

Wednesday Afternoon, November 12, 2014

Nanometer-scale Science and Technology

Room: 304 - Session NS+AS-WeA

Nanoscale Imaging and Materials Characterization

Moderator: Craig Prater, Anasys Instruments, Paul Sheehan, Naval Research Laboratory

2:20pm NS+AS-WeA1 2014 AVS Albert Nerken Mark Award Lecture - **Brilliant Nanodiamond Particles**, *Olga Shenderova**, Adámás Nanotechnologies Inc., *G.E. McGuire*, International Technology Center
INVITED

Despite that nanodiamond (ND) particles were discovered more than 50 years ago and were mass produced in the early 80s, for a long time they were in the shadow of their more famous sp^2 carbon cousins. Two recent major breakthroughs, production of individual 4-5nm particles and particles containing colour centres exhibiting stable luminescence and unique spin properties have brought ND particles to the forefront of materials research.¹ Nanometer size particles are produced by detonation of carbon-containing explosives or by grinding of microdiamond powders. Besides well-known outstanding mechanical and thermal properties, diamond particles have remarkable optical properties in combination with biocompatibility, high specific surface area, and tuneable surface structure. Applications of ND which have captivated the imagination of scientist in areas which have broad societal impact, such as energy preservation and biomedical imaging, will be briefly illustrated and a more in-depth review of their optical properties provided.

The optical emission, scattering and attenuation of ND are finding unique applications. In life sciences nanoparticles are increasingly used as fluorescent probes to monitor cellular interactions and study cellular dynamics at the single molecular level. Foreign atoms can be incorporated into the lattice of ND particles providing photostable particles as well as systems for quantum sensing that may be used to probe the intracellular environment at the nanoscale. Development of multimodal imaging probes based on 5-10nm ND and doping of ND with different elements to generate photoluminescence at alternative wavelengths are future directions for this field. Carbon dot-decorated ND is another means of generating photoluminescent nanoparticles with tuneable emission over the visible to near-infrared portion of the electromagnetic spectrum. The photoluminescent ND is increasingly being viewed as a means of drug delivery. Encapsulating ND in a porous silica shell is a means of achieving stable fluorescent imaging with nanoparticles with a high loading capacity for bioactive molecules.

Due to its high refractive index, wide bandgap and crystalline lattice, ND highly attenuates and scatters ultraviolet radiation. High attenuation and scattering in combination with large surface area has been shown as a means of increasing the radiation resistance of polymer nanocomposites. This can be beneficial in sunscreens as well as in polymers used in the construction of satellites to be placed in low Earth orbit.

¹V.Mochalin, O.Shenderova, D.Ho and Y.Gogotsi, "The properties and applications of nanodiamonds", (2012) *Nature Nanotechnology*, 7 (1) 11-23.

3:00pm NS+AS-WeA3 **Oxidation State Sensitive Imaging of Ceria Nanoparticles**, *Aaron Johnston-Peck*, National Institute of Standards and Technology (NIST)

Scanning transmission electron microscopy (STEM) coupled with electron energy loss spectroscopy (EELS) has been successfully applied to track changes to composition as well as bonding environment with atomic resolution. These measurements impose exacting experimental and instrumentation requirements that include aberration-corrected optics, electron sources with narrow energy spreads, and extremely stable room environments. Therefore it seems prudent when possible that other techniques with less demanding experimental requirements supplement EELS measurements. Imaging or diffraction techniques greatly relax these aforementioned requirements as the need for corrective optics and narrow energy spreads can be eliminated. Moreover the possibility of beam induced artifacts is reduced because the total electron dose needed to form an image or diffraction pattern is less than an EELS spectrum image.

Low angle annular dark field (LAADF) STEM is presented as an alternative to EELS measurements to identify changes to local changes of oxidation state in ceria (CeO_2) nanoparticles. This relationship was established

through the use of EELS, *in-situ* measurements, and image simulations. Ceria has numerous energy related applications due to the ability of ceria readily store and release oxygen. The formal charge of the cerium ions transition from 4+ to 3+ as oxygen vacancies are formed. These oxygen vacancies cause local distortions to the crystal and subsequently produces additional diffuse scattering to low angles. The LAADF STEM signal is sensitive to this change in scattering and contrast variations in the image become resolved. Additionally, preliminary experiments on other metal oxide nanoparticles suggest that this approach may be applied to other material systems and processes as well.

3:20pm NS+AS-WeA4 **Shape and support interaction of size-selected Pd and Pt NPs on $\text{TiO}_2(110)$** , *Mahdi Ahmadi*, *F. Behafarid*, University of Central Florida, *B. Roldan Cuenya*, Ruhr-University Bochum, Germany

The shape and the support interaction of 3D palladium and platinum nanoparticles (NPs) deposited on $\text{TiO}_2(110)$ was investigated using scanning tunneling microscopy (STM). The NPs were synthesized using inverse micelle encapsulation. In spite of the initial random location of the micelle-prepared NPs on the support, step edge decoration was observed after annealing at high temperature ($>1000^\circ\text{C}$). In general, resolving the shape of 3D NPs using STM is very challenging due to the tip-convolution effects. However, a combination of ultra-sharp STM tips and samples containing structurally well-defined NPs allowed us to resolve the NP shape, with the highest features on the NPs being unaffected by tip artifacts. It was found that all NPs had a truncated octahedron shape, with $\{111\}$ top and interfacial facets. Furthermore, the alignment of the NP edges (or symmetry axes) with the $\text{TiO}_2(110)$ -[001] atomic rows evidenced the epitaxial relationship with support achieved after annealing. The STM data were analyzed following the Wulff-Kaischew theorem, and a MATLAB code was used to reconstruct the NP shape, eliminating overestimations in the lateral size inherent to the STM technique due to tip effects. The surface energy ratio $\gamma_{100}/\gamma_{111}$ was calculated for each Pd NP with an average value of 1.12 ± 0.07 , which is in good agreement with theoretical values. Moreover, the adhesion energy was found to display a size-dependence, with larger NPs having smaller adhesion energy. This phenomenon can be explained based on the minimization of the interfacial strain by reducing the contact area. Following similar analysis of Pt NPs on $\text{TiO}_2(110)$, a higher $\gamma_{100}/\gamma_{111}$ ratio of 1.18 ± 0.1 was obtained as compared to Pd. Also, the rate of decrease in the adhesion energy with increasing NP height was lower for Pt as compared to Pd.

4:20pm NS+AS-WeA7 **Nanoscale Imaging and Spectroscopy of Plasmonic Hot Spots and Dark Modes with the PTIR Technique**, *Andrea Centrone*, National Institute of Standards and Technology (NIST)
INVITED

Localized surface plasmon resonances couple propagating light with nanoscale volumes of matter (hot-spots), enabling new applications in sensing and therapeutics. Surface-Enhanced Infrared Absorption (SEIRA) Spectroscopy exploits such hot-spots for sensitive chemical detection. Calculations predict large SEIRA enhancement factors but the diffraction of long IR wavelengths ($2 \mu\text{m} - 16 \mu\text{m}$) has hindered the experimental determination of SEIRA enhancements with nanoscale resolution.

Photo Thermal Induced Resonance (PTIR) combines the chemical specificity of IR spectroscopy with the lateral resolution of Atomic Force Microscopy (AFM). PTIR circumvents the limitations of light diffraction by employing an AFM tip as a local detector for measuring the transient thermal expansion induced by the absorption of light pulses in the sample. Local IR spectra and composition maps are obtained recording the amplitude of the tip deflection as a function of the laser wavelength and position, respectively. Notably, the PTIR signal is proportional to the absorbed energy (not scattering) and the PTIR spectra are directly comparable with IR spectral libraries, enabling materials identification.

In this work, the PTIR technique is applied to image the dark plasmonic resonance of gold Asymmetric Split Ring Resonators (A-SRRs) in the mid-IR with nanoscale resolution. Additionally, the chemically-specific PTIR signal is used to map the local absorption enhancement of PMMA coated A-SRRs, revealing hot-spots in the resonators' gaps with enhancement factors up to ≈ 30 .

The local information gathered with in the PTIR experiments can provide insightful information and possibly help to engineer nanomaterials for greatest efficacy. As an additional example the PTIR technique will be applied to image phase separated domains in Metal-Organic Frameworks single crystals, a novel class of materials that find application in catalysis, sensing and separation.

* Albert Nerken Award Winner

5:00pm **NS+AS-WeA9 AFM-based Infrared Spectroscopy—Nanoscale Chemical Analysis with Sensitivity Down to Single Monolayers**, *Craig Prater, K. Kjoller, M. Lo, E. Dillon, R. Shetty*, Anasys Instruments, *C. Marcott*, Light Light Solutions, *F. Lu, M. Jin, M. Belkin*, University of Texas at Austin, *A. Dazzi*, Université Paris-Sud, France

The ability to perform chemical analysis at the nanoscale has been considered one of the “holy grails” of the scanning probe microscope community. Many techniques have been developed to provide material contrast in SPM images based on a variety of properties (electronic, optical, mechanical, etc.), but there had not been the ability to perform broadly applicable chemical analysis on diverse samples. We have developed AFM-based infrared spectroscopy (AFM-IR)¹ that enables broadly applicable chemical analysis on samples with nanoscale spatial resolution and with sensitivity down to the scale of individual molecular monolayers. The AFM-IR technique illuminates a sample with light from a tunable infrared laser source and then uses the tip of an AFM to measure the sample’s local photothermal expansion due to the absorption of infrared light at specific wavelengths.² Measuring absorption as a function of wavelength creates an IR absorption spectrum that acts as a chemical fingerprint to characterize and identify chemical components. Mapping IR absorption spatially over a sample at different wavelengths can be used to create maps of nanoscale chemical composition. Recently we have implemented two techniques to extend both the applicability and sensitivity of the AFM-IR technique. First, we implemented top side illumination to enable AFM-IR on a much wider array of samples and sample substrates. Second, we developed a resonance enhanced mode³ where the IR laser pulses are synchronized to a contact resonance of the AFM cantilever. Combined with “lightning rod” enhancement of the incident IR light, the resonance enhanced technique can achieve chemical analysis with single monolayer sensitivity⁴ and spatial resolution ~25 nm. We will describe the AFM-IR technique, recent innovations and applications in materials, life sciences, photonics, and semiconductors.

References:

1. A. Dazzi, R. P., F. Glotin, and J. M. Ortega. *Opt. Lett.* 2005, 30, 2388-2390.
2. Dazzi, A.; Prater, C. B.; Hu, Q.; Chase, D. B.; Rabolt, J. F.; Marcott, C. *Appl. Spectrosc.* 2012, 66, (12), 1365-1384.
3. Lu, F.; Belkin, M. A. *Opt Express* 2011, 19, (21), 19942-19947.
4. Lu, F.; Jin, M.; Belkin, M. A. *Nat Photon* 2014, 8, (4), 307-312.

5:20pm **NS+AS-WeA10 Schottky Barrier Height Mapping of Nanoengineered Metal/Semiconductor Interfaces**, *Robert Balsano, C. Durcan*, University of Albany-SUNY, *A. Matsubayashi, V.P. LaBella*, University at Albany-SUNY

Metal/semiconductor junctions form rectifying contacts known as Schottky diodes, which have an energy barrier determined by charge transfer and bonding at the interface. Current-voltage and capacitance-voltage spectroscopy measurements yield a spatially averaged barrier height. Ballistic electron emission microscopy (BEEM) is a scanning tunneling microscopy (STM) technique that can measure transport of hot electrons through materials and interfaces locally with high spatial and energetic resolution due to the precise positioning of the STM tip. This presentation details work done to map the Schottky barrier height with nanoscale resolution at several metal/semiconductor interfaces. These maps can give insight into the homogeneity of the barrier height as well as the spatial distribution of individual metal species. Potentially this technique can be used to image nanoengineered interfaces.

5:40pm **NS+AS-WeA11 Scanning Electron Microscopy to Probe Electron Transport of Working Nanodevices under Realistic Operation Conditions**, *Ana Stevanovic, A. Kolmakov*, National Institute of Standards and Technology (NIST)

The interplay between the electron transport and chemical status of the surface of working nanodevices can be affected by local electroactive inhomogeneities (defects), presence of near surface depletion regions and Schottky contacts. In spite of tremendous progress achieved in understanding of semiconductor chemical sensors, very little experimental data are available on aforementioned interplay in working devices under realistic operation conditions. Ambient pressure electron microscopy is used in this work to address *in situ* imaging of a formation of electroactive inhomogeneities inside a model SnO₂ nanowire device as a function of gas environment and temperature under realistic operating conditions. In addition, using scanning photoelectron and Auger microscopy with the lateral resolution of ca 80 nm, we are able to access spectroscopically the fine changes in surface condition of an individual SnO₂ nanowire during their operation. It is possible to monitor the changes in a conductance of the SnO₂ nanodevice in operando mode upon exposures to different redox gases and relate them to the formation of the specific surface groups.

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