

Wednesday Afternoon, November 2, 2011

Biomaterial Interfaces Division

Room: 108 - Session BI+AS+NS+SS-WeA

Functionalization and Characterization of Nanostructures

Moderator: A. Belu, Medtronic, Inc.

2:00pm BI+AS+NS+SS-WeA1 Characterization of Nano-objects by Cluster-SIMS, E.A. Schweikert, Texas A&M University INVITED

Secondary ion mass spectrometry, SIMS is a method of choice for the chemical analysis of nanodomains embedded in solids. We examine here a case which has received little attention, the analysis of individual, free-standing nano-objects. Our approach uses a variant of SIMS. The nano-objects are bombarded with a sequence of individual projectiles resolved in time and space, in the present case Au_{400}^{4+} of up to 520 keV impact energy. The successive projectiles impact stochastically the nano-objects dispersed on a solid support. Typically tens of secondary ions are ejected from each impact. They are identified with time-of-flight mass spectrometry and recorded individually. This approach reveals molecules co-located within the 10-20 nm diameter area of emission from one Au_{400}^{4+} impact. We demonstrate that the event-by-event bombardment-detection mode is sensitive to the chemical and/or physical nano-scale separation of molecular species. The performance is illustrated with the determination of the relative abundance of the oxide layer in the near surface of 50-100 nm nanoparticles; the nature and abundance of different nano-objects (5-20 nm in diameter) in mixtures of nano-sized solids; the composition of bio-objects such as a bacteriophage including the amino acids of the proteins surrounding the phage and the bases from the encapsulated DNA. The distinct feature of the nanoprobe technique presented here is in the detection of co-emitted ejecta from individual projectile impacts which allows to test chemical composition, in a nonimaging mode, yet at an exquisite level of spatial resolution. Moreover the co-emission of fragment and parent ions enhances the accuracy of molecular identification.

Work supported by NSF grant CHE-0750377

2:40pm BI+AS+NS+SS-WeA3 Strategies for Studying the Surface Chemistry of Engineered Nanoparticles with SIMS, C. Szakal, J. McCarthy, National Institute of Standards and Technology, K. Louis, R.J. Hamers, University of Wisconsin-Madison, R.D. Holbrook, National Institute of Standards and Technology

The environmental toxicity of engineered nanoparticles (ENPs) is of increasing importance as these materials become more widely used in manufacturing processes and consumer products. Nanoparticles have extremely high surface-to-volume ratios, which makes the surfaces more critical than their corresponding bulk materials in terms of reactivity, aggregation, and toxicity to various life forms. Therefore, it is critical that we develop methods to distinguish small chemical changes on nanoparticle surfaces in order to understand how these materials will interact outside of controlled laboratories. Conventional approaches of nanoparticle characterization have focused on high resolution morphological imaging (TEM, SEM) and physical property measurements such as surface charge. However, chemical information is generally only inferred from these materials with most current methods. If it is possible to obtain both elemental and molecular information from ENP surfaces, we may be able to determine the eventual fate of ENPs in the environment.

We have developed a comprehensive approach for studying the surface chemistry of ENPs, including 1) preparation of ENPs to controllably study desired variables, 2) development of methods such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) and environmental scanning electron microscopy (ESEM) to probe small changes in ENP surface chemistry and/or aggregation, and 3) development of methods to improve the speed and reproducibility of ENP aggregation for batch studies. These approaches will be utilized as the basis of future toxicity studies of selected ecosystems.

3:00pm BI+AS+NS+SS-WeA4 Unusual Hydrogenation Isotherms for Pd Nanoring Model Systems Observed Via Nanoplasmonic Sensing, C.B. Langhammer, E.M.K. Larsson, I.L. Zoric, Chalmers University of Technology, Sweden, V.P. Zhdanov, Boreskov Institute of Catalysis, Russian Federation

Nanostructured materials have been proposed as a solution for the development of efficient hydrogen storage systems. As the size of the system gets reduced in the nanometer range enthalpies and entropies of hydrogen dissolution in the metal (α -phase) and hydride formation (β -

phase) as well as activation barriers for diffusion and desorption of hydrogen become size dependent thus influencing both thermodynamics (pressure-composition isotherms) and kinetics (loading/unloading kinetics). The pressure-composition isotherms for a H₂/M system show a well-known behavior typical for an α -phase in the low pressure-composition range followed by a plateau signaling the onset of a hydride formation (β -phase) via a first order phase transition and a coexistence of the two over a wide composition range. At higher pressure a pure β -phase exists characterized by a pressure-composition curve with a steep slope. The plateau pressure of the H₂/M system is determined by the requirement of equilibrium between the three phases in coexistence, thus primarily by the enthalpy and entropy of hydride formation. In case of more than one hydride type a coexistence region exhibits multiple plateaux determined by appropriate energetics as described above. In all known cases the same multiple plateaux features were observed both during the charging and discharging process, i.e. when hydrogen pressure was increased/decreased, accompanied of course by a perennial hysteresis.

In this work we report unusual pressure-composition isotherms for H₂/Pd nanosized rings where a double plateau isotherms are observed during the charging process and a single plateau one during the hydrogen discharging. The Pd nanorings were fabricated using colloidal lithography. Hydrogen isotherms were followed by monitoring the shift in the ring Localized Surface Plasmon Resonance, LSPR, upon exposing the system to increasing/decreasing hydrogen pressure steps (and equilibrating the sample at each pressure step). The shift of the LSPR resonance was calibrated by preparing the same ring structure on a quartz crystal microbalance and "weighing" directly absorbed hydrogen. A linear relation between the LSPR shift and QCM frequency shift (proportional to hydrogen concentration) was observed.

We present a simple model, based on the observed heterogeneity of the nanorings (as seen in TEM) and by taking into account the defect induced lattice strain, that accounts for the unusual behavior of the observed isotherms.

4:00pm BI+AS+NS+SS-WeA7 Surface Functionalization and Analysis of Functional "Soft" Nanostructures: From 2 to 3 Dimensions, H. Schönherr, University of Siegen, Germany INVITED

The local properties of soft matter, e.g. for the fabrication of functional biointerfaces or nanostructures, are of tremendous importance for ultimate functionality. In this presentation, the closely interrelated areas of surface chemical functionalization / engineering and analysis of properties will be discussed based on three key examples. These examples include: (i) synthesis and modification of polymer brushes with particular focus on the nanomechanical properties, (ii) ultra small diameter nanotubes obtained by the layer-by-layer assembly of polyelectrolytes inside a sacrificial porous template and (iii) block copolymer nanocapsules that are developed for advanced wound management. In all examples, confinement effects are expected to play a significant role in determining e.g. the mechanical properties, as assessed by atomic force microscopy (AFM) nanoindentation.

For thin polymer films (2D) the dependence of the mechanical properties on the film architecture was unraveled. Compared to spin-coated films, brushes synthesized on gold surface by surface initiated polymerization showed higher elastic moduli, which is attributed to entropy effects. Upon chemical crosslinking tunable elastic properties are obtained, which provides interesting pathways for the fabrication of defined cell - surface contacts.

Similarly important are defined nanoscale objects that can be obtained via the replication of small templates by the so-called layer by layer (LbL) deposition of polyelectrolytes (G. Decher Science 1997, 277, 1232). LbL deposition in porous Anodic Aluminum Oxide (AAO) was only very recently expanded to the 100 nm length scale due to an alleged entropic barrier caused by adsorbed polyelectrolytes close to the pore orifice [Y. Cho et al. Small 2010, 6, 23, 2683]. However, in contrast to this report, we show that the adsorption of polyelectrolytes on the top plane of the AAO and polymer sedimentation have been identified as main bottlenecks. Suppressing these processes enabled us to produce free standing polymer nanotubes with external diameters of < 55 nm.

Finally, first steps in the development of active nanocapsules filled with a reporter dye or an antimicrobial agent for applications in burn wound management will be presented. In particular the case of burn wounds and the devised biomimetic strategy of BacterioSafe will be introduced. Subsequently, the fabrication and characterization of a polystyrene-block-poly(acrylic acid) amphiphile-based model vesicle system, in particular the loading and release behavior and mechanical properties will be discussed.

4:40pm **BI+AS+NS+SS-WeA9 Large Area Fabrication of Biological Nanostructures**, *G. Tizazu, O. El-Zubir*, University of Sheffield, UK, *S. Brueck*, University of New Mexico, *D. Lidzey, G. Leggett*, University of Sheffield, UK, *G.P. Lopez*, Duke University

There has been enormous interest in the control of biological interactions at interfaces with nanometer spatial resolution, but important challenges still remain to be addressed. Of the established fabrication techniques, electron beam lithography is expensive, and requires exposure under vacuum, while scanning probe methods are slow and (with few exceptions) do not permit fabrication over large areas. In contrast, interferometric lithography (IL) is a simple approach that uses inexpensive apparatus to fabricate sub-wavelength structures over macroscopic areas. When two coherent laser beams interfere, they yield a sinusoidal pattern of intensity that may be used to modify photosensitive materials. Previously IL has been used extensively for semiconductor nanofabrication, but our recent data show that combined with self-assembled monolayer resists it provides a fast, simple method to create molecular nanostructures over macroscopic areas. Illustrations will be provided of bionanofabrication using interferometric modification of protein-resistant (oligo ethylene glycol) functionalised surfaces, where feature sizes as small as 30 nm ($\lambda/8$) have been achieved over square cm areas, and the controlled growth of protein-resistant brush structures from patterns of initiators for atom-transfer radical polymerisation. The fabrication of metallic nanostructures over macroscopic regions, including Ti structures as small as 35 nm, and gold nanostructures of controlled size and periodicity will also be demonstrated.

5:00pm **BI+AS+NS+SS-WeA10 Functionalization of Mesoporous Silicon Biosensors to Achieve Tunable DNA Bioreceptor Density**, *J. Lawrie, R.R. Harl, B.R. Rogers, P. Laibinis, S.M. Weiss*, Vanderbilt University

Porous silicon has become a widely studied material for sensing over the last decade based on its large surface to volume ratio and easily tunable morphology. With growing interest in the detection and analysis of genetic material, DNA oligos have become an increasingly important bio-recognition element in porous silicon and many other sensor platforms. As aptamers, nucleic acids serve as high affinity bioreceptors to a wide range of small molecules and biological materials, opening up a number of potential applications in environmental science, chemical and biological defense, and medical diagnostics. In this work, tuning of the porous silicon surface chemistry is described. Controlling surface silanization, bioreceptor density, and bioreceptor charge and secondary structure enables the fabrication of reusable, label-free optical sensors toward specific nucleic acid targets. Detection limits in the nanomolar range have been demonstrated.

We have previously shown that in situ DNA synthesis via the phosphoramidite method in porous silicon produces high bioreceptor coverage for label-free optical biosensing applications. Low hybridization efficiency, despite high sensitivity, for such sensors indicated that tuning the receptor surface density could further improve detection limits. To modify surface receptor density, two-component trichlorosilane monolayers were deposited from solution onto porous silicon. One monolayer component remained active to phosphoramidite chemistry while the second component was inert. This method enabled a range of surface probe densities to be achieved and controlled via silanization conditions. Monolayer composition and DNA receptor density were verified using XPS, contact angle, and UV-Vis spectrophotometry. For a 16mer DNA oligo bound within a porous silicon waveguide, detection of the complementary target nucleic acid was maximized when 25% of the internal pore surface area was active toward DNA synthesis. Tuning surface DNA density increases sensitivity by a factor of 2-3. Label-free, target-specific detection of oligos was observed at concentrations of 25nM.

We will present results from hybridization efficiency studies in which DNA bioreceptor surface density, length, and secondary structure are varied. These parameters are vital to nucleic acid aptamer sensing strategies in label-free optical biosensors. Predicting appropriate receptor surface density for aptamer sensors based upon oligo sequences will provide advantages in achieving fast and sensitive waveguide sensors for detection in complex media.

Acknowledgements: This work is supported in part by the Army Research Office (W911NF-08-1-0200).

5:20pm **BI+AS+NS+SS-WeA11 Composite Fluorocarbon Membranes by Surface-Initiated Polymerization**, *C.A. Escobar, A.R. Zulkifli, G.K. Jennings*, Vanderbilt University

This presentation describes the fabrication and characterization of a novel composite membrane that consists of two types of nanoporous materials, namely, nanoporous gold leaf (NPGL) and nanoporous alumina, and a selective poly(perfluorohexyl norbornene) (pNBF6) polymer. Integration of the three materials is achieved by means of silane and thiol chemistry, and

the use of surface-initiated ring-opening metathesis polymerization (SI-ROMP). The former two provide functionalization of the nanoporous substrates, and the latter promotes the generation of the polymer film within and atop of the alumina-NPGL membrane. The synthetic process is versatile in that simultaneous or selective growth of the polymer film in each nanoporous layer is straightforward. The use of SI-ROMP allows tailoring of the extent of polymerization of pNBF6 throughout the structure by varying polymerization time. Advancing contact angle measurements show that the surface of these composite membranes exhibits both hydrophobic and oleophobic behavior. Scanning electron microscopy (SEM) images indicate that the thin polymer films cover the porous substrates entirely. Results from electrochemical impedance spectroscopy (EIS) confirm that the membranes provide effective barriers to aqueous ions and that sulfonation of the polymer backbone substantially enhances ion transport through the composite membrane. Ion transport and selectivity of the membrane change by regulating the polymerization time. The fluorinated nature of the polymer thin film renders the membrane selective towards molecules with similar chemical characteristics.

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