

Tuesday Afternoon, November 10, 2009

Applied Surface Science

Room: C2 - Session AS+NS-TuA

Nanoparticle and Nanoscale Surface Chemistry I

Moderator: V. Grassian, University of Iowa

2:00pm **AS+NS-TuA1 Hydrogen Interactions on Nanostructured Carbon Aerogel Surfaces**, *T.M. Willey*, Lawrence Livermore National Laboratory, *A. Deriy*, Argonne National Laboratory, *B.J. Kozioziemski*, *M. Worsely*, *G. Nyce*, *J.R.I. Lee*, Lawrence Livermore National Laboratory, *J. Ilavsky*, Argonne National Laboratory, *S. Ghosal*, *K.J. Wu*, *A.V. Hamza*, *T. van Buuren*, Lawrence Livermore National Laboratory

Generating clean power from nuclear fusion has been an elusive goal over the past several decades. Although many incremental improvements continue towards this goal, one of several challenges for inertial confinement fusion (ICF) is to produce inexpensive, highly symmetric and/or highly controlled deuterium-tritium ice layers within millimeter-sized spherical targets. Ultra low density, nanostructured materials such as aerogels could be useful to serve as scaffoldings for forming uniform hydrogen ice layers. We have studied the aerogel structure and as well as nanoscale wetting of liquid hydrogen onto aerogel surfaces using ultra small angle x-ray scattering (USAXS). We have focused on two 30 mg/cc carbon aerogel structures; the first is a dicyclopentadiene (DCPD) polymer aerogel and the second, a carbon nanotube based aerogel. We are able to observe and control nanoscale hydrogen droplet formation within the DCPD structure, while scattering from nanotube-based aerogels indicates wetting with little or no indication of droplet formation. The combination of ultra-low density, hydrogen uptake, and wetting differences are promising developments for materials to be used in designer targets for ICF. Both aerogels, but especially the nanotube-based aerogel exhibit minimal structural changes when submerged and frozen in cryogenic hydrogen.

2:20pm **AS+NS-TuA2 Probing the Surface Chemistry and Catalytic Activity of Bimetallic and Oxide Nanoparticles**, *L. Jones*, *M. Gordon*, University of California Santa Barbara

Catalysis by metallic nanoparticles offers a wide variety of model systems to study and understand the fundamental mechanisms involved in surface chemistry. In addition, dramatic changes in catalytic activity have been observed when transitioning from the bulk phase to nanoscale dimensions. This behavior is mainly due to finite size effects (i.e., unsaturated atoms at surfaces, edges, kinks, and corners), preferred morphologies, or modification of the nanoparticle's electronic structure by the support. Being able to observe these changes as nanoparticles are decreased in size can give more insight into how to tune electronic and structural changes for particular catalytic applications.

In this talk, we will highlight several routes to synthesize monodisperse metallic nanoparticles (Cu, Pt, Au) of sizes <10 nm with different shapes and compositions. We will also discuss the formation of ordered arrays of supported metallic nanoparticles via plasma reduction of micelles containing metallic precursors. The talk will include catalytic studies, in-situ vibrational spectroscopy, and XPS on Cu and its oxides for CO oxidation as a function of particle size, support, and promoters. The Cu/Cu₂O/CuO system has been studied using controlled oxidation and CO/O₂ dosing at various temperatures and pressures, using Raman bands of adsorbates and phonons to investigate changes in catalytic mechanisms, activity, and nanoparticle morphology.

2:40pm **AS+NS-TuA3 STXM Spectroscopy of Individual Polymer-Wrapped Carbon Nanotube**, *J.J. Pireaux*, *X. Gillon*, *S. Abou Rich*, *A. Felten*, University of Namur (FUNDP), Belgium

The intrinsically inert nature of the pristine carbon nanotube (CNT) surface is a severe constraint for several applications such as fabrication of composites in which the CNTs should be homogeneously dispersed in a matrix. To overcome this problem, functionalisation of the CNT surface has been attempted with different methods (chemical or electrochemical modification, polymer grafting, fluorination...). Our most recent approach consists in the use of Inductive RF plasma (13.56 MHz) to polymerize a monomer (acrylic acid or styrene) onto the CNT surface. But when characterizing the composition of such a nano-material with a conventional technique like X-ray Photoelectron Spectroscopy, one faces the problem that typically a sample area of some μm^2 or even mm^2 is probed: this prevents the analysis of an individual modified nanostructure. Moreover, signal originating from impurities present on the nanotube (amorphous carbon, onion-like particles, catalysts residues) cannot be avoided. Clearly, one would like to be capable to carry out the analysis at much higher spatial

resolution. In this context, Scanning Transmission X-ray Microscopy (STXM) has recently been shown to be one of the most appropriate techniques to study carbon nanotubes since it combines both spectroscopy and microscopy with a spatial resolution better than 30 nm: STXM allows indeed to study isolated nanotubes [1,2,3]. In this report, electronic, structural and chemical properties of pristine and plasma treated isolated multiwall carbon nanotubes were studied with STXM at beamline 5.3.2. from the Advanced Light Source (ALS), Berkeley (CA). Analysis of the C1s near-edge absorption fine structure (NEXAFS) was performed showing clear differences between grafted polystyrene, polyacrylic acid and the carbon nanotubes. Chemical mapping at the nanoscale was performed, highlighting polymer rich regions on the nanotubes.

This work is financially supported by the Nano2Hybrids project (EC-STREP-033311) and the RCO Marshall plan.

1. A. Felten et al. Appl. Phys. Lett. 89, 093123(2006).
2. A. Felten et al. Nano Lett., 7, 2435(2007).
3. E. Najafi et al. Small, 4 (12), 2279 (2008).

3:00pm **AS+NS-TuA4 Nanoparticle Characterization using Advanced FESEM/STEM and XPS Instrumentation**, *K.L. Bunker*, *T. Lersch*, *J. Marquis, Jr.*, *G. Casuccio*, *J.D. Piasecki*, *B.R. Strohmaier*, RJ Lee Group, Inc.

Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) are valuable tools for characterizing the structure, morphology, and composition of nanoparticles and nanostructures. TEM can provide high-resolution imaging, crystallographic information, and elemental composition, when combined with energy dispersive X-ray spectroscopy (EDS), but no detailed surface information. FESEM on the other hand, can provide extremely detailed information on surface morphology. Combining the high resolution secondary electron imaging capabilities of FESEM with TEM data to utilize the strengths of each technology provides the opportunity to more fully and accurately characterize nanomaterials. However, the process of transferring samples between separate FESEM and TEM instruments and relocating such small particles is time consuming and tedious. Recently, Hitachi commercialized a high resolution electron microscope that combines the benefits of FESEM and low-kV scanning transmission electron microscopy (STEM) in a single instrument (Model S-5500).

The electron optical design of the S-5500 places the sample at the optimum analytical and imaging working distance. This allows simultaneous acquisition of high-resolution FESEM and STEM images, as well as EDS information. Therefore, a variety of signals can be collected simultaneously including secondary electron and backscattered electron FESEM images and bright field (BF) and dark field (DF) STEM images. Combining this instrument with new silicon drift detector (SDD) technology (Bruker 30 mm^2) allows for high resolution elemental analysis and mapping of nanostructures.

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a highly surface-sensitive and quantitative technique for nanostructured materials characterization. Nanometer scale sampling depth and its ability to provide chemical state information makes XPS an ideal analytical technique for investigating the elemental and chemical composition of nanoparticles. Hence, XPS can provide valuable complementary information to high resolution electron microscopy studies of nanomaterials. This presentation will illustrate the power of using combined FESEM/STEM and XPS analysis through an examination of a variety of nanomaterials. Examples will include (among others): functional thin organic layers on metal surfaces, multi-layer thin film coatings on glass, activated carbon nanoparticles, antimicrobial metal nanoparticles, and carbon nanotubes containing nanoparticle metal catalysts.

4:00pm **AS+NS-TuA7 Behavior of Engineered Nanoparticles in Aquatic Environments – An Overview**, *R.D. Holbrook*, National Institute of Standards and Technology **INVITED**

The behavior of engineered nanoparticles in aquatic systems will be influenced by three main factors: the physiochemical conditions encountered in a specific environment; the nanoparticles' bioavailability; and any transformation that may occur during biological uptake and excretion. Physiological conditions, such as the type and concentration of organic matter and inorganic species, will dictate aggregation kinetics. Environments that encourage nanoparticle stability may increase their persistence in the water column while those that favor instability may result in nanoparticle deposition among bottom sediments. Nanoparticle bioavailability will be dictated by both spatial and phase distribution; large

nanoparticle aggregates bound to sediment material may be less available to aquatic organisms than, for example, single nanoparticles remaining in solution. Biological ingestion and subsequent excretion may result in nanoparticle degradation and/or changes to aggregation behavior. The objective of this presentation is to provide an overview of these three factors as they apply to the fate, transport, and bioavailability of engineered nanoparticles. Information gained from studying naturally-formed nanoparticles (colloids) will be reviewed and case studies will illustrate our current knowledge of engineered nanoparticle behavior.

4:40pm **AS+NS-TuA9 Heads and Tails: Simultaneous Exposed and Buried Interface Imaging of Self-Assembled Monolayers**, *P.X. Han, A.R. Kurland*, The Pennsylvania State University, *S.U. Nanayakkara*, University of Pennsylvania, *M. Blake, C.M. Pochas, P.S. Weiss*, The Pennsylvania State University

We have simultaneously imaged the chemically bound head-groups and exposed tail-groups in bi-component alkanethiolate self-assembled monolayers with molecular resolution. This has enabled us to resolve the controversy of scanning tunneling microscopy image interpretation, and to measure the molecular polar tilt and azimuthal angles. Our local measurements demonstrate that ordered domains with different superstructures also have varied buried sulfur head-group structures.

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