Chemistry Seminar Abstracts for the Year 2009

Microalgase-Based Bioremediation and Biofuels

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Abstract: Aquatic microalgae are photosynthetic microorganisms that have great potential to be the solution to growing energy and environmental challenges, as more practical and environmentally benign methods for renewable biofuel production, carbon dioxide sequestration and wastewater remediation. Multidisciplinary collaborative research is conducted to develop economical and environmentally-sustainable technologies for microalgae that utilize carbon dioxide and wastewater as nutrient sources and yield algal biomass that can be converted to biofuels. Unicellular microalgae are fast growing and efficient converters of solar energy and carbon dioxide, thereby producing many times the biomass per unit area of land when compared to terrestrial plants. We have established a collection of microalgae species, specifically native species that adapt well to local environmental conditions and can resist the invasion by undesirable species. Cultivation conditions for the maximum production of algal biomass and target biochemicals have been investigated. Efficient techniques for harvesting and dewatering algal biomass are developed in the lab and tested for the field application. A pilot open-pond cultivation system that can utilize carbon dioxide in the flue gas generated from a coal-fired power plant is constructed for the demonstration of large-scale (10,000 gallons) algae cultivation and harvesting processes. Supercritical catalyst-free transesterification reaction is evaluated for the efficient production of biodiesel from oil-bearing crops including microalgae. Improved methods for pretreatment and hydrolysis of microalgae as cellulosic ethanol feedstock are also being investigated. Ultimately, these innovations will contribute in the development of an integrated self-supported system/process that incorporates the microalgae cultivation process with bio-refinery that is dedicated to algae-based biofuels and products.

Assemblies of Nanoparticles as 3D Scaffols for New Materials: from Mechanically Strong Polymer Crosslinked Aerogels to Porous Iron and Silicon Carbide

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Abstract: Monolithic, low-density 3-D assemblies of nanoparticles, known as aerogels, are pursued for unique properties above and beyond those of their individual building blocks. Specifically, since those materials are characterized by large internal void space (>80% v/v) they demonstrate low thermal conductivity, low dielectric constants and high acoustic impedance. The most common type of aerogels are based on silica and they are environmentally sensitive (hydrophilic, fragil*e*) limiting their practical applications in certain nuclear reactors as Cherenkov radiation detectors, as devices for capture of hypervelocity particles in space (NASA's Stardust Program), and as thermal insulation of electronic boxes aboard planetary vehicles such as the Sojourner Rover on Mars (1997), and the two Mars Exploration Rovers Spirit and Opportunity (2004).

The fragility problem of silica aerogels is traced to well-defined weak points in their skeletal framework, the interparticle necks. Using the surface functionality of the inorganic nanoparticles as a focal point, we have directed attachment of a conformal polymer coating over the entire skeletal framework, bridging the nanoparticles and rendering all necks wider [1,2]. Thus, although the bulk density may increase by a factor of 3 (still an ultra-lightweight material), the mesoporosity (pores in the range 2-50 nm) remains almost unchanged, while the strength of the material can increase by up to a factor of 300 above the strength of the underlying inorganic framework. In that regard, polymer crosslinked aerogels may

combine a multiple of the specific compressive strength of carbon fiber reinforced composites with the thermal conductivity of styrofoam. The crosslinked aerogel technology has been demonstrated with several different polymers such as polyurethanes/polyureas, epoxies and polyolefins, while ~35 different metal and semimetal sol-gel oxides from the periodic table have been crosslinked successfully yielding a combination of structural, magnetic and optical properties. Currently polymer crosslinked aerogels are evaluated as starting materials for the carbothermal synthesis of carbide and pure metal aerogels [3,4], while applications being explored include thermal and acoustic insulation, ballistic protection (armor), membranes for use in separation technology, dielectrics and supports for catalysts.

Transparent Conductors: From Basic Principles to Controllable Properties

Dr. Julia Medvedeva, Dept. of Physics, MS&T

Abstract: Many optoelectronic technologies, including photovoltaic cells, flat panel displays, organic light-emitting diodes and energy-efficient windows, require materials which possess a unique combination of two seemingly contradictory properties - optical transparency and electrical conductivity. Such a combination is attained in a few oxides - doped In_2O_3, ZnO, CdO and SnO_2.

Here, we summarize the key electronic features essential for achieving good carrier transport while maintaining sufficient optical transmission in a typical transparent conducting oxide (TCO). The role of the following factors governing the electrical and optical properties is discussed: (i) the local and long-range crystal symmetry; (ii) the electronic configuration of the cations; and (iii) the carrier generation mechanism employed. The results not only provide microscopic insight into the underlying phenomena in conventional TCOs but also serve as a solid foundation for further search for efficient transparent conductors beyond those traditionally employed.

Investigation of Pharmaceuticals and Personal Care Products in Missouri Natural and Drinking Water Using LC-MS/MS

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Abstract: The trace amount of pharmaceuticals and personal care products (PPCPs) in natural waters has dramatic effects on the aquatic environment. Furthermore, the PPCPs in surface water may also have possible health impacts on humans because surface water is used as drinking water after treatment by water treatment facilities. Therefore, the analysis of pharmaceuticals and personal care products in natural and treated waters become very important to provide information about the removal of PPCPs in drinking water and waste water treatment processes.

In this presentation, a comprehensive method has been developed and validated in two different water matrix for the analysis of sixteen important PPCPs by a single solid phase extraction (SPE) of 0.25 L water sample followed by analysis using liquid chromatography coupled with tandem mass spectrometry.

Sixteen compounds which representing antibiotics, hormones, analgesics, stimulants, antiepileptic and X-ray contrast media were analyzed in both untreated and treated drinking waters. Water samples were collected from 34 different water treatment facilities across Missouri in both winter and summer seasons. The method detection limit for these compounds ranged from 1 to 20 ng/L. The details about method development, method validation, occurrence data, quality assurance and the trend of the PPCPs in different types of water and seasons will be discussed. In addition, the treatability of PPCPs by free chlorine will also be presented.

Synthesis and Fluoride Anion Binding Studies of Fluorinated Boron-Based Anion Receptors

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Abstract: A series of fluorinated boron based anion receptors were synthesized and their fluoride ion binding was studied using spectroscopic techniques. Structures of the fluorinated boroxines, tris(2,6-difluorophenyl)-boroxin (DF), tris(2,4,6-trifluorophenyl)boroxin (TF), and tris(pentafluorophenyl)boroxin (PF), and boroxin-fluoride complexes have been confirmed by comparing their ^{19}F and ^{11}B NMR chemical shifts with those obtained by DFT-GIAO method and also by mass spectroscopic studies.

The stoichiometry of the fluoride anion binding to these boroxines has been shown to be 1:1 using ^{19}F NMR, UV-vis spectroscopy. Further confirmation was obtained by mass spectroscopic studies for DF. UV-vis spectroscopic studies show the co-existence of more than one complex, in addition to 1:1 complex, for perfluorinated boroxin, PF. DFT calculations (B3LYP/6-311G**) show that the fluoride ion complex of DF prefers unsymmetrical, covalently bound structure over the symmetrically bridged species by 12.5 kcal/mol.

Analysis and Occurrence of Disinfection By-Products in Fresh and Salt Water

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Abstract: Haloacetic acids (HAAs), trihalomethanes (THMs), and bromate are toxic water disinfection by-products (DBPs) that US Environmental Protection Agency regulated in drinking water. Iodoacetic acids, halonitromethanes (HNMs) are the emerging DBPs that have been recently found in the disinfected drinking waters with much higher toxicity than the regulated DBPs at the same concentrations. This seminar will present our new rapid and sensitive methods [1] for the analysis of these DBPs, the occurrence screening study of the DPBs in 34 Missouri drinking water treatment systems, occurrence and formation studies of these DBPs in seawater/saltwater based aquaria in the SeaWorld Parks. Several types of State-of-the-Arts analytical instrumentations were used to perform the experiments, including ion chromatography-inductively couple plasma/mass spectrometry (IC-ICP/MS), liquid-liquid extraction

followed by gas chromatography-mass spectrometry (LLE-GC-MS), and solid phase microextraction (SPME)-GC-MS. The highly cytotoxic and genotoxic emerging HNMs were detected in most of the Missouri drinking waters with the concentrations in the range from non-detectable to 6.71 μg/L, within the range of the national wide screening studies (up to 10 μg/L). All of these DBPs were formed in the aquaria of SeaWorld Parks at much higher concentrations than those in the drinking water. These DBPs are not only harmful to the SeaWorld Park workers and marine animals; they may also be the major causes of the eye irritation problems in the SeaWorld Park aquaria [2].

Mesoscopic Physics of Photons: Particle Versus Wave Trasport Through Random Media

Dr. Alexey Yamilov, Dept. of Physics, MS&T

Abstract: The term mesoscopic physics refers to a wide range of quantum (or, more precisely, interference) phenomena which occur in solids between the macroscopic and microscopic size. Quantum or not, the interferencephenomena are common to waves of any nature, including the electromagnetic waves. I will explore the similarities and differences between mesoscopic electronic transport and the light propagation in disordered media. In particular, I will discuss an exciting possibility of coherent amplification of photons which adds a new dimension to the fundamental study of mesoscopic transport and leads to a new physical phenomenon - random lasing.

Traditional and Non-traditional Chemistry Careers

Lisa Balbes, ACS Career Personnel

Abstract: A chemistry background prepares you for much more than just a laboratory career. The broad science education, analytical thinking, research methods, and other skills learned are of value to a wide variety of types of employers, and essential for a plethora of types of positions. By understanding your own personal values and interests, you can make informed decisions about what career paths to explore, and identify positions that match your needs. This talk will discuss a variety of traditional and nontraditional careers for chemists, including positions in industry, academia and government, chemical information, patent work, technical writing, education, human resources, sales and marketing, and much more. We will discuss typical tasks, education or training requirements, and personal characteristics that make for a successful career in each field, illustrated with specific examples. Valuable tips and advice about planning career transitions will also be provided.

Dynamics of Polymers at Interfaces using TMDSC and Deuterium NMR

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Abstract: The effect of molecular mass on the adsorption of poly(methyl methacrylate) (PMMA) on silica was determined by using temperature-modulated differential scanning calorimetry (TMDSC). A two-component model, based on loosely-bound polymer with a glass transition temperature (T_g) similar to that of bulk polymer and more tightly-bound polymer with a T_g higher than that of the loosely bound polymer, was used to interpret the thermograms. PMMA (with a high and medium molecular masses of 450 kDa and 85 kDa, respectively) had similar amounts of tightly bound polymer (approximately 0.78 mg/m^2) adsorbed on the surface of silica with a corresponding thickness of about 0.65 nm.The low molecular mass, 32 kDa PMMA, had a smaller amount of tightly bound polymer (about 0.48 mg/ m^2) adsorbed on the silica surfaces, corresponding to a thickness of 0.40 nm. The ratios of heat capacity increments of the loosely bound and tightly bound components ($\Delta C_{pA}/\Delta C_{pB}$) in the glass transition regions, indicating the relative mobility of the two components, were also estimated.

A study of the effect of functional groups on adsorbed polymers, such as poly(methyl methacrylate) (PMMA), poly(vinyl acetate) (PVAc) and poly(methyl acrylate) (PMA) on silica surfaces, was also determined using TMDSC. In this study, polymers of high molecular mass (200-450 kDa) were used. The results showed little difference in the amount of the tightly bound component for adsorbed PMMA and PVAc on silica (0.78 mg/m^2), while the amount of the tightly bound in adsorbed PMA on silica showed less, but not significantly different (0.72 mg/m^2) amounts. These tightly bound amounts of polymers adsorbed on the silica surfaces corresponded to the thicknesses of about 0.65 nm for PMMA and PVAc and 0.60 nm for PMA.

The dynamic behavior of a plasticizer that affects bulk and adsorbed PVAc on silica was also studied using deuterium NMR (^{2}H NMR). This study probed the effect of plasticizer on small adsorbed amounts of polymer (PVAc) on silica (approximately 0.8 mg polymer/m^{2}silica). The deuterated plasticizer, dipropylene glycol dibenzoate (DPGDB-d^{10}), was synthesized and used as a plasticizer for PVAc. Bulk PVAc and adsorbed PVAc on silica were prepared with approximately 10% and 25% plasticizer and used for this study. The changes of the lineshape of ^{2}H NMR spectra suggested that, as the temperature increased the motion of the polymer segments also increased, and was even more pronounced in the presence of plasticizer. Additionally, the relaxation times of both pure deuterated plasticizer (DPGDB-d^{10}) and plasticized bulk PVAc were observed.