Chemistry Seminar Abstracts for the Year 2015

Theoretical Tools to Study Dynamics of Planetary Atmospheres

Moumita Majumder, Dept. of Chem., MS&T

Abstract: The evolution of planetary atmospheres speaks to the history of the creation of the universe. The physical and chemical environments of planetary atmospheres vary greatly between different planets, moons and other celestial objects. The types of life found on Earth rely on a limited range of conditions. Understanding the physical and chemical behavior of atmospheres requires tools to treat collisional reaction dynamics in the gas phase. This talk presents methods to compute accurate potential energy surfaces needed to predict the spectroscopy and dynamics of small species.

DNA Engineering: from Structure to Application

Risheng Wang, Dept. of Chem., MS&T

Abstract: Deoxyribonucleic acid (DNA) is the carrier of generic information in living cells, which can replicate itself through Watson-Crick base paring. Over the past three decades, researchers in the emerging field of DNA nanotechnology are using the DNA as structural nanomaterials to build addressable artificial nanostructures in one, two and three dimensions. These self-assembled nanostructures have been used to precisely organize functional components into deliberately designed patterns which have a wide applications in material science, biomedical, electronic and environmental fields. The development of DNA nanotechnology and its potential application will be covered. Then my talk will discuss the design and construction of several DNA nanostructures including: self-assembly of DNA six-helix nanotubes from two half-tube components; Using DNA origami template to organize semiconducting quantum dots (QDs) and gold nanoparticles (AuNPs) and discussing the methods to integrate “top-down” nanofabrication technique with “bottom-up” self-assembly.

In Vitro Study of Wound-healing Capabilities of Bioactive Glass Nanofibers under Various Culture Conditions

Sisi Chen, Dept. of Chem., MS&T

Abstract: Bioactive glass materials have been developed and widely used for biomedical applications such as hard or soft tissue repair and regeneration. Recently developed borate-based, nanometer-scale, fiber-shaped glasses integrated many promising features and study results have

shown that borate bioglass can promote both osteogenesis and angiogenesis, and thus triggered increasing interest in future wound-healing applications especially on soft tissues. However, the underlying biochemical mechanism is still largely unknown. In this study, three different micro- or nano-fibers, one silicate-based (45S5) and one bioactive borate glasses (13-93B3), and one copper/zinc (Cu/Zn) doped borate glass (1605), were examined to investigate their stimulation of vascular endothelial growth factor (VEGF) under varied culture conditions. An *in vitro* dynamic flow control system that mimics the niche environment of the vascular depletion and hyperplasia area in wound-healing regions was used to demonstrate the actual biological compatibility and functionality of the borate glass nanofibers. Cell growth and the secretion of VEGF were monitored along with the release of boron and other nanofiber constituents. The detailed experimental conditions and results under both static condition and dynamic flow condition will be presented and discussed at the seminar.

Terrestrial and Extraterrestrial Studies of Nonexistent Compounds

Dennis J. Clouthier, Dept. of Chem., University of Kentucky

Abstract: Powerful laser-based techniques have been developed over the last two decades for detecting transient and very reactive molecules in very low concentrations. With these methods we have been able to thoroughly characterize species which had previously been classified as "nonexistent" and unlikely to be observable. This talk will describe the technology and experimental techniques for preparing and studying such compounds including our first determination of the length of the carbon-silicon triple bond and the detection of a new phosphorus carbide in the laboratory and in outer space. Practical applications in the characterization of semiconductor growth intermediates, upper atmospheric chemistry, and the chemistry of the interstellar medium will also be discussed.

Toward Automating Two-Dimensional Electrophoresis- a Hybrid Chip Devise for Protein/Peptide Separation

Prof. Shaorong Liu, Dept. of Chem. & Biochem., University of Oklahoma

Abstract: In this presentation, we introduce a chip-capillary hybrid device to integrate capillary isoelectric focusing (CIEF) with parallel capillary sodium dodecyl sulfate – polyacrylamide gel electrophoresis (SDS-PAGE) or capillary gel electrophoresis (CGE) toward automating two-dimensional (2D) protein separations. The hybrid device consists of three chips that are butted together. The middle chip can be moved between two positions to re-route the fluidic paths,

which enables the performance of CIEF and injection of proteins partially resolved by CIEF to CGE capillaries for parallel CGE separations in a continuous and automated fashion. Capillaries are attached to the other two chips to facilitate CIEF and CGE separations and to extend the effective lengths of CGE columns. Specifically, we illustrate the working principle of the hybrid device, develop protocols for producing and preparing the hybrid device, and demonstrate the feasibility of using this hybrid device for automated injection of CIEF-separated sample to parallel CGE for 2D protein separations. Potentials and problems associated with the hybrid device are also discussed.

Cytotoxicitiy is a Function of Multiple Chemical and Physical Properties of Engineered Nanomaterials

Prof. Yue-Wern Huang, Dept. of Biological Science, MS&T

Abstract: It is estimated that by 2017, this field will represent a $48.9 billion market. As engineered nanoparticles (NPs) currently occupy a significant portion of the market and are anticipated to proliferate commercially, there is an urgent need to study their potential impact on human health and the environment. In this seminar, I will present information with regard to what physicochemical properties of nanomaterials influence cytotoxicity. The properties investigated include band-gap energy, surface charge, relative available particle surface binding site, and metal dissolution. Furthermore, I will also present our recent findings in altered cell cycle and inhibition of cell proliferation. Collectively, this information could inform design of safer engineered nanomaterials.

Give Vitamin E Another Chance

Prof. Nukhet Aykin-Burns, Division of Radiation Health UAMS-College of Pharmacy, Little Rock, AR

Abstract: Radiation therapy is frequently used to treat malignant conditions either alone or concomitant with other modalities. 95% of patients who have had radiotherapy suffer from both acute and chronic side effects. Thus, despite discoveries in radiation biology and improvements in radiation technology, there is still a significant need for a safe and effective radio-protector/radiomitigator compound to alleviate the side effects of radiotherapy on normal tissues.

Among the few most promising alternatives are the vitamin E analogs δ-tocotrienol (DT3) and g-tocotrienol (GT3). These compounds have shown significant radioprotectant and radiomitigator

activities with minimal side effects. However, the expense of purification limits their potential use. Two inexpensive natural sources with abundant tocotrienol content have shown protection against radiation induced mitochondrial dysfunction and oxidative stress in human cells and in a murine model, suggesting they are viable sources for tocotrienols that can be used as radioprotectors.

Continuous Flow Reactor for Carbonic Acid Hydrolysis of Biomass

Nicholas Dudenhoeffer, Dept. of Chem., MS&T

Abstract: The increasing need for renewable fuels sources has led to the investigation of different methods that can maximize the bioethanol production from the fermentation of carbohydrate-rich biomass.

The two most commonly used hydrolysis methods for carbohydrate-rich biomass are enzymatic hydrolysis and mineral acid hydrolysis. However, enzymatic hydrolysis is a slow process and mineral acid hydrolysis requires neutralization and generates a waste stream. In this study high temperature water and carbonic acid was used as an alternative to the common mineral acid hydrolysis. Unlike mineral acids, carbonic acid generated from dissolved CO_2 does not require neutralization and eliminates the production of waste. A high pressure continuous flow reactor designed for the treatment of wet biomass using pressurized carbon dioxide was used for the hydrolysis of microalgae biomass. The reaction conditions such as resident time and temperature were optimized for the formation of simple sugars and degradation byproducts. The yield of simple sugars from the direct treatment of whole biomass for 5 minutes reaction at 210°C using 7 MPa CO_2 was very low, but increased to levels similar to the dilute mineral acid hydrolysis when a small amount (0.05%) of sulfuric acid was added. The amount of thermal degradation byproducts such as 5-HMF and furfural was approximately one order higher, however, no inhibition was observed during the subsequent fermentation of hydrolysis substrates to ethanol.

Nanostructured Catalysts Prepared by Atomic/Molecular Layer Deposition

Xinhua Liang, Dept. of Chemical & Biochemical Engineering, MS&T

Abstract: Catalysts are responsible for the production of over 60% of all chemicals and are used in some 90% of all chemical processes worldwide. Heterogeneous catalysts enable many chemical transformations of fossil resources (natural gas, methane, liquid petroleum, coal, etc.)

into useful products. Normally, heterogeneous catalysts consist of small metal particles dispersed on a high surface area porous oxide support. Traditional methods, such as wet-chemical processing, can produce metal particle catalysts as small as several nanometers, but these methods cannot precisely control the size of the catalytic nanoparticles and disperse them homogeneously within the porous substrates. In addition, heterogeneous catalysts cannot selectively convert specific molecules in the reactant mixture to catalyze only desired reactions. Novel approaches are required to synthesize and characterize stable metal nanoparticles catalysts with tightly controlled sizes to further advance the knowledge of their unique size-dependent catalytic behavior. Recently, atomic layer deposition (ALD) has been used to prepare highly active, highly dispersed metal nanoparticles. ALD is a thin film growth technique based on sequential, self-limiting surface chemical reactions, and has focused principally on the formation of thin film oxides with precise atomic layer control. Molecular layer deposition (MLD), which is similar to ALD, can be utilized to deposit pure polymer films or hybrid organic/inorganic polymer films using suitable precursors. Highly porous metal oxide films with well-defined porous structures and precisely controlled thickness down to several angstroms can be prepared from dense organic/inorganic hybrid metal alkoxide films grown by MLD. These ultra-thin films can be used for catalyst encapsulation. In this presentation, I will introduce ALD/MLD chemistry, particle surface functionalization by ALD/MLD, and examples of nanostructured catalysts prepared by ALD/MLD, such as thermally stable size-selective catalysts.

Conversion of Glasses into Biologically Useful Products

Prof. Mohamed N. Rahaman, Dept. of Materials Science & Engineering Director, Center for Biomedical Science and Engineering, MS&T

Abstract: There is growing interest in glasses for use in healthcare. Glasses have the advantage of ease of fabrication and compositional modification. The reactivity of a glass can be controlled over a wide range, from nearly inert to highly reactive, by controlling its composition. While bioinert glasses are used in some medical applications, glasses that react in an aqueous solution such as the body fluid (referred to as bioactive glasses) are There is growing interest in glasses for use in healthcare. Glasses have the advantage of ease of fabrication and compositional modification. The reactivity of a glass can be controlled over a wide range, from nearly inert to highly reactive, by controlling its composition. While bioinert glasses are used in some medical applications, glasses that react in an aqueous solution such as the body fluid (referred to as bioactive glasses) are receiving more research and development interest for medical and dental applications. Bioactive glasses degrade and convert to hydroxyapatite (the mineral constituent of bone) in an aqueous phosphate solution such as the body fluid, releasing ions in the process which can stimulate the gene expression of cells and, thus, enhance bone regeneration and soft tissue healing. The reaction of certain glasses in a phosphate solution can also be used to create phosphate materials near room temperature which have unique architectures, such as hollow

hydroxyapatite microspheres being researched for drug and growth factor delivery. This presentation will describe methods for creating biomedical glasses and converting them into a variety of compositions and architectures for use in applications such as bone regeneration, wound healing and drug delivery.

How Chemistry Promotes Modern Medical Imaging: a Bench-to-Bedside Story about Chemical Exchange Saturation Transfer MRI

Prof. Guanshu Liu, Kennedy Krieger Institute & Russel H. Morgan Dept. of Radiology and Radiological Science, John Hopkins Medical School

Abstract: MRI has become one of the most important medical imaging modalities and is playing indispensable roles in the diagnosis and treatment of many diseases. MRI detection can be further advanced from the anatomical level to the molecular level, with the help of specific molecular probes. Recently, along with the development of MR molecular imaging, Chemical Exchange Saturation Transfer (CEST) has emerged as an attractive MRI contrast mechanism. The CEST MRI contrast is generated simply by transferring the modulated magnetization from water-exchanging protons (OH, NH, or NH2) to their surrounding water molecules (the source of MRI signal), which makes it possible to directly use MRI to detect many diamagnetic molecules in as low as mM concentration range. Thus CEST opens a new gate to accomplish MR molecular imaging with biodegradable and biocompatible compounds, including those already approved for clinical use and even many endogenous biomolecules. In this talk, a brief introduction of CEST MRI mechanism will be first provided, followed by several examples showing its biomedical applications, which are either being tested or ready to be used in the clinic. The importance of chemistry in the development of modern MR imaging will be then discussed.

Functional Nanoporous Polymeric Aerogels: Polyurea and Polyamides

Malik Adnan Saeed, Dept. of Chem., MS&T

Abstract:

Part A: Nanoporous Polyurea from Triisocyanates Reacting with Mineral Acids

Isocyanates react with carboxylic acids and yield amides. What is reported herewith is that transferring that reaction to a range of mineral acids, (anhydrous H_3BO_3, H_3PO_4, H_3PO_3, H_2SeO_3, H_6TeO_6, H_5IO_6 and H_3AuO_3) yields urea. The model system for this study was a triisocyanate,

tris(4-isocyanatophenyl)methane (TIPM), reacting with boric acid in DMF at room temperature yielding nanoporous polyurea networks that were dried with supercritical fluid CO_2 to robust aerogels. Residual boron in the model system was quantified with prompt gamma neutron activation analysis (PGNNA). It was found very low (≤0.05 % w/w) and was shown to come primarily from B_2O_3 (by ^{11}B NMR). Thus, any mechanism for systematic incorporation of boric acid in the polymeric chain, by analogy to carboxylic acids, was ruled out. Retrospectively, it was fortuitous that this work was conducted with aerogels, and the model system utilized H_3BO_3, whereas the byproduct, B_2O_3, could be removed easily from the porous network leaving behind pure polyurea. With other mineral acids results could have been misleading, because the corresponding oxides are insoluble and remain within the polymer (via skeletal density determinations and EDS). On the positive side, the latter is a convenient method for *in situ* doping robust porous polymeric networks with oxide or pure metal nanoparticles (Au in the case of H_3AuO_3) for possible applications in catalysis.

Part B: Ferrocene-based Polyamide Aerogels: Graphitization, Transmetalation, and Use in Heterogeneous Catalysis

Ferrocene-polyamide aerogels (Fc-PA) incorporating one ferrocene moiety in every polymer repeat unit were prepared in one pot via an underutilized reaction between a triisocyanate and ferrocene dicarboxylic acid. Fc-PA aerogels have high porosities (up to 92% v/v of empty space) and surface areas (up to 456 m^2g^{-1}). Upon pyrolysis (800-1400 °C / H_2), Fc-PA aerogels decompose to Fe(0) and carbon but remain monolithic. Fe(0) catalyzes low-temperature graphitization in its vicinity, thus the resulting materials consist of Fe(0) nanoparticles (20-25 nm in diameter, wrapped in graphitic ribbons (4-5 nm thick), and the whole assemblies are embedded in the nanoporous matrix of amorphous/graphitic carbon (C-) aerogels. Such monolithic Fe(0)-doped C-aerogels (Fe@C) were transmetalated (*tm*-) quantitatively with several noble metals without sacrificing the intricate C-aerogel nanostructure. Surface areas and porosities of transmetalated C-aerogels (*tm*-M@C, M: Au, Pt, Pd) remain high (about 100 m^2g^{-1} and 90% v/v, respectively), and their open structure facilitates rapid diffusion of reactants to the metal particles, rendering those materials particularly attractive as heterogeneous catalysts. The latter was demonstrated with reduction of nitrobenzene (Fe@C), oxidation of alcohols (*tm*-Pt@Cand *tm*-Pt@C) and Heck couplings (*tm*-Pd@C). Conversions were consistently high (80-100%), and at the end of each reaction the monolithic *tm*-M@C catalyst was harvested and reused several times without noticeable loss of activity.