Friday Morning, November 11, 2016

In-Situ and Operando Spectroscopy and Microscopy for Catalysts, Surfaces, & Materials Focus Topic
Room 101C - Session IS-FrM

In situ Characterization of Nanomaterials

Moderators: Stephen Nonnenmann, University of Massachusetts - Amherst, Xiao-Ying Yu, Pacific Northwest National Laboratory

8:20am **IS-FrM1 In-situ High-Energy X-ray Scattering for Probing Colloidal Nanoparticles in Solution*, Yugang Sun,*** Temple University **INVITED**

Growth and transformation of colloidal nanoparticles are important for synthesizing functional nanoparticles with tailored properties that represent the foundation for enabling nanotechnology. However, the involving chemical and physical processes are very complicated and barely understood, which limits the precise control over the properties of the nanoparticles. In this presentation, high-energy x-ray scattering techniques will be discussed to serve as unique in-situ approach to monitor these processes in real time. High-energy x-rays have strong penetration in reaction solutions, enabling the possibility to probe the solid colloidal nanoparticles with small volume fractions. In addition, the weak absorption of high-energy x-rays in materials can eliminate the possible side reactions. Reaction systems including the synthesis of colloidal silver nanocubes and microwave synthesis of silver nanoparticles have been successfully studied with the high-energy x-ray scattering at the beamline 1ID of Advanced Photon Source (APS)

9:00am **IS-FrM3 Microfluidics Applied to Ultrafast Spectroscopy*, Adrien Chauvet,*** University of Sheffield, UK **INVITED**

The use of ultrafast laser technologies became essential in the characterization of molecular complexes, as these techniques have opened new doors for the study of fundamental photo-chemical and photo-physical behaviour. However the application of laser-based spectroscopy for the study of biological samples came along with technical challenges: On one hand, purified biological samples are sensitive to their environment (e.g. oxygen) and are only available in small (sub-millilitres) quantities. On the other hand, the use of ultrafast laser systems primarily demands that the sample is refreshed at each laser shot, at a few kHz repetition rate. Consequently, there exists a pressing need to apply microfluidics systems in the field of ultrafast spectroscopy.

After a brief introduction on laser spectroscopy, I will describe some of the most common solutions that are currently in use in order respond to the constraints of both, the sample and the analytical system. I will then present our newly developed microfluidic flow cell: the cell, while it is convenient to set-up and to use, is suitable to most laser systems up to ~10 kHz repetition rate, and requires a minimal sample amount of ~ 250 microL. The benefits of such a microfluidic system will be illustrated through the analysis of multi-hemes cytochromes.

9:40am **IS-FrM5 Adsorbate-Induced Structural Changes Precious Metal Nano Catalysts*, Zheng Lu,*** *Y. Lei,* University of Alabama in Huntsville

Metal nanoparticles can exhibit dramatically different catalytic properties compared to their bulk counterparts. The structure of the supported metal nanoparticles can change dynamically under reaction condition such as when molecules adsorb on the surface. A fundamental understanding of the structure of supported nano catalysts under reaction conditions is an important step towards achieving precise structure-reactivity relationship in catalysis and will ultimately lead to better catalysts.

In this work, we combined X-ray absorption spectroscopy (XAS), pair distribution function (PDF) and small angle X-ray scattering (SAXS) measurements to reveal the lattice contraction and expansion of supported small platinum, palladium and Au nanoparticles as a function of the particle size and the adsorbates. X-ray absorption spectroscopy measurements were performed at the sector 10 beamline at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). Scattering data of PDF were collected at beamline 11-ID-B at the APS. High energy X-rays (58 keV) were used in combination with a large area detector. SAXS experiments were performed at the APS 12-ID-B station. The 2D SAXS data were collected on an area detector, a q range of 0.006−0.7 Å-1 with an incident energy of 12 keV.

The support precious metal nano catalysts were studied under selective oxidation reaction conditions.These findings will help us to understand adsorbate-induced structural and chemical changes in precious metal nano catalysts and be useful for improving catalytic activity.

10:00am **IS-FrM6 Understanding the Role of Atmospheric Surface Adsorbates on the Chemical Reactivity of Zirconium Hydroxide Nanopowders using *Operando* Vibrational Spectroscopy*, Robert Balow,*** NRC/NRL Postdoctoral Fellow*; W. Gordon,* Edgewood Chemical Biological Center*; D.E. Barlow,* Naval Research Laboratory*; I. Iordanov, C. Knox,* Edgewood Chemical Biological Center*; V. Bermudez, J. Lundin, J. Wynne,* Naval Research Laboratory*; G.W. Peterson, C. Karwacki,* Edgewood Chemical Biological Center*; P.E. Pehrsson,* Naval Research Laboratory

Much effort has been focused on developing materials and sorbents for decontamination of chemical warfare agents (CWAs); however, CWAs can have different reactivity and decomposition pathways, making it difficult to find an all-in-one decontamination solution. Zirconium hydroxide ($Zr(OH)_4$) has excellent sorption properties and wide-ranging reactivity towards numerous types of CWA and simulants.[1] This reactivity has been attributed to a combination of diverse surface hydroxyl species (terminal, bridging, etc.) and under-coordinated Zr defects. Unfortunately, these promising preliminary results were often obtained under pristine and unrealistic operating conditions in which the potential impact of atmospheric components (e.g. H_2O and CO_2) and trace contaminants (e.g. NO_x, SO_2, H_2S and various hydrocarbons) was not a factor.

A more complete picture of the reactivity under *operando* conditions is necessary to evaluate the potential field use of $Zr(OH)_4$ for CWA decontamination. We couple insights from theory with a suite of *operando* infrared spectroscopy techniques to probe the $Zr(OH)_4$ surface, at ambient pressure, under atmospheric components such as humidity and CO_2. Contaminated surfaces are then exposed to a sarin CWA simulant, dimethyl methylphosphonate, to evaluate the impact of these adsorbed surface contaminants on the decomposition performance of $Zr(OH)_4$.

1. Bandosz, T. J., Laskoski, M., Mahle, J., Mogilevsky, G., Peterson, G. W., Rossin, J. A., & Wagner, G. W. (2012). Reactions of VX, GD, and HD with Zr(OH)4: Near Instantaneous Decontamination of VX. *The Journal of Physical Chemistry C, 116*(21), 11606-11614. doi:10.1021/jp3028879

10:20am **IS-FrM7 *In Situ* Molecular Characterization of the Solid-Electrolyte Interface on Lithium Metal Anode**, *Y. Zhou,* ***Xiaofei Yu****, R. Cao, W. Xu, M. Su, Z. Xu, D.R. Baer, C. Wang, Z. Zhu,* Pacific Northwest National Laboratory

Currently, the main stream anode material in Li ion battery industry is graphite. Though it has been a great commercial success, the energy density of graphite-based Li-ion batteries will reach their limit soon. Li metal is an ideal anode material for next generation rechargeable Li batteries because of its extremely high theoretical specific capacity and very low negative electrochemical potential. It has been over 40 years since the first attempt of using Li metal as an anode; however, large-scale commercial applications are still not achieved due to a few challenges, such as dendritic Li growth and limited Columbic efficiency. Recent years, it has been reported that highly concentrated electrolytes, such as 4.0 M lithium bis(fluorosulfonyl)imide (LiFSI) in 1,2-dimethoxyethane (DME), can result in the dendrite-free plating of Li metal and with high Columbic efficiency. However, the detailed mechanism is not clear. In this research, in situ liquid SIMS was used to molecularly characterize the structure of the Solid-Electrolyte Interfaces (SEI) formed in 1.0 M and 4.0 M LiFSI in DME. The thickness of the SEI in 4.0 M electrolyte is thinner than that in 1.0 M electrolyte. More importantly, less solvent molecules (DME) and Li metal residuals were found in the SEI layer formed in 4.0 M electrolyte. In addition, more F^- was found in the SEI layer formed in 4.0 M electrolyte, indicating that more LiF stays in the SEI layer formed in 4.0 M electrolyte. Our data suggest that the residual solvent molecules (DME) in the SEI layer may play an important role in formation of dendrite and decreasing of Columbic efficiency.

10:40am **IS-FrM8 *In Situ* DRIFTS of TiO_2 Nanoparticles*, Michelle Foster,*** University of Massachusetts, Boston

This project describes recent work focused on the surface chemistry of TiO_2 nanoparticles. These materials are commonly used in photocatalytic systems, where light induced reactions take place at the interface between the nanoparticle and an adsorbed sensitizing molecule. There are two primary classes of photocatalytic reactions: an adsorbate is excited by the light and interacts with the substrate, or the substrate is excited by the light and transfers an electron to the molecule. In both types of catalysis, it is the interaction of the adsorbate with the nanoparticle that truly drives the entire system. To optimize these catalytic processes, a better understanding of the interactions between the nanoparticles and the adsorbate is needed. *In situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is well suited for analyzing the surface reactions on

TiO_2 nanoparticles. These powders are mostly transparent to the infrared and the multi-bounce nature of the diffuse reflectance helps to increase the signal from these low coverage reactions. This project explores, on a molecular level, the reactions between acetic acid and TiO_2 nanoparticles using *in situ* DRIFTS as a function of both temperature and relative humidity. To better understand the reactivity, different crystal structures of TiO_2, including anatase, rutile, and the commercially available P25 are investigated. Using DRIFTS and a high-temperature reaction chamber, we monitor surface changes when the TiO_2 is exposed to water and acetic acid. It is important to first understand how water alone reacts with the surface, creating a surface hydroxyl layer. After the reactivity between water and TiO_2 nanoparticles is clarified, the reaction of acetic acid with the surface of TiO_2 nanoparticles is investigated under a variety of different water coverages to better understand the role surface hydroxyls play in the reaction between acetic acid and TiO_2 nanoparticles.

11:00am **IS-FrM9 In situ Characterization of Green Rust Synthesized in Ionic Liquids by Liquid ToF-SIMS and SALVI***, **Juan Yao**, X. Sui, D. Lao, J. Weisenfeld, Y. Zhou, S. Nune, D. Heldebrant, Z. Zhu, X.-Y. Yu,* Pacific Northwest National Laboratory

Ionic liquids as green solvents have wide applications in material synthesis, catalysis, and separation. A model switchable ionic liquids (SWILs) consisting of 1,8-diazabicycloundec-7-ene (DBU) and 1-hexanol with carbon dioxide (CO_2) gas was chosen to synthesize nanocrystalline green rust. Under anoxic conditions, a nanoparticulate green rust with carbonate (nano GR) was synthesized by the addition of methanol to the degassed switchable ionic liquid (SWIL) solution consisting of 1-hexanol, DBU, CO_2 and iron (II) acetate ($Fe(C_2H_3O_2)_2$). The structure and oxidation state of nanocrystalline green rust were confirmed using SEM, TEM and Mössbauer spectroscopy. More importantly, the molecular structure change of the ionic liquid leading to green rust formation was characterized using in situ liquid using time-of-flight secondary ion mass spectrometry (ToF-SIMS) coupled with a vacuum compatible microfluidic reactor, SALVI (System for Analysis at the Liquid Vacuum Interface). Principal component analysis (PCA) was conducted to identify the key components of the solvated iron acetate in methanol and the green rust synthesized in the SWILs. Our results show that liquid SIMS can be a useful tool to study complex liquids at the molecular level providing insights in predicative synthesis of nanomaterials using environmentally friendly solvents.

11:20am **IS-FrM10 Direct Observation of the Growth and Dissolution Process of SnO_2 Nanowires***, **Bethany Hudak**, Y.-J. Chang,* University of Kentucky*; L.F. Allard,* Oak Ridge National Laboratory*; B.S. Guiton,* University of Kentucky

The vapor-liquid-solid (VLS) nanowire growth mechanism is a widely used synthesis technique known to produce high-quality, single crystalline nanowires. This method was first developed by Wagner and Ellis to grow silicon nanowires, and has evolved to utilize many different catalyst materials with facile control over nanowire length, diameter, and dopant concentrations. While this method is prevalent for the growth of inorganic nanowires, the growth kinetics of the VLS mechanism are not well understood, especially for binary and ternary crystal systems. Theoretical predictions suggest that the VLS growth mechanism is governed by steady-state kinetics, and that the crystal chemistry of the reverse process may be different from that which governs nanowire growth. The use of *in situ* microscopy techniques has advanced the understanding of the VLS growth process and nanowire growth kinetics. Through the use of *in situ* heating and atmosphere control in the transmission electron microscope (TEM), we have developed a method to study the forward and reverse growth mechanism of Au-catalyzed SnO_2 nanowires, the reverse process being dubbed solid-liquid-vapor (SLV) nanowire dissolution. By controlling the total pressure of the sample environment, the forward and reverse growth mechanisms can be directed. This method of observing the growth and dissolution of SnO_2 nanowires should provide an experimental platform to explore features relevant to the VLS growth mechanism, such as saturation concentration of a reactant within a VLS catalyst droplet and the use of VLS catalyst metals for controlled etching of semiconducting materials.

11:40am **IS-FrM11 Probing Glyoxal Aqueous Surface Chemistry by In Situ Molecular Imaging***, **Fei Zhang**, Y. Zhou, X. Sui,* Pacific Northwest National Laboratory*; J. Chen,* Shandong University*; Z. Zhu, X.-Y. Yu,* Pacific Northwest National Laboratory

Aqueous surfaces after photochemical and dark reactions of glyoxal and hydrogen peroxide (H_2O_2) have been studied by a microfluidic reactor coupled with in situ liquid Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) for the first time. Both positive and negative ion mode mass spectra provided complementary information of the surface reactions. Compared with previous results using bulk solutions, our unique liquid surface molecular imaging approach made it possible to observe glyoxal hydrolysis (i.e., first and secondary products, hydrates), oxidation products (i.e., glyoxylic acid, oxalic acid, formic acid, malonic acid, tartaric acid), oligomers, and water clusters (i.e., $(H_2O)_nH^+$, $(H_2O)_nOH^-$) with sub-micrometer spatial resolution. Spectral principal component analysis was used to determine similarities and differences among various photochemical aging and dark reaction samples and controls. Observations of oxidation products give the physical foundation to deduce new reaction pathways at the aqueous surface. The first chemical mapping of water cluster changes between dark and photochemical aging provides the direct physical evidence that glyoxal oxidation affects the hydrophobicity and water microenvironment at the surface. SIMS three-dimensional chemical mapping enables visualization of the surface mixing state at the molecular level. We potentially provide a new way to investigate complex surface reaction mechanisms as an important source of aqueous secondary organic aerosol (SOA) formation in atmospheric chemistry.

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