COLL 1

Vibrationally mediated chemistry at the gas-surface interface

Arthur L Utz(1)*, arthur.utz@tufts.edu, 62 Talbot Ave, Medford MA 02155, United States ; Victoria Campbell*(1)*; Deno DelSesto*(1)*; Nan Chen*(1)*; Eric Peterson*(1)*; Eric Dombrowski*(1)*; Yongli Huang*(1)*. (1) Department of Chemistry, Tufts University, Medford MA 02155, United States*

Vibrationally energized polyatomic molecules are abundant under thermal processing conditions, and vibrational energy can play an important role in activating reactions at the gas-surface interface. Beam-surface scattering studies performed with laser-excited and internal state selected molecules provide insight into how vibrational excitation of the molecule and surface activate reaction. Observations of mode- and bond-selective reactivity reveal the extent of vibrational energy redistribution prior to reaction. Surface-temperature-dependent studies using internal-state-selected gas-phase reagents show that surface vibrations can play a dramatic role in promoting methane activation on Ni. The presentation will highlight recent results from our lab that explore the role of surface excitation and of vibrationally hot precursor molecules in promoting reaction at the gas-surface interface.

COLL 2

Electronically nonadiabatic chemical dynamics at metal surfaces

Alec M. Wodtke(1)(2)*, alec.wodtke@mpibpc.mpg.de, Fassberg 11, Goettingen Lower Saxony 37077, Germany . (1) Department of Dynamics at Surfaces, Max Planck Institute for Biophysical Chemistry, Goettingen Lower Saxony 37077, Germany (2) Department of Physical Chemistry, Georg August University of Goettingen, Goettingen Lower Saxony 37077, Germany*

Developing a predictive understanding of surface chemistry based on the first principles of Physics must include possible breakdown of the Born-Oppenheimer approximation. Reaching this goal means progressing beyond what is now possible for gas-phase bimolecular reactive encounters. This represents one of the most important challenges to current research in chemical physics; since, to the extent that the Born-Oppenheimer approximation breaks down, we have no predictive theory of surface chemistry. This means we are working in an exciting environment where new phenomena might be discovered through experiments and inspire new theoretical developments. This lecture will present recent experimental results that demonstrate the importance of Born-Oppenheimer breakdown. I will emphasize quantitative measurement that can be directly compared to dynamical theories that go beyond the Born-Oppenheimer Approximation.

White et al., *Nature*, 2005. **433**: 503; Huang et al., *Science*, 2000. **290**: 111; Cooper et al., *Chem. Sci.*, 2010. **1**: 55; Shenvi et al., *Science*, 2009. **326**: 829; Larue et al., *Phys.Chem.Chem.Phys.,* 2011. **13**:97.

COLL 3

Ethanol electrooxidation on Pt(111)-supported SnOx: A surface science approach to study the metal oxide-metal interaction in electrocatalysis

Wei-Ping Zhou(1)*, wpzhou@bnl.gov, Bldg 555 Brookhaven Ave, Upton New York, United States ; Stephanus Axnanda*(1)*; Michael G White*(1)*; Radoslav R. Adzic*(1)*. (1) Chemistry Department, Brookhaven National Laboratory, Upton New York 11973, United States*

Recent studies demonstrated that the SnOx promoted Pt electrocatalysts have high performance in ethanol electrooxidation and may have the potential for use in direct ethanol fuel cells. However, the nature of the active phase in SnOx/Pt nanocatalysts still remains elusive and their performance is highly dependent on the preparation methods and activation conditions. To examine the activity – SnOx-Pt interaction correlation, we used a surface science approach to prepare and characterize the model catalyst system consisting of SnOx nanoislands grown on a Pt(111) electrode. The SnOx/Pt(111) model systems were characterized using XPS and LEIS and then the ethanol oxidation reaction (EOR) was studied under electrochemical conditions without exposure to air. Correlating the surface properties of the SnOx/Pt(111) electrode with the observed EOR activity will provide critical information for improving the understanding of SnOx-Pt interaction in the EOR reaction. A detailed discussion of these findings will be presented at the meeting.

COLL 4

Using nanoscale amorphous solid films to create and study deeply supercooled liquids

Bruce D Kay(1)*, bruce.kay@pnl.gov, PO Box 999 MSN K8-88, Richland Washington 99352, United States ; Scott Smith*(1)*. (1) Chemical and Materials Sciences Division, Pacific Northwest National Laboratory, Richland Washington 99352, United States*

Molecular beam vapor deposition on cryogenic substrates is known to produce amorphous solid films. When heated above their glass transition these films transform into deeply supercooled liquids. These nanoscale liquid films can be used to study kinetic processes such as diffusion, isotope exchange, and crystallization in unprecedented detail. This talk will highlight our recent advances in this area with a focus on hydrogen-bonded liquids such as water and alcohols.

This work was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences. The research was performed using EMSL, a national scientific user facility sponsored by

DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated by Battelle, operated for the U.S. DOE under Contract DE-AC05-76RL01830.

COLL 5

Shock compression dynamics with molecular resolution

Dana D Dlott[(1)]*, dlott@illinois.edu, Box 01-6 CLSL, Urbana IL, United States ; Christopher M Berg*[(1)]*; Alexei Lagutchev*[(1)]*. (1) School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana IL 61801, United States*

Detonation of energetic materials takes place within a traveling interfacial structure called the detonation front. The detonation front travels over a typical molecule in 0.1 ps. Chemical reaction initiation occurs in a nanometer layer near the front and ignition in a micrometer layer behind the front. These processes are studied in real time using a tabletop apparatus with a femtosecond laser to study initiation and a nanosecond laser to study ignition.

COLL 6

Free Radical Polymerization at the Vapor/Ionic Liquid Interface

Malancha Gupta[(1)]*, malanchg@usc.edu, 925 Bloom Walk, HED 216, Los Angeles CA 90089-1211, United States . (1)*

This talk will describe vapor-phase free radical polymerization of hydrophilic and hydrophobic monomers in the presence of ionic liquids (ILs). We will explain how the polymerization kinetics at the vapor/IL interface can be varied to produce several novel polymeric structures such as films and skins. We will discuss the effect of key parameters such as deposition time, temperature, and monomer solubility. Molecular weight data and thickness measurements will be presented to show the morphology and conformality of the resulting skins and films produced at the vapor/IL interface.

COLL 7

Measuring Environmental Transformation of Multi-walled Carbon Nanotubes using Integrated Thermal Analysis and Related Hyphenated Techniques

Endalkachew Sahle-Demessie[(1)]*, sahle-demessie.endalkachew@epa.gov, Nationla Risk Management Research Lab, 26 W. Martin Luther King Dr,, Cincinnati OH 45268, United States ; Amy Zhao*[(1)]*; Andrew W. Salamon*[(2)]*; Stephen Harrmon*[(1)]*. (1) Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati OH 45040, United States (2) Perkin Elmer Inc., 710 Bridgeport Ave. Shelton, CT 06484, United States*

With the increase in the commercialization of exploiting engineered nanomaterials increases, the future of nanotechnology rests upon approaches to making new, useful nanomaterials and testing them in complex systems. Unlike the mature analytical market for bulk and molecular matter, the current advance from discovery to application in nanotechnology is constrained due to the lack of quick, rapid, reliable and low cost technique. Thermogravimetric analysis (TGA) has demonstrated to be an effective technique to confirm dimensions and homogeneity of multiwalled carbon nanotubes (MWCNT) including the presence of trace metal catalyst or other contaminates, and structural defects. We have also demonstrated the use of TGA to study effects of exposing MWCNT to oxidative atmosphere that causes environmental aging which increases defect sites, reduces their structural stability and increase chemical functionalization. The results were compared with other characterization techniques such as spectroscopic, X-ray diffraction and transmission electron spectroscopic. TGA-GC-MS emitted gas analysis has also been used to investigate the adsorption and interaction of organic molecules with nanoparticles in the environments.

COLL 8

Aggregation and adsorption of silver nanoparticles: Effects of surface modification by humic substances

Olha Furman(1)*, Olha_Furman@baylor.edu, One Bear Place #97354, Waco Texas 76798, United States ; Boris Lau*(1)*; Sascha Usenko*(2)*. (1) Department of Geology, Baylor University, Waco Texas 76798, United States (2) Department of Environmental Science and Aquatic Systems Research, Baylor University, Waco Texas 76798, United States*

The behavior of engineered nanoparticles, many of which serve as contaminant scavengers, is an important topic for environmental health and safety. The impacts of humic acid (HA) and fulvic acid (FA) on the aggregation and adsorption kinetics of 50 nm citrate-stabilized silver nanoparticles (AgNPs) onto silica surfaces were investigated using dynamic light scattering and a quartz crystal microbalance. At pH 8 and 1mM $Ca(NO_3)_2$, both acids (5 mg/L DOC) reduced the aggregation rate, with HA showing greater stabilization than FA. The rate and extent of uncoated AgNP adsorption changed due to substrate modifications. After substrates were coated with HA and FA, the adsorbed mass decreased by ~35% and ~60% respectively. There was no observable adsorption when AgNPs and substrate were both coated with HA. However, FA-coated AgNPs adsorbed significantly onto FA-coated substrate. These results suggested that HA and FA exert different influences on the fate and transport of AgNPs.

COLL 9

Adsorption of Copper Species on Commercially Available Functionalized Multiwall Carbon Nanotubes – Regeneration and pH effect

Shirley Rosenzweig(1)*, shrosenzweig@fuse.net, 5090 Westsand Ct, West Chester OH 45069, United States ; George Sorial*(1)*; E. Sahle-Demessie*(2)*. (1) Environmental Engineering Department, Cincinnati, University of Cincinnati, Cincinnati OH 45221-0071, United States (2) Office of Research and Development, NRMRL, U.S. Environmental Protection Agency, Cincinnati OH 45268, United States*

MWCNTs can be purchased with hydroxyl (OH-) or carboxyl groups (COOH-) attached to the surface. In aggregate state the network forces within the bundles is stronger on acid-group. Characterization techniques have measured more oxygen groups on alcohol groups. The method used to add surface oxygen groups to MWCNT is usually not disclosed by manufacturers. It is assumed to be preferentially plasma process, which is faster and more efficient than chemical functionalization. FTIR is carefully performed to quantitatively evaluate the different oxygen groups present, as well as impurities and copper species. XPS is used to compare results. Deprotonation techniques are used to “break-open” network forces within the bundles. By removing van der Waals forces from the alcohol and acid network, we expose more adsorption sites for metallic species such as copper. This method is expected to accelerate the adsorption process. FTIR is used to measure the different amount of oxygen groups exposed. MWCNTs are washed with different base solutions in the deprotonation process. TEM and Zeta potential techniques are used to confirm the change of aggregate state. Isotherm and kinetic experiments are performed to compare results. Copper chemistry in water is controlled by changing pH. MWCNTs are expensive and their regeneration for multiple uses of adsorption is highly recommended. There are more copper ions than copper solids species at low pHs in water. Therefore, by washing copper-adsorbed-MWCNTs with acids, it will dissolve copper solid species back to copper ionic state, “cleaning” the MWCNTs and enhancing them. AAS, FTIR and ICP are used to evaluate traces of copper and other impurities. Adsorption mechanisms of copper ions versus copper solid species on MWCNTs are also evaluated.

COLL 10

Aggregation, deposition and transport of CeO_2 nanoparticles in a sand filtration process at water treatment facilities

Zhen Li(1)*, liz2@mail.uc.edu, 2600 Clifton Ave., Baldwin Hall 765, Cincinnati OH 45219, United States ; E Sahle-Demessie*(2)*; Ashraf Aly Hassan*(2)*; George A Sorial*(1)*. (1) Environmental Engineering Program,School of Energy, Environmental, Biological, & Medical Engineering, University of Cincinnati, cincinnati OH 45220, United States (2) Office of Research and Development, NRMRL, U.S. Environmental Protection Agency, Cincinnati OH 45268, United States*

The increased production and use of manufactured nanoparticles presents concerns for environmental and human health. When CeO_2 nanoparticles (NPs) are increasingly used into a wide range of products such as coatings, ultraviolet blockers, additives and catalysts, questions have been raised that if they can be removed by traditional water treatment procedure once they are released into the water system. In this study, the

aggregation and stability of CeO2 NPs was studied in a water matrix which was provided by a drinking water treatment plant. The water was collected prior to the sand filtration system and was characterized by measuring the pH, total organic carbon, conductivity, turbidity, phosphate, sulfate and nitrate. The stability of the CeO_2 NPs was investigated by measuring their particle size distribution with time, and the EMP/Zeta potential in the water. Column studies were conducted using the sand used in the sand filtration system. Breakthrough results were obtained to investigate the deposition of CeO_2 NPs onto the sand surface and their transport. The results were compared with the breakthrough experiments using synthesized water matrices (which have simpler water chemistry) and clean sand. This study provides important insights to the interaction of NPs and the traditional sand used in the filtration system in water treatment plants.

COLL 11

Retention of nano-particles in sand filters at water treatment plant using CFD simulations

Ashraf Aly Hassan(1)*, hassan.ashraf@epamail.epa.gov, 26 W. Martin Luther King Drive, Cincinnati OH 45268, United States ; Zhen Li*(2)*; Endalkachew A Sahle-Demessie*(1)*; George Sorial*(2)*. (1) Office of Research and Development, NRMRL, U.S. Environmental Protection Agency, Cincinnati OH 45268, United States (2) School of Energy, Environmental, Biological, and Medical Engineering, Environmental Engineering Program, University of Cincinnati, Cincinnati OH 45268, United States*

In aquatic environment fate and transport of nano-particles (NP) depend on various factors; most important the water chemistry. Several metal oxide NPs were studied in sand columns, under actual operating conditions, simulating a water treatment plant in Cincinnati, OH. We used mathematical models to validate and simulate the experimental effluent stream profile. Partial differential equations were solved simultaneously using Mathematica®. The experimental data were accurately simulated using a different numerical model that solves conservation of mass and momentum, and the interaction and deposition of nano-particle with bed material. The mathematical model is based on a specific area-to-volume ratio for the porous media. The model predications were performed using computational fluid dynamic (CFD) software, Fluent®. The simulations predicted the maximum concentration of NPs that could be retained within the column in addition to buffer capacity of the maximum NP spike concentration.

COLL 12

Design of *in vivo* assays for probing of physiochemical dependent biocompatibility and toxicity of naomaterials

X. Nancy Xu(1)*, xhxu@odu.edu, 4541 Hampton Blvd., Alfreind Chemistry Bldg., Norfolk VA 23529, United States ; Kerry J. Lee*(1)*; Lauren M. Browning*(1)*; Prakash D.*

Nallathamby[(1)]; Tao Huang[(1)]. (1) Department of Chemistry and Biochemistry, Old Dominion University, Norfolk VA 23529, United States

Nanomaterials possess distinctive physiochemical properties, which promise their unique functions and applications. For instance, their tiny sizes enable them to penetrate into living organisms. Their larger surface areas permit effective surface modification with desired molecules for sensing and for effective treatments. Notably, their distinctive larger surface areas also make them highly active, which may cause adverse effects on living organisms. Therefore, it is important to develop high-throughput inexpensive in vivo assays for effective screening of their biocompatibility and toxicity. We have synthesized and characterized a mini-library of stable and purified nanomaterials and used them as a model system. We have developed new imaging tools to track and characterize their transport and potential toxic effects on embryonic development at single nanoparticle resolution in real time. Our studies show that early development zebrafish embryos can serve as effective in vivo assays for screening physiochemical dependent biocompatibility and toxicity of nanomaterails.

COLL 13

Understanding the microbial communities that influence nanoparticle fate and transport via polymer coating degradation

***Teresa L. Kirschling**(1)(2), tlphilli@andrew.cmu.edu, 5000 Forbes Avenue, Pittsburgh PA, United States ; Patricia L. Golas(3)(2); Kelvin B. Gregory(4)(2); Gregory V. Lowry(4)(2); Robert D. Tilton(1)(5)(2). (1) Department of Chemical Engineering, Carnegie Mellon University, United States (2) Center for the Environmental Implications of Nanotechnology, United States (3) Department of Chemistry, Carnegie Mellon University, United States (4) Department of Civil and Environmental Engineering, Carnegie Mellon University, United States (5) Department of Biomedical Engineering, Carnegie Mellon University, United States*

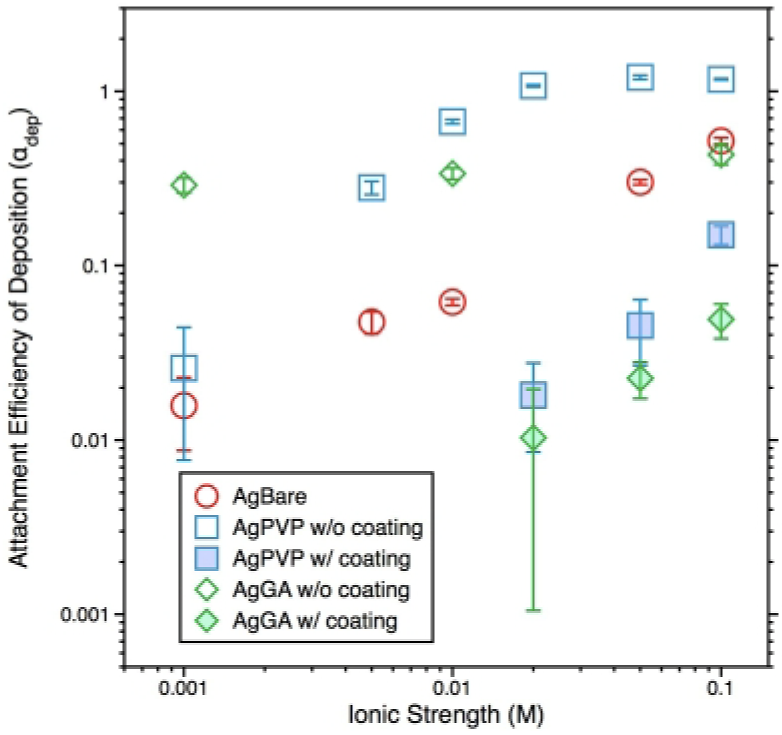
The fate of polymeric surface coatings is expected to dictate the long-term fate, partitioning and ecological impact of engineered nanoparticles in the environment. Microorganisms likely will mediate polymer coating degradation, but direct microbiological removal of nanoparticle coatings has not been demonstrated. In this study, we synthesized cross-linked bottle brush copolymers consisting of 2000 molecular weight polyethylene oxide (PEO) arms emanating from dense polystyrene-like core. These copolymers serve as model nanoparticles with a covalently grafted polymer coating for a study of direct coating degradation by microbes. A mixed PEO degrading culture was enriched from urban river water. Growth of this culture on the PEO copolymer nanoparticles as the sole carbon source indicates that the PEO coating is bioavailable. Microbial processing resulted in particle aggregation indicating that microbial degradation of polymeric coatings may be an important transformation mechanism. The structure of microbial communities which degrade nanoparticle coatings will also be discussed.

COLL 14

Polymeric coatings on nanoparticles prevent auto-aggregation but enhance attachment to un-coated surfaces

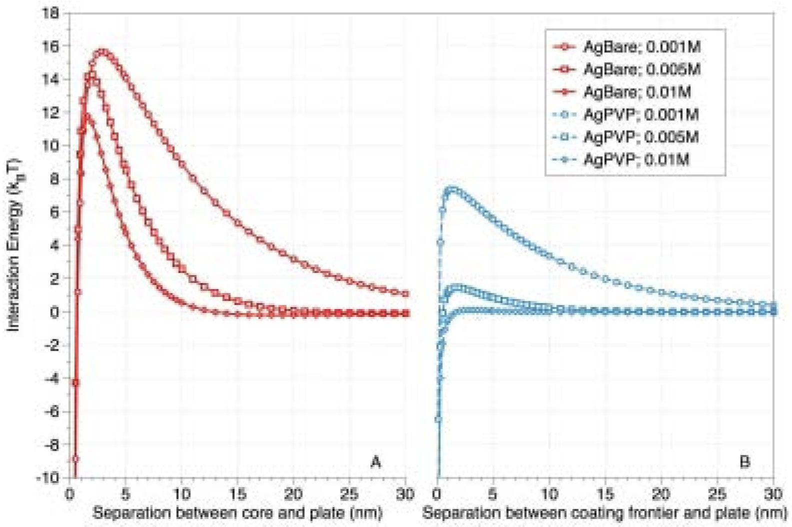
Shihong Lin[(1)], *shihong.lin@duke.edu, 121 Hudson Hall, Durham NC 27708, United States ; Yingwen Cheng*[(2)]*; Jie Liu*[(2)]*; Mark R. Wiesner*[(1)]*. (1) Department of Civil and Environmental Engineering, Duke University, Durham NC 27708, United States (2) Department of Chemistry, Duke University, Durham NC 27708, United States*

The aggregation and deposition kinetics of three different types of silver nanoparticles (AgNPs) were studied: AgNPs that are charge-stabilized only (AgBare), AgNPs that are coated by uncharged polymers (e.g. AgPVP) and AgNPs that are coated with charged polyelectrolyte (e.g. AgGA). It is found that while polymeric coatings may always help stabilizing the AgNPs against aggregation by steric stabilization mechanism, they might in fact destabilize the AgNPs for deposition with the absence of a corresponding coating layer on the collector surface, which is demonstrated by a remarkable discrepancy between the affinity of the coated AgNPs for an uncoated collector surface and that for a coated surface.



DLVO theory was applied considering the effect of the polymeric coating on particle-surface interaction. We propose that the drastic increase in particle-surface might be

attributable to the shifted "interaction frontier" which would significantly decrease the barrier of total interaction energy.



COLL 15

Hydrate particle aggregation determined by interfacial interactions

***Zachary M. Aman**(1), zaman@mines.edu, 1600 Illinois St., Golden CO 80401, United States ; Erika P. Horning(1); E. Dendy Sloan(1); Amadeu K. Sum(1); Carolyn A. Koh(1). (1) Chemical Engineering, Colorado School of Mines, Golden CO 80401, United States*

Hydrate aggregation is a critical factor in determining where and when hydrates may plug a deepwater flow line. Quaternary ammonium salts are typically used as flowline anti-agglomerant. Some additives of this type are categorized with acute and chronic Category 1 aquatic toxicity, and may be harmful to the environment. Carboxylic acids are naturally occurring amphiphiles and have been previously shown to reduce cyclopentane hydrate cohesion force. Direct measurements show that 1-, 2- and 4-membered polynuclear aromatic carboxylic acids reduce hydrate cohesive force by 23%, 27% and 87%, respectively. Acids with 0-, 1- and 3-carbon spacing between the carboxyl and 4-membered polynuclear aromatic groups reduce hydrate cohesion force of 56%, 87% and 74%, respectively. Combined with direct interfacial tension measurements between water and mineral oil, these data suggest that the 4-membered polynuclear aromatic group with 1-carbon functional group spacing may be affecting the hydrate surface wettability, in addition to weakening the capillary bridge between particles.

COLL 16

Effects of anions and organic matter on reactivity and surface characteristics of nanoscale zero-valent iron particles

Hong-Seok Kim[(1)]*, khs4011@pusan.ac.kr, Room 2514, 2nd Eng. bdlg., Pusan National University, Jangjeon-dong, Geumjeong-gu, Busan Busan 609-735, Republic of Korea ; Jun-Young Ahn*[(1)]*; Kyung-Yup Hwang*[(1)]*; Inseong Hwang*[(1)]*; Diem T.N. Le*[(1)]*; Jin-Yong Lee*[(2)]*; Jeong-Yong Chun*[(3)]*. (1) Department Civil and Environmental Engineering, Pusan National University, Busan, Republic of Korea (2) Department of Geology, Kangwon National University, Republic of Korea (3) Geogreen21, Republic of Korea*

Nanoscale zero-valent iron (NZVI) particles were tested as remediation media for groundwater contaminated by organic pollutants. The contaminated groundwater contained anions (NO_3^-, Cl^-, SO_4^{2-}, HCO_3^-) and natural organic matter (NOM). Treatability of commercial NZVI particles (NANOFER 25, Nanoiron, Czech) was tested by using synthetic groundwater and the field groundwater samples. Interactions between NZVI and adsorbates and the resulting characteristics on the surface of the NZVI were also investigated. More than 95% of 1.8 mM TCE was removed within 20 hours with a NZVI dosage of 25 g/L ($k= 0.15\ hr^{-1}$). TCE degradation reactions were not substantially affected by the presence of each anion with concentrations as high as 100 times the average field concentrations. However, when four anions (NO_3^-, Cl^-, SO_4^{2-}, HCO_3^-) were present simultaneously, the degradation reactivity was decreased by 60% ($k=0.069\ hr^{-1}$). The k value of TCE degradation in the presence of NZVI (25 g/L) with dissolved organic carbon of 2.5 mg/L was also decreased by 84% ($k=0.025\ hr^{-1}$). In the experiments with the field groundwater, more than 90% of 1.8 µM TCE, which is the concentration of TCE at the source zone, was removed within 10 hours with a NANOFER 25 dosage of 25 g/L. TEM and XRD analyses revealed that iron precipitates containing anions were formed during the reaction and electrochemical analyses such as zeta potential and corrosion potential measurements were carried out to investigate the changes on the surface of the NZVI particles.

COLL 17

Oil-mineral interactions with applications in oil-spill clean-up

Marina Tsianou[(1)]*, mtsianou@buffalo.edu, 304 Furnas Hall, Buffalo New York 14260-4200, United States ; Ankitkumar I. Fajalia*[(1)]*; Biswa P. Das*[(1)]*. (1) Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York (SUNY), Buffalo NY 14260-4200, United States*

The wetting and adhesion of model hydrocarbons on a variety of surfaces is characterized with contact angle, atomic force microscopy (AFM), and quartz crystal microbalance (QCM) measurements. The contact angle data are analyzed in terms of surface free energy parameters that can be subsequently used to predict wetting/adhesion behavior in a variety of conditions. The AFM and QCM experiments reveal the mechanism and timescales of oil spreading and detachment from surfaces immersed in an aqueous environment. Effects of added surface active agents are considered. The findings add to our oil-mineral interactions knowledge that is needed for coastline remediation following an oil spill.

COLL 18

Oxide nanomaterials as reactive environmental interfaces

Vicki H. Grassian[(1)]*, vicki-grassian@Uiowa.edu, Chemistry Building, Iowa City IA, United States . (1) Department of Chemistry, University of Iowa, Iowa City IA 52242, United States*

Oxide nanomaterials have highly reactive surfaces and are important environmental interfaces. In this talk, the focus is on the size-dependent surface chemistry and surface photochemistry of atmospheric gases with oxide nanomaterials. In particular, dark and light driven reactions of sulfur dioxide, carbon dioxide and nitrogen oxides with TiO_2, ZnO and FeOOH nanoparticles and nanorods are discussed. These reactions are investigated using a several different spectroscopic probes that provide important information on gas-phase products, surface speciation and the nature of reactive sites. The effect of relative humidity on the surface chemistry is also explored. As will be discussed, adsorbed water can both enhance and inhibit the reactive properties of environmental interfaces depending on the exact nature of the reaction and the active sites involved.

COLL 19

Tailoring (bio)chemical activity of semiconducting metal (hydr)oxide nanoparticles: critical role of deposition and aggregation

Irina Chernyshova[(1)]*, ic2228@columbia.edu, 500 W 120th Str., Mudd Bldg, Rm. 905C, New York NY 10027, United States ; Sathish Ponnurangam*[(1)]*; Ponisseril Somasundaran*[(1)]*. (1) Columbia University, United States*

The impact of deposition and aggregation on (bio)chemical properties of semiconducting metal (hydr)oxide nanoparticles (NPs) is perhaps among the least studied aspects of aquatic chemistry of solids. Employing a combination of in situ FTIR and ex situ X-ray photoelectron spectroscopy (XPS) and using the Mn(II) oxygenation on hematite (α-Fe2O3) NPs as a model catalytic reaction, we discovered that the catalytic performance of these NPs in the dark can be manipulated by depositing them on different supports or mixing them with other semiconducting NPs. We introduce the electrochemical concept of the catalytic redox activity to explain these findings and to predict the effects of (co)aggregation and deposition on the catalytic and corrosion properties of ferric (hydr)oxides. These results offer new possibilities for rationally tailoring the technological performance of semiconducting metal oxide NPs and provide a new framework for modeling their fate and transport in the environment and living organisms.

COLL 20

From single crystals to nanoparticles: Probing reactive interfaces using the long-period x-ray standing wave approach

Marc Michel[(1)(2)]*, fmichel@stanford.edu, 450 Serra Mall, Braun Hall, Bldg. 320, Stanford CA 94305-2115, United States ; Yingge Wang*[(2)]*; Clement Levard*[(2)(3)]*; John R Bargar*[(1)]*; Yong Choi*[(4)]*; Peter Eng*[(4)]*; Gordon E Brown, Jr.*[(1)(2)(3)]*. (1) SLAC National Accelerator Laboratory, Menlo Park CA 94025, United States (2) Department of Geological & Environmental Sciences, Stanford University, Menlo Park CA 94025, United States (3) Center for Environmental Implications of NanoTechnology, Duke University, Stanford CA 94305, United States (4) Consortiums for Advanced Radiation Sources, University of Chicago, Chicago IL 60637, United States*

The mobility and geochemical cycling of metal ions in contaminated aquatic systems are controlled by a number of surface chemical properties such as complexation, sorption, precipitation, and redox transformations at mineral-water interfaces. Such processes are further complicated by the presence of various forms of organic matter coatings on the mineral surface. To evaluate these effects, we have applied the long-period x-ray standing wave (XSW) approach to samples ranging from natural single crystals of metal oxides to nanoscale thin films composed of synthetic silver and hematite nanoparticles. Coatings of organic substances such as microbial biofilms or natural organic matter are applied to more closely simulate natural conditions. A practical introduction to the XSW method will be given and a variety of x-ray scattering and fluorescence yield-based measurements will be discussed. Examples will include our recent studies of metal partitioning between biofilms and minerals and of the corrosion of synthetic Ag nanoparticles.

COLL 21

Role of desorption kinetics on colloid-facilitated transport of cesium and strontium

Timothy M Dittrich[(1)]*, timothy.dittrich@colorado.edu, 1111 Eningeering Dr., ECOT 441, Boulder CO 80309, United States ; Joseph N Ryan*[(1)]*; James E Saiers*[(2)]*. (1) Department on Civil, Environmental, and Architectural Engineering, University of Colorado-Boulder, United States (2) Department of Engineering and Applied Science, Yale University, United States*

The goal of our research was to identify and quantify the effects of desorption kinetics from illite clay colloids on the transport of cesium and strontium through a quartz sand column at different degrees of saturation (moisture contents). Cesium and strontium were used as model contaminants because they are common contaminants found on Department of Energy sites in the US and because they have contrasting sorption kinetics with illite. Breakthrough experiments were conducted with a column (12.7 cm diameter and 33.5 cm long) packed with quartz sand. The effluent was collected and measured for total and dissolved ions, pH, and colloid concentration. The presence of illite colloids increased the transport of both cesium and strontium; however, the

transport of cesium was increased more than strontium, likely due to cesium binding more strongly to the frayed edges of illite. A previously developed model for colloid-facilitated transport of cesium and strontium has been extended to accommodate partially-saturated conditions.

COLL 22

Density functional theory study of the structures, energetics, and vibrational spectra of phosphate adsorbed onto the (100), (010), (001), (101), and (210) surfaces of Goethite

Qing Zhu(1)*, quz3@psu.edu, 303 Deike Building, University Park PA 16802, United States ; James D Kubicki*(1)*; Masoud Aryanpour*(2)*; Kristian W Paul*(3)*; Lara Kabalan*(1)*. (1) Department of Goesciences, The Pennsylvania State Univeristy, University Park PA 16802, United States (2) Department of Mechanical Engineering, Stanford University, Stanford CA 94305, United States (3) DuPont Crop Protection, Stine-Haskell Research Center, Newark DE 19714, United States*

Planewave density functional theory (DFT) and hybrid molecular orbital-DFT (MO-DFT) calculations were performed on periodic and cluster models of phosphate on the (100), (010), (001), (101) and (210) surfaces of α-FeOOH (goethite). Potential energies of monodentate and bidentate surface complexes obtained from both molecular dynamics simulations and energy minimization calculations were compared to outer-sphere models to estimate adsorption energies in each configuration on each face. Structures were extracted from the periodic DFT calculations as starting configurations of the MO-DFT cluster calculations. Calculated frequencies from MO-DFT method were correlated with observed infrared frequencies. Configurations that resulted in favorable adsorption energies were also found to produce theoretical vibrational frequencies that correlate well with observation. The model relative stability of monodentate versus bidentate configurations is dependent on which goethite surface was under consideration. Furthermore, the protonation state of the model adsorbed phosphate corresponded in a reasonable way with the pH of the solution from which phosphate was observed in experimental studies. Overall, the results suggest that phosphate adsorption onto goethite may occur as a variety of surface complexes depending on the habit of the mineral (i.e., surfaces present) and pH.

COLL 23

Structure and reactivity of the uraninite (111) surface

Joanne E Stubbs(1)*, stubbs@cars.uchicago.edu, 9700 S. Cass Avenue, Building 434A, Argonne IL 60439, United States ; Peter J Eng*(1)*; Glenn A Waychunas*(2)*; John R Bargar*(3)*. (1) Consortium for Advanced Radiation Sources, University of Chicago, Chicago IL 60637, United States (2) Lawrence Berkeley National Laboratory, Berkeley CA 94720, United States (3) Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park CA 94025, United States*

Corrosion of uraninite (UO2) is a surface-mediated process fundamental to controlling uranium mobility in contaminated environments, to the performance of nuclear power systems, and to nuclear waste stability. The structures of hydrated uraninite-water interfaces are seminally important to corrosion mechanisms and rates. Until now, UO2 surface studies have been limited to vacuum-based techniques, with none conducted in the presence of liquid water.

The crystal truncation rod (CTR) x-ray diffraction method is ideally suited to such measurements, as it specifically probes structures at two-dimensional interfaces. The (111) surface structure of single-crystal UO2 has been measured under both dry and hydrated conditions. Even during nominally anaerobic handling, a nm-dimensioned layer of UO2+x can form, which is commensurate with the underlying UO2. This overlayer is partially dissolved by exposure to liquid water, consistent with the relatively high solubility of oxidized uranium. These results indicate that UO2 is highly reactive with water.

COLL 24

DFT investigation of the oxidation of the uranium dioxide (111) surface

Anne M. Chaka(1)*, anne.chaka@nist.gov, 100 Bureau Drive Mailstop 8443, Gaithersburg Maryland 20899-8443, United States ; Gloria A.E. Oxford*(1)*; JoAnne Stubbs*(2)*; Peter Eng*(2)*. (1) Physical Measurement Laboratory, NIST, Gaithersburg Maryland 20899-8443, United States (2) Consortium for Advanced Radiation Sources, University of Chicago, Chicago Illinois 60637, United States*

Oxidation of uranium dioxide is an important process to understand and control, as it plays a key role in the weathering and release of uranium into the environment from natural mineral sources, mines, and micron-sized particles resulting from deployment of depleted uranium penetrators in munitions, as well as the corrosion and structural failure of nuclear fuel rods. Density-functional theory is used to investigate the surface and subsurface oxidation processes of the UO_2(111) surface as a function of oxygen partial pressure, and understand the structural and chemical implications.

COLL 25

Structural characterization of novel aluminum hydroxide nanoclusters as geochemical model compounds for contaminant transport

Tori Z. Forbes(1)*, tori-forbes@uiowa.edu, CB W374, Iowa City IA 52242, United States . (1) Department of Chemistry, University of Iowa, Iowa City IA 52242, United States*

Aluminum oxyhydroxide nanoclusters are effective coagulants for water purification and are suspected to be a component of the flocculent precipitated during acid mine drainage. Due to their affinity for binding heavy metals, the presence of nanoclusters in solution can impact the transport and fate of contaminants in aqueous environments.

Aluminum oxyhydroxide nanoclusters can be structurally characterized, thus they may serve as ideal geochemical model compounds to investigate the structural details, surface chemistry, and reactivity of small colloidal particles and amorphous solids. Less than ten aluminum oxyhydroxide nanoclusters have been crystallized and additional compounds are needed to ensure that the system is adequately characterized. Using a supramolecular approach, we have crystallized a new Keggin-type cluster containing 26 aluminum cations ($[(AlO_4)(Al_{12}(\mu\text{-}OH)_{25}(H_2O)_{10}]_2^{12+}$). The significance of this cluster in aluminum-bearing solutions and the overall importance of nanoclusters as geochemical model compounds for colloidal-mediated transport will be discussed.

COLL 26

Can we activate oxide catalysts by anion doping?

Horia Metiu[(1)]*, metiu@chem.ucsb.edu, University of California, Santa Barbara California 93106-9510, United States . (1) Department of Chemistry & Biochemistry, University of California, Santa Barbara, United States*

I will spend the early part of this talk reminiscing about my contacts with Professor Ruckenstein while we were both employed by the "Institutul Politechnic din Bucuresti". After that I will present quantum mechanical calculations that attempt to determine whether it is a good idea to try to activate oxide catalysts by using a controlled amount of a halogen source in the feed. Our main interest is in improving the catalytic activity or selectivity for oxidative dehydrogenation or for oxidative halogenation of alkanes.

COLL 27

Single-Molecule Insights into Heterogeneous Catalysis, Substrate-Mediated Interactions, and Buried Interface Structures

Paul S Weiss[(1)]*, psw@cnsi.ucla.edu, 570 Westwood Plaza, Los Angeles CA 90095, United States . (1) CNSI and Departments of Chemistry & Biochemistry and of Materials Science & Engineering, UCLA, Los Angeles CA 90095, United States*

Interactions within and between surface adsorbates can be designed, directed, measured, understood, and exploited at unprecedented scales. In these and other measurements, we collect substantial data sets in order to generate distributions with the statistics of ensemble-averaging techniques, while retaining all the single-molecule and environmental information. This requires new automated tools for acquisition and analyses. This approach, in combination with multiple modalities of atomic-resolution measurements, enables new insights into precise and hierarchical assembly, as well as function at the nanoscale.

COLL 28

Understanding Enantioselectivity on Chirally Modified Surfaces in Ultrahigh Vacuum

Wilfred Tysoe[(1)]*, wtt@uwm.edu, 3210 N Cramer Street, Milwaukee WI 53211, United States . (1) Chemistry and Biochemistry, University of Wisconsin-Milwaukee, Milwaukee WI 53211, United States*

Since different enantiomers of pharmaceuticals and agrochemicals can have different physiological properties, they generally require the synthesis of enantiopure compounds. An attractive option to achieve this is to use heterogeneous catalysts. In order to understand how this might be achieved, the enantioselectivity of model chirally modified single-crystal surfaces is explored in UHV by following the chemistry of chiral probe molecules on chirally modified surfaces. This allows the structure of the modifier to be determined in detail using a wide range of surface science strategies including infrared spectroscopy, STM and LEED. Enantioselectivity is measured by adsorbing chiral probe molecules such as R- or S-propylene oxide onto a chirally modified as a function of modifier coverage, allowing detailed correlations to be made between the structure and coverage of a surface modifier and its resulting enantioselectivity. This approach is illustrated using chiral modifiers consisting of alcohols, acids, amino acids, and naphthylethylamine.

COLL 29

Designed metal nanoparticle placement on carbon microspheres through a facile one-step process: Applications to the development of multifunctional materials for environmental remediation.

Vijay T John[(1)]*, vj@tulane.edu, 300 Lindy Boggs Bldg., New Orleans Louisiana (LA) 70118, United States ; Jingjing Zhan*[(1)]*; Bhanukiran Sunkara*[(1)]*; Gary McPherson*[(1)]*. (1) Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans LA 70118, United States*

A one step aerosol-based process (ABP) is developed to vary the placement of iron nanoparticles on the external surface of carbon microspheres or within the interior. This is accomplished through the competitive mechanisms of sucrose carbonization and the precipitation of soluble iron salts, in an aerosol droplet passing through a high temperature heating zone. At lower aerosolization temperatures, carbonization occurs first leading to iron salt precipitation on the external surface, while at higher temperatures interior placement occurs through concurrent iron salt precipitation and sucrose carbonization. The resulting composites are highly conducive to the reductive dechlorination of compounds such as trichloroethylene (TCE). Since both iron and carbon are widely used catalysts and catalyst supports, the simple process of modifying iron placement has significant potential applications in heterogeneous catalysis. Colloidal stability, partitioning characteristics and transport through groundwater is facilitated by the addition of designed polyelectrolytes to the system.

COLL 30

Characterization and performance of Fischer-Tropsch catalysts modified by a chelating agent

***Dady B. Dadyburjor**(1)(2), dady.dadyburjor@mail.wvu.edu, PO Box 6102, Morgantown WV 26506-6102, United States ; Ashish Bambal(1)(2); Alaa Kababji(1)(2); Vidyasagar Guggilla(1)(2); Todd H. Gardner(1); Edwin L. Kugler(1)(2). (1) National Energy Technology Laboratory, US Department of Energy, Morgantown WV 26507, United States (2) Department of Chemical Engineering, West Virginia University, Morgantown WV 26507, United States*

Fischer-Tropsch synthesis (FTS) is a key step for converting fossil fuels into usable fuels and chemicals. Catalyst deactivation has been reported as a major challenge for cobalt-based FTS catalysts. Preliminary work is presented on the modification with chelating agents of the silica support used for the FTS catalyst. Nitrilotriacetic acid and ethylenediamine tetraacetic acid are used as the chelating agents. Characterization of the catalysts by x-ray diffraction, x-ray photoelectron spectroscopy and temperature-programmed reduction is presented. CO hydrogenation experiments have been carried out in a computer-controlled system centered around a fixed-bed reactor. Support modification of the Co/SiO_2 catalysts is expected to minimize metal-support interaction and to improve the stability and activity of the FTS catalysts.

COLL 31

Enhanced CO_2 adsorption on H_2O-treated zeolitic imidazolate framework (ZIF)

***Yun Hang Hu**(1), yunhangh@mtu.edu, 1400 Townsend Drive, Houghton MI 49931, United States ; Lei Zhang(1). (1) Department of Materials Science and Engineering, Michigan Technological University, Houghton MI 49931, United States*

Metal-organic
frameworks (MOF) have the tunable pore structures and ultra-high surface areas, which makes them better than other porous materials for gas adsorption. Zeolitic Imidazolate Frameworks (ZIF), which have excellent chemical and thermal stability, are a particularly interesting type of MOFs for CO_2 adsorption and separation. Herein, it is reported that the structure of ZIF-8 can be changed by H_2O-treatment. Furthermore, the H_2O-treated ZIF-8 exhibited higher CO_2 capacity than the original ZIF-8. This indicates that the H_2O treatment, which can increase the interaction between CO_2 and ZIF-8, constitutes an effective approach to tune the structure of ZIF-8 for CO_2 adsorption.

COLL 32

Surface chemistry in humid environments: Bridging the divide between colloid and surface science

Vicki H. Grassian[1]*, vicki-grassian@Uiowa.edu, Chemistry Building, Iowa City IA 52242, United States . (1) Department of Chemistry, University of Iowa, Iowa City IA 52242, United States*

The Division of Colloid and Surface Chemistry with its approximately 2500 members and rich history is one of the more active Technical Divisions of the American Chemical Society. The interdisciplinary nature of the division is reflected in the programming offered by the division and the research interests of the members which are sometimes discussed in terms of “wet chemistry” to reflect colloid science in aqueous phase and “dry chemistry” to reflect surface science in ultrahigh vacuum. As we look back and move forward, the division should honor those who have made outstanding contributions – either wet or dry chemistry (or both) – to these areas. We do so here in this symposium for Eli Ruckenstein and his enormous contributions by each of us presenting our own unique contributions. In this talk, I will attempt to bridge the divide between “wet” and “dry” chemistry by focusing on molecular-based studies of the surface chemistry of oxides in humid environments – a water activity regime between aqueous phase (colloid science) and ultrahigh vacuum (surface science). Understanding the detailed molecular-based surface chemistry in this water activity regime is important in atmospheric and environmental chemistry as well as corrosion science and, until recently, has been largely ignored.

COLL 33

Electrical Double Layer and Specific Ion Effects at Interfaces between Thermotropic Liquid Crystals and Aqueous Phases

Nicholas L Abbott[1]*, abbott@engr.wisc.edu, 1415 Engineering Drive, Madison WI 53706, United States ; Rebecca Carlton*[1]*. (1) Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison WI 53706, United States*

Ions play a central role in a wide range of interfacial phenomena, including colloidal stability, formation of emulsions, fusion events involving biological membranes and charging of electrochemical interfaces. At relatively low concentrations, the effects of ions often reflect the presence of electrical double layers, whereas at high concentrations of ions, phenomena connected to the hydration of ions can dominate and pronounced specific ion phenomena are observed. In this presentation, observations of orientational ordering transitions of thermotropic, water-immiscible liquid crystals (LCs) at aqueous interfaces (i.e., an oil-water interface) that are triggered by the interactions of simple ions will be described. Because the ordering of the molecules in the LC phase is long range, the interfacial ionic events are amplified into bulk ordering transitions within the LC phase that are readily quantified by optical methods. A particularly surprising finding is salt-induced patterned orientations of LCs, suggesting the lateral segregation of species at these oil-water interfaces. The results are significant in that they offer new fundamental insights into ionic phenomena at oil-water interfaces and provide guidance for the design of dynamic and responsive materials based on LCs.

COLL 34

Interfacial properties and applications of polymer-grafted nanoparticles

Robert D. Tilton(1)(2)*, tilton@andrew.cmu.edu, 5000 Forbes Avenue, Pittsburgh Pennsylvania 15213, United States ; Trishna Saigal*(1)*; Nicolas J. Alvarez*(1)*; Gunnar Duner*(3)*; Shelley L. Anna*(1)(4)*; Lynn M. Walker*(1)*; Krzysztof Matyjaszewski*(5)*; Andra Dedinaite*(3)*; Esben Thormann*(3)*; Per M. Claesson*(3)*. (1) Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh Pennsylvania, United States (2) Department of Biomedical Engineering, Carnegie Mellon University, Pittsburgh Pennsylvania, United States (3) Department of Surface and Corrosion Science, Royal Institute of Technology, Stockholm, Sweden (4) Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh Pennsylvania, United States (5) Department of Chemistry, Carnegie Mellon University, Pittsburgh Pennsylvania, United States*

The development of “grafting from” methods of brush formation by polymerization from surface-bound initiators makes it possible to create brush-decorated nanoparticles with large grafting densities. Such particles have proven to be effective emulsifying agents by virtue of their high affinity adsorption to oil/water interfaces. Also, adsorbing brush-grafted nanoparticles as brush building blocks potentially can be used to create a brush-like coating on a larger surface. This presentation will focus on silica nanoparticles with poly(dimethylamino ethylmethacrylate) brushes. The interfacial properties of these particles, at oil/water, air/water, or silica/water interfaces, depend on the grafting density and solution conditions that affect brush ionization and long-range colloidal forces. The interfacial tension and Gibbs elasticity of particle monolayers on fluid interfaces will be discussed in connection with Pickering emulsion applications, and adsorption isotherms, layer organization, normal forces and lateral forces on solid surfaces will be discussed with application to tribology.

COLL 35

Ligand-mediated repulsion enables nanoparticle desorption from compressed oil-water interfaces

Kathleen J Stebe(1)*, kstebe@seas.upenn.edu, 220 South 33 St, Philadelphia PA 19104-6393, United States ; Valeria Garbin*(1)*; John Crocker*(1)*. (1) Department of Chemical and Biomolecular Engineeirng, University of Pennsylvania, Philadelphia PA 19104-6393, United States*

The trapping of nanoparticles at fluid-fluid interfaces has been exploited to build self-assembled structures, to stabilize emulsions and foams, and in phase-transfer catalysis. However, little is known about how interactions between adsorbed nanoparticles affect their exchange between the interface and the bulk. We study ligand-capped gold nanoparticles adsorbed from suspension to an oil-water interface. Using a pendant drop, we measure pressure-area isotherms of the nanoparticle monolayer. The drop shape allows us to determine the surface tension; an image analysis technique based on absorbance enables us to determine the fractional coverage of the drop surface. We interpret features in the pressure-area isotherm in terms of interparticle interactions, and explore their consequences on nanoparticle partitioning. For this nanoparticle-ligand system, the particles can be forced to desorb at high surface compression-a result that motivates the study of how ligands influence interparticle interactions to promote forced desorption to facilitate nanoparticle recovery and re-use.

COLL 36

Structure and interactions of grafted neutral polymer brushes

Marian Manciu(1)*, mmanciu@utep.edu, 500 West University Ave, El Paso TX 79968, United States . (1) Physics, University of Texas at El Paso, El Paso TX 79912, United States*

The partition function of each polymer chain of a grafted polymer brush can be obtained as a sum over all possible 1D random walks with a reflecting barrier at origin, to each walk corresponding a free energy due to monomer-monomer and monomer-solvent interactions. Most of the random walks have very high free energies (e.g. because of monomer overlapping) and therefore very small Boltzmann factors, hence providing a negligible contribution to the partition function. We calculated an approximate partition function, in which the latter contributions have been discarded. For non-adsorbing polymer brushes, the model can be used for both good and poor solvents, is compatible with a parabolic-like profile at moderate grafting densities, as well as an almost step-like profile at high densities or a collapsed brushed at lower densities, and leads in certain conditions to the well known scaling laws. In poor solvents, the interactions between brushes might become attractive for some ranges of separation distances. For adsorbing polymer brushes, the structure of the brush is described in terms of the fraction of monomers belonging to loops, trains and tails and structural transitions between normal and collapsed brushes (loops-to-trains transitions) or normal and stretched brushes (loops-to-tails transitions) are investigated. It was shown that there is an optimal grafting density to maximize the attraction induced by the adsorbing polymer.

COLL 37

Stimuli-responsive polymer brushes: design and applications

Sergiy Minko(1)*, sminko@clarkson.edu, 8 Clarkson Ave, Potsdam NY 13699, United States . (1) Chemistry and Biomolecular Science, Clarkson University, Potsdam NY 13699, United States*

The talk provides an overview of recent results from our laboratory on the design, synthesis, characterization, and applications of nanostructured polymeric and colloidal systems used for the fabrication of smart responsive surfaces, micro/nano-actuators, colloidal particles, and biosensors based on stimuli-responsive tethered functional polymeric chains (polymer brushes). Various architectures of polymer brushes were

engineered to regulate and balance intermolecular forces (electrostatic, hydrophobic, magnetic, steric and guest-host interactions) and to become functional components of novel nanostructured materials that can undergo structural reconfiguration (or switching) triggered by specific external stimuli.

COLL 38

Multifunctional Nanoclusters from Nanoparticles: Fundamentals, Design and Biomedical/Energy Applications

Keith P Johnston(1)*, kpjaustin@sbcglobal.net, Speedway and Dean Keeton, CO400, Austin TX 78712, United States . (1) Department of Chemical Engineering, University of Texas, Austin TX 78712, United States*

A major challenge in nanoparticle engineering is to devise a flexible and robust synthetic strategy to pack sufficient multifunctionality into nanoparticles smaller than ~100 nm, even below 50 nm. Commonly, nanoparticles are synthesized from atoms, where the difficulty in controlling the morphology of the various components often limits the strength of multifunctional properties and biodegradability. A novel approach is to build nanoparticle clusters from primary nanoparticles, instead of from atoms, based on tuning colloid interactions. A key objective will be to control nanocluster size and particle spacing within the clusters by manipulation of the particle concentration pathways and the total interaction potential between particles. The interaction potential, which depends upon the electrostatic, van der Waals, steric and depletion forces, governs the kinetically-controlled aggregation and particle morphology. This “bricks and mortar” interfacial dynamic assembly technique allows essentially unlimited flexibility choosing and mixing the nanoparticle building blocks in any proportion to engineer desired function. For the case of iron oxide and gold nanoparticles, this approach is providing unprecedented strengths of optical, magnetic, and optical/magnetic responses, in biodegradable particles as small as 50 nm. A general paradigm for engineering multifunctional biodegradable nanoclusters has the potential to revolutionize fundamental nanoscience and nanotechnology. The biodegradation of nanoclusters into primary nanoparticles can overcome the major roadblock in nanotechnology that is toxicity upon accumulation in humans and in the broader environment. Concentrated protein nanoclusters are assembled from protein monomers by tuning the colloidal intereactions. A hierarchy of intracluster and intercluster interactions may be controlled to provide colloidal stability, low viscosities, and stable protein.

COLL 39

Colloids of luminescent silicon nanocrystals: Synthesis, functionalization, and applications in bioimaging

Mark T. Swihart(1)*, swihart@buffalo.edu, 303 Furnas Hall, Buffalo New York 14260-4200, United States . (1) Chemical and Biological Engineering, University at Buffalo (SUNY), Buffalo NY 14260-4200, United States*

Photoluminescent silicon nanocrystals (silicon quantum dots, Si QDs) have great potential in biological imaging and diagnostic applications, where they provide an attractive alternative potentially toxic heavy-metal-containing QDs. However, they have been much less studied than more easily prepared QDs of compound semiconductors such as CdSe. In all of their potential applications, stability and tunability of optical and electronic properties are important. In addition, the Si QDs must remain stably dispersed in biological fluids, over a wide range of pH and salt concentration. High luminescence quantum yield at near-infrared wavelengths is also a key requirement. Meeting these requirements requires engineering both the crystalline silicon core and its interface with the surroundings. This talk will outline our efforts in developing scalable, economical methods of preparing and modifying Si QDs, with an emphasis on biological applications. We have confirmed the biocompatibility of phospholipid polymer-micelle-encapsulated Si QDs (MSiQDs) and demonstrated *in vivo* targeted tumor imaging in live mice. More recently, we have explored encapsulation of SiQDs with low-cost, biocompatible pluronic block copolymers or biodegradable chitosan, as well as combination of SiQDs with magnetic iron oxide nanoparticles, chelated gadolinium ions, plasmonic gold nanoparticles, or chemotherapeutic agents for multimodal imaging and treatment.

COLL 40

Redox-responsive gels as reversible extractants for polar organics: Synthesis and electrochemical characterization

T. Alan Hatton*(1)**, tahatton@mit.edu, Room 66-309, MIT 77 Massachusetts Ave, Cambridge MA 02139, United States ; Abhinav Akhoury(1); Lev Bromberg(1). (1)*

The recovery or removal of polar organics from aqueous media is an important step during the fermentative production of biofuels such as ethanol and butanol. To overcome problems of entrainment or solubility of organic solvents use as extractants, we have developed redox-responsive gels that have hydrophobic domains with good selectivity and capacity for, e.g., butanol, in the reduced state, but on oxidation these domains become charged and expel the butanol in favour of water. The gels are crosslinked so that there is no leaching of the solvent into the feed phase, and are immobilized on electrode surfaces, ensuring that there is no entrainment by the feed phase, nor emulsion formation. Electrical potential swings are used rather than changes in temperature, pH or ionic strength to alter the distribution coefficients, which can have some advantages in operations.

This presentation will describe the general concepts underlying the design and synthesis of the redox-responsive gels, their electrochemical characterisation, and the partitioning behaviour of polar organic molecules between the gels and the aqueous feed phase. In particular, we show through reconciliation of model predictions and experimental results that electron transport in polymer coated Redox Polymer Electrodes is diffusion controlled. Diffusion of electrons through the polymer film occurs either by 'hopping' of electrons from one redox site to the next, or by the motion of the polymer chains themselves ('bounded diffusion'), or both, depending on the concentration of redox-active centers in the gel.

COLL 41

Surface Science for the Soldier

Lynne Samuelson(1)*, lynne.samuelson@us.army.mil, Kansas Street, Natick MA 01760, United States ; Lian Li*(2)*; Jayant Kumar*(2)*. (1) U.S. Army Natick Soldier RDEC, Natick MA 01760, United States (2) Center of Advanced Materials, University of Massachusetts Lowell, Lowell MA 01754, United States*

Surface science has broad reaching applicability in both the civilian and military sectors. At Natick Soldier RDEC, our primary mission is to maximize a Soldier's Survivability, Sustainability, Mobility, Combat Effectiveness and Quality of Life while treating the Soldier as a System. Towards this, for Soldier protection, advanced materials and surfaces are needed which are lighter in weight, multifunctional, and can provide improved blast, ballistic, flame/thermal, camouflage, chemical/biological, environmental, situational awareness and laser eye protection. For combat feeding, new materials and surface science solutions are needed for improved food pathogen sensing, performance enhancement and nutrient delivery and revolutionary packaging for enhanced shelf-life stability. For aerial delivery of personnel and cargo, fundamental advancements are needed to optimize air flow over irregular surfaces and permeability through materials for precision airdrop and personnel safety. Lastly, for shelter technologies, advanced materials and structures are needed for rigid and softwall shelters that could improve chemical, biological, blast and ballistic protection, lighting, power management, anchorage, and deploy-ability (airbeam). This talk will give an overview of the science and technology being carried out at our laboratory and provide examples of current research efforts where surface science is helping to play an important role in material enhancements to Soldier capabilities. Some examples of surface science for the Soldier will include superhydrophobic surfaces for antifouling, electrically conductive nanofibrous membranes for sensing and EMI shielding, functionalized graphene surfaces for food pathogen sensing, surface modified metal oxide nanoparticles for electronic applications and polydiactylene coated metal oxides for photovoltaics.

COLL 42

Etching of diamond by hyperthermal atomic oxygen

Timothy K. Minton(1)*, tminton@montana.edu, 103 Chem/Biochem Bldg., Bozeman Montana 59717, United States ; Linhan Shen*(1)*; William Alexander*(1)*; Zeev Shpilman*(2)*; Irina Gouzman*(2)*; Eitan Grossman*(2)*; Rozalia Akhvlediani*(3)*; Alon Hoffman*(3)*; Jeffrey T. Paci*(4)*; George C. Schatz*(5)*. (1) Department of Chemistry and Biochemistry, Montana State University, Bozeman Montana 59717, United States (2) Space Environment Section, Soreq NRC, Yavne 81800, Israel (3) Schulich Faculty of Chemistry, Technion, Haifa 32000, Israel (4) Department of Chemistry, University of Victoria, Victoria British*

Columbia V8W 3V6, Canada (5) Department of Chemistry, Northwestern University, Evanston Illinois 60208, United States

The reactivity of single crystal diamond surfaces to hyperthermal (5 eV and 7.5 eV) atomic oxygen (AO) was studied by high resolution electron energy loss spectroscopy (HREELS) and atomic force microscopy (AFM) and by beam-surface scattering techniques. Theoretical calculations of reactions on these surfaces were also conducted using SCC-DFTB-based and PBE/DZP-based direct dynamics simulations. Selective etching of the diamond surfaces was observed in the experiments: (111) oriented surfaces were severely etched, while (100) oriented surfaces had high resistance. Scattering experiments identified the production of volatile CO and CO_2 products on the reactive surface. Both surfaces can be damaged by the incoming oxygen during the initial stages of exposure, resulting in the removal of carbon as CO_2 molecules and functionization of the surfaces with oxygen. Theoretical results show that, on the (111) surface, oxy radical formation, graphitization, and direct CO_2 production are important, whereas on the (100) surface, O-atoms add to give ketone and ether groups.

COLL 43

Single impacts of fullerenes on surfaces : from postcollision multifragmentation to pick-up reactions

***Eli Kolodney**[(1)], eliko@tx.technion.ac.il, Technion city, Haifa Israel 32000, Israel . (1) Department of Chemistry, Technion-Israel Institute of Technology, Haifa Israel 32000, Israel*

Multifragmentation (MF) phenomena where highly energized complex finite system disintegrates simultaneously into several of its constituents are sometimes of a universal nature regarding the general patterns revealed. We show that surface impact induced MF of C_{60} can be a fully velocity correlated event. By measuring kinetic energy distributions of C_n (n= 1-12) fragment ions following collisions of 300-900 eV C_{60} anions with a gold surface we have observed the transition from MF with a common average energy for all fragments (“during- collision event”) to a one with a common average velocity for all fragments (“post-collision event”). The results were reproduced within a “precursor mediated statistical MF” model and molecular dynamics simulations. We will also report reactive ion shattering of C_{60} on gold and silver targets at higher impact energies (3-14 keV). Formation and ejection of gold and silver carbide cluster ions is shown to be a single impact pickup event.

COLL 44

Energetic xenon sputtering and embedding at ice surfaces

***Daniel Killelea**[(1)], dkillelea@uchicago.edu, 929 E 57th St GCIS E012, Chicago IL 60637, United States ; Kevin Gibson[(1)]; Hanqiu Yuan[(1)]; Steven J Sibener[(1)]. (1)*

Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago IL 60637, United States

Energetic collisions between gas-phase atoms or molecules and ice surfaces are ubiquitous in nature. Such collisions occur under non-equilibrium conditions given the disparity between the temperature of the substrate and that of the incident species. Moreover, metastable absorption states can be accessed at sufficiently high collision energies, opening up enhanced channels for species collection and concentration. Such events are of importance to many astrophysical and environmental chemical phenomena. Here, we present results of a study where the energetically accessed absorption states of the network of molecules in an ice surface were probed with translationally activated gas-phase Xe atoms, focusing on sputtering, energy accommodation, and a new mechanism for the incorporation of volatile species into ice surfaces: collisionally activated embedding. Evidence for embedding comes from the observation of Xe desorption at temperatures nearly 100 K above the normal desorption temperature for xenon adsorbed onto an ice surface.

COLL 45

Bright coherent ultrafast x-rays in the keV region and applications in surface science

Margaret M. Murnane[(1)]*, murnane@jila.colorado.edu, University of Colorado, Boulder CO 80309-0440, United States ; Henry C. Kapteyn*[(1)]*. (1) Department of Physics and JILA, University of Colorado, Boulder CO 80309-0440, United States*

This talk will discuss recent advances in high harmonic generation and applications. Phase matching using mid-infrared driving lasers has now resulted in bright soft x-ray supercontinua reaching photon energies > 1 keV. These ultrabroad bandwidths can support few-attosecond pulses and span the elemental x-ray absorption edges relevant to surface science, biological and materials spectroscopy, as well as nanoscale imaging. Applications in ultrafast, element-specific, dynamics in magnetic and correlated-electron materials, as well as nanoscale imaging with 20nm spatial resolution, will also be discussed.

COLL 46

Manipulation of Adsorbed Atoms and Molecules

Paul S Weiss[(1)]*, psw@cnsi.ucla.edu, 607 Charles Young Drive East, Los Angeles CA 90095, United States . (1) California Nanosystems Institute and Departments of Chemistry and Biochemistry, University of Calfornia-Los Angeles, Los Angeles CA 90095, United States*

We use the manipulation of adsorbed atoms and molecules with the scanning tunneling microscope (STM) to probe interadsorbate and adsorbate-substrate interactions. The

STM has the unique ability to map the perturbed electronic structure of and due to adsorbates. We use this capability to quantify such interactions and to elucidate the roles of perturbed electronic structure in surface chemistry, structures, dynamics, and catalysis.

COLL 47

Effects of interfacial forces on crystal nanoscale motion visualized with four-dimensional electron microscopy

***David J. Flannigan**(1), flanniga@caltech.edu, 1200 E. California Blvd., Pasadena CA 91125, United States ; Sang Tae Park(1); Ahmed H. Zewail(1). (1) Department of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena CA 91125, United States*

We directly visualized the effects of interfacial forces on crystal motion using ultrafast electron microscopy (UEM). Specifically, UEM is used to follow the driven movement of a single crystal of copper-tetracyanoquinodimethane on an amorphous membrane of silicon nitride. The movement results from the elongation of the crystal, which is initiated by a laser pulse *in situ*. We examined two distinct arrangements: (1) crystals anchored to the membrane at one end and free to move, and (2) crystals lying flat on the membrane. Oscillations of the free crystals occur at MHz frequencies with quality factors of 1000 or more. No such oscillations are seen for the crystals lying flat on the membrane. From the nanosecond dynamics, we find that the gravitational load cannot fully explain the motion. An additional effective load being six orders of magnitude larger than that due to gravity is therefore attributed to adhesive forces at the interface.

COLL 48

Viscosity enhancement of supercritical CO_2

***Stephen D Cummings**(1), Stephen.Cummings@bris.ac.uk, Cantock[apos]s Close, Bristol Avon BS8 1TS, United Kingdom ; Julian Eastoe(1). (1) School of Chemistry, University of Bristol, Bristol Avon BS8 1TS, United Kingdom*

A series of semi-fluorinated hybrid surfactants, pentadecafluoro-5-dodecyl (F7H4) sulphates, have been shown to form reversed micelles in dense CO_2; the aggregates evolve to form water-in-CO_2 (w/c) microemulsion droplets on addition of water. Aggregates in w/c phases have been characterised by small-angle neutron scattering (SANS) and probed with high pressure viscometry, showing the presence of viscosity enhancing cylindrical droplets, which become dispersed lamellar phases at higher water loadings. Also investigated are high internal phase emulsions (HIPEs) formed with brine, and supercritical CO_2, stabilized by certain commercial nonylphenol ethoxylates (Dow Tergitol NP-, and Huntsman Surfonic N- surfactants). These HIPE systems were characterised by SANS, with quantitative analyses of the profiles showing behaviour similar to hydrocarbon-water emulsions, regarding total interfacial areas and the effects

of surfactant concentration on the underlying structures. Finally, the advantages of both approaches for controlling the physico-chemical properties of liquid/supercritical CO_2 in sequestration and subterranean storage will be compared.

COLL 49

Wettability Gradient-Driven Directional Water-Transport across Thin Fibrous Materials

Tong Lin(1)*, tong.lin@deakin.edu.au, Pigdons Rd, Geelong Vic, Australia ; Hongxia Wang*(1)*; Jie Ding*(2)*; Xungai Wang*(1)*. (1) Institute for Technology Research and Innovation, Deakin University, Geelong Vic 3217, Australia (2) Human Protection and Performance Division, Defence Science & Technology Organisation, Melbourne Vic 3207, Australia*

We demonstrate that thin fibrous materials having a wettability gradient from superhydrophobic to hydrophilic through the thickness direction have a novel directional water transfer effect: water can transfer only from the superhydrophobic to the hydrophilic side, but not in the opposite direction unless an external force is applied. A sol-gel technology was used to prepare a superhydrophobic coating on fabrics, and the coated fabrics showed water contact-angle as high as 165 degrees. When the coated fabric was subjected to a photochemistry treatment from one fabric side, the irradiated surface turned hydrophilic permanently, while the back side still maintained the superhydrophobicity. The treated fabric can transfer water droplet rapidly from hydrophobic to hydrophilic side, and the pressure allowing water breakthrough the fabric is different considerably between the two fabric sides. The directional water transfer effect is also affected by the wettability gradient.

COLL 50

Insights into skin barrier functions with monolayer studies of stratum corneum lipids

Guangru Mao(1)(2)*, guangrumao@gmail.com, 199 Grandview Rd, Skillman NJ 08558, United States ; Catherine Mack*(1)*; Dina VanWyck*(1)*; Sheela Bhandarkar*(1)*; Euen Gunn*(1)*; Richard Mendelsohn*(2)*; Russel M Walters*(1)*. (1) Baby Care Science & Technology, Johnson & Johnson, Skillman nj 08558, United States (2) Department of Chemistry, Rutgers University, Skillman nj 08558, United States*

The stratum corneum (SC) intercellular lipids, which are packed in a lamellar structure, maintain most of the skin barrier functions. The structure and packing order of these lipids determines many skin properties such as transepidermal water loss (TEWL), barrier to external substances, and mechanical properties. In this study a monolayer for an equal molar mixture of ceramide (Cer), cholesterol (Chl), and fatty acid (FA) was used to model intercellular SC lipids. The surface behavior and phase transitions of monolayers were studied by surface pressure-molecular area isotherm and Brewster

Angle Microscopy. The model SC lipids formed a closely packed, solid-like film at the air/water interface. This model Cer/Chl/FA system was then perturbed with the introduction of a series of saturated and unsaturated fatty acids/triglycerides and also changes in the ratios of the Cer/Chl/FA. The resultant changes in monolayer model in terms of molecule packing and phase transitions were found complimented with in vivo studies on skin barrier function probed by TEWL and ATR-IR measurements on skin lipid order. The in vivo results confirmed the importance of the SC lipid molecular order changes observed in vitro.

COLL 51

Rheology of water coated glass beads dispersed in mineral oil

Eric B Webb(1)*, ewebb@mymail.mines.edu, 1600 Illinois St, Golden CO 80401, United States ; Amadeu K Sum*(1)*; Carolyn A Koh*(1)*; E. Dendy Sloan*(1)*; Matthew W Liberatore*(1)*. (1) Department of Chemical Engineering, Colorado School of Mines, Golden CO 80401, United States*

Glass beads coated in water and dispersed in mineral oil will flocculate via capillary bridges. Adding just 1% water by volume to a solution of 20% glass beads dispersed in mineral oil dramatically increases the viscosity. Under shear, the glass bead aggregates may align, deform, break up, or further aggregate. We use rheology to learn about these microstructure changes by measuring the viscosity at varying shear rate or shear stress. Both solid and hollow glass beads are studied separately. We measured viscosity at varying shear rate with solid glass beads using a parallel plate geometry. The particles settle rapidly and beads are sometimes ejected due to centrifugal force effects. Experiments with hollow glass beads corrected the settling issues, while moving to concentric cylinders geometry prevented particle ejection by centrifugal forces.

COLL 52

Photothermal oxidation of PbS quantum dot solids

Rachelle R Ihly(1)*, rihly@uci.edu, 10433 Adobe Circle, Irvine CA 92617, United States ; Jason Tolentino*(1)*; Yao Liu*(1)*; Markelle Gibbs*(1)*; Matt Law*(1)*. (1) Department of Chemistry, University of California, Irvine, Irvine CA 92697, United States*

PbSe and PbS quantum dot (QD) thin films have become technologically relevant as active layers in opto-electronic devices including field-effect transistors and solar cells. The spontaneous, thermally activated oxidation of these solids renders most devices non-functional, limiting their practical use. QDs are especially susceptible to oxidation due to large surface areas and energies, with oxidation causing a reduction in QD size and increased quantum confinement. A combination of optical absorption and Raman spectroscopy, and ex-situ TEM measurements was used to characterize the photothermal degradation of films exposed to heat and UV-light in air and nitrogen atmosphere. A UV-induced localized heating mechanism was identified and suppressed by illuminating films in oxygen at low temperature. Oxidation could be prevented by infilling QD films using atomic layer deposition of amorphous alumina which acts as a gas diffusion barrier. This work may have broad impacts in understanding solar cell stability in harsh conditions.

COLL 53

Cryo-microscopy study of freeze-thaw stabilization of paint

Manish Mittal[(1)]*, mmittal@umn.edu, 421 Washington Avenue SE, 151 Amundson Hall, Minneapolis MN 55455, United States ; Catheryn L Jackson*[(2)]*; Gregory Monaghan*[(2)]*; John A Roper*[(3)]*; Lorraine F Francis*[(1)]*. (1) Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis MN 55455, United States (2) Core R&D Analytical Sciences, Dow Chemical Company, Spring House PA 19477, United States (3) Dow Coating Materials R&D, Dow Chemical Company, Midland MI 48674, United States*

Stability of latex paints during freezing and thawing cycles is an important performance criterion. Adding volatile organic compounds (VOCs) in the paint formulation depresses its freezing point and imparts stability. However, environmental concerns have increased the pressure to reduce the amount of VOCs in the paint. In order to design dispersions that are freeze-thaw (FT) stable we need to understand the mechanism of stabilization. We use propylene glycol additive to FT stabilize an acrylic paint formulation. The paint is frozen and thawed in a controlled rate freezer and the microstructure at various stages in the process is observed using cryogenic scanning electron microscopy (cryoSEM). We report the effect of freezing rate, thawing rate and the amount of additive on the frozen microstructure. The results are compared with the (FT unstable) acrylic paint without the additive. We observed that the size of ice crystals formed during freezing increases when either the cooling rate is reduced or the amount of glycol in the paint is increased. However, it is only during thawing that the particles aggregate. Similarly, we observed that the thawing rate also greatly affects the microstructure and eventually the stability of the paint. Finally, we elucidate the cryoSEM results reported here and propose a mechanism of FT stabilization of paint due to VOCs.

COLL 54

Structure-property correlation of surfaces using thermal scanning probe microscopy

Khoren Sahagian[(1)]*, khoren@anasysinstruments.com, 121 Gray Ave., suite 100, Santa Barbara California, United States . (1) Anasys Instruments, Santa Barbara California 93101, United States*

Atomic Force Microscope (AFM) probes can now be micro fabricated with an internal resistive heater allowing for localized heating of nano-scale feature or domains; nano-

TA. As the temperature of the probe is scanned the region in contact will expand pushing upward on the AFM probe. At a transition temperature the surface softens and the AFM probe slightly indents downward into the sample much like in the case of a bulk Thermo-Mechanical Analyzer (TMA) but with lateral resolutions approaching 100nm. Structure-property correlation of surfaces is of keen interest where a wide range of surface kinetics can be directly observed via their impact on transition temperature. Applications will be drawn from a range of surfaces in industries including but not limited to biomedical devices, aerospace, coatings, & polymer blends.

COLL 55

Preparation of shape-switching colloids using electrohydrodynamic co-jetting

Kyung Jin Lee(1)*, lkyungjin@gmail.com, 3434 G.G. Brown 2300 Hayward St, Ann Arbor Michigan 48109, United States ; Joerg Lahann*(1)*. (1) Department of Chemical Engineering, University of Michigan, Ann Arbor Michigan 48109, United States*

Recent achievement on electrohydrodynamic co-jetting with side-by-side needle geometry provides promising tool to prepare anisotropic micro-building blocks. Herein we report Janus microcylinders and fibers composed of diverse pairs of polymer compartments using electrohydrodanamic co-jetting with dual-core/shell needles. Poly (latic-co-glycolic acid) (PLGA) solution introduced into shell needles can act as a sacrificial barrier, and simultaneously PLGA electrospinning makes it possible to produce perfectly aligned microfiber, which can transfer microcylinder by cryo-sectionning. Diverse range of polymers can be delivered into each core, resulting in Janus microcylinder or microfibers containing different pair of polymers. These compartmentalized microcylinders or fibers can undergo reversible shape shifting and thus offer utility in a number of different applications, such as smart colloidal particles and stimulus responsive building blocks.

COLL 56

Nanostructured, nanoporous Palladium alloys from consolidation of dendrimer encapsulated nanoparticles for Hydrogen isotope separation and storage

Patrick J Cappillino(1)*, pcappil@sandia.gov, PO Box 969, Mail Stop 9292, Livermore CA 94551, United States ; Michelle A Hekmaty*(2)*; David B Robinson*(1)*. (1) Energy Nanomaterials, Sandia National Laboratories, Livermore CA 94550, United States (2)*

Due to its high surface area, porous Palladium is a promising material for high value applications including chromatographic separation and storage of Hydrogen isotopes. In the case of Tritium storage, it has been hypothesized that pores should mediate destructive nucleation of Helium-3 bubbles arising from background tritium decay. A technique for preparing nanoporous Palladium alloys based on consolidation of dendrimer encapsulated nanoparticles (DEN) will be presented. Destabilization of a colloidal suspension of DEN and purification yields a high surface area material with

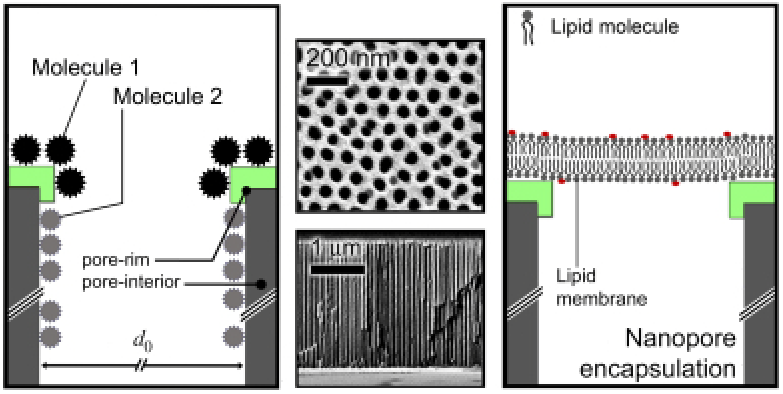
pore diameters between 20 and 200 nm. Compared to other aqueous chemical reduction methods, this approach has the advantage of compositional uniformity that is tunable based on the composition of the DEN. Nanoporous $Pd_{0.9}Rh_{0.1}$ alloys with uniform composition or with Rh enrichment at pore walls and grain boundaries have been prepared and characterized. Their Hydrogen and Deuterium storage properties were evaluated and compared to nonporous $Pd_{0.9}Rh_{0.1}$ powders.

COLL 57

Orthogonal Functionalization of Nanoporous Alumina: Control of 3D Surface Chemistry for Directed Chemistry at the Pore Rims.

Thomas D. Lazzara(1), *thomas.lazzara@gmail.com, Tamannstrasse 2, Göttingen Niedersachsen 37077, Germany ; Claudia Steinem*(1)*; Andreas Janshoff*(2)*. (1) Institute of Organic and Biomolecular Chemistry, Georg-August University Göttingen, Göttingen Niedersachsen 37077, Germany (2) Institute of Physical Chemistry, Georg-August University Göttingen, Göttingen Niedersachsen 37077, Germany*

Nanoporous anodic aluminum oxide was silanized and selectively plasma treated to create dual-functionality substrates, which had different pore-rim and pore-interior surface chemistries. We tailored the pore-rim surface chemistry to direct the assembly of components: proteins and giant liposomes. By modifying the pore-rims with dodecyltrichlorosilane, we directed the rupture of giant liposomes and formed hybrid pore-spanning lipid membranes, which were tethered. By modifying the pore rims with silanols, we directed the formation of fluid pore-spanning membranes, without pore-rim pinning points.



COLL 58

Atomistic Modeling of ISCC in Fuel-Pellet Interactions

Matthew L Rossi(1), *mrossi@lanl.gov, MS-G755, Los Alamos NM 87545, United States ; Christopher D Taylor*(1)*. (1) Materials Science and Technology, Los Alamos National Lab, Los Alamos NM 87545, United States*

Recent events, such as those in Fukushima, Japan, have caused much scrutiny over the nuclear industry. One significant concern in current nuclear technology is the low burn-up rates of nuclear fuel. The average fuel cycle for nuclear reactors in the United States is ~50GWd/kgU. This equates to the initial ~3% enriched U-235 ending at ~0.5% enriched U-235. The lifetimes of such fuel rods are however reduced due to stress corrosion cracking which occurs in the Zircaloy cladding. It has been shown that irradiation and operating stresses alone are not sufficient to induce material failure [Jacques, P., Lefebvre, F., and Lemaignan, C. J. Nuc. Mater. 1999, 264, 239-248]. During fission of the fuel pellets, considerable yields of cesium (~13%) and iodine (~10%) are produced. We seek to study the initiation of iodine-influenced stress corrosion cracking (ISCC) [Sidky, P.S. J. Nuc. Mater. 1998, 256, 1-17], commencing with $Zr\text{-}I_x$, and progressing to more complex interactions, such as those occurring between ZrO_2 and CsI at grain boundaries, using *ab initio* methods modeling the behavior. Ultimately, we will develop a reactive force-field (ReaxFF) which is suitable for the ISCC process to comprehensively simulate the reactions which occur within a nuclear reactor at the pellet-cladding interface. Our atomistic model may provide insight into the initiation of cracking in the cladding, and ultimately, prescriptive solutions to reducing corrosion.

COLL 59

Manipulating interdiffusion for mediated LbL drug delivery

Paula T. Hammond(1)*, hammond@mit.edu, 77 Massachusetts Avenue, 66-352, Cambridge MA 02139, United States . (1) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge Massachusetts 02139, United States*

The polyelectrolyte layer-by-layer (LBL) assembly process has been demonstrated to be an excellent platform for localized delivery of drugs from surfaces. We have investigated the direct incorporation of a broad range of molecular species, from small molecule drugs with very little charge to large globular proteins and DNA siRNA that exhibit meaningful charge densities. By using hydrolytically degradable polyions in conjunction with naturally occurring biomacromolecules, it is possible to generate surface eroding thin films that release their content gradually, thus introducing the potential for sequential drug release. On the other hand, many proteins and small molecule drugs of interest undergo significant interdiffusion, effectively mixing the content of multi-drug LbL complexes. Although interdiffusion can create challenges in achieving sequential release of multiple drugs; on the other hand, it can also be used as a vehicle for achieving high loadings of drug. Specific non-electrostatic interactions between different components in the film can further impact the loading and release behavior of LbL systems. When these interactions are understood, and the degree of interdiffusion can be manipulated, it is possible to generate multifunctional drug release systems with ideal release behavior based on given applications. In this talk, means of manipulating and modulating interdiffusion in thin release films will be discussed, as well as approaches that capitalize on these effects. Differences in assembly behavior based

on the means of generating LbL films will also be addressed. Examples of applications will range from biomedical implant coatings to vaccines.

COLL 60

Saloplastic macroporous polyelectrolyte complexes: Towards biomaterials

Haifa H Hariri(1), *hhariri@chem.fsu.edu, 180 Moore Court apt # 10, Tallahassee Florida 32310, United States ; Joseph B Schlenoff*(1). *(1) Chemistry and Biochemistry, Florida State University, Tallahassee Florida 32310, United States*

Polyelectrolyte complexes of sodium poly(4-styrenesulfonate) (NaPSS) and poly(diallyldimethylammonium chloride) (PDADMAC) were formed upon mixing equimolar solutions at high salt conditions. Under ultracentrifugal fields, the complex precipitates were transformed into compact transparent hydrogels, known as compact polylectrolyte complexes (CoPECs); these showed extensive porosity and considerable mechanical stability that render them good candidates for bioimplants. Free NaPSS chains were detected in the pores of CoPECs creating excess osmotic pressure, which controls the pore size and contributes to the mechanical resistance of the material under loading. This mechanism of load bearing aided by osmotic contribution from the pores is known for the articular cartilage. The mechanical properties of CoPECs in different salt concentrations were studied by uniaxial tensile testing and the stress-strain data were fit to a three-element generalized Maxwell model which explains the different relaxation mechanisms of these soft, water-saturated porous structures.

COLL 61

Photo-crosslinkable polyelectrolyte multilayers: Enhanced mechanical properties for cell culture applications

Ali M. Lehaf(1), *alehaf@chem.fsu.edu, 178 Moore Drive apt # 09, Tallahassee Florida 32310, United States ; Maroun D. Moussallem*(1)*; Jessica Martinez*(2)*; Joseph B. Schlenoff*(1)*; Thomas C. S. Keller III*(2). *(1) Chemistry and Biochemistry, Florida State University, Tallahassee FL 32306, United States (2) Biological Science, Florida State University, Tallahassee FL 32306, United States*

Photocrosslinkable polyelectrolyte multilayers (PEMUs) were prepared from poly(acrylic acid) grafted with photosensitive benzophenone, and poly(allylamine) hydrochloride. The Young's modulus measured by nano-indentation increased smoothly in a controlled fashion after irradiation with UV light. The permeability of the PEMU towards iodide ion measured with a rotating disc electrode decreased significantly. The surface wettability and charge density were not affected by irradiation, suggesting the surface chemistry and charge remained essentially unaltered. This provides a substrate material for cell culture where the only variable is mechanical property. Photocrosslinking provides a level of control over regions of crosslinking which is not achieved by chemical and thermal crosslinking. A multilayer with an elasticity gradient was prepared using a

gradient neutral density filter. Osteoblasts cultured on this gradient showed a preference for the stiffer part.

COLL 62

Tunable dual growth factor co-delivery from polyelectrolyte multilayer films for biomedical implants

Nisarg J Shah[(1)(2)]*, nisarg@mit.edu, 77 Massachusetts Ave, 76-573, Cambridge MA 02139, United States ; Mara L Macdonald*[(1)(3)]*; Yvette M Beben*[(4)]*; Robert F Padera*[(5)]*; Raymond E Samuel*[(1)]*; Paula T Hammond*[(1)(2)]*. (1) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge MA 02139, United States (2) David H. Koch Institute for Integrative Cancer Research, Massachusetts Institute of Technology, Cambridge MA 02139, United States (3) Harvard MIT Division of Health Sciences and Technology, Massachusetts Institute of Technology, Cambridge MA 02139, United States (4) Department of Biology, Massachusetts Institute of Technology, Cambridge MA 02139, United States (5) Department of Pathology, Brigham and Women's Hospital, Boston MA 02215, United States*

A promising strategy to speed up joint implant integration, reduce recovery time and failure rates is to deliver a combination of certain growth factors to the integration site. However, there is a need to control the quantity of growth factors delivered at different times during the healing process to maximize efficacy. Here, we present a characterization of polyelectrolyte multilayer films that sequester physiological amounts of osteogenic rhBMP-2 (recombinant human bone morphogenetic protein - 2) and angiogenic rhVEGF$_{165}$ (recombinant human vascular endothelial growth factor) in a degradable [poly(β-amino ester)/polyanion/growth factor/ polyanion] LbL tetralayer repeat architecture. rhBMP-2 released over a period of 2 weeks, while rhVEGF$_{165}$ eluted from the film over the first 8 days. Both growth factors retained their efficacy, as quantified with relevant dose dependent *in vitro* assays. Mineral density of bone formed in *vivo* by rhBMP-2/rhVEGF$_{165}$ coated scaffolds was approximately 33% higher than scaffolds coated with only rhBMP-2. This study demonstrates a promising approach to delivering precise doses of growth factors where control over spatial and temporal release profile of the biologic is desired.

COLL 63

Promotion of preosteoblast cell proliferation on complex coacervate substrates

Dimitrios Priftis[(1)]*, dpriftis@berkeley.edu, 281 Stanley Hall, Berkeley CA 94720-1462, United States ; Katie Megley*[(1)]*; Matthew Tirrell*[(1)]*. (1) Bioengineering, University of California, Berkeley, Berkeley CA 94720-1462, United States*

Mixing of oppositely charged polyelectrolytes in aqueous solutions may result in the formation of polyelectrolyte complexes (PEC). Phase separation and complex coacervation of different polyelectrolytes was investigated in such solutions. Sample

turbidity, which is an indicator of complex formation, and optical microscopy, was utilized for this study. The polymer rich coacervate phase was used as a substrate for cell proliferation of preosteoblast cells (MT-3T3). To investigate the effect of coacervates on cell proliferation different assays, which measure metabolic activity of viable cells, were used. Confocal microscopy was also utilized to visualize cell interaction and proliferation on the coacervate surface. To optimize MT-3T3 cell proliferation parameters that affect complex coacervation, such as polyelectrolyte ratio, were adjusted. Specific bioactive peptide sequences such as $(Lys)_5$(Arg-Gly-Asp) were also introduced in the coacervate substrates and their effect on cell proliferation was studied.

COLL 64

Three-dimensional tissue models fabricated by controlling cell interface using a layer-by-layer nanofilm

Michiya Matsusaki(1)*, m-matsus@chem.eng.osaka-u.ac.jp, 2-1 Yamada-oka, Suita Osaka 565-0871, Japan ; Koji Kadowaki*(1)*; Mitsuru Akashi*(1)*. (1) Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Osaka, Japan*

The creation of artificial three- dimensional (3D) tissues possessing a similar structure and functions as natural tissue is a key challenge for implantable tissues in tissue engineering, and for model tissues in pharmaceutical assay. Recently, we developed unique bottom-up approach, “hierarchical cell manipulation using a layer-by-layer nanofilm”, which applies the use of nanometer-sized fibronectin-gelatin (FN-G) films to control cell interfaces (**Fig. 1**)[1)]. Since the nanofilms with approximately 6 nm acted as a scaffold for the cell adhesion of the second layer[2,3)], we successfully developed various layered tissues such as blood vessel models[4-5)]. These cellular hierarchical structures would be useful as a 3D-tissue model for tissue engineering and pharmaceutical assay.

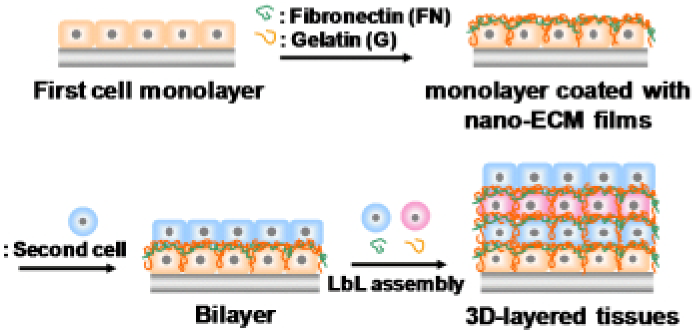


Fig. 1. Fabrication of 3D-tissue models by hierarchical cell manipulation.

References:
1) M. Matsusaki et al., *Angew. Chem. Int. Ed.*, **46**, 4689 (2007); 2) *J. Biomater. Sci. Polymer Edn.*, **18**, 1565 (2007); 3) *Langmuir* **26**, 5670 (2010); 4) *BBRC* **402**, 153 (2010); 5) *J. Biomater. Sci. Polymer Edn.*, *in press*.

COLL 65

Aggregation of human gamma-crystallin proteins and loss of transparency in cataracts

Benjamin G Mohr[(1)]*, bmohr@mail.pse.umass.edu, 120 Governors Drive, Amherst MA 01003, United States ; Cassidy M Dobson*[(1)]*; Scott C Garman*[(1)]*; Murugappan Muthukumar*[(1)]*. (1) University of Massachusetts, Amherst MA 01003, United States*

The human lens derives its transparency and refractive index from the interactions between crystallin proteins (α-, β-, ɣ-crystallin). When the ordering of these crystallins is perturbed, insoluble macromolecular aggregates of crystallin proteins can occur resulting in cataracts. We have performed a detailed study on the intermolecular interactions of ɣ-crystallin proteins using dynamic light scattering (DLS) and fast protein liquid chromatography (FPLC). The ɣD- and ɣS-crystallin proteins were exposed to a variety of environmental conditions (temperature, pH, salt) in addition to being exposed to reducing conditions and α-crystallin proteins, which naturally behave as heat shock proteins in the lens of the eye. Our DLS results provide strong evidence that there are non-covalent intermolecular hydrophobic or electrostatic forces which lead to individual ɣ-crystallins (Rh ~ 3nm) along with large aggregates of ɣ-crystallin (Rh ~ 200nm). We will present data demonstrating the disruption of aggregation in the presence of α-crystallin at physiological concentrations and at sufficiently high salt concentrations.

COLL 66

Hemostatic layer-by-layer assembled coatings

Anita Shukla[(1)]*, anitas@mit.edu, NE47-487, 77 Massachusetts Avenue, Cambridge Massachusetts 02139, United States ; Paula T Hammond*[(1)]*. (1) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge Massachusetts 02139, United States*

Uncontrolled bleeding is the leading cause of death in military trauma and a severe cause of increased patient mortality in civilian trauma. Many of the techniques commonly employed to control bleeding have adverse effects, such as tissue necrosis. As an alternative, we have developed a layer-by-layer (LbL) assembled coating that promotes hemostasis and can be applied to any surface. Spray LbL assembly was used

to build bilayers of the small molecule, tannic acid, and a clotting factor, thrombin, making use of hydrogen bonding interactions between these species to build up a multilayer coating. These films were applied to gelatin sponges commonly used to absorb blood during invasive procedures, without altering their absorbent capabilities. Films of just 10 bilayers, approximately 100 nm thick, were highly effective in causing fibrin clot formation *in vitro*, and promoted hemostasis instantaneously in a porcine spleen bleeding model *in vivo*.

COLL 67

Surface charging properties of minerals by site-specific AFM colloidal probe technique

***Yang Gan**(1), ygan@hit.edu.cn, No.92, West Da-Zhi Street, Harbin Heilongjiang 150001, China . (1) School of Chemical Engineering & Technology, Harbin Institute of Technology, Harbin Heilongjiang 150001, China*

Regardless of intensive interests in the surface chemistry of (hydr)oxide minerals, the surface charging behavior in aqueous solution is still not well understood. Using skillfully both AFM high-resolution imaging technique and site-specific colloidal probe technique, we showed unambiguously that the basal plane of gibbsite developed significant net positive charge in the acidic pH range, and that the PZC of polished corundum single-crystal (sapphire) was sensitive to the change in off-cut angle of samples. The series of study demonstrated that studying samples with carefully controlled microscopic structures was an essential step towards to a better understanding of the charging properties of (hydr)oxide minerals. We also found that wearing of microspheres against a hard substrate like corundum needed to be seriously considered for accurate force measurements, particularly in high salt concentrations cases and for adhesion studies where surface roughness of microspheres plays a critical role.

COLL 68

Photocatalytic activity of oxide nanoparticles

***Mary Jane Shultz**(1), Mary.Shultz@tufts.edu, Pearson Lab, 62 Talbot Ave, Medford MA 02155, United States . (1)*

Small mineral particles in the environment contain a variety of metal ions. Some of these, including iron and titanium oxides, are photo active. The presence of water in either small or large concentration modifies the photo activity. This paper will present evidence showing that metal ions either doped or in solution increase the photo activity of titania. Water inhibits the photo activity in two ways: by directly competing with adsorbates for surface sites and by limiting binding of molecular oxygen to the surface. Iron ion modification serves to trap electrons and to increase adsorption of molecular oxygen.

COLL 69

Linear and non-linear optical spectroscopic investigations of anion adsorption at environmentally relevant aqueous/mineral interfaces: Sulfate adsorption at fluorite and hematite surfaces

Aaron M Jubb(1)*, ajubb@chemistry.ohio-state.edu, 100 W. 18th Ave., Columbus OH 43210, United States ; Heather C. Allen*(1)*. (1) Department of Chemistry, The Ohio State University, Columbus OH 43210, United States*

Interactions between aqueous chemical species and environmental surfaces determine the mobility and fate of the chemical species within the environment. An understanding of these interactions, such as adsorption, is necessary for the prediction of the behavior and life-time of aqueous environmental contaminants. The adsorption of the ubiquitous aqueous anionic species sulfate (SO_4^{2-}) at environmentally relevant buried water/mineral (e.g. fluorite, hematite) interfaces was investigated as a function of pH, concentration, and solution ionic strength utilizing the linear vibrational spectroscopic technique total-internal-reflection Raman spectroscopy (TIR-Raman) and the non-linear optical spectroscopy vibrational sum frequency generation (VSFG). TIR-Raman and VSFG allow for the resolution of inner-sphere versus outer-sphere adsorption complexes at the mineral surface as well as enhanced surface specificity compared to other vibrational spectroscopic techniques (e.g. attenuated total reflectance Fourier transform infrared (ATR-FTIR)) commonly used to study adsorption processes. Results indicate that sulfate predominantly forms mono-dentate inner-sphere adsorption complexes at the fluorite and hematite surfaces.

COLL 70

Solvent effects on molecular adsorption and solvation at solid/liquid interfaces

Robert Walker(1)*, rawalker@chemistry.montana.edu, PO Box 173400, Bozeman MT 59715, United States ; Brittany L. Woods*(1)*; Eric A. Gobrogge*(1)*; A. R. Siler*(2)*. (1) Department of Chemistry and Biochemistry, Montana State University, Bozeman MT 59715, United States (2) Department of Chemistry and Biochemistry, University of Maryland, College Park, College Park MD 20742, United States*

Resonance enhanced second harmonic generation (SHG) spectroscopy was used to characterize the interfacial adsorption and solvation behavior of two solutes: p-nitrophenol (pNP) and p-nitroanisole (pNAs). The two solutes are sensitive to solvent polarity and show similar solvatochromic behavior in bulk solvents. Several silica/liquid interfaces were used in this study including weakly associating solid/liquid interfaces formed between silica and n-hexane, decane, cyclohexane, and methyl-cyclohexane and strongly associating interfaces formed between silica and water, dimethyl sulfoxide, and acetonitrile. On average, pNP has ~10 kJ/mol more adsorption energy at the measured interfaces than pNAs. This result was attributed to the relatively low solubility of pNP in alkane solvents. SHG spectra showed that the two different solutes sample

different interfacial polarities at the *same* silica/liquid interfaces. Adsorbed pNAs is sensitive to solvent identity but the excitation spectrum of pNP adsorbed to the silica surface changed very little regardless of adjacent solvent.

COLL 71

Temperature dependent water uptake by eicosanoic acid films using attenuated total reflection infrared spectroscopy

Annabel M Edwards(1)*, edwardsa@denison.edu, 100 West College Avenue, Granville OH 43023, United States . (1) Department of Chemistry and Biochemistry, Denison University, Granville OH 43023, United States*

Eicosanoic acid films supported on functionalized silicon surfaces serve as a simplified model for the epicuticular wax layer of plant cuticles. The cuticular wax layer present on all above ground plant surfaces inhibits large scale water loss. We investigate water movement through the eicosanoic acid films using attenuated total reflection (ATR) infrared spectroscopy measurements. These uptake studies are performed at various temperatures and are compared to similar studies that explore water uptake in eicosane films. A dodecyltriethoxysilane layer on a silicon ATR crystal prevents water adsorption to the silicon crystal and allows measurement of trace water signals that arise from water diffusion into the hydrophobic film. A goal of this work is to gain a clearer molecular-level picture of water's pathways through the largely hydrophobic plant cuticular interface.

COLL 72

Insights into manganese oxide surface chemistry: A DFT investigation

Gloria A. E. Oxford(1)*, gloria.oxford@nist.gov, 100 Bureau Drive, MS 8443, Gaithersburg MD 20899, United States ; Anne M. Chaka*(1)*. (1) National Institute of Standards and Technology, Gaithersburg MD 20899, United States*

Manganese oxides help to regulate groundwater contaminant concentrations due to their high reactivity and prevalence in geological settings. Understanding manganese oxide surface structures and redox behavior under environmentally relevant conditions provides an important foundation for studying mechanisms of heavy metal adsorption and oxidation. Periodic density functional theory calculations combined with *ab initio* thermodynamics have been applied to identify stable clean and hydrated β-MnO_2 and γ-MnOOH surfaces and to probe their redox behavior in response to varying oxygen and water chemical potentials. Oxidation and reduction of the clean surfaces lead to significant surface reconstructions that demonstrate the competition between optimizing *d* orbital energies and manganese coordination geometries and electrostatic and steric constraints of the bulk. Jahn-Teller distortion of surface manganese allows for the existence of multiple oxidation states at the surface. Preliminary studies have been performed to investigate Cr(III) adsorption geometries on stable hydrated surfaces.

COLL 73

Overlayer growth and reaction mechanisms of iron-(hydr)oxide nanoparticles on magnetite (111) surfaces

***Sarah C Petitto**(1), scpetitto@stcloudstate.edu, Wick Science Building 371, 720 Fourth Avenue South, St. Cloud MN 56301-4498, United States ; Jacob R Harguth(1); Michael D. Workman(1). (1) Department of Chemistry, St. Cloud State University, St. Cloud MN 56301-4498, United States*

Iron-(hydr)oxides, in particular magnetite, play a significant role in geochemical and industrial processes due to their wide-spread occurrence and unique chemical reactive properties. Under these conditions, a passivating overlayer and iron-(hydr)oxide nanoparticle surface precipitates form, decreasing magnetite's redox capabilities. Our studies examine both the formation of the oxidation overlayer and iron-(hydr)oxide nanoparticles surface precipitates to determine their effects on the magnetite surface and redox capabilities. An electrochemical redox study combining chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) was used as a function of time and applied potentials to examine surface roughness, film thickness, and density. The size, texture, and growth mechanisms of these iron-(hydr)oxide nanoparticles was investigated using complementary surface topography atomic force microscopy (AFM). These measurements will provide a comprehensive description of the molecular to nanoscale interface structure to model a pathway for how a magnetite surface might evolve and its implications on the surface reactivity will be discussed.

COLL 74

Surface chemical processes controlling pollutant transformation in zero-valent iron based treatment systems

***Yang Xie**(1), yxie001@ucr.edu, A242 Bourns Hall, Riverside CA 92521, United States ; David M. Cwiertny(1). (1) Department of Chemical and Environmental Engineering, University of California, Riverside, Riverside CA 92521, United States*

To investigate the entity responsible for pollutant transformation in iron-based treatment systems, trends in zero-valent iron (Fe(0)) and palladium-iron (Pd/Fe) bimetallic reductant reactivity toward 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA), a model chlorinated solvent, were examined as a function of pH, solvent concentration, reductant loading, reductant particle size and suspension aging time. In batch systems, rate constants for 1,1,1,2-TeCA reduction by Pd/Fe exhibited different dependencies relative to Fe(0) with respect to solution pH, solvent concentration and reductant loading, collectively supporting a scenario in which different reactive species are at play in each system. Subsequent investigations support atomic hydrogen from water reduction as a key reactive entity in Pd/Fe systems because a substantial solvent isotope effect was observed between systems with H_2O and D_2O. The magnitude of this isotope effect appears to increase with increasing Pd/Fe loading, suggesting that the

involvement of atomic hydrogen may depend on the relative concentrations of the target solvent and bimetallic reductant in treatment systems.

COLL 75

Protonation and electron transfer reactions of vanadium oxides affected by surfactant interfaces

Debbie C Crans(1)*, crans@lamar.colostate.edu, Department of Chemistry, Fort Collins Colorado 80523, United States ; Alejandro M Trujillo*(1)*; Pabitra B Chatterjee*(1)*; Ernestas Gaidamauskas*(1)*; Michael D Johnson*(2)*; Nancy E Levinger*(1)*. (1) Department of Chemistry, Colorado State University, Fort Collins Colorado 80523, United States (2) Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces New Mexico 88003, United States*

Membrane-like interfaces affect vanadium chemistry, specifically complex stability and reactivity. Changes in stability are readily monitored by ^{51}V NMR spectroscopy. Previously, changes in reverse micelle (RM) size showed alteration in ^{51}V NMR spectra, indicating changes to vanadium-complex composition and environment. Furthermore, vanadium-dipicolinate compounds have been shown to exhibit one and two electron transfer reactions based on environment. Anionic AOT and cationic CTAB RM systems are selected to explore the effect of charge on vanadium compounds with regard to protonation and electron transfer. Infrared (IR) studies probing the water pool identify the effect of protonation on vanadium-containing decavanadate as its location changes. Additionally, we explore the effect of surface charge and spatial proximity on the deprotonation of decavanadate. Using the combination of NMR and IR, significant differences in the properties and surface interactions are observed.

COLL 76

Non-Equilibrium Collision Dynamics at the Gas-Liquid Interface with Quantum State Resolution

David J. Nesbitt(1)*, djn@jila.colorado.edu, University of Colorado, Boulder CO 80309, United States ; Joseph R. Roscioli*(1)*; Andrew W. Gisler*(2)*; Michael P. Ziemkiewicz*(2)*; Daniel Nelson*(1)*. (1) Department of Chemistry and Biochemistry, JILA/NIST, Boulder CO 80309, United States (2) Department of Physics, JILA/NIST, Boulder CO 80309, United States*

Liquids are arguably the chemically most important and yet often the least well understood state of matter, with the gas-liquid interface representing a true frontier challenge for the tools of chemical physics. This talk will present recent results from studies in our group on non-equilibrium collision dynamics at the gas-liquid interface, invoking a suite of IR/visible/UV laser based approaches. The first is based on colliding supersonically cooled molecules (e.g., DCl, CO_2) in skimmed jets from freshly prepared room temperature ionic liquid (RTILs) surfaces in vacuum, exploiting high resolution

diode and IR quantum cascade lasers to probing the rovibrational and translational states of the recoiling projectiles. A second approach investigates scattering of open shell species (e.g., NO) from molten metals and molten salts (e.g., Ga, RTILs, KOH) as a function of temperature, taking advantage of laser induced fluorescence (LIF) to probe non-adiabatic energy transfer and electron-hole pair dynamics at the gas-liquid conductor interface. A third set of studies probes hyperthermal collision dynamics at gas-liquid mimetic interfaces such as self assembled monolayers (SAMs) on Au, using REMPI and velocity map imaging to obtain a fully correlated quantum state/vector momentum map of the collision dynamics.

COLL 77

Gas-liquid and gas-solid reaction dynamics studies

George C Schatz(1)*, schatz@chem.northwestern.edu, 2145 Sheridan Road, Evanston IL 60208-3113, United States . (1) Department of Chemistry, Northwestern University, Evanston IL 60208, United States*

This talk will describe our recent theoretical studies of hyperthermal atomic oxygen reacting with hydrocarbon liquids, with ionic liquids and with diamond surfaces. In these studies, the high energies shorten the time-scale of the dynamics to the few ps range, and this makes it possible to use molecular dynamics methods within a QM/MM framework to directly simulate the reactive dynamics. I show how these theoretical methods can be used to understand primary reaction mechanisms, as well as angular and energy distributions of the gaseous products which emerge from the surface after reaction. Related studies of sodium atoms at water and glycerol surfaces will be described, and in all studies there will be comparisons with experiment.

COLL 78

Reactions of solvated electrons initiated by collisions of sodium atoms at the vacuum-liquid interface

William A Alexander(1)*, alexander@chemistry.montana.edu, 103 Chemistry and Biochemistry Building, Bozeman Montana 59717, United States ; Timothy K Minton(1); Justin P Wiens(2); Gilbert M Nathanson(2). (1) Department of Chemistry and Biochemistry, Montana State University, Bozeman MONTANA 59717, United States (2) Department of Chemistry, University of Wisconsin-Madison, Madison Wisconsin 53706, United States*

Na atoms are used to initiate reactions of solvated electrons at the surface of liquid glycerol. The electrons are created by adsorption and ionization of Na atoms deposited effusively on a glycerol film in vacuum. The velocity and angular distributions of the scattered Na atoms indicate that only directly recoiling Na atoms escape into the gas phase; those that are trapped at the surface remain behind and ionize. Gas-phase reaction products identified by mass spectrometry include: hydrogen atoms, hydrogen

molecules, water molecules, and glycerol radicals. Each product desorbs from solution in a Maxwellian velocity distribution and follows a cosine angular pattern. Mechanisms for each reaction are presently being investigated using isotopic H and D substitution. The direct observation of desorbing hydrogen atoms implies that Na atom bombardment can be used to produce reactive species at or near the surface of a protic liquid.

COLL 79

Localized and delocalized energetic reaction at surfaces

John C. Polanyi[(1)]*, jpolanyi@chem.utoronto.ca, 80 St. George Street, Toronto Ontario, Canada . (1) Department of Chemistry, University of Toronto, Toronto Ontario M5S 3H6, Canada*

Halides react in a localized fashion with semiconductors (Si(111) or Si(100)) surfaces and metal (Cu(110)), despite the presence of excess energy in the reagents and exoergicity in the product. The 'localization' consists in the fact that the chemisorbed product is formed closely adjacent to the reagent. The localization is attributed primarily to the fact that the barrier to reaction is lowered by the concurrent existence of reagent and product bonding, i.e., 'concerted' reaction dynamics. A further contributing factor to localization is the nature of the energy release which deposits energy in the newly-formed bonds at the surface, and for vertical transition states into recoil of product into the gas-phase. In rare cases a horizontal transition state experiences an asymmetric force that sends a physisorbed intermediate cartwheeling hundreds of angstroms across the rough surface of silicon, before it finally slows and reacts at a substantial distance exemplifying 'delocalized' reaction.

COLL 80

Towards heterogeneous photocatalysis at subnanometer length and subpicosecond time scales

Nicholas Camillone[(1)]*, nicholas@bnl.gov, Building 555, Upton NY 11973, United States ; Peter Sutter*[(2)]*; Dolocan Andrei*[(1)]*; Danda P Acharya*[(2)]*; Percy Zahl*[(2)]*. (1) Department of Chemistry, Brookhaven National Laboratory, Upton NY 11973, United States (2) Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton NY 11973, United States*

Electron-mediated substrate–adsorbate energy transfer is central to photoinduced surface chemistry. To probe relevant processes at molecular length and time scales, we are leveraging cryogenic scanning tunneling microscopy in two converging lines of investigation: (i) single-molecule imaging of the adsorption and electron-induced chemistry of small molecules on model catalysts and (ii) local probing of ultrafast surface electron dynamics. Our imaging studies have revealed a complex adsorption behavior for a model system: CO_2 on rutile TiO_2 (110). We will describe the multiple binding sites, inferred potential energy landscape, and reactions driven by electron

injection in this system. We will also discuss new strides made towards measuring surface electron dynamics with simultaneous subnanometer and subpicosecond resolution using ultrafast-laser-excited STM. We will describe a two-color pump–probe approach that eliminates thermal instabilities present in one-color experiments. Our results will be presented from the perspective of subnanometer-scale studies of the dynamics of heterogeneous photocatalysis.

COLL 81

CO photooxidation on reduced TiO_2(110) surface

Nikolay Petrik[1]*, nikolai.petrik@pnl.gov, MS K8-88; P.O. Box 999, Richland Washington 99352, United States ; Gregory Kimmel*[1]*. (1) Division of Chemical and Materials Sciences, Pacific Northwest National Laboratory, Richland Washington 99352, United States*

Photo-induced reactions between O_2 and CO on reduced rutile TiO_2(110) surface are studied at low temperature (~30K). Photon stimulated desorption (PSD) of O_2, CO_2 and CO are observed with comparable yields. Results indicate that CO_2 is produced from the chemisorbed O_2 molecule residing in the oxygen vacancy and CO molecule physisorbed on the Ti site next to it. The PSD angular distribution for CO_2 is non-cosine, narrow and off-normal: it peaks at ~ 40 degrees to the surface normal in the (001) plane (across the Ti and O rows on the surface). The results are consistent with CO_2 produced from the (Ti)-O-C-O-O-(V_O) transition state complex predicted theoretically. CO PSD from the TiO_2(110) surface is enhanced dramatically by the presence of chemisorbed O_2 molecules, where photo-desorbing CO may be a by-product of the CO photooxidation process.

COLL 82

Gold nanoparticles for delivery of molecular and biomacromolecular therapeutics

Vincent M. Rotello[1]*, rotello@chem.umass.edu, 710 North Pleasant St., Amherst MA 01003, United States . (1) Department of Chemistry, University of Massachusetts, Amherst MA 01003, United States*

Drug Delivery Systems (DDSs) provide an important tool for increasing the efficacy of pharmaceuticals through improved pharmacokinetics and biodistribution. Additionally, DDSs can be used to target specific cell types (e.g. tumor cells), enhancing therapeutic efficiency and minimizing side effects of current therapeutic agents. We have used gold nanoparticles for the creation of DDSs and biomacromolecule delivery systems. Four important attributes of these vehicles are: 1) AuNPs can be fabricated with a wide variety of monolayer structures, allowing facile conjugation of drugs as well the “tuning” of the particle surface in terms of charge and hydrophobicity. 2) The thiol functionality of glutathione (GSH) can displace sidechains from AuNPss, providing a mechanism for drug release, relying on the ~1000-fold higher intracellular concentration of GSH relative to extracellular (e.g. plasma) levels. 3) The monolayer can be "tuned" to bind hydrophobic guests, providing a novel method for drug release through membrane fusion. 4) Gold has low inherent toxicity. Our research in the area of small molecule, DNA, and protein delivery using covalent and non-covalent particle-payload delivery systems will be discussed.

COLL 83

Molecular engineering of cell-nanoparticle interactions

Catherine J. Murphy(1)*, murphycj@illinois.edu, 600 S. Mathews Ave., Urbana IL 61801, United States . (1) Department of Chemistry, University of Illinois, Urbana IL 61801, United States*

The interaction of nanoparticles with cells is an extraordinarily interesting area, with potential applications in new cellular imaging probes, drug delivery vehicles, and even nanoparticle therapeutics. In addition to direct interaction of nanoparticles with cells, nanoparticles can also exert effects on cells through the extracellular matrix. In this talk I will discuss our efforts to engineer the surface chemistry of gold nanoparticles to tune their interactions with living cells both directly (through peptide targeting on the particles) and indirectly (through the effects different "flavors" of nanoparticles have on the ability of cells to engage with the extracellular matrix).

COLL 84

Binary heterogeneous assembly of quantum dots and gold nanoparticles into clusters and superlattices with DNA

Dazhi Peter Sun(1)*, psun@bnl.gov, 735 BNL, Upton NY 11973, United States ; Oleg Gang*(1)*. (1) Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton NY 11973, United States*

The ability to generate assemblies containing different types of nano-scale objects, such as quantum dots (QDs) and gold nanoparticles (AuNPs), would allow for a systematic investigation of the collective optical effects in heterogeneous nanomaterials. The incorporation of nucleic acids into nanoparticle assembly design provides a powerful tool for the fabrication of nano-architectures in a highly controllable fashion. Here, we report the heterogeneous assembly of QDs and AuNPs into clusters and three-dimensional (3D) superlattices by means of DNA encoding. Carboxylic CdSe/ZnS core-shell QDs were functionalized with amino-single stranded (ss) DNA to obtain a stable aqueous dispersion of QD-DNA conjugates, which maintains the optical properties of the original QDs. By introducing AuNPs modified by complementary ssDNA, QD-AuNP aggregates were assembled. Using synchrotron-based small angel X-ray scattering, we found that QD-AuNP assemblies form a body center cubic (BCC) lattice, while each nanoparticle type, QD and AuNP, are positioned in a simple cubic (SC) manner. For fabricating QD-Au clusters, we introduce a novel strategy that permits the use of

double-strand (ds) DNA as addressable template for particle positioning via a site-specific molecular intercalator. Dynamic light scattering and transmission electron microscopy results indicated the successful assembly of QDs and AuNPs into clusters. The optical properties of these assembles will also be discussed.

Research was supported by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division. Research was carried at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. Experimental help from Dr. Andrea L. Stadler and Mikhail Gurevich was also appreciated

COLL 85

Vesicle-based biomimetic platforms for water purification and biosensor applications

Bingfang Wang(1)*, wangbingfang@hotmail.com, WS2-04-15E, Engineering Drive 3, Singapore Singapore 117576, Singapore . (1) Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117576, Singapore*

Vesicles were fabricated from different lipids, as well as amphiphilic block copolymers using film rehydration, followed by sonication and extrusion to obtain small unilamellar vesicles of uniform sizes. The vesicles were characterizaed by dynamic light scattering, transmission electron microscopy, field emission scanning electron microscopy and confocal laser scanning microscopy. The highly permeable and selective membrane water channel protein AquaporinZ (AqpZ) extracted from *E. Coli* was reconstituted into the vesicles by detergent-mediated dialysis. The functionalized vesicles were either ruptured on mica for examination of the surface morphology of the planar bilayer membrane using atomic force microscopy, or immobilized onto surface-functionalized substrates such as porous membranes made from cellulose acetate, alumina or polyethylene terephthalate using chemical conjugation. Stopped-flow light scattering spectroscopy was used to test the permeability of the AqpZ-incorporated vesicles. These vesicle-based biomimetic systems can be used for a wide range of applications such as water purification and biosensors.

COLL 86

Modified semiconductor quantum dots (QDs) for novel bioanalytical platforms

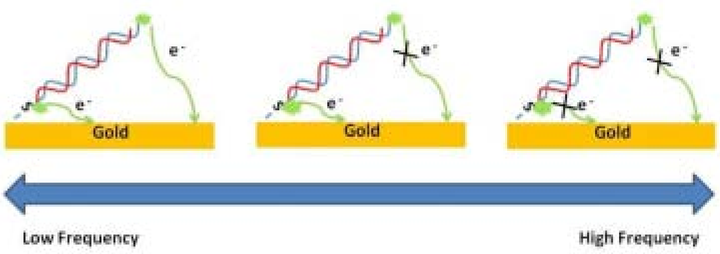
Itamar Willner(1)*, willnea@vms.huji.ac.il, Edmond J. Safra Campus, Givat-Ram, Jerusalem Israel 91904, Israel ; Ronit Freeman*(1)*. (1) Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

The unique photophysical properties of semiconductor QDs are implemented to develop new sensing platforms. These will be discussed with the following examples: (i) Fluorescence resonance energy transfer reactions (FRET) from QDs to dye labels are used to follow different biocatalytic transformations (NAD$^+$-dependent enzymes, protein kinase, endonuclease). (ii) Hairpin-functionalized CdSe/ZnS QDs are used for the detection of DNA and aptamer complexes using hemin/G-quadruplex as electron-transfer quenching labels. (iii) A chemiluminescence resonance energy transfer (CRET) from Hemin/G-quadruplex labels to CdSe/ZnS QDs is used to develop generic DNA or aptamer sensing platforms. Also, the CRET process from the Hemin/G-quadruplex to CdS QDs associated to electrodes is applied for the photoelectrochemical detection of DNA or aptamer-substrate complexes.

COLL 87

Electrochemical Monitoring of DNA-Protein Interactions

Keeshan Williams(1)*, Kwilli03@students.poly.edu, 6 Metrotech Center, Brooklyn NY 11201, United States ; Rastislav Levicky*(1)*. (1) Department of Chemical and Biological Engineering, The Polytechnic Institute of New York University, Brooklyn NY 11201, United States*



Alternating Current Voltammetry (ACV) is used to capture the thermal motions of electroactively-labeled DNA chains tethered to gold surfaces, before and after association with a transcription factor protein. As shown by several research groups, the faradaic current resulting from collisions of the DNA labels with the electrode surface tapers off at higher frequencies, resulting in a frequency-dependent tracking of chain dynamics and enabling detection of protein binding. In situations when such methods are to be used for continuous monitoring of biomolecular layers, susceptibility of the redox labels towards degradation must be recognized and calibrated for if necessary. In the case of electroactive labels based on ferrocene derivates, oxidation causes the ferrocene moiety to transition to the oxidized ferrocenium cation which is vulnerable to attack by nucleophilic species. In measurements, this leads to gradual loss of signal with the number of redox cycles performed. To counteract the loss of signal, changes in experimental conditions and/or signal processing methods may need to be implemented. This presentation will discuss recent attempt to monitor protein-DNA interactions as well as practical considerations involved with signal maintenance.

COLL 88

Packing of DNA-assembled nanocubes and nanooctahedra

Fang Lu[(1)]*, flu@bnl.gov, Bldg 735, NC, Upton NY, United States ; Yugang Zhang*[(1)]*; Kevin G Yager*[(1)]*; Daniel van der Lelie*[(2)]*; Oleg Gang*[(1)]*. (1) Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton NY 11973, United States (2) Center for Agricultural and Environmental Biotechnology, Research Triangle Institute (RTI) International, Research Triangle Park NC 27709-2194, United States*

Nanoparticle shape has a profound effect on assembly behavior. Due to the contribution of surface-attached molecules, the packing of nanoscale objects can differ markedly from the well-known geometric packing rules that apply to macroscopic objects. Here, we describe the phase behavior of nanocubes and nanooctahedron assembled by DNA-mediated interactions into three-dimensional structures. Our measurements using small angle x-ray scattering show that the packing of these nanoscale anisotropic objects depends strongly on the details of the DNA linkers. Using electron microscopy and optical spectroscopy, we elucidate the factors that drive assembly and dictate the spatial organization of the nano-objects. The relationship between particle shape and the mechanism of phase formation for nanocubes has been also investigated. Research was supported by the U.S. DOE Office of Science and Office of Basic Energy Sciences under contract No. DE-AC-02-98CH10886.

COLL 89

Reduction of metal ions by boranephosphonate DNA: potential applications from nanotechnology to biosensing

Subhadeep Roy[(1)]*, subhadeep.roy@colorado.edu, 215 UCB, Boulder CO 80309, United States ; Magdalena Olesiak*[(1)]*; Marvin H Caruthers*[(1)]*. (1) Department of Chemistry and Biochemistry, University of Colorado, Boulder CO 80309, United States*

Oligodeoxyribonucleotides (ODNs) bearing boranephosphonate internucleotide linkages have been the subject of research for a number of years for diagnostic and therapeutic applications. We have recently discovered that in addition to these properties the boranephosphonate group is also able to reduce various metal ions such as Au(III),

Ag(I), Pd(II) etc. forming the corresponding metallic nanoparticles. This juxtaposition of the expected Watson-Crick binding
properties and a chemically functional moiety that is incorporated into the backbone makes these oligonucleotide analogs uniquely suited for a wide range of applications from nanotechnology to nucleic acids based sensors. Additionally, in comparison to other DNA/RNA analogs that have been reported for DNA based nanotechnology applications, boranephosphonate DNAs has several advantages such as compatible phosphoramidite chemistry for incorporation into synthetic oligonucleotides as well as being effective substrates for DNA polymerases. Here we present results from the systematic study of the reduction of metal ions by boranephosphonate DNA and demonstrate some of the potential applications.

COLL 90

Adhesive complex coacervates inspired by the sandcastle worm

Russell J. Stewart(1)*, rstewart@eng.utah.edu, 20 S. 2030 East, Room 506C, Salt Lake City UT 84112, United States ; Sarbjit Kaur*(1)*; Hui Shao*(1)*. (1) Department of Bioengineering, University of Utah, Salt Lake City UT 84112, United States*

The underwater glue of sandcastle worms is comprised of divalent cations, polyacidic, and polybasic proteins. Synthetic polyelectrolyte analogs with the same sidechain chemistries (phosphates and amines) and sidechain molar ratios as the glue proteins, when mixed in similar proportions as the natural glue, formed complex coacervates with ideal properties for underwater adhesives, medical adhesives in particular. The coacervates are self-organized in water, water-borne yet water-immiscible, denser than water, adhere to wet surfaces, are ejectable through narrow cannulas, are containers for small molecules, and after crosslinking are dimensionally stable fully submerged in water. In a rat model, biodegradable adhesive coacervates secured and maintained alignment of calvarial bone fragments during healing, did not impede new bone growth, showed no evidence of significant toxicity or persistent inflammation, and was largely degraded after 12 weeks. Combining bioinspiration with engineering practices, bond strengths were substantially increased by incorporating additional phases into the adhesive coacervates.

COLL 91

Multilayer bio-hybrid assemblies of synthetic and biological macromolecules

Eugenia Kharlampieva(1)*, ekharlam@uab.edu, 901 14th Street South, Birmingham AL, United States ; Veronika Kozlovskaya*(2)*; John Ankner*(3)*; Hugh O’Neill*(4)*. (1) (2) Chemistry, University of Alabama at Birmingham, Birmingham AL 35294, United States (3) Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge TN 37831, United States (4) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge TN 37831, United States*

This talk is focused on polyelectrolyte layer-by-layer films (LbL) with incorporated biomolecules where interactions between adjacent layers are controlled by electrostatic or by hydrogen-bonding forces. We demonstrate highly-structured biohybrid materials obtained by localized incorporation of Green Fluorescent Protein (GFP) within electrostatically assembled polymeric matrices. The internal film structure is evaluated with neutron reflectometry by using deuterated GFP. GFP forms tightly packed molecularly-thin layers upon deposition with no intermixing with polymeric matrices. Hydrogen-bonded LbL films with incorporated natural polyphenols are discussed in potential application in cell-based transplantation therapy for diabetic recipients. The films are deposited on surfaces of pancreatic islets and provide cytocompatible biologically active coatings with diminished inflammatory immune responses. The coatings are crucial for long-term studies of *in vitro*/*in vivo* islet function and open new avenues in the area of advanced islet transplant materials.

COLL 92

Competitive adsorption between the cationic surfactant, octadecyltrimethylammonium bromide, and ssDNA at an aqueous-liquid crystal interface

Patrick S Noonan(1)*, patrick.noonan@colorado.edu, 1111 Engineering Drive, 424 UCB, ECCH 111, Boulder CO 80309, United States ; Daniel K Schwartz*(1)*. (1) Department of Chemical and Biological Engineering, The University of Colorado, Boulder CO 80309, United States*

Interactions between single stranded DNA (ssDNA) and octadecyltrimethylammonium bromide (OTAB) at an aqueous-liquid crystal (LC) interface induce a response that has demonstrated potential as a biosensor for detection of DNA hybridization events.[1] The mechanism behind ssDNA adsorption at an OTAB laden aqueous-liquid crystal interface is of interest toward understanding the limitations of a potential biosensor application. One proposed mechanism involves DNA and OTAB competing for adsorption sites. Polarized microscopy and epifluorescence images of ssDNA at the interface provide evidence for this mechanism. Furthermore, diffusion studies of ssDNA at an OTAB-laden aqueous-LC interface are consistent with competitive adsorption between ssDNA and OTAB. Comparison with theoretical models for 2D diffusion reveals that this diffusion coefficient is within an interfacial viscosity dominant regime with a value on the order of 0.1 – 1 μm²/sec.

[1] Price, Andrew D.; Schwartz, Daniel K.; *J. AM. CHEM. SOC.* 2008, 130, 8188-8194

COLL 93

Biocompatible extruded saloplastic polyelectrolyte complexes

Rabih F. Shamoun(1)*, rfs08c@fsu.edu, 316 Pennell Cir, Apt 1, Tallahassee Florida 32310, United States ; Andreas Reisch*(1)*; Joseph B. Schlenoff*(1)*. (1) Department of*

Chemistry and Biochemistry, Florida State University, Tallahassee Florida 32306, United States

Biocompatible stoichiometric
polyelectrolyte complex (PEC) was formed by the complexation of equimolar solutions of poly(styrene sulfonate) sodium salt and poly(diallyldimethylammonium chloride) at low salt concentrations. The PEC could be extruded in a standard laboratory extruder while hydrated and doped by salt. Under the effect of heat, compression, and shear forces the PEC formed a compact material of different shapes such as tubes, rods, and tapes. When soaked in dilute salt solution, the extruded PEC is rehydrated up to 40% by weight. It also exhibits elastic properties with an equilibrium modulus of 10 MPa. Since this material is saloplastic, soaking it in solutions of high salt concentration allows multiple extrusions to take place, making it ideally recyclable. The material becomes easily moldable at high temperature and at high salt concentration, acquiring a permanent shape at physiological conditions. Therefore, extruded PECs are promising for use in tissue engineering.

COLL 94

Binding and speciation of Sr(II), Ca(II), Mg(II), Ba(II), Mn(II), Zn(II), and Cd(II) to surface-bound oligonucleotides

Joseph Holland(1)*, josephholland2012@u.northwestern.edu, 2145 Sheridan Rd., Evanston IL 60208, United States ; Franz Geiger*(1)*. (1) Chemistry, Northwestern University, Evanston IL 60208, United States*

The binding of Sr(II), Ca(II), Mg(II), Ba(II), Mn(II), Zn(II), and Cd(II) to silica/water interfaces functionalized with a $A_{15}T_6$ oligonucleotides was quantified at pH 7 and 10mM NaCl using the Eisenthal $\chi^{(3)}$ technique. Binding free energies were found to range from -31.1(6) kJ/mol for Ba(II) to -33.8(4) kJ/mol for Ca(II). In addition, it was found that ion densities range from 2(1) ions/strand for Zn(II) to 11(1) ions/strand for Cd(II), respectively. A binding free energy versus interfacial potential analysis allowed us to identify the speciation of the bound Mg(II) ions and to propose three possible binding pathways. These findings suggest that Mg(II) binds as a fully hydrated divalent cation, which most likely displaces previously DNA-bound Na ions. Additionally, we were able to deconvolute the specific (base) and nonspecific (sugar and phosphate) contributions to the overall free energy of binding of Mg^{2+}. The specific interaction of Mg^{2+} with adenine, thymine, guanine, and cytosine was found to be 10.0 ± 0.3, 11.2 ± 0.3, 14.0 ± 0.4, and 14.9 ± 0.4 kJ/mol, and the nonspecific interactions with the sugar and phosphate backbone was found to be 21.0 ± 0.6 kJ/mol for each Mg^{2+} ion bound. We hope this work will serve as a surface-specific analog to the existing body of bulk studies on the interaction of divalent metal cations with oligo- and polynucleotides and will aid in the design of future surface-based biosensors.

COLL 95

Non-ionic hydrogen-bonded LbL shells with improved biocompatibility for cell encapsulation

Irina Drachuk[1]*, irina.drachuk@mse.gatech.edu, 771 Ferst Dr., Atlanta Georgia 30332-0245, United States ; Svetlana Harbaugh*[2]*; Jessica Carter*[1]*; Olga Shchepelina*[1]*; Nancy Kelley-Loughane*[2]*; Morley Stone*[2]*; Vladimir V. Tsukruk*[1]*. (1) Materials Science and Engineering, Georgia Intsitute of Technology, Atlanta Georgia 30332, United States (2) Air Force Research Laboratory, Wright-Patterson AFB, Dayton Ohio 45433, United States*

Surface engineering of cells through layer-by-layer (LbL) assembly provides an effective control over important functional properties of cells, such as cell adhesion, cell proliferation, and cellular stability in hostile environment. True hydrogen-bonded multilayer structures of tannic acid (TA) and poly(N-vinylpyrrolidone)(PVPON) were constructed on *S. Cerevisiae* cell membranes using LbL approach. Exceptionally high cell viability (94%) was observed for hydrogen-bonded encapsulated cells compared to traditionally used polyelectrolyte LbL systems, such as PSS/PAH (17%). Both growth kinetics and fluorescence intensity (resulting from green fluorescent protein expression) showed comparable growth and intensity when compared to control (non-encapsulated) cells, even with possible fast degradation of weakly-bonded hydrogen-bonded multilayers. Potential applications of true hydrogen-bonded cell encapsulation rely on combination of high viability, biocompatibility and preserved cell functionality, which can be useful for tissue engineering used in tissue engineering, cell transplantation, and cell-based sensors.

COLL 96

Targeting the Immune System with Biodegradable Nano Engineered Polyelectrolyte Microcapsules

Bruno G. De Geest[1]*, br.degeest@ugent.be, Harelbekestraat 72, Ghent Flanders 9000, Belgium ; Stefaan De Koker*[1]*. (1) Department of Pharmaceutics, Ghent University, Ghent 9000, Belgium*

Vaccines that can elicit strong T-cell responses are undoubtedly one of the major challenges for medicine today. For this purpose, dendritic cells (DCs) have to internalize antigen, process them into peptide fragments and present them to T-cells. Whereas soluble antigen largely fails to induce potent cellular immune responses, formulation of antigen into microparticles has emerged as an attractive alternative. Here, we report on efficient *in vitro* and *in vivo* antigen delivery to DCs using biodegradable polyelectrolyte capsules as antigen carrier. A first proof of concept is demonstrated using polyelectrolyte multilayer (LbL) capsules based on dextran sulfate and poly-L-arginine coated antigen loaded sacrificial calcium carbonate micro-templates. Upon dissolution of these micro-templates hollow capsules are obtained which retain the antigen within their hollow void. Subsequently we show in a number of mice based in vitro and in vivo experiments that by engineering the capsule surface it is possible to modulate the

immune activating properties of these capsules. Finally we show that using a spray-approach, rather than an LbL approach we can very well mimic the versatility of LbL capsules, but then on an industrial relevant production scale.

COLL 97

London dispersion interactions and molecular surface dynamics

Valentino R. Cooper(1)*, coopervr@ornl.gov, 1 Bethel Valley Rd, P.O. Box 2008 MS-6114, Oak Ridge TN 37831, United States . (1) Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge TN 37831, United States*

A molecular level understanding of molecule-surface interactions is crucial for tuning surface selectivity and reactivity. While it is clear that strong chemisorption bonds facilitate these interactions, the role of weaker van der Waals (vdW) forces, which include dispersion, hydrogen-bonding, and π-π stacking interactions, are often unknown or overlooked. The fact that the energy differences between reaction pathways is typically smaller than the dispersion interactions between the organic adsorbates, suggests that vdW forces will be important in many catalytic reactions. In this paper, I will discuss our use of density functional theory (employing the vdW non-local correlation functional) to demonstrate the critical importance of dispersion interactions for the adsorption and self-assembly of organic molecules on metal and semi-conducting surfaces. These studies are an important step in developing a fully first-principles description of molecular surface dynamics; thus having broader impacts for catalysis, molecular electronics, molecular storage and self-assembled coatings.

COLL 98

Complex flluid structures at polymeric interfaces

Scott K. Shaw(1)*, skshaw@email.arizona.edu, 1306 E Univ. Blvd, Tucson Arizona 85721, United States ; Colleen M. Burkett*(1)*; Jeanne E. Pemberton*(1)*. (1)*

The structures of fluid films over polymer modified and bare substrates are reported. Films are created via forced dewetting from bulk solutions in a sealed environment, and are probed via ellipsometry, vibrational spectroscopy, and contact angle measurements. Initial data for polymer-oligomer fluid layers on silver and silicon substrates have revealed disparate thickness values (2 to 125 nm) across a relatively small oligomer weight range (160 to 950 MW). The present study examines polymer modified substrates and a much larger molecular weight range of oligomers. Results are compared to theoretical film thickness predicted by long range van der Waals forces or classical hydrodynamic forces. Data are presented to differentiate the behaviors associated with these two model regimes. Trends in fluid film thickness with respect to viscosity, contact angle, and possible physical interactionswith the polymer substrate over a range of independently measured fluid properties are presented.

COLL 99

Impact of DNAPLs on the Structure of Clay in the Subsurface

Derya Ayral[(1)]*, ayrald@umich.edu, Room 7 EWRE Building, 1351 Beal Avenue, Ann Arbor Michigan 48109-2125, United States ; Margarita Otero Diaz*[(1)]*; Avery Demond*[(1)]*. (1) Department of Civil and Environmental Engineering, University of Michigan, Ann Arbor Michigan 48109-2125, United States*

Because DNAPLs (dense nonaqueous phase liquids) have low aqueous solubilities and are denser than water, they migrate vertically downward in the subsurface, collecting on and in clay lenses and layers. Understanding the transport of DNAPLs into and out of these zones requires an assessment of the impact of these liquids on the structure of clay minerals. This impact was characterized by ESEM and X-ray diffraction. The organic solvent matrix of the DNAPL caused the flocculation of clay particles and a decrease in the basal spacing, the extent of which was related to the dielectric constant of the solvent. On the other hand, surfactants typically contained in DNAPLs increase the basal spacing. Measurements of the basal spacing using DNAPLs from the field suggest that the impact is dominated by the solvent matrix; however, the surfactants can alter the wettability of the clay, allowing for imbibition of DNAPL into the clay pores.

COLL 100

Thermodynamics and Speciation of Adsorbed Cations at the Muscovite (001) - Water Interface

Sang Soo Lee[(1)]*, sslee@anl.gov, 9700 South Cass Avenue, Argonne IL 60439, United States . (1) Chemical Sciences and Engineering, Argonne National Laboratory, Argonne IL 60439, United States*

Adsorption of cations at the muscovite-solution interface was investigated using resonant anomalous X-ray reflectivity. In-situ observations revealed that cations adsorb as distinct inner-sphere (IS), outer-sphere (OS), and extended outer-sphere (OS_{ext}) species; that these species coexist at the interface; and that their proportions are controlled by the balance between electrostatic and cation hydration energies[1]. Measurements of competitive adsorption showed a complex coupling between adsorption structure and thermodynamics. Adsorption strength of a cation to the surface increases with increasing charge of the cation but decreases with increasing the magnitude of the hydration enthalpy. The IS/OS partitioning of a cation is altered by competitive adsorption. This effect will be discussed in the context of interfacial energetics and ion compatibility.
This work is supported by the U.S. Department of Energy (BES Geosciences Research Program) and National Science Foundation, and performed in collaboration with P. Fenter, C. Park, N.C. Sturchio, and K.L. Nagy.

1. S.S. Lee, et al., *Langmuir*, **26**:16647, 2010.

COLL 101

X-Ray Reflectivity Study on the Sorption of tetravalent Actinides on Muscovite

Moritz Schmidt(1)*, mschmidt@anl.gov, 9700 S Cass Ave, Lemont IL 60439, United States ; Paul Fenter(1); Lee Sang Soo(1); Richard E Wilson(1); Lynne Soderholm(1). (1) Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne I, United States*

Reliable long-term predictions about the safety of a potential nuclear waste repository must be based on a sound, molecular-level comprehension of radionuclide geochemical behavior. We apply *in situ* crystal truncation rod measurements and resonant-anomalous X-ray reflectivity to elucidate the sorption behavior of tetravalent actinides on the muscovite (001) basal plane under varying solution conditions (ionic strength, actinide concentration, background electrolyte). Measurements were performed using a purpose-built sample cell for radiological experiments. The data are complemented by precise quantitative analyses by means of alpha-counting experiments. The results clearly show the strong influence of the actinides' aqueous chemistry on their sorption behavior. It will be shown that a full description of the sorption behavior requires parameters such as the hydration enthalpy, complexation constants, hydrolysis constants, and polymer formation constants. This work is supported by the DOE (OBER), NIH, and EPA, under contract DE-AC02-06CH11357.

COLL 102

Applications of density functional theory modeling to the understanding and prediction of environmental interface reactivity

Sara E. Mason(1)*, sara-mason@uiowa.edu, Chemistry Building, Iowa City IA 52242-1294, United States . (1) Department of Chemistry, University of Iowa, Iowa City Iowa 52242-1294, United States*

The complexity of environmental interfaces makes both experimental and theoretical approaches to the study of reactivity trends challenging. Full consideration of all of the geochemical parameters contributing to contaminant adsorption from aqueous sources is prohibitive to a first principles modeling approach. We hypothesize that the gross reactivity trends governing inner-sphere adsorption of contaminant species are traceable to contaminant-surface interactions. Our approach is to robustly model a constrained set of adsorption complexes by periodic DFT calculations, using experimental details of sorption geometries for guidance where available. We design and carry out comparative theoretical studies to explore reactivity trends and to associate these trends with the physical parameters of the adsorbates and substrates. We report details of studies involving hydrated oxide surfaces interacting with cation and oxyanion adsorbates.

COLL 103

Adsorption of amino acids on montmorillonite surfaces: A theoretical study

Lorena Tribe(1)*, lut1@psu.edu, Tulpehocken Road, Reading Pennsylvania 19610, United States ; Aman Chugh*(1)*; Meserret Zekarias*(1)*; Peter M Balliet*(1)*. (1) Division of Science, The Pennsylvania State University - Berks Campus, Reading Pennsylvania 19610, United States*

The interactions of small biological molecules with mineral surfaces are at the heart of phenomena of fundamental importance in areas as diverse as drug delivery systems, soil remediation, fate of herbicides, catalysis, and origins of life theories. The combination of surface structures, presence or absence of water molecules, interlayer ions, and moieties of the biological molecules leads to a rich variety of structural possibilities. The interactions of amino acids such as lysine, leucine, and 5-aminovaleric acid with montmorillonite are studied here. Density Functional Theory calculations of the vibrational infra red and Raman spectra of amino acids surface complexes will be presented in conjunction with experimental data from the literature to provide a detailed map of the most likely surface complexes in each case. The structural differences between amino acids will be correlated with the differences in surface complex formation.

COLL 104

Line activity of hybrid lipids: stabilization of 2d ”oil in oil” microemulsions (lipid rafts)

Sam Safran(1)*, sam.safran@weizmann.ac.il, Herzel St, Rehovot Rehovot 76100, Israel ; Tetsuya Yamamoto*(1)*; Robert Bewster*(2)*; Phillip Pincus*(3)*. (1) Dept. Materials and Interfaces, Weizmann Institute of Science, Rehovot 76308, Israel (2) Dept. Applied Physics, CalTech, Pasadena CA, United States (3) Dept. Physics, UCSB, Santa Barbara CA, United States*

Lipid rafts are metastable or even stable and their size is believed to be of the order of 10-100 nm. On the other hand, the phase separated domains in model systems of membranes containing saturated lipids, unsaturated lipids, and cholesterol, are generally on the order of the system size because the positive line tension of the interfaces between saturated-rich and unsaturated-rich domains drives domain coarsening. Hybrid lipids such as POPC, which are abundant in biological membranes, have one saturated and one unsaturated tail, and may stabilize finite domains. We have analyzed theoretically a liquid crystal model that takes into account the various types of chain ordering in mixtures of saturated, hybrid, and unsaturated lipids in membranes. In these systems, the hybrid lipids can show line activity and in some cases, reduce the line tension between saturated and unsaturated lipids to zero, in a type of "oil in oil" microemulsion.

COLL 105

Modeling the micellization of complex surfactants through the complementary use of computer simulations and molecular thermodynamics

Daniel Blankschtein(1)*, dblank@mit.edu, 77 Massachusetts Avenue, Building 66 - Room 444, Cambridge MA 02139, United States . (1) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge MA 02139, United States*

Surfactant micellization in aqueous solution is of continuing fundamental importance and relevance to industry due to the widespread use of surfactants in commercial product formulations. Much effort has been devoted to theoretically predict micellization behavior, with the goal of reducing costly trial-and-error experimentation. An important example includes the development of molecular-thermodynamic theories, in which the free energy of micellization is decomposed into contributions arising from the hydrophobic effect and other considerations. These theories have been applied successfully to simpler surfactants where the hydrophilic (head) and hydrophobic (tail) regions of each surfactant are readily identified. Here, we demonstrate how surfactants of increased complexity (e.g., containing branching or rings) may also be modeled, using complementary computer simulations which allow more precise quantification of local hydration in surfactant monomer and micellar states. A novel method for head/tail identification is also demonstrated, which can be readily applied to any surfactants forming stable, simulated micelles.

COLL 106

Physical chemical properties of anionic/cationic surfactant mixtures

Ammanuel Mehreteab(1)*, ammanuel_mehreteab@colpal.com, 909 River Road, Piscataway New Jersey 08855-1343, United States . (1) Global Technology, Colgate Palmolive Co., Piscataway New Jersey 08855-1343, United States*

Typical straight chain anionic and cationic surfactants are usually incompatible in aqueous solutions and result in phase separation, significantly reducing each other's surfactant property. However, such incompatibility can be alleviated or even eliminated by changing the relative molar ratio and/or the structure of the individual surfactant molecules. The effect of molecular structure of the surfactants on their complexation and the physical chemical properties of their solution will be discussed.

COLL 107

Microemulsions from anionic and non-ionic surfactants: A novel HIPE structure

Heinz Hoffmann(1)*, heinz.hoffmann@nmbgmbh.de, Gottlieb-Keim-Str. 60, Bayreuth Germany D-95448, Germany ; L Wolf*(1)*. (1) Bayreuther Zentrum für Kolloide und Grenzflächen (BZKG) und BayKoll, Universität Bayreuth, Bayreuth Germany D-95448, Germany*

In contrast to the well established behavior for non-ionic surfactants microemulsions we have observed that microemulsions from mixtures of anionic and non-ionic surfactants show a different phase behavior. Such systems show only one optically isotropic channel which passes from the water side to the oil side. The second channel begins at the L_1/L_a phase boundary and ends in the middle of the phase diagram with equal amounts of water and oil. In addition a narrow liquid crystalline channel is observed for some of the systems that also passes continuously from the water side to the oil side. The isotropic channel has a bi-continuous morphology that is however different from the morphology in non-ionic microemulsions. With increasing oil content the morphology changes from the morphology of a L_3-phase to the morphology of a HIPE structure in which the small oil fraction of as little as 6 % forms the continuous foam structure and the water is enclosed inside the foam structure. With increasing oil content the viscosity in the channel passes over a high maximum at small oil fractions.

COLL 108

Green chemistry and sugars: a fruitful mixing for new amphiphilic molecules (or surfactants)

Isabelle Rico-Lattes(1)*, rico@chimie.ups-tlse.fr, 118 Route de Narbonne, Toulouse Toulouse Cedex 31062, France . (1) Laboratory of the IMRCP, UMRCNRS 5623, University of Toulouse, Toulouse Toulouse Cedex 31062, France*

Amphiphilic molecules (or surfactants) are key components of organized systems as emulsions and microemulsions. Depending of the applications of these systems, it is important to use an appropriate amphiphile for the process under consideration. In this context, surfactants based on sugars are very important, the sugar part bearing together hydrophilicity, biocompatibility and/or bioactivity. Moreover, considering the crucial importance of developing green chemistry, the use of renewable sugars is also an important goal. Generally, these derivatives from sugars are not readily synthesized as the starting sugars require protection. We present here routes, avoiding protection of the starting carbohydrates, to new series of surfactants derived from lactose and rhamnose, two natural sugars. All these compounds form aggregates in aqueous solutions with corresponding biological properties and vectorization ability (of drugs) depending of the nature of the aggregates. Moreover some of these compounds are now commercialized leading to new formulations of drugs for different cutaneous applications .

COLL 109

Effects of ion solvation on phase equilibrium and interfacial tension of liquid mixtures

Zhen-Gang Wang(1)*, zgw@caltech.edu, 1200 E. California Blvd., Pasadena CA 91125, United States ; Rui Wang*(1)*. (1) Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena CA 91125, United States*

We study the bulk thermodynamics and interfacial properties of electrolyte solution mixtures by accounting for electrostatic interaction, ion solvation and inhomogeneity in the dielectric medium in the mean-field framework. Difference in the solvation energy between the cations and anions is shown to give rise to local charge separation near the interface, and a finite Donnan potential between two coexisting solutions. The ion solvation affects the phase equilibrium of the solvent mixture, depending on the dielectric constants of the solvents, reflecting the competition between the solvation energy and translation entropy of the ions. Miscibility is decreased if both solvents have low dielectric constants, and is enhanced if both solvents have high dielectric constant. At the mean-field level, the ion distribution near the interface is determined by two competing effects: accumulation in the electrostatic double layer and depletion in a diffusive interface. The interfacial tension shows a non-monotonic dependence on the salt concentration: it increases linearly with the salt concentration at higher concentrations, and decreases approximately as the square root of the salt concentration for dilute solutions, reaching a minimum near 1mM. For a fixed cation type, the interfacial tension decreases as the size of anion increases. These results offer qualitative explanation within a unified framework for the long-known concentration and ion size effects on the interfacial tension of electrolyte solutions.

COLL 110

Association of telechelic hydrophobically-modified polymers in water: past, present , and future.

Françoise M Winnik[(1)]*, Francoise.winnik@umontreal.ca, BP 6128, Succursale centre ville, Montreal QC Quebec H3C 3J7, Canada . (1) Department of Chemistry and Faculty of Pharmacy, University of Montreal, Montreal QC Quebec H3C 3J7, Canada*

Amphiphilic polymers consisting of a water soluble bloc linked to two hydrophobic chains, known as associative polymers, are commercial additives employed in coatings, oil production and transportation, water treatment systems, as well as thickeners for food, cosmetics and health care products. All these applications exploit the unique self-assembly of associative polymers: in dilute solution, they assemble in the form of “flower” micelles consisting of a core containing the hydrophobic end-group surrounded by looped hydrated polymer chains. In concentrated solutions, flower micelles connect via bridging chains and form extensive networks leading to macroscopic gelation. Association parameters can be adjusted by subtle modifications of the composition and architecture of the polymers, as illustrated by results taken from our current studies of poly(N-isopropylacrylamides) and poly(2-isopropyl-2-oxazolines) bearing hydrophobic groups, such as n-octadecyl, cholesteryl, pyrenyl, or perfluoroalkyl.

COLL 111

Self-assembled templates for nanoparticle synthesis, surface modification, colloidal dispersion, and long-range organization

***Paschalis Alexandridis**[1], palexand@buffalo.edu, 304 Furnas Hall, Buffalo NY 14260-4200, United States . (1) Department of Chemical and Biological Engineering, University at Buffalo - The State University of New York (SUNY), Buffalo NY 14260-4200, United States*

Amphiphilic block copolymers (ABCs) can self-assemble in selective solvents to provide nanoscale environments of varying and tunable shape, dimensions, mobility, local polarity, concentration, and reactivity. The presentation will utilize findings from our research to highlight the interplay between ABC self-assembly fundamentals and ABC applications in (a) the surface-modification and organization of pre-formed nanoparticles, and (b) the size- and shape-controlled synthesis of nanoparticles inside these self-assembled templates.

COLL 112

Meniscus-Shear Particle Detachment in Foam-Based Cleaning of Silicon Wafers

***Clayton J Radke**[1], radke@berkeley.edu, 210 Gilman Hall, Berkeley CA 94720, United States . (1) Department of Chemical & Biomolecular Engineering, University of California, Berkeley CA 94720, United States*

We describe a new wet-cleaning method to remove 100-μm contaminant particles from silicon wafers using a foamed aqueous dispersion of fatty-acid solids. Contaminant removal is up to 100 % effective due to binary collision between suspended, insoluble fatty-acid platelets and adhered particles. Foam enhances the collision efficiency by increasing the wall shear rate and by constraining the platelet particles to flow parallel to the wall. Upon wafer immersion/withdrawal in a rectangular dip cell, contaminant removal along the wafer surface is nonuniform. To explain the observed nonuniform particle removal, we adopt a binary-collision model that demands a linear dependence of removal rate on surface shear rate. Hydrodynamic analysis shows that the wall shear rate on the wafer surface is strongly peaked in the meniscus just above the liquid-filled slot. Thus, the meniscus zone dominates the overall removal process. Agreement between experimental removal distribution and amount is excellent.

COLL 113

On adsorption barriers at liquid interfaces

***Dominique Langevin**[1], dominique.langevin@u-psud.fr, UMR CNRS 8502, Orsay Ile de France, France . (1) University Paris Sud 11, France*

It is generally assumed that adsorption of surface active agents at liquid interfaces is diffusion-controlled (when the liquids are at rest). Evidence is growing that most frequently, adsorption is slowed down by energetic barriers, electrostatic in the case of charged surface active agents. We will show examples of this situation with ionic surfactants and colloidal nanoparticles. In the case of electrostatic barriers, the classical

diffusion model of Ward and Tordai can be implemented, leading to a good agreement with the experiments. One missing feature is the determination of the time after which the barrier is overcome, which theory is not yet able to predict. We will show that this time is drastically affected by the presence of convection. We will also show important consequences of the presence of these barriers in various phenomena : withdrawal of thin films on plates (Landau-Levich problem), foaming and emulsification, and foam and emulsion coarsening.

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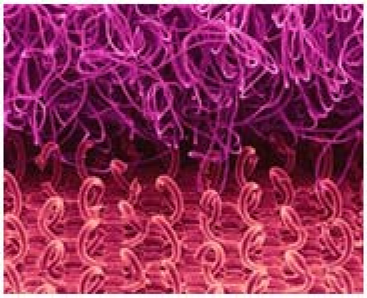
COLL 114

Streaming potentials near a rotating disk bearing a thick fuzzy surface layer

Dennis C. Prieve[(1)]*, dcprieve@cmu.edu, 5000 Forbes Ave., Pittsburgh PA 15213, United States ; Reza M. Rock*[(1)]*; Paul J. Sides*[(1)]*. (1) Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh PA 15213, United States*

In *Langmuir* **22**, 9765-9769 (2006) we present a model for predicting the streaming-potential profile near a rotating disk immersed in a dilute aqueous electrolyte. This geometry represents a promising new method for determining the zeta potential of flat surfaces (e.g. silicon wafers). We call this new technique ZetaSpin. Since then we have measured streaming potentials which are an order of magnitude larger than for flat surfaces when a 2 mm thick, highly porous sample (e.g. Velcro) is affixed to the rotating disk. A 20x view of Velcro appears below. In this paper, we present a simple model which predicts the enhanced streaming potential arising when a porous layer is affixed to the disk.



COLL 115

Self-organized fabrication of nanolens and lens-arrays: Raising the bar on dewetting of thin films

Ashutosh Sharma[(1)], *ashutos@iitk.ac.in, IIT Kanpur, Kanpur U.P. 208016, India ; Ankur Verma*[(1)]*. (1) Department of Chemical Engineering, Indian Institute of Technology, Kanpur, Kanpur U.P. 208016, India*

Inspired by the pioneering work of Ruckenstein and Jain on dewetting of thin liquid films **(**Faraday Trans. II 70, 132, 1974), this talk summarizes some of our recent results on the control of kinetics, shape, size and order of dewetted domains in thin (< 50 nm) polymer films. In particular, limitations on slow dewetting kinetics and relatively large (> 1 micron) length scales of the dewetting structures can be removed by dewetting induced under an optimal mix of water, a poor solvent and a good solvent. This room temperature technique reduces both the time and the length scales of dewetted structures by at least one order of magnitude. Further, physico-chemical modifications of the substrate and/or the film by the top-down techniques (e.g., e-beam, photolithography, nanoimprint) can be combined with dewetting for fabrication of ordered nanostructures. Such directed and enhanced dewetting of ultrathin (5 nm-50 nm) polymer films produce arrays of nano-lenses of tunable size and curvature, ~100 nm-10 microns, (*Advanced Materials* **22**, 5306, 2010), which are useful in applications ranging from the near-field imaging, amplification of weak optical signals, sub-wavelength lithography to fundamental studies of nano-optics.

COLL 116

Spreading dynamics of nanofluidic films on solids

Darsh Wasan[(1)], *wasan@iit.edu, 10 W. 33rd Street, Chicago Illinois 60616, United States ; Kirti Kondiparty*[(1)]*; Alex Nikolov*[(1)]*. (1) Department of Chemical and Biological Engineering, Illinois Institute of Technology, Chicago Illinois 60616, United States*

The wetting and spreading of nanofluids comprising of liquid suspensions of nanoparticles have significant technological applications. The nanofluid is confined in a three-phase: oil-nanofluid-soild contact region (e.g. the wedge film between an oil drop

and a solid surface). Here, we present our experimental observations and the results of a model for the dynamics of spreading of the nanofluid as a film on a solid surface based on the lubrication approach. The model takes into account the effect of the structural disjoining pressure gradient, based on the film energy isotherm determined from the data for the film-meniscus microscopic contact angle and the film viscosity of the structural nanofluidic film. The predictions of the continuum lubrication model for the dynamics of spreading are validated by experimentally determining the nanofluid spreading rate.

COLL 117

Thermodynamic theory of adsorption induced deformation

Alexnader V. Neimark(1)*, aneimark@rci.rutgers.edu, 98 Brett Road, Piscataway NJ 08854, United States . (1) Department of Chemical Engineering, Rutgers University, Piscataway NJ 08854, United States*

Phenomenon of adsorption-induced deformation attracted recently a considerable attention owing to its relevance to practical problems of mechanical stability and integrity of novel nanoporous materials and their adsorption properties. Guest molecules adsorbed in nanopores cause a substantial stress in the host matrix leading to its contraction or swelling depending on the specifics of host-guest interactions. Although various experimental manifestations of adsorption-induced deformation have been known for a long time, a rigorous theoretical description of this phenomenon is lacking. I will present a thermodynamic approach suggested for predicting adsorption stress and respective deformation in various microporous and mesoporous materials. A special attention will be paid to the enigmatic phenomenon of breathing of metal-organic frameworks and the deformation of coal during CO_2 sequestration at geological conditions.

COLL 118

Forces and stability in binary colloid dispersions

John Y. Walz(1)*, jywalz@vt.edu, Mail Code 0211, Blacksburg Virginia 24061, United States ; Shunxi Ji*(1)*; David Herman*(1)*. (1) Department of Chemical Engineering, Virginia Tech, Blacksburg Virginia 24061, United States*

The effect of charged nanoparticles on the interparticle force profile between two charged microparticles and the stability of a dispersion of such microparticles was measured. The particular system of interest was that of weakly-charged microparticles and highly-charged nanoparticles (same charge sign), which has been suggested as leading to the formation of nanoparticle halos (i.e., a halo of nanoparticles surrounding each microparticle). Such halos would create an enhanced repulsion between the microparticles and could potentially be sufficiently strong to stabilize an otherwise unstable microparticle dispersion. Our results indicate that significant deposition of the

nanoparticles still occurs in this system, leading to an increase in the electrostatic repulsive force between the microparticles. Nonetheless, this increased repulsion is still not strong enough to stabilize the microparticles against aggregation.

COLL 119

Trapping light in strongly coupled nanoparticle arrays by dark plasmons

Teri W. Odom[1]*, todom@northwestern.edu, 2145 Sheridan Road, Evanston IL 60208, United States . (1) Department of Chemistry and Materials Science and Engineering, Northwestern University, Evanston IL 60208, United States*

Plasmonic nanostructures can concentrate optical fields into highly confined, nanoscale volumes. These nano-localized optical fields are critical for optimizing plasmonic nanolasers, SERS, and white-light generation. However, the short lifetimes of the normally observed or “bright” plasmons preclude further enhancement of local fields because of the rapid depletion of the plasmon energy. To overcome this problem, we have found “dark” or subradiant plasmons that can be dynamically tuned in 2D arrays of large (> 100 nm) metal nanoparticles (NPs). At subradiant resonance wavelengths, the incident light is trapped in the NP array plane, and accumulated plasmon energy results in strong nano-localized fields on each NP. This new mechanism can potentially be exploited to enhance photochemical reactions or amplify molecular processes at molecule NP interfaces.

COLL 120

Probing charge separation dynamics at buried interfaces by a femtosecond electric field meter

Xiaoyang Zhu[1]*, zhu@cm.utexas.edu, 1 University Station, A5500, Austin TX 78712, United States . (1) Department of Chemistry & Biochemistry, University of Texas at Austin, Austin TX 78712, United States*

Charge separation at interfaces is a fundamental problem at the heart of a number of emerging scientific disciplines and technologies, such as solar photovoltaics, photocatalysis, and molecule or nanomaterial based electronics/optoelectronics. This lecture will discuss a “femtosecond electric field meter” based on time-resolved second harmonic generation (TR-SHG). SHG from an interface is highly sensitive to the presence of electric field and has been used to study metal-electrolyte interfaces and buried interfaces in field-effect transistors. We have recently developed this approach into a time-resolved probe of transient electric field established by exciton dissociation and charge-transfer across an interface. Interfacial charge separation establishes a transient electric field normal to the interface. In a four-wave mixing process, two optical fields of frequency v mix with the transient charge separation field (frequency $<< v$) to give a product signal with frequency at $\sim 2v$. The pump-induced change in SHG intensity is directly proportional to the transient electric field and this can be used to follow the

dynamics of charge separation at the interface. I will illustrate this approach in probing charge separation dynamics at both organic semiconductor and inorganic semiconductor/nano-material interfaces that of particular interest to next generation solar cells.

COLL 121

Destabilization of Ag Nanoislands on Ag(100) by Adsorbed Sulfur

Selena M. Russell(1)*, smrussel@iastate.edu, 331 Spedding Hall, Ames Iowa 50014, United States ; Mingmin Shen*(1)(2)*; Da-Jiang Liu*(3)*; Patricia A. Thiel*(1)(3)(2)(4)*. (1) Department of Chemistry, Iowa State University, Ames Iowa 50014, United States (2) Materials and Chemical Sciences Division, Fundamental and Computational Sciences Directorate, Pacific Northwest National Laboratory, Ames Iowa 50014, United States (3) Ames Laboratory - US DOE, Ames Iowa 50014, United States (4) Department of Materials Science & Engineering, Iowa State University, Ames Iowa 50014, United States*

Sulfur accelerates coarsening of Ag nanoislands on Ag(100) at 300 K, and this effect increases with sulfur coverage over a range spanning a few hundredths of a monolayer, to nearly 0.25 monolayers. We propose that acceleration in this system is strongly tied to sulfur adsorption close to kink and corner sites on island edges. Adsorption at four-fold hollow terrace sites is more favored energetically, so terrace sites are populated first, at low coverage. As coverage increases and the terrace sites become filled, some sulfur adsorbs at island edges. This leads to an increasing probability that a AgS_2 complex forms and detaches from step edges, which plausibly enhances the rate of coarsening.

COLL 122

Chemical dynamics at metal surfaces: The role of electronic excitations

John Tully(1)*, john.tully@yale.edu, PO Box 208107, New Haven Connecticut 06520-8107, United States . (1) Chemistry, Yale University, New Haven Connecticut 06520-8107, United States*

The adiabatic (Born-Oppenheimer) approximation underlies most of our understanding of chemical reaction dynamics. It has become clear, however, that nonadiabatic electronic transitions can sometimes play an important role, particularly in photo-initiated and highly energetic reactions. It is not as widely known that for reactions at metal surfaces, even at thermal energies, nonadiabatic behavior is the rule rather than the exception. Electron-hole pair transitions, charge transfer and hot-electron-induced motion can be dominant pathways for energy flow and can drastically alter reaction pathways. Recent experiments have demonstrated that molecular vibrational energy and reaction exothermicity can produce highly excited electrons, even resulting in electron emission. This talk will present progress toward a unified picture of

nonadiabatic dynamics at metal surfaces, with application to multi-quantum vibrational-to-electronic energy transfer in the scattering of nitric oxide from a gold surface.

COLL 123

Photo-induced excited state electron transfer at liquid/liquid interfaces

Ilan Benjamin(1)*, ilan@ucsc.edu, 1156 High St., Santa Cruz CA 95064, United States . (1) Department of Chemistry and Biochemistry, University of California, Santa Cruz CA 95064, United States*

Photoinduced Electron transfer at liquid interfaces is of fundamental importance to understanding basic biological and technological processes. We discuss our recent molecular-level modeling of electron transfer between excited coumarin molecules at the interface between water and dimethylaniline, in which the organic solvent acts as an electron donor. Calculated reorganization free energy and solvation dynamics are in good agreement with experiments carried out in the Eisenthal group. The effect of surface fluctuations on donor-acceptor electronic coupling will also be discussed.

COLL 124

Vibrational characterization of adsorbed phenantherenequinone on carbon onions

Daniela M Anjos(1)*, anjosdm@ornl.gov, Bethel Valley rd, Oak Ridge TN 37830, United States ; Alexander Kolesnikov*(1)*; Zili Wu*(1)*; John McDonough*(2)*; Yuri Gogotsi*(2)*; Kee S Han*(1)*; Edward W Hagaman*(1)*; Gilbert M Brown*(1)*; Steven H Overbury*(1)*. (1) Oak Ridge National Laboratory, United States (2) Drexel University, United States*

Proton-coupled electron transfer (PCET) reactions play an essential role in a broad range of energy conversion processes, as in many types of solar cells, fuel cells and others electrochemical devices. Attaching redox molecules to a conductive and defined surface is conveniently used to investigate PCET kinetics on fuid-solid interfaces. In this work, carbon nano-onions with high active surface area were modified by adsorption of phenanthrenequinone (PQ). Our goal is to understand the role of the structure of the adsorbed molecules on PCET reactions. The reversibility of the redox reaction of PQ on carbon and coverage of 0.1ML was determined by cyclic voltammetry. The nature of adsorption of this molecule on carbon was investigated by Raman, NMR and Inelastic Neutron Scattering (INS) and the features were compared with bulk PQ. Substantial differences between bulk and adsorbed PQ were identified in the very low (<440 cm^{-1}) vibrational modes only detected by INS.

COLL 125

Gold nanocages for theranostic applications

Younan Xia(1)*, xia@biomed.wustl.edu, One Brookings Drive, St. Louis MO 63130, United States . (1) Department of Biomedical Engineering, Washington University in St. Louis, St. Louis MO 63130, United States*

Gold nanocages can be prepared in relatively large quantities using a remarkably simple procedure based on the galvanic replacement between silver nanocubes and aqueous chloroauric acid. The surface plasmon resonance peaks of gold nanocages can be readily and precisely tuned to any wavelength in the near-infrared region by controlling their size and/or wall thickness. In this talk, I will present some of the most recent advances in the use of gold nanocages for a broad range of theranostic applications, including their use: *i*) as tracers for tracking by multi-photon luminescence; *ii*) as contrast agents for photoacoustic (PA) and mutimodal (PA/fluorescence) imaging; *iii*) as photothermal agents for the selective destruction of cancerous or diseased tissue; and *iv*) as drug delivery vehicles for controlled and localized release in response to external stimuli such as near-infrared radiation or high-intensity focused ultrasound (HIFU).

COLL 126

Single molecule plasmonic nanoparticle biosensors for molecular imaging of single live cells

X. Nancy Xu(1)*, xhxu@odu.edu, 4541 Hampton Blvd., Alfreind Chemistry Bldg., Norfolk VA 23529, United States ; Tao Huang*(1)*; Lauren M. Browning*(1)*; Prakash D. Nallathamby*(1)*. (1) Department of Chemistry and Biochemistry, Old Dominion University, Norfolk VA 23529, United States*

Single molecule detection (SMD) provides unique opportunities to probe distinctive functions of individual molecules in single live cells. At the cellular level, a small number of protein molecules (ligand-receptor) can induce significant cellular responses, emphasizing the importance of molecular detection of trace amounts of protein in single live cells. We have designed and synthesized single molecule nanoparticle optical biosensors (SMNOBS) and new imaging tools to mapping single ligand-receptor interactions on single live cells and tracking them to initiate signaling transduction pathways in single live cells. Unlike fluorescence probes, SMNOBS resists photodecomposition and blinking, allowing us to image single protein molecules and track their binding with single receptors on single live cells, and initiating cascade events in single live cells in real time. Updated results and experimental designs will be discussed in this presentation.

COLL 127

Using the eukaryotic intracellular space to template complex nanomaterials

Bryan Kaehr(1)(2)*, bjkaehr@sandia.gov, 1001 University Blvd. SE Ste - 100, Albuquerque NM 87106, United States ; Jason L. Townson*(2)*; C. Jeffrey Brinker*(1)(2)*. (1)*

Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque NM 87106, United States (2) Department of Chemical and Nuclear Engineering, University of New Mexico, Albuquerque NM 87106, United States

A long standing goal of nanoscience is the controlled fabrication of nanomaterials that mirror the function and complexity of biological materials. Using a “if you can't beat them join them” strategy, numerous routes to generate functional nanomaterials have been developed that simply employ biological structures (proteins, peptides, DNA, viruses, cells, plant tissues, etc.) as templates for inorganic materials resulting, in general, in encapsulation/coating of the template. Here we take a further step and show that the eukaryotic intercellular space can be used to template an inorganic silica imprint. Substrate bound and solution cultured mammalian cell lines (Aspc1, 4T1, 3T3, and others) were chemically fixed and subjected to silicification using a procedure that was shown to direct silica condensation to protein microstructures of diverse properties (e.g., isolectric point; *ACS Nano*, 2011, 5, 1401-1409). Whole cell morphology, both exterior and interior, appear preserved–potentially down to the molecular (imprinting) level following calcination (500C, 3hrs). Solution phase processing yields spherical microparticles with nano-scale features that mirror cellular structures (e.g., filopodia, nuclear pore complexes). Particles are shown to template an artificial lipid bilayer and be loaded with both small and macromolecular cargo. Further, we show retention of intrinsic enzyme (phosphatase, esterase, and others) activity in biocomposite (cell/silica) particles. This combination of retained activity and supported function (i.e., high thermal stability), post functionalization with cell-like membranes and cargo loading provides enormous opportunities to develop hierarchical nanomaterials for sensing, biocatalysis, and targeted delivery.

COLL 128

Graphite-coated magnetic nanoparticles as multimodal imaging probes and cooperative therapeutic agents for tumor cells

***Prasad Subramaniam**[(1)], prasads@rci.rutgers.edu, 610 Taylor Road, Piscataway New Jersey 08854, United States ; JoungKyu Park[(1)(2)]; Jongjin Jung[(1)]; Birju Shah[(1)]; Cheoljin Kim[(1)]; Jong Kyo Lee[(2)]; Jee-Hyun Cho[(3)]; Chulhyun Lee[(3)]; Ki-Bum Lee[(1)]. (1) Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway New Jersey 08854, United States (2) Center for Nano-Biofusion Research, Kore Research Institute of Chemical Technology, Piscataway New Jersey 08854, United States (3) Division of Magnetic Resonance Research, Korea Basic Science Institute, Ochang 363883, Republic of Korea*

An effective therapeutic approach against cancer requires the combination of several modalities such as chemotherapy, radiation, and hyperthermia. However, the development of multifunctional nanomaterial-based systems having combined therapeutic and molecular imaging capabilities with high sensitivity and selectivity is limited and not fully explored. This talk will focus on the synthesis of graphitic-carbon protected FeCo MNPs (FeCo/C NPs) using a novel hydrothermal approach, for the

targeted delivery of siRNAs for sensitizing tumor cells to hyperthermia and for the selective knockdown of a key oncogene expressed and implicated in brain cancer cells. In addition, the FeCo/C NPs could be used as multimodal imaging (MRI and Raman) agents, both *in vitro* and *in vivo.* Hence, a combined therapeutic approach using our multifunctional FeCo/C MNP constructs would facilitate the development of novel therapeutic systems aimed at the successful diagnosis and therapy of malignant cancers such as brain and breast tumors

COLL 129

FePt nanoparticles as Fe reservoir for controlled Fe release and tumor inhibition

Shouheng Sun(1)*, ssun@brown.edu, 324 Brook St, Providence Rhode Island 02912, United States . (1) Department of Chemistry, Brown University, Providence Rhode Island 02912, United States*

With the composition-dependent magnetism, FePt nanoparticles have been studied as a new nano-platform for magnetic resonance imaging and for magnetic fluid hyperthermia. Recently chemically disordered *face centered cubic* (*fcc*) FePt nanoparticles (NPs) were found to release Fe in a low pH environment. The released Fe catalyzes H_2O_2 decomposition into reactive oxygen species within cells, causing fast oxidation and deterioration of cellular membrane. Functionalized with *luteinizing hormone-releasing hormon* (*LHRH*) peptide via phospholipid, the *fcc*-FePt NPs can bind preferentially to the human ovarian cancer cell line (A2780) that over-expresses *LHRH receptors*, and exhibit high toxicity to these tumor cells. The work demonstrates that *fcc*-FePt NPs may function as a new type of agent for imaging and controlled cancer therapy.

COLL 130

Relevant Studies of Nanostructures for Bionanotechnology

Stanislaus Wong(1)(2)*, sswong@notes.cc.sunysb.edu, Department of Chemistry, Stony Brook New York, United States . (1) Chemistry, SUNY Stony Brook, United States (2) Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, United States*

The influence of ZnO nanoparticle morphology on its toxicity for marine diatoms was evaluated. Four ZnO nanoparticle motifs, possessing distinctive sizes and shapes, were synthesized without adding surfactants. Their effects on the growth of the marine diatoms, *Thalassiosira pseudonana, Chaetoceros gracilis*, and *Phaeodactylum tricornutum*, were determined in laboratory cultures. The overall results suggest that toxicity studies assessing the effects of nanoparticles on aquatic organisms need to consider both the dissolution of these particles and the cellular interaction of nanoparticle aggregates. In separate experiments, we have characterized biologically relevant heterostructures consisting of functionalized CdSe quantum dots (QDs) and

double-walled carbon nanotubes (DWNTs) and find evidence of efficient and unidirectional charge transfer. We find that the essential feature is the use of an active chemical linker between the two materials that also functions as an efficient hole trap.

COLL 131

How to achieve selective targeting by nanoparticles?

***Elena E. Dormidontova**(1), eed@po.cwru.edu, 2100 Adelbert Rd., Cleveland Ohio 44106, United States ; Shihu Wang(1). (1) Macromolecular Science and Engineering, Case Western Reserve University, Cleveland Ohio 44106, United States*

One of the important properties of polymer nanoparticles in drug/gene delivery is its capability of selective targeting of diseased cells with a high density of receptors. Achievement of selective targeting is often challenging, as there are multiple factors, including nanoparticle design, that influence the outcomes of nanoparticle targeting. Using computer simulations we analyze the influence of nanoparticle design on its efficiency in achieving selective targeting of cell surfaces with a high density of mobile receptors. We discuss how the selectivity of nanoparticle targeting can be enhanced by modifying the nanoparticle design: changing nanoparticle size, ligand valence, tether length or polydispersity. The obtained results provide practical guidance for designing polymer nanoparticles with high affinity and selectivity of cell targeting for diagnostic and therapeutic applications.

COLL 132

Electroless deposition of metal clusters on Tobacco Mosaic Virus

***Jing C. Zhou**(1), jingczhou@yahoo.com, 4555 Overlook Ave. SW, Wasington DC 20375, United States ; Mu-San Chen(1); Michael A. Bruckman(1); Carissa M. Soto(1); Banahalli R. Ratna(1); Bradley R. Spies(2); Tammie S. Confer(2). (1) Ceter for Bio/Molecular Science and Engineering, Naval Research Laboratory, Washington DC 20375, United States (2) Code 5711, Naval Research Laboratory, Washington DC 20375, United States*

We have synthesized straight and well-dispersed Cu nanorods using wild type TMV as a biotemplate. Using electroless deposition methods, Pd nanoparticles were synthesized *in situ* on the TMV biotemplate by reducing Pd^{2+} onto the virus surface. The Pd metal clusters served as catalytic sites for the reduction of Cu^{2+} to Cu^0. The thickness of the deposited Cu layer was controlled by adjusting the concentration of Cu^{2+} and ethylenediaminetetraacetic acid (EDTA) in the plating reaction. UV/vis spectroscopy was used to monitor the Cu deposition process in solution. TEM and SEM images showed that Cu nanorods were straight and uniform, 300 nm in length and 40 ± 10 nm in diameter. Additives were used to improve the dispersion of the nanorods in solution. The effective dispersion of the Cu-nanorods in solution was demonstrated by a

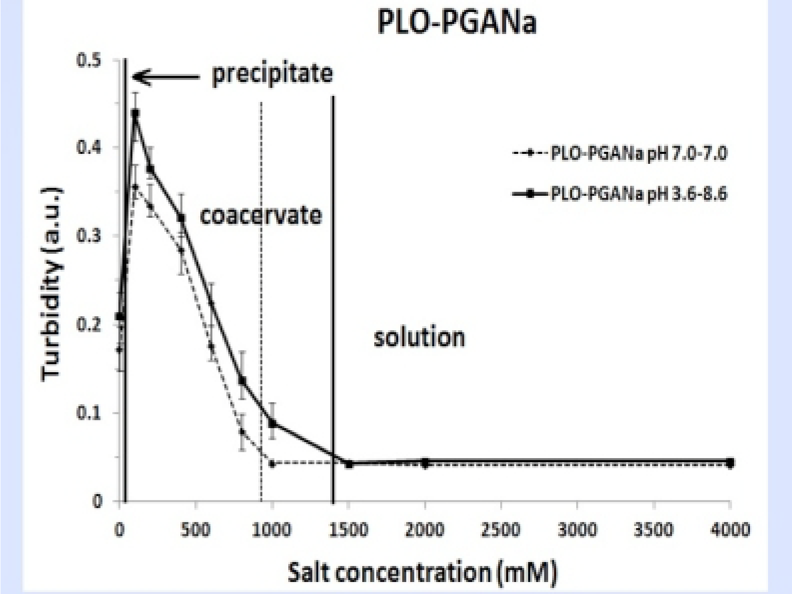
nanoparticle tracking system. The results agreed with SEM and TEM images of Cu nanorods dried on surfaces.

COLL 133

Phase behavior and self-assembly driven by polyelectrolyte complexation

Matthew Tirrell(1)*, mvtirrell@berkeley.edu, 306 Stanley Hall #1762, Berkeley CA 94720-1762, United States ; Dimitris Priftis*(1)*. (1) Department of Bioengineering, University of California, Berkeley, Berkeley CA 94801-1762, United States*

Oppositely charged polyelectrolyte molecules or blocks of copolymers can associate with one another in fluid phases known as complex coacervates. Bulk coacervates have very low interfacial tension with water and therefore produce very well-spread, uniform coatings and encapsulants. As blocks in copolymers, interactions between oppositely charged blocks can lead to new self-assembled structures such as micelles, vesicles and gels. Our work examines oppositely charged polypeptides as well-defined polymers and blocks to look at coacervate formation and self-assembly. We have mapped the phase behavior in detail for several polypeptide pairs as a function of molecular weight, degree of neutralization and other relevant variables. See for example



. In addition, we have made block copolymers including some of these same pairs to make a number of micellar structures. Our objective is a comprehensive understanding of phase behavior in multicomponent polyelectrolyte systems akin to our understanding of neutral polymer blends and block copolymers.

COLL 134

Responsive surfaces based on triblock terpolymer micelles with pH-sensitive interpolyelectrolyte complex shell

Julia Gensel^(1)^*, julia.gensel@uni-bayreuth.de, Universitätsstr. 30, Bayreuth Bavaria 95440, Germany ; Andreas Fery*(1)*; Eva Betthausen*(2)*; Axel H. E. Müller*(2)*; Fouzia Boulmedais*(3)*; Christoph Hasenöhrl*(1)*. (1) Department of Physical Chemistry II, University of Bayreuth, Bayreuth 95440, Germany (2) Department of Macromolecular Chemistry II, University of Bayreuth, Bayreuth 95440, Germany (3) Institut Charles Sadron, Centre National de la Recherche Scientifique, Strasbourg 67034, France*

We report on stimuli-responsive surfaces based on the surface immobilization of charged ABC terpolymer micelles of polybutadiene-*block*-poly(metylacrylic acid)-*block*-poly{[(2-methacryloyloxy)ethyl]trimethylammonium methylsulfate} (PB-PMAA-PDMAEMAq). In alkaline media, this triblock terpolymer forms core-shell-corona micelles with a hydrophobic PB-core, a PMAA/PDMAEMAq intramicellar interpolyelectrolyte complex (IPEC) shell, and a positively charged corona of uncomplexed PDMAEMAq. The micelles were directly adsorbed on charged silica creating a monolayer of individual micelles. Exposure of surface micelles to external stimuli (pH < pKa of PMAA) induces IPEC dissolution due to changes in ionization degree of the PMAA block resulting in the changed composition of the shell and the length of the corona. The pH-triggered response was shown to be reversible on the short-term scale while the long-term exposure to applied solution causes irreversible changes in morphology of micelles. In contrast, surface micelles with covalently cross-linked PB-cores show reversible response to pH-cycling on both, the short and the long-term scale.

COLL 135

Hysteresis during humidity-driven swelling/deswelling in a polyelectrolyte multilayer film

Kimberly E. Secrist(1)*, secriske@rose-hulman.edu, 5500 Wabash Ave, Terre Haute IN 47803, United States ; Adam J. Nolte*(1)*. (1) Department of Chemical Engineering, Rose-Hulman Institute of Technology, Terre Haute IN 47803, United States*

We demonstrate that polyelectrolyte multilayer (PEM) films comprised of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) created via spin-assisted layer-by-layer assembly (SA-LbL) display hysteretic swelling effects when exposed to changes in relative humidity. In situ reflectometry was used to monitor hysteresis in the film thickness during absorption and desorption humidity cycling of PEMs; the same technique revealed essentially no hysteretic swelling in films of either pure polyelectrolyte. We propose based on time-varying experiments that the structural response to humidity in PEMs has both short-time and long-time kinetic components. Furthermore, our results demonstrate that PEMs may retain a memory of past humidity exposure that will affect subsequent thickness measurements of the PEM. Overall, the data support the notion that swelling hysteresis may emerge in certain PEMs due to

frustration of structural relaxations within the electrostatic crosslink network. Our results suggest the importance of careful control over PEM drying and storage, as these procedures may exert a persistent effect on the film thickness and swellability.

COLL 136

Thermal properties of polyelectrolyte multilayers demonstrating linear or exponential growth

Ajay K Vidyasagar(1)*, ajayvsagar@mail.che.tamu.edu, 1M2A Brown Engineering Building, 3122 TAMU, College Station Texas 77843, United States ; Jodie L Lutkenhaus*(1)*. (1) Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station Texas 77843, United States*

Understanding thermal properties of polyelectrolyte multilayers and complexes remains a challenge. In this study, we present results on thermochemical properties of two model layer-by-layer assemblies. The LbL process involves alternate deposition of positively and negatively charged polymers resulting in interpenetrating networks of layers with fine structural control. Films may grow linearly or exponentially, and each type of growth is expected to give varied internal structure. Poly(allylamine hydrochloride)/poly(styrene sulfonate) (PAH/PSS) and poly(diallyldimethylammonium chloride)/poly(styrene sulfonate) (PDAC/PSS) multilayers assembled with and without added salt are selected as linear (or exponential) ``growth models.'' Calorimetry and ellipsometry were used to determine glass transition temperatures in both the dry and hydrated states of the polyelectrolyte multilayers. A standing hypothesis is that linear (or exponential) growth is observed for glassy (or rubbery) multilayers. The aim of this work is to understand the origin of linear versus exponential growth in polyelectrolyte multilayers with respect to their thermal properties.

COLL 137

Temperature- and pH-responsive clay-containing multilayers films

Aliaksandr Zhuk(1)*, azhuk@stevens.edu, 1 Castle Point on Hudson, Hoboken NJ 07030, United States ; Svetlana Sukhishvili*(1)*. (1) Department of Chemistry, Chemical Biology and Biomedical Engineering, Stevens Institute of Technology, Hoboken NJ 07030, United States*

We report on temperature- and pH-responsive clay/polymer layer-by-layer (LbL) films. Solely temperature-responsive films were constructed using hydrogen-bonding assembly between poly(N-isopropyl acrylamide) (PNIPAM) and montmorillonite clay nanosheets. Dual temperature- and pH-response was achieved by depositing and crosslinking hybrid clay/PNIPAM/polymethacrylic acid (PMAA)/PNIPAM LbL assemblies. Confocal laser microscopy showed that clay/PNIPAM films swelled up to ~ 15 times their dry thickness in low-salt solutions at 25^{o}C, and showed significant reversible deswelling at temperatures higher than PNIPAM's LCST of 32^{o}C, or in 0.3

Na_2SO_4 solutions at room temperature. At ambient temperature, the films showed a significant decrease in permeability of fluorescein-tagged dextrans of various molecular weights. Importantly, film permeability to dextran molecules could be reversibly controlled by temperature: permeability of clay-PNIPAM films to dextrans decreased at temperatures above PNIPAM's LCST. We also discuss synergistic effects of pH and temperature on film swelling and permeability properties using hybrid, dual-network clay/PNIPAM/PMAA/PNIPAM films.

COLL 138

Multilayers of Metal Nanoparticles with a Temperature-Responsive Polymer: Light-Controlled Swelling, Shape Anisotropy and Small Molecule Release

ZHICHEN ZHU(1)*, zzhu@stevens.edu, 1 Castle Point on Hudson, Hoboken NJ 07030, United States ; Svetlana Sukhishvili*(1)*. (1) Department of Chemistry, Chemical Biology and Biomedical Engineering, Stevens Institute of Technology, Hoboken NJ 07030, United States*

We use the layer-by-layer (LbL) approach to create light-responsive multilayers of poly(N-isopropylacryamide)-grafted Au nanoparticles (Au@PNIPAM) and linear polymers with controlled internal structure. “Nanoparticle bilayered” films with homogeneous internal structure were assembled through hydrogen bonding between Au@PNIPAM and polymethacrylic acid (PMAA). Hybrid films were constructed by depositing additional all-polymer strata of PMAA and PNIPAM homopolymer. All Au@PNIPAM-containing films showed reversible, light-induced swelling/deswelling transitions, and demonstrated light controlled diffusion of model dye molecules. The delivery rate of entrapped functional molecules could be conveniently controlled by the intensity of the incident radiation. Importantly, the internal structure of Au@PNIPAM-containing films determined the anisotropy of material size changes. While light-induced deswelling of “nanoparticle-bilayered' films was isotropic, hybrid multilayers deswelled anisotropically, and the degree of their swelling anisotropy could be controlled by the relative fractions of “nanoparticle” and polymer strata. These light-controlled, reversibly swelling materials might be useful in actuation, permeability control, and drug delivery applications.

COLL 139

Switching shape of hollow layer-by-layer hydrogel microcontainers

Veronika Kozlovskaya(1)*, vkozlovs@uab.edu, 901 14th Street South, CHEM 201, Birmingham Alabama 35294, United States ; William Higgins*(1)*; Jun Chen*(1)*; Eugenia Kharlampieva*(1)*. (1)*

We report on ultrathin poly(methacrylic acid) (PMAA) hydrogel capsules capable of switching from their cubical geometry to non-cubical in response to environmental changes. The capsules are produced from layer-by-layer (LbL) assembled poly(methacrylic acid)/poly(N-vinylpyrrolidone) capsules and fabricated as hollow hydrogel replicas of inorganic manganese carbonate particles via chemical crosslinking. The hydrogel PMAA capsules preserve the geometry of the initially cubical template at both acidic and basic conditions after core dissolution. However, the capsules change their initial shape followed by transformation into bulged structures at basic pH after EDTA treatment. Confocal microscopy, zeta-potential measurements, ellipsometry, and X-ray photoelectron spectroscopy were used to elucidate the mechanism of the pH-induced changes in the capsule geometry. The hydrogel capsules of pH-tunable geometry hold significant promise for controlled drug delivery.

COLL 140

How the speciation of metal ions changes upon adsorption to environmental Interfaces

Franz M Geiger[(1)]*, geigerf@chem.northwestern.edu, 2145 Sheridan Road, Evanston IL 60202, United States . (1) Department of Chemistry, Northwestern University, Evanston IL 60202, United States*

Metal cations can undergo changes in their speciation when they approach a charged surface from bulk aqueous solution. Here, we quantify this change using nonlinear optical methods, specifically resonantly enhanced second harmonic generation and the Eisenthal chi(3) method. Adsorption isotherms for the alkali earth metal cations, as well as uranyl and chromate, recorded as a function of electrolyte concentration show that speciation changes are favored if electrostatic repulsion within the electrical double layer can be minimized. The implications of our findings for environmental transport and fate of toxic metal ions are discussed in the context of the exponential sensitivity of the surface coverage of a metal ion on its charge.

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COLL 141

Effect of surface modification on TiO_2 phase transition temperature

Clifton C. Watkins[(1)]*, watki013@crimson.ua.edu, University of Alabama-Dept. of Chemistry, Box 870336, Tuscaloosa Alabama 35487-0336, United States ; Shane C. Street*[(1)]*; David E. Nikles*[(1)]*. (1) Department of Chemistry, University of Alabama, Tuscaloosa Alabama 35487, United States*

Titanium dioxide (TiO_2) powders, both pristine and surface modified, were prepared at room temperature by an acid-catalyzed sol-gel method. The surfaces were modified by organic and inorganic species with carboxylate, sulfonate, and phosphonate serving as the anchoring group for the respective samples. The powders were then annealed to determine the effect of surface modification on the phase transition temperature. The phase transition temperatures were measured via differential scanning calorimetery (DSC). Samples were characterized before and after annealing by SEM, EDS, FTIR, TEM, XRD, Raman, and UV-Vis for both physical and chemical properties.

COLL 142

Sorption of arsenate using CO_2 sequestered red mud

RAMESH CHANDRA SAHU$^{(1)}$*, rcsahu.chem@gmail.com, ROURKELA, ROURKELA ORISSA 769008, India . (1)*

In this preliminary laboratory study sorption of arsenate from the aqueous solutions using CO_2 sequestered red mud was investigated. The mechanisms involved in adsorption of arsenate ions on activated red mud were characterized by using AAS, XRD, SEM/EDX, FT-IR, and UV–vis. The maximum removal capacity was found at pH ~4. The adsorption kinetic studies revealed that adsorption process followed pseudo-second-order kinetics and equilibrates within 24 h. FT-IR spectra of activated red mud before and after adsorption reveals the strong bonding of carcinogenic arsenate to the adsorbent.

COLL 143

Mechanistic studies on self-assembly of natural organic material

Lee W Hoffman$^{(1)}$*, lee.hoffman@sdstate.edu, Avera Health Center, Brookings South Dakota 57007, United States ; Gabriela Chilom*$^{(1)}$*; Nathan L Netzer*$^{(2)}$*; Chaoyang Jiang*$^{(2)}$*; James A Rice*$^{(1)}$*; Chaoyang Jiang*$^{(2)}$*. (1) Chemistry & Biochemistry, South Dakota State University, Brookings SD 57007, United States (2) Chemistry, University of South Dakota, Vermillion South Dakota 57069, United States*

Humic acids are molecular aggregates representing a major component of natural organic matter. Recent studies have shown the components (non-amphiphilic, amphiphilic, and lipid-like) making up these aggregates play a significant role in the self-assembly of humic acid. In this study, component interactions were further analyzed using surface and interfacial techniques including Langmuir-Blodgett (LB) isotherms, AFM, and SEM. Amphiphilic and lipid components as well as the self–assembled composite formed from them were separated from environmental samples with different chemical characteristics. “Synthetic” composite samples were also prepared by mixing the components in various ratios. Characterization of these individual components and their 'synthetic' constructs will be described. LB data suggests different phase transitions for each component and compressibility/aggregation of all three components

of humic acid. SEM data of LB films supported isotherm data indicating aggregation at monolayer coverage. AFM analysis allowed different phases present for each component adsorbed on a flat surface.

COLL 144

Towards predicting the environmental persistence and transformations of silver nanoparticles

Robert I MacCuspie(1)*, robert.maccuspie@nist.gov, 100 Bureau Drive, Mailstop 8520, Gaithersburg MD 20899-8520, United States ; Justin M Gorham*(1)*; Stephanie L Chinnapongse*(1)*; R David Holbrook*(1)*; D Howard Fairbrother*(2)*; Nelson Akaige*(3)*; Divina A Navarro*(4)*; Diana S Aga*(4)*; Sarbajit Banerjee*(4)*; Mary Sohn*(3)*; Virender K Sharma*(3)*; Vincent A Hackley*(1)*. (1) Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg MD 20899, United States (2) Department of Chemistry, Johns Hopkins University, Baltimore MD 21218, United States (3) Department of Chemistry, Florida Institute of Technology, Melbourne FL 32901, United States (4) Department of Chemistry, University at Buffalo, The State University of New York, Buffalo NY 14260, United States*

Assessing the potential risks silver nanoparticles pose on environmental health and safety (EHS) has attracted much attention in recent years. Understanding and predicting how silver nanoparticles might behave if released into the environment would be a useful guide to both nanoEHS researchers and science-based regulatory policy. This talk will summarize recent findings on how the silver nanoparticle surface interacts and reacts with environmental waters, with the aim of better predicting what environmental compartments might be at greatest risk. The three main results include: 1) role of dynamic adsorption of natural organic matter in the mechanisms of colloidal stability in actual and reconstituted surface waters, 2) a potential mechanism for environmentally-formed silver nanoparticles by humic acids reducing silver ions, and 3) solar UV light-induced photo-oxidation of silver nanoparticle surfaces.

COLL 145

Effect of coadsorbent properties on the photovoltaic performance of dye-sensitized solar cells

Jongchul Lim(1)*, polymn@postech.ac.kr, San 31, Hyoja-dong,, Pohang Kyuongbuk, Republic of Korea ; Inyoung Song*(1)*; Young Soo Kwon*(1)*; Sung-Hae Park*(1)*; Taiho Park*(1)*. (1) Department of Chemical engineering, Pohang University of Science and Technology, Republic of Korea*

We report that the nature of the coadsorbent end groups anchored to the TiO_2 surface strongly influences the interfacial properties of dye-sensitized solar cells (DSSCs). Additionally, coadsorbent sensitization of nanoporous TiO_2 films plays an important role in organizing and orienting the adsorbed dyes. The stearic acid (SA) as coadsorbent,

which has a low dipole moment and high solubility, retards the rate of dye adsorption via a competitive anchoring process on the TiO_2 layer, thereby increasing the surface concentration of strongly bound dye on the TiO_2 surface. As a result, both short circuit current density and the power conversion efficiency were improved by 25% (11.4 to 14.2 mA/cm^2 and 5.9 to 7.4%, respectively, without and with the SA coadsorbent), even for much lower coverage of the dye. We are currently systematically optimizing the adsorption conditions and structures of the coadsorbents to further reduce cost and facilitate the preparation of DSSCs

COLL 146

Mechanistic understanding of interactions between quaternary ammonium cations and cellulose

JeongKyung Kim(1)*, jeongkyung.kim@kcc.com, 416-1, Gongse-dong, GiHeung-gu, Yongln-si GyeongGi-do, Republic of Korea ; YoonHee Cho*(1)*; Marsha Forthofer*(2)*; Keyur Desai*(2)*; Denise Taylor*(2)*. (1) Kimberly-Clark Innovation Center Asia, GiHeung GyeongGi-do, Republic of Korea (2) Kimberly-Clark Corporation, Roswell GA 30076, United States*

Quaternary ammonium cations are disinfectants commonly used with sanitizing wipe products, such as hard surface and hand sanitizing wipes. Quats are adsorbed by cellulosic materials and as a result the concentration of quats needed to effectively sanitize is not delivered to the surface. Today, products avoid this issue by using 100% synthetic wipe substrates, by “over quatting” or using an alcohol-based formulation. Understanding the mechanisms of interaction between quats and cellulose would allow for cellulose-based sanitization products. These products could provide advantages such as lower cost, environmentally friendly, higher absorbency, and/or improved wiping performance. Adsorption isotherms were generated to understand the adsorption mechanism of quats onto cellulose substrates. Data obtained for the adsorption of quats onto cellulose seemed to best fit the Langmuir adsorption isotherm. Cellulose materials with different degrees of crystallinity and chemical modifications were studied for their quat binding characteristics and a correlation with binding efficiencies was shown. Increasing the degree of crystallinity in the cellulose led to a decrease in quat adsorption whereas increasing the degree of substitution led to a decrease in quat adsorption. The alkyl chain length of the quats used for the study also affected the adsorption behavior. Results from the mechanistic studies will be presented.

COLL 147

Calcite Growth-Rate Inhibition by Fulvic Acid and Magnesium Ion at 25 C, pH = 8.5, and Calcite Supersaturation (IAP/K_{sp}) = 4.5: Potential Reduction of Calcite Formation Rate in Marine Calcifying Organisms

Michael M Reddy[(1)]*, mmreddy@usgs.gov, Po Box 25046, MS 406, Denver Colorado 80225, United States . (1) National Research Program, US Geological Survey, Water Mission Area, Denver Colorado 80225, United States*

Calcite seeded crystallization rates, at constant solution composition and calcite supersaturation, are measured in the presence and absence of a natural organic acid (fulvic acid, FA, 0.5 mg/L), in the presence and absence of magnesium ion (Mg, 10-4 M), and in the presence of both FA and Mg. FA and Mg reduce calcite crystal-growth rates by 47 % and 38 %, respectively, compared to control experiments containing no added growth-rate inhibitor. Growth-rate experiments in the presence of both FA and Mg reduce the calcite growth rate to 5 % of the control rate. In combination, FA and Mg interactions in solution and/or on the growing calcite surface dramatically decrease calcite growth rates. This result suggests that FA and Mg concentrations at biocalcification sites in marine calcifying organisms mediate calcite crystallization rates. FA and Mg influence rate-dependent metal-ion partitioning and must be considered when using carbonate trace-metal records as paleoclimate proxies.

COLL 148

Azide functional monolayer grafted to Germanium surface: an initiator to study kinetics of CuAAC interfacial reaction

Shuo Zhang[(1)]*, sz2257@columbia.edu, Mudd 385, 500 West, 120 street, New York NY 10027, United States ; Jeffrey T. Koberstein*[(1)]*. (1) Department of Chemical Engineering, Columbia University, New York NY 10027, United States*

11-bromoundecyltrichlorosilanes are shown to react readily with UV-ozone treated Germanium surfaces at low temperature and then substituted by sodium azide to form a high-quality monolayer. The resulting films are characterized by contact angle analysis (CAA), X-ray photoelectron spectroscopy (XPS), attenuated total reflectance infrared spectroscopy (ATR-IR) and ellipsometry. In addition, two models,a molecular model and a substrate-overlayer model, are built to confirm the existence of the monolayer. In presence of copper(I) catalyst these azide-modified surfaces are shown to react rapidly and quantitatively with terminal 5-chloro-pentyne forming 1,4-triazoles, via “click chemistry”. Time-resolved ATR-IR measurements have enabled us to follow the disappearance of azide on the surface, thus measuring the rate of the surface “click” reaction. Under optimal conditions, this well-behaved azide-dependent first-order reaction takes place with a rate constant of 0.00043 s^{-1}.

COLL 149

Influence of crosslinking on gas barrier behavior of polymer multilayers

You-Hao Yang[(1)]*, yangyouhao@gmail.com, 401 Lincoln Dr., Apt. 53, College Station Texas 77840, United States ; Merid Haile*[(2)]*; Jaime C Grunlan*[(1)(3)]*. (1) Department of Chemical Engineering, Texas A&M University, College Station Texas 77843, United*

States (2) Department of Chemistry, Texas A&M University, College Station Texas 77843, United States (3) Department of Mechanical Engineering, Texas A&M University, College Station Texas 77843, United States

Layer-by-layer assemblies of cationic polyethylenimine (PEI) and anionic poly (acrylic acid) (PAA) were crosslinked in an effort to improve their gas barrier behavior and reduce moisture sensitivity. Glutaraldehyde (GA), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide (EDC) and thermal crosslinking were compared with regard to film thickness, microstructure and oxygen permeability. Crosslinking, in general, was found to increase multilayer density and improve barrier at 100% RH. This relatively simple recipe may be of use for a variety of packaging applications, including flexible electronics that require high flexibility and transparency.

COLL 150

Colloidal silica-based flame retardant thin film on cotton and PET fabric

Galina Laufer(1)*, galina2405@tamu.edu, 3123 TAMU, College Station TX, United States ; Federico Carosio*(2)*; Jaime Grunlan*(1)*; Rico Martinez*(1)*. (1) Department of Mechanical Engineering, Texas A&M University, United States (2) Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Italy*

Thin films of colloidal silica were deposited on fabrics via layer-by-layer (LbL) assembly to reduce fabric flammability. Negatively-charged silica nanoparticles of two different sizes (8 and 27 nm) were paired with either positively charged silica (12 nm) for PET fabric or cationic polyethylenimine (PEI) for cotton. Micro combustion calorimetry confirmed that all coated fabrics exhibited a reduced peak heat release rate relative to the uncoated control, with 10 bilayers of PEI and 8 nm silica being the most effective for cotton and 10 bilayers of all-silica coating for PET fabric. These results demonstrate that LbL assembly is a useful technique that is able to dramatically improve flame retardant properties of complex substrates with relatively few bilayers.

COLL 151

Influence of clay suspension concentration on clay-polymer thin films properties

Morgan A Priolo(1)*, mapriolo25@tamu.edu, 3123 TAMU, College Station TX 77843, United States ; Kevin M Holder*(2)*; Daniel Gamboa*(1)*; Jaime C Grunlan*(1)*. (1) Department of Mechanical Engineering, Texas A&M University, College Station TX 77843, United States (2) Department of Chemistry, Texas A&M University, College Station TX 77843, United States*

Thin films of anionic clay and cationic polyethylenimine (PEI) were produced by alternately dipping a substrate into dilute aqueous mixtures containing each ingredient. Clay concentration in the aqueous deposition suspension was altered to analyze its influence on gas barrier and mechanical properties. Films created with 20 bilayers of

PEI with 2.0 wt. % clay exhibited enhanced mechanical and barrier behavior. After 24 clay-polymer layers were deposited onto 7-mil PET, the resulting transparent film exhibits an oxygen transmission rate below the detection limit of commercial instrumentation (< 0.005 cm^{-3} $m^{-2}day^{-1}$). This level of oxygen barrier (unprecedented for a clay-filled polymer composite) is believed to be due to a nano brick wall structure, comprised of completely exfoliated clay bricks in polymeric mortar. With a thickness below 120 nm and optical transparency greater than 95%, this thin film composite is a good candidate for foil replacement in food and flexible electronics packaging.

COLL 152

Influences of surfactants and chelating agent on the formation of manganese oxide nanoparticles through coprecipitation method

Jun-Hwan Park(1)*, junhpark@hanyang.ac.kr, 216 Adv. Mater. and Chem. Eng. Bldg., 17 Haengdang-dong, Seongdong-gu, Seoul Seoul 133-791, Republic of Korea ; Boseong Kwon*(1)*; Seong-Geun Oh*(1)*. (1) Department of Chemical Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Republic of Korea*

Manganese oxide nanoparticles were synthesized through coprecipitation method using various surfactants including Tween 20, cetyltrimethylammonium bromide (CTAB), and sodium dodecyl sulfate (SDS). First, the phase I of manganese source with surfactant and the phase II of precipitation agent with surfactant were prepared separately. Manganese nitrate hexahydrate and ammonium hydroxide were used as a manganese salt and a precipitation agent, respectively. Secondly, the phase II was added into the phase I and $Mn(OH)_2$ was formed. Also, ammonium oxalate monohydrate (AOM) was used as a chelating agent to control the activity of manganese cations and the precipitation of $Mn(OH)_2$. Morphology and size of particles were controlled with the variations of concentrations of surfactant and AOM, reaction time, and chelation time. Finally, manganese oxide nanoparticles were obtained by the calcination of $Mn(OH)_2$ at 700 °C for 6 hours. The formations of particles were investigated by FE-SEM, HR-TEM, XRD, PSA, and BET.

COLL 153

Correcting for a density distribution: particle size analysis of core-shell nanocomposite particles using disc centrifuge photosedimentometry

Lee A Fielding(1)*, l.a.fielding@sheffield.ac.uk, Dainton Building, Brook Hill, Sheffield South Yorkshire S3 7HF, United Kingdom ; Patrick W Fowler*(1)*; Steven P Armes*(1)*. (1) Department of Chemistry, The University of Sheffield, Sheffield S3 7HF, United Kingdom*

Core-shell colloidal polystyrene/silica nanocomposite particles with mean diameters of approximately 300 nm can readily be prepared by aqueous emulsion polymerization.[1] Electron microscopy studies have previously confirmed that these nanocomposite particles consist of a polystyrene core and a particulate shell that comprises a well-defined monolayer of 19 nm silica particles. Given this core-shell morphology, small 'core-shell' polystyrene/silica nanocomposite particles necessarily have higher densities than large 'core-shell' particles due to the higher silica mass fraction in the former case. Thus, for nanocomposite particles with finite polydispersity, a *density distribution* is expected in addition to a size distribution. This hypothesis has been confirmed by analytical ultracentrifugation, which was used to determine a particle density range of 1.17 to 1.23 g cm^{-3} for a specific polystyrene/silica nanocomposite sample. Disc centrifuge photosedimentometry (DCP) is a popular high resolution particle sizing technique that traditionally requires a single value of the particle density as an input parameter. In the context of this technique, the inherent density distribution of these nanocomposite particles is shown to lead to an artificial narrowing of the weight-average particle size distribution. This is likely to be a general problem for core-shell type particles where there is a significant difference in density between the core and shell components. Furthermore, the corrected weight-average particle size distribution can be readily recalculated from the DCP raw data by allowing for the known particle density distribution.

1. A. Schmid, S. P. Armes, C. A. P. Leite and F. Galembeck, *Langmuir*, 2009, **25**, 2486-2494.

COLL 154

Synthesis of various ZnO morphologies by using surfactants and oxidizing agents via hydrothermal method

Kyeongmuk Choi[(1)]*, idestar@lycos.co.kr, 216 Adv. Mater. and Chem. Eng. Bldg., 17 Haengdang-dong, Seongdong-gu, Seoul Seoul 133-791, Republic of Korea ; Taeho Kang*[(1)]*; Seong-Geun Oh*[(1)]*. (1) Department of Chemical Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Republic of Korea*

ZnO has been applied in optics, optoelectronics, and sensors because of its direct wide band gap energy of 3.37 eV at room temperature. In this study, ZnO particles with various morphologies were synthesized by hydrothermal method at 120 °C using surfactants and oxidizing agents. Zinc chloride ($ZnCl_2$) and sodium hydroxide (NaOH) were employed as the starting materials. Short rod-like or plate-like ZnO were prepared when sodium dodecyl sulfate (SDS) and isobutyl alcohol (isobutanol) were used as a surfactant and a co-surfactant, respectively. On the contrary, the length of ZnO rods was increased with the addition of oxidizing agents such as hydrogen peroxide (H_2O_2) and potassium permanganate ($KMnO_4$). The synthesized particles were characterized by FE-SEM, TEM, and XRD. Also, the effects of ZnO morphologies on the PL spectra were investigated.

COLL 155

Podocytes as specific targets for cyclo(RGDfC) modified nanoparticles

Klaus Pollinger(1)*, Klaus.Pollinger@chemie.uni-regensburg.de, Universitaetsstrasse 31, Regensburg Bavaria 93053, Germany ; Miriam Breunig*(1)*; Joerg Tessmar*(1)*; Ralph Witzgall*(2)*; Achim Goepferich*(1)*. (1) Department of Pharmaceutical Technology, University of Regensburg, Regensburg 93053, Germany (2) Department of Molecular and Cellular Anatomy, University of Regensburg, Regensburg 93053, Germany*

It is a well-accepted fact, that nanoparticles such as quantum dots (Qdots) can undergo renal filtration. Therefore it was of great interest to investigate, if it is possible to target Qdots to certain kidney cells by specific receptor-ligand interactions. In this study podocytes, which constitute an integral part of the renal filter, were investigated for nanoparticle binding and internalization. Therefore Qdots were modified with cyclo(RGDfC) to allow for binding to the αVβ3 integrin receptor expressed on podocytes. Flow cytometry experiments with isolated podocytes revealed a strong αVβ3 mediated binding of Qdots to the cells, which could be blocked using an excess of free cyclo(RGDfC). Confocal microscopy furthermore gave evidence that the targeted Qdots are located in endocytotic structures inside the cells. Further experiments with whole glomeruli, containing podocytes in their natural environment, additionally proved a podocyte associated accumulation of Qdots. These results indicate that nanoparticles can be actively targeted to individual kidney cell species.

COLL 156

Covalent grafting of antibacterial polymers onto PVC surfaces

Issam Mtimet(1)*, issam.mtimet@insa-rouen.fr, avenue de l[apos]université, Rouen haute normandie 76100, France ; Jérôme LAFARGE*(1)*; Nasreddine KEBIR*(1)*; Fabrice BUREL*(1)*. (1) Chemestry, INSA de Rouen, laboratory of Polymer Biopolymer Surface (PBS), UMR 6270 CNRS, Rouen 76100, France*

Polymers are a class of materials which are very used in the biomedical field. However, their applications are limited by the bacterial infection phenomenon which is a very serious problem. Among the strategies developed to prevent bacterial attachment onto surfaces, the covalent grafting of bioactive polymers is considered as a very recent strategy and a promising solution. In this work, the objective is to graft several antibacterial copolymers onto surfaces of PVC, which is one of the most used materials in the biomedical field. The chemical pathway consisted on click addition between azide groups and carbon-carbon triple bond. PVC surfaces as well as a serial of antibacterial copolymers bearing these two anchorage groups were successfully prepared and characterized. Two strategies in terms of antibacterial properties were envisaged, namely the bactericidal and the anti-adhesive (bacteriophobe) ones.

COLL 157

Photocurrent generation on phospholipid/alkanethiol hybrid bilayer membranes

Hong Xie(1)*, hzx0001@auburn.edu, 179 Chemistry Bldg, Auburn AL, United States ; Wei Zhan*(1)*. (1) Department of Chemistry and Biochemistry, Auburn University, Auburn AL 36849, United States*

A new photocurrent generation system based on phospholipid/alkanethiol hybrid bilayers in aqueous media is reported. First, a self-assembled monolayers (SAM) of alkanethiol is formed on gold, and separately, liposomes containing either photoactive fullerenes or ruthenium tris(bipyridyl)($Ru(bpy)_3^{2+}$) complexes are spread on top of SAM to form hybrid bilayer membranes (HBMs). The formed hybrid structures are characterized by quartz crystal microbalance, UV-vis spectroscopy, cyclic voltammetry and impedance analysis. Either anodic or cathodic photocurrent generation can be obtained, when ascorbate (anodic) or methyl violgen/oxygen (cathodic) is used as a sacrificial electron donor/acceptor, respectively.

COLL 158

Thermal analysis and FTIR spectroscopy studies of CTAB on silica

Tan Zhang(1)*, tan.zhang@okstate.edu, 107 Physical Science Building, Stillwater Oklahoma 74078, United States ; Gu Xu*(2)*; Frank D Blum*(1)*. (1) Department of Chemistry, Oklahoma State University, Stillwater Oklahoma 74078, United States (2) Brewer Science Inc., Rolla Missouri 65401, United States*

Temperature modulated differential scanning calorimetry (TMDSC), thermogravimetric analysis (TGA) and fourier transform infrared spectroscopy (FTIR) were used to probe the structure of cetyltrimethylamonium bromide (CTAB) in the presence of fumed silica nano-particles. It is found that two types of CTAB molecules were present in the adsorbed samples, which we interpret as due to tightly-bound and loosely-bound bulk-like structures. The silica surface is found to affect both melting and freezing of the tails of CTAB and their lateral interactions. Higher decomposition temperatures were also observed for the surface surfactant. The enthalpy change for CTAB during the melting and freezing indicates that the CTAB undergoes a significant structural transition from a surface dominated structure to bulk with increased adsorbed amount on surface. TMDSC, TGA and FTIR were important tools in understanding the effects of the surface on the surfactant structures.

COLL 159

Binding studies of C-reactive protein to lipid coated nanoparticles utilizing fluorescence techniques

Reid E Messersmith(1)*, reid.messersmith@ucdenver.edu, Campus Box 194, PO Box 173364, Denver CO 80217-3364, United States ; Scott M Reed*(1)*; Min S Wang*(1)*. (1)*

Department of Chemistry, University of Colorado Denver, Denver CO 80217, United States

C-reactive protein (CRP) is an acute phase protein that binds to C1q and activates the complement pathway. CRP exists in blood serum in a pentameric form (pCRP), but upon binding to phosphocholine residues on damaged cell membranes can dissociate into a biologically active form modified CRP. Phosphatidylcholine coated gold nanoparticles (PC-AuNP) were synthesized as membrane mimics so the effects of membrane structure on CRP binding could be observed. Stable PC-AuNP were created with varying alkanethiols that anchor the lipid layer to the gold nanoparticle (AuNP). A mixed bilayer containing phosphatidylcholine and cholesterol was utilized to coat the AuNP and sodium oleate was initially added to prevented aggregation. Cyanide stability tests were performed to confirm a full coverage of the lipid layer around the AuNP. Conformational changes in CRP on binding to PC-AuNP were studied by the intrinsic tryptophan fluorescence of the protein, hydrophobic fluorophores and gel assays.

COLL 160

Plasmonic and SERS properties for Ag@Au and Au@Ag core@shell nanoparticles as a function of the size and structure

***Anh Thi Ngoc Dao**[(1)], ngocanh@jaist.ac.jp, 1-1 Asahidai, Nomi Ishikawa 923-1292, Japan ; Thuy T.B. Nguyen[(1)]; Cheshta Shankar[(1)]; Derrick M. Mott[(1)]; Shinya Maenosono[(1)]. (1) Department of Materials Science, Japan Advanced Institute of Science and Technology, Nomi Ishikawa 923-1292, Japan*

In the field of bio-molecular diagnostics and sensing, gold and silver nanoparticles have received much attention because of the novel optical and SERS properties. However, in the current synthetic approaches, there are still many challenges in the formation of core@shell structures (i.e. Ag@Au or Au@Ag). The current class of core@shell particles typically has non-controllable size, composition or structure, which limits the ability to manipulate the resulting optical and SERS properties. In this study, nanoparticles with monodisperse size, structure and composition provide the ability for correlating the optical and sensing properties. This poster focuses on our recent advances and results in the study of core@shell nanoparticles with Ag@Au and Au@Ag structure and the subsequent correlation of the particle structural characteristics to the resulting optical/SERS properties. In addition the particle stability is studied in presence of different electrolytes. The results are discussed in terms of UV-Vis, TEM, HR-TEM, EDS, XPS, and HAADF-STEM.

COLL 161

Tracking the role of OH in the plasma-based synthesis of composite nanomaterials

Jeffrey C. Shearer(1)*, jeff.shearer@colostate.edu, 200 W. Lake Street, Campus Delivery 1872, Fort Collins CO 80523-1872, United States ; Ellen R. Fisher*(1)*. (1) Department of Chemistry, Colorado State University, Fort Collins CO 80523-1872, United States*

The use of composite magnetic nanomaterials in biological applications (i.e. site specific drug delivery, MRI contrast agents) has grown rapidly in recent years. The presence of surface functional groups is essential for many of these applications to be viable. Plasma enhanced chemical vapor deposition effectively deposits conformal thin films onto Fe_2O_3 nanoparticles, thereby creating composite materials with specific surface functionality. The focus here is on the incorporation of OH into films deposited using allyl alcohol plasmas. Surface characterization studies show that film characteristics, including OH incorporation, are highly dependent on the duty cycle of the plasma. Additional studies of SiO_2/Fe_2O_3 composite nanoparticles explore the contributions of gas-phase OH radicals to the deposition process. Scatter coefficients and gas-phase density measurements derived from our imaging of radicals interacting with surfaces (IRIS) technique provides additional insight on the molecular-level chemistry occurring at the interface between gaseous plasma species and nanoparticle substrates.

COLL 162

A fundamental study of the adsorption of POSS-silanols onto model stone surfaces

Bradley J. Sparks(1)*, bradsparks08@gmail.com, 118 College Dr. #5050, Hattiesburg MS 39406, United States ; Derek L. Patton*(1)*. (1) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg MS 39406, United States*

In this study, we aim to gain a fundamental understanding of the adsorption of POSS-silanols onto model oxide and carbonate surfaces. POSS-silanols are incompletely condensed frameworks possessing a hybrid inorganic–organic, three-dimensional structure and containing one–to–four silanol (Si-OH) groups. The adsorption of the silanols will be monitored using ellipsometry, where the thickness can of the adsorbed molecule will be measured. Contact angle goniometry will also be used to study the surface energy of the substrate before and after adsorption. Quartz crystal microbalance will also used to measure the mass and adsorption kinetics of POSS-silanols that adsorb to the surface using the Saeurbrey Equation, where the change in frequency can be directly related to the change in mass on the surface of the crystal.

COLL 163

Plasma enhanced chemical vapor deposition of mixed hydrocarbon/fluorocarbon thin films with a compositional gradient

***Brendan Tompkins**[1], Brendan.Tompkins@colostate.edu, 200 W. Lake St., Fort Collins Colorado 80523-1872, United States ; Ellen R. Fisher[1]. (1) Department of Chemistry, Colorado State University, Fort Collins Colorado 80523-1872, United States*

Thin organic films are important to a broad range of applications, such as low-k dielectrics, passivating films, and adhesion interlayers. We have recently developed a PECVD system for preparing mixed hydrocarbon/fluorocarbon films with a compositional gradient as a function of film depth. Films were deposited from an inductively coupled rf plasma utilizing a pre-programmed variable mixture of H_2 and C_3F_8 or C_3F_6 as feedgases. Gas phase plasma species were characterized using time-dependent actinometric optical emission spectroscopy (OES) and correlated with film composition determined using x-ray photoelectron spectroscopy (XPS). Spectroscopic ellipsometry data were used to develop a model for the film deposition rate from a plasma wherein H_2/C_3F_8 or H_2/C_3F_6 ratios were time-variant. Angle resolved XPS data show that local film composition was confined within the sampling depth of the technique. These techniques may be applied to a range of plasma systems for the fabrication of “made to order” thin films.

COLL 164

Surface properties and colloidal stability of zeolites in organic solvent and polymer-doped solutions for use in mixed matrix membranes (MMM)

***Megan E. Lydon**[1], melydon@gatech.edu, 901 Atlantic Drive, Atlanta GA 30332-0400, United States ; Sven Behrens[2]; Chris Jones[2]; Sankar Nair[2]. (1) Department of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta GA 30332, United States (2) Department of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta GA 30332, United States*

“Mixed matrix membranes” (MMMs), containing nanoparticles (e.g. zeolites) dispersed in a polymer, have been proposed as next-generation gas separation membrane technology. However, their current performance is below theoretical expectations, because of (i) particle aggregation during membrane fabrication, and (ii) defects at the zeolite/polymer interfaces. We have focused on understanding the colloidal properties of the membrane precursor solution by studying the influence of the organic solvent, zeolite surface chemistry, and polymer type. In particular, zeta potential and dynamic light scattering measurements are used to study the dispersion and degree of aggregation of zeolite particles in the polymer dope solution. We have suggested that water adsorption, the formation of charge-transfer complexes at the interface, and the inherent zeolite particle charge contribute to the zeolite zeta potential in these non-aqueous solutions. These results indicate that careful component selection and processing of the dope suspension play a significant role in fabrication of defect-free MMMs.

COLL 165

Characterization of DNA and cationic surfactant at the nematic/aqueous interface using epi-fluorescence

Aaron C McUmber[(1)]*, aaron.mcumber@colorado.edu, ECCH 111 424 UCB, Boulder Colorado 803039, United States ; Daniel K Schwartz*[(1)]*. (1) Department of Chemical Engineering, University of Colorado at Boulder, Boulder Colorado 80309, United States*

We have studied the self-assembly of DNA and cationic surfactant at the interface between aqueous solution and the liquid crystal (LC) 5CB. The response of LC anchoring to the DNA/surfactant complex provides information about intermolecular interactions, and has potential applications in the detection of DNA hybridization. The impact LC elastic free energy (F_e) has on the DNA/surfactant complex was examined by comparing epi-fluorescence images of fluorescently labeled DNA at the nematic/aqueous and isotropic/aqueous interfaces. Both the ssDNA/surfactant complex and the dsDNA/surfactant complex were observed to separate into DNA-rich and DNA-poor regions at the nematic/aqueous interface. Phase separation was also observed for the dsDNA/surfactant complex at the isotropic/aqueous interface, but not for the ssDNA/surfactant complex. This suggested that intermolecular interactions within the adsorbed layer dominate the phase behavior of the dsDNA/surfactant complex, but that the ssDNA/surfactant complex interfacial self-assembly is strongly influenced by effective interactions associated with the F_e.

COLL 166

Green route to carbon aerogels

Anand G Sadekar[(1)]*, agsqp8@mst.edu, 129, Schrenk Hall, 400 W. 11th St., Rolla MO 65409, United States ; Abhishek Bang*[(1)]*; Nicholas Leventis*[(1)]*; Chariklia Sotiriou-Leventis*[(1)]*. (1) Chemistry, Missouri Institute of Science and Technology, Rolla MO 65409, United States*

Interest in porous carbon and carbon aerogels stems from their demonstrated utility as electrodes for batteries and fuel cells, absorbers for separation and purification media, etc. For their preparation to be environmentally benign and economically efficient, one should eliminate the cost associated with multiple solvent exchanges and supercritical fluid drying. Here, we demonstrate the preparation of carbonizable aerogels based on polyacrylonitrile (PAN), using a polymerization method that can be carried out in water and does not utilize supercritical fluid drying. Specifically, since PAN is a water insoluble linear polymer, and its high molecular weight gel collapses even after supercritical fluid drying in order to maximize Van der Waals (VdW) forces, we resorted to emulsion polymerization, while to halt VdW-collapse acrylonitrile was crosslinked with commercially available bifunctional acrylates, ethylene glycol dimethacrylate (EGDMA) and hexanediol diacrylate (HDDA). Those crosslinkers engage PAN and develop 3D networks, which can be dried into macroporous aerogels at ambient pressures with no collapse. Controlled pyrolysis of those aerogels resulted in electrically conducting

carbon aerogels with BET surface areas varying from 39 to 300 m^2 g^{-1} and porosities in the range of 41-68% v/v. -

COLL 167

Regulation of local structure of ternary self-assembled monolayers using nanografting

Donglei Bu[(1)]*, dbu@ucdavis.edu, One Shields Avenue, Davis CA 95616, United States ; Jie-Ren Li*[(1)]*; Gang-yu Liu*[(1)]*. (1) Department of Chemistry, Uiniversity of California, Davis, Davis California 95616, United States*

Mixed self-assembled monolayers (SAMs) provide a platform to study and to regulate interfacial property at nanoscale. Additionally, mixed SAMs serve as better model systems in mimicking bio-membranes than single-component or binary SAMs do, due to their complex composition and domain structures. In this presentation, we will reveal the surface structure of ternary SAMs and introduce a non-conventional method of structural regulation, *i.e.,* nanografting. In a typical system such as octadecanethiol (C_{18}), 11-mercapto-1-undecanal disulfide ($C_{10}CHO$), and 3-mercaptopropionic acid (C_2COOH), phase segregation is observed. The tall phases are primarily closely-packed C_{18} molecules, surrounded by short phases of the $C_{10}CHO$ and C_2COOH components. The nanoscale phase segregation can be altered using conventional methods of surface chemistry. This presentation introduces an alternative approach of nanografting which enables production of various surface structures, from molecular level mixing to phase segregation at the nanometer level, and to the phase segregation formed in natural growth.

COLL 168

Supported lipid bilayer nanosystems stabilization by undulatory-protrusion forces, and destabilization by lipid bridging

Sushma Savarala[(1)]*, tua82725@temple.edu, 1901 N. 13th Street, Philadelphia PA, United States ; Frederick Monson*[(2)]*; Marc A. Ilies*[(3)]*; Stephanie L. Wunder*[(1)]*. (1) Chemistry, Temple University, Philadelphia PA 19122, United States (2) Chemistry, Westchester University, Westchester, United States (3) School of Pharmacy, Temple University, Philadelphia PA, United States*

Colloidal stabilization/precipitation of zwitterionic lipid/SiO_2 nanosystems was investigated as a function of ionic strength and ratio of lipid/SiO_2 surface area. Salt is necessary for supported lipid bilayer (SLB) formation, but also causes precipitation of the SLBs, due to electrostatic shielding and suppression of undulation/protrusion forces. Addition of excess SUVs (equal populations of SUVs and SLBs) restored these repulsive forces, resulting in restabilization. We suggest that SUVs separate SLBs in the suspension, as observed by TEM, and that SLB-SLB interactions are replaced by SLB-SUV interactions. When there was less lipid available than required for complete bilayer

coverage of the SiO_2, the nanosystem precipitated. We postulate a process in which lipid patches on one nanoparticle collide with bare silica patches on another SiO_2 nanoparticle, forming a single bilayer bridge between them. TEM data confirmed these findings and showed that lipid bridges are therefore composed of half bilayers adsorbed on adjoining nanoparticles.

COLL 169

Formation of cationic/zwitterionic lipid sheaths that can envelope and release SiO_2 nanoparticle supported lipid bilayers

Selver Ahmed(1)*, selver@temple.edu, 1901 N. 13th Street, Beury Hall 130, Philadelphia Pennsylvania 19122, United States ; Sushma Savarala*(1)*; Yanjing Chen*(2)*; Geoffrey Bothun*(2)*; Stephanie L Wunder*(1)*. (1) Chemistry, Temple University, Philadelphia PA 19122, United States (2) Chemical Engineering, University of Rhode Island, Kingston RI 02881, United States*

Assemblies of SLB silica nanoparticles can be collected and released from bilayer sacks by temperature modulation. The sacks, composed of the same lipid as the SLBs, encapsulate ca 20 SLBs in a tight-fitting sheath-like structure, formed upon cooling a nanosystem composed of equal populations of SLBs and SUVs below $T_{m.}$ We propose a mechanism for formation of the sheaths in which the SUVs adsorb to aggregates of SLBs just above T_m, and then fuse with each other upon cooling below T_m, forming a contiguous “peas in a pod” structure. The contents of the sacks can be released by heating the nanosystem above T_m. Although the lipid bilayer in direct contact with the SiO_2 nanoparticles always remains attached to the support, the sheath is removed above T_m, forming vesicles that keep the released SLBs in suspension via undulation/protrusion forces. Replacement of excess DMPC/DMTAP (50/50) SUVs with DOPC/DOTAP, results in RT stabilization.

COLL 170

Design and use of fluorous amphiphilic polymers for nanoparticle formation

Florian Ernst Golling(1)*, golling@mpip-mainz.mpg.de, Ackermannweg 10, Mainz Rheinland-Pfalz 55128, Germany . (1) Synthetic Chemistry, Max Planck Institute for Polymer Research, Mainz Rheinland-Pfalz 55128, Germany*

The syntheses of inorganic metal and polyolefinic nanoparticles by means of fluorous polymers are presented. The production of silver and copper particles is utilized by laser ablation in an organic solvent and *in situ* functionalized with a statistical amphiphilic terpolymer bearing fluorinated side chains. The surface modified particles are then homogenously incorporated into poly(pentafluorostyrene) to simulate a PTFE matrix, often used for implants. The antibacterial properties of the silver particles are studied with *E.coli* bacteria. For the synthesis of high molecular weight polyolefine nanoparticles, nonaqueous Oil-in-Oil emulsions based on a perfluorinated solvent and a non-coordinating hydrocarbon were utilized for the polymerization of gaseous ethylene and propylene. In order to prevent phase separation of the immiscible solvents, an appropriate blockcopolymer was designed consisting of a lipophilic and a strongly fluorophilic segment. In contrast to most waterborne heterophase techniques, the presented system can be employed for water sensitive monomers and catalysts.

COLL 171

Fabrication of layer-by-layer assembled thin films based on κ-casein fibrils

Ji-Hye Lee(1)(2)*, ebenezer7@snu.ac.kr, Building 302, Room 616, 599 Gwanak-ro, Gwanak-gu Seoul 151-742, Republic of Korea ; Jiyeong Chun*(2)*; Seung R. Paik*(2)*; Kookheon Char*(1)(2)*. (1) The National Creative Research Initiative Center for Intelligent Hybrids, Gwanak-gu Seoul 151-742, Republic of Korea (2) School of Chemical and Biological Engineering, Seoul National University, Gwanak-gu Seoul 151-742, Republic of Korea*

Abnormal accumulation of amyloid fibrils in a organ has been known to associate with several neurodegenerative diseases. Although amyloid fibrils could be regarded as pathological materials from a biomedical point of view, the amyloid fibrils has recently received great attention for advanced biofibrillar materials due to their unique properties such as highly ordered hierarchical structure and robust mechanical strength but still with some flexibility. In present study, we propose a unique strategy to fabricate multilayered films with amyloid-like fibrils derived from κ-caseins of bovine milk, which is not linked to any disease. Prior to the build-up of multilayered films based on κ-casein fibrils, the kinetics of fibril formation as well as charge density was analyzed in detail (i.e., AFM and SANS) under various conditions. The multilayer films were prepared with diverse pairs of κ-casein amyloid fibrils and polycations, and their film growth and mechanical properties of free-standing multilayer films were investigated with different polycations. Multilayered films containing κ-casein amyloid fibrils as a component would offer many opportunities to use as novel biomaterials with robust mechanical strength as well as biocompatibility.

COLL 172

New polymeric emulsifiers for aqueous and non-aqueous emulsions

Katrin Wunderlich(1)*, wunderlich@mpip-mainz.mpg.de, Ackermannweg 10, Mainz Rheinland-Pfalz D-55128, Germany ; Dilyana Markova*(1)*; Markus Klapper*(1)*; Klaus Müllen*(1)*. (1) Synthetic Chemistry, Max Planck Institute for Polymer Research, Mainz Rheinland-Pfalz D-55128, Germany*

Emulsifiers are essential for the stabilization of emulsions. It is known from aqueous emulsion systems that amphiphilic block copolymers are very effective emulsifiers as manifested by the small amount of block copolymers required for emulsification. Typically, emulsifiers contain sulfonate groups or polyethylene glycol as hydrophilic

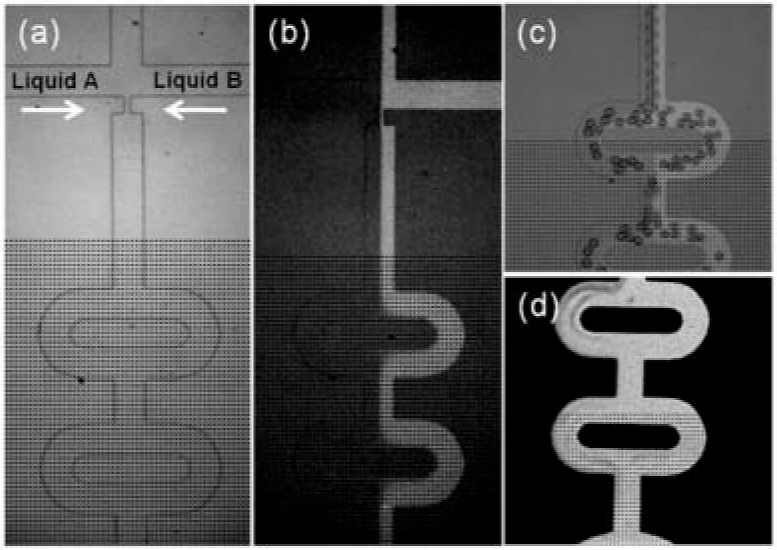
block. In order to extent the concept of the aqueous and non-aqueous emulsions, specially designed diblock copolymers with phosphonic acid groups were designed. Emulsifiers consisting of polyphenylene oxide (PPO) and poly(diethyl p-styrene phosphonate) (PDESP) were elaborated by atom transfer radical polymerization (ATRP) using PPO as macroinitiator and diethyl p-styrene phosphonate as monomer. Subsequent hydrolysis led to diblock copolymers of PPO and poly(styrene phosphonic acid) (PSPA). The success of the synthesis was confirmed by 1H NMR spectroscopy and by gel permeation chromatography (GPC). The diblock copolymers can be applied as emulsifiers in aqueous and non-aqueous emulsions.

COLL 173

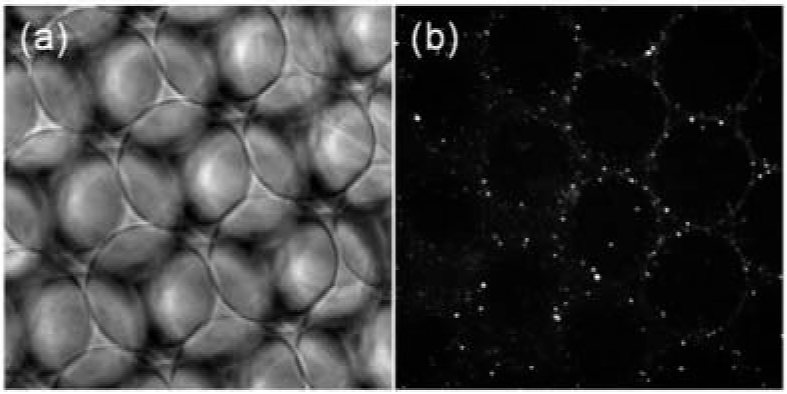
Preparation of polyacrylamide foam scaffold with microfluidic mixer

Yi-hsuan Lee[(1)]*, leey@seas.wustl.edu, 128 Sec. 2, Academia Rd., Nankang, Taipei Taiwan 11529, Taiwan Republic of China ; Keng-hui Lin*[(1)]*. (1) Institute of Physics, Academia Sinica, Taipei Taiwan 115, Taiwan Republic of China*

Design and fabrication of tissue engineering scaffolds with different biomaterials have been widely developed to study the cell behaviors. We have utilized a flow-focusing microfluidic device to generated monodisperse foam as template for constructing ordered scaffolds. To extend our system for different materials, we combined (a) a flow-focusing system with branched mixing channel to perform homogenous reaction in microfluidic system, (b)Without bubbles, the flows are laminar due to the low Reynolds number, and (c-d) when introducing bubbles into the branched channels, the circulating flow field created by the bubble slug in the biphasic flow can provide homogenous mixing.



By using this system, (a) 3D ordered polyacrylamide foam scaffold with different pore size and stiffness have been successfully prepared. (b) The surface of scaffolds can also be modified with fibronectin for cell culturing. The cell behavior such as migration and morphology in these scaffolds also be studied.



COLL 174

Thin Films of Diblock Copolymers and Their Micelles for the Fabrication of Inorganic Nanostructures

Sung-Soo Kim$^{(1)}$*, sskim12@snu.ac.kr, 599 Gwanak-ro, Gwanak-Gu Seoul 151-747, Republic of Korea ; Jin-Hyung Kim*$^{(1)}$*; Yeonju Lee*$^{(1)}$*; Byeong-Hyeok Sohn*$^{(1)}$*. (1) Department of Chemistry, Seoul National University, Seoul 151-747, Republic of Korea*

Diblock copolymers composed of two different polymers spontaneously assemble into periodic nanostructures, of which the size and morphology can be controlled by the molecular weight and composition of copolymers. In a selective solvent for one of the blocks of diblock copolymers, nanometer-sized micelles consisting of a soluble corona and an insoluble core are formed. The diblock copolymers and their micelles can be coated on solid substrates to form nanostructured thin films, which can be used as nanoscale lithographic masks for etching processes and nanotemplates to generate arrays of inorganic nanomaterials. In this study, we applied the diblock copolymer approach to the fabrication of a variety of inorganic nanostructures, including nanostructured graphenes, graphene-nanoparticle hybrids, nanorods-nanoparticle arrays, and nanostructured oxides for potential applications in optoelectronic devices.

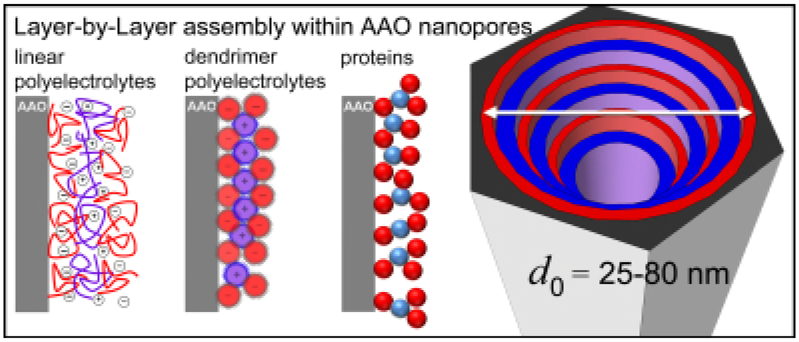
COLL 175

The Importance of Macromolecular Shape and Interactions in Layer-by-Layer Assemblies within Cylindrical Nanopores

Thomas D. Lazzara$^{(1)(2)}$*, thomas.lazzara@gmail.com, Tamannstrasse 2, Göttingen Niedersachsen 37077, Germany ; K.H. Aaron Lau*$^{(3)}$*; Wolfgang Knoll*$^{(4)(2)}$*; Jean-Pierre Majoral*$^{(5)}$*; Anne-Marie Caminade*$^{(5)}$*; Andreas Janshoff*$^{(6)}$*; Claudia Steinem*$^{(1)}$*. (1) Institute of Organic and Biomolecular Chemistry, Georg-August University Göttingen, Göttingen*

Niedersachsen 37077, Germany (2) Max Planck Institute for Polymer Research, Göttingen Niedersachsen 37077, Germany (3) Department of Biomedical Engineering, Northwestern University, Evanston IL 60202, United States (4) Austrian Institute of Technology, Vienna 1220, Austria (5) Laboratoire de Chimie de Coordination du CNRS, Toulouse 31077, France (6) Institute of Physical Chemistry, Georg-August University Göttingen, Göttingen Niedersachsen 37077, Germany

The Layer-by-Layer (LbL) deposition of macromolecules within anodic aluminum oxide was studied in-situ for: polyelectrolyte dendrimers, linear polyelectrolytes and proteins. Low ionic strength was found to inhibit deposition. Under optimal charge screening, LbL proceeded as on a planar surface, until growth became inhibited because of the confined cylindrical geometry. The physical structure of the LbL film strongly influenced the number of deposition steps before steric hindrance was reached, at a pore diameter of 25-30 nm.



COLL 176

The Effect of Surfactant on the Shear-induced Structure and Rheological Properties of SAA/Oil/Fatty Alcohol/Water Quaternary System

***Sung-Ho Moon**(1), prudentmoon@amorepacific.com, 17 Haengdang-dong, Seoul Seongdong-gu 133-791, Republic of Korea ; **Sung-Ho Moon**(2), prudentmoon@amorepacific.com, 17 Haengdang-dong, Seoul Seongdong-gu 133-791, Republic of Korea ; Chang Seok Ki(2); Woori Bae(2); Byung-guen Chae(2); Sang-Hoon Han(2); Jun-Hwan Park(1); Seong-Geun Oh(1). (1) Department of Chemical Engineering, Hanyang University, Seoul 17 Haengdang-dong, Seongdong-gu 133-791, Republic of Korea (2) Cosmetics & Personal Care Research Institute, AMOREPACIFIC R&D CENTER, Yongin-si, Gyeonggi-do 314-1, Bora-Dong Giheung-Gu 446-729, Republic of Korea*

The effect of surfactant on the rheological properties of quaternary systems consisting of surfactant, oil, fatty alcohol and water is studied to improve the stability of O/W cream. The basic ternary systems show the formation of lamella liquid crystals called ∝ gel. On the other hand, the quaternary systems behave lamella liquid crystals including

M and D2 Phase. It is the study of the diverse rheological responses was done by a polarizing microscope, differential scanning calorimetry, small angle X-ray scattering, Rheometer and cryogenic scanning electron microscopy. When the different kinds of surfactant is added, quaternary systems show the diverse rheological responses. Several surfactants are used as emulsifier which is nonionic surfactant, anionic surfactant, cationic surfactant and surfactant mixtures.

COLL 177

Nanodetoxification: Reduction of target compounds on iron oxide nanoparticles

Lauren M Graham(1)*, grahaml@umd.edu, 091 Chemistry Building, Rm 2112, College Park MD 20742, United States ; Sang Bok Lee*(1)(2)*; Thao M Nguyen*(1)*; Sung-Kyoung Kim*(1)*. (1) Department of Chemistry and Biochemistry, University of Maryland, College Park MD 20742, United States (2) Graduate School of Nanoscience and Technology, Korea Advanced Institute of Science and Technology, College Park MD 20742, United States*

Magnetic iron oxide nanoparticles can act as reduction reaction sites for toxic target compounds. Iron oxide nanoparticles are synthesized using a polyol method. The reducing capability of the nanoparticles has been confirmed with benzoquinone as the target toxin. The nanoparticles are embedded into silica nanotubes to improve biocompatibility and selectivity. Silica nanotubes are prepared via sol-gel template synthesis, allowing for differential surface functionalization and facile size control. These nanotubes provide the foundation for a nanoparticle-based detoxification system. This approach goes beyond capturing toxic compounds by reducing the molecule to a less active form.

COLL 178

Detection of homocysteine oxidative stress biomarker using molecular beacon - based fluorescent assay

Magdalena Stobiecka(1)*, hepelmr@potsdam.edu, 44 Pierrepont Avenue, Potsdam New York 13676, United States ; Agata Chalupa*(1)*; Maria Hepel*(1)*. (1) Department of Chemistry, The State University of New York at Potsdam, Potsdam New York 13676, United States*

The investigations of oxidative stress biomarkers are important to understand their role in organisms and to develop assays for rapid diagnosis of stress-related disorders. Homocysteine (Hcys) is formed during a metabolism of methionine to cysteine but the increased concentration of Hcys in plasma (> 20μM) is a risk factor for many disorders including cardiovascular or Alzheimer's. Molecular beacons (MB) are a new class of the nucleic acid probes and are designed to have a stem and loop structure. The main goal of this work was to develop a simple fluorescence turn-on molecular beacon probe for the detection of Hcys. In these investigations the MB with a

FAM dye attached to 5' end of the oligonucleotide and the DABCYL quencher molecule attached to the 3' end of the MB was used. The influence of the temperature, concentrations of Hg^{2+} and Hcys on the fluorescence signal of MB will be presented.

COLL 179

Fluorimetric assay for determination of nitrotyrosine and chlorotyrosine

Agata Chalupa(1)*, hepelmr@potsdam.edu, 44 Pierrepont Avenue, Potsdam New York 13676, United States ; Magdalena Stobiecka*(1)*; Maria Hepel*(1)*. (1) Department of Chemistry, The State University of New York at Potsdam, Potsdam New York 13676, United States*

3-chlorotyrosine and nitrotyrosine (NT) have very important clinical significance as they have been observed in a variety of human diseases. Both serve as markers for heme-containing enzyme myeloperoxidase released by inflammatory cells such as monocytes, macrophages and neutrophils. They are detected in patients with rheumatoid arthritis, atherosclerosis and Alzheimer's disease. Nitrotyrosine formation in proteins has been also detected in diabetes and 3-chlorotyrosine serves as a marker for oxidative damage in arteries. In this work, interactions of biomarkers with gold nanoparticles and two fluorescence dyes: Rhodamine B (RhB) and Coumarin 120 (C120) have been investigated. The quenching of fluorescence signal of C120 after addition of NT was observed and attributed to the fluorescence resonance energy transfer (FRET) from dye to NT. In interactions of NT with RhB, the FRET is unlikely. In measurements, the resonance elastic light scattering (RELS) spectroscopy has been employed and molecular dynamics simulations have been carried out.

COLL 180

True critical coagulation concentrations for SWCNT dispersions determined by aggregation kinetics

Jordan C. Poler(1)*, jcpoler@uncc.edu, 9201 University City Blvd., Charlotte NC 28223, United States ; Anjail L. Ameen*(1)*; Michael W. Forney*(1)*. (1) Department of Chemistry, University of North Caroline at Charlotte, Charlotte NC 28223, United States*

Measuring true critical coagulation concentrations (CCCs), as defined by DLVO theory, for single-walled carbon nanotube (SWCNT) dispersions is quite challenging experimentally. We demonstrate a new method to monitor the aggregation kinetics of SWCNT dispersions that allows us to study aggregation rates in the reaction-limited and diffusion-limited regimes using inorganic salts. Our results agree with our previous work studying the onset of aggregation (much lower coagulant concentration), showing that mixed solvent systems can yield significantly higher dispersion stability than pure solvents. We have also applied our method for studying aggregation kinetics to measure CCCs for novel charged Ru coordination complexes.

COLL 181

C-reactive protein binding to model curved membranes

Joshua C Black[(1)]*, josh.black@du.edu, 2199 S. University Blvd, Denver CO 80208, United States ; Travis Cambell*[(1)]*; Kathryn M. Palma*[(1)]*; Min Wang*[(2)]*; Aml Alnaas*[(1)]*; Scott Reed*[(2)]*; Michelle Knowles*[(1)]*. (1) Department of Chemistry and Biochemistry, University of Denver, Denver CO 80208, United States (2) Department of Chemistry, University of Colorado - Denver, Denver CO 80217, United States*

This project is advancing research into cardiovascular disease by investigating C-reactive protein's (CRP) interaction with curved membrane surfaces, a condition present in apoptotic cells. We have induced curvature in a phospholipid bilayer independent of other factors typically present in a biological system. Nanoparticles were deposited onto a glass substrate prior to creation of a supported lipid bilayer, which induces curvature in the bilayer as it forms. Using confocal microscopy, fluidity was observed and diffusion rates characterized for bilayers formed over the nanoparticles (20-100 nm in diameter). CRP binding to the apoptotic mimics has been explored. To complement our *in vitro* work, we have measured CRP binding to apoptotic cells. Preliminary work has been done to determine if CRP undergoes isoform conversion from pentamer to monomer and if membrane bound CRP interacts with C1q in an effort to better understand the role of curved membranes in the clearance of apoptotic cells.

COLL 182

Membrane transport activity and dynamics of the ABC transporter, P-glycoprotein

Philip P Cheney[(1)]*, philip.cheney@du.edu, SG Mudd Room 259, 2101 E. Wesley Ave, Denver CO 80207-3438, United States ; Halima Assoudani*[(1)]*; Michael Stachler*[(1)]*; Michelle K Knowles*[(1)]*. (1) Department of Chemistry and Biochemistry, University of Denver, Denver CO 80208, United States*

ATP binding cassette (ABC) transporters regulate the lipid asymmetry of the plasma membrane by exporting a wide variety of lipids to the outer leaflet. P-glycoprotein (PGP) is an ABC transporter responsible for the efflux of a large number of hydrophobic small molecules, such as drugs and fluorescent dyes. The interactions of PGP with its local environment on the plasma membrane are studied here using confocal and total internal reflection fluorescence microscopy (TIRFM). A fusion protein of PGP with enhanced green fluorescent protein (EGFP) and several rhodamine-derivative and cyanine fluorescent dyes make the transporter and its substrates visible. Here we use fluorescence recovery after photobleaching (FRAP) techniques to assess bulk protein mobility on the membrane. To complement this technique, TIRFM is used to track single PGP molecules and PGP clusters across the surface of the plasma membrane. Using these microscopic methods, the localization and dynamics of PGP on the membrane in the inactive, active, and inhibited states are determined and a preliminary mechanistic model is proposed.

COLL 183

Identifying trends in density functional theory chemisorption energies for NO on transition metals

Daniel J. Gillette[(1)]*, daniel-gillette@uiowa.edu, Chemistry Building, I IA 52242-1294, United States ; Sara E. Mason*[(1)]*. (1) Department of Chemistry, University of Iowa, Iowa City IA 52242-1294, United States*

Density functional theory (DFT) calculations are used to investigate the adsorption NO on transition metal surfaces in an effort to track and correct for quantitative errors in the theoretical chemisorption energy. While DFT correctly predicts the preferred adsorption site of NO on metal surfaces, the absolute values of the chemisorption energy are known to vary considerably based on the choice of exchange correlation functional or other details of the calculation. In our approach we vary the design of N and O pseudopotentials to obtain trends in chemisorption energy as a function of NO electronic structure. We apply this method to a variety of metal surfaces and NO adsorption sites, and use the obtained trends in DFT chemisorption energies to suggest correction schemes for more consistently accurate DFT predictions of adsorption energetics.

COLL 184

Monolayer-protected gold nanocluster scaffolds for hydroxyapatite biomineralization

Aren E. Gerdon[(1)]*, gerdoar@emmanuel.edu, 400 The Fenway, Boston MA 02115, United States ; Sean McHugh*[(1)]*; Kayla Vasconcellos*[(1)]*; Katherine Dapsis*[(1)]*; Alexander Petty*[(1)]*. (1) Department of Chemistry, Emmanuel College, Boston MA 02115, United States*

Important properties of tiopronin-protected gold nanoclusters (MPCs) suggest their usefulness as scaffolds in the field of biomineralization. This research focuses on functionalized MPCs in the formation of hydroxyapatite ($Ca_5(PO_4)_3OH$; HAP), the major mineral in bones and teeth. Experiments show that when MPCs are reacted with physiologically relevant concentrations of calcium chloride and sodium phosphate precursors, the formation of HAP is accelerated as compared to equivalent concentrations of the tiopronin molecule or in the absence of any template. Precipitate could be detected after ~30 minutes, which is several hours faster than in the absence of the nanoparticle scaffold. IR transmission experiments confirm the presence of HAP as opposed to amorphous phases. Additional experiments are currently being performed to study the effects of DNA-presenting and PEG-presenting MPCs. These results suggest that MPCs are an excellent scaffold for HAP biomineralization and may have far ranging applications in the formation of other minerals.

COLL 185

Emulsion stabilization by polymeric surfactants : Colloidal and interfacial rheological behaviours

Sophie Bistac[(1)], *sophie.bistac-brogly@uha.fr, 2 rue des frères Lumière, Mulhouse Alsace 68093, France ; Léonard Atanase*[(1)]*; Gérard Riess*[(1)]*. (1) LPIM, Université de Haute Alsace, Mulhouse 68093, France*

In this work, three poly(vinyl acetate-co-vinyl alcohol) copolymers (PVA), with similar hydrolysis and polymerization degrees but with different “blockiness” were used. These surfactants are combined with sodium dodecyl sulphate (SDS). A complex is then formed by hydrophobic interaction between the acetate sequences of the PVA and the hydrophobic moiety of SDS. The objective of this work was to demonstrate, in a first stage, by dynamic light scattering that, by complex formation, the aggregates initially present in aqueous solutions of PVA, so-called nanogels, can be disaggregated in the presence of SDS. In a second stage, interfacial viscoelasticity of a chlorobutane/H_2O system containing PVA is investigated by the oscillating drop technique. It turned out that excellent emulsion stability could be obtained for higher elastic interfacial modulus. In conclusion it is shown that the molecular characteristics of PVA have a very important role in interfacial properties and therefore emulsions stabilization.

COLL 186

Temperature-Induced Release of Bioactive Compounds from Multilayers of Diblock Copolymer Micelles

Zhichen Zhu[(1)], *zzhu@stevens.edu, 1 Castle Point on Hudson, Hoboken NJ 07030, United States ; Svetlana Sukhishvili*[(1)]*; Ning Gao*[(1)]*; Hongjun Wang*[(1)]*. (1) Department of Chemistry, Chemical Biology and Biomedical Engineering, Stevens Institute of Technology, Hoboken NJ 07030, United States*

We compared hydrogen-bonded and electrostatically assembled layer-by-layer (LbL) films of diblock copolymer micelles (BCM) in their ability to retain and release bioactive compounds in response to temperature variations. The systems were poly(N-isopropylacrylamide)-*b*-poly(N-vinylpyrrolidone) (PNIPAM-*b*-PVPON) BCM/tannic acid (TA) as a hydrogen-bonded film, and poly(N-isopropylacrylamide)-*b*-poly(methacrylic acid) (PNIPAM-*b*-PMAA) BCM/branched polyethyleneimine (BPEI) as an electrostatically assembled film. Both film types were stable in a wide range of pH, demonstrated reversible swelling transitions when temperature was varied below/above PNIPAM's LCST of 32-35°C, and showed temperature-controlled release of hydrophobic model molecules loaded within micellar cores. For both hydrogen-bonded PNIPAM-*b*-PVPON/TA and PNIPAM-*b*-PMAA/BPEI films, the inclusion of BCMs within the outermost film demonstrated low cytotoxicity to breast cancer cells. We also investigated the possibility of using these films for temperature-controlled delivery of doxorubicin to kill cancer cells.

COLL 187

Spatially confined photoreactions in multicompartmental colloids and fibers prepared by electrohydrodynamic co-jetting

Kyung Jin Lee(1)*, lkyungjin@gmail.com, 3434 GG Brown, 2300 hayward St, Ann Arbor Michigan, United States ; Sangyeul Hwang*(1)*; Jaewon Yoon*(1)*; Joerg Lahann*(1)*; Tae-Hong Park*(1)*. (1) Department of Chemical Engineering, University of Michigan, Ann Arbor Michigan 48109, United States*

We describe the preparation of novel colloids and microfibers with spatially confined photoreactive polymers via electrohydrodynamic (EHD) co-jetting. Multicompartmental colloids and microfibers containing photocrosslinkable polymer (PVCi) in one compartment are prepared and the selective photoreaction is achieved with simple UV irradiation on anisotropically incorporated PVCi in one compartment of either colloids or microfibers. Particle and fiber structure can be controlled by adjusting concentration of the jetting solution. After solvent treatment of biphasic particles and fibers after photocrosslinking, hemicapsules with porous structure and PVCi microfibers with small diameter can be obtained from biphasic particles and fibers, respectively, which can be evidence for successful anisotropic photocrosslinking. This study further elucidates unique physical properties that arise from the bicompartmental character of the particles and fibers. Furthermore, this technique can be extended to prepare divers anisotropic colloids and microfibers compartmentalized by functionally heterogeneous polymers.

COLL 188

DFT study of arsenate adsorption onto hydrated hematite surfaces

Christoffer J. Goffinet(1)*, christoffer-goffinet@uiowa.edu, Chemistry Building, Iowa City IA 52242-1294, United States ; Sara E. Mason*(1)*. (1) Department of Chemistry, University of Iowa, Iowa City IA 52242-1294, United States*

Arsenic is a toxic element that is regulated in drinking water by the EPA at no more than 10 ppb, and arsenate surface complexes with hydrated iron oxides are a known contamination source. Vital to the overall understanding arsenate mobility in the environment is a detailed description of surface complex structures and the physical controls of the substrate on reactivity trends. In this study we use density functional theory (DFT) to model arsenate adsorption onto (experimentally confirmed) structural models for hydrated hematite surfaces. We carry out comparative studies of adsorption at different adsorption sites on the hematite surface and in different coordiation geometries with surface and distal ligands. As both the arsenic in arsenate and the antimony in antimonate are in the +5 oxidation state with a d(10) valence electron configuration, we compare our findings to previous work detailing antimonate adsorption onto hydrated hematite surfaces. Specifically, we test the prediction that the adsorption energetics and predicted thermodynamically preferred adsorption motifs for the oxyanions will be similar and whether differences occur due to varying atomic size.

COLL 189

Gradient films for sensing applications

Anna Paola Soliani(1)*, asolian@clemson.edu, 150 Sirrine Hall, Clemson SC 29634, United States ; Bogdan Zdyrko*(1)*; Igor Luzinov*(1)*. (1) Department of Materials Science and Engineering, Clemson University, Clemson SC 29634, United States*

We report on the generation of polymeric nanostructured films that can selectively sense the immediate environment via swelling. Specifically, we prepared poly(glycidyl methacrylate) (PGMA) film with a polystyrene (PS) 1-D gradient. PGMA layer (60-100 nm) was first produced to form a non-soluble, but swellable, coating. Next, carboxylic acid terminated PS was grafted onto the PGMA layer using a specially designed stage with a temperature gradient. A 1-D gradient of temperature was established and translated into PS grafting gradient. Ellipsometry, FTIR, AFM, and contact angle were used to characterize the obtained 1-D gradient films. The film demonstrated position dependent swelling in different solvents.

COLL 190

On-demand degradation of acetal-modified dextran particles fabricated by electrospray

Tae-Hong Park(1)*, parktae@umich.edu, 2300 Hayward Street, 3074 H. H. Dow, Ann Arbor Michigan 48109, United States ; Joshua M Lumley*(1)*; Thomas W Eyster*(1)*; Sangyeul Hwang*(1)*; Joerg Lahann*(1)(2)(3)*. (1) Department of Chemical Engineering, Univeristy of Michigan, Ann Arbor Michigan 48109, United States (2) Biomedical Engineering, University of Michigan, Ann Arbor Michigan 48109, United States (3) Macromolecular Science and Engineering, University of Michigan, Ann Arbor Michigan 48109, United States*

Photo-triggered degradable polymer particles have been fabricated via electrospraying of a solution of acetal-protected dextran (Ac-Dex) that further included 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine as a photoacid generator. Mean particle size was 626 ± 88 nm and 520 nm ± 63 nm determined from dynamic light scattering measurement and SEM image respectively. The controlled degradation of dextran particles was achieved by illumination at 340 nm. The photoacid generated within the particle is responsible for the catalytic demasking of parent hydroxyl groups of dextran, leading to dissolution of particles in water. A BCA assay was used to quantify the amount released dextran. Thus, our particles may find applications as drug carriers for on-demand delivery.

COLL 191

Environment sensitive fluorescent nanoparticles with tunable properties

Maryus Chyasnavichyus(1)*, cchyasn@clemson.edu, 161 Sirrine Hall, Clemson SC 29631, United States ; Bogdan Zdyrko*(1)*; Volodymyr Tsyalkovsky*(1)*; Igor Luzinov*(1)*. (1)*

School of Materials Science and Engineering, Clemson University, Clemson SC 29634, United States

Fluorescent nanoparticles were obtained via grafting of 5 nm layer of fluorescently labeled (Rhodamine B) poly(glycidyl methacrylate) (PGMA) on the 150 nm silicon dioxide particles. To introduce affinity to the various organic solvents poly(ethylene glycol) (PEG) was attached to the PGMA layer using “grafting to” approach. Resulting nanoparticles were highly fluorescent and stable in a variety of organic solvents. Fluorescent response from the nanoparticles varied with the solvent nature suggesting sensitivity of the nanoparticles to the environment. It was also possible to introduce magnetic properties to the nanoparticles. This was done by attachment of 10-15 nm Fe_3O_4 particles to the poly(acrylic acid) layer grafted to the silica particles via PGMA. The resulting core-shell nanoparticles showed both high fluorescence and stability in water together with the response to the magnetic field.

COLL 192

Mapping surface chemistry using accumulated single molecule trajectories

Nathaniel S Nelson[(1)]*, nelsonns@colorado.edu, 424 UCB ECCH 111, Boulder CO 80309, United States ; Daniel K Schwartz*[(1)]*; Robert Walder*[(1)]*. (1) Department of Chemical and Biological Engineering, University of Colorado - Boulder, Boulder CO 80309, United States*

The dynamic behavior of individual adsorbate molecules (e.g. adsorption rate, interfacial diffusion, desorption rate) is directly related to the surface chemical functionality. By exploiting these phenomena, we have developed a novel approach to map lateral variations in surface chemistry. Individual fluorescently-labeled molecules are imaged using TIRF microscopy and their trajectories are determined by tracking the molecule's position throughout its interfacial lifetime. Combining the data from millions of molecular trajectories allows for quantitative “maps” of the adsorption rate, steady-state coverage, desorption probability, and diffusive step size to be generated. The values of these quantities have been studied as a function of surface hydrophobicity, and maps of the related properties have been determined on patterned substrates. Through the appropriate selection of probe molecule and solvent, any surface functionality can be mapped using this method. The work to be presented shows the quantitative analysis of a surface patterned with hydrophilic and hydrophobic regions.

COLL 193

Fabrication of polymer coated magnetic Fe_3O_4 nanocomposites with magnetic stirring method for the immobilization of enzymes

Joo Seob Lee[(1)]*, jlee36@uwyo.edu, Dept. 3295, 1000 E. University Ave, Laramie Wyoming 82070, United States ; Kevin J. Schilling*[(1)]*; Patrick A. Johnson*[(1)]*. (1)*

Department of chemical & Petroleum Engineering, University of Wyoming, Laramie Wyoming 82070, United States

Polymer coated magnetic Fe_3O_4 such as (1) poly vinyl alcohol (PVA) coated Fe_3O_4 nanocomposites and (2) β-Cyclodextrin (β-CD) coated Fe_3O_4 spherical aggregates have been investigated. We have studied each material for the immobilization of carbonic anhydrase (CA), which is coupled with polymeric surfaces by single or multiple attachments, in order to evaluate the enzyme binding force, diffusion, leakage, applicability, and CO_2 capture. (1) CA-PVA-Fe_3O_4 was prepared by enzyme encapsulation and embedded technology, in which CA was embedded onto PVA-Fe_3O_4 and cross-linked. Fe_3O_4, PVA-Fe_3O_4, and CA-PVA-Fe_3O_4 were characterized with FT-IR, TEM, SEM, DSC, DLS, and zeta-potential, which confirmed the surface interactions, enzyme immobilization, colloidal stability, and enzyme activity. (2) CA-β-CD-Fe_3O_4 was prepared by enzyme encapsulation and chemical bonding between β-CD and CA to form inclusion complexes. β-CD-Fe_3O_4 was fabricated with two surfactants, β-CD and polyethylene glycol nonylphenyl ether (NP30). The products were studied by FT-IR, DLS, zeta-potential, VSM, SEM and TEM.

COLL 194

Cysteine molecule covered magnetic Fe_3O_4 nanoparticles via the sonochemical method for bio-applications

Kevin J. Schilling(1)*, kschill2@uwyo.edu, 2501 Pathfinder #528, Laramie Wyoming 82072, United States ; Joo Seob Lee*(1)*; Patrick A. Johnson*(1)*. (1) Department of Chemical & Petroleum Engineering, University of Wyoming, Laramie Wyoming 82071, United States*

Cysteine covered magnetic Fe_3O_4 nanoparticles (Cys-Fe_3O_4) have been fabricated via sonochemical approaches using **(1)** metal salts mixtures and **(2)** iron pentacarbonyl ($Fe(CO)_5$) in conjunction with a small molecule surfactant. In this report, we have compared two kinds of Cys-Fe_3O_4 nanoparticles using both methods. The goal is to achieve well-dispersed Cys-Fe_3O_4 nanoparticles. Cysteine molecules bound to magnetic Fe_3O_4 nanoparticles have the desired behavior and solubility properties in aqueous and non-aqueous solutions. We found that different conditions such as sonication time and concentration of DL-Cysteine affect the magnetic properties of Cys-Fe_3O_4 colloidal suspensions. FT-IR, Raman Spectroscopy, TEM, SEM, DLS, XRD, VSM, and zeta-potential (+/-, mV) were performed to characterize the fabricated materials. However, we did observe low magnetization and long precipitation times in DI-water. Thus, we have discovered that other solvents (e.g., methanol, acetone) create more uniform dispersion of Cys-Fe_3O_4 colloids in solution.

COLL 195

Solvent-free, pore-spanning model membranes studied by fluorescence microscopy and atomic force microscopy

Marta Kocun[(1)], *marta.kocun@gmail.com, Tammannstrasse 6, Goettingen Niedersachsen 37077, Germany ; Thomas D. Lazzara*[(2)]*; Claudia Steinem*[(2)]*; Andreas Janshoff*[(1)]*. (1) Institute of Physical Chemistry, Georg August Universitat, Goettingen 37077, Germany (2) Institute of Organic and Biomolecular Chemistry, Georg August Universitat, Goettingen 37077, Germany*

Mechanical properties of native membranes govern multitude of morphological and physiological functions. However, the complexity of native organisms requires the use of model systems which mimic the behavior of their native counterparts. Black lipid membranes, solid supported membranes and tethered membranes have all been used in previous studies but only pore-spanning membranes offer the possibility of local investigation of their mechanical properties. Here, pore-spanning polymer membranes are formed by poly(butadiene)-block-poly(ethylene oxide) polymersome rupture on porous substrates. Furthermore, gold-thiol functionalization procedure of the same porous substrates was used to prepare solvent-free, pore-spanning, laterally mobile lipid bilayers. We have used fluorescence microscopy together with atomic force microscopy to characterize these membranes and investigated their mechanical response to indentation. In addition to viscoelasticity and elastic moduli of pore-spanning polymer membranes, we have prepared solvent-free, pore-spanning lipid membranes and investigated their lipid-specific lateral tension.

COLL 196

Capillary rise limited by capillary condensation in narrow gap space

Clifford B Kim[(1)], *cbkim@fas.harvard.edu, 265 Lowell Mail Center, Cambridge MA 02138, United States ; David H Waldeck*[(2)]*; Christopher W Borysenko*[(3)]*. (1) Department of Neurobiology, Harvard University, Cambridge MA 02138, United States (2) Department of Chemistry, University of Pittsburgh, Pittsburgh PA 15260, United States (3) Mellon College of Science, Carnegie Mellon University, Pittsburgh PA 15213, United States*

Capillary rise is known to be inversely proportional to tube diameter (gap size), and this implies constant contact angle of liquid to the wall. This work investigates whether this inverse relationship holds true in extremely small spaces. A wedge-shaped apparatus was devised from glass (Pyrex) plates, with a gap size ranging from the sub-millimeter to micrometer scale. For narrow gap ranges (< 50 μm for silicone oil), capillary rise was found to significantly fall off from the inverse relationship. Contact angles calculated from the measured capillary rise showed a monotonic increase in this gap regime, approaching 90 degrees at zero gap size. A possible mechanism is proposed to explain the observed phenomenon in terms of thermodynamic equilibrium in a narrow, confined space, namely that the curvature of a liquid/vapor interface lowers the equilibrium vapor pressure of the liquid, causing a reduction of solid-vapor interfacial tension via capillary condensation and therefore an increase in the contact angle.

COLL 197

Hydrogen gas sensing with networks of ultrasmall palladium-based nanowires

Xiaoqiao Zeng[(1)(2)(3)]*, xzeng@niu.edu, 1425 W. Lincoln Hwy., Dekalb Illinois 60115, United States ; Zhili Xiao*[(2)(3)]*; Tao Xu*[(1)(2)]*. (1) Department of Chemistry and Biochemistry, Northern Illinois University, Dekalb Illinois 60115, United States (2) Materials Science Division, Argonne National Laboratory, Dekalb Illinois 60115, United States (3) Department of Physics, Northern Illinois University, Dekalb Illinois 60115, United States*

Palladium nanowires show promising results in speed and sensitivity in hydrogen sensing. However, single palladium nanowires face challenges in nanofabrication, manipulation, and achieving ultrasmall transverse dimensions. Taking advantage of single palladium nanowires in high speed and sensitivity, we fabricated hydrogen sensors based on networks of ultrasmall (<10 nm) palladium nanowires which are deposited onto commercially available filtration membranes. The pure palladium nanowire network sensors show sensitivities and response times are as a function of the nanowire thickness, and demonstrate the superior hydrogen sensing performance. We also employed such novel fabrication method to achieve hydrogen sensors of ultrasmall palladium/chromium bilayer nanowire networks with the thickness of the continuous palladium layer down to 2 nm. The response time of bilayer nanowire networks sensors are faster than the pure palladium nanowire networks sensors. Furthermore, they eliminate a crucial drawback of pure palladium based sensors which saturate at hydrogen concentrations higher than 3%.

COLL 198

Ni & Ni alloy nanotubes synthesized by electrochemical deposition in AAO templates

Sung-Kyoung Kim[(1)]*, skkim@umd.edu, Chemistry Building, College Park Maryland 20742, United States ; Seung Il Cho*[(1)]*; Thao M. Nguyen*[(1)]*; Sang Bok Lee*[(1)]*. (1) Department of Chemistry and Biochemistry, University of Maryland, College Park Maryland 20742, United States*

Nickel nanostructures have attracted great attention because of their electrochemical, magnetic, and catalytic properties which are useful for the application to nanoelectronic devices, catalysis, high-density magnetic memories, and battery electrodes. We describe the growth mechanism of nickel nanotubes in electrochemical template synthesis. The composition of an electrolyte solution played an important role in determining Ni nanostructures. Our approach was applied to the synthesis of Ni alloy nanotubes, such as Ni/Co and Ni/Fe/Co.

COLL 199

Highly efficient self-decontaminating metal organic framework (SD-MOF) composite

***Lawrence Renna**[1], lawrence.renna@qinetiq-na.com, 360 Second Avenue, Waltham Massachusetts, United States ; Yongwoo Lee[1]; Philip Delaney[1]; Anastasia Manesis[1]; Navin Patel[1]; Weiss Steve[1]. (1) Technology Solutions Group, QinetiQ North America Inc., Waltham MA 02452, United States*

There is a need for an environmentally benign, cost-efficient, and reusable material that can degrade toxic chemical agents into non-toxic by-products for safe disposal. QNA has previously developed a self-decontaminating metal organic framework (Q-SD-MOF®) for this purpose. A SD-MOF composite material has been developed to improve the DECON efficacy of the SD-MOF. The MOF composite as well as the parent SD-MOF were analyzed by scanning electron microscopy (SEM) and tested for its ability to degrade organophosphorous chemical agents. The aforementioned revealed that in the composite material the SD-MOF is the dominating factor; but the manner in which the framework self-assembles on the molecular template allows for high sorption capacity and reactivity to degrade chemical agents in comparison to the parent MOF materials. This concept of a self-assembled MOF on molecular template can be applied to other decontaminating MOF's such as a zinc based SD-MOF. This new reactive self-decontamination composite material could find application for Individual Protection (cartridges for masks) and Collective Protection (military tents).

COLL 200

Development and characterization of SERS bioassays

***Ashley Driscoll**[1], ghoti@uwyo.edu, 1000 E. University Ave., Dept. 3295, Laramie WY 82071, United States ; Patrick A. Johnson[1]. (1) Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie WY 82072, United States*

Nanoparticles can be made from a variety of organic and inorganic materials and find use in a wide range of applications such as targeted drug delivery, contrast enhancement in MRIs and also act as carrier agents in bioassays. Two general approaches have been taken to develop bioassays – surface capture of the target analyte and solution based capture of the target analyte. Solution based surface enhanced Raman scattering (SERS) bioassays use functionalized gold colloids in place of a capture surface, but this presents the problem of collecting bound particles to read with a laser. One approach to solve this is a magnetic capture assay. In two particle capture systems, a gold particle with dye and a magnetic particle are both functionalized with biomolecules. The biomolecules target the same substrate and reacted species can be pulled from solution with a magnetic field for analysis. When read with the laser, only the substrates also bound with a gold particle will provide a signal due to the SERS effect. One particle capture assays incorporate the elements of the two particle system into a single gold coated magnetic particle. These provide a gold surface for attachment of biomolecules and the SERS effect, while also being able to be collected from solution by an applied magnetic field. To further the development and understanding of a single particle capture assay, modeling of a colloidal system could determine important parameters toward improving assay performance and the development of portable

detection systems that do not require moving parts. We present the synthesis and characterization of gold coated magnetic nanoparticles for use in colloidal bioassays as well as preliminary modeling of solution based assays.

COLL 201

Block-copolymer-templated Synthesis of Ultra-large-pore Ordered Mesoporous Silicas with Face-centered Cubic Structure

Liang Huang[(1)(2)]*, Liang.Huang@csi.cuny.edu, Building 6S-127, 2800 Victory Boulevard, Staten Island NY 10314, United States ; Michal Kruk*[(1)(2)]*. (1) Department of Chemistry, College of Staten Island, Staten Island NY 10314, United States (2) Graduate Center/City University of New York, Staten Island NY 10314, United States*

Ordered mesoporous silicas with spherical pores are a particularly interesting family of ordered mesoporous materials. The pore cage diameter of these materials can be adjusted from several nanometers to ~40 nm, and also their pore entrance diameter can be tuned in a range from one nm (or even lower) to the size close to the pore cage diameter. We developed ultra-large-pore FDU-12 (ULP-FDU-12) silicas with face-centered cubic structure of spherical mesopores using Pluronic F127 surfactant and xylene or other compounds as swelling agents. ULP-FDU-12 exhibited pore diameters up to at least 36 nm and unit cell parameters up to at least 55 nm. The pore entrance size of ULP-FDU-12 can be tailored in a wide range, thus changing the pore accessibility. In some cases, the pore entrance can even be eliminated or reduced to such a size that nitrogen molecules cannot access the pores, resulting in a closed-pore material.

COLL 202

Wettability gradient modulation of polyelectrolyte multilayer films

Xiayun Huang[(1)]*, sherry.huangxiayun@gmail.com, 1501 Holleman Dr, APT 186, College Station Texas 77840, United States ; Nicole S Zacharia*[(1)(2)]*. (1) Department of Mechanical Engineering, Texas A&M University, College Station Texas 77843, United States (2) Materials Science and Engineering Program, Texas A&M University, College Station Texas 77843, United States*

Intelligent surfaces with controllable wettability in response to various external stimuli have received special attentions due to theirs practical application in self-cleaning surfaces, anti-adhesive coatings, microfluidics, etc. Generally, wettability of the surface is controlled by not only the chemical natures but also geometrical structures. Here, we used water-soluble polycations, poly(diallyldimethylammonium chloride) (PDAC), polyanions, sodium poly(styrene sulfonate) (SPS), and sodium chloride (NaCl) to form polyelectrolyte multilayer films. Wettability gradient of the multilayer surfaces could be modulated by exchanging counterions with fluorinated salt (perfluoroocatanioic acid ammonium salt). A wettability gradient would be created by fluorinated counterions

exchanging by wet stamping methods. The wettability gradient and droplet motion would also be measured.

COLL 203

Green, facile synthesis of dispersible γ-AlOOH nanorods

Pham Dat Thanh[(1)]*, phamdatthanh@jaist.ac.jp, 1-1 Asahidai, Nomi Ishikawa 923-1292, Japan ; Tran Viet Thu*[(1)(2)]*; Derrick Mott*[(1)]*; Shinya Maenosono*[(1)]*. (1) School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi Ishikawa 923-1292, Japan (2) Faculty of Physics and Chemical Engineering, Le Quy Don Technical University, Nomi Ishikawa 923-1292, Japan*

In this study, *γ*-AlOOH nanorods were synthesized by a hydrothermal method, using aluminum acetate without any capping ligand. The resulting NRs are easily dispersed in polar solvents. The effect of reaction conditions on the shape and size of the *γ*-AlOOH was investigated. In addition, the mechanism of the particle dispersibility and the role of acetate anion in stabilization of the *γ*-AlOOH NRs in polar solvents was studied. Interestingly, *γ*-AlOOH NRs can be easily converted to *γ*-Al_2O_3 by heat treatment without changing morphology and dispersibility. In addition, the *γ*-AlOOH NRs were used as a precursor to produce $CuAlO_2$ by using a wet chemical process. The high surface energy *γ*-AlOOH NRs can play a role as support for the deposition of Cu precursor to form a nanoprecursor. The conversion of nanoprecursor into $CuAlO_2$ by solid-state reaction was carried out at high temperature and is part of the results discussed in this presentation.

COLL 204

Adsorption and desorption of allylamine, propylamine, and propylene on the Si(100)-2x1 surface

Lekh N Adhikari[(1)]*, lekha@unr.edu, 1664 N Virginia St, MS 216, Reno Nevada 89557, United States ; Yunfeng Zhang*[(1)]*; April J Carman*[(1)]*; Sean M Casey*[(1)]*. (1) Department of Chemistry, University of Nevada, Reno, Reno Nevada 89557, United States*

The adsorption of allylamine, propylamine, and propylene on the Si(100)-2x1 surface has been investigated using Auger electron spectroscopy, thermal desorption spectroscopy (TDS), and work function measurements. All of these molecules are three carbon chain moieties with differing terminal functional groups and were chosen to self-consistently probe amine and alkene functional group chemistry on this surface. Results from the adsorption of propylene and allylamine were mostly consistent with previous studies on adsorption of these molecules, with the main difference being the observation of a prominent m/z = 17 desorption product in the case of TDS after allylamine adsorption. TDS after propylamine adsorption gave rise to a prominent propylene desorption channel, similar to the other two species studied, but several important differences were noted between the propylamine and allylamine TDS spectra.

These differences, and their implications toward differing adsorption/desorption pathways, will be discussed.

COLL 205

Osteoblast adhesion and proliferation in response to electrospun poly(epsilon-caprolactone) /polyhedral oligomeric silsesquioxane nanocomposites

Bingbing Li(1)*, li3b@cmich.edu, 201 E Ottawa Ct Dow 268, Mount Pleasant MI 48858, United States ; Jizhou Fan*(1)*. (1) Department of Chemistry, Central Michigan University, Mount Pleasant MI 48858, United States*

Surface morphology and wettability are important factors for the design of novel biomaterials for regenerative medicine. In this presentation, electrospun poly(epsilon-caprolactone) (PCL) / octaisobutyl-polyhedral oligomeric silsesquioxane (POSS) nanocomposites of varying morphological features are used to study the influence of microstructured substrates on pre-osteoblast adhesion, morphology, and proliferation. Scanning electron micrographs showed distinct yet related morphological features of fixed osteoblasts in response to electrospun substrates of varying morphology and hydrophobicity. Cell proliferation assay based on the enzymatic cleavage of tetrazolium salt to a water soluble formazan dye was used to evaluate the effect of surface morphology and chemistry on osteoblast proliferation. Current results showed a higher proliferation rate for pre-osteoblasts cultured on microparticulate substrates fabricated by electrospinning of PCL/POSS with a higher POSS ratio. The mechanism behind above observation is currently undergoing further experimental verification.

COLL 206

Nonspecific adsorption of nucleotide triphosphates and polynucleotides on modified silica surfaces

Jon H Monserud(1)*, jmonseru@gmail.com, 424 UCB ECCH 111, Boulder CO 80401, United States ; Daniel K Schwartz*(1)*. (1) Chemical and Biological Engineering, university of colorado boulder, Boulder CO 80309, United States*

Biosensors, and other diagnostic techniques, are dependent on the specific interactions of nucleotides on a functionalized surface. However, minimizing nonspecific DNA adsorption is critical to optimizing biosensor performance in techniques such as fluorescent microscopy of deoxyribonucleic acid (DNA) microarrays. In these systems fluorescently labeled species might non-specifically adsorb near a probe molecule potentially resulting in insertion errors. Interactions between various surfaces and single stranded DNA (ssDNA) is of interest in understanding phenomena which result in DNA species adsorbing irreversibly to a surface. Total internal reflection fluorescent microscopy was used to track single molecules of fluorescently labeled ssDNA on silica, octadecyltriethoxysilane (OTES), and 3-glycidoxytrimethoxysilane (GPTMS) surfaces. Trajectories of these molecules were analyzed to extract Residence time distributions,

diffusion behavior, and fractions of species that are irreversibly bound. Analysis of these surfaces revealed that the characteristic residence times on the surface increased with the following order: GPTMS, fused silica, OTES.

COLL 207

Investigation of electric double layer of mixed micelle surfaces by potentiometric titration, indicator dye spectrometry and zeta potential measurements.

Gavin F Kirton(1)*, gavin.kirton@rocky.edu, 1511 Poly Drive, Billings Montana 59102, United States ; Kozue Kimura*(1)*. (1) Department of Chemistry, Rocky Mountain College, Billings Montana 59102, United States*

The use of indicator dyes that exhibit shifts in absorption peak position with the electric field at a charged micelle surface presents a possibility of finding surface potentials (ψ_0) in a more convenient manner than potentiometric titration of acid probes. In previous work, the spectral peak shift for cationic crystal violet was correlated to the increase in surface potential of an anionic/nonionic (SDS/TX100) surfactant mixed micelle obtained by titration. Further calibration of mixed micelles, including cationic/nonionic (CTAB/TX100) and anionic/nonionic (SDS/TX100) systems were carried out by the combination of potentiometric titration and measurement of zeta (ζ) potentials (ZetaPALS, Brookhaven Instruments) in the presence and absence of selected ionic and neutral dyes. Differences observed between measured potentials revealed increased counterion accumulation beyond certain mole fractions of charged surfactant.

COLL 208

Fabrication of layer-by-layer poly(lactic acid)s stereocomplex using a inkjet printer

Takami Akagi(1)*, akagit@chem.eng.osaka-u.ac.jp, 2-1 Yamada-oka, Suita Osaka 565-0871, Japan ; Tomoko Fujiwara*(2)*; Mitsuru Akashi*(1)*. (1) Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita 565-0871, Japan (2) Department of Chemistry, The University of Memphis, Memphis TN 38152, United States*

Poly(lactide) (PLA) is a biodegradable and biocompatible polymer that is widely used in medicine and bioengineering. It has been reported that the poly(L-lactide)/poly(D-lactide) (PLLA/PDLA) mixtures in solution form stereocomplexes with distinctive physical and chemical stability due to the van der Waals interaction between L-lactyl and D-lactyl unit sequences. Layer-by-layer (LbL) assembly promises stepwise deposition of interactive polymers to prepare ultrathin polymer films by alternate immersion of substrates into the polymer solutions. In general, electrostatic forces hydrogen bonds, van der Waals forces, or combinations of these interactions are available as the driving forces for LbL assembly. In this study, we developed an alternate technique for the stepwise assembly of enantiomeric PLAs using a inkjet

printer. Inkjet printing is considered one of the most promising methods for controlled deposition of polymers. Inkjet technology can be successfully used for stereocomplex assembly of PLAs.

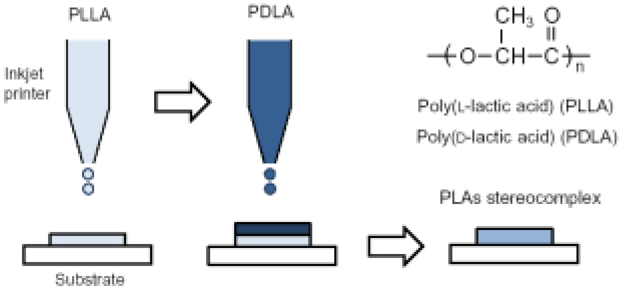


Figure 1. Schematic representation of PLAs stereocomplex formation by inkjet layer-by-layer assembly.

COLL 209

Study of surface reactions during atomic layer deposition using in situ infrared spectroscopy

Rohan P Chaukulkar[(1)], *rchaukul@mines.edu, 1500 Illinois Street, 353 Alderson Hall, Golden Colorado 80401, United States ; Nick Thissen*[(2)]*; Vikrant R Rai*[(1)]*; Sumit Agarwal*[(1)]*. (1) Chemical Engineering Department, Colorado School of Mines, Golden Colorado 80401, United States (2) Plasma and Materials Processing, Eindhoven University of Technology, Eindhoven 5600MB, The Netherlands*

Atomic layer deposition (ALD) is a thin film growth technique, which is widely used to deposit highly conformal thin films. This technique has been successfully applied to deposit various materials such as metal-oxides and nitrides, metals, semiconductors, and more recently, polymers. To enable new deposition chemistries and to achieve better control over existing ones it is important to understand the surface reaction processes that occur during film growth. We use in situ attenuated total reflection Fourier transformation Infrared spectroscopy (ATR-FTIR) to study the ALD of dielectrics, and infrared reflection absorption spectroscopy (IRAS) to probe the surface reactions during deposition of metals. We will present a study of the surface reactions during the ALD of SiO_2, Al_2O_3 and Cu. We will report on the ALD window for the processes and identify the surface reactive sites. We will also relate the surface reaction mechanism to the processing of these films.

COLL 210

Grafted layer for reduction of surface wettability with non-aqueous liquids

TUGBA DEMIR[(1)]*, tdemir@clemson.edu, Clemson, Clemson SC 29634, United States ; Guzeliya Korneva*[(2)]*; Bogdan Zdyrko*[(1)]*; Konstantin Kornev*[(1)]*; Igor Luzinov*[(1)]*. (1) Department of Material Science and Engineering, Clemson University, Clemson SC 29631, United States (2) Department of Bioengineering, Clemson University, Clemson SC 29634, United States*

We report on surface modification of different surfaces with grafted polymer layers in order to reduce their wettabilty with non-aqueous liquids. First of all, surface of silicon wafer, polyurethane coating, aluminum membrane, and cellulose non-woven material was modified with poly(glycidyl methacrylate), PGMA anchoring layer. Next, perfluoro carboxyl acid was used to attach fluorinated functional groups to the surface. Variation of the PGMA layer thickness and temperature of the attachment allowed controlling concentration of fluorinated species on the surface. Contact angles with water and hexadecane were measured and surface energy of each treated surfaces was estimated. Finally, wettability of the coatings with tributyl phosphate and 2-Chloroethyl ethyl sulfide was determined. The obtained fluorinated grafted layers demonstrated reduced wettability with the chemicals used.

COLL 211

Theoretical predications of UV-Vis spectra for Mo (VI) oxides clusters

Ahmad R Soufiani[(1)]*, razzagh@okstate.edu, 107 Physical Science, Stillwater OK 74078, United States ; Allen W Apblett*[(1)]*; Nicholas F Materer*[(1)]*. (1) Department of Chemistry, Oklahoma State University, Stillwater Oklahoma 74078, United States*

Structure optimization and UV-Vis spectra calculations were performed with the time-dependent density function framework for several Mo oxides and peroxides. The computational results were compared to experimental values from literature. Initially, optimization and UV-Vis spectra for molybdic acid and molybdate computed and methodology was validated. After which, larger molybdenum oxide clusters were investigated to ascertain possible particle size effect on visible spectra. For these calculations, structural parameters from crystallographic databases were utilized. Calculations were done for a single molecule, chain, and ribbon structures. The results show that maximum absorbance wavelength shifts to higher wavelengths, lower energy, and its intensity increases as the size of the cluster increases.

COLL 212

Formation and Immobilization of Ag Nanoparticles onto the Surface of Echinoid-like TiO_2 Particles Using Alcohol Reduction Method

Kyungho Song[(1)]*, skh123123@hanmail.net, 216 Adv.Mater.&Chem.Eng.Bldg., 17 Haengdang-dong, Seongdong-gu, Seoul Seoul 133791, Republic of Korea ; Inseok Jang*[(1)]*; Seong-Geun Oh*[(1)]*. (1) Department of Chemical Engineering, Hanyang University, Seoul 133791, Republic of Korea*

In this study, Ag nanoparticles were immobilized onto the surface of echinoid-like TiO_2 particles through novel preparation route involving alcohol reduction method. First of all, echinoid-like TiO_2 particles were synthesized via modified sol-gel method using titanium(IV) isopropoxide (TTIP) and isopropyl alcohol (IPA) in acetic acid. Secondly, the surface of TiO_2 particles was modified with 3-aminopropyltrimethoxysilane (APTMS) which acts as a chemical binder between Ag nanoparticles and the TiO_2 surface. Finally, Ag-TiO_2 composites were synthesized through alcohol reduction method using polyvinylpyrrolidone (PVP) as a stabilizer to form and introduce Ag nanoparticles onto the TiO_2 surface uniformly. To investigate the properties of Ag-TiO_2 composites, field emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), and UV-Vis spectrophotometer were used.

COLL 213

Theoretical Investigation on Cysteine Interactions with Gold Nanoparticles

Jessica Carr[(1)]*, hong.wang@mail.wvu.edu, Hodges Hall P.O.Box 6315, Morgantown West Virginia 26506-6315, United States ; James P Lewis*[(1)]*; Hong Wang*[(1)]*. (1) Department of Physics, West Virginia University, Morgantown West Virginia 26506-6315, United States*

Gold nanoparticles have been intensely investigated due to wide applications in colloidal chemistry, catalysis, medical science, etc. Lately, experiments have shown that ligand-stabilized gold nanoparticles provide a platform for precisely probing the structural and electronic properties of isolated gold nanoparticles, allowing us to further understand the interaction between gold nanoparticles and attaching ligand molecules. Using density functional theory approach, we investigate a series of gold nanoparticles with a size scale of 0.5 to 2 nm that are passivated by a monolayer of cysteine molecules [R-SH, with R=$CH_2CH(COOH)(NH_2)$]. There is a controversy about the attaching pattern of the cysteine monolayer around the gold nanoparticles. We speculate that there is hydrogen bonding between the cysteine molecules, leading to stabilized gold nanoparticles. This research shows potential hydrogen bonding forming with the gold nanoparticle surface, as well as hydrogen bonding between cysteine molecules.

COLL 214

Particle lithography with organosilanes: A molecular toolkit for studying surface chemistry

Treva T Brown[(1)]*, tbrow45@tigers.lsu.edu, 232 Choppin Hall, Baton Rouge LA 70803, United States ; ChaMarra K. Saner*[(1)]*; Jayne C Garno*[(1)]*. (1) Chemistry, Louisiana State University, Baton Rouge LA 70803, United States*

Particle lithography was used to prepare millions of nanostructures on surfaces using basic bench chemistry steps of heating, drying, centrifuging, rinsing, and mixing. A

surface mask is prepared by drying solutions of latex mesospheres on flat surfaces. Silanes attach to surfaces by successive steps of hydrolysis and condensation, therefore nanoscopic amounts of water are needed to initiate a hydrosilation reaction. Residues of water that persist on surfaces define the sites for organosilanes to bind. By controlling the drying parameters, nanopatterns of rings or pore structures can be produced. Organosilanes form bridging Si-O linkages between neighboring molecules or the substrate by covalently bonding to surfaces such as mica, gold, silicon, or glass. Though the mesoparticle diameter defines nanostructure periodicity, the sizes of the nanostructures are much smaller. The surface density, as well as the size and periodicity of the nanostructures can be tailored by the diameters of templating mesoparticles.

COLL 215

Overlayer growth and reaction mechanisms of iron-(hydr)oxide nanoparticles on magnetite (111) surfaces

Michael D Workman(1)*, womi0402@stcloudstate.edu, 1240 15th St N, Apt 18, St Cloud MN 56303, United States ; Jacob R Harguth*(1)*; Sarah C Petitto*(1)*. (1) Department of Chemistry, St Cloud State University, St Cloud MN 56303, United States*

Iron oxides perform important roles in the environment including the reduction of many aqueous metal ion species. Single crystal magnetite (111) is used to model and develop new understandings of iron oxides under aqueous conditions. Our research focuses characterizing the formation of oxide overlayers composed of other iron oxide phases that grow on the magnetite surface with exposure under environmental conditions. The initial magnetite surface was prepared using a chemical mechanical polishing (CMP) procedure that resulted in a clean, reproducible surface as determined by atomic force microscopy (AFM). The magnetite crystal was then submerged into an acidic electrolyte solution (pH 5, 0.1 M sodium perchlorate) with an applied electrical potential of +641 mV which is in the in the maghemite regime, an oxidized form of magnetite, according to the iron-oxygen stability field. The resultant changes to the magnetite surface were monitored and characterized using complementary electrochemical and AFM studies.

COLL 216

Infrared studies of photochemistry of adsorbed species over semiconducting nanoparticles

Joshua A Kristalyn(1)*, physics.is.phun@hotmail.com, 1407 North Kentucky, Iola Kansas 66749, United States ; Jeremy VanAuker*(1)*; Sateeshprashad Bandaru*(1)*; D. K. Paul*(1)*; K. J. Klabunde*(2)*. (1) Department of Chemistry, Pittsburg State University, Pittsburg Kansas 66762, United States (2) Department of Chemistry, Kansas State University, Manhattan Kansas 66506, United States*

The adsorption and decomposition mechanism of CO over TiO_2 and and Ga-doped TiO_2 were investigated at low temperatures by using a specially designed infrared cell which can be used over a wide range of temperatures. Here, the photo-induced chemical reactions were compared with reactions without light. Possible mechanisms for decomposition will be discussed with reference to a detailed IR spectral analysis.

COLL 217

Migration of colloidal spheres in electrolyte gradients

Aleksandr Chertok(1), *axc1014@psu.edu, 104 Chemistry Building, University Park PA 16802, United States ; Samudra Sengupta*(1)*; Ayusman Sen*(1)*. (1) Department of Chemistry, The Pennsylvania State University, University Park PA 16802, United States*

We show active migration of colloidal spheres along electrolyte gradients. The rate and direction of migration are dependent upon the zeta potential of the sphere and well as the nature of the electrolyte. Electrolytes with high differences between the diffusion constant of the cation and anion give higher migration rates for a given sphere type than electrolytes with similar diffusion constants for the two ions. While non-electrolyte gradients can also induce migration, this effect is shown to be significantly weaker than for electrolytes. Microspheres migrating towards an electrolyte source can navigate around obstacles, as long as significant movement away from the electrolyte source is not required in order to bypass the obstacle. We hypothesize that the mechanism of migration is diffusiophoresis. Understanding of this phenomenon may be critical to the study of more complex biological and environmental systems in which non-uniform electrolyte concentrations are present.

COLL 218

Towards the Quantitative Enhancement from Silver Colloids in Surface Enhanced Raman Spectroscopy

Jill R. Underwood(1), *s12.junderwood@wittenberg.edu, PO Box 720, Springfield OH 45501, United States ; Raymond Dudek*(1)*; Nicole Mangas*(1)*. (1) Chemistry, Wittenberg University, Springfield OH 45501, United States*

Raman Spectroscopy is the inelastic scattering of photons when light hits a molecule generating a vibrational spectrum from Raman active modes. At low concentrations Raman Spectroscopy yields little signal. Surface Enhanced Raman Spectroscopy (SERS) is used to find information about the chemical structure and composition of molecules at these low concentrations. SERS attaches an analyte (for example pyridine) to silver colloid particles and when a laser beam hits these silver particles the colloids act as antennas for the laser, amplifying the Raman scattering by as much as 10^{14} times. Although SERS is a great amplifier for Raman signals, little research has been done focusing on the quantitative effect of silver colloid size on the level of the

enhancement of the Raman signal. Preliminary results of the amount of enhancement from different monodispersed colloids will be presented.

COLL 219

Effect of cationic surfactant template and its interaction with specific anion: The case of K_2SO_4 crystallization at the liquid-liquid interface

Paul Sanstead(1)*, PSanstead1@iona.edu, 715 North Avenue, New Rochelle NY 10801, United States ;* ***Sunghee Lee***(1)*, SLee@iona.edu, 715 North Avenue, New Rochelle NY 10801, United States ;* ***Nick Florio***(1)*, NFlorio1@iona.edu, 715 North Avenue, New Rochelle NY 10801, United States . (1)*

We investigated the effects of potassium salts of varying anions upon the interfacially templated crystal nucleation of K_2SO_4 by monolayers of three different surfactants: 1-octadecylamine (ODA), 1-hexadecylamine (HDA), and dimethyldioctadecylammonium bromide (DODAB). K_2SO_4 at an initial concentration of 287 mM was contained in an aqueous microdroplet bounded by a liquid-liquid interface with 1-decanol containing surfactant. With no added salt, ODA monolayer was able to impart a regular crystal habit and low C_{onset}. Added salts exhibited varying ability to disrupt this surfactant mediated templation, which displayed a Hofmeister trend. Some anions, such as HPO_4^{2-}, exhibited almost no influence on ODA templating ability, while other, more chaotropic anions, such as SCN^- and NO_3^-, appreciably disrupted it. Results above will be compared to other cationic surfactants, including HDA, DODAB, and CTAB. Overall, these investigations have implications for the understanding of biomineralization processes which occur in heterogeneous environments.

COLL 220

Obtaining of high surface roughness copper deposits by electroless plating technique

Eugenijus Norkus(1)*, Norkus@ktl.mii.lt, A. Gostauto 9, Vilnius CO LT-01108, Lithuania ; Jane Jaciauskiene*(1)*; Irena Stalnioniene*(1)*; Giedrius Stalnionis*(1)*; Yezdi Dordi*(2)*. (1) Department of Catalysis, Center of Physical and Technological Sciences, Vilnius LT-01108, Lithuania (2) LAM Research Corporation, United States*

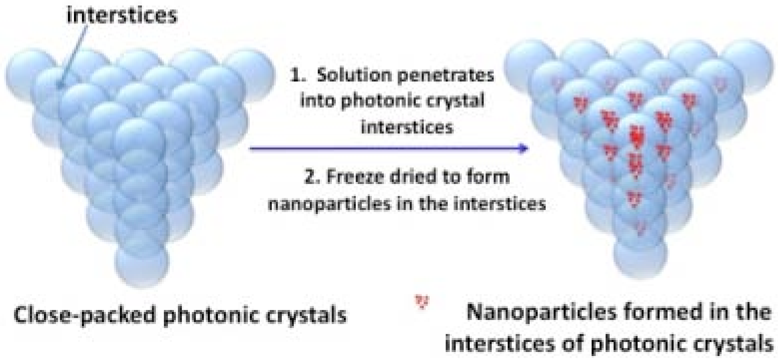
The use of pyridine-2,6-dicarboxylic and 4-hydroxypyridine-2,6-dicarboxylic acids as copper(II) ligands in formaldehyde-containing alkaline electroless copper plating solutions allowed to obtain copper layers with extremely high surface roughness factor reaching approx. 120. The Cu deposits of higher surface area were formed at highly negative open-circuit (mixed) potentials; the correlation between copper electrode overpotential and roughness of the deposit was found and discussed. The copper films obtained demonstrate a high electrocatalytic activity in anodic formaldehyde oxidation process, the oxidation rate reaches 40 mA cm^{-2} and exceeds considerably that for other copper surfaces.

COLL 221

Templated photonic crystal fabrication of nanoparticles and their resonance Raman solid cross section determinations

Luling Wang$^{(1)}$*, luw2@pitt.edu, 219 Parkman ave., Pittsburgh PA 15260, United States ; David Tuschel*$^{(1)}$*; Sanford A. Asher*$^{(1)}$*. (1)*

Development of methods to fabricate nanoparticles is important for many applications. To avoid self absorption bias it is very important to utilize small nanoparticles for solid state Raman cross section measurements. We used the defined volume interstices in close-packed photonic crystals to fabricate small $NaNO_3/Na_2SO_4$ nanoparticles with a defined stoichiometry on the surface of the photonic crystal spherical particles.



We used these stoichiometrically defined $NaNO_3/Na_2SO_4$ nanoparticles to determine the solid UV resonance Raman cross section of the NO_3^- v1 symmetric band (229 nm excitation wavelength) by monitoring the Raman spectrum of Na_2SO_4 as an internal standard. These are the first solid Raman cross section measurements that avoids self absorption biasing.

COLL 222

The thermodynamic properties of encapsulated binary n-Hexadecane/1-Octanol solutions within poly(t-butyl methacrylate) nanocapsules.

Kyle W. Tubbs$^{(1)}$*, kwtubbs@scu.edu, 500 El Camino Real, Santa Clara CA, United States ; Vincent T Nguyen*$^{(1)}$*; Paul J Henry*$^{(1)}$*; Thorsteinn Adalsteinsson*$^{(1)}$*. (1) Department of Chemistry & Biochemistry, Santa Clara University, Santa Clara CA 95053, United States*

We study the phase transition behavior of binary solutions of n-Hexadecane and 1-Octanol that are encapsulated with sub-micron sized poly(t-butyl methacrylate) polymer capsules. Systematic variation of the radius of the encapsulated oil droplet from 50 nm to 100 nm allows us to observe how the increase in the particle surface to volume ratio affects the phase transition behavior of the oil. The synthetic handle of the polymer capsules also allows us to vary the thickness of the encapsulating polymer film, and the chemical composition of the film. This allows us to change the flexibility of the film, and the surface tension between the polymer and the oil. The phase transition of the encapsulated oil is investigated through differential scanning calorimetry (DSC) and variable temperature NMR spectroscopy. This gives us a broad experimental basis in observing the actual transition temperature, the enthalpy of the phase transition, how much of the oil remains in liquid form (perceivably the surface-phase in the system) and how the composition of remaining encapsulated liquid changes during the freezing of the oil. The experiments show a dramatic change in the phase behavior and surface-liquid composition as a function of the size of the confinement. The onset of the phase transition is shifted toward lower temperatures as the confinement gets smaller, while simultaneously more liquid remains unfrozen after the main transition. The composition of the unfrozen liquid appears to be enriched in n-hexadecane, rather than 1-octanol.

COLL 223

Direct encapsulation of hydrocarbon solution nanodroplets via nucleation of polymer encapsulation from mini-emulsion templates

***Emily M Tran**(1), emtran@scu.edu, 500 El Camino Real, Santa Clara CA 95053, United States ; Lauren E Tracy(1); Paul J Henry(1); Thorsteinn Adalsteinsson(1). (1) Department of Chemistry & Biochemistry, Santa Clara University, Santa Clara CA 95053, United States*

We demonstrate that sub-micron sized droplets (nano-droplets) of hydrocarbon solutions can be captured inside nanometer thick hydrated polymer shells by directly initiating polymerization in the aqueous phase from the surface of the nano-droplet. The pre-formulated nano-droplets are prepared into a mini-emulsion, which can be made sufficiently stable to withstand the growth and deposition of the polymer unto the surface of the emulsion droplet. We have successfully deposited few nanometer thick poly(N-isopropyl acrylamide) and poly(methacrylamide) layers onto oil droplets measuring 150 to 200 nm in diameters. The oil droplets can contain potentially fragile solute molecules (dyes) without interference in the polymer deposition. Our synthetic methods allow us to vary the thickness of the polymer layer, the size and composition of the oil droplet in a single step. We also demonstrate that the polymer capsules can subsequently be used as templates for further polymer deposition. This may allow us to build up layer-by-layer capsules with liquid hydrocarbon cores in the sub-micron range. We demonstrate the polymer capsule formation by NMR spectroscopy, dynamic light scattering and gel permeation chromatography as well as SEM microscopy. NMR spectroscopy is used to verify encapsulation of solute molecules as well as to investigate molecular mobility of the molecules.

COLL 224

Microscale patterning of nanoscale roughness on Nylon-6,6 surfaces

R. Lloyd Carroll[(1)], *lloyd.carroll@mail.wvu.edu, 217 Clark Hall, Box 6045, Prospect St., Morgantown WV 26506, United States ; Matthew Payne*[(2)]. *(1) Chemistry, West Virginia University, Morgantown WV 26506, United States (2) Chemical Engineering, West Virginia University, Morgantown WV 26506, United States*

Nylon-6,6 is widely used in a variety of applications due to its desirable properties. A relatively simple procedure involving exposure of the polymer to concentrated formic acid and subsequent immersion in ethyl alcohol produces nanoscale roughness on the surface. Through selective wetting of the surface, microscale patterns of topographically roughened nylon could be produced. Potential applications of such a method could include modification of substrate wettability or controlled microfabrication of scaffolding for the growth of cellular systems. Microcontact and micromolding techniques were employed to selectively produce patterned regions of the nylon surface with dimensions as small as 3 µm. Substrate patterns were analyzed via optical microscopy, stylus profilometry and atomic force microscopy, and scanning electron microscopy (SEM). It is shown that nanoscale roughness and topography can be consistently generated in selective micropatterns ranging from 3–160 µm over an area of several square centimeters on a nylon surface through appropriate microcontact techniques.

COLL 225

Monodisperse Core/Shell Au/FePt Trimetallic Nanoparticles with Tunable Au Core and FePt Shell as a Highly Active Catalyst for Methanol Oxidation Reaction

Xiaolian Sun[(1)], *xiaolian_sun@brown.edu, 324 Brook Street Box H, Providence RI 02912, United States ; Shouheng Sun*[(1)]*; Shaojun Guo*[(1)]*; Yi Liu*[(1)]*; Sen Zhang*[(1)]. *(1)*

Pt and Pt-based nanostructures are the most efficient catalysts for fuel cell reactions nowadays. Core/shell nanoparticles (NPs) with a Pt-based shell are of great interest since the core-shell structure not only can reduce Pt usage in a controllable manner but also improve the catalytic efficiency through the electronic interaction between the core and shell. In our work, Au/FePt core/shell NPs with tunable Au core size and controlled FePt shell thickness were facilely synthesized and studied as an advanced nanoelectrocatalyts for methanol oxidation reaction (MOR). We found that the existence of Au core can not only reduce the usage of Pt metal but also promote the catalytic activity. More interestingly, it is observed that the activity of Au/FePt core/shell NPs is highly dependent on the shell thickness while the core size has a slight effect.

COLL 226

Nanoparticle size and shape series for *in vivo* fluorescence imaging

Ou Chen[(1)], *chenou@mit.edu, 77 Massachusetts Ave, 18-080, Cambridge MA 02139, United States ; Zoran Popović*[(1)]*; Wenhao Liu*[(1)]*; Vikash Chauhan*[(2)]*; Dai Fukumura*[(2)]*; Rakesh Jain*[(2)]*; Moungi Bawendi*[(1)]. *(1) Chemistry, Massachusetts Institute of Technology, Cambridge MA 02139, United States (2) Radiation Oncology,* *Massachusetts General Hospital and Harvard Medical School, Boston MA 02139, United States*

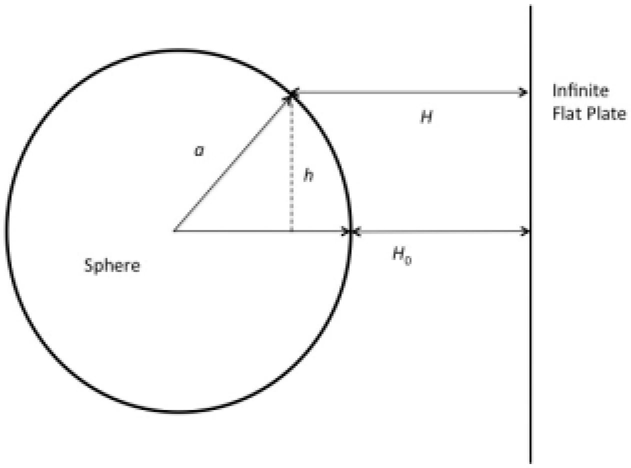
Any design of nanoparticle vectors for cancer therapy or imaging must take into account the interaction of the nanoparticles with the tumor microenvironment. Size, configuration and charge of the particles are major determinant of their behavior. However, simultaneous probing of solid tumors with particles of different size and configuration – required to account for the heterogeneity of solid tumors – has thus far been challenging due to the limitations of available nano-sized probes. Here we have designed and successfully synthesized different size (ranging from 10nm-150nm) and different configuration (sphere and rod) of quantum dot (QD) based nanoparticles that display distinct emission wavelengths for simultaneous imaging of transport *in vitro* and *in vivo*. Besides being of distinctive and narrow hydrodynamic sizes, these nanoparticles have been tested to be highly luminescent, non-aggregated, and with low protein adsorption. These properties enable the *in vivo* study of transport and distribution of nanoparticles with different size and configuration simultaneously within the same solid tumor.

COLL 227

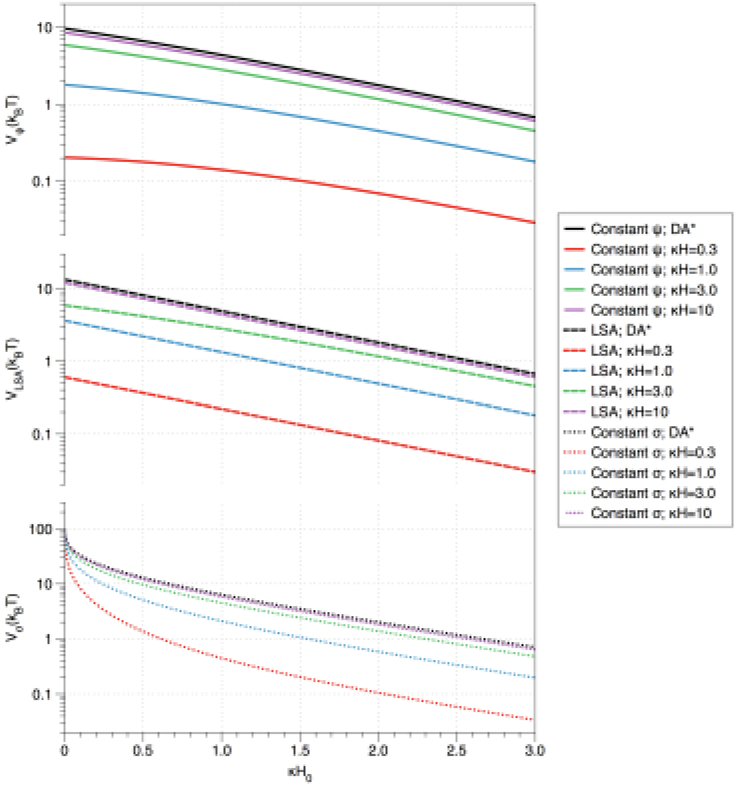
Exact analytical expression for the potential of electrical double layer interaction for a sphere-plate system

Shihong Lin(1)*, shihong.lin@duke.edu, 121 Hudson Hall, Box 90287, Durham NC 27708, United States ; Mark R. Wiesner*(1)*. (1) Civil and Environmental Engineering, Duke University, Durham NC 27708, United States*

Exact, closed-form analytical expressions are presented for evaluating the potential energy of electrical double layer (EDL) interactions between a sphere and an infinite flat plate using three different assumptions: constant potential,constant charge, and linear superposition approximation (LSA).



By taking advantage of the simpler sphere-plate geometry, simplifying assumptions used in the original Derjaguin approximation (DA) for sphere-sphere interaction are avoided, yielding expressions that are more accurate and applicable over the full range of κa. The results from these expression are exactly the same to that obtained by numerically solving the Poisson-Boltzman equation.



These analytical expressions are significant improvements over the existing equations in the literature that are valid only for large κa because the new equations facilitate the modeling of EDL interactions between nanoscale particles and surfaces over a wide range of ionic strength.

COLL 228

Experimental study and quantum-mechanical calculations of absorbance and fluorescence spectra of colloidal dispersion of CdS nanoparticles in solid solutions of fluorescent dyes in polymethylmethacrylate

Nikolay N. Barashkov(1)*, Nikolay@microtracers.com, 1370 Van Dyke Ave, San Francisco CA 94124, United States ;* ***Tamara S. Novikova***(2)*, tamara1206@hotmail.com, 10 Vorontcovo Pole, Moscow Moscow region, Russian Federation ; Artur Mantel(3); Irina S. Irgibaeva(3); Tamara V. Sakhno(2); Anuar Aldongarov(3); Moldir Bisengalieva(3). (1) Department of R&D, Micro-Tracers, Inc, San Francisco CA 94124, United States (2) Karpov Institute of Physical Chemistry, Moscow, Russian Federation (3) Department of Chemistry, Eurasian National University, Astana, Kazakhstan*

Colloidal dispersion of CdS nanoparticles in polymethylmethacrylate (PMMA) is prepared by purging hydrogen sulfide into solution of cadmium trifluoroacetate in MMA following by radical polymerization of MMA in presence of benzoyl peroxide. Absorbance and fluorescence spectra of prepared CdS/PMMA nanocomposites are investigated and compared with the spectra of colloidal dispersion of CdS nanoparticles in PMMA containing different concentration of merocyanine dye with 3H-indolilidene fragment as well as two types of perylene dyes (Lumogen Orange 240 and Lumogen Red 300). In case of CdS/merocyanine dye/PMMA nanocomposites the significant increase in the fluorescence intensity of merocyanine dye compared to merocyanine dye/PMMA system is observed. The influence of dye concentration on the fluorescence intensity of CdS/PMMA composites is investigated and possible explanation of this effect is discussed.

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COLL 229

Diffusiophoresis and osmotic diffusion of polyethylene glycol in the presence of aqueous salts

Michele D Schultz(1)*, m.d.russell@tcu.edu, TCU Box 298960, Fort Worth Texas 76129, United States ; Onofrio Annunziata(1). (1)*

Salts are known to significantly affect the equilibrium properties of macromolecules in aqueous solutions. Likewise, salts are also expected to affect their dynamic properties.

For example, salt concentration gradients can induce migration of a macromolecule (diffusiophoresis), and macromolecule concentration gradients can induce salt migration (osmotic diffusion). Better understanding of these two processes can potentially lead to applications for macromolecule self-assembly, controlled release, and separation technologies. Polyethylene glycol (PEG) was studied in the presence of aqueous salts (KCl, NaCl, Na_2SO_4, and $CaCl_2$). In all salt cases, we find that a salt concentration gradient induces PEG diffusiophoresis from high to low salt concentration, and a PEG concentration gradient induces salt osmotic diffusion, from high to low PEG concentration. Interestingly, PEG diffusiophoresis was found to be nearly constant with all salts; however, salt osmotic diffusion was found to be significantly higher for the Na_2SO_4 case than for the other salt cases.

COLL 230

In situ synthesis of bimetallic nanoparticle assemblies on functionalized surfaces

Amy Bondy[(1)]*, albondy@umd.umich.edu, 4901 Evergreen Road, Dearborn MI 48128, United States ; Krisanu Bandyopadhyay*[(1)]*. (1) Department of Natural Sciences, University of Michigan-Dearborn, Dearborn MI 48128, United States*

Metallic nanoparticles are becoming increasingly important due to their catalytic applications. Additionally, bimetallic nanoparticles are especially significant due to their unique properties. Thus, the formation of 2D metallic nanoparticle arrays that do not aggregate on various functionalized surfaces is of considerable interest. The present research involves the formation of gold-platinum and gold-paladium nanoparticles directly on silicon and indium tin oxide (ITO) coated glass surfaces. Atomic Force Microscopy (AFM) is used to characterize the structure of the nanoparticles, and UV-visible spectroscopy is used to follow the formation of nanoparticles on ITO surfaces due to the metals' characteristic absorption band in the visible region. The catalytic activity of these bimetallic nanoparticles is assessed for methanol oxidation reaction. As part of our ongoing research, the catalytic activity and mechanisms of the gold-platinum and gold-paladium nanoparticle assemblies are studied and compared.

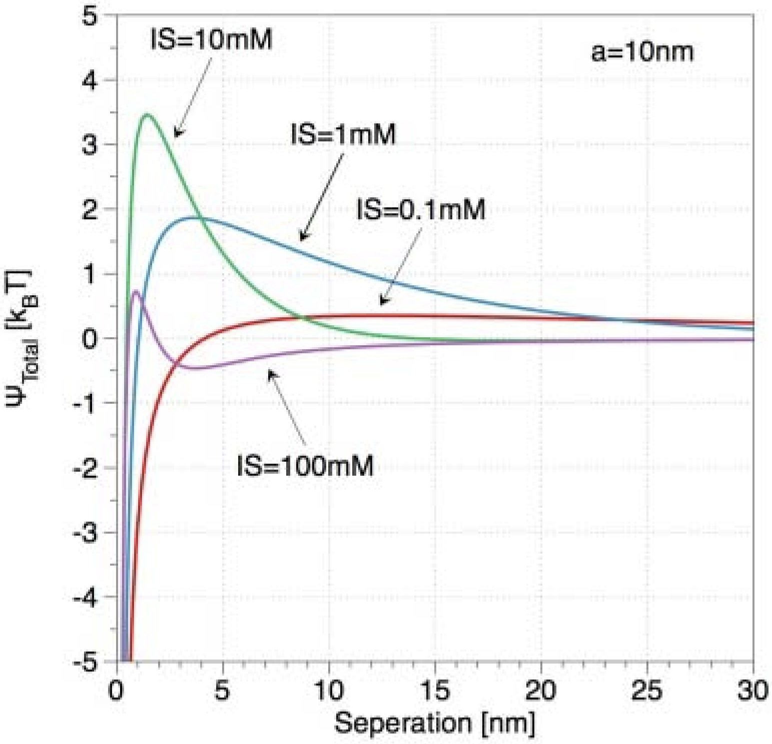
COLL 231

Theoretical prediction of decreased stability of nanosized particles at very low ionic strength

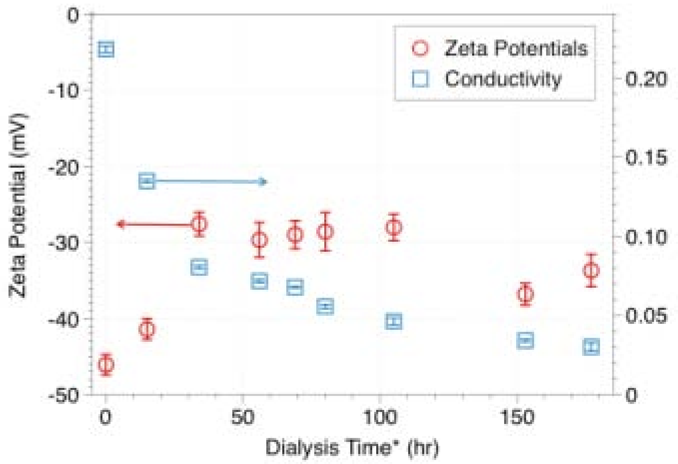
Shihong Lin[(1)]*, shihong.lin@duke.edu, 121 Hudson Hall, Durham NC, United States ; Mark R. Wiesner*[(1)]*. (1) Department of Civil and Environmental Engineering, Duke University, Durham NC 27708, United States*

The potentials of electrical double layer (EDL) interaction for a sphere-plate system ($V_{\mathrm{EDL,\ SP}}$) were calculated for fixed separations at different ionic strengths (IS) using the recently proposed exact analytical expressions. Contrary to the conclusion of Verwey and Overbeek that the stability of particle suspension would increase monotonically with

decreasing IS, the results based on the exact analytical expressions show that nanosized lyophobic particles would reach a maximum stability at relatively low IS and become destabilized at very low IS.



Such a trend should also apply to particle-particle interaction, as suggested by the potentials of EDL interaction for a sphere-sphere system ($V_{\text{EDL, SS}}$) obtained using the surface element integration method. As a qualitative experimental evidence, prolonged dialysis of a suspension of gold nanoparticles (AuNPs) was conducted. It was shown that aggregation of AuNPs occurred after a significant amount of electrolyte was removed, even though the zeta potential did not vanish.



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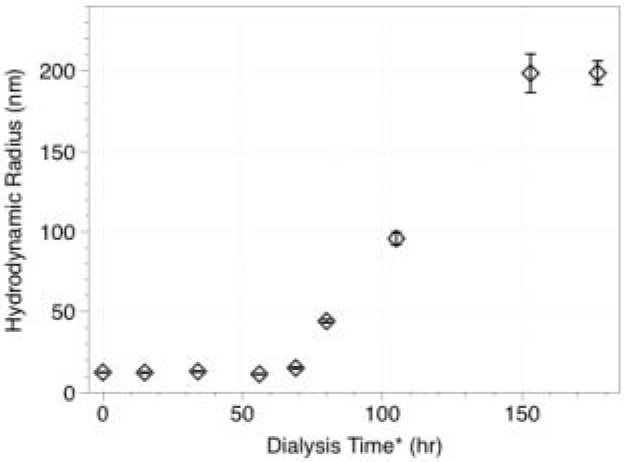

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COLL 232

Gas transport properties of polypropylene/clay nanocomposites

Mualla Oner(1), *oner@yildiz.edu.tr, Davutpasa campus, İstanbul Turkey, Turkey ; Ayla Necipoglu*(2)*; Suleyman Deveci*(3)*. (1) Chemical Engineering Department, Yıldız Technical University, İstanbul 34210, Turkey (2) (3) Yildiz Technical University Davutpasa Campus, Phase 1,, Dizayn Group Research & Technology Development Co Ltd,, İstanbul 34210, Turkey*

Polymer-clay nanocomposites are one of the newest composite types, which its importance is came out especially after 2000. Polymers are used as matrix in these types of composites and clay minerals act as reinforcement material. By combining these two different structures, new materials can be synthesized which have better physical and chemical properties according to the normal polymers. In this study polypropylene with different melt flow index was used to prepare polypropylene-clay nanocomposites via melt intercalation metod. Polypropylene / clay blends were produced with different compositions to determine the optimum amount of clay. Physical

properties of polypropylene composites were investigated using X-ray diffraction and differential scanning calorimetry. The oxygen barrier properties of the composites were determined at room temperature. The results showed that the filled polypropylene exhibit lower gas permeability compared to the unfilled polypropylene. The effect of melt flow index and crystalinity of the polypropylene on barrier properties of composites was investigated by using oxygen permeability instrument.

COLL 233

Chain length effects in the formation of Polyelectrolytes Multilayers

Samantha Micciulla(1)*, chloe.chevigny@tu-berlin.de, Strasse des 17. Juni 124, Berlin Berlin 10623, Germany ; Samuel Dodoo*(1)*; Maximilian Zerball*(1)*; Chloe Chevigny*(1)*; Regine von Klitzing*(1)*. (1) Department of Physical and Theoretical Chemistry, Stranski Lab., TU Berlin, Berlin Berlin 10623, Germany*

For the past twenty years, the Layer-by-Layer technique (LbL) has made it possible to modify surfaces by covering them with thin films. The deposition of PolyElectrolytes Multilayers (PEM) is influenced by various parameters, such as ionic strength, pH value and charge density. Here we are interested in the influence of the chains length on the formation and properties of such films. As polyelectrolytes we chose to use the two most widely spread systems, PSS/PAH and PSS/PDADMAC, with different chain lengths (from 10 to 100 monomers/chain). The thickness, roughness and aspect of the PEM are monitored as a function of the number of layers deposited by a complementary use of ellipsometry, AFM and QCM-D. Different growth models are found, depending on the chain length and the adsorption time.

COLL 234

Phase Behavior of Two-Component Thiol SAMs on Immobilized Gold Nanoparticles Characterized by XPS

Michael L. Jespersen(1)(2)*, michael.jespersen.ctr@wpafb.af.mil, AFRL/RXBN, 2941 Hobson Way, Buliding 654, Wright-Patterson Air Force Base OH 45433, United States ; Folusho T. Oyerokun*(1)(3)*; Eric S. Pitt*(1)*; Travis M. King*(4)*; Richard A. Vaia*(1)*. (1) Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base OH 45433, United States (2) UES, Inc., Wright-Patterson Air Force Base OH 45433, United States (3) National Research Council, Wright-Patterson Air Force Base OH 45433, United States (4) Department of Biomedical Engineering, Texas A&M University, College Station TX 77843, United States*

Self-assembly processes at nanoparticle interfaces are of interest for tailoring nanoparticle functionality and enabling formation of higher-order nanoparticle assemblies. We have utilized x-ray photoelectron spectroscopy (XPS) to analyze the phase behavior of two-component organothiol SAMs formed from solution onto immobilized gold nanoparticles. Citrate-stabilized gold nanoparticles are immobilized

onto thiol-terminated silane monolayers by random self-assembly. The nanoparticle-surface interaction is sufficiently stable to allow subsequent modification of the gold nanoparticle surfaces without desorption of nanoparticles or in-plane aggregation. SAMs of alkanethiols are assembled onto the surface-bound gold nanoparticles from mixed thiol solutions, and the resultant films are analyzed by XPS. Attenuation of the Au 4f photoelectron peak by inelastic scattering through the carbonaceous overlayer is analyzed in order to determine average SAM thicknesses, from which the monolayer compositions are calculated. The effects of particle size and solution composition on the phase behavior of two-component organothiol SAMs on gold nanoparticles will be presented.

COLL 235

Popcorn shape gold nano particle mediated SERS probe for low level selective detection and photothermal nanotherapy of multidrug resistance bacteria from vegetables

Sadia Afrin Khan(1)*, sadia_afrin_2006@yahoo.com, 1400 J. R. Lynch Street, Jackson MS 39217, United States ; Anant Kumar Singh*(1)*; Dulal Senapati*(1)*; Zhen Fan*(1)*; Paresh Chandra Ray*(1)*. (1) Department of Chemistry and Biochemistry, Jackson State University, Jackson MS 39217, United States*

In recent days multidrug resistance bacteria (MDRB) is an immense risk worldwide. In this condition a novel approach which does not depend on traditional methods for the selective detection and targeted killing is an urgent need. Driven by the need, herein I am presenting Rh-6G tagged S-PS8.4 RNA aptamer conjugated popcorn shape gold nanotechnology driven Surface Enhanced Raman Scattering (SERS) technique to selectively detect and photothermally destroy drug resistant *Salmonella typhimurium* from infected romaine lettuce. In the presence of S*.typhimurium*, aptamer conjugated popcorn shape gold nanoparticles are forming several hot spots which allows to get the SERS signal making it possible to detect the bacteria with higher sensitivity and when these are exposed to radiation almost all bacteria are killed due to local photothermal lysis. We believe this nanotechnology based assay will open up a new possibility for the detection and killing of MDRB from food samples.

COLL 236

Aggregation behavior and kinetics of bovine insulin

Kiersten Batzli(1)*, kbatzli@umich.edu, HH Dow Bldg, 2300 Hayward St, Ann Arbor Michigan 48109, United States ; Brian Love*(1)(2)(3)*; K. Anne Juggernauth*(1)(4)*. (1) Department of Materials Science and Engineering, University of Michigan, Ann Arbor Michigan 48109, United States (2) Department of Biomedical Engineering, University of Michigan, Ann Arbor Michigan 48109, United States (3) Department of Biologic and Materials Science, University of Michigan, Ann Arbor Michigan 48109, United States (4)*

Macromolecular Science and Engineering Research Center, University of Michigan, Ann Arbor Michigan 48109, United States

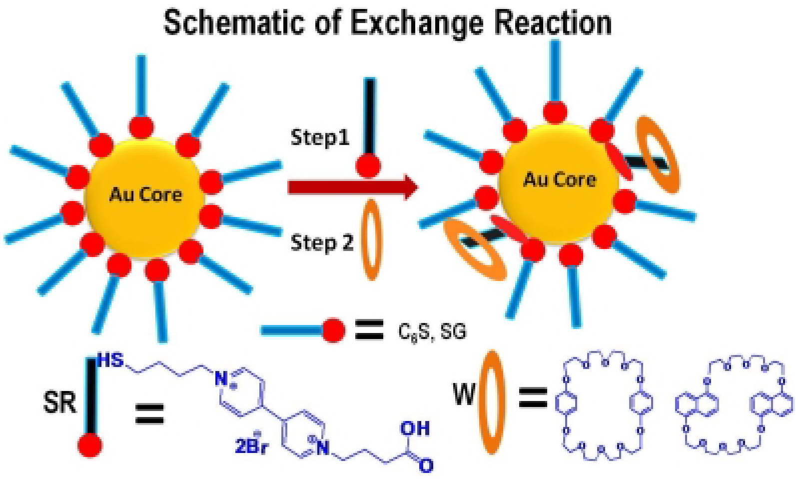
Insulin is an amyloidogenic protein associated with the occurrence of diabetes. Pharmaceutical insulin used by diabetics is often composed of a human insulin analog along with a stabilizing agent. Despite the inclusion of stabilizers such as metacresol, pharmaceutical insulin may degrade and become less effective, and to prevent this must be stored and used in specific conditions. We have used rheology and small-angle x-ray scattering (SAXS), as well as AFM, to study the aggregation kinetics of bovine insulin protein in solution at a variety of concentrations and environmental conditions, including heating rate, incubation temperature and strain. The behavior of bovine insulin is compared to tests of pharmaceutical insulin. The use of rheology in conjunction with other methods to determine the rate and behavior of insulin aggregation in denaturing conditions provides us with a means to test alternative stabilization methods for protein therapeutics in suspension.

COLL 237

Synthesis and Optoelectronic Dynamics of Supramolecular Switches Assembled on Monolayer Protected Gold Clusters

Mary Sajini Devadas(1)*, sajini_dev@yahoo.com, 3425 Wood Hall, Kalamazoo MI 49008, United States ; Isurika Fernando*(1)*; Gellert Mezei*(1)*; Ekkehard Sinn*(1)*. (1) Department of Chemistry, Western Michigan University, Kalamazoo MI 49008, United States*

Mechanically interlocked molecules (MIMs), such as catenanes and rotaxanes, have contributed significantly to the development of tunable molecular architectures on scales from the molecular to the nanoscopic levels. Efficient syntheses of rotaxane-nanoparticle hybrids have potential uses in molecular electronic devices (MEDs), molecular switch tunnel junctions (MSTJs), and nanoelectromechanical systems (NEMS). Hexanethiolate (SC_6) and glutathione (SG) gold clusters were synthesized and characterized. Ligand exchange reaction was performed in order to place exchange the hexanethiolate(SC_6) and glutathione(SG) with a new thiol based Rod(SR) molecule. This hybrid was then further modified with the wheel(W) component of the rotaxane, which is the crown ether ring. The ensuing changes in optical (UV-Vis, Fluorescence, TPA) and electrochemical properties (SWV) will be presented. The engaging-disengaging reaction between the rod and wheel components on the nanoparticle surface will be studied to sense nerve gas mimics. The electron tunneling between the gold core and the molecular switch can be tailored specifically to detect redox active species in solution



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COLL 238

In-situ photorheology: Kinetics of photogelation in Laponite based photorheological fluids

K. Anne Juggernauth$^{(1)(2)}$*, annekj@umich.edu, 2300 Hayward St., HH Dow Bldg, Ann Arbor MI 48109, United States ; Amy E. Gros*$^{(2)}$*; Brian J. Love*$^{(2)(3)(4)}$*. (1) Macromolecular Science & Research Center, University of Michigan, Ann Arbor MI 48109, United States (2) Department of Materials Science & Engieering, University of Michigan, Ann Arbor MI 48109, United States (3) Department of Biomedical Engineering, University of Michigan, Ann Arbor MI 48109, United States (4) Department of Biologic and Materials Sciences (Dentistry), University of Michigan, Ann Arbor MI 48109, United States*

Photorheological (PR) fluids represent a class of material that has generated a significant amount of interest in the recent years due to its wide variety of possible uses. Recent reports on nanoparticle based photofluids helps in eliminating the need for extensive chemical synthesis leading to PR behavior. However, the kinetics of gelation of these new PR fluids is not well understood. The kinetics of gelation and the factors affecting gel formation upon UV exposure were explored using in-situ photorheology and a Laponite based PR system. These systems were further analyzed using a variety of other techniques including light and x-ray scattering as well as differential scanning calorimetry (DSC) and microscopy.

COLL 239

Synthesis of gold nanoshell by in situ generation of gold seeds on silica core

Gabrielle McGuire(1), gmcguire@umd.umich.edu, 4901 Evergreen Road, Dearborn MI 48128, United States ; Elissa Grzincic(1); Ben Q. Li(2); Avinash Yella(2); Krisanu Bandyopadhyay(1). (1) Department of Natural Sciences, University of Michigan-Dearborn, Dearborn MI 48128, United States (2) Department of Mechanical Engineering, University of Michigan-Dearborn, Dearborn MI 48128, United States

Various core-shell combinations of nanoshells have been formed by bottom-up approach and find it applications in cancer treatment and as solar energy absorber. The synthesis procedure to generate silica/Au nanoshell is well documented in literature. In the present method, gold seeds are formed separately and then adsorb on to amine functionalized silica core surface to grow the final gold nanoshell. The present research deals with a new method to form these nanoshells, eliminating gold seed forming steps and also shortening the time needed for synthesis. Specifically, the procedure entails a new method to form silica-core and gold-shell nanoshells, involving the generation of the gold seeds in-situ, rather than forming the seeds in a separate solution. This relatively simpler route to generate nanoshells will improves their ease of use and makes them even better candidates for various potential applications. In this present reseach, different size core-shell nanoparticles will be generated including a sub-100 nm core. The heating profile of these nanoshells will also be explored.

COLL 240

Theoretical studies of the HMTD adsorption inside MCM-41 and AAO nanopores

Evgueni B Kadossov(1), evgueni@xplosafe.com, 1414 South Sangre Road, Stillwater OK 74074, United States ; Allen W. Apblett(1); Nicholas F. Materer(1). (1) Xplosafe, LLC, Stillwater OK 74074, United States

Adsorption of hexamethylene triperoxide diamine (HMTD) inside the silica (MCM-41) and anodized aluminum oxide (AAO) nanopores was studied utilizing hybrid quantum mechanics/molecular mechanics approach. The HMTD molecule and the adjacent pore region represented by the stoichiometric Si_6O_{12} (Al_6O_9) clusters were calculated on the density functional (B3LYP/6-31G*) level, while the rest of the system was treated using the universal force field method. The computed adsorption energy values of HMTD inside MCM-41 and AAO pores range from 8.9 to 54.3 kJ/mol depending on the pore size, and correspond to weak physisorption. HMTD binding energies decrease as the pore size increase and are slightly stronger for the AAO system. However, HMTD adsorption on bare $Si_6O_{18}H_{12}$ and $Al_6O_{12}H_6$ clusters is endothermic, indicating significant effect of the pore walls on the adsorption strength.

COLL 241

Phosphonosilicate gels by nonhydrolytic condensation reactions

Jiri Pinkas(1), jpinkas@chemi.muni.cz, Kotlarska 2, Brno Brno CZ-61137, Czech Republic ; Ales Styskalik(1); David Skoda(1); Zdenek Moravec(1); Craig E. Barnes(2). (1)

Department of Chemistry and CEITEC MU, Masaryk University, Brno CZ-61137, Czech Republic (2) Department of Chemistry, University of Tennessee, Knoxville Tennessee TN 37996-1600, United States

Previously, we prepared phosphosilicate gels by elimination of acetic acid esters in heterocondensation reactions between silicon acetate and trimethylsilyl ester of phosphoric acid.[1,2] Here we report a study that extends this reaction principle to the formation of hybrid phosphonosilicate gels from acetoxysilanes $^{1}R_{x}Si(OC(O)CH_{3})_{4-x}$ (^{1}R = Me, Ph) and phosphonic acid esters $^{2}RP(O)(OSiMe_{3})_{2}$ (^{2}R = $OSiMe_{3}$, c-Hex, Ph) in nonaqueous solvents.

$$2\ ^{1}R_{4-x}Si(OC(O)CH_{3})_{x} + x\ ^{2}RP(O)(OSiMe_{3})_{2} = 2x\ CH_{3}C(O)OSiMe_{3} + (^{1}R_{4-x}Si)_{2}(PO_{3}{}^{2}R)_{x}$$

The nonhydrolytic ester elimination provides clear amorphous hybrid phosphonosilicate gels which were studied by N_2 adsoprtion, ^{29}Si and ^{31}P CPMAS NMR, IR spectroscopy, and TG/DSC. Trimethylsilyl acetate was identified by NMR and GC/MS as the elimination byproduct.

[1] Styskalik, A. et al., ChemZi. Bratislava, SK: SCHS, **2009**, 164. ISSN 1336-7242.

[2] Styskalik, A. et al., Hybrid Materials, Strasbourg, FR, **2011**, B.2.7.1

The financial support by MSM0021622410, CZ.1.05/1.1.00/02.0068, and GACR P207/11/0555 is gratefully acknowledged.

COLL 242

Pyridinium gemini surfactants: Synthesis, self-assembling, and physicochemical properties

***Marc A Ilies**(1), mailies@temple.edu, 3307 N Broad Street, Philadelphia PA 19140, United States ; Vishnu Dutt Sharma(1); Eronmwon O Aifuwa(1). (1) Department of Pharmaceutical Sciences, Temple University School of Pharmacy, Philadelphia PA 19140, United States*

Gemini surfactants are defined as surfactants made up of two identical or different amphiphiles linked at the level of the polar head by a spacer. In recent years a large number of gemini surfactants with different polar heads, hydrophobic chains, linkers and counterions were synthesized and studied in respect of their self-assembling and biological properties. Cationic gemini surfactants in particular attracted a lot of interest due to their special biological properties. In the present study we have evaluated the impact of two structural components – chain length and counterion - on the physicochemical characteristics of the supramolecular assemblies generated from a small series of pyridinium gemini surfactants synthesized in our lab.

COLL 243

Anomalous diffusion in supported lipid bilayers induced by oxide surface nanostructures: Single molecule tracking on opaque and highly-refractive substrates

***Ryugo Tero**[1][2], tero@eiiris.tut.ac.jp, 1-1 Hibarigaoka, Tempaku-cho, Toyohashi Aichi 441-8580, Japan ; Gen Sazaki[3]; Toru Ujihara[4]; Tsuneo Urisu[2]. (1) The Electronics-Inspired Interdisciplinary Research Institute, Toyohashi University of Technology, Toyohashi Aichi 441-8580, Japan (2) Division of Biomolecular Sensing, Institute for Molecular Science, Toyohashi Aichi 441-8580, Japan (3) The Institute of Low Temperature Science, Hokkaido University, Sapporo Hokkaido 060-0819, Japan (4) Department of Materials Sciences and Engineering, Nagoya University, Nagoya Aichi 464-8603, Japan*

Supported lipid bilayers (SLBs), lipid bilayers stabilized at solid/water interface, are expected as a promising cell-membrane-mimicking models system as well as an interface system between solid and biological materials. One of the most important aspects of the cell membrane dynamics is its hierarchic behavior in domain structures and molecular diffusion. Lipid diffusion in SLBs on oxide surfaces at the scale of 100 nm to 10 um was observed in situ by single molecule tracking (SMT) method. SMT with various time resolutions revealed hierarchic diffusion in the SLBs artificially caused by substrate nanostructures. SMT is a powerful method to investigate the molecular behavior in the SLBs, but the substrate material has been restricted to glass and quartz since the SLB is illuminated by the evanescent light induced in the total internal reflection condition. In our experimental system the substrates with SLBs on the surface is put on the cover glass slip upside down, and the excitation light is diagonally introduced to the substrate surface through the cover slip. This experimental setup achieved SMT independent of the sample transparency and refractive index. We discuss the spatiotemporal dependence of the lipid diffusion coefficients affected by substrate nanostructures in detail.

COLL 244

Kinetics of surface-based hybridization: Deviation from Langmuir kinetics and long-lived secondary structures

***Damion L Irving**[1], damion.irving@gmail.com, 6 Metrotech Center, RH607, Brooklyn NY 11201, United States ; Rastislav Levicky[1]; Yatao Liu[1]. (1)*

Surface-based hybridization is used in DNA microarrays for a plethora of applications. However, key assumptions used to treat the thermodynamics, kinetics, and mass transport of hybridization of these systems over a wide parameter space are either unavailable or questionable. In this work a mixed SAM composed of a 20 bp probe sequence (P1) and Mercaptohexanol passivator, is end tethered to a gold electrode, to prepare a probe layer of known coverage. To study the initial kinetic rates of binding, a model system consisting of a fully complementary, 18 bp DNA target sequence (T1) is used. DNA are conjugated with Ferrocene derivative redox couples, and hybridization

kinetics are tracked with time using cyclic voltammetry; hydrodynamic conditions are controlled using a rotating disk electrode, that allows for decoupling of mass-transport effects and surface hybridization kinetics. Kinetics are studied over a wide parameter space of counterion concentration (C_{K+}) and probe coverages for P1 and T1, showing significant deviation from the Langmuir model, even in the pseudo-Langmuir regime. These results motivated a study of four additional target sequences (T2, T3, T4, T5) of varying length and complementarity, under pseudo-Langmuir (PL) and moderate probe (MP) coverages and a counterion concentration C_{K+}=1.0mol L^{-1} chosen to effectively screen electrostatic interactions. The results suggest a kinetic mechanism where long-lived imperfect duplex structures relax to perfect duplexes as equilibrium is approached. Nearest neighbor calculations are used as a benchmark for investigating the possibility of probe-probe interactions, showing two such possible secondary structures for P1. The qualitative contribution of these effects are investigated under PL and MP for C_{K+}=1.0mol L^{-1}. The results suggest that hybridization is described by: (1) electrostatic effects from membrane potentials in the probe layer before and during hybridization (2) long-lived P-T secondary structures in the layer (3) probe-probe interactions in the probe layer.

COLL 245

Dielectric Spectroscopy of the Concentrated Dispersions of Poly(N-isopropylacrylamide) Microgels

Dan Zhu(1)*, zhudan1013@gmail.com, 1# Wenyuan Road, Nanjing Jiangsu 210046, China ; Jianfeng Zhou*(2)*; Jian Shen*(1)*. (1) College of Chemistry and Materials Science, Nanjing Normal University, Nanjing Jiangsu 210046, China (2) Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei Anhui 230026, China*

Dielectric spectroscopy is a powerful tool in characteizing the complex systems and their dynamics. By detecting the interaction of the matter with the electromagnetic waves in a broad band (10^{-6} ~ 10^{12} Hz), dielectric spectroscopy provides a large amount of information on related bound and free charges, sensitively reflecting the hierarchical structures, especially those related with interfacial phenomena. In this study it provides a direct observation of the particles motions and interactions as well as the collaborative process in the concentrated collodial dispersions. There are two relaxation modes detected, the fast mode around MHz results from the Maxwell-Wagner-O'Konski polarization, correlated with the Debye length, while the slow mode at 10KHz is related with the concentration polarization of the medium solvent aroud the microgels. The latter provides us the dynamic parameters of the jamming transition of the PNIPAM colloids, when its volume fraction reaches a high value with temperaturs decreasing. The electrical characteristic method provides us not only convenience and accuracy, but also non-invasion and continuous measurement, compared with other vibrational spectroscopies, dielectric spectroscopy covers a broad range of frequencies, which makes it qualified to the studies of the non-equilibrium dynamics of soft matters.

COLL 246

Depolymerization Powered Motor and Their Application as Diffusion Pumps

Hua Zhang(1)*, huz111@psu.edu, 104 Chemistry Bldg, The Pennsylvania State University, University Park PA 16802, United States ; Jesse Robbins*(1)*; Meng Wu*(1)*; Ran Liu*(1)*; Scott Philips*(1)*; Ayusman Sen*(1)*. (1) Department of Chemistry, The Pennsylvania State University, Univeristy Park PA 16802, United States*

Poly(ethyl cyanoacrylate) (PECA) particles with the diameter of 2μm were synthesized. The diffusion coefficient of the particles increased about 55% in pH=8 and 75% in pH=8.5 solutions respectively by comparing with pH=6 control, attributed to the moderate polymer degradation in basic environment. Utilizing the stimulus-responsive depolymerization property of both PECA and poly (phthalaldehyde) (PPA), diffusion pumps were developed. With the release of small molecules, tracer particles were expelled away from bulk PECA and PPA, creating a zone of exclusion.

COLL 247

The effect of surface tension and curvature on the phase behavior of encapsulated liquid volumes in polymer nanocapsules.

Thorsteinn Adalsteinsson(1)*, tadalsteinsson@scu.edu, 500 El Camino Real, Santa Clara CA, United States ; Kyle W. Tubbs*(1)*; Vincent T. Nguyen*(1)*; Paul J. Henry*(1)*; Emily M. Tran*(1)*. (1) Department of Chemistry & Biochemistry, Santa Clara University, Santa Clara CA 95053, United States*

We present results from experiments on nano-encapsulated binary hydrocarbon solutions (n-Hexadecane and 1-Octanol). Droplets with varying size and binary composition are encapsulated within nanometer thick poly(alkyl methacrylate) shells via mini-emulsion polymerization. The thermal behavior of the encapsulated droplets is investigated using Differential Scanning Calorimetry (DSC). Composition of the oils during thermal transitions is investigated by Variable Temperature NMR spectroscopy (VT-NMR).

The variation of capsule size allows us to probe the effect of curvature on the phase transition, but our synthetic method allows us to vary the type of polymer used to encapsulate the oil droplets, and thus the interfacial tension between the oil and the polymer. The polymers are insoluble in the oils, which allows us to assume that the interface is static, or solid. The formation of the solid phase within the capsule should therefore be closer to what is observed in solid-mixtures than what is seen in surfactant stabilized emulsions.

COLL 248

Effects of salts on carbon nanotubes dispersions: understanding molecular mechanisms

Andrey I. Frolov[1], *frolov@mis.mpg.de, Inselstr. 22, Leipzig Saxony 04103, Germany ;* ***Maxim V. Fedorov***[1], *fedorov@mis.mpg.de, Inselstr. 22, Leipzig Saxony 04103, Germany ; Raz N. Arif*[2]*; Anastasia O. Romanova*[1]*; Aleksey G. Rozhin*[2]*. (1) Max Planck Institute for Mathematics in the Sciences, Leipzig Saxony 04103, Germany (2) School of Engineering & Applied Science, Aston University, Aston Triangle, Birmingham B4 7ET, United Kingdom*

Dispersions of carbon nanomaterials are important for their energy applications. In this study we consider the effects of salts on carbon nanotubes (CNTs) dispersions in aqueous [1] and non-aqueous solvents. We investigate the molecular-scale mechanisms of ion interactions with the nanotube surface and we show how the microscopic ion-surface interactions affect the stability of CNT dispersions. Our simulations reveal that an increase of the salt concentration should decrease the stability of the CNT dispersions (salting out effect) [2]. Direct experiments confirm the simulation results: for example, addition of salt into the N-methyl-2-pyrrolidone (NMP) dispersions of CNTs leads to precipitation of CNTs (bundle formation) [3]. Thus, one can stimulate the bundle formation in the CNT dispersions and regulate the overall concentration of nanotubes in the dispersions by changing salt concentration.

[1] Frolov, Rozhin, Fedorov, ChemPhysChem 2010, 11, 2612.
[2] Frolov et al., Chemical Science, submitted
[3] Fedorov et al., Nanoscale, submitted

COLL 249

Quantitative analysis of correlation between Nafion distribution in mesoporous carbon catalyst and their ORR reactivity

Ken'ichi Kimijima[1], *k-kimijima@fc-cubic.or.jp, AIST bldg., 2-3-26 Aomi, Koto-ku, Tokyo Tokyo 135-0064, Japan ; Shun Umemura*[1]*; Ichizo Yagi*[1]*. (1) Fuel Cell Cutting-Edge Center (FC-Cubic), Technology Research Association, Tokyo Tokyo 135-0064, Japan*

Nano-scale structures of catalyst and catalyst layer (electrode) in PEFC (polymer electrolyte fuel cell) are one of the important factors for their ORR reactivity, because the formation of effective reaction sites and the mass transfer of both reactants and products are finally tuned via the nano-scale structure inside catalyst layer, which includes size and structure of pores, structure and distribution of Nafion (proton conductive polymer) agglomerates. In our previous study, we have proposed a method to evaluate the effect of the nano-structure of catalysts on the ORR reactivity by constructing a series of model catalysts. It was found that the ORR activity strongly depended on the pore size in the mesoporous region and the distribution of Nafion around platinum particles inside mesopores, which could be controlled using an

ionomer with a low molecular weight instead of Nafion.[1]

In this study, to clarify the correlation between the ORR activity and Nafion distribution within the pores in a catalyst layer, the spatial distribution of Nafion in model catalyst layer has been conducted. A model catalyst layer was prepared as novel mesoporous carbon membrane, and Nafion was diluted by various solvents and was directly cast onto the membrane. Nafion distribution was measured using XPS-depth profiling method. From F1s signal in the XP spectra, the penetration of Nafion toward mesopores was directly confirmed, and the spatial distribution of Nafion, depending on the kind of dispersant, was quantitatively analyzed. Further, the kinetic ORR current at these model catalysts was also influenced by the kind of dispersant for Nafion, and a correlation between the penetration depth and ORR activity will be discussed.

(1) Kimijima, K.; Hayashi, A.; Umemura, S.; Miyamoto, J.; Sekizawa, K.; Yoshida, T.; Yagi, I. *J. Phys. Chem. C* **2010**, 114, 14675.

COLL 250

Nanoparticle mediated stabilization of immiscible polymer blends

Subhalakshmi Nagarajan(1)*, subhalakshmi.nagarajan.ctr@us.army.mil, Kansas Street, Natick MA 01760, United States ; Christopher P Drew*(1)*; Ramanathan Nagarajan*(1)*. (1) U. S. Army Natick Soldier Research, Development and Engineering Center, Natick MA 01760, United States*

Filler-reinforced polymer blends, which combine rigidity and thermal stability of inorganic materials with processability and flexibility of polymers, are of great interest. The final properties of the filler-reinforced blends are influenced by the location and distribution of fillers and processing conditions employed. It would be desirable if the equilibrium morphology would spontaneously be formed due to immiscible elements adopting a low-energy arrangement. Pickering-type emulsions, where particles act as emulsifying agents, residing at the interface of low molecular weight immiscible liquids, have been shown to have stable morphologies. This work attempts to extend this knowledge to stabilize polymer blends using nanoparticles as blend compatibilizers.The morphology of polymer blends and location of the nanoparticles were studied and effect of nanoparticle hydrophilicity on blend morphology was evaluated for some immiscible homopolymer pairs. Aggregation of nanoparticles into a third phase and a novel method of covalently sequestering the nanoparticles to the polymer were examined.

COLL 251

A visible light driven Fe-TiO_2 mesoporous nanophotocatalyst

Ying Wang(1)(2)*, wangy@nju.edu.cn, Hankou Road 22, Nanjing Jiangsu 210093, China ; L. Liu*(1)(2)*; S. Chu*(1)(2)*; L. L. Luo*(1)(2)*; F. Kong*(1)(2)*; Z. G. Zou*(2)*. (1) School of Chemistry and Chemical Engineering, Nanjing University, Nanjing Jiangsu 210093, China (2) Eco-*

materials and Renewable Energy Research Center (ERERC), Nanjing University, Nanjing Jiangsu 210093, China

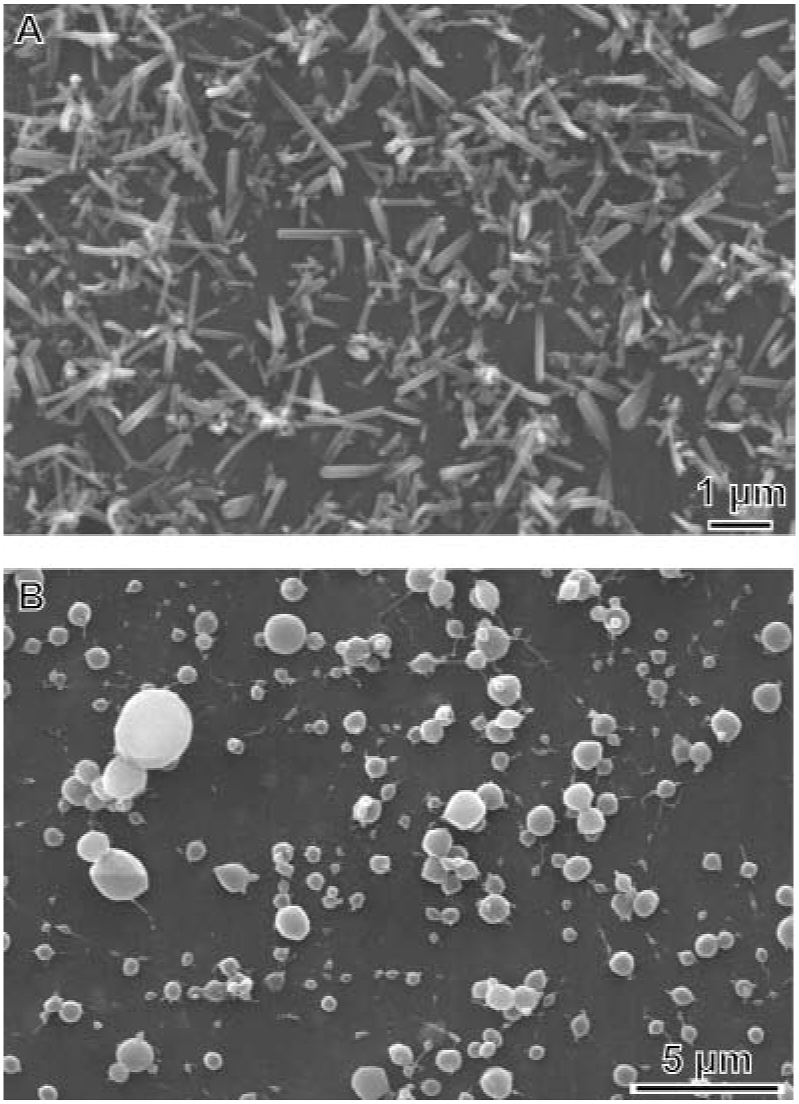
A series of novel of Fe-doped & propylthiol-functionalized organic-inorganic hybrid mesoporous TiO_2 photocatalysts have been first prepared by one-pot method. These materials possess high surface areas and mesoporous structure with uniform pore size distribution. XRD analysis confirms the anatase phase of these Fe-doped TiO_2 materials. From EPR and XPS, it was found that Fe exists in trivalent ions state substituting Ti^{4+} into TiO_2 lattice in low spin state. The XPS data also indicates the formation of Si-O-Ti bond, suggesting that MPTES has been successfully polymerized in mesoporous TiO_2. The photodegradation of PHE under visible light irradiation (λ>420nm) was investigated to evaluate the photocatalytic activity of these materials and these samples demonstrated the highest photocatalytic activity. The intermediates of PHE photodegradation were detected by gas chromatography-mass spectrometer. Based the experiment results, we proposed a possible mechanism.

COLL 252

Engineering hydrophobic drug by using electrospray system: Developing an effective drug delivery system for Niclosamide

Meng-Yi Bai(1)*, mybai@mail.ntust.edu.tw, #43,Sec.4,Keelung Rd., Taipei Taiwan 106, Taiwan Republic of China . (1) Graduate Institute of Biomedical Engineering, National Taiwan University of Science and Technology, Taipei Taiwan 106, Taiwan Republic of China*

Recently, we have found that Niclosamide is an effective drug for treating ovarian cancer. The greatest problem which strongly influences its efficacy on cancer treatment is the hydrophobic nature of this drug. In this study, we utilized electrospray (ES) technique to generate Niclosamide nano-/micro- particles and hopefully the produced pharmaceutical particles can be hence well dispersed or dissolved in water-based solution, such as phosphate buffer saline (PBS). We fabricated two forms of Niclosamide nano-/micro- particles : (A) pure Niclosamide nanorods and (B) Niclosamide-encapsulated PLGA submicro- particles



. We anticipated that these two different types of drugs carriers are going to show improved compatibility to water-based solution due to their increase in surface to volume ratio. A simple solubility test was conducted to show this enhanced water solubility/or dispersity

. We are currently investigating the efficacy of these pharmaceutical particles on the treatment of ovarian cancer through a series of *in vitro* and *in vivo* studies.

COLL 253

Characterization of Tumor Necrosis Factor (TNF) Protein Conjugation on Gold Nanoparticles

Sherrie Elzey(1)*, sherrie.elzey@nist.gov, 100 Bureau Dr, Stop 8520, Gaithersburg MD 20899, United States ; De-Hao Tsai*(1)*; Frank DelRio*(1)*; Athena Keene*(2)*; Katherine Tyner*(2)*; Jeffrey Clogston*(3)*; Jiwen Zheng*(3)*; Robert MacCuspie*(1)*; Tae Joon Cho*(1)*; Suvajyoti Guha*(1)(4)*; Michael Zachariah*(1)(4)*; Vincent Hackley*(1)*. (1) Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg MD 20899, United States (2) Center for Drug Evaluation and Research, Food and Drug Administration, Silver Spring MD 20993, United States (3) Nanotechnology Characterization Laboratory, Advanced Technology Program, SAIC-Frederick Inc., NCI-Frederick, Frederick MD 21702, United States (4) Departments of Mechanical Engineering and Chemistry, University of Maryland, Gaithersburg MD 20899, United States*

Gold nanoparticle (AuNP)-based targeted drug delivery platforms confine the therapeutic agent, such as *tumor necrosis factor* (TNF), within the tumor, reducing collateral damage to healthy tissue and reducing the required systemic dose. The capacity to characterize the surface density, conformation, and functionality of TNF-AuNP conjugates is important from a drug development and regulatory perspective. In this work, we use complementary physical and spectroscopic characterization methods to interrogate the conjugation of TNF onto AuNPs. Prior to conjugation, we use

electrospray-differential mobility analysis (ES-DMA) and gel electrophoresis to obtain the mass distribution of TNF. Based on the characterization results of unbound TNF, we evaluate changes in the molecular conformation of TNF protein conjugates in wet and dry states via particle size characterization. In addition, fluorescence assay and attenuated total reflectance-Fourier transform infrared spectroscopy are used as orthogonal methods to characterize the surface packing density of TNF proteins on AuNPs and also to provide a qualitative assessment of the binding affinity for TNF on AuNPs.

(Partially funded by NCI Contract HHSN261200800001E)

COLL 254

Compatibility of RNA with nanomaterials

John J Black[1]*, John81689@live.missouristate.edu, 316 Lakeview Lane, Galena Missouri 65656, United States ;* ***Ashley M Schaeffer***[1]*, Schaeffer123@live.missouristate.edu, 2020 E Bennett, A11, Springfield Missouri 65806, United States ; Kartik C Ghosh*[2]*; Adam Wanekaya*[3]*; Robert K DeLong*[1]*. (1) Department of Biomedical Sciences, Missouri State University, Springfield Missouri 65897, United States (2) Department of Physics Astronomy & Materials Science, Missouri State University, Springfield Missouri 65897, United States (3) Department of Chemistry, Missouri State University, Springfield Missouri 65897, United States*

For macromolecular RNA such as poly I:C, siRNA or RNA vaccines to achieve a sustained therapeutic effect, nanomaterials are sought to help bind, stabilize, deliver or target it to various tissues. As a first step in this research report, we sought to determine the biocompatibility of nanomaterials with RNA. Here we tested a panel of many common commercially available nanomaterials. Agarose gel electrophoresis and UV/VIS spectroscopy were used to analyze the integrity of the RNA after exposure to the various nanomaterials. Nanomaterials such as iron(III) oxide caused changes in the way RNA migrated through the agarose gels. UV/VIS analysis showed changes in the intensity of RNA's characteristic 260 nm absorbance peak in the presence of different nanomaterials. Further characterization is now underway by dynamic laser light scatter (DLLS) and high performance liquid chromatography (HPLC) to better understand the mechanisms underlying interaction and degradation.

COLL 255

Acrylate copolymeric nanogels for tissue engineering of articular cartilage

Sathish Ponnurangam[1]*, sp2522@columbia.edu, 500 W, 120th street, 918 Mudd, New York NY 10027, United States ; Grace O[apos]Connell*[2]*; Irina Chernyshova*[1]*; Clark T Hung*[2]*; Ponisseril Somasundaran*[1]*. (1) Department of Earth and Environmental Engineering, Columbia University, New York NY 10027, United States*

(2) Department of Biomedical Engineering, Columbia University, New York NY 10027, United States

Incorporation of nanogels in hydrogel scaffolds used in tissue engineering can have several advantages such as sustained release of nutrients and growth factors, finer control of the scaffold degradation rates, porosity modification, mediation of cell signaling and enhancement cell adhesion through appropriate functionalization. In this study, we report the synthesis, characterization and application of acrylate-based copolyermic nanogels in engineering of articular cartilages from bovine chondrocytes. Nanogels are synthesized using the inverse microemulsion technique. The degree of cross linking and functionalization of nanogels was characterized using XPS, NMR, and FTIR spectroscopy. Size and surface charge of the nanogels were characterized using dynamic light scattering and electrokinetic measurements. The effect of nanogels on the mechanical strength and biochemical composition of engineered bovine cartilages is discussed.

COLL 256

“Clicking” water soluble HB-PEI polymers onto SWNTs

***Daniel R. Holycross**(1), drholycross@gmail.com, Dow 342, Department of Chemistry, Central Michigan University, Mt. Pleasant MI 48859, United States ; Minghui Chai(1). (1) Department of Chemistry, Central Michigan University, Mt. Pleasant MI 48859, United States*

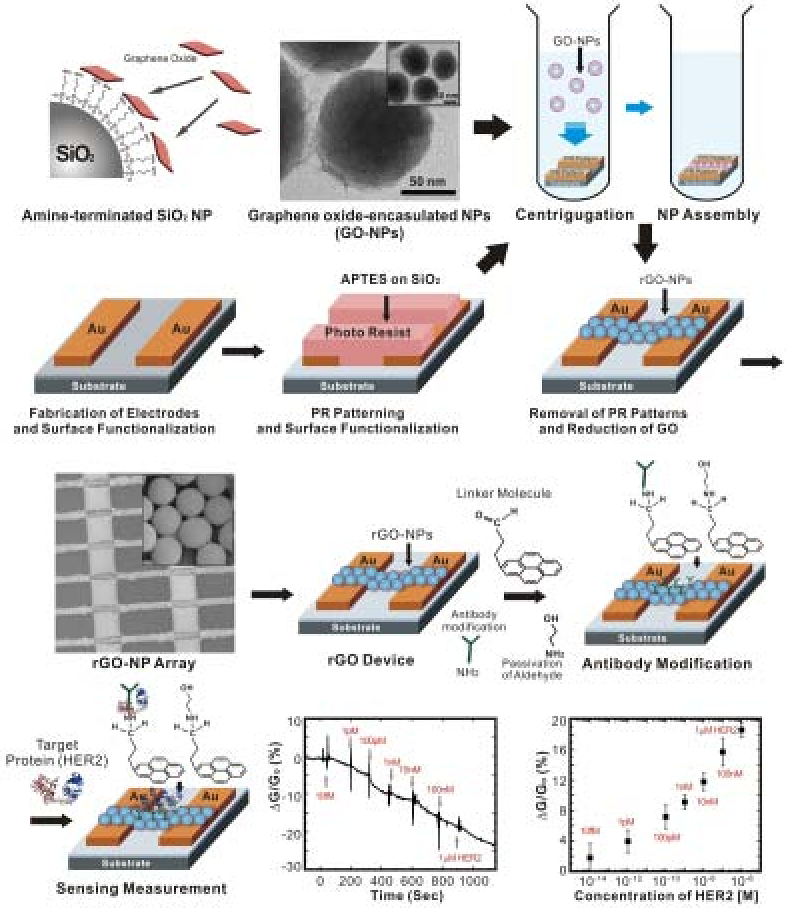
In this work, an efficient way is shown to functionalize the single-wall carbon nanotubes (SWNTs) for potential biomedical applications with water-soluble hyper-branched poly(ethyleneimine) (HB-PEI) polymers using “click” chemistry. First the alkyne functional groups are introduced on the surface of the SWNTs using the reaction of p-aminophenyl propargyl ether with isoamyl nitrite, which generates the free radicals to add onto the surface of SWNTs. Then the azide functionality is produced on the HB-PEI through the formation of imidazole-1-sulfonyl azide synthesized from sulfuryl chloride, sodium azide and imidizole in a one-pot reaction, then reacting with the primary amino groups of the HB-PEI via diazotransfer reaction. Then the two parts can be easily clicked together to form biocompatible SWNTs functionalized with HB-PEI polymers. The unreacted azide groups in the polymer entities of the water-soluble SWNT systems can be further clicked with drug molecules like acetaminophen as potential drug delivery vehicles.

COLL 257

Graphene-encapsulated Nanoparticle-based Biosensor for the Selective Detection of Cancer Biomarkers

Aniruddh Solanki[(1)]*, asolanki@rutgers.edu, 214 Calderone CT, South Plainfield NJ 07080, United States ; Sung Myung*[(1)]*; Cheoljin Kim*[(1)]*; Ki-Bum Lee*[(1)]*; Jaesung Park*[(2)]*; Kwang S. Kim*[(2)]*. (1) Department of Chemistry and Chemical Biology, Rutgers University, Piscataway New Jersey 08854, United States (2) Center of Superfunctional Materials, Department of Chemistry, Pohang University of Science and Technology, Pohang, Republic of Korea*

This talk will focus on fabrication and application of biosensors, based on graphene-encapsulated nanoparticle arrays, for highly sensitive and selective detection of breast cancer biomarkers (HER2 and EGFR). We believe the increased surface-to-volume ratio significantly helped in lowering the detection limits (1 pM) for our target biomarkers.



In addition, we demonstrated the highly selective nature of our biosensor by detecting low concentrations (100 pM) of our target biomarkers even in the presence of a highly concentrated BSA solution.

COLL 258

Highly monodisperse chemically-reactive sub-micrometer particles: polymer colloidal photonic crystal

Guofang Chen[(1)]*, cheng@stjohns.edu, 8000 Utopia Parkway, Queens NY 11439, United States ; Zhenyu Luo*[(1)]*; Saad Syed*[(1)]*. (1) Chemistry, St. John[apos]s University, Queens NY 11439, United States*

Polymer colloidal photonic crystals, which are ordered arrays of highly monodisperse polymer colloids, have demonstrated important potential applications in the fields of photonics, optics and sensing. The advantage of chemically-reactive particles for the colloidal photonic crystal is that the use of chemically-reactive monomer can allow for easy chemical modification of the particle, which is capable of monitoring biorecognition and biochemical interaction at surfaces with visibly perceptible color change. In the presence of an analyte, the structure or optical properties of the photonic crystal change, leading to a change in its optical response, which is the foundation for the photonic crystal sensors. Here we developed a simple method based on surfactant-free emulsion polymerization technique with the dropwise addition of water-soluble initiators to synthesize highly monodisperse sub-micrometer latex particles from chemically-reactive monomer. With the as-prepared chemically reactive polymer colloids, photonic crystals were fabricated on the flat glass substrates, nonplanar substrates, inside fused-silica capillaries, and so on, which produce beautifully iridescent colors. Tough photopatterned photonic crystals were also prepared from such polymer colloids without using molds or grooves.

COLL 259

Biocompatible and biodegradable silk LbL microcapsules

Irina Drachuk[(1)]*, irina.drachuk@mse.gatech.edu, 771 Ferst Dr., Atlanta Georgia 30332, United States ; Olga Shchepelina*[(1)]*; Maneesh Gupta*[(1)]*; Vladimir V. Tsukruk*[(1)]*. (1) Department of Materials Science and Engineering, Georgia Institute of Technology, Atlanta GA 30332, United States*

The importance of biocompatibility and biodegradation is of outmost importance for biomedical and cell-based bio-sensing applications. In comparison to the traditionally used layer-by-layer (LbL) polyelectrolyte-based shells, thin yet chemically stable silk-based shells give the advantage due to high biocompatibility of protein molecules. Here we report on novel composition of biocompatible and biodegradable robust microscale capsules that are fabricated based on LbL deposition of pristine silk fibroins due to formation of hydrophobic interactions between protein molecules and sacrificial silica template. An alternative route of capsule assembly was based on LbL deposition of silk fibroins with other biocompatible polymer (PVPON) due to formation of multiple hydrogen-bonding. Highly stable and robust biocompatible microcapsules demonstrated in this work provide an attractive tool for the formation of drug carriers and building blocks for tissue engineering.

COLL 260

Conformation of polyelectrolytes in saloplastic polyelectrolyte complexes by small angle neutron scattering

Marie Z. Markarian(1)*, markarian@chem.fsu.edu, 102 Varsity Way Room 2902, Tallahassee Florida 32306, United States ;* ***Haifa H. Hariri***(1)*, hhariri@chem.fsu.edu, 102 Varsity Way Room 2902, Tallahassee Florida 32306, United States ; Andreas Reisch*(1)*; Volker S. Urban*(2)*; Joseph B. Schlenoff*(1)*. (1) Department of Chemistry and Biochemistry, Florida State University, Tallahassee Florida 32306, United States (2) Center for Structural Molecular Biology, Oak Ridge National Laboratory, Oak Ridge Tennessee 37831, United States*

Compacted and stoichiometric polyelectrolyte complexes were prepared by mixing equimolar amounts of poly(styrene sulfonate) and poly(diallyldimethylammonium chloride) solutions at low ionic strength. The nascent complexes were ultracentrifuged and salt and temperature annealed for compactness and homogeneity, respectively. Small angle neutron scattering, SANS, was performed to investigate the single polyelectrolyte chain dimensions in complexes made from mixtures of deuterated and protonated forms of the polyanion with comparable degrees of polymerization. The complexation of two different molecular weight polyanions was investigated. Gaussian statistics described the conformation of the polyelectrolyte chains regardless of molecular weight. The results were confirmed by form factor fits to SANS profiles and their corresponding Kratky plots. Consequently, radii of gyration of polyanions were determined in 0.1 M to 1.5 M NaCl storing solutions.

COLL 261

Hydrogen-bonded layer-by-layer films composed of poly(vinyl alcohol) and poly(acrylic acid)

Hyomin Lee(1)*, hyomin@mit.edu, 77 Massachusetts Ave. 66-353, Cambridge MA 02139, United States ; Robert E Cohen*(1)*; Michael F Rubner*(2)*. (1) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge MA 02139, United States (2) Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge MA 02139, United States*

Poly(vinyl alcohol) (PVA) is a water soluble, biodegradable, and biocompatible polymer with excellent chemical resistance and physical properties. PVA is employed in a wide range of biomedical applications including controlled release systems and tissue engineering. Furthermore, accessibility of the hydroxyl groups makes it a promising candidate for thin film coatings. Here, we demonstrate that layer-by-layer (LbL) assembly of PVA and poly(acrylic acid) (PAA) under carefully controlled deposition conditions yields mechanically stable interdigitated multilayers. In contrast to conventional solution casting techniques, hydrogen bonded LbL assembly allows for nanometer level control of the composition throughout the film. The relatively weak hydrogen bonding of the PVA and PAA system in aqueous environment along with its ability to be cross-linked by heat-induced esterification results in tunable pH-induced

degradation behavior. Also with sufficient heat treatment, a reversible, pH-responsive thin film hydrogels could be fabricated. This multilayer system also provides a stable platform for further post-modification.

COLL 262

Mechanical properties of swollen layer-by-layer shells

Milana O. Lisunova(1)*, mlisunova3@mail.gatech.edu, 771 Ferst Dr., NW, Atlanta Georgia 30332-0245, United States ; Irina Drachuk*(1)*; Olga Shchepelina*(1)*; Kyle Anderson*(1)*; Vladimir V Tsukruk*(1)*. (1) School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta Georgia 30332-0245, United States*

The effect of the fluid environment on the mechanical properties, in particular elastic modulus, rigidity, elasticity and surface morphology of layer-by-layer (LbL) multilayer shells, was studied by force spectroscopy in air and liquids. The Young's modul of swollen LbL shells drastically reduced by two order of magnitude comparatively to the collapsed dried state. The embedding polyethyleneimine precursor and *1*-ethyl-*(*3-3-dimethylaminopropyl) carbodiimide cross-linking to LbL shell leads to the improvement of the elastic properties. In addition, the elastic modulus value for the shells based on poly(vinylpyrrolidone) increases from 0.76 to 4.3 MPa as molecular weight of polymer increases from 55 to 1,300 kDa. The buckling morphology caused by large deformation or core dissolving; wrinkles formation due to compression, collapse all have been addressed in this study. The correlations between the surface morphology and transport properties of shells, such as permeability, release mechanisms and final mechanical properties are discussed.

COLL 263

Uranyl sorption onto hematite: Effects of aqueous inorganic carbon and surface structure

Frances N Skomurski(1)*, frances.skomurski@pnl.gov, 902 Battelle Boulevard, PO Box 999 MSIN P7-25, Richland WA 99352, United States ; Kevin M Rosso*(2)*; Steven C Smith*(3)*. (1) Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland WA 99352, United States (2) Fundamental and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland WA 99352, United States (3) National Security Directorate, Pacific Northwest National Laboratory, Richland WA 99352, United States*

In subsurface environments when contaminant uranium exists as the oxidized uranyl cation (UO_2^{2+}), aqueous inorganic carbon species are important complexing agents that may enhance its mobility. Hence, it is necessary to understand how the presence of dissolved carbonate species affect uranium sorption behavior onto ubiquitous substrates, such as iron oxides. Here, quantum-mechanical calculations were performed to determine the relative stabilities of hypothetical uranyl and uranyl (bi-

)carbonate surface complexes on a hematite (α-Fe_2O_3) molecular model at two unique adsorption sites. Adsorption energies were calculated for six different uranyl (bi-)carbonate complexes to mimic pH-induced uranium-carbonate speciation effects. Results suggest that site selectivity may reduce the number of active adsorption sites for uranyl (bi-)carbonate species on hematite surfaces. Moreover, the apparent high stability of aqueous uranyl-carbonate complexes relative to the considered inner-sphere surface complexes suggests other, weaker sorption modes such as outer-sphere complexes may predominate.

COLL 264

Sorption of selenium(VI) and selenium(IV) onto anatase and rutile

Norbert Jordan(1)*, n.jordan@hzdr.de, Bautzner Landstr. 400, Dresden Sachsen 01328, Germany ; Harald Foerstendorf*(1)*; Andreas Scheinost*(1)(2)*; Johannes Lützenkirchen*(3)*; Stephan Weiß*(1)*; Karsten Heim*(1)*; Vinzenz Brendler*(1)*. (1) Institute of Radiochemistry, Helmholtz-Zentrum Dresden-Rossendorf, Dresden 01328, Germany (2) The Rossendorf Beamline at ESRF, Dresden 01328, Germany (3) Institute for Nuclear Waste Disposal, Karlsruhe Institute for Technology, Eggenstein-Leopoldshafen 76344, Germany*

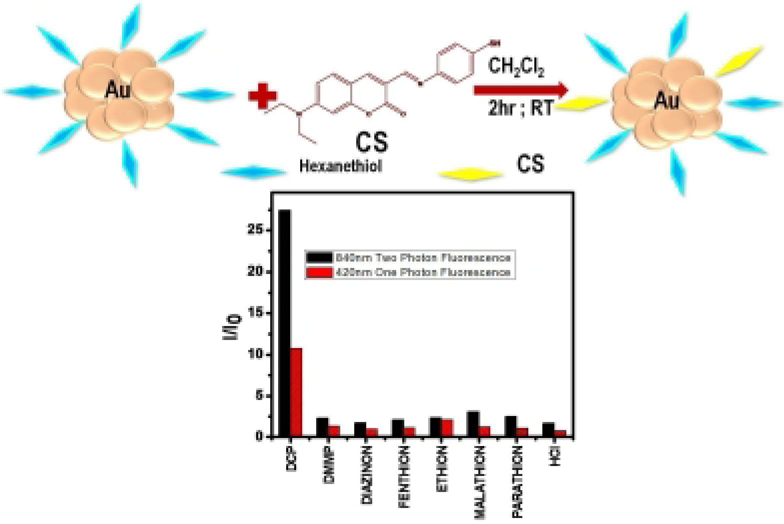
In the context of nuclear waste management, long-term safety assessments have shown that selenium-79 could be one of the major isotopes contributing to the global radioactivity potentially reaching the biosphere. The present study focuses on the sorption of selenium oxyanions, i.e. selenium(VI) and selenium(IV), onto pure anatase and rutile phases, in order to complete the thermodynamic databases used for safety assessments of water contamination. A combination of both macroscopic and microscopic measurements have been used. Results showed that both phases have higher affinity towards selenium(IV) compared to selenium(VI). Batch experiments evidenced ionic strength dependence of the selenium(VI) sorption, while no impact was noticed for selenium(IV). During electrophoretic mobility measurements, no shift of the isoelectric point of anatase (pH_{IEP}) upon selenium(VI) sorption was observed, while selenium(IV) retention decreased the pH_{IEP} to lower pH values. Based on ATR FT-IR and EXAFS spectroscopic observations, we concluded that selenium(VI) is sorbed onto TiO_2 as outer-sphere surface complexes, while selenium(IV) forms primarily inner-sphere complexes. Finally, selenium sorption onto TiO_2 was described by a multisite surface complexation model (CD-MUSIC).

COLL 265

Unique Optical and Electrochemical Properties of Quantum Sized Gold Clusters and Their Applications as Single/Multi Photon Sensors and Imaging Agents

Mary Sajini Devadas(1)*, sajini_dev@yahoo.com, 1903 W Michigan Avenue, 3425 Wood Hall, Kalamazoo MI 49008, United States ; Guda Ramakarishna*(1)*; Ekkehard Sinn*(1)*; Fasil Abebe*(1)*. (1) Department of Chemistry, Western Michigan University, Kalamazoo MI 49008, United States*

Semiconductor metal clusters in the nanometer regime display many interesting optical, electronic and chemical properties due to quantum size effect. For example, electrochemical and optical properties of gold nanoclusters (AuNCs) that are smaller than 1.5nm are completely different from larger than 1.6nm AuNCs and their bulk counterparts. Hence, different core sized nanomaterial can be applied to produce advanced sensors, light harvesting devices and “green” high efficiency catalysts. Nerve Gas Agents (NA) are used in chemical warfare. Our major goal is to synthesize gold clusters (AuNCs) with different dimensions and varying compositions in order to design novel sensors to detect NA mimics. The mimics are the organophosphorus pesticides and their sulfur analogs. These mimics have the same chemical action as the NAs on the neurotransmitter Acetylcholine esterase (AChE). We use both optical and electrochemical detection techniques to assess the use of AuNCs as sensors. We have synthesized AuNCs with a variety of surface passivating ligands such as ferrocenylhexanethiol, coumarins and pyrenes. They have shown good selectivity towards Diethylchlorophosphate (DCP) and Fenthion. To understand the electron transfer mechanisms, fluorescence upconversion lifetimes and transient absorption measurements were conducted which correspond to changes in the square wave voltammogram. These clusters exhibit good two photon crosssections and are good single and multi photon sensors.



COLL 266

Physiological Characteristics of Octylphenol Polyethoxylate Biodegradation in Soil/water Systems

Yi-Tang Chang$^{(1)}$*, ytchang@scu.edu.tw, 70, Linhsi Rd.,, Shinlin, Taipei, Taiwan 11102, Taiwan Republic of China ; Shin-Ling Chou*$^{(1)}$*. (1) Department of Microbiology, Soochow University, Shinlin, Taipei Taiwan 11102, Taiwan Republic of China*

Octylphenol polyethoxylates surfactants are widely applied as commercial clean products and agricultural pesticides. In this study, community-level physiological

profiling (CLPP), carbon degradation potential (CDP) and API ZYM enzymatic activities are analyzed for TX-100 (octylphenol[9.5]polyethoxylates) biodegradation in the monomer or micelle status. The results indicated the CLPP of TX-100 biodegradation was divided into four obvious regions. Organic composition of clay/soil and TX-100 in monomer or micelle didn't affect microbial utilization of 95 carbon sources. The chemical interactions between TX-100 and media were related to the performance of CLPP. Higher CDP values were presented in free-living bacteria in the natural soil/water system and attached bacteria in the clay/water system. Significant activities of esterase, esterase lipase and lipase, as the range of 8.3-54.1% were detected due to the hydrophilic group of TX-100. Positive reaction of alkaline phosphate was detected in two soil/water systems, which was referred to the bioactivities of phosphate-solubilizing bacteria.

COLL 267

Effects of surface-active agents and natural organic matter on the colloidal behavior of titanium-dioxide nanoparticles

Biplab Mukherjee(1)*, mukherjee.biplab@epa.gov, 960 College Station Road, Athens GA, United States ; Termaine Powell*(2)*; James W. Weaver*(3)*; Dermont Bouchard*(2)*; Xin Ma*(4)*; Rajani Goursihetty*(5)*. (1) National Exposure Research Laboratory, U. S. Environmental Protection Agency/ National Research Council Associate, Athens GA, United States (2) National Exposure Research Laboratory, U. S. Environmental Protection Agency, Athens GA, United States (3) NRMRL, U. S. Environmental Protection Agency, Ada OK, United States (4) NRMRL, U. S. Environmental Protection Agency, Cincinnati OH, United States (5) National Exposure Research Laboratory, U. S. Environmental Protection Agency/ Student Service Contractor, Athens GA, United States*

To restrict adversaries on our ecosystem arising from NP exposure, there is an urgent need to understand the effects of different physicochemical factors on the colloidal behavior of NPs. The focus of this research was on the investigation of the aggregation, deposition, and charge behavior of TiO_2 (anatse) NPs in the presence of surfactants (sodium dodecyl sulfonate, SDS; triton X-100, TX both at 160 mg/L) and Suwannee river humic acid (HA) at 7.5 mg/L. The aggregation propensity was lowest when both surfactant and HA was present, but greatest in the presence of TX. The critical coagulation concentration (CCC, mM) at pH 7.5±0.4 in NaCl and $CaCl_2$ was 80 and 1for bare-TiO_2, 80 and 5 in SDS, 80 and 1 in TX, 500 and 10 in HA, > 1000 and 10 in SDS-HA, and > 1000 and 50 and in TX-HA, respectively. The iso-electric point pH (pH_{iep}) for bare-TiO_2 was 5.1, which was reduced to 2.3, < 1.0, and 3.3 in HA, SDS, and TX, respectively. The pH_{iep} in SDS-HA and TX-HA was similar to that in SDS and HA, respectively. Deposition of the NPs at pH 7.5±0.4 on the model SiO_2 surface was found to be minimal in all the cases (< 1ng/cm^2-min) except when TX was present. In the presence of TX, the deposition rate was found to be 100 ng/cm^2-min and was attributed to the strong ability of TX molecules to interact, neutralize, and readily adsorb on to SiO_2, resulting in bridging between NPs and SiO_2 surfaces. In combination, the HA and

the surfactants exerted effects, which were much greater than the individual effects of either the surfactants or HA indicating that the synergistic effects of surface-active agents can play a dominant role in determining the fate and transport of engineered/natural NPs in environmentally relevant systems.

COLL 268

Molecular dynamics simulations of the liquid surface of imidazolium-based [Tf_2N^-] ionic liquids

Martin Lisal(1)(2)*, lisal@icpf.cas.cz, Rozvojova 135, Prague 6-Suchdol Bohemia 165 02, Czech Republic . (1) E. Hala Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals of the ASCR, v. v. i.,, Prague 165 02, Czech Republic (2) Department of Physics, J. E. Purkinje University, Faculty of Science, Prague 165 02, Czech Republic*

We present molecular dynamics simulations of the liquid-gas interface of three room temperature ionic liquids with a common anion, namely, the bis(trifluoromethylsulfonyl) imide ([Tf_2N^-]), and imidazolium-based cations that differ in the alkyl tail length, namely, the 1-butyl-3-methylimidazolium ([C_4mim^+]), the 1-hexyl-3-methylimidazolium ([C_6mim^+]), and the 1-octyl-3-methylimidazolium ([C_8mim^+]). The CHARMM force-field is utilized for description of the bonded and van der Waals non-bonded interactions while partial charges used are based on quantum calculations for isolated [C_nmim^+][Tf_2N^-] ion pairs. The total charges of anions and cations are around -0.9 and 0.9, respectively, which somewhat mimics the anion to cation charge transfer. The surface tension at 300 K is calculated using the mechanical route and its value agrees within statistical uncertainties with experimental values. The simulation configurations are analyzed using the novel method of identification of the truly interfacial molecules. Structural and dynamic properties of the interfacial layer, the first layer beneath the interface and the central (bulk) layer are calculated. Regarding the structural properties, we determine density and charge profiles, and orientation ordering. Concerning the dynamic properties, we calculate the normal and tangential diffusion coefficients, and the survival probability to characterize ions mobility in particular layers. In addition, we also evaluate the re-orientation correlation functions for short and long molecular axis to describe re-orientation dynamics of cations and anions in each layer.

COLL 269

Reactivity of platinum-gold monolayer bimetallic surfaces: Structure-dependent surface chemistry

Robert E Rettew(1)*, r-rettew@gatech.edu, 771 Ferst Dr., Atlanta GA 30332, United States ; Shuang Cheng*(1)*; Faisal Alamgir*(1)*. (1) Department of Materials Science and Engineering, Georgia Institute of Technology, Atlanta GA 30318, United States*

Bimetallic structure-dependent catalysts currently show great promise for many applications. Of particular recent interest are bimetallic electrode surfaces consisting of a nanofilm of one metal grown on top of a substrate metal. These surfaces can be fabricated by a technique called surface limited redox replacement (SLRR), which allows metals to be deposited iteratively with submonolayer-scale degrees of precision per iteration. This talk presents an experimental study of the reactivity of SLRR-grown Pt nanofilms at single and multi-atomic overlayer thicknesses. This reactivity is then correlated with changes in surface chemistry and atomic structure for Pt grown on monolithic and nanoparticle Au substrates. We correlate the influence of the substrate on the oxidation state of platinum with electrochemical performance for methanol and carbon monoxide oxidation. Furthermore, we examine changes in the metal d-band for Pt nanofilms using x-ray photoemission and absorption spectroscopic techniques.

COLL 270

Surface-architecture-determined electrochemistry of Pt on Au, TiO_2, CeO_2, and MnO_2 surfaces

Faisal Alamgir(1), *faisal.alamgir@mse.gatech.edu, 771 Ferst Dr., Atlanta GA 30332, United States ; Robert E Rettew*(1)*; Shuang Cheng*(1)*; Marc Sauerbrey*(2)*. (1) Department of Materials Science and Engineering, Georgia Institute of Technology, Atlanta GA 0332, United States (2) Department of Physics, Universitaet Bremen, Bremen, Germany*

The surface atomic structure and chemical state of Pt is consequential in a variety of surface-intensive devices. Here we present the direct interrelationship between the support material employed for ultrathin Pt films, the resulting atomic and electronic structure of Pt species, and the consequent electrochemical reactivity for Pt deposits on a variety of metal and metal oxide supports. These supports include high surface area electrodes composed of Au, TiO_2, MnO_2, and CeO_2 . X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) measurements were performed to relate the observed electrochemical behavior to the oxidation state and the atomic structure of the deposited Pt species. The atomic structure and the oxidation state of the deposited Pt were found to depend both on the growth method used to deposit Pt on the substrate, and the chemical identity of the substrate itself.

COLL 271

Enhanced supercapacitor nano-composite SWCNT electrodes functionalized non-covalently with rigid dinuclear ruthenium coordination complexes

Jordan C. Poler(1), *jcpoler@uncc.edu, 9201 University City Blvd., Charlotte NC 29223, United States ; Jeffrey R. Alston*(1)*. (1) Department of Chemistry, University of North Carolina at Charlotte, Charlotte NC 28223, United States*

Nanocomposites of single-walled carbon nanotubes (SWCNTs) loaded with dinuclear ruthenium coordination complexes forming electrochemical capacitors will be presented.

These supercapacitor electrodes were characterized using cyclic voltametry and galvanostatic charge/discharge. Energy storage mechanisms of these composites derive from an electrical double layer as well as pseudo-capacitance effects within the ruthenium complexes. Binding of SWCNTs and the ruthenium complexes by mechanical docking interactions forgoes the need of binders or harsh chemical functionalization of the SWCNT. Due to excellent conductivity, chemical resistance and large specific surface area (≤ 1300 m^2 g^{-1}), the SWCNTs facilitate charge transfer and enable a large specific capacitance and electrochemical window. We will present the experimental methods, theoretical models and the capacitive enhancement due to the binding of the coordination complex. We will present nanocomposit electrodes with specific capacitance values of 500 F g^{-1} for 1% wt. loading of ruthenium complex versus 30 F g^{-1} for pristine SWNT electrodes.

COLL 272

Novel phenol capturer derived from the mesoporous silica coated with liquid film

Jian Hua Zhu(1)*, jhzhu@nju.edu.cn, 22 Hankou Road, Nanjing Jiangsu 210093, China ; Yu Zhou*(1)*; Yu Fei Tao*(1)*; Jing Yang*(1)*; Wei Gang Lin*(1)*; Mi Mi Wan*(1)*. (1)*

The gaseous adsorption of phenol by zeolite and mesoporous silica was investigated by using the instantaneous adsorption method, examining the influence of pore structure, morphology and chemical composition of porous materials on the adsorption. Novel phenol-capturer was prepared by modifying the as-synthesized mesoporous silica MCM-41 with tetraethylenepentamine (TEPA), not only saving the energy and time for removal of template, but also opening the way to utilize the micelles for adsorption. Once the organic modifier was distributed in the template micelle of MCM-41 to form a web within the mesoporous channel, the composite could adsorb more phenols in gas stream than activated carbon for the first time. With an unwonted high adsorption capacity, this mesoporous silica-amine composite represented potential application for trapping phenols, especially in tobacco smoke to protect environment. Moreover, this new material could adsorb more phenols in gas stream than activated carbon for the first time.

COLL 273

Visible light driven Fe-TiO_2 mesoporous nanophotocatalyst

Ying Wang(1)*, wangy@nju.edu.cn, 22 Hankou Road, Gulou, Nanjing Jiangsu 210093, China ; Long Liu*(2)*; Sheng Chu*(2)*; Leilei Luo*(2)*; Fei Kong*(2)*; Zhigang Zou*(2)*. (1) School of Chemistry and Chemical Engineering, Eco-materials and Renewable Energy Research Center (ERERC),, Nanjing Jiangsu 210093, China (2)*

A series of novel of Fe-doped & propylthiol-functionalized organic-inorganic hybrid mesoporous TiO_2 photocatalysts have been first prepared by one-pot method. These materials possess high surface areas and mesoporous structure with uniform pore size

distribution. XRD analysis confirms the anatase phase of these Fe-doped TiO_2 materials. From EPR and XPS, it was found that Fe exists in trivalent ions state substituting Ti^{4+} into TiO_2 lattice in low spin state. The XPS data also indicates the formation of Si-O-Ti bond, suggesting that MPTES has been successfully polymerized in mesoporous TiO_2. The photodegradation of PHE under visible light irradiation (λ>420nm) was investigated to evaluate the photocatalytic activity of these materials and these samples demonstrated the highest photocatalytic activity. The intermediates of PHE photodegradation were detected by gas chromatography-mass spectrometer. Based the experiment results, we proposed a possible mechanism.

COLL 274

Stable and responsive electrostatic multilayer nanoparticles for systemic delivery to tumors

Paula T. Hammond(1)*, hammond@mit.edu, 77 Massachusetts Avenue, 66-352, Cambridge MA 02139, United States ; Zhiyong Poon*(1)*; Stephen Morton*(1)*. (1) Department of Chemical Engineering and Koch Institute for Integrative Cancer Research, Massachusetts Institute of Technology, Cambridge MA 02139, United States*

Layer-by-layer approaches have been promoted for several years as a means of micro- and nanoparticle for systemic delivery because they present, for many reasons, strong advantages for their use in place of more complex synthetic colloidal systems. Despite the many advances in designing these systems as highly effective drug and gene carriers, there has been a significant lag between materials system development and actual systemic application of these systems in vivo due to issues regarding stability in the bloodstream, and sufficient blood circulation lifetimes for the effective accumulation of particles in the desired regions. We have found that the stability of the LbL nanoparticle systems can be modulated with both the numbers of layers and layer composition, and here we demonstrate the ability to observe andtrack in vivo systemic stability of LbL coated quantum dots and other nanoparticles using simple labeling methods. Furthermore, we find that when the composition of the outer layer of the particle is manipulated, we can see very distinct differences in the biodistribution, even with the subtle compositional differences between two negatively charged polysaccharides that yield equal zeta potential. With appropriate tuning of these parameters, we can greatly increase lifetime and reduce accumulation of the nanoparticle in the liver and spleen. Recently, we have also used dynamic LbL layers on a nanoparticle to generate a stealth outer corona layer that 'sheds' at the lower pH of hypoxic tumors; this step reveals positively charged nanoparticle surfaces that are rapidly taken up by tumor cells. We have found specific LbL layers that act as highly effective, and in some cases pH responsive, stabilizing layers for nanoparticles to yield long distribution times.

COLL 275

Virus-like particles: Multifunctional antigen carriers

Marta Comellas-Aragones[(1)]*, comellas@scripps.edu, 10550 North Torrey Pines Road, La Jolla CA 92037, United States ; M.G. Finn*[(1)]*; Zinaida Polonskaya*[(1)]*; Lisa Kain*[(2)]*; Luc Teyton*[(2)]*. (1) Department of Chemistry, The Scripps Research Institute, La Jolla CA 92037, United States (2) Department of Immunology, The Scripps Research Institute, La Jolla CA 92037, United States*

The low immunogenicity of some glycans is a major obstacle in the development of vaccines. Virus-like particles (VLPs) have been shown to be promising carriers for immunization due to their inherent immunogenicity, a consequence of their nanometer size, nucleoprotein content, and regular structure. Since VLPs are highly monodisperse and possess structures known to atomic resolution, their surfaces provide multiple functionalities that can be addressed in a rational manner both chemically and genetically. This provides a unique and robust platform on which to explore parameters for optimization of antigen delivery. We are investigating the potential use of carbohydrate antigen-presenting VLPs as immunogenicity enhancers and their possible use as vaccines. We will describe the use of tailored VLPs in this effort, and report on the correlation of structural features with immunogenicity and the activation of different immunological pathways.

COLL 276

Biodistribution and pharmacokinetics of magic number gold nanoclusters.

Christopher J Ackerson[(1)]*, ackerson@colostate.edu, 1872 Campus Delivery, Fort Collins CO 80521, United States . (1) Chemistry, Colorado State University, Fort Collin CO 80521, United States*

Our objective is to test the hypothesis that small molecularly defined nanoclusters such as Au25(SR)18, Au102(SR)44, and Au144(SR)60 have narrow a biodistribution, rapid equilibration between intra- and extravascular spaces, blood circulation lifetimes tunable through choice of SR ligands and total and predictable clearance from the blood through renal filtration. Our work is justified because these compounds like other potential nanoparticle therapeutics may allow simultaneous diagnosis and therapy, when targeted to specific proteins that are overexpressed on disease cells. Diagnosis for these 'magic number' metal clusters is by medical imaging such as MRI or CT. Therapy is by joule heating of the particles in a radiofrequency field. Because radiofrequency wavelengths are large it is especially important to understand particle fates.

COLL 277

Rational Design, Development, and Optimization of Nanopharmaceuticals for Targeted Drug Delivery in Nanomedicine-An Interfacial and Colloidal Science Approach

Heidi M. Mansour[(1)]*, heidi.mansour@uky.edu, 789 S. Limestone St., Office 331 Biological Pharmaceutical Bldg, Lexington Kentucky 4053t6-0596, United States . (1)*

Department of Pharmaceutical Sciences, University of Kentucky College of Pharmacy, Lexington Kentucky 40536, United States

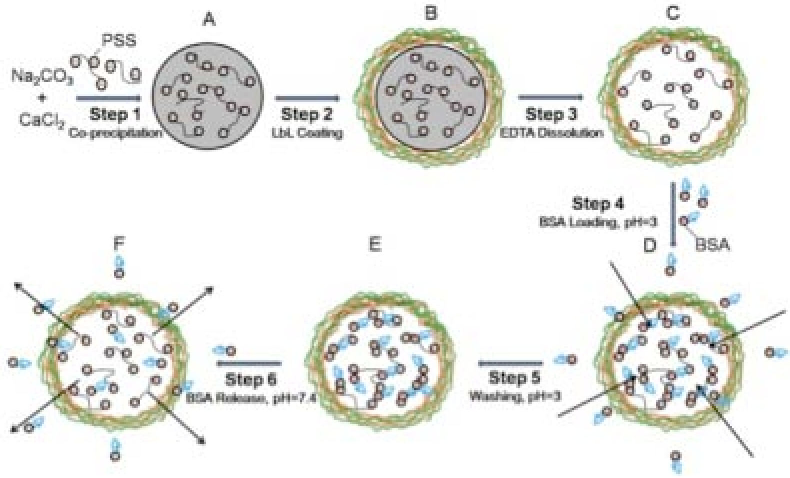
The physicochemical and interfacial aspects of nanomedicine drug delivery systems, including phospholipid and lipopolymeric colloidal self-assemblies for nanopharmaceutical applications, will be presented. These nanomedicines include liposomes and polymeric liposomes in the colloidal dispersion state and in the solid-state as multifunctional lipospheres. The surface chemistry, interparticulate interfacial interactions, Langmuir surface spreading behavior, biophysics of biomembrane phase behavior, material science and water-solid surface interactions that influence performance of these nanomedicine systems will also be discussed. Additionally, novel particle engineering design methods will be presented for rationally designing and tailoring multifunctional nanopharmaceutical systems for targeted drug delivery and combination dual-drug delivery. Through an interfacial and colloid science approach, nanomedicine delivery systems can be rationally designed, developed, and optimized with tailored multifunctional properties for enhanced penetration through biofilms and targeted delivery, while possessing the necessary nanopharmaceutical properties for stability and performance.

COLL 278

PSS-doped nanostructured polyelectrolyte capsules for delivery of proteins

***Ashok M Raichur**(1), amr@materials.iisc.ernet.in, Sir C V Raman Avenue, Bangalore Karnataka 560012, India ; Anandhakumar S(1). (1) Department of Materials Engineering, Indian Institute of Science, Bangalore Karnataka 560012, India*

Nanostructured microcapsules of poly(allylamine hydrochloride) (PAH) and poly(methacrylic acid) (PMA) were prepared by coating the polyelectrolytes on to polystyrene sulfonate (PSS) doped $CaCO_3$ particles using the layer-by-layer technique and subsequent removal of $CaCO_3$.



This procedure produced hollow microcapsules having a unique property of undergoing changes in capsule wall permeability as a function of pH. Bovine serum albumin (BSA) could be spontaneously loaded at pH below the isoelectric point of the capsule. FITC-dextran and FITC-BSA were used to demonstrate the reversible pH dependent open and closed state of the capsules. Confocal laser scanning microscopy showed that FITC-BSA was homogeneously distributed inside the capsules. Loading of protein was dependent on pH and decreased with increase in pH from 3 to 4.5. With increase in initial protein concentration, the protein content inside the capsules was nearly 200 times higher than the feeding concentration. At lower BSA concentration, spontaneous deposition was the predominant mechanism of loading while at higher BSA concentrations, it was diffusion controlled. Circular dichroism and FTIR measurements suggested no conformational changes to the BSA structure. Sustained released of BSA could be obtained up to 5 h following a initial burst release in the first 30 min. Biocompatibility studies with mouse embryonic fibroblast cells indicated that the capsules were biocompatible. Thus such pH sensitive polyelectrolyte microcapsules offer a promising delivery system for water-soluble proteins and peptides.

COLL 279

Single molecule detection in cell by fluorescence metal nanoprobe

Jian Zhang(1)*, jian@cfs.umaryland.edu, 725 West Lombard Street, Baltimore MD 20855, United States ; Yi Fu*(1)*; Joseph R. Lakowicz*(1)*. (1)*

Fluorescence metal nanoparticles are developed as molecular imaging agents for cell imaging. Compared with organic fluorophores, these metal nanoprobes are observed to display increased brightness, decreased lifetime, increased photostability, and reduced photoblinking because of near-field interactions of fluorophores with the metal nanoparticles. The metal nanoprobes are found to be able to conjugate with target molecules including genomic targets in cells and receptors on cell surfaces. Fluorescence intensity and lifetime images of single cells are recorded on a lifetime-resolved confocal microscope. Because of brighter emission signals and unique lifetimes of metal nanoprobes, their emission signals can be identified distinctly from the cellular autofluorescence at the single probe level on the collected cell images. Consequently, the single target molecules can be detected by cell imaging. As novel molecule imaging agents, the metal nanoprobes are developed for the quantification and distribution of target molecules in the cells. The approach is also considered to have great a potential for the clinical diagnostic research.

COLL 280

DNA-Capped Nanoparticles Designed for Doxorubicin Drug Delivery

Mathew M. Maye(1), *mmmaye@syr.edu, 111 College Place, Syracuse New York 13244, United States ; James C. Dabrowiak*(1)*; Colleen M. Alexander*(1)*. (1) Department of Chemistry, Syracuse University, Syracuse New York 13905, United States*

Metal compounds and complexes are widely used for treating and detecting disease, and metal nanostructures are playing an increasingly important role in the emerging field of nanomedicine. Gold nanoparticles (AuNP) in particular offer a number of attractive features for the visualization, detection, and treatment of disease. In this presentation we will discuss our recent work in loading the anticancer drug doxorubicin (DOX) onto DNA-capped AuNPs designed for specific DOX intercalation. Drug binding was confirmed by monitoring an increase in DNA melting temperature, AuNP plasmon resonance, and a hydrodynamic radius increase, as a function of [DOX]/[DNA] ratio. Using this approach, up to a few hundred DOX molcules can reside at each AuNP, depending on NP size, and DNA length. The capacity for drug release to target DNA was confirmed. The potential for this method to be tailored for a number of existing anti-cancer drugs will also be discussed.

COLL 281

Regulatory Challenges Presented by Nanotechnology Applications – FDA's Perspective

Ritu Nalubola(1)*, Ritu.Nalubola@fda.hhs.gov, 10903 New Hampshire Ave, Silver Spring MD 20993, United States . (1) U.S. Food and Drug Administration, Silver Spring MD 20993, United States*

The U.S. Food and Drug Administration (FDA) regulates a broad range of products under the Federal Food, Drug, and Cosmetic Act (FFDCA) and other statutes. FDA is generally responsible for overseeing the safety and, as applicable, effectiveness of a wide range of products, including drugs, devices, foods, veterinary products, and cosmetics. Nanotechnology allows scientists to create, explore, and manipulate materials at the nanoscale. Such materials can have chemical, physical, and biological properties that differ from those of their larger counterparts. FDA believes that nanotechnology-enabled products present regulatory challenges similar to those posed by products using other emerging technologies. FDA experts recognize, however, that properties of a material relevant to the safety and (as applicable) effectiveness of FDA-regulated products might change repeatedly as size enters into or varies within the nanoscale range. Scientific considerations and broad policy issues relevant to FDA's regulation of nanotechnology applications will be discussed.

COLL 282

Formation and applications of cyclodextrin nano and micro structures

Pradipta Purkayastha(1)*, pradiptp@gmail.com, Mohanpur Campus, Mohanpur West Bengal 741252, India ; S. Syed Jaffer*(1)*; Prasun Ghosh*(1)*. (1) Department of Chemical*

Sciences, Indian Institute of Science Education and Research, Kolkata, Mohanpur West Bengal 741252, India

The primary purpose of drug delivery systems is delivering the necessary amount of drug to the target efficiently and precisely. Host-guest chemistry has emerged as a necessary service to such processes. Hosts like cyclodextrins (CDs) are considered to be potential candidates because of their ability to alter the physicochemical, and biological properties of guest molecules through the formation of inclusion complexes. Considering drug molecules that can fluoresce, methods can be developed by observing their fluorescence emission inside various hosts. For example, cyclodextrins are generally found to have three different cavity dimensions, *viz.*, α-, β- and γ-CDs, and they have their own abilities to form inclusion complexes with specific guests depending on the proper inclusion of the guest molecule into the hydrophobic cavity. The CDs have been observed to undergo formation of molecule induced nanotubular suprastructures in aqueous medium. These structural morphologies are dependent on the concentration of the guest molecule.

COLL 283

Adsorption and Conformation of Serum Albumin Protein on Gold Nanoparticles Investigated using Dimensional Measurements and In Situ Spectroscopic Methods

De-Hao Tsai(1)*, dhtsai@nist.gov, 100 Bureau Dr, Stop 8520, Gaithersburg MD 20899, United States ; Frank DelRio*(1)*; Athena Keene*(2)*; Katherine Tyner*(2)*; Robert MacCuspie*(1)*; Tae Joon Cho*(1)*; Michael Zachariah*(1)(3)*; Vincent Hackley*(1)*. (1) Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg MD 20899, United States (2) Center for Drug Evaluation and Research, Food and Drug Administration, Silver Spring MD 20993, United States (3) Departments of Mechanical Engineering and Chemistry, University of Maryland, Gaithersburg MD 20899, United States*

The adsorption and conformation of bovine serum albumin (BSA) on gold nanoparticles (AuNPs) is interrogated both qualitatively and quantitatively via complementary physicochemical characterization methods. AuNP hydrodynamic size exhibits a greater proportional increase due to BSA conjugation at pH values below 2.5 compared with less acidic pH values, corresponding with the reversibly denatured (E or F form) conformation of BSA. Due to the difference in the measurement environment, a larger increase of AuNP size is observed following BSA conjugation when measured in the fluid state compared to the dry state. BSA surface density reaches 90 % of saturation (~0.015 nm^{-2}) at a solution phase concentration between (10 and 30) µmol/L. The equilibrium binding constant for BSA on AuNPs is calculated by applying the Langmuir equation, with resulting values ranging from (0.51×10^6 to 1.65×10^6) L/mol, suggesting a strong affinity due to bonding between the single free exterior thiol on N-form BSA (associated with a cysteine residue) and the AuNP surface.

COLL 284

Bio-applications of SERS tags

Michael J. Natan(1)*, michael.natan@cabotcorp.com, 325 E. Middlefield Rd., Mountain View CA 94043-4003, United States . (1) Department of Chemistry, Cabot Security Materials Inc., Mountain View CA 94043, United States*

We have developed a series of encapsulated SERS-active labels and several different assay formats that are designed to be used with small or handheld Raman readers for chemical and biochemical sensing applications. We will describe the basic nanomaterials-driven compositions, highlighting the challenges and successes in synthesis, characterization, and scale-up. We will then highlight current applications, ranging from *in vivo* imaging to ultrasensitive detection of proteins and DNA to antibody-enabled detection of low molecular weight species such as aflatoxin and TNT.

COLL 285

Gold nanoparticles, antibodies, and surface-enhanced Raman spectroscopy: Integrated tools for the early detection of infectious diseases

Marc D. Porter(1)*, marc.porter@utah.edu, 383 Colorow Drive, Salt Lake City UT 84108-1201, United States . (1) Nano Institute of Utah, University of Utah, Salt Lake City UT 84108, United States*

Early detection of infectious diseases demands marked advances in the performance of today's diagnostic tools in terms of sensitivity and speed. This presentation will describe efforts to develop a readout methodology that potentially addresses these needs by coupling gold nanoparticle (i.e., spheres and rods) labeling concepts with surface-enhanced Raman scattering (SERS) and approaches to increase antigen and label flux. This presentation will detail strategies for both the fabrication and readout of chip-scale platforms by examining fundamental dictates for optimal performance (e.g., plasmonic coupling, antibody specificity and immobilization, and nonspecific adsorption). Drawing on insights from such studies, results from experiments that focus on the use of immunoassays for the ultralow-level detection of viral and microbial infectious agents will be discussed.

COLL 286

SERS nanoparticles for detection of cell surface proteins

Christina M MacLaughlin(1)*, cmaclaug@chem.utoronto.ca, 80 St. George Street, Walker Lab, Toronto ON M5S 3H6, Canada ; Shell Ip*(1)*; Edward Parker*(2)*; Natalie Tam*(3)*; Nisa Mullaithilaga*(2)*; Gang Zheng*(3)*; Chen Wang*(2)*; Gilbert Walker*(1)*. (1) Department of Chemistry, University of Toronto, Toronto ON M5S 3H6, Canada (2) Department of Pathology and Laboratory Medicine, Mount Sinai Hospital, Toronto ON*

M5G 1X5, Canada (3) Institute of Biomaterials and Biomedical Engineering, University of Toronto, Toronto ON M5G 1L7, Canada

Development of surface enhanced Raman scattering (SERS) Au nanoparticles with various SERS tags, particle protection chemistries and targeting modalities are reported for 60nm Au nanoparticles. Coating and conjugation of targeting moieties were characterized. A comparison of different dye labels which represent various classes of dyes has been made. Longevity during storage, and stability in *in vitro* biological conditions have been evaluated. The attributes of dyes that are well suited to multiplexing will be discussed. SERS particles were targeted to lung cancer, and leukemia cells, which serve as models for adherent and circulating malignancies. At least one SERS platform to be reported upon has the advantage that it can be used simultaneously with traditional pathology stains, such as giemsa.

COLL 287

Development of Colloidal SERS Biosensors

Patrick A Johnson[(1)], *pjohns27@uwyo.edu, 1000 E. University Ave, Dept. 3295, Laramie WY 82071-2000, United States . (1) Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie WY 82071-2000, United States*

The development of colloidal based SERS bioassays for portable diagnostics will be presented. DNA, antigen and antibody detection systems have been developed using paramagnetic capture assay schemes. For nucleic acid assays, gold colloids and paramagnetic nanoparticles were functionalized with DNA, as well as DNA analogues, to capture target DNA or RNA from solution. The development of gold-coated magnetic nanoparticles provided an alternative, single nanoparticle assay scheme. The nanoparticles function as SERS substrates while simultaneously providing a separation / concentration mechanism. In similar fashion, both antibody and antigen multiplexed detection strategies for Rift Valley Fever virus and West Nile virus demonstrated sensitivities comparable or greater than ELISA assays utilizing the same reagents. In addition, considerations of the advantages of using colloidal systems over surface based systems for biological assays will be discussed.

COLL 288

Antibody conjugated gold nanorods for SERS based biosensing

Mark T. McDermott[(1)], *mark.mcdermott@ualberta.ca, 11227 Saskatchewan Drive, Edmonton Alberta T6G 2G2, Canada ; Shereen Elbayomy*[(1)]*; Lars Laurentius*[(1)]*. (1) Department of Chemistry and National Institute for Nanotechnology, University of Alberta, Edmonton Alberta T6G 2G2, Canada*

Chemically modified spherical gold nanoparticles have been used as extrinsic labels for surface enhanced Raman scattering (SERS) detection of surface based assays. Rod-

shaped gold nanoparticles should provide higher sensitivity and potentially stronger binding via multivalent interactions. The challenge in employing gold nanorods for this application is the replacement of the shape directing surfactant layer on the surface. We have developed a modification procedure to replace the cetyltrimethylammonium bromide (CTAB) layer on gold nanorods with a self-assembled monolayer (SAM) teminated with ethylene glycol (EG) and COOH groups. The nanorods are made SERS active by place exchange with 4-nitrobenzenethiol (NBT). We will present results that track the modification procedure. Antibodies are conjugated to the nanorods through the terminal –COOH group. The antibody conjugated nanorods were used for SERS readout in sandwich immunoassays and provide extremely low detection limits. A direct comparison with spherical nanoparticles will be presented.

COLL 289

Novel SERS fiber sensors for bioanalytical applications

Jin Z Zhang(1)*, zhang@ucsc.edu, 1156 High Street, Santa Cruz CA 95064, United States ; Claire Gu*(2)*. (1) Department of Chemistry and Biochemistry, University of Californoia Santa Cruz, Santa Cruz CA 95064, United States (2) Department of Electrical Engineering, University of Californoia Santa Cruz, Santa Cruz CA 95064, United States*

Novel SERS (surface-enhanced Raman scattering) sensors based on conventional optical fibers as well as photonic crystal fibers have been developed to detect chemicals and biochemicals with molecular specificity and high sensitivity. We have demonstrated that the SERS fibers sensors are significantly more sensitive than traditional bulk detection using various samples including dye molecules, proteins, and bacteria. In addition, we have demonstrated synergistically enhanced SERS activities in a double substrate “sandwich” structure using either two Ag nanoparticle substrates or a combination of Ag nanopartciles and nanowires. Furthermore, we have shown that substrates with uniform structures, e.g. highly uniform hollow gold nanospheres, can afford highly consistent SERS at the single nanostructure level. These sensors are very compact, highly sensitive, molecular specific, and low cost,
and have remote detection capability. These studies clearly demonstrate that fiber-based SERS sensors are promising for practical application for chemical and biochemical analysis.

COLL 290

Design of biodegradable gold nanoclusters for NIR optical imaging

Avinash K Murthy(1)*, amurthy0106@gmail.com, 1 University Station C0400, Austin TX 78712, United States ; Jasmine M Tam*(1)*; Justina O Tam*(2)*; Davis Ingram*(1)*; Morgan Schulze*(1)*; Robin Nguyen*(1)*; Robert Stover*(1)*; Robert Schramm*(1)*; Li Ma*(1)*; Konstantin V Sokolov*(2)*; Keith P Johnston*(1)*. (1) Department of Chemical Engineering, University of*

Texas at Austin, Austin TX 78712, United States (2) Department of Biomedical Engineering, University of Texas at Austin, Austin TX 78712, United States

Gold nanoparticles which exhibit surface plasmon resonance in the near-infrared region (NIR) of the optical spectrum are extremely useful for biomedical imaging applications but are often unable to be efficiently cleared. We have developed biodegradable clusters of controlled size from 20 to 100 nm made from 4 nm primary gold nanoparticles with surface charges optimized for efficient clearance. These nanoclusters absorb strongly from 650 to 900 nm, due to close interparticle spacings and high gold loadings. Cluster formation was induced by the addition of various weakly-adsorbing polymer stabilizers. The cluster sizes and optical properties were tuned varying gold particle concentrations and polymer/gold ratios to moderate interparticle interactions. Surface charge measurements explain the mechanism of aggregation and deaggregation. This kinetically-controlled nanocluster assembly using physical methods offers broad opportunities for the design of nanoclusters for multi-modal imaging/therapeutic systems, cell-specific targeting, and biodegradable clusters for rapid clearance from the body.

COLL 291

Going for the gold: organothiols can penetrate the protein-stabilizing layer of BSA-stabilized gold nanoparticle and be adsorbed onto the gold surface.

Dongmao Zhang[(1)]*, dz33@msstate.edu, 310 Presidential Circle, Mississippi State Mississippi, United States ; Karthikeswar Vangala*[(1)]*; George Salomons*[(1)]*; Vu Le*[(1)]*; Lewis Edwin*[(1)]*. (1) Chemistry, Mississippi State University, Mississippi State Mississippi 39762, United States*

Understanding how bovine serum albumin (BSA)-stabilized gold nanoparticle (AuNP) interacts with physiologically and biomedically relevant organothiols is fundamentally important in understanding the structure of the AuNP/protein complex and its stability, toxicity, and biocompatibility. With AuNP sequentially mixed with BSA and a series of organothiols ((cysteine, homocysteine, glutathione, mercaptobenzimidazole (MBI)), we have found that all of the tested organothiols penetrate the protein stabilizing layer and are adsorbed onto the AuNP surface without causing significant BSA displacement. Using MBI as the probe organothiol, we have found that the BSA adsorption layer only passivates ~10% of the AuNP surface and ~90% of the surface is available for organothiol adsorption. Surface plasmonic resonance studies indicate that MBI adsorption onto the BSA-stabilized AuNP is a rapid process, indicating that the BSA adlayer is highly permeable. Implications of these findings for nano / bio material fabrications and applications will be discussed.

COLL 292

Functional multilayer films and complexes based on the molecular interactions of polyelectrolytes

Kookheon Char[(1)(2)]*, khchar@plaza.snu.ac.kr, Rm.616, Bldg.302, Daehak-Dong, Gwanak-Gu Seoul 151744, Republic of Korea . (1) School of Chemical & Biological Engineering, Seoul National University, The National Creative Research Initiative Center for Intelligent Hybrids, Gwanak-Gu Seoul 151744, Republic of Korea (2) Seoul National University, The WCU Program of Chemical Convergence for Energy & Environment, Gwanak-Gu Seoul 151744, Republic of Korea*

Functional polymeric platforms including multilayered films as well as complexes based on polyelectrolytes (PEs) have been explored, exploiting molecular interactions strongly dependent upon external environments. In particular, the layer-by-layer (LbL) deposition has received enormous attention for the fabrication of functional multilayer films due to many advantages such as programming functionalities at desired positions within the films. In this presentation, the LbL assembled multilayer films containing diverse functional objects (i.e., quantum dots, polymeric micelles, carbon objects including graphenes, and proteins) and their unique properties will be discussed. Moreover, external stimuli-driven changes of multilayer films have been investigated by adjusting the molecular interactions between PEs. In addition to multilayer films based on charged PEs, the formation and morphological transition of charged micelle complexes have also been studied in various solution conditions, again taking advantage of specific interactions between two charged micelles. These diverse polymeric platforms based on the molecular interactions between charged functional objects offer great potentials for many applications ranging from optoelectronics to biomedicines.

COLL 293

Advance Materials with Record Properties Made by the Layer-By-Layer Assembly

Nicholas A. Kotov(1)*, kotov@umich.edu, 2300 Hayward, Ann Arbor Michigan 48109, United States ;* ***Christine Andres***(1)*, kotov@umich.edu, 2300 Hayward, Ann Arbor Michigan 48109, United States . (1) Chemical Engineering, University of Michigan, Ann Arbor Michigan 48109, United States*

Nanoscale composites with exceptional structural control and record properties can be made by the layer-by-layer assembly. In this presentation this will be demonstrated for the nanoscale composites for (1) load bearing and military applications with exceptional mechanical properties, (2) energy applications for batteries and fuel cells, (3) optoelectronic applications, and (4) biomedical applications, such as neuroprosthetic devices.

COLL 294

Ultrathin nano brick wall super gas barrier quadlayer assemblies

Morgan A Priolo(1)*, mapriolo25@tamu.edu, 3123 TAMU, College Station TX 77843, United States ; Daniel Gamboa*(1)*; Kevin M Holder*(2)*; Jaime C Grunlan*(1)*. (1) Department of Mechanical Engineering, Texas A&M University, College Station TX 77843, United*

States (2) Department of Chemistry, Texas A&M University, College Station TX 77843, United States

Thin films of sodium montmorillonite clay and weak polyelectrolytes were prepared by alternately dipping a PET substrate into four different dilute aqueous mixtures (polyethylenimine, poly(acrylic acid), polyethylenimine, and montmorillonite clay). After depositing four of these quadlayers (QL), the resulting transparent film exhibits an oxygen transmission rate below the detection limit of commercial instrumentation (< 0.005 cm^3 m^{-2} day^{-1}). This level of oxygen barrier, which is unprecedented for a clay-filled polymer composite, is believed to be due to a nano brick wall microstructure comprised of completely exfoliated clay bricks in polymeric mortar and clay layer spacing on the order of tens of nanometers. This 4 QL film has a thickness of only 51 nm and an optical transparency of 95%, making it a true foil replacement technology useful for flexible electronics and microwaveable food packaging.

COLL 295

Layer-by-layer (LbL) assembly of charged species in non-polar solvents: Generation of conductive and photocatalytic thin films

Daeyeon Lee[(1)]*, daeyeon@seas.upenn.edu, 220 S. 33rd St. Towne 311A, Philadelphia PA 19104, United States ; Kwadwo E. Tettey*[(1)]*; Michael Q. Yee*[(2)]*. (1) Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia PA 19104, United States (2) Department of Bioengineering, University of Pennsylvania, Philadelphia PA 19104, United States*

LbL assembly, to date, has mostly been limited to the fabrication of thin films using materials dissolved in aqueous solutions. Considering that a large number of functional materials are synthesized and stable in non-polar solvents, it would be highly advantageous to enable LbL assembly in such media. In this study, we demonstrate LbL assembly in non-polar media by imparting charge onto various materials using a charge inducing agent (CIA). Our study shows that the composition, growth behaviors and physical properties of these LbL films can be tailored by varying the concentration of the CIA. We also demonstrate that MWCNT/TiO_2 films assembled in non-polar media show excellent conductivity and photocatalytic activity. Our results demonstrate that LbL assembly can indeed be performed in non-polar media, which will widen the library of materials that can be incorporated into thin films based on the LbL technique.

COLL 296

Interactions of surfactant/polyelectrolyte complexes with water soluble organics dyes and subsequent adsorption of these complexes to the surface of TiO_2 colloids.

Dion Rivera(1)*, riverad@cwu.edu, 400 East University Way, Ellensburg WA 98926-7539, United States ; Brittany Best*(1)*. (1) Chemistry, Central Washington University, Ellensburg WA 98926, United States*

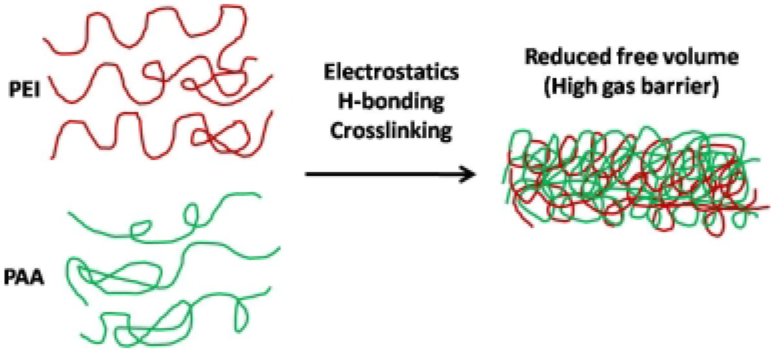
Ultraviolet visible spectroscopy (UV-visible) has been used in conjunction with multivariate least squares analysis to understand complex interactions of aqueous polyelectrolyte/surfactant complexes with water soluble organic dyes and the subsequent adsorption of the complex containing the dye onto a TiO_2 colloid. This technique allows concentrations of the polyelectrolyte poly(sodium-4-styrenesulfonate), the surfactant cetylpyridinium bromide, and the water soluble dyes phenol red or bromothymol blue to be calculated from the overlapped UV-visible spectral data. The data analysis indicates that all three species come out of solution as a complex at a mole ratio of surfactant to polyelectrolyte of 360:1. Addition of NaCl at concentrations of 50 mM and 500 mM influences the amount of dye removed from the system. The number of dye molecules associated with the polyelectrolyte/surfactant complex is estimated to be 21 +/- 2 dye molecules per complex for both dye molecules at low ionic strengths.

COLL 297

Super Gas Barrier of All-Polymer Layer-by-Layer Assemblies

You-Hao Yang(1)*, yangyouhao@gmail.com, 401 Lincoln Dr., Apt. 53, College Station Texas 77840, United States ; Jaime C Grunlan*(1)(2)*; Merid Haile*(3)*; Yong Tae Park*(2)*; Frank A Malek*(1)*. (1) Department of Chemical Engineering, Texas A&M University, College Station Texas 77843, United States (2) Department of Mechanical Engineering, Texas A&M University, College Station Texas 77843, United States (3) Department of Chemistry, Texas A&M University, College Station Texas 77843, United States*

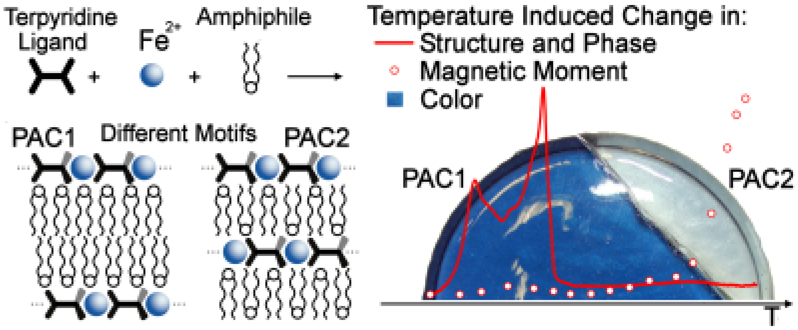
Layer-by-layer assembly of cationic polyethylenimine (PEI) and anionic poly (acrylic acid) (PAA) was investigated with regard to pH of each polymer during deposition. Thickness and surface roughness can be altered dramatically due to the pH-responsive morphology of PEI and PAA. The oxygen permeability of an 8-bilayer, glutaraldehyde-crosslinked PEI/PAA film (305 nm thick) is below 3.2×10^{-21} $cm^3\cdot cm/cm^2\cdot s\cdot Pa$, which is believed to be the lowest permeability of an all-polymer system ever reported. This relatively simple recipe may be of use for a variety of packaging applications, including flexible electronics that require high
flexibility and transparency.



COLL 298

Design principles for tuning the magnetic properties of polyelectrolyte-amphiphile-complexes

Guntram Schwarz(1)*, guntram.schwarz@matsyn.uni-wuerzburg.de, Röntgenring 11, Würzburg Bayern 97070, Germany ; Dirk G Kurth*(1)*. (1) Department of Advanced Materials, University of Würzburg, Wuerzburg 97070, Germany*



Self-assembly of Fe^{2+}-ions and the rigid ditopic ligand 1,4-bis(2,2´:6´,2´´-terpyridin-4´-yl)benzene results in metallosupramolecular coordination polyelectrolytes (MEPE). Sequential self-assembly of MEPE and dialkyl phosphoric acid esters of varying chain length via electrostatic interactions between MEPE and the amphiphiles leads to the corresponding polyelectrolyte-amphiphile-complexes (PAC). The PACs have a stratified architecture where the MEPE is embedded in between the amphiphile layers. Upon heating above room temperature, the PACs show either a reversible or an irreversible spin-crossover (SCO), depending on the the architecture of the amphiphilic matrix. We describe, how the structure and the magnetic response function of PACs can be tailored through the design of the ligand and the composition.

COLL 299

Hydration phenomena at the interface of physics and biology: A new fluctuations-based perspective

Shekhar Garde(1)*, gardes@rpi.edu, 110, 8th Street, Troy NY 12180, United States . (1) Howard P. Isermann Department of Chemical & Biological Engineering, Rensselaer Polytechnic Institute, Troy NY 12180, United States*

Water-mediated interactions (e.g., hydrophobic interactions) govern a host of biological and colloidal self-assembly phenomena from protein folding, micelle and membrane formation, to molecular recognition. Macroscopically, hydrophobicity is often characterized by measuring a droplet contact angle on a surface. At the nanoscale, such measurements are not feasible, e.g., for surfaces of proteins or nanoparticles. Using theory and molecular simulations, we present a new perspective that connects the behavior of water near nanoscale interfaces to their hydrophobicity/philicity. Specifically, we show that water density fluctuations (and not the average local density) provide a quantitative characterization of interfacial hydrophobicity. Density fluctuations are enhanced near hydrophobic interfaces and suppressed near hydrophilic ones. This new perspective provides a computational tool for characterizing the hydrophobicity patterns on protein surfaces, which are relevant for binding, recognition, and aggregation. Simulations also show how the properties of water at interfaces influence binding, folding, and dynamics of flexible molecules in interfacial environments. Our current understanding of the hydration of ions, osmolytes, and solution additives, when combined with this new perspective, provides additional insights into the role of water in multicomponent biological interactions.

COLL 300

Microemulsions and Micellar Solutions for the Conservation of Cultural Heritage

Piero Baglioni(1)*, piero.baglioni@unifi.it, VIA DELLA LASTRUCCIA 3 - SESTO FIORENTINO, FLORENCE FLORENCE 50019, Italy . (1) Department of CHemistry and CSGI, University of FLorence, Florence Florence 50019, Italy*

Works of art and artifacts that constitute our cultural heritage are subject to deterioration, both from internal and external factors. Surfaces that interact with the environment are the most prone to aging and decay; accordingly, soiling is a prime factor in the degradation of surfaces and the attendant disfigurement of a piece. Coatings, that were originally intended to protect or contribute aesthetically to a work of art, should be removed if they begin to have a destructive impact on its appearance or surface stability. This talk addresses the removal or organic coating from pictorial surfaces by using new colloidal systems: (1) Microemulsions and micellar solutions optimized for acrylic and vinyl polymers. (2) Nanomagnetic gels with embedded microemulsions or micellar solutions. With illustrative examples, I will report on the applications of these systems in recent restoration workshops.

COLL 301

Going forward: Green colloids for a healthy planet

***Ponisseril Somasundaran**[(1)], ps24@columbia.edu, 500 W 120th Str, Mudd Bldg, Rm.905, New York NY, United States . (1) Department of Earth and Environmental Engineering, Columbia University, New York NY 10027, United States*

We are all just tenants on this planet and we can not afford to continue to mess it up lest the landlord becomes angrier and punishes us with extreme events. Each of us needs to contribute to the reform with our expertise. As colloid chemists, we can do our part by developing greener efficient technologies for industries ranging from minerals to energy to consumer care to pharmaceuticals to the newcomer nanotechnology. I will present recent research at the Langmuir Center for Colloids and Interfaces in collaboration other institutions on greener reagents and their synergistic mixtures with conventional reagents. On going applications of green reagents for oil spill remediation, mineral beneficiary, biosolar cells, detergency, personal care products and bio-catalytic nanoparticles will be discussed along with our efforts to develop needed metrics to monitor and measure greenness. Importantly, the unlimited potential of the application of dynamics of surface active agents, engineered nanoparticles and tethered surfaces will be explored.

COLL 302

Controlling phase morphology in phospholipid vesicles through membrane tension and history

***Maria M Santore**[(1)], santore@mail.pse.umass.edu, 120 Governors Drive, Amherst MA 01003, United States ; Dong Chen[(2)]. (1) (2) Department of Polymer Science and Engineering, University of Massachusetts - Amherst, Amherst MA 01003, United States*

This work explores phase transitions in mixed DOPC-DPPC giant unilamellar vesicles, focusing on the effects of membrane tension and cooling rates on the types and shapes of the resulting solid domains and on the phase diagram which includes metastable curves. Two domain types, “patches” (which include rounded, hexagonal, and dendritic shapes) and striped (which include needles with finite ends and stripes which terminate in other stripes without ends) are observed to incorporate /exclude fluorescent tracers differently, evidencing distinctly different molecular structures for the two solid types. The patch phase, thought to be comprised of ordered ripples, forms on rapid cooling, independent of membrane tension, with the composition-dependence of the phase separation temperature resembling phase diagrams typical of DPPC-containing mixtures. At moderate cooling rates, order 1C /min, the nature of the phase (stripes or patches, tilt or ripple) depends on the membrane tension, with high tension favoring stripes. There is also tendency to form stripes at slow cooling rates at lower temperatures, providing additional curves on the phase diagram, depending on the tension. At the slowest cooling rates with low tension membranes, a few patches nucleate at the expected temperature, but are consumed by stripes which initiate at lower temperatures. The dynamic loss of patches and simultaneous growth of stripes

near 25C evidences the preferred equilibrium nature of the stripes, though to be comprised of the tilted gel in its orthorhombic ordering. The robust nature of the patches formed at high tension and rapid cooling demonstrates a history-dependent energy barrier between the patch and striped phases which, at most conditions can be difficult to cross, providing great stability to the patch phases when they do form rapidly and extensively.

COLL 303

Dark Antimicrobial Activity of Cationic Conjugated Phenylene Ethynylene Polymers and Oligomers against E. coli and Other Pathogens

David G Whitten(1)*, whitten@unm.edu, Centennial Engineering Center Rm 2041, Albuquerque New Mexico 87131-1341, United States ; Ying Wang*(2)*; Zhijun Zhou*(1)*; Yanli Tang*(1)*; Jingshu Zhu*(1)*; Taylor D Canady*(1)*; Steven W Graves*(1)*; Eva Y Chi*(1)*; Kirk S Schanze*(3)*. (1) Center for Biomedical Engineering, University of New Mexico, Albuquerque New Mexico 87131-1341, United States (2) Chemistry and Chemical Biology, University of New Mexico, Albuquerque New Mexico 87131-1341, United States (3) Department of Chemistry, University of Florida, Gainesville Florida 32611-7200, United States*

The interactions of poly(phenylene ethyneylene) (PPE)-based cationic conjugated polyelectrolytes (CPE) and oligo-phenylene ethynylenes (OPE)with *E. coli* cells and other pathogens such as phages have been investigated to gain insight on the origin of the different dark killing abilities among the CPEs/OPEs. In agreement with previous findings, these compounds can efficiently perturb the bacterial cell wall and cytoplasmic membrane; resulting in the death of bacteria. The electron microscope observations and cytoplasmic membrane permeability assays reveal the detail of the interaction between *E. coli* cells and CPEs/OPEs. The oligomers can penetrate the bacterial outer membrane and interact efficiently with the bacterial cytoplasmic membrane; in contrast, the polymers can cause serious damage to the cell surface. The minimum inhibitory concentration (MIC) and hemolytic concentration (HC) measurements compare the antimicrobial activities of CPEs/OPEs against two different strains of *E. coli* cell and cytotoxicity against human red blood cells (RBC).

COLL 304

Amphiphilic peptides: From mode of action to drug delivery aspects

Martin Malmsten(1)*, martin.malmsten@farmaci.uu.se, Uppsala Biomedicinska Centrum BMC, Husarg. 3, 752 37, Uppasala Sweden, Sweden . (1) Pharmaceutical Physical Chemistry, Uppasala University, Uppasala, Sweden*

Due to increasing resistance development, antimicrobial peptides (AMPs) are receiving increasing attention since these may provide rapid and broad-spectrum response to a host of pathogens. Some of these peptides also provide strongly antiinflammatory

responses. Membrane interactions are critical for the antimicrobial action of AMPs, where current efforts are directed to identifying peptides displaying pronounced selectivity for microbial membranes. In inflammation, additional aspects are of importance, including interaction with lipopolysaccharide and related microbial membrane components. Focusing on endogenous peptides generated during infection, we combine basic biophysical investigations of peptide-membrane interactions with modern biotechnological tools for peptide design, and with biological experiments including bacteria, cells, and various animal models. Some recent examples of the work done in these contexts will be provided, aiming at synthesizing biophysical and biological aspects of these peptides. In addition, examples are provided on the incorporation of such peptides in drug delivery and implant systems, with emphasis on polymer microgels.

COLL 305

Conformation of antimicrobial peptide Cecropin P1 C immobilized on silica surface using Molecular Dynamics Simulation

Ganesan Narsimhan$^{(1)}$*, narsimha@purdue.edu, 225 S. University Street, West Lafayette IN 47907, United States ; Xiayou Wu*$^{(1)}$*; Ramanathan Nagarajan*$^{(2)}$*; Charlene Mello*$^{(2)}$*. (1) Department of Agricultural and Biological Engineering, Purdue University, West Lafayette IN 47907, United States (2) Natick Soldier Research, Development & Engineering Center (NSRDEC), Natick MA 01760, United States*

Molecular Dynamics simulation of Cecropin P1 C (CP1C), an antimicrobial peptide, using AMBER showed an equilibrium structure consisting of two regions of high α helix probability with a sharp bend. The α helix probability for different residues of adsorbed CP1C on silica surface is not significantly different from that of CP1C in solution at low ionic strength of 0.02 M whereas there is a decrease in the probability only in the second region of residues EGI at higher ionic strength of 0.12 M. The conformation of CP1C tethered to silica surface with a $(PEO)_6$ linker exhibited two regions of high α helix probability as opposed to that with a $(PEO)_3$ linker which exhibited only one α helical region; the conformation of CP1C in solution is closer to the former than latter as a result of less surface interaction of tethered polypeptide with a longer linker.

COLL 306

Use of QCM-D overtone data to infer nature of antimicrobial peptide interactions with model bilayer membrane

Ramanathan Nagarajan$^{(1)}$*, ramanathan.nagarajan@us.army.mil, Kansas Street, Natick MA 01760, United States ; Kathleen Wang*$^{(2)}$*; Terri A Camesano*$^{(2)}$*. (1) Molecular Sciences and Engineering Team, U. S. Army Natick Soldier Research, Development and Engineering Center, Natick MA 01760, United States (2) Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester MA 01609, United States*

Many naturally occurring peptides have been shown to possess antimicrobial activity against both Gram-positive and Gram-negative bacteria. Their unique ability to prevent development of microbial resistance has been generally attributed to their cell killing mechanism involving the by destabilization of the cell membrane through non-specific physical interactions. The membrane destabilization has been suggested to occur by a combination of events such as surface adsorption of the peptides on the membrane, transmembrane insertion of the peptides to generate cylindrical or toroidal pores and lysis of the membrane by formation of lipid-peptide aggregates. In this study we propose that frequency and dissipation changes at various overtones measured using Quartz Crystal Microbalance with Dissipation monitoring can be used to infer the different pathways of membrane destabilization caused by antimicrobial peptides. We illustrate the approach with results obtained for chrysophsin 3 and alamethicin interacting with supported bilayers of egg phosphotidyl choline.

COLL 307

Janus colloids

Steve Granick[(1)]*, sgranick@uiuc.edu, 1304 West Green St., Urbana IL 61821, United States . (1)*

The specially-designed colloidal building blocks known as Janus present a new paradigm in colloid science because their interactions are directional. The “diblock” motif, mutually attractive on one domain and repulsive on another, makes this a prototypical system for elucidating, on a mechanistic level, how concepts of chemical reaction kinetics explain the development of stable and highly ordered nonequilibrium structures. With the “triblock” motif, spheres that attract one another on two polar regions but repel at the middle band, we go beyond this to demonstrate the self-assembly of a useful low-density lattice of spheres, the colloidal Kagome lattice, and visualize its aqueous assembly dynamics on the single-particle level. The generalization of these design rules will be discussed.

Work performed with Erik Luijten, Qian Chen, Jonathan Whitmer, Eric Diesel, Shan Jiang, Jing Yan, and Sung Chul Bae.

COLL 308

Catalytic model systems studied by high-resolution, video-rate Scanning Tunneling Microscopy

Flemming Besenbacher[(1)]*, fbe@inano.au.dk, Ny Munkegade, Building 1521, room 309, Aarhus C Denmark DK-8000, Denmark . (1) Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus C DK-8000, Denmark*

For decades single-crystal surfaces have been studied under ultra-high vacuum (UHV) conditions as model systems for elementary surface processes. This “surface science approach” has contributed substantially to our understanding of the processes involved in especially catalysis. In this talk I will show how STM can reveal fundamental processes in relation to catalysis, and how we can extract quantitative information on surface diffusion of adatoms and molecules. We use time-resolved, high-resolution STM images/movies to understand diffusion of vacancies, interstitials and molecules, e.g. water molecules on oxide surfaces, sintering and diffusion of nanoclusters on oxide surfaces, diffusion of intermediate species, and to identify active sites and to determine new nanostructures with novel catalytic properties (see www.phys.au.dk/spm). The atomic-scale information obtained may even lead to the design of new and improved catalysts in certain cases .

COLL 309

Computer-Simulation/Molecular-Thermodynamic (CS-MT) framework to predict micellization properties of surfactant mixtures

Jaisree Iyer(1)*, jaisree@mit.edu, 77 Massachusetts Avenue, 66-257, Cambridge Massachusetts 02139, United States ; Jonathan D Mendenhall*(1)*; Shangchao Lin*(1)*; Daniel Blankschtein*(1)*. (1) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge Massachusetts 02139, United States*

In most industrially relevant surfactant formulations several surfactants are mixed in an effort to satisfy all the performance specifications. Therefore, the ability to predict the composition-dependent micellization behavior of surfactant mixtures would facilitate the development of new formulations by reducing the need for costly trial-and-error experimentation. Recently, we developed a Computer-Simulation (CS)/Molecular-Thermodynamic (MT) framework to model the micellization behavior of complex surfactants in which hydration information from molecular dynamics simulations of surfactant monomers and micelles is combined with our MT theory for micellization. In this talk, we discuss the extension of the CS-MT framework to surfactant mixtures in which hydration information from simulated mixed micelles is used. In addition, we address the challenges associated with the practical implementation of the CS-MT framework by formulating a simpler CS-MT model for surfactant mixtures, including testing its ability to predict critical micelle concentrations of binary surfactant mixtures.

COLL 310

Mechanistic insights into the sphere-to-worm and worm-to-vesicle transitions during RAFT aqueous dispersion polymerization of amphiphilic diblock copolymers at high solid contents

Adam J Blanazs(1)*, a.blanazs@sheffield.ac.uk, Dainton Building, Sheffield S. Yorks S3 7HF, United Kingdom ; Jeppe Madsen*(1)*; Steven P Armes*(1)*. (1) Department of Chemistry, The University of Sheffield, Sheffield S. Yorks S3 7HF, United Kingdom*

We report polymerization-induced block copolymer self-assembly via aqueous dispersion polymerization of 2-hydroxypropyl methacrylate (HPMA) at 70^{o}C using RAFT chemistry with a water-soluble poly(glycerol monomethacrylate)-based chain transfer agent. TEM studies confirm that spherical micelles, worm-like micelles or vesicles are produced within 2 h at 70^{o}C at 10 % solids. The onset of micellar nucleation leads to a significantly enhanced rate of polymerization, which suggests that solvation of the growing PHPMA chains by unreacted HPMA monomer leads to a high local monomer concentration. Moreover, monitoring of the polymerization reveals a wide range of intermediate morphologies are formed during the growth of the water-insoluble PHPMA chains, which provide important mechanistic insights regarding the sphere-to-worm and worm-to-vesicle transitions. The former transition simply involves micellar fusion, whereas the latter transition involves a complex sequence of events, including the formation of branched worms, partially coalesced worms, nascent bilayers, 'jellyfish' structures and finally a pure vesicle phase.

COLL 311

From Solubilization of Organic Compounds in Block-copolymer Surfactant Micelles to Micelle-templated Synthesis of Ultra-large-pore Ordered Mesoporous Materials

Michal Kruk(1)(2)*, Michal.Kruk@csi.cuny.edu, Building 6S-241, 2800 Victory Boulevard, Staten Island NY 10314, United States ; Manik Mandal*(1)*; Liang Huang*(1)(2)*; Tiffany Man*(1)(2)*; Liang Cao*(1)(2)*. (1) Department of Chemistry, College of Staten Island/City University of New York, Staten Island NY 10314, United States (2) Graduate Center/City University of New York, Staten Island NY 10314, United States*

Micelle swelling agents (expanders) are commonly used in surfactant-templated syntheses of ordered mesoporous materials (OMMs). The micelle expander is solubilized in the hydrophobic cores of the micelles and thus increases their diameter and volume, leading to the enlarged pore size and volume of the surfactant-templated material. However, the swelling process is often accompanied by the loss of size uniformity or change in shape of the micelles, which affords heterogeneous or/and disordered porous materials. Recently, we proposed that the synthesis of well-defined OMMs with appreciably enlarged mesopores can be facilitated by selecting swelling agents that are solubilized in the micelles to an appreciable extent, but not to an excessive extent. Further, we proposed to select swelling agents from series of organic compounds that exhibit gradually increasing extent of solubilization in micelles of surfactants of interest. The success of this strategy will be illustrated for ordered mesoporous silicas and organosilicas.

COLL 312

Biocatalytic synthesis of polypyrrole in amphiphilic block copolymer micelles

Subhalakshmi Nagarajan**(1)**, *Subhalakshmi.Nagarajan.ctr@us.army.mil, Kansas Street, Natick MA 01760, United States ; Ferdinando F Bruno(1); Christopher P Drew(1); Ramanathan Nagarajan(1). (1) U S. Army Natick Soldier Research Development and Engineering Center, Natick MA 01760, United States*

Enzyme catalyzed polymerization of pyrrole in the presence of various dopants including surfactants results in formation of processable and water-soluble doped polypyrrole complexes. Biomimetics such as Hematin are known to catalyze the polymerization of pyrrole in the presence of anionic surfactants. However all these reactions involve the use of significant amount of dopants which are almost impossible to remove after polymerization. Here we report a biocatalytic route to the synthesis of processable polypyrrole in amphiphilic block copolymer micelles using very small amounts of 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) diammonium salt as a redox mediator in the absence of other dopants. Amphiphilic symmetric triblocks based on PEO-PPO-PEO are commercially available (trade name Pluronics®) biocompatible copolymers known to form stable micelles over a range of temperatures and concentrations. Pluronics P123 and F127 were found to be effective in solubilizing both the pyrrole monomer and catalyst hematin. Synthesis and characterization of the Polypyrrole-pluronic conjugates will be presented.

COLL 313

Kinetics of chain exchange between polymer micelles at equilibrium: DPD simulations

Elena E. Dormidontova**(1)**, *eed@po.cwru.edu, 2100 Adelbert Rd., Cleveland Ohio 44106, United States ; Zhenlong Li(1). (1) Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland Ohio 44106, United States*

Chain exchange kinetics between polymer micelles at equilibrium have become a subject of growing interest because of both its fundamental importance and the potential practical applications of polymer micelles. Using dissipative particle dynamics simulations we studied the equilibrium chain-exchange between micelles formed by short diblock copolymers in solution. By performing micelle hybridization simulations, we found that equilibrium chain exchange follows a first-order kinetic process and the characteristic time is mainly determined by chain expulsion and does not depend on polymer concentration. The chain exchange characteristic time, τ, increases exponentially with core block length, N_A and interaction parameter between blocks, χ_{AB} as $\tau \sim \exp(0.67\chi_{AB}N_A)$. We also found that in contrast to theoretical predictions, chain exchange between micelles occurs more rapidly for micelles with a longer corona-block length due to a higher compatibility of diblock copolymers and therefore a lower potential barrier for chain expulsion.

COLL 314

Effect of oil-to-oater ratio on the stability of water-in-crude oil emulsion

Mehrnoosh Moradi[(1)], *mmoradib@uwyo.edu, Dept. 3295, 1000 E. University Ave, Laramie WY 82071, United States ; Vladimir Alvarado*[(1)]*. (1) Chemical & Petroleum Engineering, University of Wyoming, Laramie WY 82071, United States*

Stability of water-in-crude oil (W/O) emulsion is attributed to the presence of polar materials indigenous to crude oil such as asphaltene and resins. Availability of organic interfacial compounds in the oil is a function of the oil volume fraction. In this study, we determine the stability of W/O emulsions as a function of oil-to-water volumetric ratio. Emulsion stability is determined by using Electrorheology (ER), which serves as proxy of droplet coalescence through measurements of electrical current and provides information on structural changes of the emulsion. Current percolation allows one to estimate the Critical electric field (CEF), a value of the voltage-to-gap ratio in the rheometer at which the emulsion structure breakdown occurs. Time evolution of viscosity, elasticity and electrical current are measured to indicate the microstructure and interfacial properties. Results show that by increasing the oil fraction, the CEF value increases, indicating higher stability of the emulsion.

COLL 315

Computer simulation studies of structure and dynamics of aqueous reverse micelles

Branka M Ladanyi[(1)], *Branka.Ladanyi@colostate.edu, Department of Chemistry, Fort Collins CO 80523-1872, United States ; Janamejaya Chowdhary*[(1)(2)]*. (1) Department of Chemistry, Colorado State University, Fort Collins CO 80523-1872, United States (2) Department of Biochemistry and Molecular Biology, University of Chicago, Fort Collins CO 80523-1872, United States*

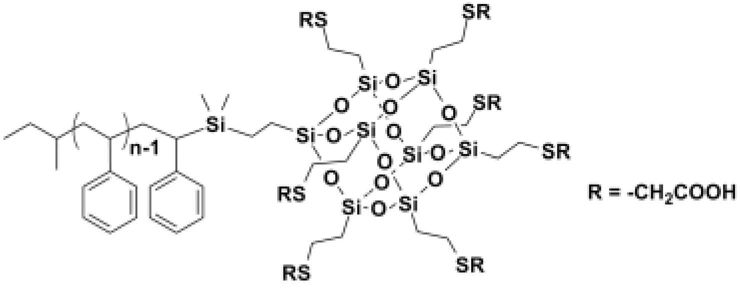
This presentation deals with the results of molecular simulation studies of our atomistic models for aqueous reverse micelles (RMs) of varying water content w_0 = [water]/[surfactant]. The results are for the anionic surfactant AOT (= sodium bis (2-ethylhexyl) sulfosuccinate) as well as for other water/surfactant/oil systems. Structural properties of the RMs are characterized in terms of radial density and hydrogen bond profiles, pair distributions, and fluctuations in the size and shape of the aggregates. The mobility of water in different interfacial layers is quantified in terms of orientational time correlations, translational mean squared displacements, and survival probabilities. We find that interfacial structure changes as w_0 is varied due to the increase in the surface area per headgroup with increasing w_0 and that water mobility in a given layer depends on w_0 in addition to the distance from the interface. Comparison of our results for water dynamics to data from time-resolved IR and quasielastic neutron scattering experiments will be discussed.

COLL 316

Giant surfactant: Polystyrene−(carboxylic acid-functionalized POSS) amphiphile

***Xinfei Yu*[1]**, *xy5@zips.uakron.edu, 170 University Ave Rm 929, Akron OH, United States ; Wen-Bin Zhang[1]; Roderic P Quirk[1]; Stephen Z. D. Cheng[1]; Hao Liu[1]. (1) Department of Polymer Science, The University of Akron, Akron OH 44325, United States*

PS-APOSS has been designed and synthesized with a polar rigid head and a hydrophobic flexible polymeric tail.



PS-APOSS

PS-APOSS forms micelles in selective solvents, and the micellar morphology can be tuned from vesicles to wormlike cylinders and further to spheres by increasing the degree of ionization of the carboxylic acid. The PS tails in these micellar cores were found to be highly stretched in comparison with those in traditional amphiphilic block copolymers.

COLL 317

Graphene oxide as colloidal surfactant

***Jiaxing Huang*[1]**, *jiaxing-huang@northwestern.edu, 2220 Campus Drive, 3051 Cook Hall, Evanston IL 60208, United States . (1) Department of Materials Science & Engineering, Northwestern University, Evanston IL 60208, United States*

Graphite oxide sheet, now named as graphene oxide (GO), is the product of chemical exfoliation of graphite that has been known for more than a century. Interest in this old material has resurged with the rapid development of graphene since 2004, as GO is considered to be a promising precursor for bulk production of graphene. However, apart from making graphene, GO itself has many intriguing structural features and properties. For example, it can be viewed as an unconventional type of soft material as it has characteristics of polymers, membranes, colloids, liquid crystals and as highlighted here, amphiphiles. GO has long been described as hydrophilic due to its ionizable edge functional groups, however, it should be amphiphilic since there are also hydrophobic graphitic nano domains in its basal plane. Indeed, GO readily adsorbs to air-water and oil-water interfaces, and can lower the interfacial energies. As the “world's thinnest bar of soap”, GO shows some intriguing size dependent solution properties, and can act as dispersing agent for insoluble materials in water such as graphite, carbon nanotubes or insoluble conjugated polymers. Some exciting opportunities and new materials created by this novel sheet-like surfactant, such as a photovoltaic fullerene/nanotube/graphene all-carbon composite will be presented.

COLL 318

Biomimetic vesicular membrane with incorporated Aquaporin-Z for forward osmosis

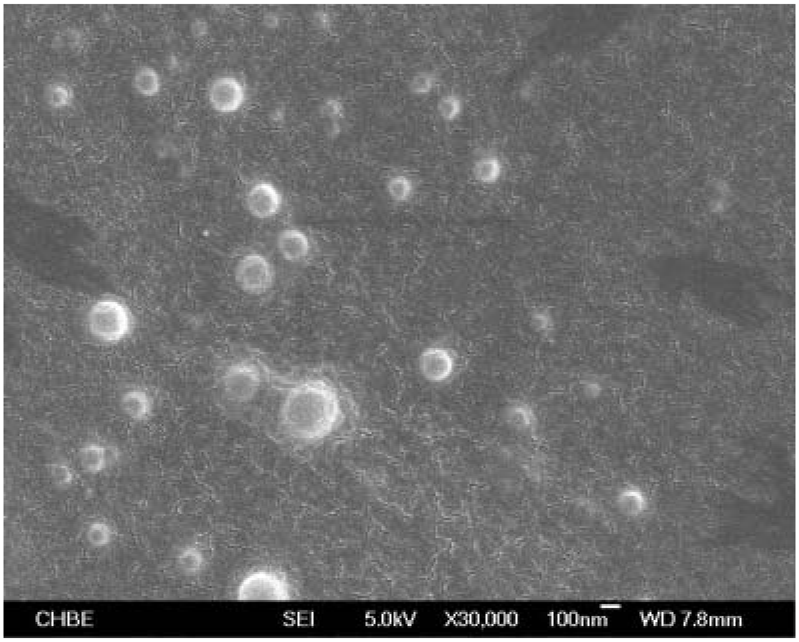
Fang He(1)*, fang.he@nus.edu.sg, Centre for Life Sciences (CeLS), #05-01, 28 Medical Drive, Singapore Singapore 117456, Singapore ; Yen Wah Tong*(1)*. (1) NUS Graduate School for Integrative Sciences and Engineering (NGS), National University of Singapore, Singapore Singapore 117456, Singapore*

Biomimetic membranes for forward-osmosis have seen their advances in recent years for their exceptional performance but the research has been intercepted by several technical limitations such as coverage and mechanical instability. We proposed the use of Aquzporin-Z incorporated
vesicles to design and construct a novel biomimetic membrane that can potentially overcome
such constraints.

This study proceeds from the fabrication of Aquaporin Z-incoporated polymersomes to the immobilization of these vesicles on an appropriate support before an investigation of the membrane's bulk water permeability with a forward-osmosis test unit. Here we show biophysical studies on four different vesicular formulations of diblock-copolymer polybutadiene-polyethylene oxide. They include morphological observations with AFM, CLSM and TEM, chain rigidity studies, 2-dimensional lateral-diffusivity studies with FRAP and post-incorporation functionality tests of proteins with stopped-flow spectroscopy.

Sample	Solvent	Permeability (m/sec)
PBD PEO	DI water	1.06E-5
PBD PEO	1XPBS	1.9E-5
Aqp-Z incorporated PBD PEO	1XPBS	3.98E-4
Crosslinked PBD PEO	DI water	6.5E-6
Crosslinked Aqp-Z incorporated PBD PEO	1XPBS	4.5E-4

Using the optimised vesicular formulation for protein incorporation, we immobilized and coated solid supports with intact vesicles via various surface coupling reactions.



COLL 319

Microrheological Studies of Gelation Behavior for a Poly(ethy1ene oxide)-Poly(propy1ene oxide)-Poly(ethy1ene oxide) Triblock Copolymer in Aqueous Solution

***Ren-Jye Wu**(1), RJWU@itri.org.tw, Rm 104, Bldg 67, 195, Sec. 4 Chung Hsing Rd., Chutung, Hsinchu Taiwan 31040, Taiwan Republic of China ; Yen-Cheng Li(1). (1) Department of High Throughput Synthesis and Analysis, Industrial Technology Research Institute, Hsinchu Taiwan 31040, Taiwan Republic of China*

Control of gelation is important for industrial applications. The gelation behavior of a poly(ethy1ene oxide)-poly(propy1ene oxide)-poly(ethy1ene oxide) triblock copolymer (Pluronic® F127) in aqueous solution was studied by diffusing wave spectroscopy technique. The frequency dependent viscoelastic moduli (G' and G”) were obtained from the mean square displacement by using the generalized Stokes-Einstein equation in the range of 0.1 s^{-1} to 10^6 s^{-1}. The G' and frequency at the crossover of G' and G” decreased rapidly with temperature before the gel temperature, while, depending on the concentration, remained constant or slightly increased with temperature after gelation. This could be explained by the micellar gelation mechanism of gel formation. It is interesting to note that the level-off G' at high frequency seems to be independent of the concentration of F127 at temperatures higher than gel point. This implies that the micelle size and arrangement of F127 gel could be the same for the concentration range studied.

COLL 320

Liquid-Liquid Phase Separation of a Monoclonal Antibody and Nonmonotonic Influence of Hofmeister Anions

Jifeng Zhang(1)*, jifengz@amgen.com, One Amgen Center Drive, Thousand Oaks CA 91320, United States . (1)*

Liquid-liquid phase separation was studied for a monoclonal antibody in the monovalent salt solutions of KF, KCl, and KSCN under different pH conditions. A modified Carnahan-Starling hard-sphere model was utilized to fit the experimental data, establish the liquid-liquid coexistence curve, and determine antibody-antibody interactions in the form of T_c (critical temperature) under the different solution conditions. The liquid-liquid phase separation revealed the complex relationships between antibody-antibody interactions and different solution conditions, such as pH, ionic strength, and the type of anion. At pH 7.1, close to the pI of the antibody, a decrease of T_c versus ionic strength was observed at low salt conditions, suggesting that the protein-protein interactions became less attractive. At a pH value below the pI of the antibody, a nonmonotonic relationship of T_c versus ionic strength was apparent: initially as the ionic strength increased, protein-protein interactions became more attractive with the effectiveness of the anions following the inverse Hofmeister series; then the interactions became less attractive following the direct Hofmeister series. This nonmonotonic relationship may be explained by combining the charge neutralization by the anions, perhaps with the ion-correlation force for polarizable anions, and their preferential interactions with the antibody.

COLL 321

Correlation of Metal Oxide Nanoparticle Physicochemical Properties with Cytotoxicity

Charles C Chusuei(1)*, chusuei@mtsu.edu, 1301 East Main Street, Box 390, Murfreesboro TN 37132, United States ;* ***Shravan Mallavarapu***(1)*, shravanm1122@gmail.com, 1301 East Main Street, Box 68, Murfreesboro TN 37132, United States ; Chi-Heng Wu*(2)*; Yue-wern Huang*(2)*. (1) Chemistry Department, Middle Tennessee State University, Murfreesboro TN 37132, United States (2) Department of Biological Sciences, Missouri University of Science and Technology, Rolla MO 65409, United States*

Over the last decade, metal oxide nanoparticles have been widely used in biomedical applications such as sunscreens, toothpastes, and even food products. There has been a growing concern over the toxicity of these metal oxide nanoparticles as they interact with the living cells, and other intracellular parts at the nanoscale. Studies examining 4th-period transition metal oxide nanoparticles (20 to 60 nm in diameter) using human bronchial epithelial cells shows a trend in toxicity that roughly corresponds with transition metal periodicity. We have investigated a variety of factors that govern these observed trends. Point-of-zero charge (PZC), metal oxide dissolution, and the degree of surface hydroxylation on the nanoparticle surfaces were studied. Nanoparticles were

placed in a constant composition reactor (16 hours) to maintain pH conditions and mimic physiological conditions at pH = 7.4. Surface hydroxylation was studied by comparing integrated peak area ratios of hydroxyl versus metal oxide oxygen using X-ray photoelectron spectroscopy (XPS) O 1s core levels. The PZC of these nanoparticles largely match observed PZC trends: Mn_2O_3 > ZnO = CuO > NiO > CoO > Fe_2O_3 > Cr_2O_3 > TiO_2. In addition to analysis of PZC and degree of surface hydroxylation, effects of nanoparticle dissolution, BET surface area and the interplay of these physicochemical properties that govern the degree of cytoxicity were probed.

COLL 322

Self assembling gold nanoparticle based breast cancer imaging agent

Ziyan Zhang(1)*, zzhangb@go.wustl.edu, One Brookings Drive, Saint Louis MO 63130, United States ; Yongjian Liu*(2)*; Michael J Welch*(2)*; John-Stephen A Taylor*(1)*. (1) Department of Chemistry, Washington University in St. Louis, Saint Louis MO 63130, United States (2) Division of Radiological Sciences, Mallinckrodt Institute of Radiology, School of Medicine, Washington University in St. Louis, Saint Louis MO 63110, United States*

Gold nanoparticles have attracted much interest as a platform for development of multifunctional delivery agent. In this study, we developed ODN (oligodeoxyribonucleotide) based self-assembled gold nanoparticles as targeted breast cancer imaging agents. We first synthesized ODN modified gold nanoparticles, and then assembled them with DOTA (1,4,7,10-tetraazacyclododecane-N,N',N'',N'''-tetraacetic acid) functionalized complementary PNA (peptide nucleic acid) as ^{64}Cu chelating moiety for PET imaging, and PEG (polyethylene glycol) functionalized PNA for stealth effect. To target MCF7 cells, we synthesized a DNA aptamer that was also complementary to the gold modifying ODN. For *in vitro* studies with fluorescent microscopy, we also assembled the gold nanoparticles with a Cy5 labeled complementary PNA. The size, optical absorption, fluorescent properties and ODN loading of the nanoparticle were characterized. Bio-distribution of the PEGylated gold nanoparticles in normal mice was studied by PET imaging. The MCF7 targeting ability of the aptamer based PEGylated gold nanoparticles is under investigation.

COLL 323

Gold Nanoparticle Dimers as Tags for SERS-based Cancer Detection

Laura Fabris(1)(2)*, lfabris@rci.rutgers.edu, 607 Taylor Road, Piscataway New Jersey 08854, United States ; Bryan J. Paladini*(1)*; Robert C. Wadams*(1)*. (1) Department of Materials Science and Engineering, Rutgers University, Piscataway New Jersey 08854, United States (2) Institute for Advanced Materials Devices and Nanotechnology, Rutgers University, Piscataway New Jersey 08854, United States*

Early cancer detection is of fundamental importance to reduce morbidity and recurrence, especially for highly invasive cancers. A great potential has been recognized for the use of nanoparticle (NP)-based imaging agents, capable of specifically visualizing only the targeted diseased cells. The possibility of achieving early detection at the single cell level could enable the visualization of tumor margins and the analysis of post-surgical histological samples with fast detection times and high sensitivity. Surface enhanced Raman scattering (SERS)-based imaging tags are starting to attract increasing attention due to their brightness and the possibility of multiplexing. In this contribution we will report on the development of SERS-based imaging tags, composed of gold NP dimers held together by a Raman active small molecular linker. Synthesis, characterization, and application in human glioblastoma will be reported and future implementations of the system will be described.

COLL 324

Structural basis for ligand exchange: Progress toward artificial proteins

Christine L. Heinecke(1)*, christine.heinecke@colostate.edu, 200 W Lake Street, Campus Delivery 1872, Fort Collins Colorado 80523, United States ; Christopher J. Ackerson*(1)*. (1) Department of Chemistry, Colorado State University, Fort Collins Colorado 80523, United States*

Thiolate ligand protected gold clusters (LPGCs) are widely studied nanoparticles with biological applications in imaging, drug delivery and drug enhancement. Ligand place exchange reactions represent a universal avenue for preparing chemically and biologically functionalized LPGCs. We have solved the X-ray crystal structure of 4-bromobenzenethiol ligand exchanged Au_{102}(*p*-mercaptobenzoic acid)$_{44}$, which has revealed an initial structural understanding of the ligand place exchange reaction. Our results enhance the concept of LPGCs as 'artificial proteins' and suggest the possibility of 'site-directed mutagenesis' on LPGCs.

COLL 325

Analytical methods for determining nanoparticle purity and the presence of nanoparticle surface coatings

Elisabeth Mansfield(1)*, elisabeth.mansfield@nist.gov, 325 Broadway, Boulder CO 80305, United States ; Stephanie Hooker*(1)*; Karl Sebby*(1)*. (1) Materials Reliability Division, NIST, Boulder CO 80305, United States*

Use of nanoparticles in some applications (*i.e.*, nanomedical, nanofiltration or nanoelectronic) require small-scale samples with well known purities and composition. In addition, when nanoparticles are introduced into harsh environments (*i.e.*, biological fluids) the particle may become coated with matter from the media, such as proteins or lipid layers. Many of today's analytical techniques are not able to address small scale samples of nanoparticles to determine purity and presence of surface coatings and

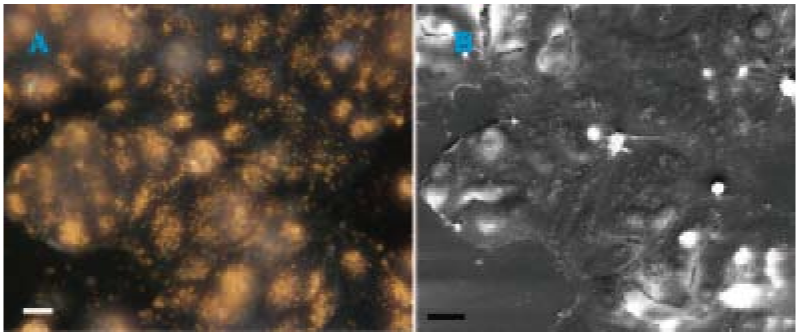
purity. Quartz crystal microbalances (QCMs) are extremely sensitive mass sensors capable of measuring mass changes on the scale of nanograms to picograms with total sample volumes of less than 10 micrograms. Recent advances at NIST (National Institute of Standards and Technology) have expanded the QCM technique to include measurements at elevated temperatures (up to 575°C). We will present use of elevated temperature QCM methods to measure the properties of nanomaterials at elevated temperatures, demonstrating how these techniques can be used to perform micro-thermogravimetric measurements to determine purity. Elevated temperature QCM methods are used to determine coverage of gold and silica nanoparticles with surface ligands and compared to traditional analytical techniques and characterize carbon nanotubes for purity.

COLL 326

Complete characterization, cytotoxicity, and cell uptake of a functionalized gold nanorods

Leonid Vigderman[(1)]*, lvigder@gmail.com, 6100 Main Street MS-60, Houston TX 77005, United States ; Pramit Manna*[(1)]*; Eugene R Zubarev*[(1)]*. (1) Department of Chemistry, Rice University, Houston TX 77005, United States*

We report the synthesis of a thiol-stabilized gold nanorod system which addresses the stability and cytotoxicity issues of as-synthesized surfactant-stabilized nanorods and whose structure can be definitively determined by traditional techniques such as ^{1}H-NMR and thermogravimetric analysis. Using darkfield optical imaging (A), SEM (B), TEM, and ICP we show that the gold nanorods can be taken up in large amounts by MCF-7 cells in vitro while maintaining low cytotoxicity.



COLL 327

Chemically-Modified Single Glass Conical Nanopore for Biomimetic Stimuli-Responsive Ion Channel

Yao-Qun Li(1)*, yqlig@xmu.edu.cn, Shiming Road, Xiamen Fujian 361005, China ; Li-Xiang Zhang*(1)*; Sheng-Lin Cai*(1)*; Yu-Bin Zheng*(1)*; Xiao-Hong Cao*(1)*. (1) Department of Chemistry and Key Lab of Analytical Sciences, Xiamen University, Xiamen Fujian 361005, China*

Biological ion channels that regulate ion permeation through cell membranes play important roles in maintaining various significant physiological functions. By designing functional molecules modified synthetic nanopore systems, we can control ionic transport through nanometer-scale opening in response to surrounding stimuli. We have made a modification of the inner surface of a single glass conical nanopore channel amphoteric with biocompatible 6-carboxymethyl-chitosan (CMC) to achieve a smart device responsive to surrounding pH stimuli. The response of the CMC modified nanopore channel was highly sensitive, reversible and reproducible. Furthermore, we have integrated a smart homopolymer which undergo both temperature and pH induced conformational transitions to a single glass conical nanopore channel to realize the pH and temperature dual-stimuli responsive ion transport properties. Surface-initiated atom transfer radical polymerization (SI–ATRP) has been used to prepare poly (2-(dimethylamino) ethyl methacrylate) (PDMAEMA) brush on the single glass conical nanopore channel. The conductance of the PDMAEMA–nanopore complex was highly reversibly switched under pH and temperature double stimuli control, with perfect gating efficiency. The smart biomimetic nanochannels may suggest its future applications in biosensors and drug-delivery.

COLL 328

Organic self assembled monolayers on bio-metallic alloys

Anil Mahapatro(1)*, amahapatro@nsu.edu, 700 Park Avenue, Norfolk VA, United States . (1) Department of Chemistry, Norfolk State University, Norfolk VA 23504, United States*

Cobalt Chromium (Co-Cr) alloys has been widely used in the biomedical arena for cardiovascular, orthopedic and dental applications. Surface modification of the alloy allows us to tailor the interfacial properties to address critical challenges of Co-Cr alloy in these medical applications. Nanosized self assembled monolayers (SAMs) of Octadecylphosphonic acid (ODPA) have been formed on the Co-Cr alloy surface. These SAMs formed were investigated for their stability to oxidative and physiological conditions over periods of 1, 3, 7 and 14 days. The formation and stability of the nanosized monolayers was characterized using Fourier Transform Infrared Spectroscopy (FTIR) with Attenuated Total Reflectance (ATR) attachment, Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS), Ellipsometry and Contact Angle measurements. Experimental results confirmed that ODPA SAMs were successfully coated on Cobalt Chromium (Co-Cr) alloy surface and were found to be stable and strongly bound after oxidative and PBS exposure over 14 days.

COLL 329

Biological Application of Novel Cobalt-based Metal Organic Frameworks

Jingbo Louise Liu(1)*, jingbo.louise@gmail.com, MSC 161, 700 University Blvd, Kingsville TX 78363, United States ; Wendy Zhuang*(1)*; Hongcai L Zhou*(1)*. (1) Chemistry, Texas A&M University, College Station TX 77842-3012, United States*

Metal organic frameworks (MOFs) have drawn attention due to their tunable molecular architectures and electronic functionalities, leading to novel applications in the biological field. Our goals are to optimize the synthesis variables and characterize the structure of the engineered materials. This work presents new discoveries of bacteria inactivation using novel cobalt (Co)-based MOFs, derived using solvothermal technique. These Co-MOFs were effective at inactivating *Escherichia coli* (*E. coli*) gram-negative bacteria. From our study, it was found that MOFs displayed high potency to inactivate bacteria within a short time (ca. 30 min) compared with our previous work, using silver modified TiO_2 nanoparticles (NPs, > 4 hr). The contributions of this work are: (a) The novel Co-MOFs were derived via solvethermal method with optimal fabrication parameters; (b) The textural and crystalline structure were obtained using the state-of-the-art techniques; and (c) The new application of Co-MOFs to improve the potency of bacteria inactivation.

COLL 330

Redox-responsive molecular delivery vehicles

Robin L McCarley(1)*, TUNNEL@LSU.EDU, 232 Choppin Hall, Baton Rouge LA 70803-1804, United States ; Nicole H Carrier*(1)*; Jerimiah C Forsythe*(1)*; Maria Fabiana Mendoza*(1)*; William C Silvers*(1)*; Sreelatha Balamurugan*(1)*; Martin Loew*(1)*. (1) Department of Chemistry, Louisiana State University, Baton Rouge LA 70803-1804, United States*

Described here is a group of stimuli-responsive container molecules, based on lipids, that has the ability to have their contents released to the environment upon activation by a redox stimulus. Redox activation leads to cleavage of chemical moieties attached to the container lipids, and this event results in disassembly of the container (liposome), thereby causing the delivery of the container's contents. These systems release their responsive units in a fashion that allows for the programmed delivery of the container's contents, as indicated by time-lapse spectroscopy measurements of guest release. Light scattering, transmission electron microscopy, and electrochemical methods are used to probe the mechanism of liposome opening after redox activation.

COLL 331

Factors controlling the localized surface plasmon resonance response of surface-bound gold nanoplates to protein binding and applications in cancer diagnostics

Francis P Zamborini[(1)]*, f.zamborini@louisville.edu, 2320 South Brook Street, Louisville KY 40292, United States ; Srinivas R Beeram*[(1)]*; Radhika Dasari*[(1)]*; Daniela Hazel*[(1)]*; Michelle Maune*[(1)]*. (1) Chemistry, University of Louisville, Louisville KY 402922, United States*

Gold and silver nanostructures effectively absorb and scatter light in the visible range due to the excitation of localized surface plasmons. The wavelength and intensity of the absorbed/scattered radiation is highly sensitive to the refractive index of the medium surrounding the metal nanostructures. This has been exploited for biosensing applications. In this presentation, we describe the effect of coverage, location, and binding distance of the proteins on the localized surface plasmon resonance response. The response is significantly increased by selective binding of proteins to edge and vertex sites of the nanoplates due to enhanced local fields at these locations. The response also increases with increasing protein coverage and decreases exponentially with increasing distance between the binding protein and the nanoplate surface according to theory. Selective detection of human IgG occurred in the range of 0.01 ng/mL to 100 ng/mL by selective attachment of anti-IgG onto the edges of the nanoplates. It is possible to use this strategy for the detection of biomarkers for cancer diagnostics.

COLL 332

Bottom-up assembly and characterization of artificial multienzyme complexes

William M Aumiller Jr[(1)]*, wma111@psu.edu, 104 Chemistry Building, University Park PA 16802, United States ; Bradley W Davis*[(1)]*; Jacqueline D Keighron*[(1)]*; Songon An*[(1)]*; Stephen J Benkovic*[(1)]*; Christine D Keating*[(1)]*. (1) Department of Chemistry, The Pennsylvania State University, University Park PA 16802, United States*

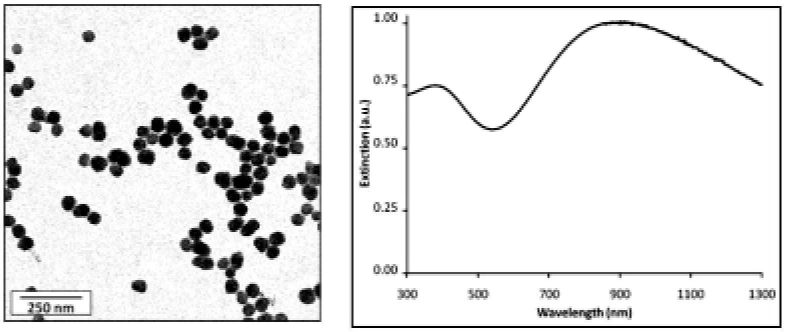
Dynamic proximity between sequential enzymes has been proposed to regulate metabolic pathways such as the de novo purine biosynthesis pathway. Progress toward the bottom-up assembly and characterization of enzyme-nanoparticle bioconjugates where proximity can be controlled will be discussed. Sequential enzymes of the purine pathway were expressed and purified with hexa-histidine (His_6) tags, followed by chemically labeling the enzymes with fluorescent dyes. The labeled proteins were immobilized to surface functionalized gold nanoparticle scaffolds via His_6 / nickel(II) – nitrilotriacetic acid (Ni^{2+}–NTA) attachment chemistry. The number of enzyme molecules per particle was determined by fluorescence and the specific activity of the enzyme was calculated. The gold nanoparticle scaffolds were structurally characterized using dynamic light scattering and UV-vis absorbance. The kinetic advantages of sequential enzyme colocalization are also discussed. This approach allows for the study of sequential enzyme kinetics as a function of proximity alone.

COLL 333

Polypyrrole nanoparticles: A new class of contrast agent for cancer imaging

Kin Man Au(1)*, K.M.Au@shef.ac.uk, Brook Hill, Sheffield Sheffield S3 7HF, United Kingdom ;* ***Steven Armes***(1)*, s.p.armes@sheffield.ac.uk, Brook Hill, Sheffield Sheffield S3 7HF, United Kingdom ; Zeng Lu*(2)*; Steven Matcher*(2)*. (1) Department of Chemistry, University of Sheffield, Brook Hill, Sheffield S3 7HF, United Kingdom (2) Department of Materials Science and Engineering, University of Sheffield, Brook Hill, Sheffield S1 3JD, United Kingdom*

Cancer is a major cause of death in the western world. Diagnosis of early-stage cancers is a major challenge for biomedical science in the 21st century. In the past decade, several high resolution medical imaging techniques have been developed which are potentially useful for the diagnosis of early-stage cancers. As for traditional medical imaging techniques (e.g. X-ray CT, MRI, PET), contrast agents are often used to enhance the sensitivity and selectivity of cancer detection. Polypyrrole (PPy) absorbs strongly in the UV-Vis-NIR region and has relatively low toxicity. Although the synthesis of PPy nanoparticles has been reported more than two decades ago, biomedical applications of PPy nanoparticles are rather limited. Herein we demonstrate the first biomedical application of PPy nanoparticles as contrast agents for high resolution cancer imaging. The synthesis and characterisation (e.g. SEM, TEM, DLS and XPS) of PPy nanoparticles and a preliminary investigation of their *in vitro* performance will be highlighted.



(Left) Transmission electron micrograph of polypyrrole nanoparticle contrast agent. (Right) Extinction spectrum obtained for PPy nanoparticles.

COLL 334

Direct Bioattachent to Qdot Interfaces for Short FRET Distances

Mathew M. Maye(1)*, mmmaye@syr.edu, 111 College Place, CST 1-014d, Syracuse NY 13244, United States ; Joshua Zylstra*(1)*; Hyunjoo Han*(1)*; Rabeka Alam*(1)*; Valerie N. Valle*(1)*. (1) Department of Chemistry, Syracuse University, Syracuse New York 13244, United States*

In this presentation we first describe a new quantum dot phase transfer protocol using ligand exchange and the amino acid histidine. The phase transfer from non-polar solvents to aqueous buffers is homogeneous, and no appreciable precipitation occurs. The molecule histidine was chosen in order to first displace the organic encapsulation and second to provide a weakly chemisorbing intermediate at the qdot interface. This allows the histidine to act as an intermediate shell upon which further direct ligand exchange can occur. Characterization via 1D and 2D NMR revealed the extent of ligand exchange, and provide insights into the interfacial binding mechanism. In addition to monolayers, these qdots can be directly modified with biomaterials of choice, including designer peptides, oligonucleotides, and proteins. Using this, we have designed qdot-dye and qdot-qdot FRET assemblies with highly tunable distances. Here, assembly and disassembly, concurrent with FRET responses, were driven by DNA-encoded interactions leading to a number of potential energy transfer and biodiagnostic applications.

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Low Temperature Synthesis of Various Ligand Capped Magic-Sized CdSe Clusters

Rajesh Sardar(1)*, rsardar@iupui.edu, 402 N. Blackford Street, Indianapolis IN 46202, United States . (1) Department of Chemistry & Chemical Biology, Indiana University Purdue University Indianapolis, Indianapolis IN 46202, United States*

Synthesis of monodispersed, ligand-protected cadmium selenide (CdSe) nanoparticles has received great attention due to their potential applications in electronics, bio-imaging, solar cells and photocatalysis. It still remains a major challenge to synthesize ultra-small clusters with well-defined composition. Previously magic–sized clusters were synthesized using the reverse micelle technique. Mass-spectroscopic analysis had shown the formation of a well-defined number of atoms with the predicted formulas of $(CdSe)_{33}$ and $(CdSe)_{34}$, which only exist at certain stable sizes.[1] The synthesis of this cluster required careful synthetic experimental conditions; which include the presence of specific capping ligands, as well as the reaction temperature.[2] Here for the first time we show that trioctylphosphine (TOPO) capped magic- size CdSe clusters can be synthesized at low temperatures (<70 ^{0}C).[3] UV-vis spectroscopic analysis of the TOPO capped magic-sized particles displays a sharp peak at 424 nm with FWHM of 20 nm, which corresponds to 1.7-1.9 nm diameter CdSe clusters. Photoluminescence spectroscopy shows a deep trap broad emission at the 560 nm region. The X-ray diffraction (XRD) profiles confirm the presence of reflections corresponding to magic-size clusters. We also observed continuous formation of magic-sized clusters over the course
of 48 hrs. It was also found that the formation of magic-size clusters is sensitive to reaction temperature and concentration of capping agents. Our synthetic protocol is extended to prepare oleylamine, lauric acid, and phosphonic acid capped magic-sized CdSe particles. We also studied the ligand-exchange chemistry of the TOPO capped particles by various alkanethiols.

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COLL 336

Biocompatible Nanochelators Surface Functionalized with Phytochelatin Peptide Derivatives for Metal Chelation Studies

Marilyn R. Mackiewicz[(1)]*, mackiewi@pdx.edu, 1719 SW 10th Ave, Portland OR 97201, United States . (1) Chemistry, Portland State University, Portland OR 97201, United States*

Nanochelators with biocompatible tailored ligands can play a profound role in the capture and stabilization of metals with different oxidation states. These types of nanochelators that possess good solubility and potential to cross the blood brain barrier with minimal side effects are of significant interest as sensors and as therapeutic chelating agents. We have prepared a new class of biocompatible water-soluble gold nanomaterials for metal chelation studies. The nanomaterials are surface-functionalized with small peptide derivatives of phytochelatins (PC). Natural PC chelators are cysteine-rich peptides found in certain plants have high metal uptake, tolerance, and specificity. The small dimensions and high surface to volume ratio of nanomaterials make these ideal ligand transport vehicles and the local surface plasmon resonance (LSPR) of gold nanoparticles which are sensitive to changes in refractive index can be used as a probe for metal chelation. The synthetic methodology will be discussed and the UV-vis, TEM as well as dynamic light scattering measurements will be presented. Metal binding studies using LSPR and fluorescence techniques will demonstrate the use of these peptide-coated nanomaterials to chelate metals with high specificity and affinity. These multi-functional nanochelators will serve as a new platform for developing optical metal sensors and nanochelating therapeutic agents.

COLL 337

DNA-guided assembly of binary mixtures of Au nanoparticles

Yugang Zhang[(1)]*, yuzhang@bnl.gov, Brookhaven National Laboratory, Upton NY 11973, United States ; Fang Lu*[(1)]*; Kevin G Yager*[(1)]*; Lelie Daniel van der*[(2)]*; Oleg Gang*[(1)]*. (1) Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton NY 11973, United States (2) Center for Agricultural and Environmental*

Biotechnology, Research Triangle Institute International, Research Triangle Park NC 12194, United States

Recently, DNA-mediated nanoparticle assembly has emerged as a powerful strategy that allows for the programmable and predicable fabrication of 3D ordered superstructures of nano-objects. The observed structures in systems assembled from DNA-coated spherical particles typically exhibit a body centered cubic or a face centered cubic phase, with assembly found to depend on the recognition type of DNA. However, the assembly behavior for multi-component systems is still not well explored. We report the DNA-guided assembly of binary mixtures of Au nanoparticles of different designs. Using in-situ small angle x-ray scattering methods, we have mapped the phase behavior of these systems and correlated the findings with previously observed results. Research was supported by the U.S. DOE Office of Science and Office of Basic Energy Sciences under contract No. DE-AC-02-98CH10886.

COLL 338

Polyelectrolyte multilayers: Building polymer complexes one step at a time

Michael Rubner(1)*, rubner@mit.edu, Building 13-5106, Cambridge Mass 02139, United States . (1) Materials Science and Engineering, MIT, Building 13-5106, Cambridge Mass 02139, United States*

Layer-by-layer assembly provides an opportunity to create highly functional, molecular-level blends of a wide variety of polymers and nanomaterials. In this stepwise process, materials that often form strongly or weakly associated complexes in solution can be assembled together in a highly controlled manner. As a result, complex multilayer heterostructures with well-defined nanoscale and functionally distinct regions can be created in a manner not possible by simple solution complexation. In this presentation, the layer-by-layer assembly, characterization and properties of a number of different molecularly blended polyelectrolyte multilayers will be discussed including systems based on polysaccharides, living cells, poly(vinyl alcohol) and nanoparticle/polymer combinations. By controlling composition, layering sequence and crosslinking levels, it will be shown that mechanically robust functional thin film coatings with properties ranging from anti-fogging to structural color to bioactivity can be produced on demand

COLL 339

Flame retardant thin film assemblies from completely renewable materials

Galina Laufer(1)*, galina2405@tamu.edu, 3123 TAMU, College Station TX, United States ; Jaime Grunlan*(1)*; Christopher Kirkland*(1)*; Aaron Ham*(1)*. (1) Department of Mechanical Engineering, Texas A&M University, College Station TX 77843, United States*

In an effort to create an environmentally-friendly flame retardant system for foam and fabric, layer-by-layer (LbL) thin films were assembled using “green” materials obtained from completely renewable sources. Ten bilayers of pH 3 chitosan (CH), as the cationic layer, and pH 10 montmorillonite (MMT) as the anionic layer, were deposited on cotton fabric and foam. The total coating thickness is approximately 10 nm. Cotton fabric was found to retain a significant amount of residue, following vertical flame testing, and its weave structure was undamaged. For open-celled polyurethane foam, only the outermost surface was charred after being exposed to the direct flame from a propane torch for 10 seconds. When cut open, white flexible foam was revealed under a black char layer. These results demonstrate the first truly “green” LbL flame retardant.

COLL 340

Strategies to Incorporate Micelles of Selectively Betainized Block Copolymers into Electrostatic Layer-by-layer Films

Irem Erel(1)*, erel@metu.edu.tr, ODTU Universiteler Mahallesi, Dumlupinar Bulvari No.1, Cankaya Ankara 06531, Turkey ; Vural Butun*(2)*; Adem Levent Demirel*(3)*. (1) Department of Chemistry, Middle East Technical University, Cankaya Ankara 06531, Turkey (2) Department of Chemistry, Osmangazi University, Meselik Eskisehir 26480, Turkey (3) Department of Chemistry, Koc University, Sariyer Istanbul 34450, Turkey*

We report on strategies to incorporate micelles of selectively betainized poly[3-dimethyl(methacryloyloxyethyl) ammonium propanesulfonate-*block*-2-(diisopropylamino)ethyl methacrylate] (PDMAPS-b-PDPA) within layer-by-layer (LbL) films. Multilayers were fabricated at pH 8, above critical micellization pH of 6.5 for PDMAPS-*b*-PDPA. To impart net electrical charge on PDMAPS-corona, we studied phase behavior of micelles with PDMAPS-corona in the presence of salt as well as formation of interpolymer complexes between PDMAPS-corona and polyelectrolytes (PEs) in solution prior to film deposition. Using information obtained, strategies were developed to incorporate micelles within multilayers. We found that when positive charges on PDMAPS-corona were screened by I^- of NaI, micelles could be assembled using only weak PEs (e.g. PAH). However, when PDMAPS-corona was complexed with PAH (screening negative charges), micelles were successfully self-assembled using strong PEs (e.g. PSS). Fundamental understanding of selectively betainized block copolymer micelle (BCM) multilayers is important due to interesting biological properties of polybetains and high loading capacity of BCMs.

COLL 341

Effect of molecular interactions on the release mechanism of multilayer films

Yeongseon Jang(1)*, jys0419@snu.ac.kr, Rm.616, Bldg.302, Seoul National University, Daehak-Dong, Gwanak-Gu Seoul 151744, Republic of Korea ; Jooyeon Seo*(1)*; Bulent Akgun*(2)*; Sushil Satija*(2)*; Kookheon Char*(1)*. (1) School of Chemical and Biological Engineering, Seoul National University, The National Creative Research Initiative*

Center for Intelligent Hybrids, Gwanak-Gu Seoul 151744, Republic of Korea (2) NIST Center for Neutron Research, NIST, Gaithersburg MD 20899-6100, United States

Controlled release platforms, with multi-functionality and controllable release kinetics tailored for biomedical applications, have been explored for many years. Among various systems explored for the controlled release, layer-by-layer (LbL) assembled multilayer films have advantages to insert functionalities at desired nanoscale positions within the films. However, detailed release mechanism of the LbL films, triggered by external stimuli, has not been well established in terms of the changes in internal film structure as well as the release motion of polymer chains from a film. In present study, we have systematically investigated pH-triggered release mechanism of multilayer films by adjusting molecular interactions, which are related to the type (i.e., strong and weak polyelectrolytes) as well as the molecular weights of polyelectrolytes. The release behavior of deuterated polyelectrolytes has been studied with neutron reflectivity and quartz crystal microbalance. These results give insights on the controlled release of target materials from multilayer films and, ultimately, offer functional stimuli-responsive polymeric release platforms.

COLL 342

Anti-flammable intumescent nanocoatings prepared using layer-by-layer assembly

Jaime C Grunlan[(1)]*, jgrunlan@tamu.edu, 3123 TAMU, College Station TX 77843-3123, United States ;* ***Yu-Chin Li***[(1)]*, yuchin1024@gmail.com, 3123 TAMU, College Station TX 77843-3123, United States . (1) Department of Mechanical Engineering, Texas A&M University, College Station TX 77843, United States*

Cotton fabric is the most used natural textile, but it is highly flammable. By treating fabric with intumescent nanocoatings, composed of poly(ally amine) and poly (sodium phosphate), prepared via layer-by-layer (LbL) assembly, the fabric structure and integrity is highly preserved following vertical flame testing. In some cases, no ignition occurs (*i.e.*, the fabric did not burn when exposed to direct flame). Postburn analysis of coated fabric shows a cellular (foamed) layer and significant bubble formation on fibers with SEM imaging. Cone calorimetry shows that peak heat release rate and total heat release has 30 % and 65 % reduction, respectively, compared to the uncoated fabric, with only 4 wt% added to the original fabric weight. This study marks the first intumescent flame retardant nanocoating, which dramatically reduces the flammability of cotton.

COLL 343

Modulation and mechanical reinforcement of all-nanoparticle layer-by-layer thin films

Kwadwo E Tettey[(1)], *kwadwo@seas.upenn.edu, 220 South 33rd Street, Room 311A Towne Building, Philadelphia PA 19104, United States ; Majemite I Dafinone*[(1)]*; Gang Feng*[(2)]*; Teresa Brugarolas*[(1)]*; Jeanne W.C Ho*[(1)]*; Daeyeon Lee*[(1)]*. (1) Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia PA 19104, United States (2) Department of Mechanical Engineering, Villanova University, Villanova PA 19085, United States*

Layer-by-layer (LbL) assembly of charged nanoparticles such as SiO_2 and TiO_2 leads to generation of all–nanoparticle thin films with multifunctionality. However, there are some drawbacks to these LbL films, which limit their widespread utilization. Favorable film growth occurs in a narrow pH range, and films are easily abraded. In this study, the processing window of TiO_2/SiO_2 LbL films is broadened by introducing a small amphiphilic molecule, hexylamine, into SiO_2 nanoparticle suspensions. Hexylamine in SiO_2 nanoparticle suspensions widens the processing window by suppressing the negative surface charge of SiO_2 nanoparticles and by inducing complete charge inversion of LbL films. Meanwhile, the mechanical durability of all-nanoparticle films on glass and polycarbonate substrates is significantly improved by using atomic layer deposition (ALD). Nanoindentation and abrasion tests demonstrate that LbL films can be reinforced without the need for high temperature calcination. ALD-treated films retain their superhydrophilicity and anti-reflection properties.

COLL 344

The effect of shape and core release methods on the mechanical and transport properties of LbL capsules

Milana O. Lisunova[(1)], *mlisunova3@mail.gatech.edu, 771 Ferst Dr NW, Atlanta Georgia 30322, United States ; Olga Shchepelina*[(1)]*; Wenbin Mao*[(2)]*; Aleksandr Alexeev*[(2)]*; Vladimir V Tsukruk*[(1)]*. (1) School of Materials Science and Engineering, Georgia Institute of Thechnology, Atlanta Georgia 30332, United States (2) School of Mechanical Engineering, Georgia Institute of Thechnology, Atlanta Georgia 30332, United States*

The anisotropic capsules based on organic and inorganic cubes and tetrahedral cores were synthesized by layer-by-layer (LbL) assembly. The capsules of different geometries exhibited different mechanical stability under osmotic pressure variation. We found that the anisotropic microcapsules do not undergo random buckling, collapse typical for spherical capsules under a similar change in the internal volume. Moreover, the anisotropic microcapsules maintain their structural integrity for much greater deformation in sharp contrast to the conventional spherical microcapsules. The permeability of anisotropic capsules has been compared with that for isotropic capsules. We suggest that the diffusion coefficient across hollow shells of anisotropic capsules is higher comparatively to the isotropic spherical capsules due to different core release processes. Computational studies demonstrated increased mechanical stability of the anisotropic capsules under osmotic pressure variation due to sharp edges and vertices

acting as a reinforcing frame in contrast to spherical microcapsules that undergo random buckling.

COLL 345

Stabilization of aqueous carbon nanotubes/graphene dispersions: insights from molecular dynamics simulations

Alberto Striolo[(1)], *astriolo@ou.edu, Sarkeys Energy Center T-235, 100 East Boyd St, Norman OK 73019, United States ; Naga Rajesh Tummala*[(1)]*; Manaswee Suttipong*[(1)]*. (1) School of Chemical, Biological and Materials Engineering, The University of Oklahoma, Norman OK 73019, United States*

Preventing the agglomeration of carbon nanotubes, and that of graphene sheets in aqueous media remain some of the biggest hurdles towards the application of such interesting nanomaterials. Surfactants have been used to stabilize aqueous dispersions, achieving promising results. A detailed understanding of the molecular driving forces responsible for such important results could lead to innovative technologies. Towards achieving such detailed understanding, we conducted equilibrium MD simulations for the structure of self-assembled aggregates of SDS, SDBS, FMN, and AOL surfactants on carbon nanotubes and graphene sheets of different sizes. We quantified the effect of surface density, and that of surfactant molecular structure on the aggregates morphology. The results have been compared, favorably, to available experimental data. The structural results have been used to calculate nanotube – nanotube potential of mean forces. We will summarize here the features the surfactants should offer to secure stabilization of the dispersions.

COLL 346

Significantly enhanced SWCNT dispersion stability in mixed solvent systems

Jordan C. Poler[(1)], *jcpoler@uncc.edu, 9201 University City Blvd., Charlotte NC 28223, United States ; Michael W Forney*[(1)]*. (1) Department of Chemistry, University of North Carolina at Charlotte, Charlotte NC 28223, United States*

Research on the dispersion of pristine single-walled carbon nanotubes (SWCNTs) is mostly focused on measuring the dispersion limit in various organic solvents, yet little attention has been paid to the dispersion stability of SWCNTs in viable organic solvents. We have studied SWCNT dispersion stability for mixtures of the organic solvents N,N-Dimethylformamide (DMF) and N-methyl-2-pyrrolidinone (NMP). We will show that mixing DMF and NMP yields dispersion stabilities that are 60% to 115% greater than the pure solvents with a 50/50 mixture (v/v). SWCNT aggregation process is described by a physical model that combines the Maxwell-Boltzmann energy distribution function and DLVO theory for quantitative comparison between solvent systems. The ability to stabilize colloidal dispersions without functionalizing the particles will be discussed.

Correlations between dispersion limits and the stability of the dispersion with regard to solvent properties will be presented.

COLL 347

Reactivity of CoMoCAT® single-walled carbon nanotubes under Bingel conditions and their dispersibility in unsaturated polyester resin

Matthew J Kayatin(1)*, kayatmj@tigermail.auburn.edu, 212 Ross Hall, Auburn AL 36849, United States ; Virginia A Davis*(1)*. (1) Department of Chemical Engineering, Auburn University, Auburn AL 36849, United States*

Sidewall esterification of single-walled carbon nanotubes (SWNT) can be achieved via the Bingel reaction; however, undesired sonopolymer is generated in-situ. We provide a fresh perspective on this topic by examining the Bingel reaction on CoMoCAT® SWNT and the subsequent dispersibility in isophthalic unsaturated polyester resin (UPR).

Sonopolymer removal was studied using thermal gravimetric analysis (TGA), attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIR), resonant Raman spectroscopy (Raman), and via Hansen solubility parameters. The extent of reaction and inherent doping effect on the SWNT with treatment time was examined using Raman. Coupled TGA-FTIR and ATR-FTIR data was gathered to examine surface functional groups present. Finally, the high-shear dispersibility of the functionalized SWNT in to UPR was studied. We provide comparative analysis of dispersion stability under conditions previously found to induce low shear aggregation of SWNT-UPR dispersions using a rheological-optical shear cell.

COLL 348

Locking rigid rods in a matrix: Sucrose co-dispersant enables ultrahigh aqueous concentration of individually dispersed single-walled carbon nanotubes

Jarrett D Leeds(1)*, jleeds@umd.edu, Bldg 091 Room 0107, College Park MD 20740, United States ; John T Fourkas*(1)*; YuHuang Wang*(1)*. (1) Department of Chemistry and Biochemistry, University of Maryland, College Park MD 20740, United States*

Single-walled carbon nanotubes were individually dispersed in aqueous solutions of the surfactant sodium dodecylbenzene sulfonate using sucrose as a co-dispersant. The amount of raw nanotube material converted to individually dispersed nanotubes, known as mass conversion, was more than three times higher when using a co-dispersant. Strikingly, with a co-dispersant, as the raw nanotube mass was increased the mass conversion remained constant far beyond previously reported values. Using our new processing conditions, ultra-high concentrations of individually dispersed nanotubes in the g/L range became possible. We attribute the significant improvement of dispersion to an increase in solvent viscosity due to sucrose. This change in viscosity decreases the free movement of nanotubes, preventing re-bundling and allowing adequate time for

stabilization by surfactant molecules. Spectroscopic data confirm that there is no interaction between sucrose and nanotubes, indicating the role of sucrose as an aggregation preventing matrix which increases the efficiency of the dispersion process.

COLL 349

Interactions of ionic liquids and their mixtures with carbon nanomaterials: insights from molecular modeling

Andrey I. Frolov[(1)], *frolov@mis.mpg.de, Inselstr. 22, Leipzig Saxony 04103, Germany ;* ***Maxim V. Fedorov***[(1)], *fedorov@mis.mpg.de, Inselstr. 22, Leipzig Saxony 04103, Germany ; Tom Kirchner*[(1)]*; Kathleen Kirchner*[(1)]*. (1) Max Planck Institute for Mathematics in the Sciences, Leipzig Saxony 04103, Germany*

Room Temperature Ionic Liquids and their mixtures with organic solvents become widely used as electrolytes in super capacitor applications nowadays [1,2]. We investigate the basic mechanisms of the electrical double layer formation in ionic liquids and their mixtures with organic solvents (e.g. acetonitrile) near different nanocarbon electrodes: flat graphene sheets, carbon nanotubes and carbon “nano-onions”. We use Molecular Dynamics simulations with coarse-grained and fully-atomistic models. We analyze the structural transitions at the electrode surface in response to the variation of the voltage across the double layer. We study the effects of ion size/shape asymmetry and short-range correlations on the properties of the electrical double layer. We also analyze how the presence of an organic solvent affects the structure of the double layer.

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COLL 350

Dependence of aggregation/deposition properties of metal oxide nanoparticles on their size in the presence of fatty acids

Sathish Ponnurangam[(1)], *sp2522@columbia.edu, 500W, 120th Street, 918 Mudd, New York NY 10027, United States ; Irina Chernyshova*[(1)]*; Ponisseril Somasundaran*[(1)]*. (1) Department of Earth and Environmental Engineering, Columbia University, New York NY 10027, United States*

The aggregation/dispersion properties of metal (hydr)oxide NPs play key roles in many technological and natural processes including catalysis, dyeing, electrochemical deposition, MRI imaging, drug delivery, mineral separation as well as the role and fate of these NPs in the environment. However, one of the persistent obstacles in rationally manipulating these properties is the lack of understanding of how nano-size or synthesis-induced variations in the surface structure of the NPs influences the

adsorption forms and density of surfactants or dispersants. We discovered that size of hematite (a-Fe_2O_3) and ferrihydrite NPs controls stability of their suspensions in the presence of sodium laurate (dodecanoate). Also, both the sorption capacity (characterized by the adsorption isotherms) and hydrophobicity (characterized by the contact angle) of these NPs vary remarkably with their size. To rationalize these findings, a multi-technique approach based on *in situ* FTIR and *ex situ* XPS spectroscopies, and DFT calculations is employed. These results allow discussing the possible origin of the size-dependence in terms of the acid-base properties of the adsorption sites as well as the interfacial pH. The impact of this study is significant because carboxylate additives are commonly used to disperse metal (hydr)oxide NPs in paints, coatings, personal care products, lubricants, polishing agents and adhesives.

COLL 351

Magnetic Janus ball toward single magnet manipulation

***Sangyeul Hwang**(1), sangyeul@umich.edu, 3418 G.G.Brown, 2300 Hayward St., Ann Arbor MI 48109, United States ; Srijanani Bhaskar(2); Joerg Lahann(1)(2)(3). (1) Department of Chemical Engineering, The University of Michigan, Ann Arbor MI 48109, United States (2) Macromolecular Science and Engineering, The University of Michigan, Ann Arbor MI 48109, United States (3) Department of Materials Science and Engineering, The University of Michigan, Ann Arbor MI 48109, United States*

Magnetic Janus particles (MJPs) consisting of two distinct compartments within the same particle have been prepared and fully characterized. We found unusual magnetodynamic behavior of these particles in magnetic fields that was due to their unique magentic anisotropy. Magnetic control of MJPs using simple experimental procedures is of great interest to the area of tunable electro/magneto-responsive materials, such as rheological fluids or displays. Herein, we report the preparations of various bicompartmentalized magnetic micro/nanoparticles via the electrohydrodynamic (EHD) co-jetting based on two distinctive solvent systems (organic and water). Both, fundamental dynamic behaviors of magnetically anisotropic particles, as well as their magnetic self-assembly will be discussed.

COLL 352

Preparation of monodisperse silicon nanocrystals through density-gradient ultracentrifugation in organic solvents

***Joseph B. Miller**(1), joseph.b.miller@ndsu.edu, 218 South Engineering, 1211 Albrecht Blvd, Fargo North Dakota, United States ; Austin R. Van Sickle(1); Ganjigunte R. S. Iyer(1); Rebecca A. Anthony(2); Uwe R. Kortshagen(2); Erik K. Hobbie(1). (1) North Dakota State University, United States (2) University of Minnesota, United States*

Monodisperse colloidal suspensions of ligand-stabilized silicon nanocrystals, synthesized through a nonthermal low-pressure plasma reaction, are prepared through density-gradient ultracentrifugation in mixed organic solvents. Density-gradient profiles of mixed chloroform and m-xylene are used to control the settling speed of the nanoparticles and hence optimize their transient separation by size along the depth of polyoxymethylene ultracentrifuge tubes. The mean size and polydispersity of the extracted fractions are characterized through photoluminescence spectroscopy and transmission electron microscopy, and the self-assembly of fractions into close-packed crystal lattices is achieved using an immiscible two-fluid evaporation scheme. The photophysical properties of the nanocrystal lattices are compared with those of the starting materials and suspensions, and the influence of atmospheric oxygen on the stability of the nanocrystal photoluminescence is measured. Supported by the DOE through DE-FG36-08GO88160.

COLL 353

Seed-mediated synthesis and characterization of Gold nanoparticles of various morphologies

Robert C. Wadams[(1)]*, wadamro@eden.rutgers.edu, 607 Taylor Road, Piscataway New Jersey 08854, United States ; Laura Fabris*[(1)]*. (1) Department of Materials Science and Engineering, Rutgers University, Piscataway New Jersey 08854, United States*

Gold nanoparticles absorb visible and near-infrared light due to the coupling of the electromagnetic field with the nanoparticle's localized surface plasmon resonances (LSPRs). The excitation energy of LSPRs is largely dependent on nanoparticle size and morphology. Tuning LSPR modes is achieved in bottom-up syntheses by altering nanoparticle shape through precise control over reaction conditions and reagent selection. Herein, is described the synthesis of gold nanoparticles and the characterization of their optical properties.

COLL 354

Wetting Characteristics of Carbon-Ionomer Nanocomposites

Chris J Cornelius[(1)]*, ccornelius@engr.uconn.edu, 191 Auditorium Road, Storrs CT, United States ; Sonal Mazumder*[(2)]*. (1) Department of Chemical Engineering, University of Conneticut, Storrs CT 06269, United States (2) Department of Chemical Engineering, Virginia Tech, Blacksburg VA 24061, United States*

The role of roughness and composition on the wetting characteristics of a series of Nafion based ionomer nanocomposites were studied in order to evaluate its hydrophobic and hydrophilic properties. In this study, idealized surfaces were created using a smooth silicon wafer and two 3M micro-replicated Brightness Enhancement Films (BEF) with different textured surfaces. All surfaces were coated with ionomer nanoparticle alcohol solutions in order to generate films of variable compositions using mixtures of Nafion, a series of Pt/C catalysts, and a commercial single walled carbon nanotube (SWCNT). Nanocomposite films of various surface compositions were created and studied in this work. A general trend of increasing hydrophobicity was observed for nanocomposite surfaces as compared to the bare substrate. Individual contact angles were dependent on the nature of the underlying substrate, relative surface pattern, roughness, and concentration of ionomer. Apparent surface contact angles on these substrates exhibited behavior that followed both the Wenzel and Cassie models. Overall wetting properties were dependent upon composition and micro scale roughness of the nanocomposites.

COLL 355

Facile synthesis of multifunctional hollow nanoparticles via self-assembly of random copolymers as responsive drug and gene carriers

***Apiradee Honglawan**[1], apih@seas.upenn.edu, 3231 Walnut St. LRSM, Room 200, Philadelphia PA 19104, United States ; Shu Yang[1][2]; Shiqi Wang[2]. (1) Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia PA 19104, United States (2) Materials Science and Engineering, University of Pennsylvania, Philadelphia PA 19104, United States*

Polymeric nanoparticles are of great interest as efficient drug and gene delivery carriers due to their high robustness compared to liposomes and amenability to chemical modifications for specific targeting cells. However, synthesis of these nanoparticles with controlled size and chemistry often requires laborious multistep processes, leading to low throughput and limited functionalities. Here, we report a facile route to synthesize multifunctional hollow nanoparticles via assembly of random copolymers through photopolymerization of acryloyl chloride (AC) and comonomers. Random copolymers composed of poly(acryloyl chloride) (PAC), a small amount of hydrolyzed product, poly(acrylic acid) (PAA), and their partially crosslinked components (X) exhibited amphiphilic character, enabling the assembly of vesicle-like hollow particles in various organic solvents, including acetone, tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO). Depending on solvent quality and photoexposure dosage, the average particle size could be varied ranging from 20 nm to 100 nm with a narrow size distribution. When transferred to an aqueous solution, the particles were hydrolyzed and demonstrated pH responsiveness due to the formation of carboxyl terminals on the particle shell. The latter could be further functionalized with polymers that are commonly used in drug and gene delivery, including positively charged poly(ethylene imines) (PEI) and anti-fouling poly(ethylene glycol) (PEG), respectively. Through copolymerization, we also successfully incorporated a variety of functional groups, including thermoresponsive N-isopropylacrylamide (NIPAM) and PEG, respectively, to the random copolymer particles. This study presents a simple yet versatile approach to synthesize well-defined hollow nanoparticles with multiple functionalities. We currently investigate their application to systemic gene encapsulation and targeted delivery.

COLL 356

Long Circulating Liposomes Modified by Zwitterionic Polymers

Zhiqiang Cao(1)*, zqcao@u.washington.edu, Benson Hall 320, Seattle WA 98195, United States ; Shaoyi Jiang*(1)*. (1) Chemical Engineering, University of Washington, Seattle WA 98195, United States*

Polyethylene glycol (PEG) is almost exclusively used to modify nanoparticles (NPs) to improve their blood residence time for both diagnostic and therapeutic purposes. One of the most successful example is Doxil®, a PEG modified liposome with encapsulated doxorubicin (DOX) that has been approved by FDA to treat several types of cancer and solid tumors. PEG lengthens the circulation time of liposome in blood so that the liposome is more likely extravasated through the abnormally permeable vessels of tumors (passive tumor targeting). Recently zwitterionic polymers such as poly(carboxybetaine) (PCB) has shown excellent stealth properties. Rather than non-ionic PEG, we used zwitterionic PCB to modify liposomes, and comapred them with PEG versions side by side. Their unique properties were explored such as a remarkably improved blood circulation life-time.

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Formulation and in vitro evaluation of serum stable bioactive polymeric nanoparticles for managing atherosclerosis

Adam W York(1)*, adamyork@rci.rutgers.edu, 599 Taylor Road, Piscataway New Jersey 08854, United States ; Kyle R Zablocki*(1)*; Daniel R Lewis*(2)*; Li Gu*(3)*; Kathryn E Uhrich*(3)*; Robert K Prud[apos]homme*(4)*; Prabhas V Moghe*(1)(2)*. (1) Department of Biomedical Engineering, Rutgers University, Piscataway New Jersey 08854, United States (2) Department of Chemical & Biochemical Engineering, Rutgers University, Piscataway New Jersey 08854, United States (3) Department of Chemistry & Chemical Biology, Rutgers University, Piscataway New Jersey 08854, United States (4) Department of Chemical & Biological Engineering, Princeton University, Princeton New Jersey 08544, United States*

We report a new class of bioactive nanoparticles (NPs) fabricated from "nanolipoblockers", a family of polymeric macromolecules that inhibit oxidized low-density lipoprotein (oxLDL) accumulation in inflammatory cells (i.e., macrophages). The fabrication, via nano-flash precipitation, yields a NP with a stabilizing amphiphilic macromolecule, consisting of poly(ethylene glycol) and mucic acid functionalized with lauroyl groups, and a chosen hydrophobic solute as the NP core. Dynamic light scattering quantified NP hydrodynamic diameters and confirmed colloidal stability in the presence of serum proteins. Cytocompatibility, oxLDL uptake and foam cell formation, in human monocyte derived macrophages, were investigated for both NP systems and analogous micellar systems via fluorescence and light microscopy. In the presence of serum, NP formulations demonstrate higher efficacy at inhibiting oxLDL uptake and foam cell phenotype than conventional polymeric micellar systems. This increased stability and efficacy highlight the possible utility of these serum-stable NPs for managing atherosclerosis, a key inflammatory disorder underlying the progression of cardiovascular disease.

COLL 358

Polymeric Nanoparticles for Sensor and drug delivery applications

Stephanie Schubert(1)(2)(3)*, stephanie.schubert@uni-jena.de, Lessingstrasse 8, Jena Thuringia 07743, Georgia ; Antje Vollrath*(1)(2)*; Igor Perevyazko*(1)(2)*; Dagmar Fischer*(2)(3)*; Ulrich S Schubert*(1)(2)*. (1) Laboratory of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Germany (2) Jena Center for Soft Matter (JCSM), Friedrich-Schiller-University Jena, Germany (3) Institute of Pharmaceutical Technology, Friedrich-Schiller-University Jena, Germany*

The precise control over specific properties enables polymers to be promising materials for drug delivery systems. For the manifold requirements of nanocontainers *in vivo*, specific challenges have to be fulfilled by the polymeric carrier, like biocompatibility, active or passive targeting, controlled drug release or sensing properties to gain online information about the intracellular environment. Defined synthesis strategies in combination with a selection of formulation techniques allow the design of well-defined particles in the nanoscale range. For this purpose, synthetic as well as natural polymers (polysaccharides) were modified with multiple functionalities and characterized using state-of-the-art analytical tools. The formulation of the materials into nanoparticle systems was performed by emulsion techniques and nanoprecipitation. In particular nanoprecipitation provides a mild and facile tool for the production of defined nanostructures. With the help of high throughput formulation techniques it is further possible to screen nanoparticle systems in a broad range. Advanced characterization techniques such as dynamic light scattering, electron microscopy, analytical and preparative ultracentrifugation, and asymmetric flow field flow fractionation allow both the analysis and the selective separation of particle fractions. The defined functional nanoparticle systems were then investigated *in vitro* according to their drug delivery and sensing abilities.

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Design and synthesis of nanoscale amphiphilic macromolecules: Effect of hydrophobicity on inhibition of oxidized low-density lipoprotein uptake

Dawanne E Poree(1)*, deporee@gmail.com, 610 Taylor Road, 371 Wright Reiman Labs, Piscataway New Jersey 08854, United States ; Daniel Lewis*(2)*; Kubra Kamisoglu*(2)*; Kyle Zablocki*(2)*; Prabhas V Moghe*(2)*; Kathryn E Uhrich*(1)*. (1) Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway New Jersey 08854, United States (2) Department of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, Piscataway New Jersey 08854, United States*

Atherosclerosis, the occlusive artery disease, is characterized by a buildup of oxidized low-density lipoprotein (oxLDL) in the vascular intima. Our research group has previously prepared nanoscale amphiphlic macromolecules (AMs) comprised of a mucic acid backbone, four aliphatic side chains and a poly(ethylene glycol) tail that are capable of inhibiting oxLDL uptake through competitive inhibition of scavenger receptors. Because hydrophobicity plays a major role in polymer-protein binding, we are preparing AMs of varying hydrophobicity and evaluating their ability to inhibit oxLDL uptake in both peripheral blood mononuclear cells (PBMCs) and endothelial cells (ECs). Preliminary studies involving two (T12P5) and four (M12P5) aliphatic chains suggest that increased hydrophobicity results in increased oxLDL inhibition with M12P5 inhibiting 90% and 99% oxLDL uptake in PBMCs and ECs, respectively, compared to the 18% and 82% inhibition of T12P5. We are currently preparing AMs bearing eight aliphatic chains and investigating their effect on oxLDL inhibition.

COLL 360

Cyclodextrin-modified polyamine nanoparticles for targeted co-delivery of siRNA and anti-cancer drugs for inhibiting brain cancer cell proliferation

Birju Shah(1)*, birju20@rci.rutgers.edu, 610 Taylor Road, Piscataway NJ 08854, United States ; Prasad Subramaniam*(1)*; Cheoljin Kim*(1)*; Ki-Bum Lee*(1)*. (1) Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway New Jersey 08854, United States*

Tumors harbor multiple dysregulated pathways owing to their cellular heterogeneity, thereby limiting the utility of single target agents. Hence it would be desirable to target multiple oncogenic elements using complementary therapeutic modalities, such as short-interfering RNAs and small molecules in order to achieve a cooperative effect, thereby enhancing their individual efficacy, but also simplifying biological applications. However, for this purpose, a major hurdle is the scant availability of delivery platforms capable of simultaneously translocating multiple payloads to the target cell. Herein we describe the synthesis of cyclodextrin-modified dendritic polyamine nanoparticles and their application to simultaneously deliver multiple payloads -siRNA and anti-cancer drugs - in an efficient and target-specific manner to glioblastoma cells. This talk will mainly focus on demonstrating that the simultaneous delivery of two orthogonal therapeutic modalities significantly inhibited cell proliferation and induced apoptosis in brain tumor cells as compared to the individual drug/siRNA treatments.

COLL 361

Cationic lipids as nonviral compacting agents of DNA

Emilio Aicart(1)*, aicart@quim.ucm.es, Avda. Complutense, s/n, Madrid Madrid 28040, Spain ; Elena Junquera*(1)*; Monica Munoz-Ubeda*(1)*; Alberto Rodriguez-Pulido*(1)*; Ana L. Barran*(1)*; Alberto Martin-Molina*(2)*. (1) Department of Physical Chemistry I, University Complutense, Madrid 28040, Spain (2) Department of Applied Physics, University of Granada, Granada 18071, Spain*

Cationic lipids compact negative DNA by forming lipoplexes (liposome/DNA complexes) that can act as nonviral vehicles in gene therapy. In this work, a variety of cationic colloidal aggregates are presented as potential DNA vectors together with experimental and theoretical tools for their characterization. Zeta potential allows to determining the isoneutrality ratio of the colloidal aggregate-DNA complex, together with its surface density charge. The shape, morphology and size of the lipoplexes are analyzed by cryo-TEM. Lamellar and hexagonal structures of the lipoplexes have been determined with SAXS. Fluidity of the lipidic bilayer is studied through fluorescence anisotropy, and the interaction DNA-colloidal vector has been evaluated by ethidium bromide fluorescence intercalation assays. The influence of the mixed lipid composition and the charge ratio between the cationic lipid and DNA on the lipoplex properties have been also analyzed. Calculated phase diagrams have confirmed the experimental concentration domains and the isoneutrality conditions

COLL 362

Multifunctional nanomateiral-based targeted siRNA delivery for inducing the apoptosis of brain tumor cells

KiBum Lee(1)*, kblee@rutgers.edu, 610 Taylor Road, Piscataway New Jersey, United States ; Prasad Subramaniam*(1)*; Birju Shah*(1)*; Cheoljin Kim*(1)*. (1) Department of Chemistry and Chemical Biology, Rutgers University, Piscataway New Jersey 08854-8087, United States*

This talk will focus on developing methods for synthesizing multi-functional nanoparticles and utilizing the functional nanomaterials as chemotherapeutic agents against brain tumor cells in a highly selective and sensitive way. More specifically, we are working on two orthogonal nanotechnology-based approaches: i) application of multi-functional nanoparticles for non-viral siRNA delivery to manipulate oncogene expression levels of GBM cells, which results in inducing the apoptosis of target cells; and ii) harnessing the potential of the multivalent nanoparticles for delivering anti-cancer therapeutics into the glioblastoma cell lines with high efficacy. In our research, we typically synthesize inorganic/organic nanomaterials such as gold nanoparticles, quantum dots, magnetic nanoparticles, and functional polymers that are readily tuned and possess novel electronic, optical, magnetic, and chemical properties. In such projects, we carefully design the ligand/conjugation chemistry to make biocompatible nanoparticles. A summary of the results from these efforts and the future directions will be discussed in this presentation.

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Nano polyampholyte gels prepared by amphoteric poly (amino acid) for protein nanocarrier

Heyun Shen(1)*, shen@chem.eng.osaka-u.ac.jp, 2-1 Yamada-oka, Suita Osaka 565-0871, Japan ; Takami Akagi*(1)(2)*; Mitsuru Akashi*(1)(2)*. (1) Department of Applied*

Chemistry, Graduate School of Engineering, Osaka University, Osaka 565-0871, Japan (2) Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), Osaka 565-0871, Japan

We synthesized a amphoteric poly(amino acid), Poly(γ-glutamic acid) -*graft*-Arginine (γ-PGA-Arg), to prepare a novel polyampholyte nanogels.

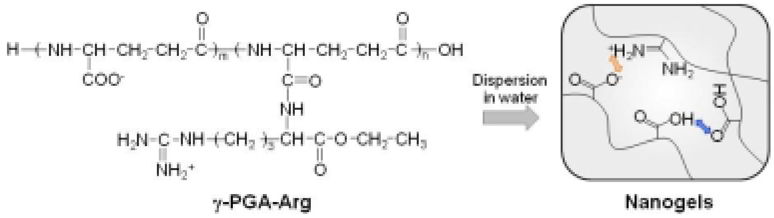


Figure 1. Chemical structure of γ-PGA-Arg and illustration of non-covalent chemical cross-linking in the nanogels.

Arginine is one kind of cationic amino acid which can simply graft on the γ-PGA backbone in aqueous solution. In the case of 28% grafting degree of the γ-PGA-Arg, the sizes of nanogels were 632, 793, and 311 nm for the concentration with 10, 5, and 1 mg/mL, respectively.

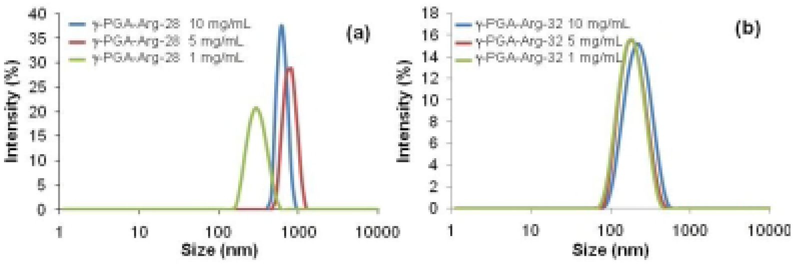


Figure 2. Particle sizes of the γ-PGA-Arg-28 (a) and γ-PGA-Arg-32 (b) in different concentration. The sizes were measured by dynamic light scattering.

In contrast, 32% grafting degree of nanogels were stable in the different concentration which sizes approximately were 200 nm. This result indicated that the size of polyampholyte gels can be changed by numbers of the ion namely that the balance of the cationic charged of Arg side chain and the anionic charged of γ-PGA unit. On the other hand, γ-PGA-Arg-44 could not form monodispersed naongels. We consider that the nanogels should regulate behavior of the protein adsorption by the surface charge.

COLL 364

Multiplexed magnetic labeling amplification

Monty Liong(1)*, liong.monty@mgh.harvard.edu, 185 Cambridge St., Boston MA 02114, United States ; Carlos Tassa*(1)*; Stanley Y Shaw*(1)*; Hakho Lee*(1)*; Ralph Weissleder*(1)*.*
(1) Center for Systems Biology, Massachusetts General Hospital, Harvard Medical School, Boston MA 02114, United States

The use of magnetic materials is expected to afford significant advances in cell separation, diagnostics, and therapy of scant cell population. We describe a highly sensitive and multiplexable magnetic tagging method that amplifies the loading of magnetic nanoprobes (MNPs) onto targeted cells. The method utilizes linker oligonucleotides as the binding agents between the oligonucleotide-functionalized antibodies and the oligonucleotide-modified MNPs (MNP-DNA). We validated the method by surface plasmon resonance measurements, labeling of specific growth factor receptor, and detection of human cancer cells. To further amplify the magnetization signal intensity, we labeled cells with multiple rounds of complementary MNP-DNA. A set of labeling experiments, which combined multiplexed analysis and signal amplification, was designed to take advantage of the hybridization specificity between

oligonucleotide strands. We demonstrated this method by simultaneously targeting three cancer markers of interest (HER2/*neu*, EpCAM, and EGFR) that have varying abundance level on a panel of cancer cell lines.

COLL 365

Self-assembly of CdTe nanoparticles with biomolecules into advanced architectures

Sudhanshu Srivastava(1)*, ssrivass@umich.edu, 2300 Hayward Street, Ann Arbor Michigan 48109, United States ; Nicholas A Kotov*(1)*. (1) Chemical Engineering, University of Michigan, Ann Arbor, MI, United States*

A big challenge in the self-assembly of nanoparticles (NPs) with biomolecules is to understand if controlled architectures similar to the protein-protein or biomolecular interactions inspired from nature can be created. Reproduction of such controlled self-assembly routes under conditions of living systems from non-biological systems, would indicate that one can replicate a part of biological component using synthetic tools. Advanced properties have been reported for the inorganic NPs once they self-assemble in to 1D, 2D and 3D architectures. On the same scale protein-protein interaction and protein-DNA interactions have been also widely studied for fabricating advanced morphologies. As NPs show a lot of similarity with biomolecules, introducing the inorganic NPs with known assemblies of biomolecules or biomolecules with known assemblies of NPs can lead to generate hybrid materials. Numerous NP-biomolecule conjugates have been reported in past for controlled enzymatic reactions, protein-protein couplings, delivery agents, sensors and other diagnostic applications. But not much emphasis is given to understand the self-assembly routes for introducing biomolecules structures in the already known assemblies of inorganic NPs. For the study CdTe NPs which in general forms 1D wire and 2D sheets were tested for the incorporation of DNA and proteins like Cytochrome C. The assemblies lead to new structures with very controlled incorporation of biomolecules with NPs. The approach provides: 1) biomolecular assemblies with NPs to create new architectures, b) a fundamental understanding of the parameters for the NP-biomolecule interaction will provide the foundation to predict structures similar to protein-protein or protein-DNA interactions, c) while some superstructures created can potentially be dynamic, i.e. responsive to different stimuli can lead to new switchable materials, e) reversible geometry of nanocomposites from one structure to other can be controlled by the conformation change of biomolecules.

COLL 366

Nanogenerator for self-powered biomedical applications

Guang Zhu(1)*, gzhu7@gatech.edu, 500 Northside Cir NW APT JJ4, Atlanta Georgia, United States ; Zhou Li*(1)*; Rusen Yang*(2)*; Zhonglin Wang*(1)*. (1) Department of Materials Science and Engineering, Georgia Institute of Technology, Atlanta Georgia 30309,* *United States (2) Department of Mechanical Engineering, university of minnesota, United States*

Nanostructures of zinc oxide (ZnO) have attracted much interest because of their unique piezoelectric, semiconducting, and catalytic properties. Recently, utilizing the coupled piezoelectric and semiconducting properties, ZnO nanowire (NW) based nanogenerator (NG) has been developed for converting mechanical energy into electricity. One of the objectives for harvesting mechanical energy is to build self-powered nanosensors for implantable biomedical detections. To examine the biosafety of ZnO nanostructures, we demonstrated the cellular level biocompatibility of ZnO NWs, which proved to be reliable for further biomedicine and engineering application. To investigate the possibility of scavenging weak and irregular biomechanical energy, we tested the ZnO NW based NG both in vitro and in vivo. The NG was demonstrated to be capable of effectively converting mechanical energy, such as body movement, breath, and heart beat, into electricity. The research opens up a new path towards providing power source for implantable biomedical applications.

COLL 367

Biocompatible and antibacterial biomimetic hybrid films

***M. Carme Coll Ferrer**(1)(2), macoll@seas.upenn.edu, 3231 Walnut Street, Philadelphia PA 19104-6202, United States ; Noreen J. Hickok(3); David M. Eckmann(4); Russell J. Composto(2). (1) The Institute for Medicine and Engineering, University of Pennsylvania, Philadelphia PA 19104-6202, United States (2) Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia PA 19104-6202, United States (3) Department of Orthopaedic Surgery, Thomas Jefferson University, Philadelphia PA 19107, United States (4) Department of Anesthesia, University of Pennsylvania, Philadelphia PA 19104-6202, United States*

In this work, we present a novel method to prepare a unique hybrid biocoating based on dextran embedded with silver nanoparticles (Ag NPs). Here, the Ag NPs are synthesized *in situ* in a presence of oxidized dextran in solution. The NPs loading is controlled by the silver nitrate and the aldehydes concentration in solution. Two different $AgNO_3$ concentrations, 2 mM and 5 mM, and two aldehydes concentrations, 5 and 10 %, have been studied. The dextran surfaces show patches with a diameter of ~ 50 nm. For the dextran/NP films, the dextran patches are still observed but now with well dispersed individual Ag NPs (~4nm) and clusters of NPs. The antibacterial efficiency of these surfaces has been measured against *S. aureus.* Studies show that dextran/NP(2mM, 5 % aldehydes concentration) exhibits higher resistance to bacteria adhesion relative to control surfaces of silicon and dextran coated silicon.

COLL 368

Nanostructured models of apoptotic cell membranes

Scott M. Reed(1)*, scott.reed@ucdenver.edu, 1201 5th St., Denver CO 80217, United States ; Min S. Wang*(1)*; Joshua Black*(2)*; Michelle K. Knowles*(2)*. (1) Department of Chemistry, University of Colorado Denver, Denver CO 80217, United States (2) Department of Chemistry and Biochemistry, University of Denver, Denver CO 80208, United States*

The membranes of apoptotic cells differ in lipid composition and structure because they contain damaged lipids that cause nanoscale and microscale protrusions. Changes in membrane shape influence protein binding and may be one way in which the body identifies damaged cells for removal. Damaged lipids, membrane curvature, or the combination of those two factors may influence protein binding to apoptotic cells. We have created nanostructured membranes using nanoparticles and two-dimensional supported bilayers on glass. These nanostructured models of apoptotic cell surfaces allow for separate control of membrane curvature and lipid composition. Binding of C-reactive protein (CRP) to nanoparticles coated with lipids reveals a preference of CRP to bind highly curved membranes. CRP also binds to nanostructured supported lipid bilayers formed on glass surfaces. Binding of CRP to the membranes and to nanoparticles is being quantified to determine what features of an apoptotic membrane are critical for protein recognition.

COLL 369

Biomarkers of oxidative stress in autism

Maria Hepel(1)*, hepelmr@potsdam.edu, 44 Pierrepont Avenue, Potsdam New York 13676, United States ; Magdalena Stobiecka*(1)*. (1) Department of Chemistry, The State University of New York at Potsdam, Potsdam New York 13676, United States*

Autism spectrum disorders, is a pervasive development disorder, which is characterized by impairment in communication skills, sensory disturbances and repetitive motor behaviors. In addition the associated complications such as seizures or mental retardation are observed. The autistic children were found to have altered plasma homocysteine (Hcys) levels, significantly lower major intracellular antioxidant total glutathione (tGSH) levels and higher concentrations of oxidized glutathione disulfide. The levels of nitrotyrosine (NT) in cerebellar tissue from autistic subjects were also higher as compared to control subjects. In this work, the simple methods for detection of oxidative stress biomarkers such as: GSH, Hcys, cysteine and NT based on their interactions with gold nanoparticles (AuNP) is presented. Interactions of biomolecules with citrate-, cysteamine- or ZONYL- capped spherical AuNP have been investigated using the high sensitivity of the resonance elastic light scattering spectroscopy, UV-Vis spectroscopy and transmission electron microscopy to study biomarker induced interparticle cross-linking AuNP network.

COLL 370

Arrays from Surface-Modified Pt Nanoparticles Assembled in Polyelectrolyte for Electrochemical Sensing

Lara Halaoui[(1)], *lh07@aub.edu.lb, Bliss Street, Beirut Beirut 110236, Lebanon ; Sarah Jaber*[(1)]*; Pierre Karam*[(1)]*; Pamela Nasr*[(1)]*. (1) Department of Chemistry, American University of Beirut, Beirut 110236, Lebanon*

Pt nanoparticles (NP) modified with polyvinylpyrrolidone (PVP), polyacrylate (PAC), or glucose oxidase (GOx) were assembled in polydiallyldimethylammonium chloride (PDDA) in one layer or in multilayers on electrodes, resulting in electrochemically active films. Pt NPs were tetrahedral or spherical/ellipsoidal with average size from 2.5 nm to 4.3 nm, depending on the synthesis and capping molecule. The active surface site distribution was determined using hydrogen underpotential deposition and depended on the surface modification. Random arrays of Pt NP/PDDA were electrocatalytic for several reactions such as oxygen reduction and hydrogen peroxide oxidation, and featured significant stability facing anodic polarization due to the NPs more difficult surface oxidation relative to bulk Pt. Pt NP/PDDA amperometric sensors exhibited high sensitivity and a low detection limit (42 nM) for H_2O_2 at submonolayer NP coverage on PDDA. Sensing of glucose was also demonstrated at assemblies of Pt NPs coupled *in-situ* with GOx.

COLL 371

Nanoparticle alignment on various surfaces using insulin fibrils as a biotemplate

Shuchen Hsieh[(1)], *shsieh@facmail.nsysu.edu.tw, 70 Lien-hai Rd, Kaohsiung Kaohsiung 80424, Taiwan Republic of China ; Chiung-Wen Hsieh*[(1)]*. (1) Department of Chemistry, National Sun Yat-sen University, Kaohsiung Kaohsiung 80424, Taiwan Republic of China*

Nanoparticles (NPs) have drawn increased attention from researchers due to their unique size-dependent optical, electronic, magnetic, and catalytic properties. These properties may be further modified by controlling NP spatial arrangement on surfaces. For example, when metallic NPs are placed close together, near-field coupling between surface plasmons occurs which can lead to enhancement. Synthetic methods for producing NPs are well-developed, and provide good control over NP size, shape, and composition. However, methods for patterning and aligning NPs on varied surfaces continue to be explored. In the experiments described here, insulin fibrils were used as a biotemplate to attach Au NPs to wafer-grade polished glass and ITO substrates, and to attach Au and CdSe NPs to PDMS substrates. The NPs adhered preferentially to the insulin fibrils via electrostatic interactions, forming chains. This method provides a general approach for aligning NPs into chains on functional surfaces for applications such as optical waveguides.

COLL 372

Protein-specificity in binding to silica nanpoarticles

Bhuvnesh Bharti[(1)]*, bhuvneshbharti@gmail.com, Strasse des 17 Juni 124,, TC 7, Berlin Berlin 10623, Germany ; Jens Meissner*[(1)]*; Gerhard H. Findenegg*[(1)]*. (1) Department of Chemistry, Technical University Berlin, Berlin Berlin 10623, Germany*

We report a comparative study of the attachment of lysozyme and cytochrome c to silica nanoparticles. For both proteins a pronounced increase in maximum adsorption Γ_m with increasing pH and a decrease of Γ_m with increasing ionic strength is observed, emphasizing the role of electrostatic and hydrophobic interactions. Lysozyme is causing hetero-flocculation of silica particles in a wide range of pH and ionic strength, but no flocculation is found with cytochrome c on 40 nm silica particles. This difference is attributed to a different charge distribution on the outer surface of the two proteins. The flock structure of the lysozyme-silica aggregates was studied by small-angle X-ray scattering (SAXS) and cryo-TEM. The inter-particle structure factor $S(q)$ of the aggregates can be represented by a square-well potential with small extension of the well, in agreement with the picture that the silica particles are glued together by lysozyme molecules.

COLL 373

Saloplastics: A new horizon for polyelectrolyte complexes

Joseph B Schlenoff[(1)]*, schlen@chem.fsu.edu, Dittmer Laboratory, Tallahassee Fl 32306, United States . (1) Department of Chemistry and Biochemistry, Florida State University, Tallahassee FL 32306, United States*

Polyelectrolyte complexes become soft and processible when they are doped with salt. This saloplasticity enables the formation of large, rugged articles of complex suitable for applications as biomaterials. Understanding and exploiting saloplasticity relies on a thorough understanding of the fundamentals for the formation of polyelectrolyte complexes, PECs, whether they are precipitated from solution or formed by the newer multilayering method. This talk will present the driving forces for PEC formation and dissociation. Examples will be given of the types of morphology obtained with saloplastic processing. Finally, possible applications and properties of PECs as cartilage mimics will be discussed.

COLL 374

Temperature and charge dependence of ion diffusion coefficients through polyelectrolyte multilayers

Ramy Abdo Ghostine[(1)]*, rghostine@chem.fsu.edu, 174 brittain drive apt 5, Tallahassee FL 32310, United States ; Joseph B Schlenoff*[(1)]*. (1) Chemistry and Biochemistry, Florida State University, Tallahassee FL 32306, United States*

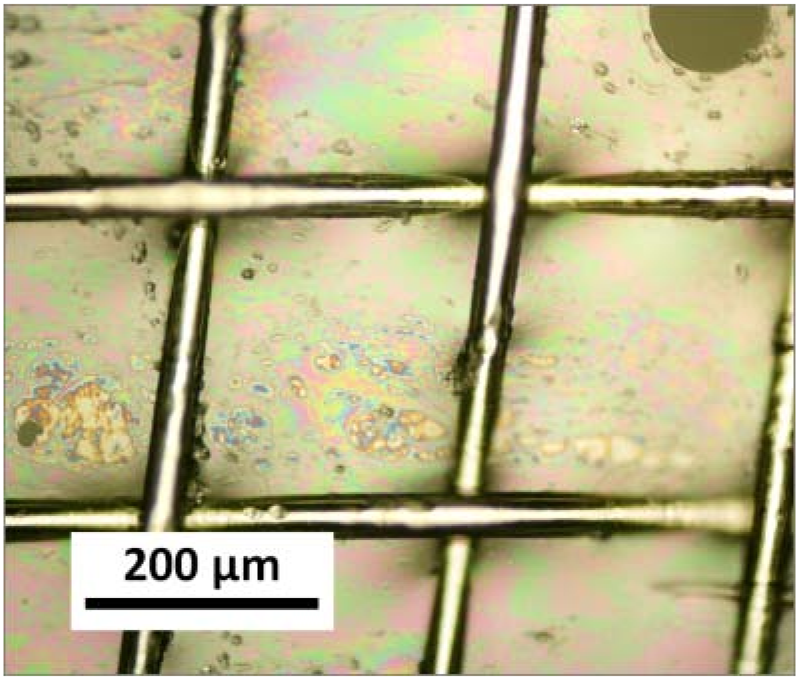
The permeability of a triple charged redox active ion, ferricyanide, through polyelectrolyte thin films of poly(diallyldimethylammonium) chloride (PDADMA) and polystyrene sulfonate (PSS) were investigated at different temperature and different salt concentration. The concentration of ferricyanide inside the membrane was measured by Attenuated Total Reflectance Fourier Transform Infra Red Spectroscopy (ATR-FTIR). A rotating disk electrode (RDE) was used to measure the fluxes across the film, and to calculate the diffusion coefficients of ferricyanide inside the membrane. It was found that the amount of ferricyanide inside the film decreases with temperature when salt ions are present. Membrane transport is strongly thermally activated with an activation energy of 126 kJ mol^{-1}. A potential shift was recorded on the cyclic voltammograms at different salt concentration between the bare electrode and the coated electrode, due to the difference in ferri/ferrocyanide concentration gradients inside the film.

COLL 375

Beyond conformal coating: Superdeposition and pore bridging phenomena exhibited by LbL films

Rebecca Ladewski[(1)]*, ladewski@mit.edu, 76-553, 500 Main St., Cambridge MA 02139, United States ; Paula Hammond*[(1)(2)]*; Angela Belcher*[(2)(3)]*; Rebekah Miller*[(2)(3)]*. (1) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge Massachusetts 02139, United States (2) Department of Biological Engineering, Massachusetts Institute of Technology, Cambridge Massachusetts 02139, United States (3) Department of Materials Science, Massachusetts Institute of Technology, Cambridge Massachusetts 02139, United States*

One universally-acknowledged beneficial attribute of layer-by-layer (LbL) assembly is its ability to conformally coat substrates of all shapes and sizes. In this work we discuss LbL coatings that bridge pores over 200 microns wide in metal meshes, creeping beyond the wetted areas of substrates (see the figure below). This phenomenon has applications in membrane assembly or solar device construction. The effects of polymer chain length, polymer backbone charge density, interdiffusion, and surface hydrophilicity/hydrophobicity will be discussed.



COLL 376

From LbL to simultaneously sprayed polyanion/polycation polyelectrolyte nanoscale coatings.

Mathias Lefort(1), *mathias.lefort@ics-cnrs.unistra.fr, 23 rue du Loess, BP 84047, 67034 STRASBOURG Alsace Cedex 2, France ; Fouzia Boulmedais*(1)*; Joseph Hemmerle*(2)*; Arnaud Ponche*(3)*; Pierre Schaaf*(1)*. (1) Departement of Macromolecular Engineering at Interfaces, ICS UPR 22, CNRS, Strasbourg 67034 Strasbourg Cedex 2, France (2) UMR 977 INSERM, Strabourg 67085 Strasbourg, France (3) IS2M - LRC 7228 CNRS, Mulhouse 68057 Mulhouse, France*

Layer-by-Layer (LbL) deposition of polyelectrolytes has received considerable attention during the last years leading to polyelectrolyte multilayers. We first present a brief history of LbL from dipping to spraying. We then introduce a method inherited from the spray-assisted LbL deposition : “Simultaneous Spray Coating of Interacting Species” (SSCIS). Instead of bringing species step-by-step to form LbL-films, SSCIS brings two or more interacting components simultaneously against a surface. This results in a fast buildup of a non-layered coating while the excess material is removed by drainage. Different components can be used and were studied (pair of complementary polyelectrolytes, a polyelectrolyte and a small multicharged organic molecule) providing different film morphologies (stack of complexes or liquid-like film). We will also discuss the influence of different parameters (spraying time, solution concentration,…) and present the rules (different from the LbL) driving the construction of these films.

COLL 377

Microcalorimetric studies on ion and water exchange in redox-active polyelectrolyte multilayers

Raphael Zahn(1)*, zahn@biomed.ee.ethz.ch, ETZ F 76, Gloriastrasse 35, Zurich Zurich 8092, Switzerland ; Katrin R Bickel*(2)*; Rolf Schuster*(2)*; Fouzia Boulmedais*(3)*; Janos Vörös*(1)*; Pierre Schaaf*(3)*; Tomaso Zambelli*(1)*. (1) Department of Information Technology and Electrical Engineering, ETH Zurich, Zurich 8092, Switzerland (2) Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT),, Karlsruhe 76131, Germany (3) Institut Charles Sadron, CNRS, Strasbourg CEDEX 2 F-67034, France*

We present a polyelectrolyte multilayer (PEM) consisting of Poly-L-Glutamic Acid and Poly-(AllylamineHydrochloride) containing ferrocyanide ions. The oxidation of the incorporated ferrocyanide ions caused an expansion of the PEM. This behavior was attributed to the reversible uptake of counterions and water into the film. Using electrochemical quartz crystal microbalance with dissipation monitoring (EC-QCM-D) it was possible to determine the number of ions and water molecules exchanged during the swelling.

Electrochemical microcalorimetry experiments showed that the entropy of the counterions and water molecules taken up by the film is lower than the entropy of the corresponding molecules in solution. This indicated a reduced mobility of the molecules in the PEMs. We performed microcalorimetry experiments with different counterions at several concentrations and relate the results to the Hofmeister series and the different modes of charge compensation in the PEMs (intrinsic *vs.* extrinsic charge compensation).

COLL 378

Coupling Ellipsometry and Quartz Crystal Microbalance with Dissipation Monitoring to Quantify Interfacial Changes in Polyelectrolytes

Mark A Poggi(1)*, mark.poggi@biolinscientific.com, 514 Progress Dr., Suite G, Lithicum Heights MD 21090, United States ; Matthew Dixon*(1)*; Archana Jaiswal*(1)*. (1) Biolin Scientific (Q-Sense), Linthicum Heights MD 21090, United States*

There are many surface sensitive techniques (such as AFM and SEM) which are routinely used to study nano-scale properties of interfaces. However, these techniques sometimes lack the ability to probe in-situ phenomena in-real time. In materials engineering, understanding how an engineered material will perform in-situ has relevance in understanding molecules behave at interfaces. Recently we have coupled two analytical techniques that allow scientists to quantify changes at material interfaces. We recently reported the coupling of quartz crystal microbalance with dissipation monitoring (QCM-D) and ellipsometry. By combining these two analytical measurements we are successfully able to monitor changes in thickness, mass and structural properties. With the QCM-D component, we can determine the solvated mass

and structural rigidity of a film and with the corresponding ellipsometric information we can determine the molecular mass, thus allowing us to de-convolute solvent contributions in a thin film. In this discussion we will review analytically how we are making these measurements and recent experiments that have been performed studying polyelectrolyte interfaces.

COLL 379

Strategies to Selective Patterning of Polyelectrolyte Multilayers: Transfer, Molding, and Electric-Field-Assisted Deposition

Pil J. Yoo[(1)(2)]*, pjyoo@skku.edu, Chunchun-Dong 300, Suwon Gyunggi-Do 440746, Republic of Korea ; Young Hun Kim*[(1)]*; Yong Man Lee*[(2)]*. (1) School of Chemical Engineering, Sungkyunkwan University, Suwon Gyunggi-Do 440746, Republic of Korea (2) SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon Gyunggi-Do 440746, Republic of Korea*

We introduce a simple and robust method for varying the phase of the patterns in transfer printing of polyelectrolyte multilayers. Simply transferred positive patterns, edge-defined intermediate patterns, and negatively engraved/molded patterns are obtained by manipulating the capillarity of the plasticized polymeric layer from weak to strong. A phase diagram of the pattern transfer is suggested to account for the influences of the temporal and spatial factors in the experiments. In addition, we propose the electric-field-assisted layer-by-layer (LbL) assembly of polyelectrolyte multilayers, whereby the rate of deposition of polyelectrolytes can be significantly enhanced by increasing the magnitude of the externally applied electric field. By exploiting this phenomenon, we are able to achieve successful film deposition even at pH values that are typically not available in the conventional LbL assembly, which is further utilized to pattern the polyelectrolytes via selective deposition onto suitable electro-conductive substrates for various downstream applications.

COLL 380

Monte Carlo simulation of fluorescence correlation spectroscopy data for large and rigid fluorescenty labeled particles undergoing both the translational and rotational diffusion

Karel Prochazka[(1)]*, prochaz@vivien.natur.cuni.cz, Albertov 6, Prague 2, Prague Czech Republic CZ-12843, Czech Republic ; Filip Uhlik*[(1)]*; Peter Kosovan*[(1)]*; Jitka Kuldova*[(1)]*; Zuzana Limpouchova*[(1)]*. (1)*

Fluorescence correlation spectroscopy (FCS) is a non-invasive optical technique used for studying the diffusion of fluorescent or fluorescently labeled species. While the interpretation of FCS results for small molecules based on the theory of diffusion of point-like particles is straightforward, data on large, flexible or multiply labeled macromolecules are affected also by the rotational diffusion, internal motion and other

effects and therefore have to be interpreted with care. We present results of Monte Carlo simulations aimed at the interpretation of FCS data for large spherical particles (labeled on their surface) that undergo both the translational and rotational diffusion. The most important conclusion from the study is the following: The autocorrelation curve for large spheres can be fitted by the function derived for the point-like particles very precisely. However, the obtained diffusion coefficients and other parameters of the fit are significantly incorrect and have to be recalculated.

COLL 381

Novel polymerization powered colloidal motor: Enhanced diffusion and directed motion

Ryan A Pavlick(1)*, rap251@psu.edu, 104 Chemistry Building, University Park PA 16802, United States ; Samudra Sengupta*(1)*; Timothy McFadden*(1)*; Ayusman Sen*(1)*. (1) Chemistry, Pennsylvania State University, University Park PA 16802, United States*

The development of colloidal motors that function at low Reynolds number regimes was been an increasing area of research over the past couple of years. Our group reports the first motor to be powered by a polymerization reaction outside a biological system. This motor employs a bound form of Grubbs' catalyst asymmetrically fashioned on a gold-silica Janus microsphere. These motors show increased diffusion up to 70% when placed in solutions of monomer. These motors also display chemotaxis when placed in a gradient of monomer. This property is useful for the development of self repair systems.

COLL 382

Drainage behavior of electrically destabilized thin liquid films and characterization of resulting nanoscale patterned surfaces

Arnab Atta(1)*, arnab.atta@ualberta.ca, 4-9 Mechanical Engineering Building, Edmonton Alberta T6G 2G8, Canada ; Amir Ehsan Hosseini*(1)*; Subir Bhattacharjee*(1)*. (1) Department of Mechanical Engineering, University of Alberta, Edmonton Alberta T6G 2G8, Canada*

Electrically induced destabilization of thin liquid film has been numerically studied assuming long-wave asymptotic analysis of the governing equations. Morphological evolution of the film interface is captured for different configurations of applied field to identify the effect of field heterogeneity on the film drainage time and nanoscale surface pattern formation. Influence of substrate heterogeneity combined with heterogeneous field has also been demonstrated. Results indicate that faster film drainage can be achieved by introducing minimal field heterogeneity as compared to other periodically heterogeneous configurations which produces structured surface patterns as well. Additionally, envisaging those nanoscale patterns as roughness, DLVO interactions between resulting surface morphologies and spherical as well as flat objects have been

evaluated by surface element integration technique to gain insights into particle deposition behavior on the surface. This developed methodology will contribute in understanding the drainage behavior of thin film and impact of consequential surface patterns on colloidal interactions.

COLL 383

Novel approach for altering the density of permanently confined surfactant in mesoporous silica

Rubal Dua[(1)]*, rubal.dua@kaust.edu.sa, Office: 4230 WS-14, Building 4, Level 4, Thuwal Jeddah 23955-6900, Saudi Arabia ; Peng Wang*[(1)]*. (1) Water Desalination and Reuse Center, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia*

A co-surfactant synthesis based approach is presented for obtaining mesoporous silica samples with varying density of permanently retained surfactant. In particular varying amounts of two similar cationic surfactants: Cetyl trimethylammonium bromide (CTAB) and [3-(trimethoxysilyl)propyl]-octadecyldimethylammonium chloride (TPODAC) were used, while keeping the total number of moles of surfactant constant. Both CTAB and TPODAC contribute in the formation of templating micelles which upon addition of silica oligomers and a base catalyst give rise to mesoporous silica. However among the two, only TPODAC forms covalent bond with the silica framework and is thus permanently retained while CTAB can be removed via acidified ethanol washing at high temperature, once the meso-structure is obtained. Both X-ray Diffraction (XRD), N_2 adsorption-desorption measurements indicated that the synthesized mesoporous silica samples had similar structural properties. Thermogravimetric (TG) analysis results confirmed the varying levels of percentage weight fraction of retained TPODAC in different samples. One of the applications of these surfactant containing mesoporous silica samples is their use for contaminant removal from water. Thus the obtained mesoporous silica samples with different permanently retained surfactant density were used to test the sorption of diuron, a moderately hydrophobic organic compound (HOC). The results from the sorption tests clearly indicate the expected correlation between the density of the retained surfactant in the pore and the overall removal of the contaminant. The optimum density resulted in a more than two fold increase in the adsorption capacity of the material for diuron removal as compared to the mesoporous silica sample synthesized using only TPODAC. All the results show that co-surfactant synthesis is an efficient method for tuning the density of permanently confined surfactant in mesoporous silica for enhancing their contaminant sorption capacity.

COLL 384

The interactions between PGPR and milk proteins at the oil-water interface as determined by interfacial tensiometry

Ibrahim Gulseren[(1)]*, igulsere@uoguelph.ca, 129 Food Science Bldg., Guelph Ontario N1G 2W1, Canada ; Milena Corredig*[(1)]*. (1) Department of Food Science, University of Guelph, Guelph Ontario N1G 2W1, Canada*

Due to the labeling concerns, food producers are interested in limiting the usage of synthetic emulsifiers such as PGPR, a lipophilic emulsifier commonly used in the stabilization of water-in-oil emulsions. The objective of this work was to further our understanding of the possible synergistic interactions between PGPR and milk proteins, namely, sodium caseinate and b-lactoglobulin, using interfacial tensiometry. These proteins are widely employed as emulsifiers in food systems. b-lactoglobulin or sodium caseinate lowered interfacial tension synergistically with PGPR. However, PGPR dominated the elasticity of the interface. When b-lg was present in isolation the interfacial elasticity was higher compared to PGPR alone. The addition of PGPR to a b-lactoglobulin interface lowered the elasticity, possibly through partial displacement of the protein. At high concentrations of b-lactoglobulin or sodium caseinate, the rigidity of the interfacial film decreased, indicating conformational changes in the film due to modified surfactant-surfactant interactions.

COLL 385

NMR Characterization of Canopy Dynamics in Nanoscale Ionic Materials

Michael L. Jespersen[(1)(2)]*, michael.jespersen.ctr@wpafb.af.mil, AFRL/RXBN, 2941 Hobson Way, Building 654, Wright-Patterson AFB OH 45433, United States ; Peter A. Mirau*[(1)]*; Ernst D. von Meerwall*[(3)]*; Richard A. Vaia*[(1)]*; Nikhil J. Fernandes*[(4)]*; Emmanuel P. Giannelis*[(5)]*. (1) Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB OH 45433, United States (2) UES, Inc., Wright-Patterson AFB OH 45433, United States (3) Department of Physics, University of Akron, Akron OH 44325, United States (4) School of Applied and Engineering Physics, Cornell University, Ithaca New York 14853, United States (5) Department of Materials Science and Engineering, Cornell University, Ithaca New York 14853, United States*

Nanoscale ionic materials (NIMS) are organic-inorganic hybrids in which a core nanoparticle is functionalized with a covalently attached corona and an ionically tethered polymer canopy. NIMS exhibit liquid-like character under ambient conditions in the absence of solvent and are of interest for a variety of applications. We have used nuclear magnetic resonance (NMR) relaxation and pulse-field gradient (PFG) diffusion experiments to measure the canopy dynamics of NIMS prepared from 18-nm silica nanoparticles. NMR studies show that the fast (ns) local dynamics of the canopy are insensitive to the presence of the silica nanoparticles unless the system is deficient in canopy. Canopy diffusion in NIMS is slowed relative to the neat copolymer, but crowding at the nanoparticle surface results in two canopy populations with different diffusion coefficients. Electrostatic interactions with other dipolar or ionic species alter the dynamics by decreasing the strongly-bound population.

COLL 386

Electrically tunable photonic crystal for reflective display element

Moon G. Han$^{(1)}$*, moongyu.han@samsung.com, San 14, Nongseo-dong, Gihung-gu, Yongin-si Gyeonggi-do 446-712, Republic of Korea ; Seog-Jin Jeon*$^{(2)}$*; Chang Gyun Shin*$^{(2)}$*; Hong Shik Shim*$^{(2)}$*; Jung Woo Kim*$^{(2)}$*. (1) (2) Display Device Lab, Samsung Advanced Institute of Technology, Yong-in Gyeong-gi 446-712, Republic of Korea*

Over the past few decades, photonic crystal, which is a three dimensional periodically structured materials, in which dielectric function suffers a spatially periodic variation leading to forbidding of the propagation of certain range of electromagnetic wave, has been successfully used in many modern optical devices, such as lasers, waveguides, optical filters, and light emitting diodes. We will report our recent efforts in developing reflective display element utilizing electrically tunable photonic crystal using charged colloids, which responds to electrical field and exhibit electrokinetic movement while maintaining ordered array due to strong electrostatic repulsion between particles. By applying voltage, the change of reflective, structural color of the pixel has been achieved by modulating the spacing between spherical colloidal particles with high surface negative charge. Potential performance of this display technology in terms of reflectivity, color, gamut, switching speed will also be discussed.

COLL 387

Control of anisotropic particle suspensions for bioinspired composite technology

Randall M Erb$^{(1)}$*, randall.erb@mat.ethz.ch, Wolfgang-Pauli-Strasse 10, HCI-F-511, Zurich Zurich 8093, Switzerland ; A. R. Studart*$^{(2)}$*. (1) (2) Department of Materials, ETH Zürich -Swiss Federal Institute of Technology, Zurich Zurich 8093, Switzerland*

Due to the large strength to weight ratio of composites, their implementation as load-bearing materials is exponentially growing especially in aerospace, the automobile industry, and construction. The majority of commercial composites today are produced with continuous aligned fibers that lead to significant material strength along a single axis. The primary weakness of commercial laminates remains the stiffness in the third, out-of-plane direction. Instead, natural composites utilize unique orientation of its inorganic reinforcement to provide significant 3-D strength not typical in manufactured composites. If discontinuous fibers can be deliberately aligned within a composite, then isotropic reinforcement similar to these natural systems becomes a possibility. Here we present our recent characterization of an ultra-high response of $Al2O3$ platelets under magnetic fields. To achieve this response we modify the platelets first with <0.1% $Fe3O4$ nanoparticles This modification allows for the remote control of particle orientation under magnetic fields that can, among numerous exciting possibilities, lead to platelet alignment that can mimic the structures in natural systems. We have developed an energy model for these particle suspensions that explain this ultra-high response and suggest the key parameters essential in these systems. To help validate these parameters, we employed this model in suspensions of rods and successfully predicted the best size regime for high responsiveness. We extend this model to

describe the exciting alignment of the platelets second major axis under rotating magnetic fields. We have found a relationship between the viscosity of the suspension and the critical frequency required to change from 'phase-locked' to 'fullyaligned' modes. Finally, we use these techniques to create a family of advanced composites. exhibiting 3-d reinforcements, spatial gradients, and various deliberate alignments. These composites exhibit the 3-D reinforced structures predicted to have enhanced material properties, such as higher stiffness and 'wear-free' characteristics.

COLL 388

Model of Dispersion Polymerization Process

Zhipeng Song(1)*, zsong2@mmm.com, 3M Center, Bldg 0236-03-B-01, St. Paul MN 55144, United States ; Eric S Daniels*(2)*; E David Sudol*(2)*; Mohamed S El-Aasser*(2)*; Andrew Klein*(2)*. (1) 3M Company, St. Paul MN 55144, United States (2) Emulsion Polymers Institute and Department of Chemical Engineering, Lehigh University, Bethlehem PA 18015, United States*

A model was developed to describe the particle nucleation, aggregation and growth processes that occur in dispersion polymerization based on the discretized particle population balance theory. The simulation results show that dispersion polymerization is a two-particle population system. The second population of particles grow to become the final particles and are small in number (10^{12} L^{-1}). The size of the first population of particles is small (2-30 nm), but the number of these particles is large (10^{14} L^{-1}). The first population of particles does not grow to a larger size. The destiny of these particles is to be captured by the second population of particles and contribute to the volume increase of the latter.

COLL 389

Characterization of casein micelles suspensions in skim milk concentrated using osmotic stressing: Interactions and changes in the composition of the serum phase

Pulari Krishnankutty Nair(1)(2)*, pkrishna@uoguelph.ca, Building #038, Guelph ON, Canada ; Marcela Alexander*(1)*; Milena Corredig*(1)*. (1) Department of Food Science, University of Guelph, Guelph ON N1G 2W1, Canada (2) Department of Dairy Development, Guelph ON N1G 2W1, Canada*

Casein micelles were concentrated using of osmotic stressing with poly-ethylene-glycol, to reach high volume fractions (Φ, from 0.1 to 0.78) while keeping the ionic balance constant. The soluble protein, calcium content, viscosity and refractive index of the serum were analyzed. There was no release of colloidal calcium phosphate from the micelles, even at high volume fractions. The viscosity of the concentrated milk followed the Eilers equation. The turbidity parameter measured by Diffusing Wave Spectroscopy, increased up to a Φ of ~0.4 and at higher Φ the experimental data could no longer be

predicted by hard sphere theory. At the low Φ <0.32%, the particles showed a free diffusing Brownian behaviour, while at higher Φ, the particles were no longer free diffusing and experienced restrictions in their movement. This research brings new insights on the interactions and changes in the serum phase on the characterisation casein micelles during concentration.

COLL 390

Shear thickening and changes in particle structure of chemical mechanical polishing slurries

Nathan Crawford[(1)]*, mliberat@mines.edu, 1600 Illinois St, Golden Colorado 80401, United States ; Matthew Liberatore*[(1)]*; S. Kim R. Williams*[(2)]*; David Boldridge*[(3)]*. (1) Department of Chemical Engineering, Colorado School of Mines, Golden Colorado 80401, United States (2) Department of Chemistry and Geochemistry, Colorado School of Mines, Golden Colorado 80401, United States (3) Department of Research and Development, Cabot Microelectronics Corporation, Aurora Illinois 60504, United States*

Chemical mechanical polishing (CMP) is a fundamental technology used in the semiconductor manufacturing industry to polish and planarize a wide range of materials for the fabrication of microelectronic devices (i.e., computer chips). The CMP slurry is a mixture of a colloidal abrasive, a suspension fluid (usually water) and active chemicals that react with the material to be removed. During the polishing process, the slurry will undergo shear rates in excess of 10^6 s^{-1}. Under this extreme shear environment, it is hypothesized that individual slurry particles begin to interact and collide with one another forming large agglomerates (≥ 0.5 μm) that cause the slurry to portray solid-like behavior (shear thickening). These agglomerates trigger the formation of defects such as scratches, gouges, pits, and corrosion during polishing. On the order of 10-15% of failed integrated circuits can be linked to CMP induced defects which is estimated to be $4.5 to $9 billion of lost production per year.

Our overall effort seeks to obtain a detailed understanding of the high shear rheological behavior of CMP slurries as well as changes in particle characteristics, both temporary and permanent. Utilizing high shear rheology to mimic the CMP process, the goal is to correlate shear thickening of the CMP slurry to the formation of agglomerates (or hydroclusters). The slurries of interest are a concentrated fumed silica suspension in water with added KOH for electrostatic stabilization at alkaline pH. A controlled stress rheometer with a parallel plate geometry at small gaps measures the non-linear rheological responses of the high solids slurry. Rheo-optical techniques were used to identify the formation, shape, and size of agglomerates generated under shear. Flow field-flow fractionation with single particle optical sensing were employed to size and quantify the relative number of large particles (≥0.5 μm) produced from shearing experiments.

COLL 391

Structure evolution and kinetics in PEO-PPO-PEO triblock copolymer solutions with added pharmaceuticals

Norman A K Meznarich*(1)*, *nakm@umich.edu, 3062 HH DOW, 2300 Hayward Street, Ann Arbor MI 48109, United States ; Brian J Love(1). (1) Department of Materials Science and Engineering, University of Michigan, Ann Arbor MI 48109, United States*

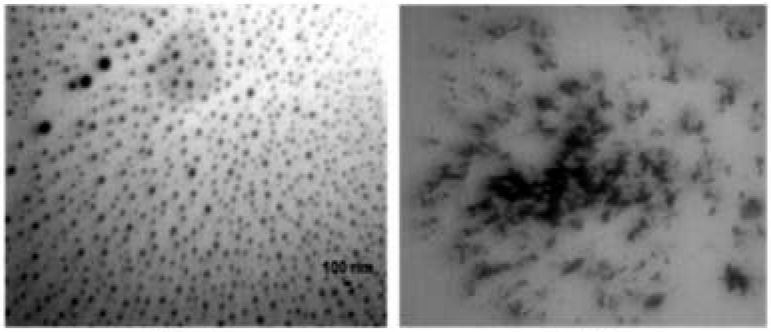
Aqueous solutions of polyoxyethylene-polyoxypropylene-polyoxyethylene triblock copolymers (Pluronics) undergo micellization and structural arrangement as their temperature is raised. This property has made Pluronics a material of interest for drug delivery applications. Previously, we have investigated the effects of added methylparaben on the kinetics of Pluronic F127 gelation using rheology, DSC, and DLS. We found that methylparaben lowers the gelation temperature of these solutions, and observed an increase in the gelation rate. Here we examine directly the structures formed by F127 solutions using small-angle x-ray scattering (SAXS) as they have been heated through their phase transitions. We found that methylparaben alters the evolution of ordered structure to a more gradual process as the temperature is raised. Neat solutions of equivalent concentration exhibited a more rapid change from the disordered to the ordered state. Methylparaben also stabilizes the micelle lattices, allowing them to persevere at higher temperatures; they also homogenize the structures throughout the solution. Finally, we have collected some preliminary data involving F127 solutions with other pharmaceuticals.

COLL 392

Fluorescent pH -responsive nanoGUMBOS for drug delivery to cancer cells.

Susmita Das*(1)*, *susmita@lsu.edu, 444A Choppin Hall, Baton Rouge LA 70803, United States ; Paul Magut(1); Sergio L de Rooy(1); Lijie Zhao(1); Isiah M Warner(1). (1) Chemistry, Louisiana State University, BATON ROUGE LA 70802, United States*

Nanoparticles that are capable of rapid drug release when exposed to acidic pH conditions are highly desirable for drug delivery to cancer cells. Herein, we report a novel, facile technique to synthesize phthalocyanine based fluorescent and pH sensitive nanoGUMBOS. The GUMBOS (**G**roup of **U**niform **M**aterials **B**ased on **O**rganic **S**alts) were based on a phthalocyanine based cation and a bile acid based anion. The GUMBOS synthesized were characterized using NMR and FTIR. The synthesized nanomaterials were 10-20 nm in diameter and were found to remain highly intact and spherical at the physiological pH. However, at an acidic pH (6) they were observed to expand and coalesce. This property of the nanoGUMBOS is considered to very important for target specific drug delivery to cancer cells. The fluorescence properties will allow the tracking of the nanoparticles and imaging as well. The cytotoxicity studies indicate nearly 80 % cell viability revealing fairly high biocompatibility of these nanomaterials.



pH7.4 pH6

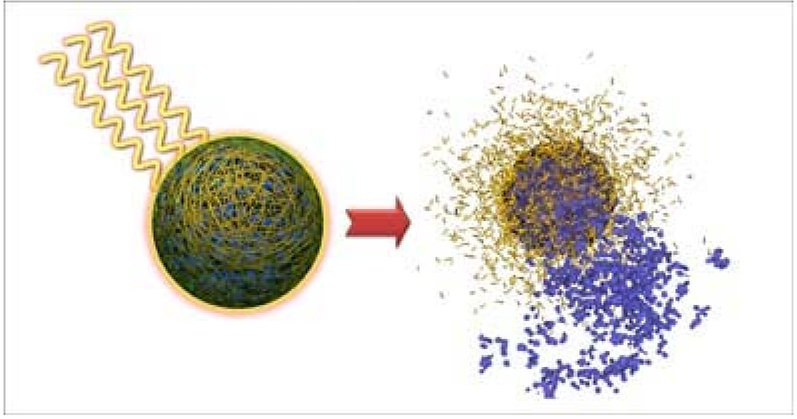
TEM images of pH sensitive nanoGUMBOS

COLL 393

UV and Near-IR triggered release from polymeric nanoparticles

Adah Almutairi[(1)], *aalmutairi@ucsd.edu, 9500 Gilman Dr., La Jolla CA, United States . (1)*

A new light-sensitive polymer containing multiple light sensitive triggering groups along the backbone and incorporating a quinone-methide self-immolative moiety was developed and formulated into nanoparticles encapsulating a model pharmaceutical Nile Red. Triggered burst release of the payload upon irradiation and subsequent degradation of the nanoparticles were observed. This system is designed to be versatile where the triggering group can be sensitive to a number of wavelengths.



COLL 394

Shape-dependent bactericidal efficacy of nitric oxide (NO)-releasing silica mesoporous nanorods

Yuan Lu[1]*, yuan.lv@gmail.com, UNC-CH, Caudill 311, Chapel Hill NC 27599-3290, United States ; Bin Sun*[1]*; Mark H Schoenfisch*[1]*. (1) Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill North Carolina 27599-3290, United States*

Nitric oxide (NO) is a diatomic free radical antibacterial agent, capable of killing bacteria via oxidative and nitrosative stress. To facilitate storage and controlled release of NO, we have previously synthesized spherical NO donor-modified silica nanoparticles. These particles were shown to be highly effective at killing bacteria. Due to the well-known roles of nanoparticle size and shape on circulation and cellular internalization, we set out to study the effect of NO-releasing nanoparticle geometry on biocidal activity to potentially increase their killing efficacy. Herein, we describe a surfactant-templated approach to design diazeniumdiolate-functionalized mesoporous silica nanorods of various shapes and NO-releasing properties. The results of this work demonstrate that the biocidal activity of NO-donor modified nanorods depends greatly on both shape and NO release profile.

COLL 395

Combinatorial micro-/nanoarrays of microenvironmental signals for controlling stem cell fate

KiBum Lee[1]*, kblee@rutgers.edu, 610 Taylor Road, Piscataway New Jersey 08854-8087, United States ; Aniruddh Solanki*[1]*; Shreyas Shah*[1]*. (1) Department of Chemistry and Chemical Biology, Rutgers University, Piscataway New Jersey 08854-8087, United States*

This talk will focus on the interface of nano-surface chemistry and stem cell biology. Two important research projects will be presented: i) development of bio-surface chemistry methods to generate combinatorial arrays of microenvironmental cues and ii) application of the combinatorial platforms to understand the *spatiotemporal* effects of microenvironmental cues on differentiation of stem cells. Developing nanotechnology-based combinatorial approaches for regulating stem cell fate and studying the functions of multiple microenvironmental cues that regulate stem cell behaviors are critical to fully achieve the therapeutic potential of stem cells. To investigate the complex neural stem cell (NSC) behaviors, we first patterned extracellular matrix (ECM) and signal molecules in combinatorial ways by using soft-nanolithographic methods and then investigated stem cell responses to multiple cues. Our combinatorial nanoarrays allowed us to selectively control the neuro-differentiation of NSC differentiation in an efficient way. Summarized results of our efforts and future directions will be discussed.

COLL 396

Synthesis and characterization of soluble and biocompatible dendritic salicylic acids

Minghui Chai(1), *chai1m@cmich.edu, Dow 342, Department of Chemistry, Central Michigan University, Mt. Pleasant Michigan 48859, United States ; Daniel B. MacHue*(1)*; Daniel R. Holycross*(1)*; Shengzhuang Tang*(1)*; Che-Hin Ho*(1)*. (1) Department of Chemistry, Central Michigan University, Mt. Pleasant MI 48859, United States*

Dendritic salicylic acid prodrugs have been developed in our previous work. However their water solubility is still rather low which limits their further biomedical applications. In this presented research we try to conjugate mono-saccharides including glucose, galactose and mannose via glycosylation onto the surface of the previously synthesized different generation normal and high-loading dendritic salicylic acid prodrugs. In this way the water-solubility and biocompatibility of the dendritic salicylic acid prodrugs can be greatly enhanced by the sugar moieties on the surface of the dendrimers. Furthermore the *in vitro* cytotoxicity tests can be easily carried out for these sugarlated dendrimers in comparison with the original ones. In addition the structures of these newly made dendrimers are characterized using NMR, MS, UV-Vis, IR and other analytical techniques.

COLL 397

Multiresponse strategies to modulate burst degradation and release from nanoparticles

Adah Almutairi(1), *aalmutairi@ucsd.edu, 9500 Gilman Dr., La Jolla CA, United States . (1)*

Logic gate nanoparticles, where two chemical transformations take place one after the other, were successfully formulated from a newly synthesized random co-polymer. This polymer, poly([2,2=-(propane- 2,2-diylbis(oxy))bis(ethane-2,1-diyl) diacrylate]-co-[hexane-1,6-diyl diacrylate]-4,4= trimethylene dipiperidine), (poly-β-aminoester ketal-2) contains two pH responsive moieties within its backbone. As nanoparticles they function akin to an AND logic gate. The ß-aminoester backbone moiety provides a pH triggered solubility switch, only when this switch is “ON” does the ketal moiety also turn “ON” to undergo rapid acid catalyzed hydrolysis. These AND logic gate polymeric nanoparticles were prepared using an oil in water emulsion method. Their degradation in the pH range of 7.4 - 5 was monitored by dynamic light scattering and showed excellent stability at pH 7.4 and rapid degradation at pH 5. Our results indicate that the prepared logic gate nanoparticles may prove valuable in delivering therapeutics and diagnostics to cells and diseased tissue.

COLL 398

Spectroscopic methods for the development of nanomaterials for controlled release

Cathryn L McFearin(1), *cmcfearin@ucsd.edu, 9500 Gilman Dr, MC 0600, PSB 2186, La Jolla CA 90263-0600, United States ; Jagadis Sankaranarayanan*(1)*; Adah*

Almutairi(1). (1) Skaggs School of Pharmacy and Pharmaceutical Sciences, University of California, San Diego, La Jolla CA 90263-0600, United States

Development of therapeutic delivery systems for controlled release requires characterization of a complex mixture of pharmaceuticals, delivery vehicle materials, and formulation components as well demonstrating the release properties of these systems. The work in this talk illustrates the specific capabilities and advantages of different spectroscopic techniques developed in our laboratory to provide information about controlled release samples. First, coupling infrared spectroscopy (IR) with the attenuated total reflection (ATR) sampling technique and fiber optic probe technology provides label free, non-destructive, chemical specific information about multi-component samples for use as a tool in the drug delivery field. Second, steady state and lifetime fluorescence methods provide a sensitive measure of model pharmaceutical payload behavior. These techniques are applied to two promising delivery vehicles, polymeric nanoparticles and hydrogels.

COLL 399

Nanoengineered antigen surfaces promote new intercellular communication routes via membrane nanotubes and dendritic filopodia

***Jie-Ren Li**(1), jierenli@gmail.com, One Shield Ave., Davis CA 95616, United States ; Huan-Yuan Chen(2); Nai-Ning Yin(1); Fu-Tong Liu(2); Gang-yu Liu(1). (1) Department of Chemistry, University of California-Davis, Davis California 95616, United States (2) Department of Dermatology, School of Medicine, University of California-Davis, Sacramento California 95822, United States*

Mast cells are widely recognized as critical effectors in allergic disorders and other immunoglobulin E-associated immune responses. The most widely known response is that leading to the secretion of histamine, proteoglycans and serine proteases from cytoplasmic granules. Using nanoengineered surfaces with antigens of dinitrophenyl (DNP) domains, two new intercellular communication routes, membrane nanotubes and dendritic filopodia, were discovered while mast cells were activated. Membrane nanotubes are tethered above the substratum and are distinct from filopodia. Membrane nanotubes have a diameter of 65 nm to 212 nm and a length ranging from 5.6 to 11.6 µm. The branches and tips of dendritic filopodia follow the pattern of nanoengineered surfaces underneath, indicating the guiding effect of nanostructured antigen. The results indicate that intercellular connections of membrane nanotubes promote transfer of IgE-FceRI complex to connected cells. Dendritic filopodia facilitate long-distance antigen recognition.

COLL 400

Counter-ion effects on ionizable biomolecules in aqueous electrolyte solutions: understanding molecular mechanisms

Anastasia O. Romanova(1), *romanova@mis.mpg.de, Inselstr. 22, Leipzig Saxony 04103, Germany ;* ***Maxim V. Fedorov***(1), *fedorov@mis.mpg.de, Inselstr. 22, Leipzig Saxony 04103, Germany ; Andrey I. Frolov*(1). *(1) Max Planck Institute for Mathematics in the Sciences, Leipzig Saxony 04103, Germany*

In this work we investigate the effects of K^+ and Na^+ ions on the structure of anionic biomacromolecules (poly-L-glutamate based polypeptides and halophilic enzymes) and on the formation of alpha-cyclodextrin complexes with ionized aromatic carboxylic acids (ACAs) in aqueous solutions. The latest can be a model for binding in more complicated systems (e.g. protein-ligand binding). In contrast to potassium ions, sodium ions tend to form direct contact pairs with the carboxylate groups in the studied systems. In the case of anionic macromolecules, sodium ions make significant effects on their secondary structure. In the CD-ACA systems, the strong interactions of Na^+ ions with COO^- groups of ACAs shift the equilibrium of complex formation towards dissociation of the complexes. We propose a molecular mechanism explaining the effects of ions, based on competition between the ions and water for binding with the ionized carboxylate groups of the studied biomolecules.

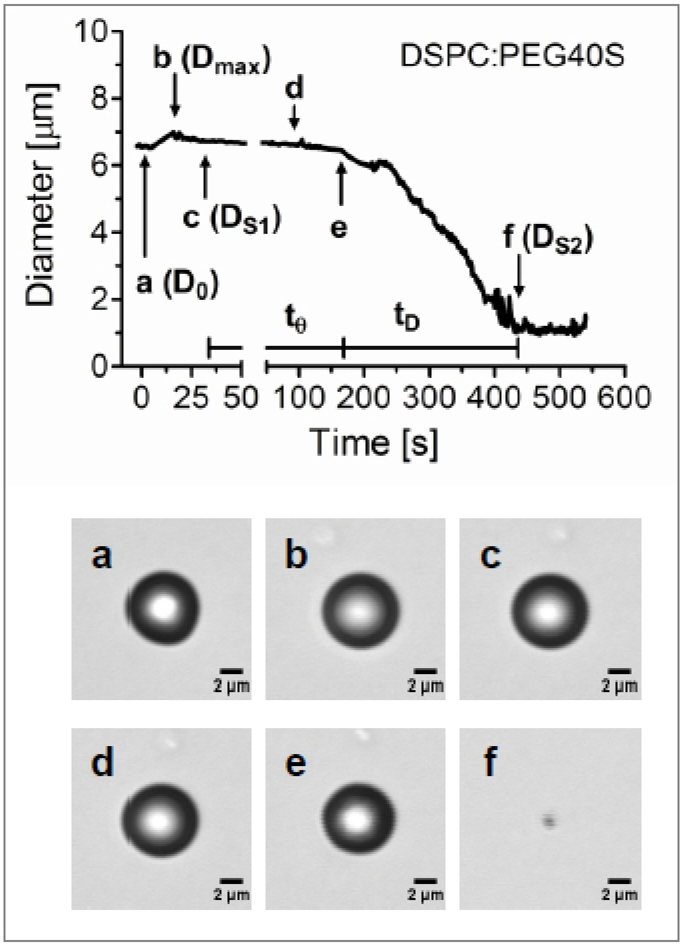
COLL 401

Dynamics of Lipid-Coated Microbubbles

Mark Borden(1), *mark.borden@colorado.edu, 1111 Engineering Drive, Boulder CO 80309, United States ; James Kwan*(2). *(1) Mechanical Engineering, University of Colorado, Boulder CO 80302, United States (2) Chemical Engineering, Columbia University, New York NY 10027, United States*

Microbubbles are prevalent in natural systems, industrial processes and biomedical applications. Each microbubble is stabilized against coalescence and Laplace pressure-driven dissolution by a self-assembled monomolecular film of lipids, which imparts mechanical stability and resistance to gas permeation. Previous experimental and modeling efforts have elucidated the mechanical properties and gas permeability for static (constant size) microbubbles. However, little is known about the effects of the microbubble shell on the dynamic properties of a microbubble subject to variable size. Such effects are critical to understanding the fate of a microbubble injected into the bloodstream or stimulated by ultrasonic acoustic waves, for example. We recently performed a series of experiments to probe the dynamic behavior of the lipid monolayer film in response to growth and dissolution in a multi-gas environment. Our results showed that the monolayer resists expansion and subsequent compression beyond the equilibrium state of the resting microbubble. These data indicate an anisotropic break-up of the shell. Interestingly, the monolayer arrests dissolution at small diameters, typically around 1-2 microns, independent of the initial size. The experimental data was analyzed using a model for the gas transport and surface viscoelastic terms. Our results show that the microbubble dynamics can be modeled fairly well with a yield stress and exponential strain-softening elasticity and viscosity terms. These results will be presented in the context of microbubble ultrasound contrast agents used for quantitative

medical imaging.



COLL 402

Correlation of the optical and SERS properties for molecular nano-probes composed of gold and silver with wide ranging size, structure and composition

Derrick Mott[(1)]*, derrickm@jaist.ac.jp, 1-1 Asahidai, Nomi Ishikawa 923-1211, Japan ; Dao T. Ngoc Anh*[(1)]*; Cheshta Shankar*[(1)]*; Priyank Mohan*[(1)]*; Shinya Maenosono*[(1)]*. (1) Department of Materials Science, Japan Advanced Institute of Science and Technology, Nomi Ishikawa 923-1211, Japan*

Gold and silver core@shell nanoparticles for bio-molecular detection are exciting because of the enhanced sensitivity and tunable optical properties. However, there are few studies that demonstrate control over a wide range of size, structure, and composition for Ag@Au or Au@Ag nanoparticles with tunable shell thickness and core size. As a result, there is a gap in understanding of how the complex structure and composition will impact the optical/SERS activity. Recently, we have synthesized

Ag@Au and Au@Ag nanoparticles over a wide range of size with tailorable shell thickness. The ability has allowed the correlation of the particle structural/composition properties to the optical/SERS activity. Particle properties were studied using techniques including HR-TEM, XPS, ICP-MS, etc,. HAADF-STEM was used with EDS elemental mapping to visualize the core@shell structures along with atomic resolution images, providing definitive elucidation of the structures. Finally, Mie modeling of the optical properties provides insight into the fine structural characteristics.

COLL 403

Screening SERS enhancement using self-assembled plasmonic polyhedral nanoparticle clusters

Joel Henzie(1)*, joelhenzie@berkeley.edu, Room 419 Latimer Hall, Berkeley CA 94720-1460, United States ; Peidong Yang*(1)*. (1) Department of Chemistry, University of California-Berkeley, Berkeley CA 94704, United States*

Optimal sensitivity and reproducibility of analytical techniques like surface enhanced Raman spectroscopy (SERS) requires precise control of metal surfaces with materials dimensions spanning millimeter to sub-nanometer length scales. At the lower end of these sizes, efforts in nanofabrication remain an interesting physical and chemical challenge because sub-nanometer control is difficult to achieve using processes such as lithography. Colloidal noble metal nanocrystals can be synthesized as monodisperse polyhedral shapes, with facets that are atomically smooth. We will show how a combination of nanoimprint lithography and hierarchical self-assembly of Ag polyhedra can be used to pattern arbitrary arrangements of plasmonic nanoparticle clusters with nanoscale, highly reproducible interparticle gaps. By controlling the geometry of these assemblies, we can screen for optimal SERS enhancement at multiple wavelengths, and also tune their optical properties from the UV to the mid-infrared.

COLL 404

Optical Sizing of Immunolabel Clusters through Multispectral Plasmon Coupling Microscopy

Bjoern Reinhard(1)*, bmr@bu.edu, 590 Commonwealth Avenue, Boston MAssachussetts 02215, United States . (1) Boston University, United States*

The wavelength dependent scattering cross sections of self-assembled silver nanoparticle clusters of known size (n) were measured on five different wavelength channels between 427 and 510 nm through correlation of multispectral imaging and scanning electron microscopy. A multivariate statistical analysis of the spectral response of this training set provided a correlation between spectral response and cluster size and enabled a classification of new measurements into four distinct nanoparticle association levels (I1-I4) whose compositions were dominated by monomers (I1), dimers (I2), trimers and tetramers (I3), and larger clusters (I4), respectively. One potential application of the optical sizing approach is to map association levels of silver immunolabels on cellular surfaces. We demonstrate the feasibility of this approach using silver immunolabels targeted at the epidermal growth factor receptor on A431 cells in a proof of principle experiment. The ability to measure immunolabel association levels on subcellular length scales in an optical microscope provides new opportunities for experimentally assessing receptor density distributions on living cells in solution.

COLL 405

High sensitivity carbon nanotube based electrochemiluminescence sensors

***Anita Venkatanarayanan**(1), Anita.Venkatanarayanan@dcu.ie, National Center for Sensor Research, Dublin City University, Glasnevin, Dublin Dublin 9, Ireland ; James F Rusling(2); Robert J Forster(1); Tia E Keyes(1). (1) School of Chemical Sciences, Biomedical Diagnostic Institute, National Center for Sensor Research, Dublin City University, National Center for Sensor Research, Dublin City University, Glasnevin, Dublin Dublin 9, Ireland (2) Department of Chemistry, University of Connecticut, Storrs, Mansfield Connecticut 06269, United States*

Microarrays of protein and DNA are emerging as powerful diagnostic tools since they allow screening of biologically important molecules in a parallel, high throughput manner. However, high density packaging of *active* biomolecules and sensitive detection continues to pose a significant challenge. Nanotube arrays which can detect picomolar concentrations of immunoglobulin G (IgG) through electrochemiluminescence (ECL) detection are reported. Patterned arrays of vertically aligned single walled carbon nanotube (SWCNT) forests were formed on indium tin oxide (ITO) electrodes. Anti-IgG was coupled to carboxyl terminals of SWCNT forests and the IgG was labeled with G1.5 acid terminated PAMAM dendrimer and 800 nm silica nanoparticles decorated with high brightness luminophore, $[Ru(bpy)_2PICH_2]^{2+}$, where $PICH_2$ is (2-(4-carboxyphenyl)imidazo[4,5-f]1,10]phenanthroline. Considerable ECL enhancement was achieved in the presence of sodium oxalate co-reactant. Significantly, these sensors show wide linear dynamic range, 10^6 - 10^{12} IgG coated spheres, very low detection limit, (1.1±0.1) $\times 10^{-12}$ M IgG and multiplexing capability.

COLL 406

Graphene-based nanomaterials and nanostructures: synthesis, characterization and applications

***Hua Zhang**(1), hzhang@ntu.edu.sg, 50 Nanyang Avenue, Singapore Singapore 639798, Singapore . (1) School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore*

In this talk, I will summarize the research on synthesis, characterization and applications of graphene-based nanomaterials and nanostructures, which my group has done

recently. I will introduce the synthesis and characterization of novel grapheme-based materials, especially the first-time synthesized hexagonal close packed Au nanostructures on graphene oxide, and patterned graphene structures. Then I will demonstrate the applications of graphene-based materials in chemical and bio-sensors, solar cells, electric devices, memory devices, conductive electrodes, cell cultures, matrix of MALDI-TOF-MS, etc.

COLL 407

Metal and magnetic nanoparticles as biomolecular probes and antibacterial agents

Chuan-Jian Zhong(1)*, cjzhong@binghamton.edu, Vestal pkwy east, Binghamton NY 13902, United States ; Elizabeth Crew*(1)*; Lingyan Wang*(1)*; Jin Luo*(1)*; Jun Yin*(1)*; Hong Yan*(1)*; Shiyao Shan*(1)*. (1) Chemistry, State University of New York at Binghamton, Binghamton NY 13902, United States*

Molecularly-engineered metal and magnetic nanoparticles have found increasing applications for probing and intervening biomolecular processes in medical diagnostics, drug delivery, bacterial inactivation, and molecular recognition. In this report recent findings in the investigation of metal and magnetic nanoparticles as biomolecular probes and antibacterial agents will be discussed. Examples will focus on gold, silver, and magnetic nanoparticles coated with gold or silver as core-shell type of nanoparticles for intervening DNA assembly/disassembly processes, regulating chiral recognition of enantiomers, inactivating microorganisms, and probing protein binding or drug delivery. Examples from use of the nanoprobes for surface-enhanced Raman scattering detection of biomolecular reactivities will also be discussed. Implications of the results for developing biomolecular nano-transduction and nano-intervention strategies will also be discussed.

COLL 408

Metal enhanced fluorescence of carbon nanotubes: Observation and application in enhanced cell imaging

Guosong Hong(1)*, guosongh@stanford.edu, 333 Campus Drive, Stanford CA 94305, United States . (1) Chemistry, Stanford University, Stanford CA 94305, United States*

Metal enhanced fluorescence (MEF) of single-walled carbon nanotubes (SWNTs) was observed for the first time on solution-phase deposited gold films by more than 10 times and applied in near infrared fluorescence enhanced (NIR-FE) cell imaging using SWNTs as fluorescent tags. This novel imaging technique allowed for short exposure, high signal-to-noise ratio and high cell targeting specificity for weak NIR fluorophores such as SWNTs and IR800. The degree of enhancement was revealed to decay monotonically as SWNTs were separated further away from the substrate, which also held tight in the NIR-FE cell imaging and showed distinct degrees of enhancement

depending on whether SWNTs were endocytosed by the cells or not. Single SWNTs were detected and tracked on and across cell membrane at ultralow staining concentrations that were impossible without NIR-FE imaging technique.

COLL 409

Enantioselective adsorption on chiral nanoparticles

Andrew John Gellman[(1)]*, gellman@cmu.edu, 5000 Forbes Ave., Pittsburgh PA 15213, United States ; Nisha Shukla*[(1)]*; Melissa Bartel*[(1)]*. (1) Department of Chemical Engineering, Carnegie Mellon Univeristy, Pittsburgh PA 15213, United States*

Nanoparticles can adsorb chiral compounds enantioselectively. The surfaces of Au nanoparticles have been modified with D- or L-cysteine to render them chiral. Their enantioselectivity has been probed by optical rotation measurements when exposed to racemic mixtures of chiral probes molecules such as propylene oxide (PO) and 2-butanol. Detect of enantiospecific adsorption by optical rotation arises from the fact that the specific rotation of polarized light by R- and S-PO is enhanced by interaction Au nanoparticles. Chiral Au nanoparticles selectively adsorb one enantiomer of PO from a solution of racemic PO, thus inducing a net change in optical rotation by the solution. A simple model has been developed that allows extraction of the enantiospecific equilibrium constants for R- and S-PO adsorption on the chiral Au nanoparticles. Temperature dependent measurements of the adsorption equilibria allow extraction of enantiospecific heats of adsorption of the chiral probe on the chiral nanoparticle.

COLL 410

Polyelectrolyte-colloid coacervates: Is soluble aggregate structure preserved?

Paul L Dubin[(1)]*, dubin@chem.umass.edu, 710 N Pleasant St, Amherst MA 01003, United States ; Ebru Kizilay*[(2)]*; Anthony Dinsmore*[(3)]*; Simona Maccarrone*[(3)]*; Elaine Foun*[(1)]*. (1) Department of Chemistry, University of Massachusetts, Amherst MA 01003, United States (2) Department of Chemistry, University of Massachusetts, Amherst MA 01003, United States (3) Department of Physics, University of Massachusetts, Amherst MA, United States*

The importance of polyelectrolyte-colloid coacervates derives from the preservation of colloid structure and function (e.g. enzyme activity, surfactant micelle solubilization), but the unique dynamic properties of the coacervate arise from hierarchal organization, on many length scales, of the two oppositely charged macrions. To understand how this self-organization develops, we applied dynamic light scattering, turbidimetry and microscopy to follow the thermally induced coacervation of a nonionic-anionic mixed micelle/polycation system, before and after the point of incipient phase separation, T_φ. Interpolymer complexes, forming above a critical micelle surface charge density, generate multipolymer complexes as T approaches T_φ. Just before phase separation, these soluble aggregates split into two species, the smaller one remaining in the dilute

phase after coacervation. This is explained according to disproportionation as suggested by Shklovskii. Its consequences for the mesophase structure of the dense macroscopically homogeneous coacervate fluid can be seen by DLS and CryoTEM.

COLL 411

Film Stability During Post-Assembly Morphological Changes in Polyelectrolyte Multilayers

Chungyeon Cho[(1)]*, cycho78@tamu.edu, Wisenbaker Bld. #156, Spence Street, College Station Texas 77843-3003, United States ; Nicole S Zacharia*[(1)]*. (1) Materials Science & Engineering, Texas A&M Univeristy, College Station / College Station Texas 77840, United States*

Reported here is an investigation of the origin and mechanism of the porous transition in polyelectrolyte multilayers consisting of linear poly(ethylenimine) (LPEI) and poly(acrylic acid) (PAA), and poly (allylamine hydrochloride) (PAH) and PAA under both post-acid and post-base treatments. Depending on the pH treatment and immersion time, these LbL films showed a number of morphological transformations, ranging from the creation of pores to collapsed structures and finally, the partial dissolution of films under post-base treatment. This porous transition is closely related to the neutralization of the polycation electrolytes and the ionization of polyanion electrolytes by exposing the LbL films to high pH solutions. Results obtained from QCM and FT-IR suggest that a selective or partial dissolution of polyelectrolytes is possible according to the pH treatment or exposure time. We conclude that the morphological transition is due to a combination of molecular rearrangements and the extent of release of polyelectrolytes during post-assembly treatments.

COLL 412

Solubility of polyelectrolyte complexes and relation to layer-by-layer films

Nicole Zacharia[(1)(2)]*, nzacharia@tamu.edu, 3123 TAMU, White (non-Hispanic) Texas 77843, United States ; Lauren Link*[(2)]*. (1) Department of Mechanical Engineering, Texas A&M University, College Station TX 77840-1833, United States (2) Materials Science and Engineering Program, Texas A&M University, College Station TX 77840-1833, United States*

Polyelectrolyte complexation is a difficult to understand process with many implications for the formation of polyelectrolyte multilayers (PEMs). Understanding of the phase diagram of polyelectrolyte coacervates may lead to greater insight to the assembly of PEMs as well. Our lab has investigated the deconstruction or dissolution of PEMs in terms of the complexes released upon exposure to extreme changes in pH or high ionic strength. Morphological changes in the PEM films can be understood in terms of the complex phase diagram. We have also looked into deposition of complex o create films.

Nonstoichiometric complex can be used to create PEMs, with both cation and anion being deposited at each step.

COLL 413

Assembly and Disassembly of Multilayered Polyelectrolyte Thin Films

Marina Tsianou(1)*, mtsianou@buffalo.edu, 304 Furnas Hall, Buffalo New York 14260-4200, United States ; Biswa P. Das*(1)*. (1) Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York (SUNY), Buffalo NY 14260-4200, United States*

Multilayered thin films have been the focus of intense research because of their vast array of applications. We investigate the growth and disassembly under different pH conditions of layer-by-layer (LbL) films composed of oppositely charged polyelectrolytes (including poly(diallyldimethylammonium chloride) (PDDA), poly(styrene sulfonate) (PSS), and poly(acrylic acid) (PAA)) and synthetic clays. We focus on the fundamentals governing the LbL assembly and triggered disassembly in order to get a better understanding of the mechanisms that control the internal ordering and organization in these films. We have confirmed the presence of layering in these nanostructures by scanning electron microscopy (SEM), obtained the surface roughness via atomic force microscopy (AFM), determined the regular spacing in these layers by X-ray diffraction (XRD), and studied the layer growth and disassembly using UV-vis absorbance spectroscopy. We evaluate the structural characteristics and properties of these multilayers, and we are especially interested in investigating their sensitivity and stability to external stimuli such as pH, temperature, humidity, and ionic strength.

COLL 414

Substrate influence on the structure and properties of polyelectrolytes multilayers

Chloe Chevigny(1)*, chloe.chevigny@tu-berlin.de, Strasse des 17. Juni 124, Berlin Berlin 10623, Germany ; Ralf Koehler*(1)*; Maximilian Zerball*(1)*; Regine von Klitzing*(1)*. (1) Department of Physical and Theoretical Chemistry, Stranski Lab., TU Berlin, Berlin Berlin 10623, Germany*

Polyelectrolytes Multilayers (PEM) are a very versatile and interesting tool for many technical applications. In order to better understand the functionalities of these systems and find new applications, fundamental studies are always needed. We focus on the properties profile across the film and on the effect of the solid substrate: over which length scale the substrate affects the film properties, and from which distance does the film reach bulk properties? Several surfaces types are studied and the properties of the multilayers determined via a combination of ellipsometry, X-rays and neutron reflectivity, QCM-D and AFM measurements. The substrate is found to have an important influence, both on internal structure (thickness of the layers close to substrate, inter-

diffusion) and on specific properties (like water-swelling capacity) of this area of the multilayers. The first PEI layer is also found to greatly influence properties of the whole PEM, like diffusion or elasticity.

COLL 415

Surface charge and molecular adsorption on poly(ethylene oxide)-containing multilayer assemblies

Michael A. Hickner[(1)]*, hickner@matse.psu.edu, 310 Steidle Building, University Park PA 16802, United States ; He Xie*[(1)]*. (1)*

Poly(ethylene oxide)-containing multilayer assemblies were created by sequential electrostatic deposition of anion and cation functionalized poly(ethylene oxide)-poly(urethane) water-soluble polymers. The electrostatic interactions between layers rendered the multilayer films insoluble in water and resistant to disassembly in saline solution. The surface charge of the assemblies depended on the charge of the last layer deposited and could be altered by annealing the assembly in salt water. Protein and poly(saccharide) adsorption on the multilayer assemblies was monitored by FTIR spectroscopy. The adsorption rate depended on the composition of the multilayer, specifically, the last layer deposited. Interestingly, the amide I/II band ratio of bovine serum albumen depended on the surface chemistry of the multilayer assembly presented to solution. This difference was attributed to local pH effects depending on whether anionic or cationic groups were present at the layer's surface.

COLL 416

Ac-electric manipulation of single polyelectrolyte conformations

Y. Elaine Zhu[(1)]*, yingxizhu@gmail.com, 182 Fitzpatrick Hall, University of Notre Dame, Notre Dame IN 46556, United States ; Shengqin Wang*[(1)]*; Richard C Gurtowski*[(1)]*. (1) Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame IN 46556, United States*

Recently we have studied the conformational dynamics of polyelectrolytes under AC-electric fields of varied AC-field frequency and strength. By using florescence correlation spectroscopy (FCS), we examine the structural dynamics of poly(2-vinyl pyridine) (P2VP) at a single molecular level in response to uniform AC-fields between two extended conducting plates, where no net force is imposed on P2VP chains. In stark contrast to an abrupt first-order coil-to-globule transition (CGT) by tuning solution pH, we surprisingly observe a gradual and hysteretic CGT of P2VP conformations within an optimum AC-frequency window and beyond a critical AC-field strength of molecular-weight dependence. The hysteresis is attributed to an asymmetric bistable energy landscape of a single hydrophobic polyelectrolyte chain, whose electrostatic barrier between coil and globule conformations can be reduced below thermal fluctuation energy by AC-field induced polarization due to counterion migration and condensation.

Currently, we further explore the AC-field induced conformational dynamics of surface-tethered P2VP brush chains to thereby control surface hydrophobicity and morphology.

COLL 417

Experimental and theoretical evaluation of ligand distributions in surface-modified nanoparticle systems

Michael R. Bockstaller$^{(1)}$*, bockstaller@cmu.edu, 5000 Forbes Ave, Pittsburgh PA 15213, United States ; Ilhem F. Hakem*$^{(1)}$*; Jeremy Walker*$^{(2)}$*. (1) Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh PA 15213, United States (2) FLIR Systems, Inc., 2240 William Pitt Way PA 15238, United States*

Because of their unique physical properties inorganic nanoparticles are at the center of innovations in technology areas ranging from sensing and imaging to active therapeutic agents. In these applications the synthesis of nanoparticles typically involves the replacement or modification of an initial surfactant with biocompatible and functional groups. In many cases modification reactions are incomplete and result in nanoparticle products with distributed functionality. In this contribution we evaluate both theoretically and experimentally the distribution of ligands of nanoparticles that are modified by incomplete surfactant replacement reactions. A bimodal-type distribution function will be introduced in order to quantitatively describe the distribution of ligands among particles that are modified by incomplete ligand exchange reactions. The theoretical predictions are confirmed using a model system comprised of monodisperse enzyme-based nanoparticles. Finally, the model is used to identify the conditions that facilitate the synthesis of surface-modified nanoparticles with uniform and discrete functionality.

COLL 418

Adsorption, conformation and structuration of thiol-, amine- and silane-based coupling agents at interfaces

Maurice Brogly$^{(1)}$*, maurice.brogly@uha.fr, 3 rue Alfred Werner, Mulhouse Alsace 68093, France . (1) ENSCMu - LPIM, Université de Haute Alsace, Mulhouse 68093, France*

Coupling agent molecules offer numerous technological applications in structural adhesive bonding, thin-film lubrication, corrosion protection. The present study contribute to understanding the mechanisms that govern adsorption, growth, structuration and nano-adhesion properties of coupling agent self-assembly monolayers (SAMs) on both metallic and polymer substrates. Thiol, amine and silane based coupling agent molecules were adsorbed from solution onto different substrates (gold, steel, aluminium, copper, PDMS etc...) in order to reveal the influence of both, the substrate, and head and tail functionalities of the coupling agents, in defining and controlling the organisation and reactivity of self-assembled coupling agents adsorbed as thin films. A variety of analytical techniques were used to characterize the different

substrates: wettability, atomic force microscopy (AFM), polarization modulation infrared reflection absorption spectroscopy[1], ellipsometry etc. All results presented in this work demonstrate the interest of multi-techniques and multi-scales approach in the characterization of ultra-thin organic films.

[1] T. Elzein, S. Bistac, M. Brogly, J. Schultz, Macromol. Chem. Phys., Macromol. Symp. 205, 181 (2004)

COLL 419

Analytical ultracentrifugation to determine polymer coverage on nanoparticle surfaces

Denise N Benoit(1)*, dnl1@rice.edu, 6100 Main Street, MS60, Houston TX 77005, United States ; Huiguang Zhu*(1)*; Hema L Puppala*(1)*; Carolina O Avendano*(1)*; Yousif Shamoo*(2)*; Vicki L Colvin*(1)*. (1) Department of Chemistry, Rice University, Houston TX 77005, United States (2) Department of Biochemistry and Cell Biology, Rice University, Houston TX 77005, United States*

Control of nanoparticle interactions with their environment can be achieved through surface modification. Differences in surface coverage will lead to variances in the particle behavior. The surface coverage of nanoparticles is assessed for two main characteristics: 1) polymer chain length and 2) grafting density. While polymer chain lengths are usually known before surface functionalization; grafting densities are more difficult to determine and will influence the solubility, stability and toxicity of the particles. The most common methods to measure grafting densities have disadvantages either requiring a destructive technique on large quantities or are only accurate for low molecular weight polymers. This work demonstrates that analytical ultracentrifugation (AUC) can be used as a non-destructive measurement on low sample volumes to effectively determine the polymer coverage on a wide variety of molecular weights. Furthermore, our work evaluates effective grafting densities for phase transfers, stability in ionic conditions and reduced toxicity.

COLL 420

Role of Base in the Formation of Silver Nanoparticles in Presence of Sodium Acrylate as Dual Reducing and Capping Agents

Shun Nishimura(1)*, neoEMECexplore@jaist.ac.jp, 1-1 Asahidai, Nomi Ishikawa 923-1292, Japan ; Derrick Mott*(1)*; Atsushi Takagaki*(2)*; Shinya Maenosono*(1)*; Kohki Ebitani*(1)*. (1) School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi Ishikawa 923-1292, Japan (2) Department of Chemical System Engineering, School of engineering, The University of Tokyo, Bunkyo-ku Tokyo 113-8656, Japan*

In order to control morphologies of nanoparticles (NPs), understanding of NP formation mechanism is one of effective procedures. The formation mechanism of silver (Ag) NPs synthesized with a wet-chemical reduction method using sodium acrylate (SA) as dual reducing and capping agent was investigated with various analytical techniques. The results from both colorimetric study and Uv-vis spectra of reaction solutions suggested the formation speed of Ag NPs was gradually increased with increasing the NaOH concentration. XANES spectra imply that another faster reaction pathway *via* Ag^+ complex and/or $Ag(OH)_x$ species were formed in the presence of NaOH. Generally, it is known that the oxidation reaction was accelerated by the addition of base. Therefore, according to these studies, the additive base such as NaOH plays an important role on the NPs formation due to not only creating new intermediates but also by enhancing the reduction rate by promoting the oxidation of SA.

COLL 421

Polypeptide-based colloidal hybrids: From cores to fuzzy shells

Cornelia Rosu(1)*, crosu1@tigers.lsu.edu, Choppin Hall, 232, Baton Rouge Louisiana 70803, United States ; Rafael Cueto*(1)*; Sreelatha Balamurugan*(1)*; Paul S Russo*(1)*. (1)*

The rapid advance in particle synthesis emerged an increased interest in new architectures targeted to specific applications. Among the other hybrid colloidal materials, polypeptide-coated particles are very appealing because their general synthetic framework can be applied over the uncharacteristically wide range of properties this class exhibits. Among chirality, solubility in oil or water, the synthetic polypeptides have the unique ability to undergo specific conformational transitions. Two methods are usually used to prepare these colloids: *growing from* and *grafting to*. A magnetite or cobalt core was synthesized. Silica and fluorescent coatings were performed and finally azide groups were attached to their surface. Alkyne end-terminated-α-helical polypeptides, such as poly (γ-stearyl-α-L-glutamate) and poly (ε-carbobenzyloxy-L-lysine) were prepared and clicked to the azide surface using CuBr and *N, N, N´, N´*- pentamethyldiethylenetriamine as the catalytic complex. A combination of methods such as FTIR, DLS, AF4, GPC, SOUID, etc., was used to characterize the hybrid particles.

COLL 422

DNA Surface Hybridization: Comparison of Theory and Experiment

Damion L Irving(1)*, damion.irving@gmail.com, 6 metrotech Center, RH607, Brooklyn NY 11201, United States ; Ping Gong*(2)*; Rastislav Levicky*(2)*. (1) Chemical and Biological Engineering, Polytechnic Institute of New York University, Brooklyn New York 11201, United States (2)*

Surface hybridization, in which double-stranded nucleic acid structures form at interfaces from sequence-specific pairing between complementary strands, is extensively encountered in the life sciences for analysis of DNA and RNA sequence composition. The design and interpretation of surface hybridization assays is complicated by poorly understood aspects of the interfacial environment that cause both kinetic and thermodynamic behaviors to deviate from those in solution. The origins of these differences lie in the additional interactions experienced by hybridizing strands at an interface. In this report, an analysis of surface hybridization equilibria is provided for a model system of end-tethered, single-stranded oligonucleotide "probes" hybridizing with similarly-sized, single-stranded solution "target" molecules. An existing theoretical description, and an extended version that also accounts for salt-dependence of duplex formation, are compared to recent experiments performed as a function of salt concentration C_B (0.012 mol L^{-1} to 1 mol L^{-1} sodium phosphate buffer) and probe coverage S_0 (1.8×10^{12} to 1.4×10^{13} sites cm^{-2}). Both models reasonably account for experimental trends when the DNA volume fraction remains below ~ 0.25, corresponding to conditions of low to moderate C_B and S_0. Comparison of the free energy and salt-dependence of surface hybridization with corresponding values in solution points to prominence of probe-probe interactions within the surface environment. Neither model, however, can account for strong suppression of hybridization as the volume fraction of DNA approaches 0.3 under high buffer strength and probe coverage. Under these conditions, experiments reveal that hybridization become insensitive to increases in target concentration despite many available probes; this is attributed to the onset of packing constraints. This suggests that surface hybridization can be understood in terms of: (1) decrease in local target concentration due to probe membrane potential (2) offset to the DG^0 of hybridization (3) change in the formal number of duplex counterions.

COLL 423

Lipid and Protein Separation in Supported Lipid Bilayers

Chunming Liu(1)*, chunming@mail.chem.tamu.edu, ILSB Room 1201A, College Station Texas 77843, United States ; Christopher Monson*(1)*; Hudson Pace*(1)*; Paul Cremer*(1)*.*
(1) Department of Chemistry, Texas A&M University, College Station Texas 77843, United States

The extraction and separation of membrane proteins from cells has traditionally involved the use of detergents and sonication, which can destroy the native structures and activities of these species. This has led to the search for new separation methods of membrane proteins within supported lipid bilayer (SLB) environments, which should help preserve protein structures and activities. Electrophoretic techniques have been previously been applied to the separation of charged lipids on SLB. We have now simultaneously separated membrane-associated proteins and charged lipid mixtures in a charged supported lipid bilayer with vastly improved resolution. Such methods may eventually be extended to the separation of real cell membrane protein samples.

COLL 424

Application of Second Harmonic Generation Spectroscopy to Probe Kinetics of Detergent Molecules Transferring between Emulsion Droplets

***Elsa C.Y. Yan**[1], elsa.yan@yale.edu, 225 Prospect Street, New Haven CT 06520, United States ; YuMeng You[1]; Jian Liu[1]; Aaron Bloomfield[1]; Seth Herzon[1]. (1) Department of Chemistry, Yale University, New Haven CT 06520, United States*

Emulsions are widely used in petroleum, food, and pharmaceutical industries. They are constantly broken and reformulated during manufacturing procedures. Hence, a fundamental understanding of detergent molecules transferring between emulsion droplets is important for optimizing their physical property and stability. However, studying detergent transfer between emulsion droplets remains challenging due to a lack of *in situ* surface-specific techniques. Here, we have developed a method using second harmonic generation (SHG) and a detergent probe molecule, namely MG-octyl. The detergent probe molecule contains an octyl chain and a charged headgroup that is the same as malachite green (MG) known to be effective in generating SHG signals. We have demonstrated that the transfer of MG-octyl between the n-tetradecane/water emulsion particles could be observed *in situ* and in real time. Our results support that the SHG method can be further applied to examine various factors controlling the kinetics of detergent transferring between emulsion droplets.

COLL 425

Monitoring of colloidal stability in sodium caseinate stabilized emulsions using electroacoustic spectroscopy

***Ibrahim Gulseren**[1], igulsere@uoguelph.ca, 129 Food Science Bldg., Guelph Ontario N1G 2W1, Canada ; Milena Corredig[1]. (1) Department of Food Science, University of Guelph, Guelph Ontario N1G 2W1, Canada*

The objective of this study was to employ electroacoustic and ultrasonic spectroscopy as novel non-destructive analysis methodologies for the characterization of concentrated (15%) oil-in-water emulsions *in situ*. Sodium caseinate stabilized emulsions were used as a model system, as their behaviour is well established. The changes in ultrasonic attenuation, and electroacoustic parameters (z-potential and dynamic mobility) were monitored over time, during acid-induced aggregation and flocculation induced by the presence of adsorbing and non-adsorbing polymers. Electroacoustic and ultrasonic parameters were shown not only to accurately measure the particle size distribution and overall charge of the emulsion droplets, but also are techniques well suited to follow *in situ,* without distruption destabilization processes such as sol gel transitions or colloidal aggregation. Electoacoustics was particularly well suited to monitor changes in the spatial distribution between the oil droplets as those occurring during the early stages of aggregation.

COLL 426

Motion analysis of light-powered autonomous silver chloride synthetic motors

Wentao Duan[(1)], *wud109@psu.edu, 104 Chemistry Building, State College PA 16801, United States ; Micheal Ibele*[(1)]*; Ayusman Sen*[(1)]*. (1) Department of Chemistry, Penn State University Park, State College PA 16801, United States*

Powered by UV light, micrometer-sized silver chloride (AgCl) motors do autonomous movement and form “schools” in aqueous solution, as our group previously reported.We track and then analyze motion of three groups of AgCl particles: particles that are in the formed “schools” with more than four particles around (within a radius of three particle body sizes), coupled particles that are outside the school yet have one to three particles around, and isolated particles. By plotting time-averaged mean squared displacement (MSD) of each particle over different time intervals , we discover different diffusion behaviors for the three groups of AgCl particles: schooled particles show subdiffusive behavior due to the confinement in the school, coupled particles mainly show normal diffusion behavior, and isolated particles show superdiffusive behavior by a combination of powered diffusion and brownian rotation. These results reveal correlation between movements of motor particles with their neighboring ones, and leads to a better understanding of the hydrodynamics properties of the synthetic motors.

COLL 427

Fluorescence-based Detection of Human Cardiac Troponin I using a Chemically-attached Mutant Antibody Modified Quartz Slide

Ravi A Patel[(1)], *r.patel12@umiami.edu, 1301 Memorial Drive, Cox Science Bldg., Coral Gables Florida 33146, United States ; Jhony Orbulescu*[(1)]*; Roger M Leblanc*[(1)]*; Anup Dadlani*[(1)]*; Mark Ensor*[(2)]*; Sanja Trajkovic*[(2)]*; Sylvia Daunert*[(3)]*; Miodrag Micic*[(4)(5)]*. (1) Department of Chemistry, University of Miami, Coral Gables Florida 33146, United States (2) Department of Chemistry, University of Kentucky, Lexington Kentucky 40506, United States (3) Department of Biochemistry and Molecular Biology, University of Miami, Miller School of Medicine, Miami Florida 33101, United States (4) Department of Mechanical and Aerospace Engineering, University of California, Irvine, irvine California 92697, United States (5) MP Biomedicals LLC, irvine California 92697, United States*

Human cardiac troponin I (cTnI) is the main biomarker released in the blood stream after a myocardial infarction episode. This work aims at the detection of cTnI using a monoclonal mutant IgG antibody immobilized onto quartz slide and labeled with fluorescein isothiocyanate (FITC). Surface modification strategies are explored through means of amino- or thiol- groups using appropriate silane derivatives. Surface characterization methods involve ATR-FTIR, UV-vis and fluorescence spectroscopies, and epifluorescence microscopy. The detection method is based on the fluorescence enhancement of FITC upon binding of cTnI to the chemically-attached antibody, caused by the change in the pH of the microenvironment of FITC. We were able to detect 0.4 ng/mL cTnI, a value better than some commercial tests to detect cTnI. Herein, a secondary antibody for detection/signaling is not required, whereas Enzyme-Linked

Immunosorbent Assay (ELISA) does. These results are very promising in developing a bioassay to detect cTnI in blood serum.

COLL 428

Nitric oxide-releasing dendritic scaffolds as novel antimicrobial agents

***Bin Sun**(1), bsun@email.unc.edu, Caudill Laboratories, Room 307, 131 South Rd, Chapel Hill NC 27599-3290, United States ; Yuan Lu(1); Shalini L Chudasama(1); Mark H Schoenfisch(1). (1) Department of Chemistry, University of North Carolina-Chapel Hill, Chapel Hill NC 27599-3290, United States*

Dendrimers are hyper-branched nanostructures possessing multivalent surfaces that allow for use in different biomedical contexts including drug delivery and tissue engineering. We have previously reported the synthesis of dendritic scaffolds capable of controlled nitric oxide (NO) release. Since NO is a diatomic free radical with broad-spectrum antibacterial activity, the design of dendritic scaffolds that store and release large payloads of NO provides opportunities to exploit the potential of these materials as novel antimicrobial agents. Herein, we describe an approach to the synthesis of *N*-diazeniumdiolate NO donor-functionalized dendritic scaffolds that allow for tunable antimicrobial activity via NO release payloads and dendrimer structures. In addition to presenting bactericidal activity of these scaffolds against Gram-positive and negative pathogens, we examine their cytotoxicity using cultured mammalian cells. These results demonstrate that sizes (i.e., molecular weights) and structural features (e.g., steric environments, hydrophobicity, etc.) of the dendrimers play important roles in governing their antimicrobial activity.

COLL 429

Conductive polymer nanotubes patch as an enhanced controlled transdermal delivery system

***Thao M Nguyen**(1), nguyent@umd.edu, 091 Chemistry bldg, College Park Maryland 20742, United States ; Lei Zhu(2); Sungkyoung Kim(1); Seulki Lee(2); Xiaoyuan Chen(2); Sang Bok Lee(1)(3). (1) Department of Chemistry and Biochemistry, University of Maryland, College Park Maryland 20742, United States (2) Laboratory of Molecular Imaging and Nanomedicine (LOMIN), National Institutes of Health, National Institute of Biomedical Imaging and Bioengineering (NIBIB), Bethesda Maryland 20892, United States (3) Graduate School of Nanoscience and Technology, Korea Advanced Institute of Science and Technology (KAIST), College Park Maryland 20742, United States*

Poly(3,4-ethylenedioxythiophene) (PEDOT) nanotubes of well controlled length, wall thickness and diameter are electrochemically synthesized in porous membranes. The intrinsic electrical properties of PEDOT allow for the controlled release of model drugs by varying the potential. The design criterion of the transdermal drug delivery patch system is based on the electrostatic interaction between the PEDOT nanotubes with

anionic model drugs. The oxidation and reduction of PEDOT results in the uptake and release of drugs accordingly. The PEDOT patch has been shown to control the release rate of drugs based on varying the potential strength. Both hydrophobic and hydrophilic drugs have been uploaded into the nanotubes and release *in vivo*. This research highlights potential biomedical applications for PEDOT nanotubes within a broad range of fields such as biomedical engineering, tumor targeting, and pharmacology.

COLL 430

Biocompatible nanocarriers to deliver hydrophobic therapeutics with high loading efficiency and stimuli-responsive release capability

Wan Zheng(1)*, wazheng@mines.edu, 1500 Illinois Street, Golden Colorado 80401, United States ; Liangju Kuang*(1)*; Daoben Hua*(2)*; Daniel L. Gustafson*(3)*; Hongjun Liang*(1)*. (1) Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden Colorado 80401-1887, United States (2) College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou Jiangsu 215123, China (3) Department of Clinical Sciences, Colorado State University, Fort Collins Colorado 80523-1620, United States*

Controlled delivery of insoluble therapeutic agents in a dose-, time-, and site-specific manner across aqueous physiological pathways remains an outstanding challenge, which is particularly troublesome in the fighting of cancers since most chemotherapy agents for the treatment of localized and metastasized cancers are fairly hydrophobic and have narrow therapeutic indices. We report here a nanocarrier design based on biocompatible chitosan and inorganic mesoporous silica. Chitosan is the *N*-deacetylated derivative of chitin, a naturally abundant polysaccharide with excellent biocompatibility, biodegradability, and biosorption properties. Mesoporous silica holds great promise for drug delivery due to its large specific surface area, tunable pore sizes (2-30nm), and abundant surface functionalization options. The nanocarriers have desirable size range (50-200nm) for prolonged circulation, high loading efficiency for hydrophobic pharmaceuticals, and smart drug release profiles in response to physiological stimuli. Preliminary results on nanocarrier design and preparation, prototypical payloads encapsulation, and stimuli-responsive drug release profiles will be discussed.

COLL 431

Aggrecan-mimetic polysaccharide nanoassemblies

Laura W Place(1)*, Laura.w.Place@gmail.com, 1370 Campus Delivery, Fort Collins CO 80523, United States ; Matt J Kipper*(2)*. (1) School of Biomedical Engineering, Colorado State University, Fort Collins CO 80523, United States (2) Department of Chemical and Biological Engineering, Colorado State University, Fort Collins CO 80523, United States*

Aggrecan is an important molecule in the extracellular matrix in articular cartilage; it contributes to the high compressive modulus of cartilage and to joint lubrication.

Aggrecan has a bottlebrush structure made up of a core protein and highly charged glycosaminoglycan (GAG) side chains. One such GAG is chondroitin sulfate (CS), which is a strong polyanion. Chitosan is a natural polysaccharide and is structurally similar to GAGs. Our goal is to graft CS side chains onto chitosan to form a nanostructured polymeric bottlebrush that mimics aggrecan for use as a viscosupplement, and as a carrier to stabilize and deliver therapeutic proteins. Amine groups in chitosan are thiolated and reacted with a maleimide-activated CS. This strategy enables one to tune the degree of substitution of chitosan with CS side chains to see how this parameter affects the solution dynamics and emergent biochemical properties of these new aggrecan-mimetic polymers.

COLL 432

Zwitteration: a step towards replacing PEGylation

Zaki G. Estephan(1)*, zestephan@chem.fsu.edu, 102 Varsity Way, Tallahassee FL 32306, United States ; Philip S. Schlenoff*(1)*; Joseph B. Schlenoff*(1)*. (1) Department of Chemistry and Biochemistry, Florida State University, Tallahassee Florida 32306, United States*

Zwitterions have been recognized as an alternative to PEG that suffers from limitations in biological media such as autooxidation. We recently reported the synthesis of a zwitterion siloxane monomer that covalently binds to silica surfaces. The excellent behavior of this zwitterion in suppressing protein adsorption led us to investigate advantages of using zwitterions as PEG replacements. The properties of the zwitterion siloxane on colloidal and planar surfaces were compared to those of a short chain PEG siloxane under challenging biomimetic conditions. Both surfaces showed similar properties under such conditions. However, the use of the zwitterion siloxane was advantageous in terms of controlling silylation and coverage. A mechanism for suppressing protein adsorption on these surfaces is described using counterion release as a driving force in contrast to the “steric hindrance” model.

COLL 433

Interaction of pyridinium surfactants with cellular membranes: Relevance to nucleic acid delivery

Marc A Ilies(1)*, mailies@temple.edu, 3307 N Broad Street, Philadelphia Pennsylvania 19140, United States . (1) Department of Pharmaceutical Sciences, Temple University School of Pharmacy, Philadelphia Pennsylvania 19140, United States*

The efficient delivery of foreign nucleic acids into target cells for therapeutic reasons using synthetic vectors implies several antagonistic processes. Thus, the vector must compact the nucleic acid and mask its charge before reaching its target, but once internalized it must rapidly disassemble and release the genetic cargo. The process of internalization occurs usually via endocytosis and should not significantly destabilize the

plasma membrane of the cell. However, once internalized, the vector must trigger the rupture of endosomal membrane in order to release the nucleic acid into the cytoplasm.

Pyridinium amphiphiles are well suited for mastering these opposite processes, having a diffuse charge and an elevated lipophilicity of the polar head. We will present our recent results towards efficient pyridinium-based synthetic gene delivery vectors, emphasizing structure-activity relationships across several classes of self-assembling pyridinium amphiphiles with different charge/mass ratios.

COLL 434

DNA Block Copolymer Assemblies with Drastically Enhanced DNA Binding Properties for DNA Detection and Delivery Applications

Xi-Jun Chen(1)*, chen6@sas.upenn.edu, 231 S 34th Street, Dept of Chemistry, Philadelphia Pennsylvania 19104, United States ; So-Jung Park*(1)*. (1) Department of Chemistry, University of Pennsylvania, Philadelphia Pennsylvania 19104, United States*

We have recently developed a novel hybrid nanostructure of DNA block copolymers and nanoparticles. Remarkably, the hybrid assemblies possessed extremely high DNA binding capability. The assemblies bind to complementary DNA even at very low salt concentrations, where plain DNA strands do not form duplex structure. In addition, these assemblies were highly selective in target DNA detection, capable of differentiating single base mismatch. The extraordinary binding capability of DNA block copolymer assemblies was attributed to the ultra-high surface DNA density (e.g., 3.5 x 10^4 strands for assemblies with a diameter of 150 nm). These exceptional DNA binding properties make this hybrid structure an ideal candidate for duplex DNA detection. Furthermore, the DNA block copolymer assemblies were shown to be an effective gene delivery vehicle for gene regulation applications. This talk will discuss the synthesis, DNA hybridization properties, and biomedical applications of the DNA block copolymer assemblies.

COLL 435

DNA hybridization detection using liquid crystals

Stephanie M Malone(1)*, malonesm@colorado.edu, ECCH 111 424 UCN, Boulder CO 80309, United States ; Daniel K Schwartz*(1)*. (1) Department of Chemical and Biological Engineering, University of Colorado, Boulder CO 80309, United States*

Sensitivity to hybridization is the basis for genetic screening techniques such as fluorescence in-situ hybridization (FISH), as well as microarray based assays. Elimination of the fluorescent marker, scanner, and the requisite labor necessary to label the DNA target, however, could allow for the fabrication of cheap and disposable point-of use devices. Previous work demonstrated that double stranded DNA aligns 5CB and MBBA liquid crystals (LC) at 30 degrees to the extension direction, while the

LC aligns parallel to extended single stranded DNA. This difference in alignment is sufficient to detect a single DNA molecule. Detection of double stranded DNA over the background of single stranded DNA will determine the sensitivity of this approach. By orthogonally labeling double and single stranded DNA it was demonstrated that LC alignment is sensitive enough to detect hybridized DNA among single stranded probe molecules. In situ detection of hybridization was also explored.

COLL 436

Hydrophobic conducting polymer films from post-deposition thiol exposure

Timothy W. Hanks(1)*, tim.hanks@furman.edu, 3300 Poinsett Hwy, Greenville SC 29613, United States ; Paul J. Molino*(2)*; Gordon G. Wallace*(2)*. (1) Department of Chemistry, Furman University, Greenville SC 29613, United States (2) ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, AIIM Facility, Innovation Campus, University of Wollongong, Wollongong NSW 2522, Australia*

Conducting polymers are being actively investigated for a broad range of applications, including biosensors, actuators, tissue engineering and many others. Methods for reducing their surface energies have focused on either derivatizing the monomer with a hydrophobic tail or to incorporate a hydrophobic dopant. Here we show that these polymers undergo a reaction with thiols in solution or in the gas phase that increases the contact angles to more than 100° for poly(3,4-ethylenedioxythiophene) and 140° for polypyrrole films. The thiols were incorporated into the films through covalent linkages that were unaffected by either acid or base. The morphology of the films was unaffected by short exposures, however the electrical conductivity was reduced. This approach to conducting polymer surface modification does not require the synthesis of new monomers or the use of special dopants, enabling these parameters to be independently varied to meet other requirements demanded by a particular application.

COLL 437

Electrostatically-driven nanoparticle-protein selectivity

Paul L Dubin(1)*, dubin@chem.umass.edu, 710 N Pleasant St, Amherst MA 01003, United States ; Kaimin Chen*(2)*; Yisheng Xu*(2)*; Vincent M Rotello*(3)*. (1) Department of Chemistry, University of Massachusetts, Amherst MA 01003, United States (2) Department of Chemistry, University of Massachusetts, amherst mA 01003, United States (3) Department of Chemistry, University of Massachusetts, amherst MA 01003, United States*

Cationic surface-modified gold nanoparticles (TTMA) bind proteins at pH below pI, due to electrostatic interaction with the protein's negative domain. Thus, despite itshigher pI, β-lactoglobulin's negative patch causes BLG to bind to TTMA more avidly than bovine serum albumin (BSA). The very different solution stabilities of NP complexes for BSA vs

BLG was attributed to their different charge anisotropy. To further support the proposed role of local protein charge, we studied the relative affinities of the two isoforms of BLG, and found that the replacement of two neutral amino acids in BLG-B by aspartate in BLG-A results in significantly stronger nanoparticle-binding for this variant. Isothermal titration calorimetry revealed that this selectivity arises from difference in the entropy of binding.

COLL 438

Interactions between proteins and stimuli-sensitive core-shell nanoparticles probed by isothermal titration calorimetry

Nicole Welsch(1)*, nicole.welsch@helmholtz-berlin.de, Hahn-Meitner-Platz 1, Berlin Berlin 14109, Germany ; Matthias Ballauff*(1)(2)*. (1) Department of Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin 14109, Germany (2) Department of Physics, Humboldt University Berlin, Berlin 14109, Germany*

For biotechnological applications the adsorption of proteins on nanoparticles has become a very important issue. The interactions with proteins are strongly affected by the surface chemistry of the nanoparticle and the temperature and salinity of the environment. Previously we identified the release of counterions as the main driving force for protein adsorption on highly charged spherical polyelctrolyte brushes using Isothermal Titration Calorimetry.[1] However, stimuli-sensitive nanoparticles change their physico-chemical properties when altering the environmental conditions.[2] Consequently, these particles exhibit a more complicated behaviour regarding the binding affinity. In case of adsorbed enzymes the particle phase transition also affects the catalytic activity.[2] Therefore, in a systematic thermodynamic analysis the role of electrostatic and hydrophobic interactions and of the physico-chemical state of the nanoparticles in protein adsorption is clarified.

[1] Henzler, K. et al *J. Am. Chem. Soc.* **2010**, 132, 3159-3163
[2] Welsch, N. et al *J. Phys. Chem. B* **2009**, 113, 16039-16045

COLL 439

Gold nanoparticle synthesis by natural amino acids: A density functional theory investigation

Stefano Corni(1)*, stefano.corni@nano.cnr.it, via Campi 213/A, Modena Italy, Italy ; Dimitrios Toroz*(1)*. (1) Center S3, CNR Institute of Nanoscience, Modena, Italy*

Gold nanoparticles can be synthesized by reducing chloroaurate(III) ions in the presence of peptides and amino acids. To date, however, the microscopic mechanisms that rule the formation of gold nanoparticles in these conditions are not understood. In this contribution, we shall present the results of a density functional theory investigation

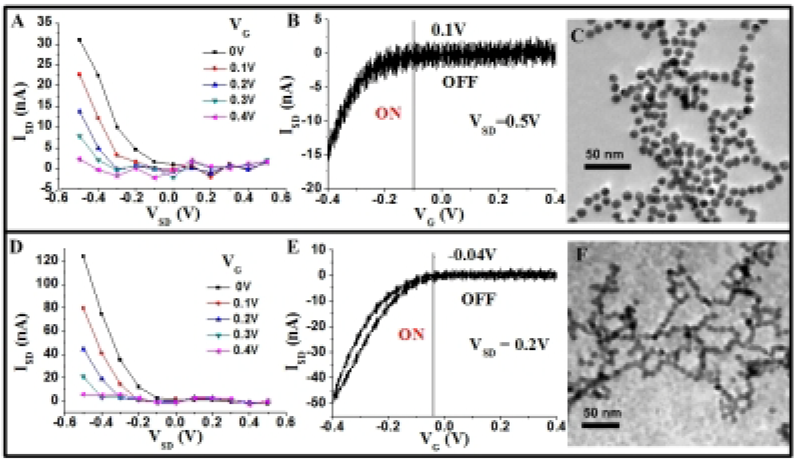
of the chloroaurate reduction in presence of serine and tyrosine. This study is focused on the early steps of the reduction, but already at this stage we find a clear difference between the two amino acids, as tyrosine facilitates the reduction of Au(III) to a greater degree than serine. Based on our results, we also suggest a possible explanation for the experimental behavior of tyrosine-intercalated peptides.

COLL 440

Electrochemical Gating of Single Electron Nanoparticles Necklace Device

Chichao Yu(1)*, cyu2@unl.edu, 220 Othmer Hall, Lincoln NE 68588-0526, United States ; Jason Ong*(1)*; Ravi Saraf*(1)*. (1) Chemical Engineering, University of Nebraska-Lincoln, Lincoln NE 68503, United States*

One dimensional (1D) nanomaterials, i.e., nanowires, have attracted great interest as a platform for detection of biological and chemical analytes in aqueous media. A novel 1D architecture composed of network of gold nanoparticle necklace is presented that behaves as a single electron device that can be electrochemically gated for biosensors. The gold nanoparticle necklaces (Au NLs) are self-assembled by electrostatic interaction (Fig.1C) or “nano-cemented” by a salt (Fig. 1F). The Au NLs are deposited between electrodes and appropriately packaged to study electrochemical gating in ionic solution by modulating the potential of the aqueous media with respect to the necklace. The electrochemical transistor exhibits effective gating phenomenon with current regulation by 13 fold (Fig.1A) and 22 fold (Fig.1D) for the un-cemented and cemented necklaces, respectively. The devices have obvious pinch off properties (Fig. 1B and 1E). The cemented device is more robust and stable in solution compared with the un-cemented device. The study is being extended to biogating where the device will be integrated to living cells to observe their cellular responses to environmental change in solution.



Upper row: Non-cemented Au NLs, Lower row: Nano-cemented Au NLs. (A) and (D) I_{SD}-V_{SD} characteristics of Au NLs devices at varying V_G. (B) and (E) Transfer characteristics (I_{SD}-V_G) with constant V_{SD}. (C) and (F) TEM images.

COLL 441

Thioester-functionalized microspheres as activated surfaces for attaching molecules permanently or reversibly

Paul J. Bracher(1)*, bracher@caltech.edu, Caltech Mail Code 139-74, 1200 East California Blvd, Pasadena CA 91125, United States . (1) Beckman Institute, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena CA 91125, United States*

This presentation will describe the fabrication of thioester-functionalized silica microspheres and their use as activated substrates for attaching molecules either permanently or reversibly. Molecules bearing primary or secondary amines bind to the spheres permanently following soft Lewis acid-mediated aminolysis of the thioesters to form amides. Molecules bearing thiols attach to the spheres by base-catalyzed thiol–thioester exchange. Once bound as thioesters, the molecules can be cleaved from the spheres using a variety of mild conditions, including the addition of base, a different thiol, or a β-aminomercaptan. While thioesters are activated derivatives of carboxylic acids, the microspheres can be stored in water for months to years because the hydrolysis reaction is slow at neutral pH. The binding system is especially amenable to biological applications—it functions in water, at room temperature, near neutral pH, and without harsh reagents.

COLL 442

Competitive Equilibrium Ligand Adsorption onto Gold Nanoparticle for Organothiol Quantification

Dongmao Zhang(1)*, dz33@msstate.edu, 310 Presidential Circle, Mississippi State MS, United States ; Xiaoxia Li*(1)*; Charles Nettles*(1)*; Siyam Ansar*(1)*. (1) Department of Chemistry, Mississippi State University, Mississippi State Mississippi, United States*

Most of AuNP analytical applications take advantage of its unique electromagnetic properties. The competitive ligand adsorption method (CELA) presented herein is a novel AuNP-based analytical method that takes advantage of the *chemical property* of AuNP that organothiols compete with each other and self-assemble onto gold surface. With this method, the analyte and the probe organothiol are mixed simultaneously with AuNP to allow equilibrium adsorption. The concentration of analyte is deduced from the amount of the probe organothiol replaced by the analyte from the AuNP. Using mercaptobenzimidazole as the probe organothiol and homocysteine as the model analyte, the detection sensitivity of this CELA method is ~10 mM. Importantly both the

dynamic range and the detection limit of this method can be readily tuned by combining this CELA with the common sample pre-concentration or dilution methods where the probe organothiol is used as the internal reference for determination of the concentration or dilution factors.

COLL 443

Theory of polyelectrolyte complexes

Murugappan Muthukumar[(1)]*, muthu@polysci.umass.edu, 120 Governors Drive, Amherst MA 01003, United States . (1) Polymer Science and Engineering, University of Massachusetts, 120 Governors Drive, Amherst MA 01003, United States*

The theory of fundamental forces behind the complexation among oppositely charged polyelectrolyte chains in solutions will be presented. The specific issues that will be addressed are the following: (a) Complexation between isolated oppositely charged chains in solution, (b) Competitive displacement of a chain inside a complex by an invading chain, and (c) Complexation of polynucleotides inside viruses.

COLL 444

Layer-by-layer assembly on porous substrates: Molecular dynamics simulations

Andrey V Dobrynin[(1)]*, avd@ims.uconn.edu, Institute of Materials Science, 97 North Eagleville Rd, Storrs CT 06269-3136, United States . (1) Polymer Program, University of Connecticut, Storrs CT 06269-3136, United States*

I will discuss results of the molecular dynamics simulations of a multilayer assembly of oppositely charged nanoparticles and polyelectrolytes on porous substrates with cylindrical pores. The film was constructed by sequential adsorption of oppositely charged nanoparticles and polyelectrolytes in layer-by-layer fashion from dilute solutions. The multilayer assembly proceeds through surface overcharging after completion of each deposition step. There is almost linear growth in the surface coverage and film thickness during the deposition process. The multilayer assembly also occurs inside cylindrical pores. The adsorption of nanoparticles and polyelectrolytes inside pores is hindered by the electrostatic interactions of newly adsorbing nanoparticles and polyelectrolytes with the multilayer film forming inside the pores and on the substrate. This is manifested in the saturation of the average thickness of the layers formed on the pore walls with an increasing number of deposition steps. The distribution of nanoparticles and polyelectrolytes inside the cylindrical pore was nonuniform with a significant excess at the pore entrance.

COLL 445

Dynamic interpolyelectrolyte complexes from ABC triblock terpolymer micelles

Eva Betthausen[(1)]*, eva.betthausen@uni-bayreuth.de, Universitätsstraße 30, Bayreuth Bavaria 95440, Germany ; Felix H. Schacher*[(2)]*; Axel H. E. Müller*[(1)]*. (1) Macromolecular Chemistry II, University of Bayreuth, Bayreuth 95440, Germany (2) Laboratory of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Jena 07743, Germany*

Dynamic interpolyelectrolyte complexes, IPECs, are formed between amphiphilic ABC triblock terpolymer micelles and oppositely charged polyelectrolytes. We demonstrate that during complexation changes in the aggregation number occur. Even more, the transfer of stimuli-responsive properties from double hydrophilic block copolymers such as poly(acrylic acid)-*block*-poly(*N*-isopropyl acrylamide) to the IPEC particles has been realized. The "precursor" micelles are formed by polybutadiene-*block*-poly(methacrylic acid)-*block*-poly{[(2-methacryloyloxy)ethyl]trimethylammonium methylsulfate} (PB-*b*-PMAA-*b*-PDMAEMAq) $B_{800}MAA_{200}Dq_{285}$ terpolymers, which self-assemble into core-shell-corona micelles in aqueous solution. At high pH, the micelles exhibit an intramicellar-IPEC shell formed by PMAA and PDMAEMAq. Excess PDMAEMAq forms a positively charged corona, which is exploited for further complexation with oppositely charged polyelectrolytes. Different charge ratios, Z, were studied via both dynamic light scattering, DLS, and cryogenic transmission electron microscopy, cryo-TEM. In addition, we investigated the synthesis and encapsulation of nanoparticles within the precursor micelles and the final IPEC particles.

COLL 446

Adsorption of spherical polyelectrolyte brushes on polyelectrolyte multilayers

Christoph Hanske[(1)]*, christoph.hanske@uni-bayreuth.de, Universitätsstraße 30, Bayreuth Bavaria 95440, Germany ; Alexander Wittemann*[(2)]*; Andreas Fery*[(1)]*. (1) Department of Physical Chemistry II, University of Bayreuth, Germany (2) Department of Physical Chemistry I, University of Bayreuth, Germany*

Ordered mesostructures of functional colloids are promising building blocks for future lab-on-a-chip devices such as sensors. The production of these materials demands full control over the effective particle-substrate interactions. We investigate the interaction between polyelectrolyte multilayers and spherical polyelectrolyte brushes (SPB), which are obtained by affixing polyelectrolyte chains to colloidal particles. The responsive surface layers on the colloids allow precise adjustment of the adsorption behavior on polyelectrolyte coated substrates. In the presence of oppositely charged surfaces the amount of adsorbed SPB monotonically increases with the ionic strength, whereas equally charged substrates efficiently prevent colloidal attachment at low salt concentrations. To elucidate the adsorption mechanism we conducted kinetic studies and compared our results with theoretical predictions based on the Random Sequential Adsorption model. The role of counterion release, secondary interactions and electrosteric repulsion is discussed. Furthermore, we present the assembly of two-dimensional arrays of SPB utilizing chemically patterned substrates.

COLL 447

Numerical modeling of polyelectrolyte layer-by-layer assembly

Qiang WANG[1]*, q.wang@colostate.edu, 1370 Campus Delivery, Fort Collins CO 80525, United States . (1) Department of Chemical and Biological Engineering, Colorado State University, Fort Collins CO 80525, United States*

Using a continuum self-consistent field theory, we first studied the adsorption of flexible polyelectrolytes on flat surfaces, and found strong charge inversion by relatively long polyelectrolytes adsorbed on oppositely charged, attractive surfaces in poor solvent at high salt concentrations, which can be understood from the adsorption behavior of neutral (uncharged) polymers in a good solvent. We then modeled the sequential process of layer-by-layer assembly of flexible polyelectrolytes on flat surfaces as a series of kinetically trapped states. Up to 60 depositions of oppositely charged polyelectrolytes (1 and 2) are performed, each followed by a washing step. We have systematically examined the effects of substrate charge density, degrees of ionization of 1 and 2, bulk salt concentrations, solvent qualities for 1 and 2, and their incompatibility on the internal structure and charge compensation of polyelectrolyte multilayers formed by either strongly or weakly dissociating polyelectrolytes. Our results agree with most experimental findings.

COLL 448

Multicompartment Micelles from Self-Assembled Ionic Triblock Terpolymers in Water

Christopher V Synatschke[1]*, christopher.synatschke@uni-bayreuth.de, Universitätsstr. 20, Geb. NW-II, Bayreuth Bavaria 95440, Germany ; Felix H Schacher*[2]*; Axel H E Mueller*[1]*. (1) Department of Macromolecular Chemistry II, University of Bayreuth, Bayreuth Bavaria 95440, Germany (2) Department of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Jena Thuringia 07743, Germany*

We report on the self-assembly of an amphiphilic triblock terpolymer polybutadiene-*block*-poly(*N*-methyl-2-vinyl pyridinium)-*block*-poly(methacrylic acid), PB-*b*-P2VPq-*b*-PMAA in water. At high pH multicompartment micelles with negatively charged PMAA corona were formed. These micelles were shown to respond to external stimuli, such as ionic strength and pH. They form further complexes with quaternized poly(2-(dimethylamino)ethyl methacrylate), PDMAEMAq or its block-copolymer with poly(ethylene oxide), PEO-*b*-PDMAEMAq. The resulting colloidal particles exhibit two dictinctly different adjacent interpolyelectrolyte complex (IPEC) layers. The inner layer consists of the intra-micellar IPEC from P2VPq and PMAA, and the outer layer was the newly formed IPEC from excess PMAA and PDMAEMAq. The resulting complex multicompartment micelles were investigated with DLS and cryo-TEM. Selective loading

of the individual compartments of the micelles (PB core and interpolyelectrolyte complex layers) with dyes or metallic nanoparticles could be shown.

COLL 449

Chain dynamics within polyelectrolyte complexes and multilayers

Li Xu(1)*, lxu3@stevens.edu, DEPT CCBBE, Stevens Inst of Tech, Hoboken NJ 07030, United States ;* ***Aliaksandr Zhuk***(1)*, azhuk@stevens.edu, DEPT CCBBE, Stevens Inst of Tech, Hoboken NJ 07030, United States ; John Francis Ankner*(2)*; Svetlana Sukhishvili*(1)*. (1) Chemistry, Chemical Biology and Biomedical Engineering, Stevens Institute of Technology, Hoboken NJ 07030, United States (2) Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge Tennessee 37831, United States*

Using a series of polycations synthesized by atom transfer radical polymerization, we investigate the relative importance of the effects of polymer charge density, steric hindrance to charge pairing and hydrophobicity on chain dynamics within polyelectrolyte complexes (PECs) and within polyelectrolyte multilayer (PEM) films. Polycations with matched chain lengths, distinct hydrophobicities, various degrees of quaternization and steric hindrance at charged groups were assembled with two different polyanions. Applying fluorescence correlation spectroscopy, ellipsometry and fluorescence recovery after photobleaching, we found that the dynamics of chain exchange within PECs is directly correlated with the mode of PEM film growth. By applying neutron reflectometry to several polycation/polyanion pairs, we have also found that more hydrophobic polycations with larger steric hindrance to ionic pairing showed faster salt-induced interdiffusion rates within PEMs. This indicates a dominant role for steric hindrance over chain hydrophobicity in determining polyelectrolyte dynamics within PECs and PEMs.