red blood cell membrane-coated nanoparticles (RBCM-NPs). A) Modification of RBC membranes with FITC-labeled HAase. B) RBCM-NPs diffusion in ECM-mimicking gels. The PLGA nanoparticle cores are in green, while the RBC membranes are in red. the co-localization of two colors illustrates that the membranes did not separate from the particles.

COLL 526

Alteration of membrane compositional asymmetry by $LiCoO_2$ nanosheets

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Given the large projected presence of redox-active nanomaterials in the next generation of consumer electronics and electric vehicle batteries, these nanomaterials are likely to come in contact with cell membranes, with biological consequences that are currently not known. Here, we present nonlinear optical studies showing that lithium nickel manganese cobalt oxide nanosheets carrying a negative zeta (ζ) potential have no discernable consequences for lipid alignment and interleaflet composition in supported lipid bilayers formed from zwitterionic and negatively charged lipids. In contrast, lithiated and delithiated $LiCoO_2$ nanosheets having neutral and positive ζ potentials, respectively, alter the compositional asymmetry of the two membrane leaflets. Furthermore, the bilayer asymmetry remains disturbed even after rinsing. The insight that some cobalt oxide nanoformulations induce alterations to the compositional asymmetry in idealized model membranes may represent an important step towards assessing the biological consequences of their predicted widespread use.

COLL 527

Scavenging components of the biomolecular corona using an *in vitro* liver model

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Nanoparticles presented in a complex biological milieu form a layer of long-lived biomolecules known as the ‘hard corona’ that forms the biological identity of the nanoparticles. Nanoparticle-biomolecular complexes then interact with biological barriers via single cell interactions and gain access to specific pathways via these molecules presented on the surface of the nanoparticles. Biomolecular patterns presented on the nanoparticle surface will determine how a nanoparticle interacts with a range of receptors on specific cells. This may define many key interactions and impacts

mediating the interactions with nanomaterials and our immune system, in particular in, *in vivo* bio-distributions, nanomedicine targeting strategies and other biological outcomes.

For instance, active pathways driven by receptors on the Kuppfer cells in the liver, such as scavenger receptors, may lead to nanoparticle accumulation via specific interactions. We also present here, the impact of the presence of apolipoproteins, specifically, ApoB-100 on the surface of silica nanoparticles which leads to low density lipoprotein receptor recognition, mostly expressed in the liver. These results suggest that the ‘labelling’ of nanoparticles by biomolecular adsorption processes allows for nanoparticle multi-pathway involvement in biological processes, in which nanoparticles may be misinterpreted to be an endogenous lipoprotein, and be taken up by low density lipoprotein receptor.

Thus, we connect the nanoparticle-surface complexes with specific cell receptor interactions using a model functional receptor library hosted in cells (HEK-293T cells). The central aim of this work was in the identification of specific receptors that can recognize nanoparticles in a complex biological milieu. Therefore, providing an understanding of how specific cell receptors interact with nanoparticle-biomolecular corona in complex biological milieu, which can be valuable to better predict and control the bio-distribution of nanoparticles and how they interaction with the immune system.

COLL 528

Magnetic actuation of intracellular signalling in mammalian cells

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Investigating the dynamics of living cells requires not only imaging tools but also methods to perturb cellular activities with high spatio-temporal resolution. Here, we present an approach based on the use of magnetic nanoparticles (MNPs) functionalized with active proteins. Once inserted in the cytosol of mammalian cells, they behave as signaling nanoplatforms which can be localized at a subcellular level with magnetic forces. For this purpose, we tailored the size and surface properties of MNPs (synthetic or protein-based) in order to ensure unhindered mobility in the cytosol. These MNPs with a core diameter below 50 nm could be rapidly displaced within living cells by exploiting biased diffusion at weak magnetic forces in the sub pico-Newton range. Furthermore, we engineered the functionalization properties of the MNPs to enable specific and in situ capturing of target proteins. We will discuss the application of the method: (i) the control of Rac1 and Cdc42 activities in live cells, (i) the manipulation of organelle dynamics in the cytosol.

COLL 529

Coordination of molecular motors during axonal transport revealed by nanoparticles

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In neurons, the axon acts as a conduit for organized transport of materials between the cell body and the synapse, a process that is essential for the function and survival of neurons. The long distance transport in axons is powered by microtubule motors, kinesins and dyneins, that drive the cargo to the axonal termini and the cell body respectively. Interestingly, axonal cargoes are often equipped with both set of motors. How the opposing motors are coordinated during the axonal transport is a topic of great interest. Using qautnum dots and gold nanoparticle as cargo labels, we show that mechanical tugs-of-war and intracellular motor regulation are complimentary features of the axonal transport process. We also developed a novel dark-field microscopy method that measure cargo rotation using gold nanorods, which reveal detailed motor coordination during axonal transport.

COLL 530

Magnetic nanoparticles: A precision tool for cell imaging and activations

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One of the important trends of next-generation biomedical sciences is the development of new tools that can accurately image, identify, and execute desired missions in a selectively programed manner. Nanotechnology is among one of the essential platform tools for targeted imaging, therapy, and simultaneous monitoring of therapeutic efficacy. In this talk, I will discuss magnetic nanoparticles as a core platform material and tool for a variety of functionalities such as sensing, targeting and signaling of cells in a selective and efficient way. Their unique utilizations in highly accurate dual-modal MR imaging, therapeutic hyperthermia of cancer cells, controlled drug/gene delivery, and molecular level cell signaling and cell fate control will be discussed.

COLL 531

Efficient and non-toxic gene delivery by triblock terpolymer micelles

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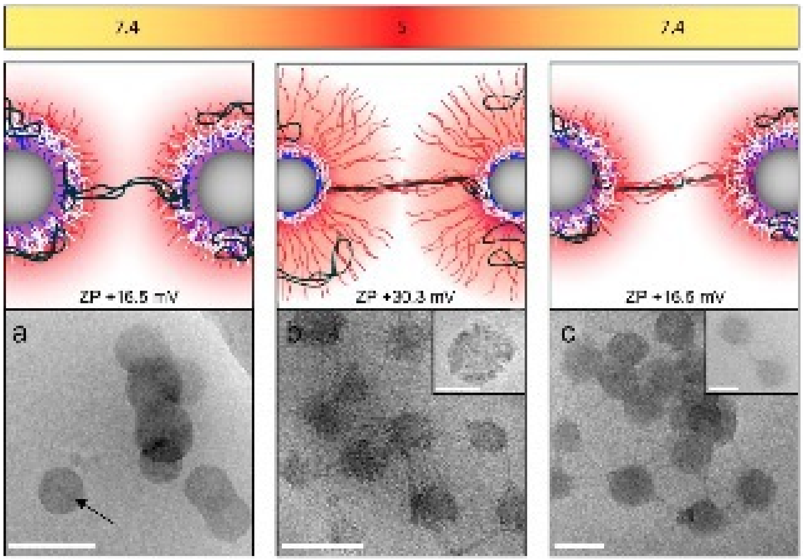
Nowadays, manipulation on a genomic level can be used to understand and influence cellular signaling, in particular since the mechanism of RNAi was discovered. The controlled delivery of genetic material into eukaryotic cells has been the focus of interdisciplinary scientific activities during the last two decades. Beside evolutionary qualified and very efficient viral transfection, non-viral delivery using polymeric systems is of high interest. Herein, a multicompartment micelle from stimuli-responsive triblock terpolymers, polybutadiene-*block*-poly(methacrylic acid)-*block*-poly(2-(dimethylamino)ethyl methacrylate) (BMAAD, PB_{800}-*b*-$PMAA_{200}$-*b*-$PDMAEMA_{285}$) will be presented as non-viral delivery agent. Such micelles are dynamic and show a strong pH dependence concerning shape, size, and surface charge. At low pH, PMAA is hydrophobic and PDMAEMA forms a cationic corona, whereas at pH 7 both blocks are charged, leading to the formation of an intra-micellar interpolyelectrolyte complex shell. Superior transfection efficiencies – better or comparable to the gold standard polyethylenimin (PEI) – were observed for both adherent as well as suspension cells (lymphocytes). The mixed micelle surface showed further advantages: (i) The high transfection efficiency is not linked to high cytotoxic effects, what is often observed with other cationic polymer systems. (ii) The efficiency was not reduced in serum-containing media. For this purpose, detailed investigations of the underlying mechanism will be presented, using cyro-TEM and asymmetric flow-field-flow-fractionation (AF4).



Scheme 1. Proposed polyplex structure and the corresponding cryo-TEM micrographs at pH 7.4, the black arrow indicates the presence of im-IPEC (a), pH 5 (b), and pH 7.4 (c). Color code: grey (PB), blue (PMAA), red (PDMAEMA), white (im-IPEC), and black (pDNA-polyplex). Scale bars indicate 200 nm and 50 nm in the insets.

COLL 532

Frizzled7-targeted nanoshells enable selective photothermal therapy and blockade of Wnt signaling in triple-negative breast cancer

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Nanoshells (NS) composed of 120 nm silica cores and 15 nm thick gold shells are an excellent platform for multimodal cancer therapy because they are efficient photothermal transducers and enable simple bioconjugation chemistry. Extensive research has demonstrated that NS coated with targeting ligands can provide tumor cell-specific photothermal therapy (PTT), but minimal research has investigated the impact of nanoparticle binding to cells on the signaling pathway to which the targeted receptor belongs. We hypothesized that, in addition to providing cell-specific PTT, antibody-coated NS could inhibit desired signaling pathways by locking the targeted receptor in a ligand-unresponsive state. We tested this hypothesis using an *in vitro* model of triple-negative breast cancer (TNBC), which is an aggressive breast cancer subtype that lacks effective treatment strategies. Hyperactive Wnt signaling drives TNBC, and is activated in TNBC cells when Wnt3a proteins bind Frizzled7 (FZD7) receptors that are overexpressed on the cells' surfaces. This activation stabilizes a molecule called β-catenin, which accumulates in the cytoplasm then enters the nucleus to promote transcription of downstream target genes including Axin2. We coated NS with antibodies specific to FZD7 receptors (FZD7-NS) to actively target TNBC cells, provide PTT, and inhibit Wnt signaling. Using fluorescent vaibility staining, we demonstrate that FZD7-NS can selectively bind TNBC cells, but not normal breast epithelial cells, to enable their photothermal ablation. Further, we demonstrate with Western blot and qRT-PCR that FZD7-NS can inhibit Wnt signaling in TNBC cells, as cells co-treated with FZD7-NS and Wnt3a exhibit 33% lower β-catenin levels and 90% lower Axin2 levels than cells treated with only Wnt3a or Wnt3a and non-targeted NS. The results presented demonstrate that NS can be utilized as multifunctional therapeutics for treatment of TNBC by carefully selecting targeting moieties to enable both cell-selective PTT and signal cascade interference. In the future, this technology could be applied to treat other cancers and diseases characterized by hyperactive Wnt signaling to improve patient outcomes.

COLL 533

Bioinorganic interface: Mechanistic studies of protein-directed nanomaterial synthesis

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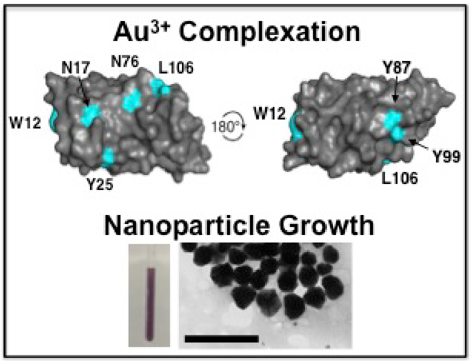
Proteins and peptides have attracted much attention as templates for one-pot synthesis of biocompatible gold nanoparticles. While numerous natural and *de novo* protein sequences have been used, the actual mechanism of nanoparticle nucleation and growth from the protein matrix is not well understood. In this study we utilized engineered consensus tetratricopeptide repeat (CTPR) protein to probe the bioinorganic interface during gold nanoparticle synthesis. The binding of CTPR to gold ions and the gold nanoparticle surface was investigated using fluorescence spectroscopy and heteronuclear single quantum coherence NMR spectroscopy to provide residue-specific measurements. We observed that the initial complexation step between gold ions and

CTPR3 is ionic strength dependent. Moreover, size and morphology of NPs can be tuned by adjusting the ionic strength. We ascertained the importance of residue identity, chemical environment, and orientation for gold ion-protein binding. Furthermore, we found that NPs preferentially interact with the negatively charged face of CTPR3 as observed in 2D NMR. This work provides a foundation for the rational design of proteins for synthesis of tailored functional nanomaterials for biological, medical, and optical applications.



Top: A surface model of CTPR3 with major binding residues to gold ions shown in cyan. Bottom: Picture of the NMR sample after gold NP formation and the corresponding TEM image of the NPs, scale bar 200 nm.

COLL 534

Thermodynamics and kinetics of Watson-Crick base pairing-driven assembly of DNA origami nanostructures

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We investigate the kinetics and thermodynamics of DNA origami dimerization using flat rectangle origami components and different architectures of Watson-Crick complementary single-stranded DNA (“sticky end”) linking strategies both in isolation and in the assembly pathways that arise during the formation of multi-unit structures. To understand the binding interactions between single origami structures, we systematically vary the number of linkers, the length of the sticky ends on the linker and linker architecture and measure the corresponding yields as well as forward and reverse reaction rate constants through fluorescence quenching assays. Further, we show that the second order forward reaction rate constant (k_on) depends on both linker architecture and number of linkers used, with typical values on the order of 10^5-10^6 1/(M*sec), which are similar to bimolecular association of small, complementary DNA strands. We use kinetic and thermodynamic information about the optimal linking architecture to extend the system to a multi-component assembly process. We characterize origami complex yields, the equilibrium constants for each possible reaction for the assembly of a heterotetrameric ring, the unit cell of a rectangular lattice using fluorescence co-localization microscopy. We find that origami interface structure controlled reaction free energies. Cooperativity, measured for the first time for a DNA nanostructure assembly reaction, was weak. Simulations of assembly kinetics suggest assembly occurs via parallel pathways with the primary mechanism of assembly being hierarchical: two dimers form which then bind to one another to complete the ring.

COLL 535

Supramolecular design of antimicrobial peptides: Balance of nanostructure, cytototoxicitity and antimicrobial activity

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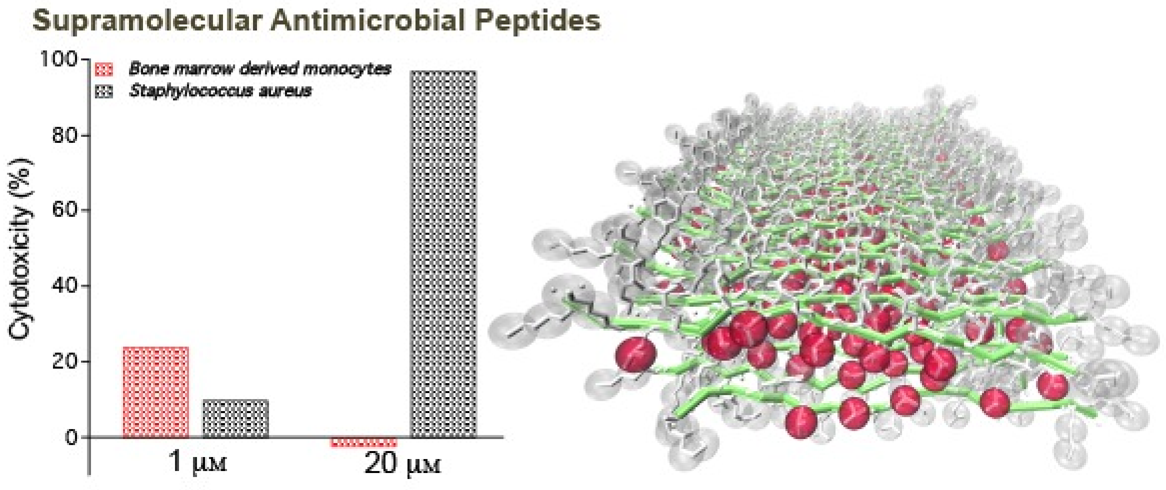
Peptide-based supramolecular assemblies represent an important class of soft nanomaterials with hierarchical structural control down to the molecular level. The well-defined molecular structure plays important roles in regulating the supramolecular nanostructure, property and various biological activities. In this work, we present the first example of *de novo* designed multidomain peptides (MDPs) that form self-assembling antimicrobial nanofibers (SAANs) with a broad-spectrum antimicrobial activity. Unlike most AMPs that exist as a monomer prior to their binding with lipid membranes, MDPs can be formulated into supramolecular nanofibers through proper balance of the number of lysine residues and repeating units of the (QL) domain. The formation of SAANs offers a huge advantage over previously designed monomeric AMPs in that the assembled nanofibers exhibit enhanced cell penetration and protects individual peptides against proteolysis while dramatically reducing their toxic and reactogenic effects on eukaryotic cells. This study details a design strategy to optimize supramolecular AMPs for minimal cytotoxicity, enhanced proteolytic stability, potent cell penetration and effective antimicrobial activity, thereby facilitating their application for systemic anti-infective treatments.



COLL 536

Free energy of pore formation by aggregates of melittin in 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) and 1,2-di-(9Z-octadecenoyl)-sn-glycero-3-phospho-(1'-rac-glycerol) (DOPG) mixed lipid bilayer by molecular dynamics simulation

Yuan Lyu[1], *Ning Xiang*[1], *Xiao Zhu*[2], ***Ganesan Narsimhan***[1], *narsimha@purdue.edu.* (1) Dept of Agric Biological Eng, Purdue University, West Lafayette, Indiana, United States (2) Research Computing, Purdue University, West Lafayette, Indiana, United States

Antimicrobial peptides (AMP) inactivate microorganisms by forming pores in cell membrane. Energetics of addition of an AMP to a transmembrane pore is important for evaluation of growth of pores. This study characterizes the potential of mean force through molecular dynamics (MD) simulation for the addition of melittin, a naturally occurring AMP, into a DOPC/DOPG mixed bilayer for different extents of penetration into either a bilayer or a pore consisting of three to six transmembrane peptides. Water channel formation occurred only for insertion into pores consisting of four or more transmembrane peptides with the radius of water channel being larger for larger number of transmembrane peptides. The energy barrier for insertion of a melittin molecule decreased for insertion into a pore with larger number of transmembrane peptides eventually approaching zero. Estimated free energy barrier for insertion of melittin into an ideal paraboloid pore were consistent with MD simulation results.

COLL 537

Membrane penetration and stability of gold nanoparticles and luminescent semiconductor quantum dots coated with of poly (oxonorbornene)-based synthetic mimics of antimicrobial peptides (SMAMPs) in aqueous media

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Semiconductor quantum dots (QDs) have unique optical properties that make them superior to organic dyes in many applications. They have broad excitation in the UV and emit brightly in a narrow emission window while possessing high photostability. Their emission wavelength can also be tuned across the UV and infrared spectrum by altering the size of the QD core. The excellent optical properties of QDs see their use in many potential medical and biological applications. However, QDs are made with inherently toxic elements such as cadmium which can be released upon nanoparticle degradation. QDs are usually coated with stabilizing ligands such as various thiol based ligands such as mercaptopropanoic acid (MPA), mercaptoundecanoic acid (MUA), dihydrolipoic acid (DHLA), or polyethylene glycol (PEG). These coatings are designed to protect the QDs from aggregation, oxidation, and stabilize the particle in aqueous solution. However, there is limited research describing toxic effects that arise from these ligands while on the surface of quantum dots. It has been shown that charge density and hydrophobicity

are primary factors in dictating membrane penetration in gold nanoparticles and it is likely similar trends occur with QDs. Synthetic mimics of antimicrobial peptides (SMAMPs) are a poly(oxanorbornene) based polyelectrolyte with two functional side chains that can be independently modified. This provides the opportunity to independently vary the surface charge density and hydrophobicity of quantum dots coated with SMAMPs polyelectrolyte. This study explore the stability of cadmium selenide and indium phosphide quantum dots coated with a series of SMAMPs polyelectrolyte with varying charge densities and hydrophobicities to determine their ability to penetrate liposome membranes. Furthermore, the stability of SMAMPs coated quantum dots in various biological media as well as their resistance towards aggregation, generation of reactive oxygen species and subsequent oxidation under illumination, and release of toxic elements will be explored.

COLL 538

Exploration of the aggregation and gelation process of short and medium sized peptide chains

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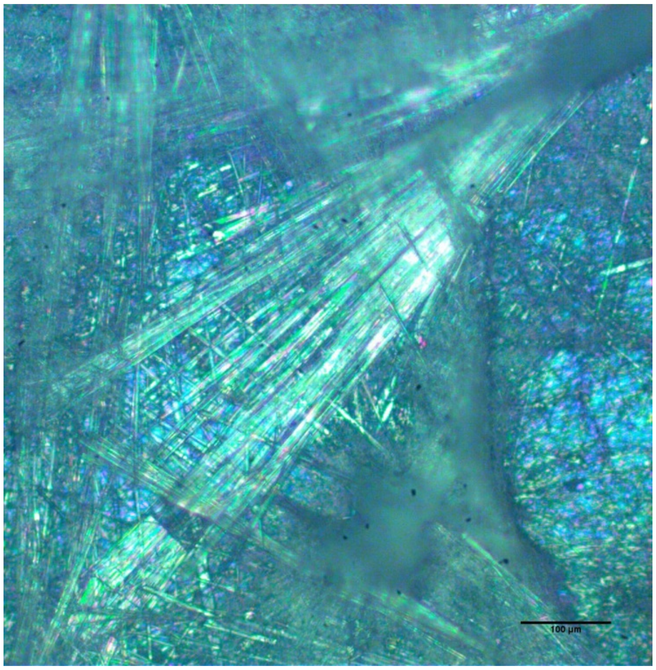
The self-assembly of biomolecules is an important issue explored in biomedical, biophysical, and bio-material research. Being able to understand how and why certain peptides prefer to self-assemble into larger gel forming networks can help shed light on their usability for drug delivery, tissue repair and environmental sensing. The biomedical use of peptides is facilitated by their biodegradability. In spite of numerous papers reporting (hydro)gel forming peptides, our understanding of which parameters govern their gel forming capabilities is still rather limited. It is generally thought that peptide fibrillization, which precedes the gelation process, requires a high content of hydrophobic residues. Recently, however, three different peptides have emerged as gelators in our laboratory, which do not meet this and other requirements. The two short unblocked peptides, i.e. Glycylalanylglycine (GAG) and glycylehystidylglycine (GHG), as well as the medium length blocked cationic peptide $(AAKA)_4$ have all been show to unexpectedly form supramolecular structures under different conditions. GAG forms crystalline fibrils in a 55%/45% mole fraction ethanol/water solution, while zwitterionic, neutral GHG has been shown to form fibrils with lengths of hundreds of μm long at neutral pH. The medium size chain, $(AAKA)_4$, forms a hydrogel at either a high enough concentration or after enough time. We will present spectroscopic and rheological data and their analysis which allow to disentangle various steps of the respective gelation processes such as peptide aggregation, fibril and network formation, and to identify the underlying physical parameters.



Brightfield microscope image of GHG in the gel phase.

COLL 539

DNA-functionalized metal oxide nanoparticles: From fundamental surface science to applications

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Metal oxides are a very important class of materials. While interfacing DNA with metallic nanoparticles have been extensively studied, relatively little is known at the metal oxide interface. In this talk, I will present our recent work on DNA adsorption by a few important metal oxides, including Fe_3O_4, CeO_2, ITO, TiO_2, and ZnO. For most of these materials, DNA adsorption is achieved via its backbone phosphate, and each conjugate as unique applications in analytical chemistry or fundamental implications. For example, the Fe_3O_4 conjugate can be used for highly sensitive arsenate detection, while the CeO_2 conjugate detects hydrogen peroxide. ZnO has high solubility, and its DNA adsorption is suggested to be the reason for many confusions in the field of Zn^{2+}/DNA interactions. A comparison between metal oxide and graphene oxide for DNA adsorption will finally be made.

COLL 540

High-density DNA-coated particles and clusters

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We demonstrate a method to create high-density DNA coatings on colloidal particles that can be used for DNA-mediated self-assembly of single and multiple-component colloidal crystals. First, we modify an amphiphilic diblock copolymer consisting of a hydrophobic polystyrene (PS) block and a hydrophilic poly(ethylene oxide) (PEO) block with azide functional groups at the end (poly(ethylene oxide)-N_3). Then, we introduce the diblock copolymers into an aqueous suspension of colloidal polymer particles swollen with a solvent. The hydrophobic PS anchoring block is incorporated into the swollen polymer spheres and physically trapped when the solvent is removed, resulting in a dense PEO polymer brush with azide functional end groups. Finally, single-stranded DNA strands with sticky ends are attached to the azide groups using strain-promoted azide alkyne cycloaddition (SPAAC, a copper-free click chemistry). This procedure results in a high areal coverage of up to 225,000 DNA strands on 1-mm-diameter particles. The ssDNA-coated particles with sticky ends can readily form either face-centered cubic (FCC) or cesium chloride (CsCl)-like crystal structures when annealed just below the melting temperature of the DNA-coated particles.

COLL 541

Molecular dynamics investigation of the sequence specific binding of single-stranded DNA (ssDNA) with chiral single-walled carbon nanotubes (SWCNTs)

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The need to sort single-walled carbon nanotubes (SWCNTs) by their chirality is an important problem in where improvement is needed in order to cost effectively pursue applications using these materials. Currently, the separation techniques used rely on a wet solution dispersion approach, in which surfactants are used to bind and individually suspend the tubes in aqueous media. This process is in conjunction with diverse techniques which sort the SWCNTs by their physiochemical properties. Previous work has shown that single-stranded DNA (ssDNA) is a very effective dispersant and this method has been used in combination with a variety of techniques such as ultracentrifugation, chromatography, and aqueous two phase extraction (ATPE). Experimental work, particularly at NIST, has shown that specific ssDNA sequences are optimal for binding particular chiralities; therefore, they are better separation agents. However, the nature of this specificity is not yet well understood and optimal bindings must be searched by trial and error. In this study, we use replica exchange molecular dynamics (REMD) simulations to study and compare the binding of experimentally determined optimal and unfavorable sequence/chirality binding pairs. Additionally, we

explore the configurational and energetic contributions to this self-assembly process and compare the effect and interplay between a number of proposed binding factors including inter- and intra-strand interactions of the ssDNA, the ratio of Kuhn length to tube diameter, and the ssDNA equilibrium conformation relative to the chiral angle of the SWCNT. From these analyses our goal is to provide better insight into the sequence/chirality specific binding mechanism, and eventually to develop a model that allows for the prediction of other pairs leading to the efficient sorting of a desired nanotube chirality.

COLL 542

Co-crystallization of nanoparticle-PEG conjugates and protein

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Dictating the three dimensional order of nanoparticles has remained an elusive goal for nanoscientists. Here we show how the process of protein crystallization can provide a means for achieving such control. The protein hen egg white lysozyme (HEWL) is an easy to crystallize biomolecule; we found when appropriately derivatized gold nanoparticles were incorporated into a biomolecular crystallization medium they co-crystallized with the protein. Such incorporation was only possible when the surface coating of the particles was over 10,000 molecular weight with low grafting densities. Light scattering and centrifugation data suggest that when poly(ethylene-glycol) has low surface grafting densities the nanoparticles and proteins had weak interactions prior to crystallization. Under these circumstances the particles enhanced protein crystal nucleation and were incorporated into lysozyme crystals imparting to them a deep red color. These crystals still diffracted in a manner similar to native lysozyme although with slightly greater mosaicity. Nanoparticles coated with short chain PEG interacted far less with proteins in solution, and did not incorporate into the growing crystals. The structure of the gold nanoparticles within the lysozyme crystal was analyzed using SAXS and TEM revealing some ordering of the particles relative to the protein crystal lattice. The phenomenon was independent of nanoparticle type and we found other nanoparticles, such as iron oxide, quantum dots and gold nanorods also occurred if the surface grafting density of PEG was low. This confirms that the surface properties of nanoparticle-PEG conjugates, rather than the nanoparticle itself, dictates the protein-nanoparticle solution interactions and the subsequence incorporation of nanoparticles into biomolecular crystals.

COLL 543

Lipid phase coexistence forms the basis of the permeability barrier of the outer skin layer

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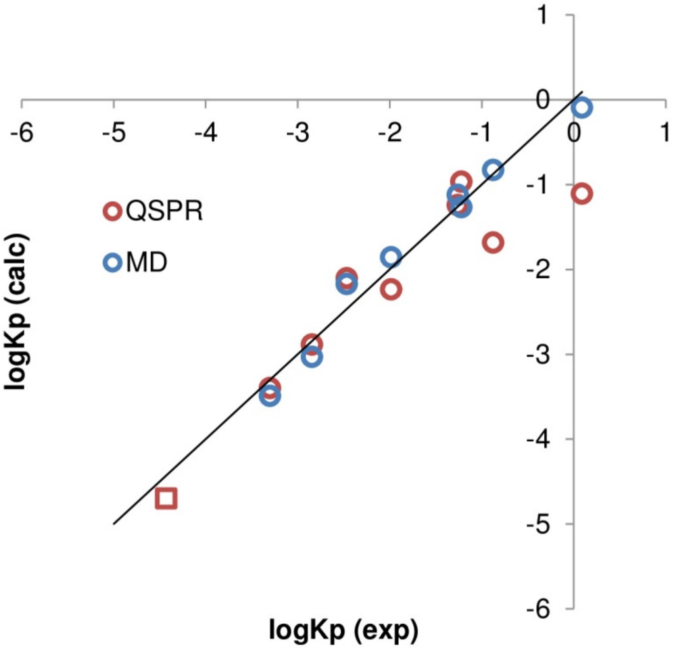
The lipid matrix of the stratum corneum (horned layer) of mammalian skin has long been studied as a biophysical model to understand and to predict the permeability of small molecules through skin. X-ray and neutron scattering, cryo-electron microscopy images, and molecular dynamics (MD) simulations show the occurrence of inverse-micellar phases or lamellar phases, alternatively. In some cases, multiple lamellar phases corresponding to lipid bilayers and more complex supra-molecular structures are detected by the same experiment. The occurrence of multiple phases parallels the availability through the skin of pathways for the permeation of hydrophilic and lipophilic molecules alike: however, there is little indication of whether such phases or pathways coexist at the microscopic scale. We used MD simulations at the atomic and coarse-grained (CG) levels of resolution to model the self-assembly of the three essential lipid components of the lipid matrix: ceramides, free fatty acids and cholesterol. Our simulations predict the phase of model mixtures, and suggest for the skin's lipid matrix an architecture where both permeation pathways coexist at the nanometer level. Calculation of the permeability coefficients from our simulation data yields an excellent agreement with whole-tissue measurements on extracted skin. Our approach can prove effective at predicting the permeabilities of small molecules in conditions that prohibit the use of empirical approaches, such as when formulations for transdermal drug delivery are used.



Comparison of permeability coefficients calculated by MD (blue) with quantitative structure-permeability relationships (QSPRs) based on data from unperturbed skin.

COLL 544

Plasmonic colloidal nanoparticles: Gateway to extreme radiative decay engineering

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Hybrid materials structured on the molecular scale hold the promise to realize optical properties that are drastically different from their bulk counterparts. For example, metal-dielectric nanocavities may tightly confine light to small mode volumes resulting in strongly increased local density of states. Placing fluorescing molecules or semiconductor materials in this region enables wide control of radiative processes including absorption and spontaneous emission rates, quantum efficiency, and emission directionality. In this talk, I will describe our recent experiments utilizing a tunable plasmonic platform where emitters are sandwiched in a sub-10-nm gap between colloidally synthesized silver nanocubes and a metal film. Utilizing dye molecules with an intrinsic long lifetime reveals spontaneous emission rate enhancements exceeding a factor of 1,000 while maintaining directional emission and high quantum efficiency. Incorporating colloidal CdSe/ZnS semiconductor quantum dots into the nanocavities enables ultrafast spontaneous emission corresponding to rates exceeding 90 GHz as well as ultrafast and efficient single photon sources. Leveraging higher-order modes of the cavity allows optical processes at multiple energies to be optimized simultaneously. We demonstrate this by enhancing both the absorption and the quantum yield in monolayer MoS_2 resulting in a 2,000-fold enhancement in the overall fluorescence. Finally, this nanocavity geometry can be tuned from the visible to the near-infrared using large-area solution-based deposition techniques promising for future ultrafast optoelectronics, bio-sensing and renewable energy applications.

COLL 545

Correlating metal-enhanced fluorescence and structural properties in $Ag@SiO_2$ core-shell nanoparticles

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Metal@silica concentric nanoparticles capable of metal-enhanced fluorescence (MEF) represent a powerful means to improve the brightness and stability of encapsulated organic fluorophores, and are finding numerous applications in biology, analytical chemistry and medical diagnostics. The rational design of MEF-enabled labels and sensors often involves comparing fluorescence enhancement factors (EF) between nanostructures having different structural properties (e.g., metal core diameter, silica shell thickness, extent of spectral overlap between plasmon band and fluorophore). Accurate determination of EFs requires the measurement of fluorescence emission

intensity in the presence and absence of the plasmonic core while minimizing the impact of physical and chemical artifacts (e.g., signal variations due to scattering, adsorption, sedimentation). In this work, Ag@SiO_2@SiO_2+*x* (where *x* is fluorescein, eosin or rhodamine B) nanostructures were synthesized with excellent control of core size, silica spacer shell thickness and fluorophore concentration. Using UV-VIS spectrometry, spectrofluorimetry, time-resolved fluorometry and transmission electron microscopy, we investigated the influence of these key structural factors on fluorescence emission intensity, and the results were used to develop a generalized methodology for the determination of fluorescence enhancement factors in Ag@SiO_2 core-shell nanoparticles. This methodology should be of general importance to designing MEF-enabled nanostructures, sensors and related analytical techniques.

COLL 546

Super-resolution imaging of plasmonic nanostructures: from ligand binding to plasmon coupling

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Super-resolution imaging is a far-field optical microscopy technique, which allows the diffraction limit of light to be overcome through the combination of photoswitchable optical probes and single molecule localization techniques. This talk describes the use of super-resolution imaging for studying the position of single ligands bound to the surface of single plasmonic nanoparticles as well as providing insight into how plasmon coupling effects impact the accuracy of single molecule localization.

COLL 547

Generalized model for the surface enhanced Raman scattering and surface enhanced/quenched fluorescence

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When a molecule or a quantum dot is placed near a metal nanoparticle or a cluster of nanoparticles, the energy transfer between them will dramatically change the optical properties of the molecule or the quantum dot. Mechanisms associated with the surface enhanced Raman scattering when a molecule is placed near a metal nanoparticle will be introduced. Using the same model, the enhanced and quenched fluorescence signal when a dye or a quantum dot is placed adjacent to a metal nanoparticle will also be discussed. The effects of the excitation and emission wavelengths, particle size, distance between the target molecule and the metal nanoparticle, and the quantum yield of the molecule on the quenching and enhancement factors will be explained.

COLL 548

Shaped, ultra-fast, ultra- intense laser processing of nanomaterials

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Nanoparticles can be produced using a number of routes including chemical, mechanical, and even biological. In the case of chemical synthesis, there is typically a nucleation step followed by a limited growth step. This produces a distribution of sizes due to the random nature of nucleation in time. Similarly, in a plasma reactor, a precursor molecule can be energized and dissociated by hot electrons at any time in the reactor, again leading to a distribution of nanoparticle sizes. If the nucleation could be constrained to a single point in time, then a more monodisperse distribution of nanoparticle sizes should be produced. I will present a new method to synthesize size tunable, narrow dispersity, metal nanomaterials using intense bursts of ultra-short duration, ultra-intense laser radiation to initiate nanoparticle nucleation from precursor molecules in the solution and gas phases. The key to monodispersity is the very short nucleation time in comparison with the nanoparticle growth time. The work is based on our recent discovery that shaped femtosecond laser pulses enable unprecedented control of rare earth nanomaterials synthesis from a minimal collection of reagents, typically precursor salt in solvent and laser light (or photonic reagent). Because the laser energy is deposited into precursor molecules in a very short time and in a non-equilibrium manner, precise control over the dimensions of the produced nanomaterials is achieved.

COLL 549

Designing multicolor long range nanoscopic ruler for imaging of heterogeneous tumor cells

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Tumor heterogeneity is one of the biggest challenges in cancer treatment and diagnosis. Multicolor optical ruler is essential to address heterogeneous tumor cells complexity. Driven by the need, current article reports the design of multicolor long range nanoscopic ruler for screening tumor heterogeneity by accurately identifying epithelial cells and cancer stem cells (CSCs) simultaneously. Nanoscopic surface energy transfer (NSET) ruler has been developed using blue fluorescence polymer dots (PDs) and red fluorescence gold cluster dots (GCDs) as multicolor fluorescence donor and plasmonic gold nanoparticle (GNP) acts as an excellent acceptor. Reported experimental results demonstrated that the multicolor nanoscopic ruler's working window is above 35 nm distances, which is more than three times farther than that of Förster resonance energy transfer (FRET) distance limit. Theoretical modeling using Förster dipole−dipole coupling and dipole to nanoparticle surface energy transfer have

been used to discuss the possible mechanism for multicolor nanoscopic ruler's long-range capability. Using RNA aptamer that are specific for the target cancer cells, experimental data demonstrate that nanoscopic ruler can be used for screening epithelial and CSCs simultaneously from whole blood sample with 10 Cells/mL detection capability. Experimental data show that nanoscopic ruler can distinguish targeted cells from non-targeted cells.

COLL 550

Treatment of emerging contaminants using advanced oxidation processes

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Traditional water and wastewater treatment facilities are designed to remove conventional pollutants such as suspended solids, human and animal waste, some dissolved material and pathogenic microbes. However, industrialisation and growth has led to the development of a large number of new chemicals that are posing to be a threat to the water bodies. These new contaminants known as Emerging Contaminants or Contaminants of Emerging Concern are a group of contaminants that comprise pharmaceuticals and personal care products (PPCPs), pesticides, household chemicals such as cleaning agents, fire retardants, animal medicines and others. In the absence of removal mechanisms, they make their way to water bodies having profound ecological and possibly health impacts. Apart from their direct impact, chemical components of many of these emerging contaminants behave as hormones leading to endocrine disruption. This new group of pollutants is proving to be quite a challenge for the water/wastewater engineers and scientists struggle with ways to deal with them.
In this presentation, advanced oxidation as a method to treat emerging contaminant will be discussed. Advanced oxidation comprises of use of hydroxyl radicals generated by photo based treatment, photocatalysis, ozonation, UV-hydrogen peroxide and the like. Hydroxyl radicals are very strong oxidants and can be successfully harnessed to oxidize the target contaminants. The short lived nature of these radicals and the non specificity of the reactions also pose challenges to their application. The mechanisms of advanced oxidation and its effectiveness in treating certain emerging contaminants will be discussed. Recent advances in their application and ways to circumvent challenges will also be discussed.

COLL 551

Competitive passivation mechanisms on copper surfaces in industrial water treatment

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Surface analysis techniques (XPS, TOF-SIMS, TEM, IR, etc.) were used to examine the relationship between chemical treatments, water chemistry, and the formation of passivation layers on copper alloy surfaces. Historically, benzotriazole and tolyltriazole (BZT and TTA) have been used in industrial open recirculating systems to treat copper alloys against general corrosion and steel alloys against galvanic corrosion. BZT and TTA have been postulated to form infinite pearl necklace arrangement with copper atoms at the metal interface forming single or multilayer films. Often industrial water is at super-saturation with several scaling salts (calcium carbonate, calcium phosphate, and metal silicates) that are treated with acrylic based polymers and passivate steel surfaces. XPS, TOF-SIMS, and TEM revealed that azoles are not sole actors in passivating copper surfaces; scaling salts whose colloidal suspension is controlled by acrylic polymers either compete for the surface or form co-films. When oxidizers (hypochlorous acid, chlorine dioxide, peroxide, etc) are used for microbiological control a spontaneous passivation mechanism speeds up the depositing of scaling layers on metal surfaces. Controlled experiments show that BZT and TTA are not able to remove these salt layers and penetrate to the metal interface. The operating pH (neutral versus alkaline) controls the scaling salt thickness, porosity, and surface chemistry at the interface of the metal and electrolyte medium. Under industrial conditions this work highlights the importance of understanding the role of scaling salts, water chemistry, and chemical treatment have in competing for the interface layer for passivation of copper metallurgies.

COLL 552

Electrocoagulation mechanisms during water and wastewater treatment: Insights from removal of viruses and boron

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Recent advances in electrochemical technologies have generated much interest in evaluating them as alternatives to conventional coagulants. One example is electrocoagulation, which is the intentional corrosion of sacrificial anodes (typically aluminum or iron) by passing electricity to release metal-ion coagulant species and destabilize a wide range of suspended, dissolved, and macromolecular contaminants. During electrocoagulation, current is passed through a sacrificial anode to dissolve coagulant precursor ions in situ, which hydrolyze rapidly to form dissolved hydroxyl complexes and insoluble hydroxide precipitates. Gas exsolution during electrolysis sometimes leads to floc-flotation. Our research has focused on employing electrocoagulation for water and wastewater treatment with regards to removal of microorganisms and dissolved contaminants and as pretreatment for microfiltration and ultrafiltration. This presentation will focus on two issues: (1) the enhanced removal of viruses from contaminated drinking water supplies and (2) boron control from hydraulic fracturing wastewater. Evidence will be presented for sweep coagulation of viruses and surface complexation of boron.

COLL 553

Capacitive deionization: Emerging trends and new directions

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Capacitive deionization (CDI) is a fast emerging technology based on the electrosorption of salt ions into micropores of charging porous carbon electrodes. CDI is most commonly applied to the desalination of brackish water, but is also being explored for other applications such as ionic separations in aqueous and organic solvents, water softening, and microfluidic sample preparation.

A year ago, members of the International Working Group on Capacitive Deionization & Electrosorption (see www.cdi-electrosorption.org) published a perspective review on the field of water desalination by CDI "Water desalination via capacitive deionization: what is it and what can we expect from it?". Since this publication, several new research directions in CDI have emerged and others have been significantly expanded, a testament to the rapid growth of this field. This presentation will cover these new emerging trends, summarizing the latest work and projecting where the field may go next.

Topics covered will include the recent advances in CDI theory, including the effect of immobile charges which capture inverted CDI behavior. Further, we will discuss the newest developments in CDI electrode and cell development, including the effect of charged surface groups on performance and CDI in organic solvents. Finally, we will discuss developments in CDI systems leveraging suspension electrodes, such as the use of fluidized bed electrodes for water desalination by CDI.

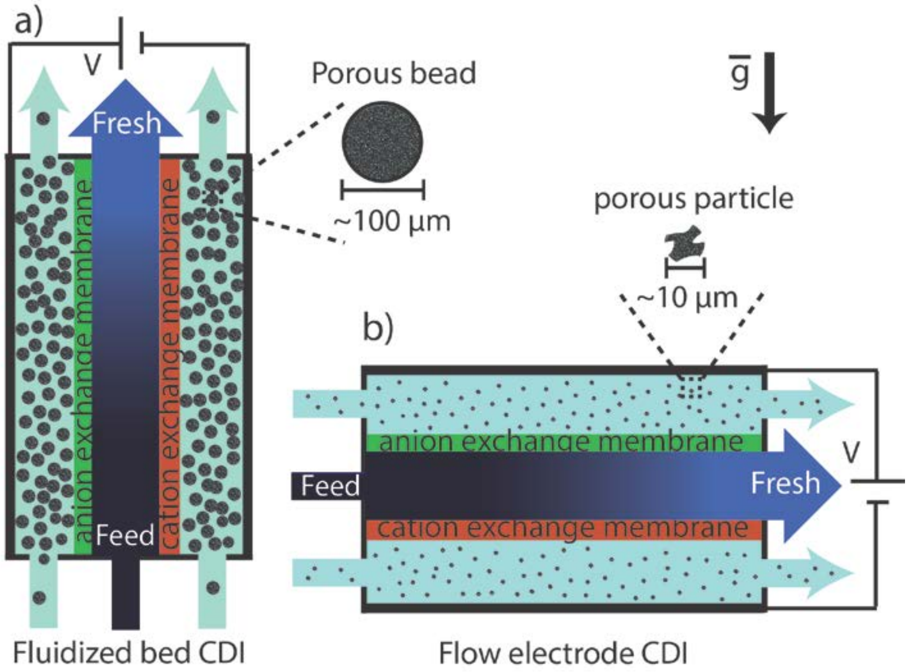

Figure 1: A comparison of suspension electrodes used in CDI. RIGHT: Flow or slurry electrodes utilize typically small carbon particles (< 10 mm) and particles are entrained by the flow. LEFT: Fluidized beds instead use larger carbon beads (order 100 mm or larger), and flow is against gravity. Sedimentation of the beads allows for the formation of densely packed fluidized beds in the electrode compartments.

COLL 554

Shock electrodialysis

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Salt transport in bulk electrolytes occurs by electro-diffusion and convection, but in microfluidic devices and porous media, electric double layer phenomena on the internal surfaces also contribute to ionic fluxes. The nonlinear coupling of bulk and interfacial transport leads to some surprising new phenomena, such as over-limiting current (faster than diffusion) sustained by a deionization shock wave, which removes salt by surface conduction (electro-migration) and surface convection (electro-osmotic flow). Propagating ion concentration shocks in glass microchannels were discovered at Stanford by Mani, Zangle & Santiago (2009), and this talk will describe extensions and applications of this phenomenon in weakly charged porous media, or “leaky membranes”. Theoretical and experimental results for scalable and continuous water purification by “shock electrodialysis” will be presented. Shock ED can achieve 99.99% salt removal with high water recovery (~80%), while also performing separation, filtration and disinfection of the feedwater. The energy efficiency (~0.5%) and current efficiency

(~60%) of the first prototype are expected to improve significantly with system optimization, according to theory. Applications of shock ED range from point-of-use water purification or recycling in gravity-fed systems, to large-scale municipal or industrial water treatment plants. The talk will also touch upon other applications of deionization shocks in porous media, such as separators or composite electrodes for rechargeable metal batteries

COLL 555

Two-dimensional carbon nanomaterials for next generation water treatment membrane

Kashif Rasool[3], *Mohamed Helal*[3], *Chang Ren*[2], *Adnan Ali*[3], *Yury Gogotsi*[1], ***Khaled A. Mahmoud***[3], *khaled.mahmoud@usask.ca.* (1) Drexel Univ, Philadelphia, Pennsylvania, United States (2) Materials Science and Engineering, Drexel University, Philadephia, Pennsylvania, United States (3) Qatar Environment and Energy Research Institute, Hamad Bin Khalifa University, Qatar, Qatar

Membrane processes including reverse osmosis (RO), forward osmosis (FO), membrane distillation (MD), and pretreatment membranes (UF/NF) are rapidly expanding as economic and efficient desalination and water purification technologies. Conventional polymeric materials often cannot tolerate high temperatures, corrosive media, and membrane fouling, which are challenges major challenges facing membrane based water treatment processes. This talk will be discussing our recent development of advanced membranes that enable ultrafast water permeation while maintaining good mechanical properties is very important for the water purification and desalination technologies.

Graphene oxide (GO) emerged recently as an alternative for manufacturing ultrathin, high-flux and energy-efficient sieving membranes because of its unique two-dimensional (2D) and atomically thin structure, outstanding mechanical strength, good flexibility, as well as possibility of facile solution processing. Difficulties in fabricating large-area, uniform GO membranes limit the utilization of this new material at the pilot scale. In our lab we have used other low-dimensional materials and developing composite membranes (e.g., with cellulose nanocrystals) containing GO which helped to achieve efficient water flux and ions sieving through size-selective nanochannels, but does not solve all problems. More recently, we have presented two-dimensional $Ti_3C_2T_x$ (MXene) as novel water desalination/purification membranes. MXenes are a new family of atomically thin, two-dimensional (2D) transition metal carbides and carbonitrides that can challenge graphene and other well-studied 2D materials due to a unique combination of properties and a large diversity of compositions. MXenes show negative surface charge and hydrophilicity, which adds a possibility to control ion flux and biofouling by applying a small potential to the membrane. The MXene membranes showed high resistant to bio-fouling and offer bactericidal properties to the new UF/NF membranes. We used density functional theory (DFT) calculations to understand the mechanisms of charge-selective ionic transport through MXene membranes. We confirmed the charge selectivity originates from the charged nature of the MXene

layers.
On the basis of these results, we expect to afford exceptional mechanical and chemical stability to the new membranes that would tolerate the harsh environmental condition with high efficiency and extended life time of the membrane.

COLL 556

One-step synthesis of {001} facet exposed TiO_2 sheets doped with sulfur on graphene with enhanced photocatalytic activity

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The highly effective composite photocatalyst composed of {001} facet exposed anatase TiO_2 sheets doped with sulfur on graphene was synthesized via a one-step hydrothermal method. The structure of the sample was characterized by XRD, SEM, TEM and Raman spectroscopy. The photocatalytic efficiency was evaluated by the degradation of methyl blue under solar light, visible light (wavelength larger than 420 nm) and UV light (wavelength between 280-400 nm). The results showed that by doping and adding graphene into the system, the degradation efficiency was enhanced under all wavelengths (solar light, visible light, UV light), especially under visible light. Reduction of band gap and improved electron mobility are considered to be reasons for the improved photocatalytic efficiency.

COLL 557

New mechanistic and predictive model for ion adsorption equilibrium in capacitive deionization

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Capacitive deionization is an emerging desalination technology that promises lower energy consumption. However, the potential of this technology has not been carefully assessed due to the lack of theoretical models applicable to realistic electrode materials. The study reported here develops a mechanistic and predictive model that takes into consideration the pore geometry and size of the electrode material and the finite size of electrolyte ions. The model builds on the Gouy-Chapman-Stern (GCS) theory, accounts for finite ion size using the Carnahan-Starling (CS) equation, and employs a rigorous numerical model to accurately determine the profiles of electric potential and ion concentration in pores of different shape and size. A series of model simulations were performed to investigate the effects of electrode characteristics, ionic

species, influent salt concentration, and applied voltage. Comparison with the commonly used GCS model and Modified Donnan model show that, unlike these previous models our model is applicable to a wide range of pore sizes and salt concentrations, and demonstrates significant inherent selectivity of CDI towards ions of different charge to size ratios. The model simulation provides important insight needed for designing high performance electrode materials.

COLL 558

Catalytic activities of transition metal nanoparticles in carbon-carbon bond cleavage of complete ethanol oxidation reaction

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Attainment of direct ethanol fuel cell technology depends critically on our ability to develop catalysts that can effectively cleave the C-C bond in complete ethanol oxidation reaction (EOR). Towards this goal, many research groups have devoted their attention to the studies of transition metal nanoparticles in complete EOR, such as alloying different metals and varying nanopaticle size. In this presentation, we will summarize the current progress and present our efforts over the past few years on the efficieny of C-C bond cleavage through different intermidiates on Cu and Pd catalysts in both gas phase and alkaline conditions

COLL 559

Controlling phase behavior and oxidation rates in core/alloy nanoparticles

Mathew M. Maye[1], *mmmaye@syr.edu*, *Laxmikant Pathade*[1], *Tennyson L. Doane*[1]. (1) Chemistry, Syracuse University, Syracuse, New York, United States

This presentation focuses on the use of metal phase behavior, redox potential, and oxidation properties to manipulate how nanoparticles nucleate, grow, and transform into new sizes, shapes, and microstructures. We explore a post-synthesis processing strategy that employs galvanic exchange and atomic interdiffusion at a core/shell interface to produce alloy-terminated nanocrystals. The resulting “core/alloy” nanoparticles have alloy compositions that are determined by shell thickness, processing temperature, and metal choice. The metals phase behavior can be used to prepare heterostructured dumbbell shapes, whereas its oxidation tendencies can be used to alter internal microstructure by controlling Kirkendall diffusion effects, or oxide shell thickness. We will also present recent success in using the core/alloy approach in the preparation of metal nanoparticles with stainless properties.

COLL 560

Nanostructured heated gold electrodes for DNA hybridization detection using enzyme labels

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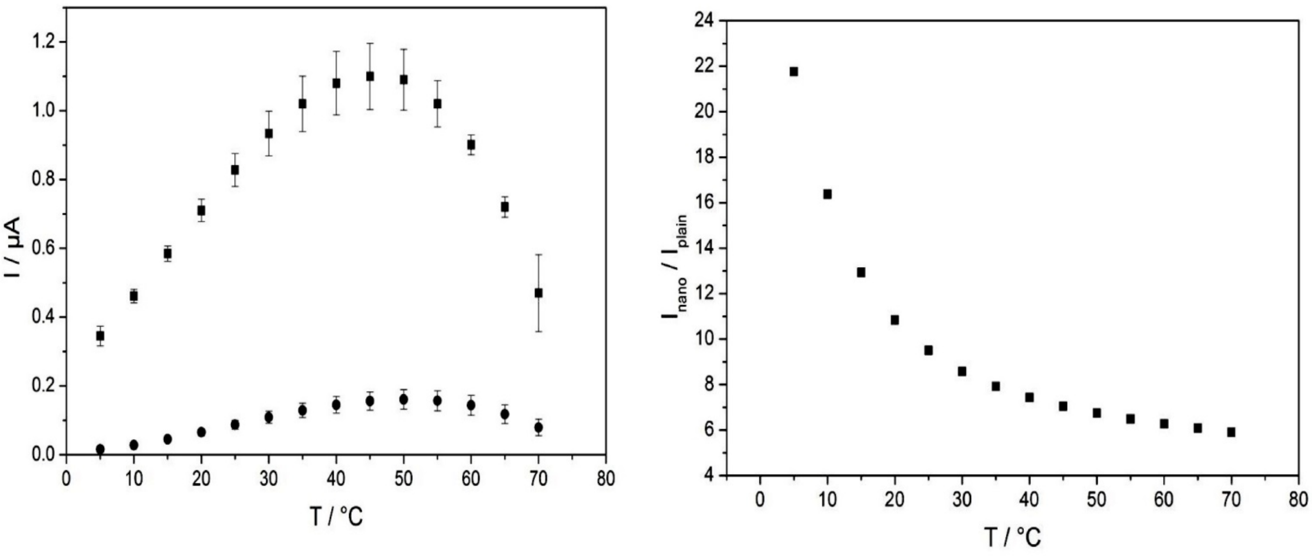
Electrically heated nanostructured gold electrodes were introduced for the detection of DNA hybridization of enzyme-labeled target strands. Template-free galvanic deposition of gold nanostructures at a gold-wire electrode lead to decreased microelectrode behavior at low temperature (5 °C). This was confirmed by cyclic voltammetry of ferrocyanide and assessment of the according wave- and peak-shaped signals. However, direct electric heating to 55 °C electrode temperature brought back the wave-like signals indicating microelectrode behavior. Another sort of heated gold electrode based on low temperature co-fired ceramics (LTCC) was modified with the same nanostructures and used for DNA hybridization detection of targets covalently modified with enzyme labels. The voltammetric signal increase for the nanostructured LTCC electrode was 22- and 6-fold at electrode temperatures of 5 °C and 70 °C, respectively. A trapping effect in the spaces between the gold nanostructures greatly increases sensitivity, in particular at lower electrode temperature. Such galvanically nanostructured gold electrodes can greatly improve sensitivity without affecting the selectivity in DNA sequence analysis.



DPV signals of alkaline phosphatase-labeled DNA at an indirectly heated LTCC gold disk electrode for plain (round dots) and nanostructured (square dots) gold surfaces at different temperatures. The right panel depicts the ratio of peak currents for each temperature. The substrate was 0.228 mM 1-naphthyl phosphate, the DPV scan rate 33 mV/s and pulse amplitude 70 mV.

COLL 561

X-ray assisted heterogeneous catalysis

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Several mechanisms associated with heterogeneous photocatalysis may be elucidated using X-ray irradiation of nanomaterials. One phenomenon is the impact of high density of electron-hole pairs created in the nanostructures due to limited penetration of light into the highly scattering nanocatalysts. With X-rays, the penetration depth is much higher. Another process that may negatively impact heterogeneous photocatalysis is the recombination of electron-hole pairs. With ionizing radiation such as X-rays, the electron-hole pairs may be separated by the intrinsic charges accumulated on the X-ray absorbing nanoparticles, which are in contact with nanoparticle catalysts. Using copper decorated titania nanoparticles as catalysts for reduction of carbon dioxide as the model reaction, these two processes are investigated and results will be presented.

COLL 562

Oxidation resistance interfaces in colloidal core/alloy nanoparticles

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In this presentation we describe a method to prepare oxidation resistant colloidal core/alloy nanoparticles. In this core/alloy system, we investigated the role of precursor deposition quantity and types. Metallic Fe cores were coated with Cr and Ni to form Fe/Cr/Ni, Fe/Ni/Cr and Fe/CrNi nanoparticles. It was observed that the oxidation patterns in this system are highly dependent on composition and deposition sequence. Nucleation and growth was monitored using TEM, and composition and oxidation states were assessed by XRD, and XPS, respectively. Oxidation was the fastest when Cr terminated the interface, whereas those with Ni or CrNi were less prone to oxidation. Oxidation resistance as a function of temperature, oxygen pressure, and environmental conditions will also be discussed. The work reported here opens a new paradigm in the development of stainless nanoparticles. We thank the NSF for support of this project (DMR-1410569).

COLL 563

Elucidating the electronic properties of colloidally-synthesized 2D nanostructures

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Colloidal-based solution syntheses offer a scalable and cost-efficient means of producing nanomaterials in high yield. Increasingly, these functional materials are finding great utility in the development of next-generation technologies across a wide array of fields, including catalysis, sensing, optoelectronics, and biomedicine. While much progress has been made in engineering nanostructured materials in solution, it still remains a substantial challenge to fully characterize their electronic properties. This is largely due to their small dimensions, which usually require the formation of polycrystalline colloidal assemblies or films prior to performing carrier transport measurements. However, such a strategy does not allow for the disentanglement of the intrinsic carrier transport within individual crystals from the transfer between separate colloids. Here we present the synthesis of 2D post-transition metal chalcogenide nanomaterials and a thorough investigation of the inherent electronic properties of individual crystals. First, we detail the development of a novel solution chemistry-based synthetic approach to produce nearly-monodisperse tin(II) sulfide (SnS) nanoribbons and nanosheets. Next, we describe the chemical and structural characterization of these nanomaterials, and how they are processed from solution to fabricate back-gated single-crystalline solid-state devices. Finally, we interrogate their electronic properties by a combination of multi-point contact probe transport measurements and time-resolved terahertz spectroscopy. These studies allow for the direct determination the materials' carrier concentration, carrier mobility, resistivity, and the majority carrier type, which have been rarely reported for individual colloidally-synthesized nanostructures.

COLL 564

SERS nanoprobes based on cyanine dye J-aggregates of gold nanoparticles

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The understanding of interparticle interactions and reactivities of spectroscopically-labeled gold based nanoparticles in the presence of chemical or biological species is important for the exploitation of them as nanoprobes based on localized surface plasmon resonance (LSPR) and surface-enhanced Raman scattering (SERS) spectroscopies. In this presentation, cyanine dye mediated small aggregates of gold and core-shell nanoparticles are investigated as a model system of the plasmonic coupling of the nanoparticles via J-aggregation of cyanine dyes to define the interparticle spatial properties. Examples will focus on the kinetic evolution of LSPR and SERS upon the assembly of gold nanoparticles via π–π interaction of indolenine cyanine dyes to from *J*-Aggregates. Effects of both the structures of the cyanine dye molecules and the size of the gold nanoparticles on the LSPR and SERS characteristics

are examined to assess the interparticle π–π interactions and J-aggregation. The experimental results are also discussed based on insights from theoretical simulations of the plasmonic coupling and the electrical field enhancements around the nanoparticles based on a dimer model.

COLL 565

Dynamic bacterial response to engineered surface features

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The interest of applied scientists and engineers in the area biofilms now supersedes the goal of avoiding their formation: The growth of bacteria on surfaces is important in energy applications and waste remediation. To this end we explore the impact of surface features, in particular nanotopography and mechanics on bacterial behavior in the initial several steps of biofilm formation, including the initial capture of bacterial cell on surfaces and the development of adhesive interactions in the first minutes of surface residence. Studies were done in gentle flow to control the interfacial forces and to make clear the precise instants in which cells became engaged with a surface. First, the near surface behavior of round (S. aureus) and capsular (E. coli) bacteria is compared near brushes of varied density and chemically similar crosslinked gels of varied crosslink density and modulus. It is found that as bacterial progress in flow along these minimally adherent surfaces, they experience intermittent contacts, time off the surface, and re-engagement with the surface that exhibits trends with crosslink density and brush thickness/softness. The round S. aureus bacteria are particularly regular in their intermittent contacts even though they never arrest on PEG surfaces. On surfaces containing cationic features, raising the features a few nanometers facilitates adhesion, presumably due to hydrodynamic features. The subsequent increase in bacterial binding, however, is strongly dependent in its kinetics on the surface distribution and density of positive charge.

COLL 566

Dynamic hydrogels for investigating YAP/TAZ-mediated mechanotransduction

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Much of what we know about cell-surface interactions comes from work on flat and hard materials that do not recapitulate the architecture, mechanics, and biology of tissues and organs. Therefore, the development of dynamic biomaterial tools that more faithfully re-create the microenvironments of physiological and pathological conditions is

essential to addressing human health challenges. Here we present a suite of hyaluronic acid (HA) hydrogel technologies to probe the effects of biophysical properties such as stiffness and viscoelasticity on mesenchymal stem cell (MSC) and liver myofibroblast spreading, cytoskeletal organization, and YAP/TAZ signaling.

HA was modified with methacrylate (Me), norbornene (Nor), β-cyclodextrin (CD), and/or adamantane (Ad) groups. Di-thiol crosslinkers and thiolated RGD were coupled to Me or Nor-modified HA via addition reactions to create elastic, covalently-crosslinked hydrogels. Hydrogels with viscoelastic character were fabricated by introducing Ad-CD dynamic supramolecular interactions. Elastic and viscoelastic hydrogels with variable crosslinking dynamics but equivalent HA content and elastic moduli were produced (E ~ 1-20 kPa). Hydrogels were amenable to *in situ* stiffening through the introduction of additional crosslinks, either by photocrosslinking reactive methacrylates or swelling in thiolated crosslinkers for light-mediated addition reactions with norbornenes.

Viscoelastic hydrogels displayed significant stress relaxation for an applied 10% strain and elevated loss moduli compared to equivalent elastic hydrogels. Hydrogel degradability could also be tuned using peptide crosslinkers susceptible to proteolysis. While MSCs showed similar spreading between elastic and viscoelastic hydrogels, YAP/TAZ nuclear localization was significantly higher on viscoelastic substrates (1.41 ± 0.04; 1.88 ± 0.05 for E ~ 5 kPa). Spatiotemporal tuning of covalent and supramolecular crosslinking was achieved by either altering light exposure during secondary photocrosslinking (covalent) or by incorporating thiolated Ad peptide to increase Ad-CD interactions (supramolecular). In conclusion, we have used exquisite control of hydrogel crosslinking dynamics to illustrate how surface mechanical properties influence YAP/TAZ-mediated mechanosensing.

COLL 567

Glycopolymer interaction with cells and bacteria: From cellular uptake to surface-functional devices

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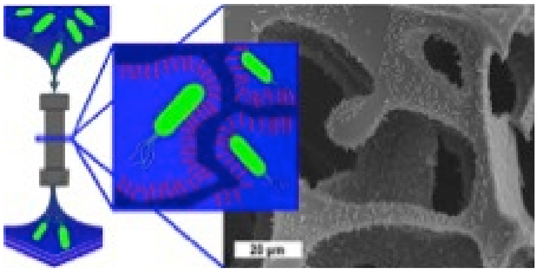
The type of sugar attached at a glycopolymer displays a strong influence on the interaction of the polymer in the biological context. Hence, it influences the uptake of the polymer into cells and can control the interaction of bacteria with a functional surface. This is demonstrated using copolymers composed of *N-iso*-propylacrylamide NiPAm and methacrylamide comonomers, where various carbohydrates are bound in an S-glycosidic fashion. The versatility and control of the reversible addition fragmentation chain transfer (RAFT) polymerization employed to obtain these copolymers not only enables the direct comparison of properties derived from the respective sugar (glucose, galactose, mannose, fructose) but allows for a labelling procedure that is broadly applicable for any kind of polymer obtained by RAFT polymerization that is to be investigated by cell studies. In particular, the fructose-functional polymer was taken up into human breast cancer cells in a significantly enhanced fashion compared to the other glycopolymers. The immobilization of the glycopolymers onto cryogels as highly porous solid support by a grafting from technique using atom transfer radical polymerization resulted in devices that can be used for selective catch and release of bacteria such as Eschericia coli since these interact selectively with mannose.



COLL 568

Living surface of a polyelectrolyte multilayer and its role in cell adhesion

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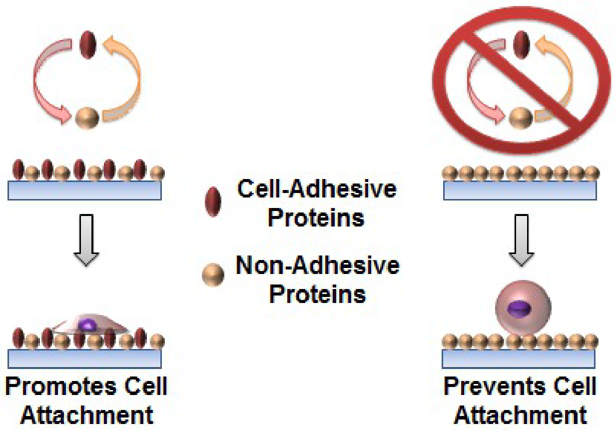
Eukaryotic cellular adhesion to a substrate is critical to surface science. For adhesion to a substrate, cells require the adsorption of extracellular proteins. Polyelectrolyte multilayer thin films made layer by layer allow a high level of control of both surface charge and composition. Fibroblasts grown on multilayers of poly(styrene sulfonate), PSS, and poly(diallyldimethylammonium), PDADMA, exhibit good adhesion with decreasing film thickness until there is a sudden transition towards non-adhesive behavior. Previous studies explain that this is due to the migration of excess positive charge within the bulk of the film that migrates towards the surface, changing its surface charge and surface morphology over time, creating a “living” surface. Precise assays of adsorbed albumin using radiolabeling showed how multilayer surface charge is related to protein adsorption. Previously we reported that at a surface charge density of -0.9 μmoles m^{-2} or greater, the cells do not attach. This study shows the reason why is because at high negative surface charge density, the surface is cytophobic and albumin is irreversibly bound to the surface inhibiting exchange between serum and cell-expressed fibronectin, otherwise seen in the Vroman Effect. A comprehensive view of cell adhesion highlights the central role of robust protein adhesion, which is required before any secondary effects of matrix stiffness on cell fate can come into play.



COLL 569

Self-assembled polymeric nanomaterials for immunomodulation

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The immune system plays an important role in many diseases, and interventions that harness the power and specificity of the immune system have enormous potential to improve human health. Cells of the immune system sense invading pathogens or pathologic issue using a network of receptors that act cooperatively to enhance and shape the type and magnitude of an immune response. Therefore, regulating the delivery of immunologic cues to the cells and pathways of the immune system is fundamental to directing immunological decision-making. Current research in our laboratory is focused on engineering nanostructured polymeric materials for intracellular delivery of immunomodulatory proteins, nucleic acids, and small molecules. This seminar will focus on our recent efforts in developing pH-responsive, endosome-destabilizing “smart” micelles and polymer vesicles for enhanced cytosolic delivery of antigens and immunostimulatory nucleotides. Data demonstrate that polymeric nanoparticles can significantly enhance the activity of several cytosolically-acting immunotherapeutics, which can be exploited to stimulate mucosal T cell responses upon pulmonary immunization and to elicit antitumor innate immune responses. Collectively, these studies demonstrate the capacity of endosomolytic nanocarriers to expand the immunotherapeutic armamentarium by opening access to cytosolic immunoregulatory machinery.

COLL 570

Nitric oxide release from PLGA-PVA nanoparticles to reduce bacteria growth

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Bacteria are capable of adapting to antibiotic treatments through many mechanisms, such as cell membrane thickening. This makes antibiotics unable to cross the membrane, increasing bacterial resistance. Nitric oxide (NO), due to its small non-polar nature, is capable of crossing the thickened cell membranes and acts as an effective antimicrobial. At low concentrations, NO has been used to induce nitrosative stress in bacterial cultures in order to disperse microbial biofilms. Polymer nanoparticles consisting of poly-lactic co glycolic acid and polyvinyl alcohol were formed and the nanoparticle surface was functionalized using thin films to deliver NO. Nanoparticles were modified with an s-nitrosothiol, s-nitrosocysteamine, as the NO delivery molecule. S-nitrosocysteamine was attached to the nanoparticle surface using phosphonic acid monolayers and traditional carbodiimide coupling. Surface reactions were confirmed using Diffuse Reflectance Infrared Fourier Transform and Ultraviolet-Visible spectroscopy. Nanoparticle size and morphology were determined using dynamic light scattering and scanning electron microscopy, respectively. Attachment of s-nitrosocysteamine and subsequent exposure to PBS at 37°C resulted in a release of 37.1 ± 2.8 nmol NO per milligram of nanoparticles. This low concentration of NO was capable of reducing *E. coli* growth by 31.9% based on a bacterial turbidity assay. The synergistic effect of these NO modified nanoparticles with a traditionally prescribed antibiotic, tetracycline, was tested. It was observed that the NO modified nanoparticles increased the effectiveness of tetracycline against *E. coli*, reducing bacterial growth by 88.7%. The functionalized nanoparticles and the released NO were not cytotoxic to mouse embryo fibroblasts in vitro. Thus, this NO delivery vehicle could be used in pharmaceutical applications to combat bacterial infections and reduce the need for antibiotics.

COLL 571

Influence of protein surface coverage on anomalously strong adsorption sites

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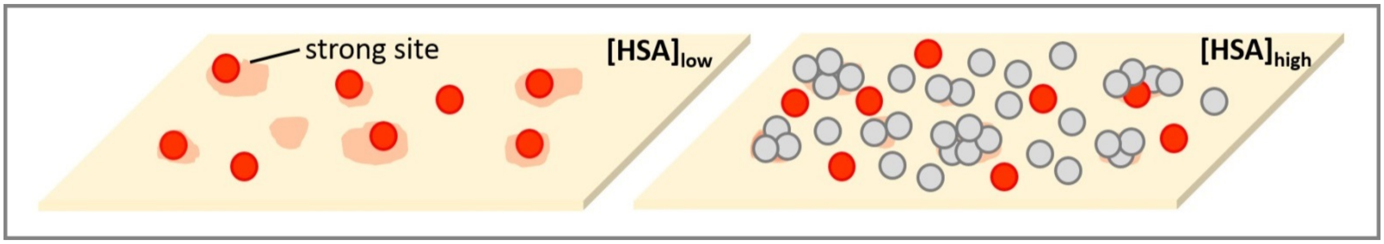
Serum albumin is commonly used as a blocking agent to reduce nonspecific protein adsorption in bioassays and biodevices; however, the details of this process remain poorly understood. Using single molecule techniques, we investigated the dynamics of human serum albumin (HSA) on four model surfaces as a function of protein concentration. By constructing super-resolution maps, identifying anomalously strong adsorption sites, and quantifying surface heterogeneity, we found that the concentration required for site blocking varied dramatically with surface chemistry. When expressed in terms of protein surface coverage, however, a more consistent picture emerged, where a significant fraction of strong sites were passivated at a fractional coverage of 10^{-4}. On fused silica (FS), “non-fouling” functionalized FS and hydrophobically modified FS, a

modest additional site blocking effect continued at higher coverage. However, on amine-functionalized surfaces, the surface heterogeneity exhibited a minimum at a coverage of ~10^{-4}. Using intermolecular Förster resonance energy transfer (FRET), we determined that new anomalous strong sites were created at higher coverage on amine surfaces, and that adsorption to these sites was associated with protein-protein interactions, i.e. surface-induced aggregation.



COLL 572

Role of bio-coronas in the enzymatic oxidation of single-walled carbon nanotubes

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Carbon nanotubes (CNTs) have been proposed for application in multiple fields including composite materials, electrocatalysis, chemical sensors, and biomedicine. However, the large scale implementation of CNT technology has been hampered by reported biological side effects, specifically that of pulmonary toxicity upon inhalation of CNTs, similarly seen with asbestos. We have investigated the use of peroxidase enzymes for safe oxidation, and effective degradation, of CNTs both *in vitro* and *in vivo*. Our research has demonstrated the ability of peroxidase enzymes to oxidize single-walled carbon nanotubes (SWCNTs), multiwalled carbon nanotubes (MWCNTs), and graphene oxide (GO), ultimately showing that introducing structural defects consisting of oxygen functionalities enhances the enzymatic oxidation of CNTs. Here, we investigate the role of bio-coronas in oxidative degradation of SWCNTs catalyzed by neutrophil myeloperoxidase (MPO) using bandgap photoluminescence and Raman spectroscopy. Our results show diameter-dependence at the initial stages of the oxidative degradation of SWCNTs coated with surfactant, protein, DNA, and lipid molecules. In addition to studying semiconducting SWCNT bandgap luminesce (E_{11}) to extract chirality information of a sample, we have also investigated the formation of a separate emission band (E_{11}^{-}) which is induced by the newly formed sp defects on the surface of SWCNTs. Understanding the role of bio-coronas in enzymatic oxidation of SWCNTs is important for design of CNT-based nanocarriers with controlled circulation times and biological compatibility for medical diagnostics and therapeutics.

COLL 573

Evaluating the role of polymer structure on cell uptake and endosomal escape of nanopolyplexes for peptide drug delivery

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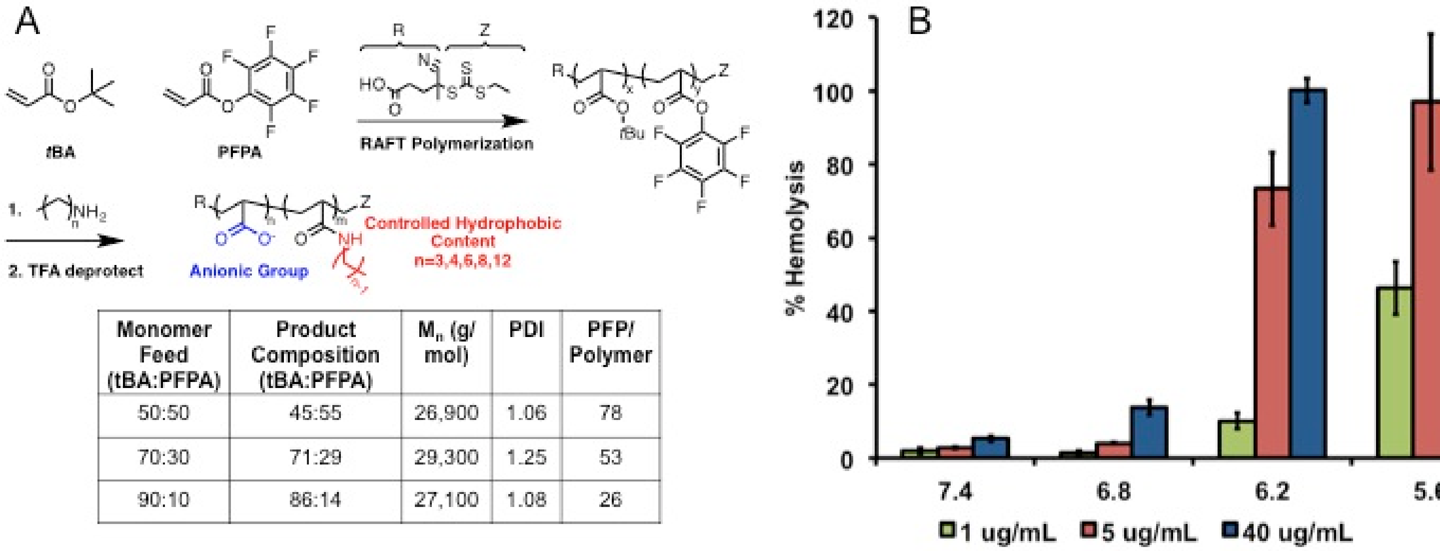
Polymers with pH-selective membrane disrupting capability are a valuable component in nanocarriers for intracellular biologic drug delivery, as endosomal escape is a critical barrier against cytosolic bioactivity. We are interested in the intracellular delivery of therapeutic peptides because they can disrupt intracellular protein-protein interactions with greater specificity than small molecule drugs. However, peptides are extensively trafficked and degraded in the endolysosomal pathway, which limits their cytoplasmic bioavailability*.* We have previously designed electrostatically bound nanopolyplexes of peptides and poly(propylacrylic acid) (PPAA), which effectively facilitated peptide uptake and translocation to the cytoplasm. However, the structural role of the PPAA polymer in facilitating membrane disruption and drug unpackaging is not thoroughly understood, and potentially not optimized. This is because PPAA is challenging and expensive to synthesize, which prohibits systematic variations of its chemical structure, specifically the length of the hydrophobic side chain and the acid:hydrophobe ratio. Herein we present a strategy for synthesizing a series of graft copolymers with controllable, well-defined anionic and hydrophobic content to investigate the relationship between polymer structure and pH-dependent membrane disruption. Copolymers containing fixed ratios of anionic groups and alkyl side chains were synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization as diagrammed in Figure 1A. A red blood cell hemolysis assay was used to model membrane disruption at pH corresponding physiological conditions as well as increasingly acidic pH found in early endosomes (6.8), late lysosomes (6.2), and lysosomes (5.6). A total of 15 polymers were screened to provide complementary understanding on the role of hydrophobe length and density, with Figure 1B showing an example formulation with desirable pH-dependent hemolysis profile. Dynamic light scattering verifies the formation of nanoscale electrostatic complexes suitable for peptide drug delivery. Ongoing studies to assess the functional role of polymer structure on peptide cargo cell uptake and endosome escape will be discussed.



Monomer Feed (tBA:PFPA)	Product Composition (tBA:PFPA)	M_n (g/mol)	PDI	PFP/ Polymer
50:50	45:55	26,900	1.06	78
70:30	71:29	29,300	1.25	53
90:10	86:14	27,100	1.08	26

COLL 574

Interactions between graphene oxide and human serum albumin proteins: Implications for nanoparticle–membrane interactions

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Graphene oxide (GO) is currently attracting much interest because of its potential applications in electrical, biomedical, and environmental engineering. Recent studies have revealed that, once GO nanomaterials enter the human body and are exposed to biological fluids, they will be coated by proteins to result in the formation of protein coronas. In this study, we investigate the adsorption of human serum albumin (HSA) proteins to GO through batch adsorption experiments and quartz crystal microbalance with dissipation monitoring (QCM-D) measurements. These experiments will be conducted under physiological conditions at pH 2 (to simulate gastric fluids) and 7 (to simulate blood serum). A QCM-D sensor is coated by GO and the GO-modified sensor is exposed to a HSA protein solution. Our preliminary QCM-D experiments show that a considerable amount of HSA proteins adsorb on GO at 150 mM NaCl under neutral pH conditions, which is consistent with the results from our batch adsorption experiments. Further experiments will be conducted with a systematic variation in the ionic strength conditions. Finally, based on the results from our adsorption experiments, we will investigate the effects of HSA adsorption on the attachment of GO to supported lipid bilayers in order to understand the interactions of GO with biological membranes in the presence of proteins.

COLL 575

Membrane interaction of PEGylated superparamagnetic nanoparticles

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Iron oxide core-shell nanoparticles are gaining ever increasing interest for separation and imaging in biotechnology and biomedicine, due to supposed low cytotoxicity and their superparamagnetic properties. Hydrophilic polymer-coated nanoparticles are believed to have low nonspecific interactions in biological systems, but much additional work in-vitro and in-vivo is needed to understand their detailed interactions with proteins, membranes and cells. We investigated monodisperse (SD<5%), single-crystalline and superparamagnetic magnetite nanoparticles of different core size and densely grafted with poly(ethylene glycol) (Mw=5kDa), with particular emphasis on their interaction with biological membranes. Membrane interactions will determine nonspecific recognition and uptake by cells. These nanoparticles demonstrated no cytotoxicity and low cell uptake in in-vitro culture of HeLa and HEK cell lines. However, using Quartz Crystal Microbalance (QCM) a strong DLVO-type interaction could be demonstrated with anionic membranes that simulate eukaryote membranes. This interaction was only present in nonphysiological buffer with low ionic strength. Only low, weak and transient binding was observed to zwiterionic phosphocholine membranes. Core size seems to have an effect, with the smallest core size (3.3nm) yielding the strongest interactions while 8nm cores displayed almost no interaction. These results imply that dense polymer grafting and nanoparticle curvature are crucial parameters to control interactions between biomedical core-shell nanoparticles and their biomolecular environment, in particular cell membranes. The interaction between nanoparticle and membrane was furthermore shown to not perturb membrane structure by Differential Scanning Calorimetry (DSC).

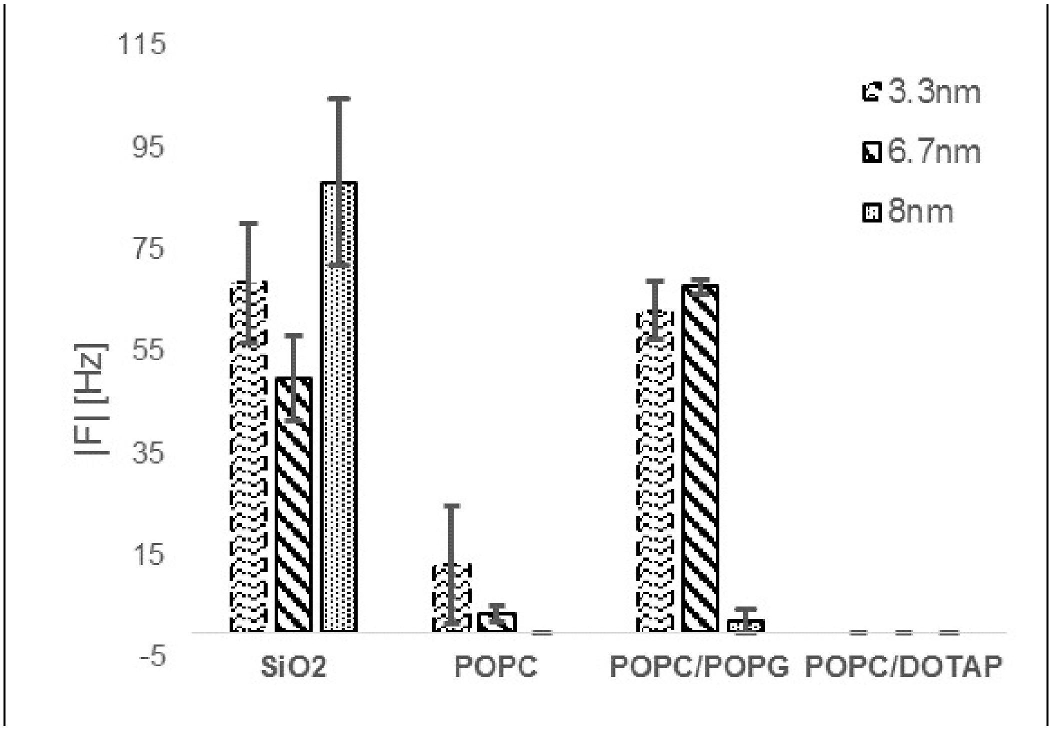

Figure 1: Nanoparticle binding to model membranes measured by QCM for different core size in MQ water

COLL 576

Biohybrid of multi-heme cytochrome and surfaces of Au and graphene: Protein adsorption and electron transfer

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Biohybrid of multi-heme cytochromes and the surfaces of gold or graphene has important applications in biofuel fuel cells (BFCs) and biosensors. Adsorbed protein's orientations and structures affect electron transfer (ET) efficiency. Our lab performed hybrid simulations (molecular dynamics (MD) simulation, free energy computation, and kinetic Monte Carlo (KMC) simulation) as well as visualization tool to predict adsorption and nonequlibrium steady-state ET of a decaheme cytochrome, MtrF onto an different surfaces (Au (111) and graphene) in water. For decaheme Cytochrome MtrF, the most possible adsorption orientation on Au(111) surface is with heme5 group approaching the gold surface, which yields a pathway for ET between the substrate and the aqueous environment. Upon adsorption, protein's secondary structures and central domains (II and IV) bonded with heme-residues remain relatively stable. MtrF surface mobility is dictated by thiol-gold interaction and strong binding between Au(111) and peptide aromatic groups. ET transfer rate across protein heme-network along the solvent-to-surface direction is slightly larger than that of the reverse direction, but lower than that of the solvation structure. In addition, the effects of protein dipole moment, hydration water and surrounding ions on the polarization response of metal surface, such as Au,

in protein adsorption are systematically quantified. On a graphene surface, for the most possible adsortpiotn, terminal-heme is not adjacent to the substrate surface. Multiple MtrF proteins packing on a graphene surface and the electron transfer pathway through proteins were predicted.

COLL 577

Developing phenylenevinylene conjugated oligoelectrolytes for membrane-targeting antimicrobial functions

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The ability of microbes to develop antimicrobial resistance underlies the emergence of drug resistant strains whose infections are increasingly difficult to treat. New molecular systems to treat multidrug resistant strains that do not elicit microbial resistance are thus a research priority attracting significant scientific interest. Compounds whose antimicrobial activity arises from inserting into and disrupting biological membranes offer alternative strategies for the development of antimicrobials and have been the focus of recent studies.

Conjugated oligoelectrolytes (COEs) with phenylenevinylene (PV) repeat units are known to spontaneously intercalate into cell membranes. Here we investigate twelve COEs, including seven structures reported here for the first time, for the relationship between their membrane disrupting properties and structural modifications, including the length of the PV backbone and the presence of either a trimethylammonium or a pyridinium ionic pendant group. Optical characteristics and interactions with cell membranes were determined by using UV-Vis absorption and photoluminescence spectroscopies, and confocal microscopy. Toxicity tests on representative Gram-positive (*Enterococcus faecalis*) and Gram-negative (*Escherichia coli*) bacteria reveal generally greater toxicity to *E. faecalis* than to *E. coli* and indicate that shorter molecules have superior antimicrobial activity. Increased antimicrobial potency was observed in three-ring COEs appended with pyridinium ionic groups but not with COEs with four or five PV repeat units. Studies with mutants having cell envelope modifications indicate a possible charge based interaction with pyridinium-appended compounds. A weakly membrane-intercalating COE with only two PV repeat units allowed us to determine the synthetic limitations as a result of competition between solubility in aqueous media and association with cell membranes. We describe, for the first time, the most membrane disrupting structure achievable within two homologous series of COEs and that around a critical three-ring backbone length, structural modifications have the most effect on antimicrobial activity.

COLL 578

Intracellular processing of nanoparticles: Novel methods to recover intracellular nanomaterials

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Engineered materials in the nanoscale are revolutionizing all areas of life ranging from industry to biomedical applications, thanks to their novel physicochemical properties. As nanotechnology is a field in full expansion, it becomes important to know how an engineered nanomaterial acts when inside a biological system.

Despite numerous studies have elucidated how nanoparticles interact with biological systems and the acute toxicity associated with their exposure, there is now no clear understanding of how many particles enter the cell, and of the possible modifications that the nanoparticles might undergo inside the cellular environment. The intracellular space, in fact, presents a hugely diverse organelle landscape, with different conditions, ranging from the highly acidic lysosomal environment to the highly basic peroxisomal one. In the case of nanomaterials different studies have shown a lysosomal colocalisation of nanoparticles. While some studies have been done in understanding the possible changes in nanomaterial structure once inside these organelles, they are somehow limited to their *in situ* nature. Moreover, in normal *in vitro* scenarios, the dilution effect affects the possibility to fully map slow dissolving materials.

Here we show a series of techniques that we developed to isolate the nanomaterials from their cellular/organelle surrounding. These approaches allow us not only to recover the full nanoparticle population, but also to efficiently calculate the real dose of nanomaterials internalized by the cells. Moreover these approaches allow us also to re-characterize the nanomaterials after cellular processing, therefore determining which modifications the nanoparticles have undergone. Here we report the application of these techniques to different formulations of nanomaterials for studying their intracellular processing.

COLL 579

Direct views of the nano-bio interface

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The interaction of engineered nanomaterials with biological membranes is important for understanding, predicting, and controlling the fate of such materials in biogeochemical environments. Yet, the nano-bio interface is notoriously difficult to access experimentally. Here, we combine nonlinear surface-specific spectroscopy, quartz crystal microbalance mass measurements, interfacial and zeta potential measurements, and scanning probe and fluorescence microscopies to obtain molecular views of structural changes that idealized model membranes undergo upon interaction with several nm-sized nanoparticles exhibiting a variety of surface chemistries. The results indicate the importance of non-contact interactions, Coulombic interactions, and corona formation under certain conditions which we identify.

COLL 580

T-cell-bound nanoparticles providing cell-regulated release of supporting signals

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Adoptive cell therapy (ACT) is a treatment for cancer where autologous tumor-specific T-cells isolated from patients are expanded *ex vivo* and then reinfused to attack metastatic cancer. ACT has led to striking clinical responses in a fraction of patients, but strategies to enhance the persistence of function and expansion of ACT T-cells *in vivo* are sought to increase the proportion of patients experiencing complete responses. We developed a strategy combining nanomedicine with ACT, based on the chemical conjugation of drug-loaded nanoparticles (“backpacks”) to the plasma membrane of live T-cells. To provide a large payload of supporting cytokines, antibodies, or other biologics in these backpacks, we synthesized protein nanoparticles based on the solution crosslinking of a protein payload with copies of itself, forming protein nanogels comprised of up to 90 wt% of the protein drug cargo. Coupling of these protein nanogels to the surfaces of T-cells enabled sustained release of drugs to the carrier T-cell. By using reducible crosslinks to form such nanogels, protein release could be coupled to the activation state-sensitive redox potential at the surface of the cell. T-cells were found to rapidly increase their redox potential following T-cell receptor triggering, leading to accelerated release of drugs from nanogel backpacks on recognition of tumor antigens. ACT T-cells carrying cytokine-loaded nanogels were capable of massive *in vivo* expansion and robust anti-tumor responses, while avoiding side effects commonly observed with systemically-administered immunomodulatory drugs.

COLL 581

Genome editing *in vivo* with the delivery of Cas9 ribonucleoprotein and donor DNA complexed to gold nanoparticles

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CRISPR/Cas9-mediated genome editing has the potential to revolutionize the treatment of genetic diseases and the development of cell-based therapies. However, gene editing with Cas9 is still challenging *in vivo*, because it requires simultaneous and efficient delivery of Cas9, guide RNA, and donor DNA into cells. In this report, we present a gold nanoparticle-based delivery vehicle, termed CRISPR-Gold, which can directly deliver Cas9 protein, guide RNA (gRNA), and donor DNA *in vitro* and *in vivo*

and efficiently induce homology directed repair (HDR). CRISPR-Gold is composed of gold nanoparticles assembled with the Cas9-gRNA ribonucleoprotein (RNP) complex, donor DNA, and an endosomal disruptive polymer. We demonstrate that CRISPR-Gold can induce HDR in human stem cells and mouse primary cells with an efficiency that is significantly higher than conventional transfection methods. Notably, we show that CRISPR-Gold can correct a nonsense mutation in the dystrophin gene that causes Duchenne muscular dystrophy in *mdx* mice, and restore dystrophin protein expression in mouse muscle after a single injection. CRISPR-Gold is the first example of a non-viral delivery vehicle that can induce HDR *in vivo* and has the potential to treat a wide spectrum of genetic diseases.

COLL 582

Active, dissipative, and dynamic behaviors of giant vesicles subject to transvesicular osmotic gradients

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A fundamental consequence of cellular organization of living systems is that the aqueous milieu, bathing the cells, is also compartmentalized. Although water equilibrates readily across the elastic cellular boundary, passive permeation of solutes is strongly hindered. As a result, gradients of concentrations of ions, salt, and soluble biomolecules are readily established across the cellular boundary, producing osmotic activity of water. To deal with any sudden environmental changes in the amount of dissolved molecules in water, free-living cells have evolved complex molecular machinaries and mechanisms (e.g., mechanosensitive channels and compatible solute accumulation), which allows them to dissipate the osmotic stress. But how might primitive cells near the dawn of life on Earth – lacking advanced biochemical or genetic capabilities and composed essentially of simple amphiphiles– have responded to such environmental insults?

Drawing from recent experiments in our labs employing simple models for the cellular chassis (i.e., giant vesicles composed of amphiphilic lipids and polymers), this talk considers how the osmotic activity of water is transduced across cell-like compartments. It highlights how water activity and accompanying dissipation of osmotic energy couples with the compartmental boundary, mechanically remodeling the membrane shape and spatially reorganizing membrane components - both through a well-orchestrated cooperative dynamics. Comparing these processes as elemental events in the homeostatic working of a living cell, these findings support the idea that water is not a mere solvent for life – a blank canvas on which biomolecules become animated – but an active medium that guides organization and dynamics of biomolecules in complex, subtle and essential ways.

The work presented is carried out with co-authors and collaborators including Doug Gettel, Jeremy Sanborn, James Ho C.S., Wan-Chih Su, Bo Liedberg, Padmini Rangamani, Rachel Kraut, Kamila Oglecka, Madhavan Nallani, and Nam-Joon Cho.

COLL 583

Nanoscale spatial regulation of epidermal growth factor receptor signaling

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The epidermal growth factor receptor (EGFR) is a receptor tyrosine kinase that plays a central role in human development, homeostasis, and disease. In the prevailing model of EGFR signal transduction, ligand binding triggers receptor dimerization, transphosphorylation, and the recruitment of signaling adapters that activate downstream pathways such as the MAPK and PI3K/Akt cascades. Subsequent internalization of the activated receptors by clathrin mediated endocytosis is thought to halt signaling. However, accumulating evidence suggests that EGFR signaling may also be regulated spatially on the cell surface. To test a role for spatial regulation of EGFR in the activation of downstream pathways, we took a chemical genetic approach. We engineered full length EGFR with an N-terminal SNAP tag, expressed the receptor at physiological levels, and synthesized a panel of multivalent nucleic acid-based probes modified with benzyl guanine to force the oligomerization of the receptors independent of ligand binding. We found that chemical dimerization of EGFR in the absence of ligand was sufficient to trigger phosphorylation of multiple tyrosines at the receptor C-terminus and recruitment of key adapters suchs as Grb2 and SOS. Surprisingly, chemically dimerized and fully phosphorylated receptors were not capable of activating Ras or Akt. We found that these full length, chemically dimerized, a phosphorylated receptors were deffective in cell-surface spatial reorganization. These data support a role for the ligand-mediated nanoscale reorganization of EGFR in the transduction of extracellular signals to intracellular pathways regulating growth, survival, motility, and differentiation.

COLL 584

Preparation, growth mechanism and uses of one-dimensional nanostructures

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One-dimensional metallic nanoparticles, such as nanowires, nanorods and nanotubes, are receiving considerable attention due to their distinctive optical, mechanical, catalytic and electronic properties. Silver is the metal which exhibits the highest electrical and thermal conductivity, and could serve as interconnects between electronic circuits, catalysts in chemical reactions or substrates for surface-enhanced Raman spectroscopy. In this presentation, I’ll describe a high-resolution transmission electron microscopy (HRTEM) analysis of the creation of silver nanowires in aqueous solution.

Electron microscopy studies and computer simulations suggest that silver nanowires with twinned crystallographic structures form through a coarsening process via an oriented attachment mechanism. An overview of this synthesis procedure and growth mechanism will be presented in detail. Silver nanowires are further used as templates for creation of complex and ordered nanomaterials with tailored and tunable structural, optical and surface properties. This consists of core-shell, nano-peapods, patchy, and hollow nanocomposites that are used in chemical sensing applications, including surface enhanced Raman spectroscopy and surface enhanced fluorescence, as well as plasmonics applications.

COLL 585

Bio-inspired synthetic giant clam system for solar energy applications

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In spite of significant efforts to develop high refractive index materials and nanostructures to enhance solar concentration in photovoltaics and photobioreactors, a major challenge remains in harvesting sunlight in low surface area devices while also reducing photodamage. Previously, we discovered that Tridacnid giant clams are highly efficient “solar transformers”. The clams have evolved a layer of forward-scattering cells, or iridocytes, overlying vertically arranged algae pillars. These iridocytes redirect downwelling light from the surface of the clam evenly to the vertically arranged algae underneath. This redistributed solar flux among the algae cells seems to allow for maximally efficient photosynthesis. We have designed and fabricated synthetic iridocytes via self-assembly of silica nanoparticles (100 - 300 nm in diameter) into micron-sized spheres-of-spheres by way of a water-oil emulsion. Our fabricated structures show similar phase functions (scattered intensity per scattering angle) to natural iridocytes. We also measured the scalar irradiance present underneath layers of synthetic iridocytes and compared it to that observed in wild giant clams. Compared to wild clam iridocytes, the synthetic analogs have a similarly wide angular distribution of light in the forward-scattering direction. We were also able to tune the wavelengths of light back-scattered from our synthetic iridocytes by tuning the size of nanoparticles, allowing us to engineer particles that preferentially forward-scatter photosynthetically efficient light while rejecting less-efficient wavelengths. We have shown that these spherical and hierarchically-ordered particles can redistribute downwelling solar irradiance in a wavelength-tunable manner. We plan to integrate these particles into photobioreactors for biofuel production.

COLL 586

Tunable optical properties of 2D nanowire lattices

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In order to build materials with switchable modality, the ability to form and rapidly reconfigure assemblies of functional particles at predetermined locations is essential. Ordered particle arrays prove particularly valuable because they often amplify the optical and electronic properties of individual particles. We employed AC electric field directed assembly of silica-coated, solid gold nanowires to form reconfigurable 2D lattices. Dielectrophoretic forces concentrated wires between electrode gaps, with their long axis aligned parallel to the field lines. The intrinsic anisotropic geometry of the nanowires enabled strong optical anisotropy arising from electromagnetic resonances. Simulations of the lattice indicated excellent discrimination between polarized light aligned parallel vs. perpendicular to the nanowires' long axes within the lattices. In order to exploit the optical anisotropy of the nanowires, a dual electrode design was developed to realize a reconfigurable polarizer in the near- and mid-IR (NIR, MIR). Two sets of electrodes were used to change the directionality of the lattice in situ. The corresponding optical response was investigated with Fourier Transform Infrared Spectroscopy. In the NIR and MIR, the nanowire lattice was almost transparent to incident light with polarization perpendicular the nanowires in the lattice, but highly reflective for the orthogonal polarization. Our experimental and simulation results were in good agreement, thus demonstrating a reconfigurable optical polarizer with high contrast between orthogonal polarization axes.

COLL 587

Design, synthesis, and characterization of mixed ionic/electronic conducting surface layers adsorbed on metal oxide particles

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Inexpensive grid-scale storage remains a major hurdle slowing the wide-scale adoption of renewable energy by public power utilities. Flow batteries have been proposed as one viable solution. Whereas, the capacity of a traditional battery is limited by its packaging, flow batteries pump redox active fluids from external storage tanks through a flow cell where electrical energy is extracted or stored via reversible redox reactions. In this way, the capacity of the battery becomes scalable independent of the specific redox chemistry and battery geometry. Semi-Solid flow batteries (SSFBs) use “flowable electrodes” for both the anode and cathode materials that consist of a mixture of lithiated metal oxide particles and carbon black particles. Carbon black is added to these dispersions to improve the utilization of lithium as the particles flow by the electrodes. Unfortunately, the presence of this percolated carbon black network leads to

significant increases in viscosity, both at low and high shear rates. In this work, we outline the synthesis of a composite polyelectrolyte/conjugated polymer adsorbed surface layer on cationic silica particles. This layer is formed through the adsorption of poly(styrene sulfonate) onto oppositely charged metal oxide particles and subsequent polymerization of the surface polyelectrolyte with 3,4-ethylenedioxithiophene (EDOT) monomer. The PEDOT:PSS layer is characterized as a function of EDOT:SO_4^{-2} loading using a combination of light scattering, neutron scattering and dielectric spectroscopy to understand the connection between the surface layer's composition, nanostructure and electrical properties.

COLL 588

Hydrogen storage by nanostructured graphene and metal hybrids enhanced with spillover mechanism

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As a fascinating 2-dimentional carbon material, graphene has been decorated with metal nanoparticles to enhance its hydrogen storage performance based on the spillover mechanism. In this work, nickel and its alloys have been used to decorate the surface of graphene. Graphene oxide was fabricated from graphite by improved Hummer method. To form Ni/graphene and Ni/Pd/graphene hybrids, the graphene oxide water dispersion was mixed with nickel chloride (and palladium chloride). $Ni(OH)_2$/graphene and $Ni(OH)_2/Pd(OH)_2$/graphene hybrids were synthesized through hydrothermal treatment, using water as a solvent and HMT as a capping agent. After heat treatment and in situ reduction with hydrogen flow, the nanostructured Ni/graphene and Ni/Pd graphene hybrids were obtained. The nanostructured Ni/Pd/Ag/graphene hybrid was synthesized from graphene oxide in the ethylene glycol solution and metal nitrates using similar reactions. XRD, Raman, SEM, AFM were used to characterize these products. ASAP 2020 was used to test the surface area, pore size, and hydrogen adsorption and desorption capacities.

COLL 589

Graphene origami for 3D functional structures and devices

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Two dimensional nanomaterials, including graphene, boron nitride and transition metal dichalcogenide monolayers, have been extensively studied in recent years, but the vast

majority of previous work utilizes the 2D materials in their original planar geometry to fabricate 2D structures and devices, while more advanced applications such as wearable and foldable electronics requires the fabrication of 3D micro- and nano-structures from those 2D materials. In this work, we use origami based approaches to self-fold graphene into 3D geometries. Briefly, the 2D materials are first patterned into arrays with predefined shape, using photolithography or nanoimprint lithography. Then the surface of graphene can be selectively modified in order to introduce structural and chemical heterogeneity. Once released from the substrate, the patterned graphene can form 3D micro or nanostructures *via* self-folding or by applying an external trigger. The surface modification of monolayer graphene is achieved using mussel-inspired polydopamine coatings, and subsequent grafting of responsive polymers including PNIPAM and polyelectrolytes, which changes the hydrophobicity, mechanical properties and introduce stimuli-responsive properties to the graphene, which is critical for their self-folding. By programming the original graphene building blocks with different size and shapes, the resulting folded graphene micro and nanostructures can have a variety of morphologies and topologies which are very different from conventional carbon nanostructures, such as carbon nanotubes and fullerenes, and have never been observed previously. We anticipate that these structures could provide new capabilities in electronics, optics and medicine.

COLL 590

Self-organization of organic molecules on graphite for photovoltaics

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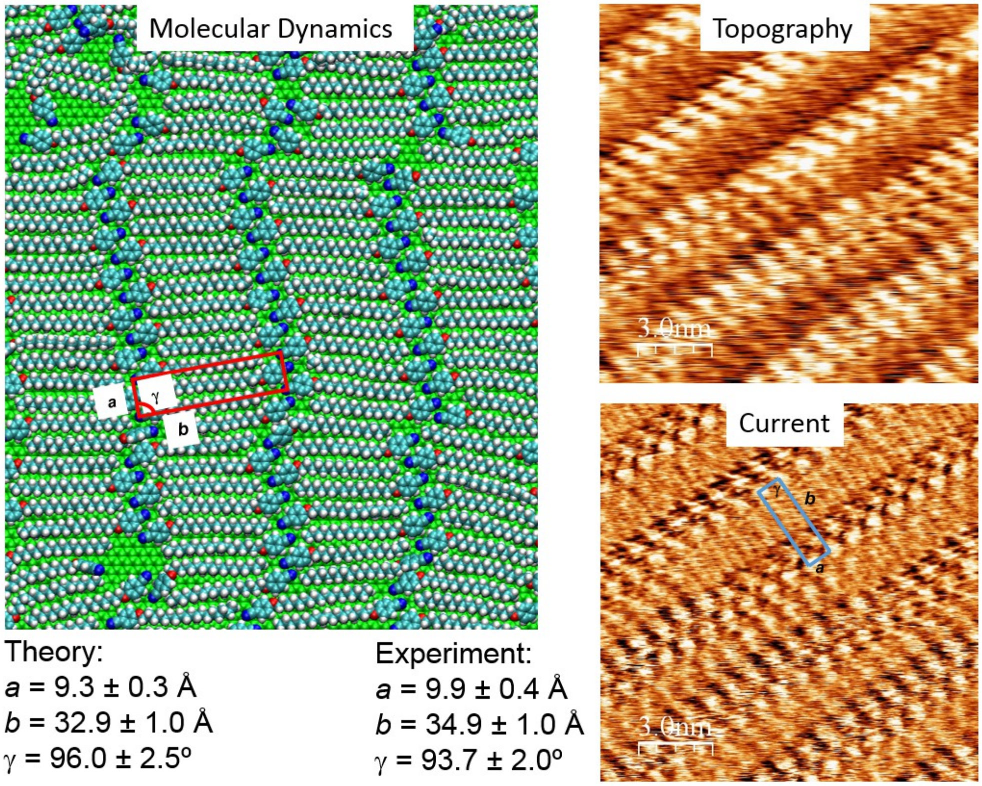
Interfacing highly oriented pyrolytic graphite (HOPG) with supramolecular organic surface assemblies is a promising approach for photovoltaics applications. To provide a basis molecular self-organization, we focus here on alkoxy-benzo-nitrile molecules on HOPG in octanoic acid as solvent is studied using molecular dynamics simulations. The phase transition between different 2D crystal structures is assessed computationally for molecules with different alkane tail lengths. The relationship between intramolecular and supramolecular structure was identified, the objective being to fill the gap between molecular design and supramolecular organization for materials design. Self-assembly pathways for various structures were identified. Yielded structures are compared with images recorded using scanning tunnelling microscopy (STM) to verify the validity of the results. The simulations yielded 2D crystal structures within 1% error compared to experiments. Multiscale techniques are used to accelerate the MD; the efficiency of the simulations allow the extension of the results to other alkane tail lengths, lattice structures and host medium conditions.



Self Assembly of alkoxybenzonitrile in octanoic acid on HOPG: Measurement of the 2D crystal unit cell - Molecular Dynamics simulation and STM characterization.

COLL 591

Designing hierarchical supramolecular interactions for organic 2D crystal assemblies at the liquid-solid interface

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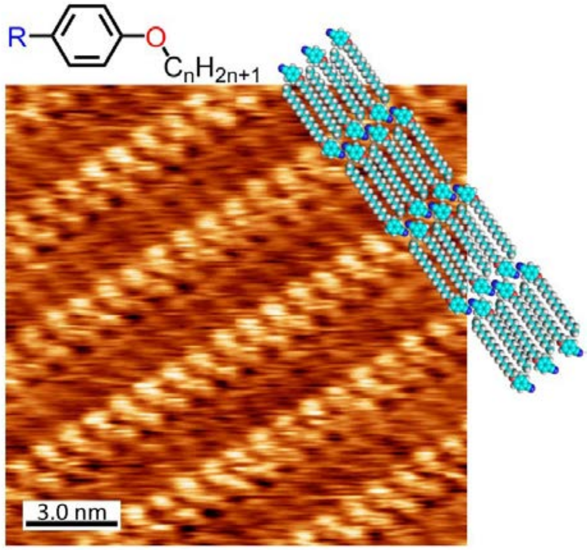
Self-assembly of organic materials into well-defined 2D architectures at surfaces offers many possibilities for applications in electronics, photovoltaics, ion sequestration, and catalysis. Growing interest in these systems has revealed a diverse range of organic assemblies with fascinating properties, but ongoing systematic studies of the hierarchy of supramolecular interactions governing self-assembly is needed. Our collaborative team is addressing this problem with a combined approach involving multiscale molecular dynamic simulations, rational design, synthesis, and surface analysis. Here, we present scanning tunneling microscopy studies to investigate the effects of varying intermolecular interactions on self-assembly at the liquid-solid interface. Functionalized

alkoxybenzenes serve as model molecules for analysis due to their facile synthesis and variety of intermolecular interactions. The contributions of dipole alignment, hydrogen bonding, and van der Waals interactions can be compared by altering alkyl chain length and functionalizing the benzene ring with various polar moieties. At least two phases of assembly have been discovered, one of which is a co-adsorption with the octanoic acid solvent. While hydrogen bonding, van der Waals, and dipole interactions are active in all phases, altering the alkoxybenzene functionalization shifts the relative strengths of the interactions and thus steers the 2D supramolecular architecture.



COLL 592

In situ synthesis of single-molecule electronic components

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Typical studies in single-molecule electronics involve surface self-assembled components first synthesized *ex situ*. Here, we will present results from single molecule measurements made using the scanning tunneling microscope based break-junction (STM-BJ) technique on molecular assemblies created using *in situ* preparations. We will discuss the suitability of surface-binding groups for these measurements, and report the results of *in situ* reactions carried out on self-assembled monolayers. We will show that these reactions can be characterized at the single-molecule level using STM-BJ experiments, as well as in bulk, for example, using surface electrochemistry, contact angle measurements and X-ray photoelectron spectroscopy. Our work shows that these techniques can ultimately be applied to construct surface-based molecular circuitry, considering this as a ‘total synthesis’ problem.

COLL 593 – Withdrawn.

COLL 594

Assembling and aligning multicomponent nanowires with van der Waals forces

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Self-assembly methods create ordered particle arrays by balancing van der Waals, electrostatics, and other forces naturally found within particle systems. While self-assembly is often spontaneous, scalable, and works under ambient conditions, predicting and/or controlling how particles self-assemble requires a strong understanding of particle interactions. Naturally, complex particles (particles with both shape and material anisotropy) have complex particle-particle and particle-substrate interactions. To better understand the assembly behavior of asymmetric particles and to create novel self-assembly methods, we explored the self-assembly behavior of multicomponent nanowires. We examined silica-coated, multi-cored, metallic nanowires (about 4 µm long and 300 nm diameter). Aqueous solutions of these particles quickly sedimented to the substrate forming particle-dense arrays, which were observed through optical microscopy. To examine small changes in interparticle forces within these systems, we varied both (1) particle segment materials and lengths and (2) the surface materials and patterns. We found that differences in van der Waals interactions (even very small differences) influenced assembly greatly, specifically how particles aligned within their assembled structures. Experimental results were compared to results from Monte Carlo simulations.

COLL 595

Self-assembling extracellular matrix proteins as materials for the condensation of silica nanostructures

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Protein based materials offer a unique platform to interface biological systems with a non-native functionality enabling their pervasive use for controlling and monitoring physiological signals inside the body. However, one barrier in the development of these materials is their seamless integration with non-biological components (metals or metal oxides) under ambient conditions. We describe a synthetic strategy derived from diatoms to reprogram extracellular matrix protein binding domains to catalyze the condensation of silicon dioxide nanostructures in water. By varying the amount of

primary amines in solution, it is possible to synthesize up 5.5g/mL silica within ten minutes of reaction time. These data suggest a method to control both the amount and morphology of silicon dioxide using extracellular matrix proteins in a process that can conceivably be used for future electronic applications while simultaneously conserving biocompatibility.

COLL 596

Study of *in vivo* efficacies of antibody dependent cell cytotoxicity of antibody functionalized gold nanoparticles

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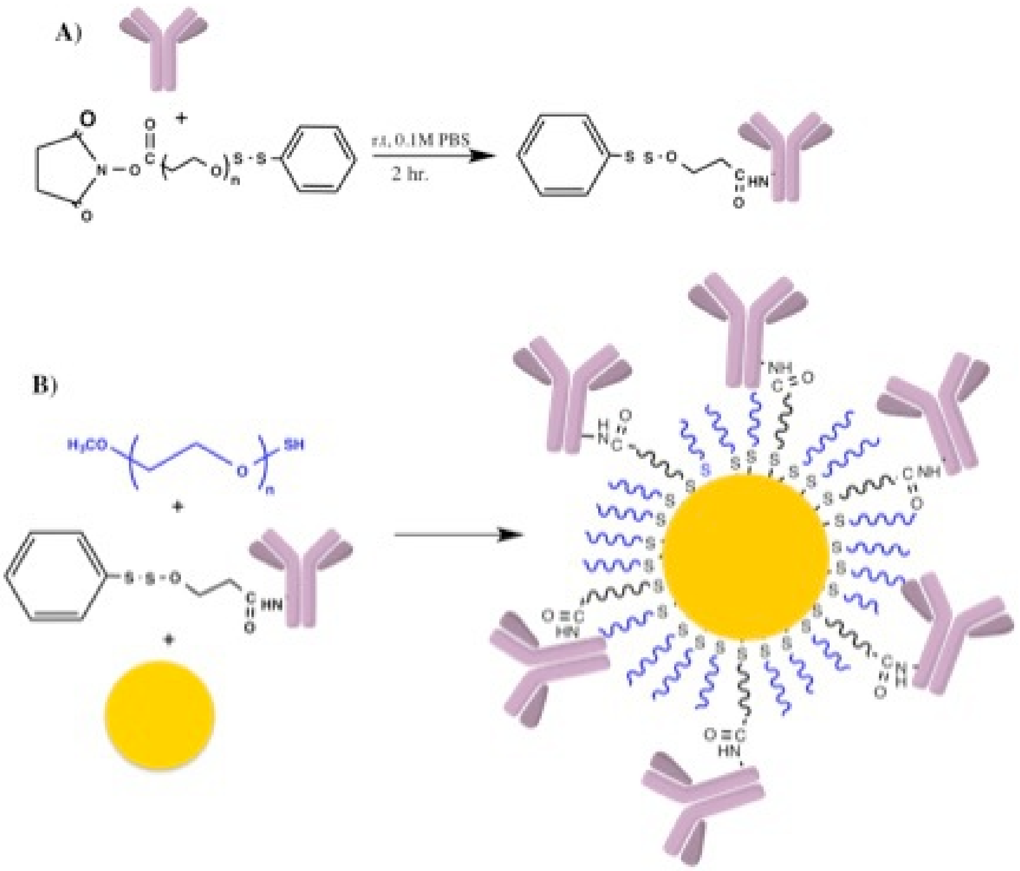
Antibody-functionalized nanoparticles are considered ideal vectors to specifically deliver therapeutics to tumor tissues. A significant amount of work is needed to understand the potential of antibody-targeted nanoparticles for cancer treatment. Antibody-dependent cellular cytotoxicity (ADCC) is a major cytolytic mechanism responsible for tumor regression under *in vivo* conditions. An antibody's ADCC activity, biodistribution, and pharmacokinetic properties can be altered upon covalent conjugation of the antibody onto nanoparticle surface. We prepared cetuximab-, rituximab-, trastuzumab- and panitumumab-functionalized PEGylated gold nanoparticles. Antibodies, PEGylated antibodies and antibody-functionalized gold nanoparticles were evaluated for their ADCC activity in epidermal growth factor receptor (EGFR)-expressing tumor cell lines *in vitro* and in athymic nude mice bearing tumor xenografts. Antibodies, PEGylated antibodies and their corresponding nanoparticles maintained their ADCC activities *in vitro*. Cetuximab treatment of EGFR-expressing H1975 tumor xenografts showed significant tumor regression due to the ADCC activity of the antibody *in vivo*. However, antibody-functionalized PEGylated nanoparticles are unable to suppress tumor growth *in vivo*, suggesting that immobilizing antibodies onto a gold nanoparticle surface decreases the ability of the antibody to prompt an ADCC response.



COLL 597

Dimensional control of orthogonal chemical interfaces using polymerizable amphiphiles

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Nanoscale control over the surface chemistry of layered materials is a growing need for fields ranging from electronics to biology. In many applications, noncovalently adsorbed ligands must simultaneously control interactions with a nonpolar substrate and a polar solvent, raising substantial challenges in terms of interfacial ligand chemistry. However, biology routinely addresses a related challenge in the context of the lipid bilayer. While conventional standing phases of phospholipids would not confer the spatially ordered interactions with the substrate needed for materials applications, we achieve the required nanoscale chemical control by instead assembling a sitting phase of polymerizable phospholipids, in which the two alkyl chains extend along the surface and the two ionizable functionalities (a phosphate and an amine) sit adjacent to the substrate and project into the solvent, respectively. Impacts of the chemically orthogonal interfacial patterning strategy on wetting and solute interactions will be discussed. For instance, we find that pKa shifts common at hydrophobic interfaces (such as graphene) are observed for the phosphate but not for the amine, suggesting that the phospholipid is an atom-efficient scaffold for creating chemically orthogonal patterns at the few-nm scale on layered materials.

COLL 598

Thermophilic ferritin: A versatile nanocontainer for the encapsulation of nanoparticles and other useful cargo

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Thermophilic ferritin (tF) is a unique nano-sized container whose multi-subunit cage structure can be disassembled and reassembled by changing solution ionic strength. Its native function is the oxidation and storage of iron as a hydrated ferric hydroxide nanoparticle. The iron can be removed and replaced with useful cargo, including other nanoparticles and proteins, granting the cargo enhanced biocompatibility, targeted delivery potential, and greater ease of functionalization. The encapsulation of gold nanoparticles by tF is particularly noteworthy, as tF maintains its native overall diameter, secondary structure, subunit stoichiometry, catalytic activity, and thermal stability after encapsulation is complete. The nanoparticle gains enhanced salt stability compared to bare particles, demonstrating the synergy of this encapsulation product. Using biophysical and materials characterization techniques, we have explored how nanoparticle size and surface ligand, as well as mutations to the protein, affect encapsulation. We are currently exploring the use of these non-native cargo–ferritin conjugates in nanoparticle templating, catalysis, and medicine.

COLL 599

Optimizing the bio-nano interface via a multi-coordinating polymer coating

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Nanomaterials, such as quantum dots, exhibit several unique photo and physical properties that are attractive for designing new bioanalytical tools. Their effective integration in biomedicine strongly benefits from tunable surface chemistry, compact size, and robust colloidal stability. Here, we present a set of multifunctional and multi-coordinating polymers as ligands for functionalizing QDs and metallic nanostructures and promote their integration within biology. The ligand design relies on the simultaneous introduction of several anchoring groups, hydrophilic segments and reactive groups along a same polymer chain, via a one-step reaction. Ligation with these polymers provides nanocrystals that are colloidally stable over a broad range of conditions. Furthermore, the tunable reactive groups in the ligands facilitate biorthogonal conjugation of the nanocrystals with distinct target molecules. We will detail the design, preparation, and characterization of such nanoparticles and their

conjugates. We will also describe the use of such conjugates in sensor design and for probing cellular processes.

COLL 600

Toward single-molecule biophysical surface-enhanced Raman spectroscopy with nanostar-liposomes bioconjugates

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Single-molecule Surface-Enhanced Raman Spectroscopy (SERS) has traditionally relied on inserting probe molecules into highly enhancing “hot spots” (<10nm gap junctions) between gold and/or silver particles. Although, this strategy leads to single molecule detection, the interactions between the probe molecule and enhancing medium often results in denaturation and inactivation of the probe molecule. To address this issue, we have constructed novel SERS substrates containing liposomes, which offer an ideal scaffold since encapsulated probe molecules retain biological and chemical activity. We present single nanoparticle SERS studies of a new construct in which probe molecules are encapsulated into surface-tethered liposomes that are conjugated to gold nanostars. The gold surface and gold nanostars offer sufficient enhancement to detect single molecules, while the core of the liposome provide an adjustable aqueous environment.

COLL 601

Bio-orthogonal coupling on hydrophilic quantum dots

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We combine the design of a set of aldehyde- or azide-appended LA-PEG (LA-PEG-CHO and LA-PEG-N_3) coordinating ligands with a mild photoligation strategy to prepare QDs with control over the fraction of intact CHO or azide groups per nanocrystal. The extremely efficient hydrazone coupling ligation is applied to react CHO-QDs with hydrozinopyridine, producing a hydrazone chromophore with a well-defined absorption signature at 350 nm. We exploit this signature to accurately measure the number of ligands per QD for several samples, when the fraction of LA-PEG-CHO per nanocrystal is varied. Additionally, we show that when the two bio-orthogonal functionalities (aldehyde and azide) are combined on the same QD platform, the nanocrystals can be “bio-orthogonally” reacted with two distinct targets and with great specificity. This strategy can be applied to other nanoparticles such as those of metals and magnetic cores, and to assemble various multifunctional bio-conjugates with great utility in biology.

COLL 602

Increased oxidation in lipid membranes from Cu^{2+} bound to phosphatidylethanolamine

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We have found that Cu^{2+} binds bivalently to phosphatidylethanolamine (PE), which is the second most abundant lipid in mammalian cells. The apparent dissociation constant of the complex at physiological pH is approximately 2 μM, and does not depend on the concentration of PE in the membrane. By contrast, at pH 10, PE lipids now have a negative charge, and increasing PE content tightens the apparent binding constant. Additionally, the oxidation of double bonds in PE-containing bilayers can be monitored in the presence of Cu^{2+}. At pH 7.4, it was found that the oxidation rate is significantly faster for bilayers containing PE than for pure phosphatidylcholine (PC) bilayers upon exposure to Cu^{2+} and hydrogen peroxide. The rate of oxidation increases linearly with increasing PE content. These results provide a link to the high level of lipid oxidation found in neurodegenerative diseases and autism, where the Cu^{2+} concentration in the body is elevated.

COLL 603

Nanocomposites hydroxyapatite: Polysaccharide hydrogels for bone regeneration

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The bone trauma are common events, which are resolved often through two surgeries. In the first step metallic prosthetic parts are implanted in the body followed by a long recovery. Then, a second surgery is required for the metallic prosthetic removal. Our study aims to show a proof of concept that alternative composite materials can be used in bone trauma surgery. Antimicrobial hydrogels of polysaccharides and polyamines crosslinked by epichlorohydrin have been previously reported to have antibacterial properties. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is a common material which promotes the osteogenesis. The osteoblast cells are growing on the surface of the hydroxyapatite, which makes this material very useful for bone tissue engineering and especially for bone regeneration.

Here we report the preparation of new antimicrobial nanocomposites between polysaccharides based hydrogels and hydroxyapatite. Hydrogels comprised of the

polysaccharide dextran and the polyamine polyethylene imine were prepared using a previously described method. Dextran was first crosslinked with epichlorohydrin and the progress of the reaction followed for the disappearance of the crosslinker. Polyethylene imine was then added to complete the gelation process. The hydroxyapatite (HA) samples which were incorporated in the hydrogel were prepared using the sol-gel method or a slurry method. The crystallite size of the hydroxyapatite were determined to be between 7.9 nm and 15.6 nm. The surface area of the sample prepared through the slurry method was higher than for the sample prepared through the sol-gel method. The polarity of the HA samples was determined by x potential measurements. Different concentrations of HA were incorporated in the polysaccharides based hydrogels. The thermal stability of those composites was investigated through thermal analysis. Their structure was explored by X-Ray diffraction and FT-IR spectroscopy. The mechanical properties of those pristine and nanocomposite gels was investigated using oscillatory rotational rheometry. Stress sweep and time sweep measurements assessed the rheology of the hydrogels and subsequently the influence of hydroxyapatite on the overall mechanical properties of the composite materials.