

Wednesday Morning, November 11, 2009

Applied Surface Science

Room: C1 - Session AS+NS-WeM

Nanoparticle and Nanoscale Surface Chemistry II

Moderator: D.J. Gaspar, Pacific Northwest National Laboratory

8:00am AS+NS-WeM1 **Size-dependent Properties and Surface Chemistry of Metal Oxide Nanomaterials**, V. Grassian, University of Iowa

Both natural and engineered oxide nanomaterials play important roles in environmental processes. In the case of engineered nanomaterials, the surface properties can be tailored for a number of different environmental applications including deNO_x catalysis and carbon dioxide removal and conversion. For naturally occurring oxide nanomaterials, e.g. iron oxides, the size dependent properties and surface chemistry will impact biogeochemical cycles. In this talk, some specific examples of the size-dependent properties and surface chemistry of both natural and engineered metal oxide nanomaterials (e.g. titanium dioxide and iron oxide) in environmental processes will be discussed.

8:20am AS+NS-WeM2 **XPS and SEM/STEM Characterization of Silver Nanoparticles Formed from the X-ray-Induced and Thermal Reduction of Silver Behenate**, B.R. Strohmeier, K.L. Bunker, C. Lopano, J. Marquis, Jr., J.D. Piasecki, K. Bennethum, RJ Lee Group, Inc., R.G. White, T.S. Nunney, Thermo Fisher Scientific, UK, R.J. Lee, RJ Lee Group, Inc.

This study is the first reported use of X-ray photoelectron spectroscopy (XPS) to characterize the organometallic compound silver behenate and its X-ray-induced and thermal reduction. Silver behenate is a long-chain silver carboxylate, CH₃(CH₂)₂₀COOAg, that crystallizes as a dimer in a head-to-head configuration. Various silver compounds, including silver behenate, are used as primary components in commercially available photothermographic (PTG) and thermographic (TG) imaging elements. Individual particles of silver behenate powder typically exist as plate-like crystals with surface dimensions of 0.2-2 μm and thicknesses of 100 nm or less. Imaging in PTG and TG devices is based on the formation of silver metal nanoparticles in the 5-30 nm range (and larger aggregates) by the thermal reduction of silver behenate dispersed in a binder incorporated with toner and development chemistry. Silver behenate has also found use as a standard reference material for low-angle calibration of X-ray diffraction instruments because its crystal structure produces a unique multi-peak diffraction pattern.

In this study, the X-ray-induced reduction of silver behenate during exposure to monochromatic Al K_α X-rays in a micro-XPS instrument was investigated as well as its thermal reduction at 100 °C and 250 °C. The X-ray induced decomposition of other silver carboxylates (silver acetate, silver benzoate, and silver trifluoroacetate) was also investigated for comparison to the behavior of silver behenate. In addition, a combined high resolution scanning electron microscope/scanning transmission electron microscope (SEM/STEM) was used in this study to provide complementary morphological information to the XPS results.

Quantitative XPS analysis of silver behenate was consistent with the theoretical C:O:Ag atomic composition. However, brown discoloration of silver behenate powder begins within a few seconds of exposure to Al K_α X-rays and increases significantly with time. Noticeable changes to the XPS spectra and the observed surface composition begin to occur after about 30 minutes of X-ray exposure. Prolonged exposure to Al K_α X-rays resulted in significant changes in the C 1s, O 1s, and Ag 3d peak shapes and positions. Changes in the XPS spectra indicated that exposure to Al K_α X-rays results in the formation of silver metal particles and decomposition of the carboxylic acid portion of the molecule to hydrocarbon species. Thermal reduction of silver behenate powder produced similar changes in the XPS spectra. This study demonstrated that XPS and SEM/STEM are complementary techniques for investigating the chemical composition, morphology, and decomposition of nanomaterials.

8:40am AS+NS-WeM3 **Surface Chemistry of Deuterium Terminated Silicon Nanocrystals and Effect of Surface Passivation on Photoluminescence**, N. Salivati, J.G. Ekerdt, University of Texas at Austin
Although silicon nanostructures exhibit size dependent light emission, which can be attributed to quantum confinement, the role of surface passivation has not yet been fully understood. Since the ratio of surface atoms to the total number of atoms is large in nanoscale systems, surface

effects play an important role in determining the electronic properties. Uncompensated dangling bonds at the surface establish localized defect states within the forbidden gap of silicon nanocrystals, providing sites for non-radiative recombination of excitons. Defect states are also associated with surface reconstructions that minimize the number of dangling bonds but result in severe distortion of the surface bonds. An effective way of capping the remaining dangling bonds is by using atomic hydrogen or deuterium. Si nanocrystals less than 8 nm in diameter are grown on SiO₂ surfaces in an ultra high vacuum chamber and the as grown surfaces are exposed to atomic deuterium. Desorption spectra are interpreted using analogies to Si (100). TPD spectra show that the nanocrystal surfaces are covered by a mix of monodeuteride, dideuteride and trideuteride species. The manner of filling of the deuteride states on nanocrystals differs from that for extended surfaces as the formation of the dideuteride and trideuteride species is facilitated by the curvature of the nanocrystal. Etching of the nanocrystal surface is observed during TPD, which is a confirmation of the presence of trideuteride species on the nanocrystal surface. No photoluminescence (PL) is observed from the as grown unpassivated nanocrystals. As the deuterium dose is increased, the PL intensity also begins to increase. Strong PL is observed only when the nanocrystals are covered with trideuteride species. The trideuteride species helps in reducing the surface stress and this is expected to enhance PL. When the deuterium dose is increased beyond a point the surface structure breaks down and amorphization of top layer of the nanocrystal takes place. Amorphization reduces the PL intensity. Finally, as the nanocrystal size is varied, the PL peak shifts, which is characteristic of quantum confinement.

9:00am AS+NS-WeM4 **Experimental Characterization of CdSe/ZnS Core/Shell Quantum Dots Encapsulated with Poly(maleic anhydride-*alt*-1-tetradecene)**, G. Zorn, S.R. Dave, T. Weidner, X. Gao, D.G. Castner, University of Washington

Semiconductor nanocrystals (Quantum Dots, (QDs)) have started to play a pivotal role in molecular labeling, cancer diagnostics and tumor imaging due to their quantum mechanical and electronic characteristics. These characteristics give them unique optical properties such as size-tunable emission profiles, broad excitation spectra, long fluorescence lifetimes, large Stokes shifts and high quantum yields. The most common QD type is a CdSe/ZnS core - shell structure surrounded by hydrophobic ligands¹; but for biological applications, QDs have to be transferred into aqueous solutions and require specific techniques for the conjugation of small peptides or antibodies onto their surfaces. In this context, a promising and widely used approach is, to encapsulate the nanocrystals with an amphiphilic polymer^{1,2}. Still, there are only few reports regarding characterization of absorbed polymer and theoretical analyses are typically based on simple geometric models.

This work is focused on characterizing the amount of the amphiphilic Poly(maleic anhydride-*alt*-1-tetradecene) (PMAT, Mw~9000) adsorbed onto a TOPO-coated CdSe/ZnS QD, as well as analyzing the polymer structure and the TOPO - PMAT interaction. An insight into the elemental composition of the nanocrystals before and after PMAT encapsulation is provided along with the orientation of the surrounding organic components. EDAX, XPS and ToF-SIMS suggest the QDs are comprised of non-stoichiometric Cd-enriched QDs with a ~0.5 monolayer ZnS shell. SFG C-H stretching of the CdSe/ZnS nanocrystals before PMAT encapsulation shows that there is a significant degree of orientational order in the TOPO film. Moreover, after PMAT encapsulation SFG C-H stretching indicates a certain degree of order in the PMAT polymer layer. Finally, from XPS analysis the number of PMAT molecules per QD is estimated to be ~7 to 1.

Reference:

1. Smith, A. M.; Dave, S.; Nie, S.; True, L.; Gao, X., *Expert Rev. Molec. Diagnos.* **2006**, 6, 231-244.
2. Rhyner, M. N.; Smith, A. M.; Gao, X.; Mao, H.; Yang, L.; Nie, S., *Nanomedicine* **2006**, 1, 209-217.

9:20am AS+NS-WeM5 **2009 AVS Albert Nerken Award Lecture - Reactivity of Nanoparticles and Other Surface Controlled Properties of Materials**, D.R. Baer*, J.E. Amonette, M.H. Engelhard, J. Liu, P. Nachimuthu, C.M. Wang, Pacific Northwest National Laboratory, J.T. Nurni, P.G. Tratnyek, Oregon Health and Sciences University, M. Kaur, Y. Qiang, University of Idaho

INVITED

Many materials properties are controlled by surface reactions, including those associated with cracking, dissolution, and corrosion. In each of these cases surface reactions alter the functional properties of the materials.

* Albert Nerken Award Winner

Detailed analysis of surface reactions in relation to the material environment has been required to understand the mechanisms involved in these processes. Many of the analysis approaches used to understand dissolution, cracking corrosion and other complex material-environment interactions are relevant to the study of some types of nanoparticles. The objective of our current research is to obtain fundamental information about the physical and chemical transformations that occur on and within mineral oxide nanoparticulates due to electron transfer reactions and other interactions with their local environment, including solution contaminants such as chlorinated hydrocarbons. The nature of the reactive surfaces, the accessibility of reactive sites, and the structures of the surface and interface layers often change significantly as particles respond to and react with their local environment (e.g. surface structure alterations, phase changes, passive layer formation ...). Although geochemically induced changes occur for bulk materials, the nature and rate of these changes can be more dramatic for nano-sized mineral phases. Our research focuses on obtaining information about these geochemically mediated transformations and how they alter particle reactivity, electron availability and particle mobility. Our research includes 1) synthesis of well-defined nanoparticles (NPs), 2) characterization of their surface and bulk composition as well as physical and electronic structure (prior to and following reaction measurements), and 3) *in situ* real-time and batch measurements of NP properties and reactivity in vacuum and solution. We will report on studies showing the impact of natural organic material (NOM) coatings on the through soil transport and reactivity of iron nanoparticles as well as the role of metal dopants on reactivity and solution aging. We have found that NOM can enhance the transport of iron metal-core oxide-shell nanoparticles through a soil column, decreasing the numbers of particles retained in the soil. We have followed up these observations and examined the impact of NOM coatings on the particle aging. Additional studies are examining the impact of S doping on particle reactivity and aging. These studies involve application of a variety of analysis methods to the particles, including XPS, XRD and TEM as well as batch and *in situ* measures of chemical reactivity and measurements of particle transport through soil columns.

10:40am **AS+NS-WeM9 Surface Characterization and Simulation of Self-Assembled Monolayer Functionalized Gold Nanoparticles**, S.D. Techane, L.J. Gamble, University of Washington, M.H. Engelhard, D.R. Baer, Pacific Northwest National Laboratory, D.G. Castner, University of Washington

In this research gold nanoparticles (AuNP) are used as model nanoparticles and self-assembled monolayers of alkyl thiols as model organic ligands to create functionalized NP with a variety of surface chemistries. The AuNP size and thiol chain length are varied to study their effects on the properties of the AuNP. Our aim is to create a series of well-defined functionalized AuNP for use in complex biological applications and to use the AuNP-SAMs as standard samples to develop XPS (X-ray photoelectron spectroscopy) data analysis methods for coated NP characterization. We have synthesized and characterized four chain lengths of COOH-SAMs (C6, C8, C11, C16 carboxylic thiols) on various sizes of AuNPs (diameter =14nm, 25nm, 40nm) and flat gold surfaces using the surface sensitive techniques of XPS and ToF-SIMS. Many of the trends expected for increasing SAM thickness are observed. In addition data shows that particle size (surface curvature) had an effect on the XPS and ToF-SIMS measurements. Complementary ATR-FTIR (attenuated total reflectance FTIR) measurements were done to characterize the SAM ordering and crystallinity. As SAMs length increased the CH₂ stretching vibration frequencies (ν_{CH_2}) decreased on both AuNPs and flat-Au surfaces. For a given chain length SAMs the ν_{CH_2} also decreased as the AuNPs particle size decreased indicating that longer chain SAMs on the smaller AuNPs (i.e. 14nm-C16 COOH-SAMs) have the most crystalline surface structure. As the XPS C/Au atomic ratio depends on the structure of the SAMs as well as the take-off angles (which range from 0 to 90° for particles) there is a need to develop XPS data analysis methods that accurately account for curved NP surfaces. SESSA (Simulated Electron Spectra for Surface Analysis) and QUASES (Quantitative Analysis of Surfaces by Electron Spectroscopy Software) have been used to simulate the experimental XPS results as a function of take-off angle for COOH-SAMs on flat-Au surfaces. Quantities such as SAM density, thickness, surface roughness and instrumental parameters were tuned in SESSA to optimize agreement between simulated and experimental XPS compositions for SAMs on flat Au surfaces. SESSA results were compared with experimental measurements taken from 3 different XPS instruments: Quantum (EMSL/PNNL), Kratos and S-probe (NESAC/BIO). Approaches are being used to apply SESSA and QUASES to analysis of the particle data.

11:00am **AS+NS-WeM10 Nanocerium Oxide as Antioxidant – Role of Environment and Surface Coating on the Interaction with Reactive Oxygen Species**, A.S. Karakoti, S. Singh, A. Kumar, University of Central Florida, S.V.N.T. Kuchibhatla, Environmental and Molecular Sciences Laboratory, W.T. Self, S. Seal, University of Central Florida

The astounding progress of nanotechnology in numerous areas of science and biotechnology is posed with a significant challenge of overcoming the nanotoxicological properties of these materials. More often than not nanomaterials produce oxidative stress when exposed to cellular environment leading to rapid cell death. While several nanomaterials are linked with oxidative stress; cerium oxide nanoparticles (CNPs) show an inverse behavior by scavenging the reactive oxygen species (ROS) thereby reducing the oxidative stress and acting as antioxidant oxides. The antioxidant properties of nanocerium originate from its redox properties, surface chemistry and nanoparticulate size. It was observed that a critical ratio of Ce³⁺/Ce⁴⁺ was required for exhibiting better antioxidant properties. Due to the reversible nature of its redox properties i.e. CNPs can regenerate its active radical scavenging oxidation state upon interaction with ROS such as peroxide and superoxide. To increase the biocompatibility and cell permeability characteristics, CNPs were synthesized in biocompatible mediums such as polyethylene glycol (PEG) and dextran. Cell viability studies showed excellent biocompatibility of the CNPs synthesized in biocompatible mediums. The antioxidant property of CNPs in these medium was compared to the water based CNPs using classical superoxide dismutase (SOD) model and it was found SOD mimetic activity was unaltered by the presence of organic coating on CNPs. Reaction of hydrogen peroxide with CNPs was used to compare the changes in oxidation state of CNPs upon interaction with peroxide species. While both PEG and dextran showed tunable redox property; it was found that the redox property of PEG based CNPs were acutely affected by medium due to change in the polarity and dielectric constant of the medium. A clear indication of formation of charge transfer complex was found with PEG while no such complex was observed with dextran. Additionally CNPs synthesized in PEG (5 – 80 vol% PEG) showed concentration dependent red shift in the formation of CNP-PEG charge transfer complex. Upon dialysis it was found that the polymer formed a stable coating on the surface of CNPs and the surface coating was linked to the observed differences in the regeneration of the oxidation state of nanoparticles. High resolution transmission electron microscopy, Fourier transform infra red spectroscopy and UV-visible spectroscopy were used to characterize the particle size, nature of coating and dynamic oxidation state of nanocerium. X-ray photoelectron spectroscopy used to probe the surface chemistry and oxidation state of CNPs.

11:20am **AS+NS-WeM11 Dynamic Nature of Cerium Oxide Nanoparticles – Influence of Aging and Local Environment**, S.V.N.T. Kuchibhatla, Pacific Northwest National Laboratory, A.S. Karakoti, University of Central Florida, C.H. Windisch Jr., P. Nachimuthu, Pacific Northwest National Laboratory, S. Seal, University of Central Florida, S. Thevuthasan, D.R. Baer, Pacific Northwest National Laboratory

Cerium oxide nanoparticles (CNPs) are a subject of increasing attention in the biomedical field in addition to many traditional applications such as catalysis, sensors and fuel cells. Most of the applications of CNPs are driven by the oxygen buffering capability, which in turn is guided by the ability of cerium to switch between 3+ and 4+ oxidation states. The thermodynamic stability of oxygen vacancies in the particles below 10 nm makes this switching more efficient. Motivated by this fact, the CNPs have been used to study their biological response (cell longevity, toxicity and related aspects) and the preliminary results have shown excellent radical scavenging ability. It has also been noted that the CNPs can effectively regenerate the active redox state. However, an unequivocal mechanism is still not reported.

We have studied, *in situ*, the influence of time (aging) and local environment (chemistry) on the chemistry and structure of CNPs. With the help of UV-Visible and Raman spectroscopy along with microXRD measurements, we have observed that the CNPs are highly dynamic in nature and respond, through changes in chemical state and possibly structure, to the variations in their local environment as a function of time. Raman data with support from XRD and some XPS results suggests that the CNPs undergo the transformation between 3+ and 4+ oxidation state through the formation of a “peroxide-complex” in presence of hydrogen peroxide, which as a function of time leads to the formation of cerium oxide nanoparticles, regeneratively. Interaction of CNPs with hydrogen peroxide was used as a model system for explaining the regenerative nature of CNPs in biological applications. Various results from this study, along with the size dependence of the transitions, will be presented while discussing the merits of the findings and their implications to the bio-medical applications.

11:40am **AS+NS-WeM12 Characterizing Environmentally Induced Changes in Nanoparticle Surface Chemistry**, *A.N. Mangham, P. Wiecinski, S.P. Yang, K.M. Louis, R.E. Peterson, W. Heideman, A. Pedersen, R.J. Hamers*, University of Wisconsin-Madison

The routes of exposure and toxicity of nanoparticles in the environment are expected to be strongly affected by the nature of surface chemical groups exposed on the outside of the particles. We have developed a laboratory-based method that simulates oxidative processes in the environment, and have applied this method to investigate the resulting changes in surface chemistry of “bare” and ligand-functionalized nanoparticles. Using CdSe as a model system, we have compared the behavior of ligands bearing different surface anchor groups including carboxylic acid groups, amines, and phosphonates. Wrapping these ligand-modified nanoparticles with amphiphilic polymers can enhance the particle stability as well as the luminescence efficiency. Surprisingly, the type of surface anchoring group has a strong effect on the stability of even the polymer-wrapped nanoparticles. Using infrared, Raman, and x-ray photoelectron spectroscopies, combined with thermogravimetric analysis, we related the differences in stability of the nanoparticles to the chemical and physical structure of the ligands. Our results show that the most thermally stable groups do not necessarily provide the best protection against degradation. As time permits, the influence of the surface chemistry on the nanoparticle toxicity using a zebrafish model will be presented and discussed.

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