

# Monday Afternoon, October 18, 2010

## Nanometer-scale Science and Technology

Room: La Cienega - Session NS-MoA

### Nanomaterials in the Environment

Moderator: U.D. Schwarz, Yale University

#### 3:40pm NS-MoA6 Nanotechnology in the Environment: Safety by Design, V. Colvin, Rice University **INVITED**

Nanotechnology-enabled systems offer much promise for solving difficult environmental problems ranging from water purification to waste remediation. These solutions must not only be cost-effective and sustainable, but they must also be safe for people and the environment. Our emerging understanding of the interface between nanomaterials and biological systems gives us the critical ability to approach the latter issue early in the development of nanotechnology. This talk will discuss in some detail how the chemical and physical properties of engineered nanomaterials impact their biological effects in model systems. Three case studies, ranging from fullerenes to metal oxides, illustrate the vast diversity of nanomaterial features and biological response. The composition of a nanomaterial is the primary factor in describing acute biological effects, and among the different examples nanoparticle charge and surface coating can be of equal importance. Interestingly, the size of the inorganic material itself – such an important feature for applications development – in these three examples is secondary in defining the materials' acute biological effect. In all cases, the biological and environmental compartments experienced by nanomaterials lead to substantial modification of their hydrodynamic size and charge. The bio-modified material that results is the central element to understand and characterize in order to detect the underlying correlations between the inorganic nanomaterial phase, composition and size with biological outcomes. These correlations form the basis for guidelines that permit researchers creating new nanoparticles to focus their energy on materials that are 'safe by design'.

#### 4:20pm NS-MoA8 Surface Functionalization of TiO<sub>2</sub> Nanoparticles: Photo-stability and Reactive Oxygen Species (ROS) Generation, K. Louis, O. Bar-Ilan, W. Heideman, M. Konrath, J. Pedersen, R. Peterson, S. Yang, R.J. Hamers, University of Wisconsin-Madison

Nanoparticles made from TiO<sub>2</sub> and other metal oxides are of increasing interest for applications including sunscreens, cosmetics, paints, biomedical imaging, and photovoltaic devices. While TiO<sub>2</sub> is generally considered to be non-toxic, TiO<sub>2</sub> and other metal oxides can generate highly toxic reactive oxygen species when exposed to water and sunlight. The ROS species can, in turn, modify the stability of the TiO<sub>2</sub> nanoparticles by altering the organic ligands that typically are present on the exterior of the nanoparticles. We are investigating the formation of ROS species by TiO<sub>2</sub> nanoparticles and the relationship between organic ligands, ROS generation, and nanoparticle stability. These factors all affect the bioavailability of TiO<sub>2</sub> nanoparticles and consequently are important factors in understanding the safety and health impacts of nanomaterials. As model systems, we have investigated TiO<sub>2</sub> nanoparticles functionalized with several ligands including citrate, 3,4-dihydroxybenzaldehyde, and rutin, a model of humic substances. Using fluorescent probes we are measuring the amount of ROS species produced from nanoparticles of different sizes and relating this to the chemical alteration/degradation of the ligands using XPS and FTIR, and examining the impact on stability of nanoparticles in aqueous media. Concurrent measurements are being made of the toxicity of the nanoparticles using zebrafish in the presence and absence of ultraviolet light in order to understand how surface chemistry of nanoparticles ultimately impacts bioavailability and environmental impact of engineered nanomaterials.

#### 4:40pm NS-MoA9 Environmental Effects on Nanoparticle Properties and Chemical Reactivity, D.R. Baer, J.E. Amonette, A. Dohnalkova, M.H. Engelhard, Pacific Northwest National Laboratory, R.L. Penn, University of Minnesota, P. Nachimuthu, J. Liu, Pacific Northwest National Laboratory, J.T. Nurmi, P.G. Tratnyek, Oregon Health and Sciences University, C.M. Wang, Pacific Northwest National Laboratory

Nanoparticles of many types are increasingly used in a variety of applications. Parts of our work have focused on the reactions of Fe metal-core oxide-shell nanoparticles with water and solution contaminants that may be found in ground water. An important factor in understanding the ability of such particles to reduce environmental contaminants and the ultimate fate of such particles is knowledge of how the particles and their properties change with time in a variety of environments. Our work has demonstrated that these particles can change rapidly over periods of hours to days in water. Our research has focused attention on three aspects of

these time dependent phenomena: 1) developing the ability to extract particles from solution, thereby stopping the reaction process and preserving, to the extent possible, the chemical and structural information; 2) how changes in the solution (adding buffers and organics) alter particle reactivity and aging in solution; and 3) using *in situ* methods to track particle changes and chemical properties. A variety of *ex situ* methods have been used to characterize the particles, including XPS, TEM, BET and XRD. Electrochemistry measurements have been used as an *in situ* real-time method. The method of sample extraction involves handling samples in a nitrogen atmosphere, a solvent rinse, and vacuum pumping to remove excess solvent. Even when particles appear dry, aggregates of particles may retain significant solvent. In addition to examining the influence of a variety of common buffers, we have examined the impact of natural organic material on the oxidation and chemical behavior of nanoparticles. Although natural organic matter (NOM) slows aging of the particles, the NOM coating helps the particles migrate relatively quickly through soil. Electrochemical measurements of various types including the open-circuit potential demonstrate the time dependence of particle changes and highlight the effects of varying environments on particle properties. Surface-potential measurements also highlight the impact of differing solutions on particle behavior.

#### 5:00pm NS-MoA10 Functionalized Ceria Nanoparticles – Influence of Coating Thickness and Density on Their Reactivity, A. Karakoti, University of Central Florida, S. Kuchibhatla, G. Orr, H. Wang, D.R. Baer, Pacific Northwest National Laboratory, S. Seal, University of Central Florida, S. Thevuthasan, Pacific Northwest National Laboratory

Topical interest in the biomedical applications of cerium oxide nanoparticles (CNPs) has emerged from its radical scavenging, antioxidant like, behavior. The ability of CNPs to carry these single electron redox processes (radical scavenging) stems from the ability of cerium to switch between the Ce<sup>3+</sup> and Ce<sup>4+</sup> oxidation states. It is essential to test and increase the biocompatibility and solubility of CNPs to be able to use these in biomedical applications as it involves a direct interface of nanoparticles with the intracellular environment. The biocompatibility as well as solubility of CNPs can be increased by modifying the surface with biocompatible polymers as ligands. Such a composite system should be able to demonstrate the unaltered characteristics of the parent CNPs and biocompatibility as well as high solubility of the polymeric system. Thorough characterization of CNP-polymer system such as thickness of polymeric coating, surface coverage and number density of the polymer per nanoparticle is necessary to relate its properties with biocompatibility.

CNPs were synthesized using two different wet chemical methods and coated with different concentration of polymer (polyacrylic acid) using conventional precipitation and redispersion technique. The molecular weight of the polymer was varied between 2,000 and 250,000 g/mol and composite system was characterized for particle size, stability/solubility of dispersion, surface charge, surface density of the polymer and thickness of the polymeric coating. Dynamic light scattering measurements were used to characterize the size as well as surface charge of the coated nanoparticles. A combination of surface area and thermogravimetric analysis was used to ascertain the number density of the polymers per unit surface area of the nanoparticles. The extent of polymeric functionalization will be determined by estimating the number of carboxyl groups on the surface of nanoparticles by chemical probing. Non linear optical (NLO) measurements are becoming increasingly popular to quantify the surface of nanoparticles. NLO analyses such as Sum Frequency Generation Vibrational Spectroscopy (SFG-VS) will be used to quantitatively estimate the polymeric ligands on the surface of CNPs. The presentation will be concluded by some of the preliminary results from the biocompatibility tests carried out on the well analyzed composite/functional CNPs.

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