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## **The Characterization of Ultrafine Particulate Matter from Combustion Processes (Continued)**

Philip D. Whitefield, Dept. of Chem., MS&T

**Abstract:** This presentation will discuss the need for ultrafine particulate matter (PM) characterization for both environmental, economic and defense related purposes. It will provide a basic introduction to the fast, real time experimental methods employed to determine PM, size distribution, number and mass concentration, composition and hydration properties using extractive sampling methods. The application of these methods will be described using examples from the work of the Aerospace Emissions Program at MS&T. In particular gas turbine engine emission characteristics using conventional and alternative aviation fuels will be described as will the changes observed in the PM properties as the engine exhaust expands and disperses in the engine exhaust plume.

## **Chelating Compounds as Potential Flash Rust Inhibitors in Waterborne Coating Systems**

Jigar Mistry, MS&T

**Abstract:**

### **Part 1: Chelating Compounds as Potential Flash Rust Inhibitors in Waterborne Coating Systems**

Waterborne coatings on ferrous substrates usually show flash rusting which decreases the adhesion of the coating and the corrosion products can form a stain. This study investigates chelating compounds as potential flash rust inhibitors. Compounds being evaluated include amine alcohols, diamines and sulfur containing amines. A new corrosion inhibitor 2,5-(S-acetic acid)-dimercapto-1,3,4-thiadiazole ( $H_2ADTZ$ ) was synthesized. The performance characteristics of this new-generation additive as a flash rust inhibitor were evaluated.

### **Part 2: 1,3,2-Thiadiazolidine-2,5-dithione: Synthesis and Structure of Alkylated Derivatives**

The observed structure of 1,3,2-thiadiazolidine-2,5-dithion (also known as 2,5-dimercapto-1,3,4-thiadiazole (DMTD)) has been previously reported in three different forms including -Dithiol and -Dithion tautomeric isomers. This paper clarifies which structure is the correct one and also reports synthesis and characterization of the structure of mono- and dialkylated DMTD. The methods of x-ray crystallography, NMR spectroscopy and ab-initio electronic structure calculations were combined to aid in understanding the reactivity and structure of each compound.

### **Part 3: Melamine & Aziridine Cure of Acrylic Colloidal Unimolecular Polymers.**

Colloidal unimolecular polymers (CUPs) were prepared and tested for application as a coating resin. These CUP particles were true nano particles and were found to be crosslinkable with melamine and aziridine. Formulations were prepared with melamine for bake cure and with aziridine for both bake and ambient cure coatings. These formulations were evaluated for MEK abrasion resistance, adhesion, hardness, gloss, flexibility, abrasion and impact resistance properties. The formulated new clear coat resin system has a low VOC and good gloss and transparency.

### **Electrodeposition/Electrochemical Reduction of Epitaxial Metal Oxide Films and Superlattices**

Zhen He, Dept. of Chem., MS&T

#### **Abstract:**

**Part 1: Electrodeposition of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  Epitaxial Films and Superlattices.** Spinel ferrites are of interest because of their potential applications in spintronics (spin-based electronics), nonvolatile memories, and magnetoreception devices. Cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) is an inverse spinel ferrite. The utility of  $\text{CoFe}_2\text{O}_4$  is mainly based on its high coercivity, and magnetocrystalline and shape anisotropy. The magnetic and electric properties of  $\text{CoFe}_2\text{O}_4$  depend on its Co:Fe ratio. Here, we present a one-step electrodeposition of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  ( $0 < x < 1$ ) thin films from an alkaline  $\text{Fe}^{3+}$ - $\text{Co}^{2+}$ -triethanolamine solution. The atomic Co:Fe ratio in the deposited  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  thin films can be tuned by controlling the deposition potential. The effects of the chemical composition on the structure and electric properties of the  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  films are investigated. Superlattices in  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  system are also electrodeposited from the same solution by simply pulsing between two potentials. Compared to  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  individual films, superlattices exhibit resistance switching and a more pronounced negative differential resistance (NDR) feature at lower current during perpendicular transport measurements.

#### **Part 2: Room-Temperature Electrochemical Reduction of Epitaxial Magnetite Films to Epitaxial Iron Films.**

The electrochemical reduction of oxides to metals has been studied for decades. Earlier work produced polycrystalline bulk metals. Here, we report that pre-electrodeposited epitaxial face-centered cubic magnetite thin films can be electrochemically reduced to epitaxial body centered cubic iron thin films in an aqueous solution on single crystalline gold substrates at room temperature. This technique opens new possibilities to produce special epitaxial metal/metal oxide heterojunctions and a wide range of epitaxial metallic alloy films from the corresponding mixed metal oxides.

# **Developing Novel Synthesis Protocols for the Fabrication of Functional Nanomaterials for Advanced Devices**

Sukhada Patil, Dept. of Chem., MS&T

## **Abstract:**

### **Patterned Growth of CdTe Nanowire Arrays for High Efficiency Solar Cells.**

In modern nanodevices while nanostructuring is expected to increase the efficiency of the device manifold, the device geometry also plays an important role in determining the practicability of the device. In that regards, the real challenge lies in assembling the semiconducting nanowires in pre-determined regions to increase the signal to noise ratio to a practically useable value. We have successfully developed a simple, reproducible and scalable technique for growing nanowires as dense arrays on patterned substrates through electrodeposition on patterned nanoelectrodes. The success of protocol was tested on CdTe as model system, as CdTe is potential economical substitute for Si. It is easily synthesizable, and has a forgiving composition where the photovoltaic efficiency is retained over a considerable stoichiometry range. The vertically aligned CdTe nanowires grown over large area by our technique were exceptionally homogeneous in terms of the nanowires diameter and length. The ensemble of the CdTe nanowire arrays covering an area of  $65 \times 65 \mu\text{m}^2$ , exhibited a photocurrent density in the mA range, which was higher than that of CdTe film grown under similar conditions. Results for patterned nanowires growth encompassing CdTe and other nanowires growth would be discussed in detail.

### **Synthesis of Superconducting Nanocables of Iron Selenide Encapsulated in Carbon Nanotubes.**

Another technically important material for nanodevices is superconductors. Recent discovery of superconductivity in iron selenide have attracted considerable attention due to the simplicity of the structure. We have synthesized superconducting FeSe nanowires encapsulated inside carbon nanotubes by a simple vapor transport reaction at  $800^\circ\text{C}$ . The superconductivity of these nanocables was determined through magnetic measurement and  $T_c$  of 10K was obtained for the ensemble of nanowires. The FeSe filling length inside the carbon nanotubes could be varied through controlling reaction conditions and the diameter of nanowires could be controlled through reaction parameters. Carbon nanotubes protect the FeSe nanowires from  $\text{O}_2$ /moisture and also under e-beam damage while preserving superconducting characteristics.

# **Designing Novel Synthesis for Production of Functional Nanowires and Nanoarrays of Superconducting and Thermoelectric Materials**

Prachi Sood, Dept. of Chem., MS&T

## **Abstract:**

### **Part A: Quest for obtaining superconducting nanowires from Fe pnictide based superconductors.**

Recently iron pnictide based compounds have been under immense scrutiny owing to discovery of superconductivity in the doped  $\text{LnFeAsO}$  (1111) and the  $\text{AFeAs}$  ( $A = \text{alkali metal}$ ) series. The iron pnictide layer is believed to be responsible for superconductivity in these compounds. Nanostructures of these superconductors are perfect low dimensional models for understanding the fundamental properties of these novel superconductors. The sacrificial template method can be possibly used to synthesize nanostructured morphologies of these superconductors, where, one of the reactants, the binary iron pnictide will be used as a morphology directing agent. We have developed a one-pot soft chemical method to synthesize monodisperse iron arsenide core-shell nanoparticles. These FeAs nanoparticles are phase pure and superparamagnetic as revealed by powder x-ray diffraction and magnetic characterization. The highest  $T_B$  achieved is 247 K. Further, attempts are being made to introduce alkali metal ions in the solution to form nanostructures of the ternary [111] superconducting phase. Results encompassing synthesis of FeAs nanoparticles and LiFeAs nanowires and [111] nanostructures will be presented.

### **Part B: Producing nanowires arrays of high ZT thermoelectric materials.**

Chalcogenides have been proven to have excellent thermoelectric properties. According to recent reports it has been proven that the nanostructures especially the nanowires increase ZT of thermoelectric materials by increasing the phonon boundary scattering. Recently, Na doped PbS-PbTe alloy thermoelectric systems have attracted attention due to their high power factor. Modification of density of states (DOS) by substitution of Te by Se effectively tunes the location of the valence bands of PbTe, which at high doping can maximize promotion of carriers into the heavy hole band to enhance power factor. It can be argued that nano columns of such a system containing basal p-type PbTe layer with cubic PbS with 2% Na doping can further increase the magnitude of ZT. Such functional arrays can be used as practical devices integrated within the device geometry. Preliminary results in this project will be shared.

## Characterization of Polymer Patterns Used in the Metal Castings Process

Hongfang Zhao, Dept. of Chem., MS&T

**Abstract:** Investment casting, known as a lost-wax casting, has been widely employed to manufacture of quality metal components in automobile, aerospace and biomedical industries because of its ability to produce accurate and complex castings. In a investment casting process, a wax pattern is dipped in ceramic slurry to form the ceramic shell and then is removed by melted or burned out in an autoclave to create cavities; molten metal is introduced in the mold and solidified to form the casting. Finally the ceramic shell is destroyed to release the metal castings. While there are some limitations of wax pattern, such as distortion when storing and handling issues due to weight and brittleness. In addition, as the demand of industry, wax pattern could be replaced by polymer pattern because of its advantages of less expansion on heating, facilitated pattern removal, in some cases less expensive and handling easily. Applicability of different low density rigid polymer pattern materials for investment casting process was experimentally investigated. Densities, elastic moduli and thermal expansion of polymer patterns were measured. Pattern removal process from the shell was examined by thermal gravimetric analysis (TGA). Comparison was done among physico-chemical properties of different low density rigid polymer pattern materials important for the investment casting process. The simulation of another metal casting process, lost foam casting, was performed by using Magmasoft to help to predict and improve the casting qualities.

## Occurrence, Degradation, and Control/Limitation of Emerging Drinking Water Contaminants in Missouri Drinking Water Systems

Dr. Honglan Shi, Dept. of Chem., MS&T

**Abstract:** Emerging contaminants in drinking water is a very active research area in recent years due to their common concurrent and uncertain risks to human health. Many drinking water emerging contaminants, including pharmaceuticals and personal care products (PPCP), *N*-nitrosamines (including NDMA), perchlorate, chlorination disinfection byproducts (including halonitromethanes, and iodo-DBPs), cyano(algal)toxins, and pesticide degradation products in Missouri drinking water and source water systems, have been studied. These studies include occurrence screening, formation and degradation, and removal. Due to the very low concentrations of these contaminants in drinking water, several ultra-sensitive and rapid analytical methods have been developed by using state-of-the-art instrumentation such as ultra-fast liquid chromatography tandem mass spectrometry and gas chromatography-mass spectrometry. Major different source waters (river water, lake water, and underground well water) have been included in these studies. Different methods for control and removal of these water contaminants have been developed/evaluated with both adsorption and oxidation

technologies. Different oxidative treatments and conditions, activated carbon and nano-materials for removal efficiency of the contaminants and their precursors will also be overviewed.

## **Rapid Screening Methods for On-Site Pharmaceutical Surveillance**

Connie M. Gryniewicz-Ruzicka, CDER, Division of Pharmaceutical Analysis, U.S. Food and Drug Administration, Saint Louis, MO

**Abstract:** Consumer exposure to poor quality, counterfeit and adulterated pharmaceutical products has prompted the FDA to develop rapid and reliable screening methods to assess the quality and safety of pharmaceutical products. Spectroscopic methods are attractive for this application because portable formats are available and samples can be analyzed on-site with analysis times on the order of minutes. This presentation will briefly describe the current spectroscopic methods, including Raman, near infrared (NIR), x-ray fluorescence (XRF) and ion mobility (IMS) spectrometries, being utilized by the FDA for field surveillance of pharmaceutical products. Method development, chemometric data analysis and field deployment will be discussed.

## **In Vivo Microdialysis Studies of Seizure Induced Oxidative Stress**

Dr. Craig E. Lunte, Dept. of Chem., University of Kansas

**Abstract:** It has been postulated that oxidative stress is a result of several neurobiological conditions, including epilepsy. Epilepsy is a disease that affects 1% of the world's population<sup>1</sup>. Of that 1%, it is estimated that 20% are resistant to current medications<sup>2</sup>. An important secondary effect of seizures is oxidative stress. Oxidative stress is a result of a deviation from the body's natural balance between reactive oxygen species (ROS) and endogenous antioxidants, which act to deplete ROS in the body. Oxidative stress due to epileptic seizures can cause localized neurotoxicity, which can in turn affect a multitude of biochemical pathways. Specifically, localized brain damage from seizures leads to imbalances in ion and neurotransmitter levels, changing membrane potentials, which results in neuronal hyperexcitability. The increase of glutamate and catecholamines and subsequent  $\text{Ca}^{2+}$  influx specifically lead to ROS formation. It has been reported that ROS levels increase during and after seizure events<sup>3,4</sup>. In addition to epilepsy, oxidative stress in the brain plays an important

role in cellular damage due to methamphetamine use<sup>5</sup>, chronic diseases (i.e. bipolar disorder<sup>6</sup>) and in degenerative diseases (i.e. scrapie<sup>7</sup> and Alzheimer's disease<sup>8,9</sup>).

The goal of this study was to use both a status epilepticus steady-state chemical model and a focal seizure model in rats using the convulsant, 3-mercaptopropionic acid (3-MPA), and to compare the changes in striatal neurotransmission to several biomarkers of oxidative stress. *In vivo* microdialysis was combined with electrophysiological methods in order to provide a complete evaluation of the dynamics of the results obtained. The biomarkers monitored included, malondialdehyde (MDA) as a marker of lipid peroxidation, nitrite as a marker of reactive nitrogen species formation, and several prostaglandins. The neurotransmitters monitored were GABA, glutamate, and the catecholamines.

In the status epilepticus (systemic dosing) model, glutamate increased and GABA decreased monotonically while changes in dopamine (DA) concentration were bimodal. Electrical activity in the brain rapidly returned to normal after administration of 3-MPA ceased, while glutamate remained elevated and GABA depressed for several hours after administration ceased. Administration of cyclothiazide (CTZ) diminished neurotransmitter activity but not the changes in GABA and glutamate, possibly indicating Glu receptor desensitization with the seizure model.

Interestingly, in the focal ischemia model, both glutamate and GABA were observed to increase. The increase in glutamate was several times greater than that of GABA, indicating that excitatory processes still dominated. The ECoG data for the focal seizure (local dosing) model were inconsistent and weak when observed. This was a result of the very local nature of the excitatory event and difficulty in co-locating the microdialysis probe and recording electrode.

In this model, MDA was observed to increase upon administration of 3-MPA, indicating that lipid peroxidation was occurring. No changes in nitrite were observed indicating that this was not a result of reactive nitrogen species being formed. A small increase in several prostaglandins has been observed, but the changes are small. We are working to improve our analytical method for determination of prostaglandins and hope to have more significant results in the near future.

## **Nanopore in Personalized Medicine: Single-Molecule Epigenetic Study**

Dr. Li-Qun Gu, Dalton Cardiovascular Research Center, Dept. of Biological Engineering, University of Missouri-Columbia

**Abstract:** Nanopores are nanometer-wide tiny pores fabricated using modern protein engineering and fashion nanotechnology. Due to the molecular-scale pore size, the binding of a single analyte molecule to the pore lumen can characteristically alter the ion current through the pore. The current change is specific to the type of target molecules and their configuration in the



pore, therefore generating a signature that serves as an electronic fingerprint for target molecule recognition. Used as a biosensor, the nanopore can simultaneously identify and quantify multiple target species for a variety of biomedical detections, with targets ranging from metal ions and cellular second messengers to protein and pathogen oligonucleotides. The nanopore is being developed as a rapid, label-free and low-cost technology for DNA sequencing and various genetic and epigenetic detections. Toward this goal, single-molecule nucleic acids and their interaction with nanopore has been extensively characterized, which includes many topics such as how the nanopore conductance is sensitively changed with the sequence of a single-stranded DNA or RNA in pore and how a double-stranded DNA is unfolded. We developed a new generation of programmable nanopore biosensors, called aptamer-integrated nanopore. Such a single molecule detector is integrated with aptamers, *in vitro* created short nucleic acids molecules that mimic antibodies to bind target proteins with high selectivity and high sensitivity. The nanopore sensor is being combined with smart polymers and microfluidics to create robust chip device for future medical diagnosis, treatment, and high-throughput screening at the molecular level. Recently, we proposed a robust nanopore method of differentiating and quantifying cancer-associated microRNAs (miRNAs) in human blood samples, an approach with the potential in non-invasive and cost-effective cancer detection. MiRNAs are small regulating RNA molecules that are recognized as potential biomarkers of cancers.

## **Microchip-based Analysis Systems for Monitoring Biological Events**

Dr. R. Scott Martin, Dept. of Chem., Saint Louis University

**Abstract:** The use of microchip-based devices for performing analytical assays such as separations has become an established research area. While one of the often stated advantages of these systems is integration of multiple processes, there are very few studies that involve the use of microchips to integrate cell-based *in vitro* mimics with an analysis system. This talk will discuss work from our labs on developing such a system. This approach uses a microfluidic device that integrates multiple processes such as cell culture, fluidic pumping, valving, electrophoresis and electrochemical detection. Issues encountered with integrating these otherwise separate techniques will be discussed as will the use of the device to continuously monitor the on-chip stimulated release of neurotransmitters from PC 12 cells. In addition, recent work towards developing polystyrene-based microchip devices to improve the success of on-chip cell culture as well as the performance of electrochemical detection will be presented.

## Chemical Doping of Topological Insulators

Yew San Hor, Dept. of Physics, MS&T

**Abstract:** A novel kind of three-dimensional insulators called topological insulators, which have a bulk insulating gap but non-trivial topological surface states has been discovered. The surface states of these topological insulators show Dirac-like behavior with the spin polarization locked perpendicular to the electron momentum by the effect of strong spin-orbit interaction. As the locking protects the surface electrons from back scattering, they are predicted to have high mobilities. The spin-resolved nature of the surface states has been confirmed in angle-resolved photoemission spectroscopy experiments. However, it has been a challenge to resolve the lack of transport information due to the dominant bulk conductance in the material. By chemical doping, the chemical potential of the material can be tuned to fall inside the band gap and therefore suppress the bulk conductivity. On the other hand, a topological insulator can also be tuned to a bulk superconductor. This means that Cooper pairing is possible in a topological insulator with implications for study of Majorana fermion physics and potential quantum computing devices. Moreover, detection of the surface currents is a crucial first step in the investigation of novel phenomena, such as axion electrodynamics, in magnetic doped topological insulators.

## Comparative Evaluation between N-Acetyl Cysteine and N-Acetyl Cysteine Amide in Acetaminophen-Induced Oxidative Stress

Ahdab N. Khayyat, Dept. of Chem., MS&T

**Abstract:** Acetaminophen (APAP) is the most widely used pharmaceutical analgesic-antipyretic agent in the world, but its toxicity is a common cause of drug-induced hepatotoxicity. With APAP toxicity, cellular glutathione (GSH) is depleted. This results in the availability of N-acetyl-p-benzoquinone imine (NAPQI) that binds to cellular macromolecules, which leads to cell necrosis. N-acetyl cysteine (NAC), a GSH precursor, is the only approved antidote for an acetaminophen overdose. It is a negatively charged molecule that diminishes its penetration into the cells, thereby requiring fairly high doses that increase the side effects. In addition, oral and I.V. administration of NAC in a hospital setting is laborious and costly. Recently, a neutral compound that is structurally very similar to NAC (an amide form of NAC, called NACA) has been developed to improve NAC's bio-availability. Therefore, in this study, we conducted an investigation to determine the mechanism of APAP-induced hepatotoxicity. We also evaluated the hepatoprotective effectiveness of NACA and compared it with NAC in the hepatic cell line, HepaRG. This comparison was based on several oxidative stress parameters, including the levels of intracellular reactive oxygen species, GSH, various antioxidant enzyme activities, mitochondrial membrane potential, and lactate dehydrogenase levels. Our preliminary data shows a dose-dependent decrease in cell viability in HepaRG cells upon exposure to APAP for

24 hours. The cell viability decreased to approximately 50% of the control when treated with 20mM APAP which increased to 70% upon NACA pretreatment. Oxidative stress parameters, upon NACA and NAC pretreatment are compared and discussed.