Thursday Morning, October 31, 2013

Applied Surface Science
Room: 204 - Session AS+BI+EM+NL+NS+SS-ThM

Nanoparticle Surface Chemistry
Moderator: H. Zuilhof, Wageningen University, Netherlands, D.Y. Petrovykh, International Iberian Nanotechnology Laboratory, Portugal

8:00am **AS+BI+EM+NL+NS+SS-ThM1 Surface Analysis as a Critical Step in Translating Nanomaterials to Technologies**, ***D.W. Grainger***, University of Utah **INVITED**

Difficulties assessing human exposure, safety, and possible toxicity from nanotechnologies have prompted questions about how to characterize nanomaterials in various experimental test beds for predictive use. While little consensus is published about human risk/benefit analysis, this is confounded by lack of accepted, sensitive and reliable characterization methods of practical value for nanomaterials in physiological milieu. Relatively few studies are conducted on these materials in biologically relevant media to understand their surface properties and physical states (i.e., sedimentation, aggregation) prior to in vitro or in vivo exposures. Few studies have standard reference materials and analytical protocols established for comparisons to other studies. The current understanding of the fate of nanomaterials of most any size and shape, both in cell culture mediawith serum or inside the mammalian body, is poor at best. Additionally, the collective published scientific record documenting fate of nanomaterials in vivo is consistent with long known tissue-based particle filtration for micro-colloids, with far less success deliberately targeting particles to specific tissue or disease sites (i.e., <5% of a nanoparticle dose reaches a disease site).

To date, most data suggest that size reductions to the nanometer dimension have not significantly changed how nanomaterials interact with physiological systems in vivo, despite in vitro distinctions observed with proteins and in cell cultures. Connecting nanomaterials properties with how they interact with proteins and cells in vitro to affect their biodistribution in vivo allows a more rational approach to designing nanomaterials with specific biomedical and toxicity properties, and to avoid the ubiquitous non-specific tissue scavenging. This is related to materials interactions with whole blood components, including platelets, cells, and plasma proteins, producing fluid transport to tissue sites, particle binding, opsonization and aggregation. However, analytical methods for nanomaterialsare not sufficiently sensitive to study these effects in vivo to alter nanomaterials biodistribution patterns. Additionally, understanding how surface coatings, ligands and contaminants change physiological behavior requires careful analysis.

The nanotechnology field must develop improved, sensitive analytical tools and methods to drive a consensus for how nanomaterials (1) should be fully and reliably characterized for biological and biomedical purposes, and (2) how different nanomaterials properties produce either beneficial (i.e., therapeutic) or toxic responses inside complex physiological systems.

8:40am **AS+BI+EM+NL+NS+SS-ThM3 Molecular Surface Characterization of Individual Nano-objects**, *C.-K. Liang, S.V. Verkhoturov*, ***E.A. Schweikert***, Texas A&M University

The importance of surface characterization of nano-objects in dimensions below 50 nm is well recognized. Indeed the most pronounced changes in chemical reactivity are expected to occur on the smallest size nano-objects. Yet, as their size shrinks, measurement techniques are lagging. A further concern, when seeking insight into size-composition-reactivity relationships, is population heterogeneity. We present here a technique for assaying individual nano-objects. The method involves bombarding dispersed nano-objects one-by-one with nanoprojectiles specifically Au_{400}^{4+}, at hypervelocity. Their impact causes abundant emission of ionized ejecta which are identified individually for each impact by time-of-flight mass spectrometry. We will describe the characterization of surfaces and environments of nano-objects as revealed by selected grazing projectile impacts.

9:00am **AS+BI+EM+NL+NS+SS-ThM4 Towards the Effective Combination of Static and Dynamic SIMS for Nanoparticle and Biological Analyses**, ***C. Szakal***, National Institute of Standards and Technology

Static SIMS and dynamic SIMS experiments, protocols, instrumentation, and laboratory groups have largely developed in separate paths. As a result, it is common to think of certain application areas for a specific SIMS analysis, such as semiconductor depth profiling with dynamic SIMS and molecule-specific imaging with static SIMS. However, a combination of the two SIMS methodologies could generate a more complete data set by utilizing the surface-sensitive characteristics of ToF-SIMS with the enhanced signal dynamic range of large geometry (LG) dynamic SIMS. Benefits and potential pitfalls of such a combined analysis are discussed for nanoparticle surface chemistry vs. bulk measurements along with other biological application areas.

9:20am **AS+BI+EM+NL+NS+SS-ThM5 Quantitation of Protein Adsorption to Gold Nanoparticles**, ***C. Minelli***, *N.C. Bell, A.G. Shard*, National Physical Laboratory, UK

The ability to quantitatively describe protein coronas of nanoparticles in biological fluids is highly sought for to understand protein corona formation, nanoparticle fate and their interaction with biological systems. A quantitative description of the nanoparticle biomolecular interface is challenging and chemical information along with structural and biofunctional characterization requires the use of complementary techniques.

The parallel use of different techniques provides in fact a range of complementary information of the materials under study, each technique being based on a specific physical principle. Here, we combine the use of liquid-based size measurement techniques such as Dynamic Light Scattering (DLS), Nanoparticle Tracking Analysis (NTA) and Differential Centrifugal Sedimentation (DCS), with vacuum techniques such as X-ray Photoelectron Spectroscopy (XPS) to provide quantitative information of core/shell nanoparticle systems.

We used a set of spherical gold nanoparticles having diameters from 20 nm to 80 nm and coated with different amount of Immunoglobulin G (IgG) antibodies as a model system. The shift of the nanoparticle Localized Surface Plasmon Resonance (LSPR) frequency measured by UV-Vis spectroscopy is known to relate to the amount of molecules adsorbed at nanoparticles' interface. We measured the LSPR shifts along with the nanoparticle sizes in liquid by using DLS, NTA and DCS. When the nanoparticles had a complete protein shell, shell thickness measurements were consistent for all the techniques. DCS sedimentation times showed excellent correlation with LSPR frequency shifts, indicating that analytical centrifugation can provide precise measurement of the thickness of complete protein shells on nanoparticles. However, in the low coverage regime, NTA and DLS techniques provided the best correlation with LSPR frequency shifts. By combining the information from the different techniques we estimated the amount of IgG molecules per nanoparticle as a function of the IgG concentration in solution. Data analysis in the high concentration regime suggested that nanoparticle curvature strongly influences the ability of a surface to allow the further adsorption of IgG.

Core/shell nanoparticle systems were also characterized by XPS. A methodology for the preparation of nanoparticle samples for analysis in vacuum was developed. XPS data was collected from nanoparticles of different core size and analysis provided quantitative chemical information of the nanoparticle. The combined use of XPS with liquid-based techniques for particle characterization provided quantitative chemical and structural information of core/shell nanoparticle systems.

9:40am **AS+BI+EM+NL+NS+SS-ThM6 Surface Characterization of Protein Functionalized Gold Nanoparticles**, *Y.-C. Wang, A. Rafati*, ***D.G. Castner***, University of Washington

Nanoparticles exhibit unique surface properties and require well-controlled surface properties to achieve optimum performance in complex biological or physiological fluids. Thus, there is a need to develop rigorous and detailed surface analysis methods for their characterization. The surface chemistries of oligo(ethylene glycol) (OEG) self-assembled monolayers (SAMs) on Au nanoparticle (AuNP) surfaces were characterized with x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), Fourier transform IR spectroscopy and high-sensitivity, low-energy ion scattering (HS-LEIS). The size, shape, and size distribution of the AuNPs was determined by transmission electron microscopy (TEM).

Both methoxy (CH_3O-) and hydroxyl (HO-) terminated OEG SAMs with chains containing 11 methylene and 4 ethylene glycol units were examined. ToF-SIMS clearly differentiates the two OEG SAMs based on the $C_3H_7O^+$ peak attributed to the CH_3 terminated SAM, while XPS didn't detect a significant difference between the two SAMs on the same surface. However, XPS did show a significant difference between the same SAM on different sized AuNPs. Both OEG SAMs were more densely packed on the 40 nm diameter AuNPs compared to the 14 nm diameter AuNPs. FTIR experiments indicates the methylene backbone groups are well-ordered on

all gold surfaces, but the OEG groups are more ordered on the 40 nm diameter AuNPs. Together the XPS and FTIR results suggest the OEG SAMs form a thicker and/or higher density SAMs on the 40 nm AuNPs compared to the 14nm AuNPs. HS-LEIS experiments showed the OEG SAMs on the 40 nm AuNPs were significantly thicker (2.6 nm) than the OEG SAMs on the 14 nm AuNPs (2.0 nm) and the flat Au surface (1.9 nm). The 2.6 nm thickness measured on the 40 nm AuNPs is consistent with thickness expected for a well-order OEG SAM (2.7 nm). TEM showed the 40 nm AuNPs had a larger size distribution and were less spherical compared to the 14 nm AuNPs, suggesting the shape of the AuNPs can have a significant effect on the structure and thickness of the OEG SAMs.

Protein G was immobilized onto the HO-terminated OEG SAMs via carbonyl diimidazole chemistry. ToF-SIMS analysis showed the relative intensities of characteristic amino acid fragments from Protein G varied with both the protein solution concentration and the type of surface.

10:40am **AS+BI+EM+NL+NS+SS-ThM9 Optical Rotation Measurements of Enantioselective Separation on Chiral Au Nanoparticles**, ***N. Shukla***, *N. Ondeck, N. Khosla, A.J. Gellman,* Carnegie Mellon University

Adsorption of chiral compounds on chiral surfaces is the initial step in enantioselective processes such as separations and catalysis. There has been a significant effort over the past decade aimed at the preparation of chiral nanoparticles based on metallic cores modified by chiral ligands. In principle, these can serve as the basis for enantioselective chemical processing. In this work we demonstrate a simple measurement of enantioselective adsorption on chiral metal nanoparticles using a method that can yield quantitative measures of the enantiospecific adsorption equilibrium constants [1].

The surfaces of chemically synthesized Au nanoparticles have been modified with D- or L-cysteine to render them chiral and enantioselective for adsorption of chiral molecules. Their enantioselective interaction with chiral compounds has been probed by optical rotation measurements when exposed to racemic propylene oxide. The ability of optical rotation to detect enantiospecific adsorption arises from the fact that the specific rotation of polarized light by R- and S-propylene oxide is enhanced by interaction Au nanoparticles. This effect is related to previous observations of enhanced circular dichroism by Au nanoparticles modified by chiral adsorbates. More importantly, chiral Au nanoparticles modified with either D- or L-cysteine selectively adsorb one enantiomer of propylene oxide from a solution of racemic propylene oxide, thus leaving an enantiomeric excess in the solution phase. Au nanoparticles modified with L-cysteine (D-cysteine) selectively adsorb the R-propylene oxide (S-propylene oxide). A robust model based on optical rotation data has been developed that allows extraction of the enantiospecific equilibrium constants for R- and S-PO adsorption on the chiral Au nanoparticles.

[1] N. Shukla, M.A. Bartel, A.J. Gellman "Enantioselective separation on chiral Au nanoparticles" Journal of the American Chemical Society, 132(25), (2010), 8575–8580

11:00am **AS+BI+EM+NL+NS+SS-ThM10 Monitoring the Citric Acid Content on Dialyzed Gold Nanoparticle**, *V. Spampinato, R. La Spina, D. Gilliland, L. Calzolai,* ***G. Ceccone***, *F. Rossi*, EC-JRC-IHCP, Italy

Gold nanoparticles (GNPs) are probably the most investigated metal nanomaterials due to their interesting properties. In fact, GNPs are applied in a several areas including material sciences, catalysis and biomedical diagnostics[1] Most of the applications of GNPs in the medical and biosensing fields require the development of careful purification to obtain afterwards a more efficient surface functionalization.[3,4] The process of purification is usually obtained by filtration, centrifugation and/or dialysis of the GNPs solution to remove part of the citrate or other stabilizing agents.[5,6] The citrate reduction Au(III) in water, known as Turkevich method, is one of the most used synthesis process to produce monodispersed and stable GNPs. [8] In this synthesis, the citrate is either the reducing agent and the stabilizer and it is used in large excess in comparison to the amount of gold.[9] In this work, we have investigated the stability and effect of dialysis on citrate stabilized GNPs by quantifying the content of citrate by Nuclear Magnetic Resonance (^{1}H-NMR), and by characterizing the GNPs/citrate interface chemistry using X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). In these studies, 15 nm gold nanoparticles stabilized with the citrate have been synthesized via the Turkevich process and the content of citrate was monitored at several or different cycles of dialysis against ultrapure water. These systematic studies showed a decreasing of the citrate content with the dialysis cycles. In particular, XPS and ToF-SIMS show that for low dialysis cycles the ratio Au/Na and Au/CHO increase almost linearly, while after 9 dialysis cycles a plateau is reached. A Similar trend is observed by^{1}H-NMR where the amount of citrate is quantified against an internal standard. The behavior of the GNPs at different dialysis cycles was also monitored by Centrifuge Particle Separation (CPS) and Dynamic Light Scattering (DLS) and UV-Vis spectra, revealing that several dialysis cycle result in a partial aggregation of the nanoparticles.

[1] P-J Debouttière, et al., *Adv. Funct. Mater*., **2006**, *16*, 2330

[3] N. L. Rosi, et al., *Science*, **2006**, 312, 1027

[4] C. Murphy et al., *Acc. Chem. Res.*, **2008**, *41* (12), 1721

[5] S. Techane, et al., *J Phys Chem C*, **2011,** 115(19), 9432

[6] S. Sweeney et al., *J. Am. Chem. Soc*., **2006**, *128* (10), 3190

[7] C. Chen, et al.*Nano Lett.*, **2006**, *6* (4), pp 611–615

[8] J. Turkevich, et al., *Discuss. Faraday Soc.*, **1951**, 11, 55

[9] M. Doyen, et al, *J. Coll. Int. Sci.*, **2013,** 399, 1

11:20am **AS+BI+EM+NL+NS+SS-ThM11 Comparison of the Structure and Solution Behaviors of 20nm Silver and 20nm Silver-Shell-Gold-Core Nanocomposites in Aqueous Biological Media**, *P. Munusamy,* Pacific Northwest National Laboratory, *S. Chen, L.B. Yen,* Imperial College London, UK, *C.W. Wang, M. Engelhard,* Pacific Northwest National Laboratory, *A. Porter*, Imperial College London, UK, ***D.R. Donald***, Pacific Northwest National Laboratory

Different synthesis routes have made it possible to produce silver nanoparticles with variety of structure properties such as size, shape, and surface functionality. Synthesizing or processing silver nanoparticles under different conditions can impart variations in properties and reactivity which can influence the biological end points. In this study we have examined how silver nanoparticles of nearly identical size, as measured by dynamic light scattering, but produced with and without gold core behave in the biological media RPMI 1640 with FBS, the cell culture media used in our laboratory for in vitro nanotoxicity studies. The initial physico-chemical characterization of citrate capped nanoparticles using DLS size and surface charge measurement showed particles of average size 27nm with negative surface charge. Structure and compositional analysis using STEM and XPS confirmed the presence of gold core of size ~7nm in one set of particles. The detailed structure of the pure silver and the core-shell particles differ significantly. Based on TEM images and XRD measurements, the pure silver particles are highly crystalline, made up of ~ 15-20 nm crystallites with well-defined grain boundary or slip plane defect structures. The silver surrounding the gold core is made up of smaller highly disordered crystallites. After 24h incubation in culture media, STEM images showed that the particles with Au core dissolved significantly and non-uniformly indicating solution attack down to the gold core. In contrast, pure silver particles underwent more uniform dissolution with some indication of varying rates for different crystal faces. In addition to the dissolution of the primary particles of both types, new smaller "daughter" silver particles were observed both nearby or some distance away from the initial nanoparticles. Centrifugation followed by ICP-MS analysis of the supernatant was used to quantify the amount of dissolved silver. The dissolution extent for core-shell particles in 24h was 3 times higher than that for pure Ag. These results highlight the significance of synthesis route and sample structure on the solution behavior of similar nanoparticles in biologically relevant environmental conditions.

11:40am **AS+BI+EM+NL+NS+SS-ThM12 Influence of Carrier Gas on the Nucleation and Growth of Nb Nanoclusters Formed Through Plasma Gas Condensation**, ***K.R. Bray***, *C.Q. Jiao,* UES, Inc., *J.N. DeCerbo,* Air Force Research Laboratory

The synthesis and characterization of metallic nanoclusters is a growing field of research due to their promising catalytic, electrical, magnetic, mechanical, and optical properties. These properties generally differ from the bulk material and can be tuned by varying the nanocluster size. Transition metal clusters have received considerable interest due to their wide range of applications. Niobium has attracted attention due to observations of ferroelectric properties at low temperature. In this work, Nb nanoclusters are deposited using a plasma gas condensation process which involves the sputtering of a Nb target to create a dense metallic vapor where clusters are formed. The concept of a temperature dependent nucleation zone in conjunction with classical nucleation theory is used to describe nanocluster nucleation and growth. Changes in the nanocluster nucleation and growth are influenced through modifications of the process parameters such as carrier gas flow rate, sputter source ion current, and aggregation length. Initial data show a novel dual peak cluster distribution under select process conditions, with the smaller cluster diameter near 1 nm and the larger cluster diameter varying from 4 to 10 nm. The larger cluster appears to be a simple condensation product while data suggest the smaller cluster may be a structured cluster with a different nucleation and growth mechanism. The effects of differing argon and helium carrier gas ratios on cluster formation in conjunction with varying sputter source currents and aggregation lengths will be discussed. These results provide the opportunity for a broader understanding into the nucleation and growth of nanoclusters

as well as insights into how process parameters interact during deposition. This knowledge will enhance the ability to create nanoclusters with desired size dispersions.

Authors Index

Bold page numbers indicate the presenter

— B —

Bell, N.C.: AS+BI+EM+NL+NS+SS-ThM5, 1
Bray, K.R.: AS+BI+EM+NL+NS+SS-ThM12, **2**

— C —

Calzolai, L.: AS+BI+EM+NL+NS+SS-ThM10, 2
Castner, D.G.: AS+BI+EM+NL+NS+SS-ThM6, **1**
Ceccone, G.: AS+BI+EM+NL+NS+SS-ThM10, **2**
Chen, S.: AS+BI+EM+NL+NS+SS-ThM11, 2

— D —

DeCerbo, J.N.: AS+BI+EM+NL+NS+SS-ThM12, 2
Donald, D.R.: AS+BI+EM+NL+NS+SS-ThM11, **2**

— E —

Engelhard, M.: AS+BI+EM+NL+NS+SS-ThM11, 2

— G —

Gellman, A.J.: AS+BI+EM+NL+NS+SS-ThM9, 2
Gilliland, D.: AS+BI+EM+NL+NS+SS-ThM10, 2
Grainger, D.W.: AS+BI+EM+NL+NS+SS-ThM1, **1**

— J —

Jiao, C.Q.: AS+BI+EM+NL+NS+SS-ThM12, 2

— K —

Khosla, N.: AS+BI+EM+NL+NS+SS-ThM9, 2

— L —

La Spina, R.: AS+BI+EM+NL+NS+SS-ThM10, 2
Liang, C.-K.: AS+BI+EM+NL+NS+SS-ThM3, 1

— M —

Minelli, C.: AS+BI+EM+NL+NS+SS-ThM5, **1**
Munusamy, P.: AS+BI+EM+NL+NS+SS-ThM11, 2

— O —

Ondeck, N.: AS+BI+EM+NL+NS+SS-ThM9, 2

— P —

Porter, A.: AS+BI+EM+NL+NS+SS-ThM11, 2

— R —

Rafati, A.: AS+BI+EM+NL+NS+SS-ThM6, 1
Rossi, F.: AS+BI+EM+NL+NS+SS-ThM10, 2

— S —

Schweikert, E.A.: AS+BI+EM+NL+NS+SS-ThM3, **1**
Shard, A.G.: AS+BI+EM+NL+NS+SS-ThM5, 1
Shukla, N.: AS+BI+EM+NL+NS+SS-ThM9, **2**
Spampinato, V.: AS+BI+EM+NL+NS+SS-ThM10, 2
Szakal, C.: AS+BI+EM+NL+NS+SS-ThM4, **1**

— V —

Verkhoturov, S.V.: AS+BI+EM+NL+NS+SS-ThM3, 1

— W —

Wang, C.W.: AS+BI+EM+NL+NS+SS-ThM11, 2
Wang, Y.-C.: AS+BI+EM+NL+NS+SS-ThM6, 1

— Y —

Yen, L.B.: AS+BI+EM+NL+NS+SS-ThM11, 2