

Monday Morning, November 9, 2009

Nanometer-scale Science and Technology

Room: L - Session NS+BI-MoM

Nanowires and Nanoparticles I

Moderator: L.E. Ocola, Argonne National Laboratory

8:20am **NS+BI-MoM1 Zirconia Nanoplatelets for use in Dental Restoratives**, K. Coulter, V.Z. Poenitzsch, S. Wellingshoff, B. Furman, M. Rubal, D. Nicoletta, K. Chan, Southwest Research Institute

Photopolymerizable composites containing very high volume fractions (>50%) of radio-opaque nanoplatelets in a low polymerization shrinkage, liquid crystalline (LC) monomer mixture are being developed as dental restoratives. The LC monomer promotes the organization of the nanoplatelets into either a smectic or columnar, colloidal liquid crystal structure with significantly enhanced strength. Further, theoretical calculations suggest that the tetragonal form of the yttria-stabilized zirconia nanoplatelets that SwRI is producing by a roll-to-roll, e-beam evaporation process can be induced to transform into a less dense monoclinic form in the presence of the hydrostatic tensile stresses expected at a growing crack tip within the composite resin. This transformational volume expansion coupled with the inherent ductility of the surrounding LC polymer matrix results in substantial improvements in dental composite wear resistance. SwRI has successfully coated onto a 200nm pitch, nanoembossed PET film in single run lengths of hundreds of meters, a 10 nm alkali halide release layer to produce a 50nm thick zirconia film of tetragonal crystal form which is subsequently removed by dissolving the alkali halide layer in water. The nanoembossed pattern transfers to the zirconia layer to produce nanoplatelets. Three specific problems have been encountered including: (1) producing tetragonal zirconia of consistent morphology in different ca 100 meter runs, (2) complete fracture along the nanoembossed pattern, (3) color in the zirconia, most probably resulting from oxygen depletion and sub-4+ zirconia oxidation states. In this paper we will present the fabrication process and challenges in producing the nanoplatelets and present some of the preliminary composite data.

8:40am **NS+BI-MoM2 Formation of Metallic Nanoclusters on TiO₂ by Deposition and Sputtering**, A.B. Arjad, J.A. Yarmoff, University of California, Riverside

The discovery that Au nanoclusters are catalytically active when supported in an oxide matrix¹ has led to an abundance of surface studies, particularly those concentrating on metal nanoclusters deposited on single crystal TiO₂. For example, STM showed that Au clusters grow on TiO₂(110) without a wetting layer and that the size of the clusters increases as more metal is deposited.² We previously used low energy alkali ion scattering to interrogate such clusters grown by evaporation, measuring the neutral fraction of the backscattered ions with time-of-flight spectroscopy.³ We were able to show that the neutralization depends on the electronic structure of the clusters, and therefore changes as a function of cluster size. Our group also demonstrated a novel method for the production of nanoclusters by Ar⁺ sputtering a thin Au film deposited on TiO₂.⁴ As this initial work was performed with Au, it is not clear whether nanoclusters displaying quantum size effects could be fabricated by sputtering other materials. In the work presented here, Ag and Pt are evaporated onto TiO₂(110) and thin films of these metals are sputtered. The materials are then interrogated via the scattering of 2.5 keV Na⁺. It was found that while both Pt and Ag form nanoclusters by evaporation, only Pt forms nanoclusters after sputtering. This may be due to differences in the surface free energy of the metals, or of the propensity of Ag to oxidize. Future efforts will include temperature programmed desorption to test the chemical activity of the metal nanoclusters, as well as the use of other substrates.

¹M. Haruta, et al., J. Catal. **144**, 175 (1993).

²M. Valden, X. Lai and D.W. Goodman, Science **281**, 1647 (1998).

³G.F. Liu, Z. Sroubek and J.A. Yarmoff, Phys. Rev. Lett. **92**, 216801 (2004).

⁴P. Karmakar, G.F. Liu, Z. Sroubek and J.A. Yarmoff, Phys. Rev. Lett. **98**, 215502 (2007).

9:00am **NS+BI-MoM3 Towards Emergence of New Function by Engineering Materials: Colloidal Nanocrystals as Building Blocks for Nanocomposites and Assemblies**, M.L. Curri, CNR IPCF, Italy **INVITED**

Increasing attention has been devoted to the properties of materials in nanophase state, which are highly dependent on their size and shape and can be dramatically different from those of the corresponding bulk phase materials. Such geometry dependent characteristics result essential for

design novel functional materials with tailored characteristics, revealing a high impact on fundamental aspects as well as on potential technology applications. Fine tuning of the nanomaterial electronic, optical, magnetic, thermal, mechanical, and chemical properties opens possibilities for their wide applications in several technological fields. In this sense the basic nanosized building blocks of such complex structures play a crucial role and the extent to which nanocrystals (NCs) and nanoparticles (NPs) can be fabricated, engineered and their properties tailored is central. Chemical strategies are now able to provide highly processable NCs, possessing an adjustable interface with the external environment, able to tune their specific chemical reactivity towards the surroundings¹. Equally decisive is the scheme used to convey the instruction for assembly and organization into the inorganic NPs. Assembly can be spontaneous (self assembly), guided by the intrinsic information coded into the building blocks, and/or driven by external stimuli, templates, chemical and/or physical forces.^{1,2} The complexity of the formed structures depend on a variety of factors, ranging from the type of the single structural component, the length scale along which the structured material is achieved, the kind of mechanism ultimately involved for the creation of the final architectures. The NC based structures, either hierarchical organized or nanocomposite in nature, can show original emergent properties which cannot be readily envisioned from the building block original properties, while can be observed to arise in the originated mesostructure of nano-objects.³ The potential to design and fabricate such nanostructured materials with unprecedented functionality open the routes for applications in biomedical, optical, electronic, catalytic and light energy conversion systems.

1. E. Fanizza, P. D. Cozzoli, M. L. Curri, M. Striccoli, E. Sardella, A. Agostiano (2007) Adv.Funct. Mater. **17** 201-211.

2. M. L. Curri, R. Comparelli, N. Depalo, E. Fanizza, M. Striccoli "Patterning and Assembling of Inorganic Nanocrystals" in Nanomaterials: Inorganic And Bioinorganic Perspectives Edited by C. M. Lukehart and R. A. Scott, Chichester, UK: John Wiley & Sons, Ltd, pp 327-356,

3. J. Y.Kim, C. Ingrosso, V. Fakhfour, M. Striccoli, A. Agostiano, M. L. Curri, J. Brugger (2009) Small **5** 1051-1057.

9:40am **NS+BI-MoM5 The Direct Writing of Nanoscale Patterns of Nanoparticles and Polymer-Nanoparticle Composites**, P. Sheehan, W.-K. Lee, Naval Research Laboratory, W. King, Z. Dai, University of Illinois, Urbana-Champaign

In thermal Dip Pen Nanolithography (tDPN), a heatable AFM cantilever regulates the deposition of an ink through controlled melting, much like a nanoscale soldering iron. Control over writing is exceptional—deposition may be turned on or off and the deposition rate easily changed without breaking surface contact. Moreover, the technique may be performed in UHV and is compatible with standard CMOS processing. tDPN has been successful at depositing materials ranging from semiconductors to insulators to metals at speeds up to 200 $\mu\text{m/s}$.

Recently, we have become interested in directly depositing nanoparticles-polymer composites. Nanoparticles and nanoparticles-polymer composites offer many new capabilities that could greatly advance nanoelectronics, data storage, biosensors, and optical imaging applications. However, these applications often require that the nanoparticles or composites be formed into nanostructures that are precisely deposited on a surface or in a device. This requirement has spurred the development of many new nanolithographies but, to date, they have exhibited relatively low resolution (>~100 nm), a lack of generality to a range of materials, or the requirement of many serial processing steps. With tDPN, we can deposit with nanoscale precision a wide range of polymers (PMMA, P(VDF-TrFE), polyethylene) that contain metallic nanoparticles, semiconducting nanoparticles, or small molecules. An oxygen plasma can remove the polymer to reveal evenly dispersed nanoparticles or, for some combinations, precisely-placed 10 nm wide rows of nanoparticles. The flexibility and precision of this approach should greatly speed the advent of AFM tip based nanomanufacturing.

10:00am **NS+BI-MoM6 Synthesis and Structural Characterization of Fe-O Nanonetworks**, G.C. Franco, C.V. Ramana, University of Texas at El Paso

Iron (Fe) oxides and hydroxides have been the subject of numerous investigations for many years. Fe oxides and hydroxides find application in chemical catalysis, magneto-electronics, energy storage and conversion, and nuclear industry. The properties and phenomena of these materials are influenced by the morphology and size. The present work is performed to grow high-quality and ordered structure Fe oxides by simple wet-chemical method at a relatively low temperature. Fe oxides and hydroxides have been prepared in aqueous media by precipitation of iron nitrate and ammonium hydroxide. Their growth and structural characteristics have been

investigated using x-ray diffraction (XRD) and high-resolution scanning electron microscopy (HRSEM). The approach is preparing different solutions of Fe particles in suspension and acetic acid at different concentrations and subject to heat treatment at 100 °C. XRD analyses indicate that the solids obtained from aqueous stage exhibit goethite (α -FeO(OH)) with average particle size 2-3 nm, while the samples with acetic acid addition shown hematite (α -Fe₂O₃) with average size ~20 nm. HRSEM images confirm the presence of particles ~100 nm in samples with no acetic acid. HRSEM indicate that the samples with acetic acid exhibit nanoparticles ~20 nm with small spots within the particles. In addition, SEM shows the presence of net-shaped structures and particles with high-density porosity within the nano-regime depending on the concentration of acetic acid. The experiments also confirm that Fe oxide nano-particles and networks are stable to a temperature of 500 °C. The results obtained on the growth, structure, and properties of the grown Fe-based nanomaterials will be presented and discussed in detail.

10:40am **NS+BI-MoM8 Synthesis of Shape Controlled Sinter Resistant Nanoparticles**, *N. Shukla, M. Nigra, A.J. Gellman*, Carnegie Mellon University

We report synthesis of shape controlled, sinter resistant, core shell nanoparticles. The synthesis conditions allow control of the shell shape and the preparation of hexagonal shells and spherical shells. The 3D structures of these particles have been studied using angle resolved high resolution TEM. 2D cross sectional TEM images show that the cores are not positioned at the centers of the shells. By rotating the nanoparticles and monitoring the apparent motions of the cores in the 2D cross sectional images it is possible to determine the radial position of the core with respect to the center of the shell. The distribution of core positions within the core shell structures is bimodal. These observations suggest that the Fe shells grow on the Pt cores by a nucleation process rather than layer-layer growth.

11:00am **NS+BI-MoM9 Fabrication and Characterization of Carbon Nanostructures; Optical, Mechanical and Chemical Properties**, *H. Fredriksson, T. Pakizah*, Chalmers University of Technology, Sweden, *J. Cardenas*, University of Oslo, Norway, *M. Käll, B.H. Kasemo, D. Chakarov*, Chalmers University of Technology, Sweden

Nanosized carbon particles are present in many different context and applications. Examples include, aerosols and interstellar dust, inks, lubricants, composite materials and electronics. Investigations of the physical properties of such nanocarbons are therefore well motivated. We present a systematic investigation of the optical, mechanical and chemical properties of graphite and amorphous carbon nanostructures with different size. Hole-mask colloidal lithography and oxygen reactive ion etching is used to fabricate supported carbon nanostructures with well-defined diameters ranging from ~100 to 350 nm and heights from ~50 to 200 nm. Optical absorption/extinction spectra of these samples, as well as finite difference time domain (FDTD) calculations, reveal resonant absorption of visible light, both for the graphitic and for the amorphous carbon structures. The spectral maxima of the absorption peaks are correlated to the nanostructure diameters and heights. These optically resonant nanostructures are then further investigated using Raman spectroscopy, and compared with measurements from macroscopic graphite crystals. We show that the limited size has little influence on the mechanical properties of the graphite, i.e. the nanostructures have the mechanical properties of crystalline graphite. However, a slight enhancement of the Raman scattering intensity, correlated to the resonant absorption in the nanostructures is observed. Upon increasing the laser power we also observe distinct peak-splits and -shifts as well as increasing anti-Stokes signal intensity, suggesting selective heating of the nanostructures. Furthermore, the correlation between size and optical absorption have been used to follow the oxidation-driven size decrease of amorphous carbon nanostructures, relevant as model systems for investigations of soot oxidation. It is shown that the peak characteristics (spectral position and amplitude) are very sensitive signatures of the nanostructure size and that this can be used to accurately measure very low oxidation rates, using simple optical absorption techniques.

11:20am **NS+BI-MoM10 Microscopic and Spectroscopic Studies of Photoactive Supermolecular Porphyrin Assemblies**, *U.M. Mazur, K.W. Hipps, B.C. Wiggins, B.A. Friesen*, Washington State University

Synthetic porphyrins form excitonically coupled ring- and rod-shaped nanostructures, which are of interest for their potential applications in optoelectronic devices and solar cells. Nanorods produced from the sodium salt of tetrakis(4-sulfonatophenyl) porphyrin, TSPP, dissolved in acidic aqueous solutions, were deposited onto Au(111) substrates and were imaged by scanning probe microscopy. Ambient and UHV scanning tunneling microscopy, STM, images revealed individual rods with diameters of 25-40 nm and lengths of hundreds of nanometers. High resolution STM images of TSPP on Au(111) showed that the rods are composed of disk-like

building blocks approximately 6.0 nm in diameter. We speculate that the disks are formed by a circular *J*-aggregation of 14-16 overlapping electronically coupled porphyrin chromophores and that this circular porphyrin organization is driven by nonplanar distortions of the porphyrin diacid. X-ray photoelectron spectroscopy, XPS, was employed to investigate the structural changes in TSPP associated with the protonation of the porphyrin ring and aggregation. Scanning tunneling spectroscopy, STS, results indicate high conductivity of TSPP nanorods that can be attributed LUMO based conductivity in the nanorods.

Our results shed light not only on the structural model for TSPP basic aggregate unit but also on the conduction mechanism within the TSPP nanorod structure.

11:40am **NS+BI-MoM11 Solid-State Tunneling Spectroscopy of Individual Nanoparticles**, *R. Subramanian, P. Bhadrachalam, V. Ray, S.J. Koh*, University of Texas at Arlington

Semiconducting nanoparticles are increasingly finding innovative applications in many areas of science and technology such as bio-medicine, solar-energy harvesting, and photonics. For effective use of nanoparticles for these applications, it is necessary to know their electronic structures and efficient and accurate techniques to measure them are desired. We present a new technique to directly probe the energy levels of individual semiconducting nanoparticles in which the units to measure the electronic structures are fabricated using CMOS-compatible processes. This technique not only enables us to probe energy levels of an individual nanoparticle, but allows carrying out many such measurements from numerous units fabricated with a single-batch parallel processing. The energy levels were directly obtained with the I-V measurement through double barrier tunnel junctions that were formed when the nanoparticles were placed between vertically separated source and drain electrodes. The band gap ($E_g \sim 1.92$ eV) and energy level spacings ($\Delta E \sim 130$ meV, $\Delta E_{p-d} \sim 96$ meV and $\Delta E_{d-f} \sim 103$ meV) were measured directly from the current-voltage and differential conductance spectra for colloidal CdSe nanoparticles (~7 nm). Measurements for core-shell semiconducting nanoparticles (such as InP/ZnS) will also be presented. (Supported by NSF CAREER (ECS-0449958), ONR (N00014-05-1-0030), and THECB ARP (003656-0014-2006))

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