Electronic Materials and Photonics
Room 102A - Session EM+NS-WeM

Nanoparticles for Electronics and Photonics

Moderators: Joseph Tischler, U.S. Naval Research Laboratory, Jessica Hilton, Mantis Deposition

8:00am **EM+NS-WeM1 Nanostructures on Surfaces: From Cluster Deposition to Low Energy Ion Bombardment**, ***Luke Hanley***, *K. Steeves Lloyd, M.W. Majeski, I.L. Bolotin,* University of Illinois at Chicago*; M. Schmeling,* Loyola University Chicago*; I.V. Veryovkin,* University of Illinois at Chicago **INVITED**

Two strategies are described for the preparation of unique nanostructures on surfaces or within thin films: cluster beam deposition and low energy ion beam irradiation. In cluster beam deposition, copper sulfide nanoparticles were prepared by magnetron sputtering under a flow of argon and hydrogen sulfide, then codeposited with evaporated pentacene to form a composite thin film (M.W. Majeski, *et al.*, ACS Appl. Mater. Interf., 2014, http://dx.doi.org/10.1021/am5028428). This all-gaseous method can prepare a variety of semiconductor nanoparticles without the surface ligand capping and oxidation effects often observed for colloidally prepared nanoparticles that can inhibit charge transfer or cause self-doping. X-ray photoelectron spectroscopy, transmission electron microscopy, and high-angle annular dark-field scanning transmission electron microscopy were used to determine that 2.3 ± 0.4 nm $Cu_{2-x}S$ nanoparticles with copper in the +1 oxidation state were deposited into pentacene films. In low energy ion beam irradiation, nanocone and nanoripple arrays were prepared on Si surfaces by grazing incidence irradiation with 1 keV Ar^+ ion beams that simultaneously sputtered away surface atoms and sputter-deposited metal impurity atoms from adjacent targets (K. Steeves Lloyd, *et al*. Surf. Sci., 2016, http://dx.doi.org/10.1016/j.susc.2016.03.016). Scanning electron microscopy and atomic force microscopy observed that when Si, Cu, or stainless steel was employed as a co-sputtering target, only stainless steel was found to assist the growth of dense arrays of nanocones. The structural characterization of samples further correlated the role of incident ion fluences on the formation of nanoripples vs. nanocones. Characterization of sample chemical composition by total reflection X-ray fluorescence and X-ray photoelectron spectroscopy revealed that the concentration of metal impurities originating from stainless steel (Fe, Cr and Ni) was relatively high in the regions with high density of nanocones and much lower in the region of nanoripples. Overall, these two strategies open up multiple possibilities for the preparation of complex nanostructures on surfaces and in thin films that are compatible with more common lithographic strategies.

8:40am **EM+NS-WeM3 Designer Nanocrystal Electronic and Optoelectronic Materials through Controlled Coupling and Doping**, ***Cherie Kagan,*** University of Pennsylvania **INVITED**

Semiconductor nanocrystals (NCs) are prized for their size- and shape-dependent electronic and optical properties and as building blocks in the assembly of NC solids. However, the long, insulating ligands commonly employed in the synthesis of colloidal NCs inhibit strong interparticle coupling and charge transport once NCs are assembled into the solids state as NC arrays. In this talk, I will describe methods to introduce atoms, ions, and more compact molecules at the NC surface that allows us to increase interparticle coupling and dope NC solids. NC coupling and doping provide control over the density of states, the carrier statistics and the Fermi energy. I will also describe the importance of engineering device interfaces to study the fundamental physics of NC solid transport and to design device architectures for applications. Examples of strong coupling and doping in II-VI and IV-VI semiconductor NC solids will be given that yield high-mobility, high-conductivity NC solids. Temperature--dependent transport measurements of these materials are consistent with a transition from localized to extended-state charge transport. These high mobility n- and p-type materials are used as the semiconductors to construct large-area, flexible, field-effect transistors and integrated circuits and for solar photovoltaics.

9:20am **EM+NS-WeM5 Au Nanoparticle Modified Indium Tin Oxide Ultramicroelectrode for Single Particle Spectro-electrochemistry Study and Ultrasensitive Electrochemistry Sensing**, ***Yanxiao Ma,*** The University of Alabama*; S. Pan,* The Univeristy of Alabama

Plasmonic active metal NPs are broadly used in electrochemical and optical sensing of molecular recognition events. However, it is extremely challenging to resolve chemical and physical transformation at single NP level using conventional optical and electrochemical methods for resolving their local structure-function relationship. We are developing an optical and electrochemical technique to resolve electrocatalytic property of single NPs. Combined methods of photolithography and electrodeposition are used for fabricating Au NP modified indium tin oxide ultramicroelectrode (ITO UME). Dark field scattering (DFS) microscopy and scanning electron microscopy (SEM) were used to characterize NPs on the surface of ITO UME. The electrochemistry voltammetric study shows that Au and Pt NPs are ideal catalytic materials for hydrazine oxidation reaction. Dark field spectroelectrochemical study of hydrazine oxidation at planer ITO and ITO UME confirmed the formation of nanobubbles on NPs surface. Relationship between DFS light intensity and hydrazine oxidation current profile was obtained.

9:40am **EM+NS-WeM6 Band Gap-Control of Spray Pyrolysis Synthesized CZTS Nanoparticles**, ***Stephen Exarhos***, *E. Palmes, A. Alvarez-Barragan, L. Mangolini,* University of California, Riverside

An innovative and scalable synthesis approach to the formation of phase-pure Cu_2ZnSnS_4 (CZTS) nanoparticles has been developed using aerosol spray pyrolysis. CZTS material is an inherent direct-band gap *p*-type semiconductor with a band gap of ~1.5 eV and absorption coefficient of $>10^4$ cm^{-1}, making it suitable for solar absorption applications. As an earth-abundant absorber material, it has been well-studied for application in thin film photovoltaics [1]. Little experimental work has been done to test the viability of the material as a photocatalyst, though the material shows low activity in driving water splitting or pollutant degradation unless synthesized in a noble metal heterostructure [2]. By its nature, CZTS is a very adaptable material system. It is relatively straightforward to alloy into the material primarily as a method of band gap control. By optimizing the band gap and band alignment of alloyed CZTS-like nanoparticles, we intend to improve the catalytic quality of CZTS-based heterostructures. We have previously shown that aerosol spray pyrolysis is an effective inexpensive and scalable technique for the synthesis of CZTS [3]. By processing a solution with copper-, tin-, and zinc-diethyldithiocarbamate precursors dissolved in a toluene solvent, we can form phase-pure, surface-ligand-free, kesterite CZTS nanoparticles with a size distribution average of ~ 20 nm. Using the same process, by adding hydrogen-terminated silicon nanoparticles — synthesized in-house by a non-thermal plasma process — to the precursor solution, we can alloy silicon into the material (making CZTSiS), and in turn increase the band gap of the material from the 1.5 eV for pure CZTS. We also have the ability to decrease the band gap by alloying different transition metals in place of zinc in the crystal lattice. We present preliminary studies characterizing CZTS and CZTSiS nanoparticles for potential use as a photocatalytic heterostructure material.

[1] Liu, Xiaolei, Yu Feng, Hongtao Cui, Fangyang Liu, Xiaojing Hao, Gavin Conibeer, David B. Mitzi, and Martin Green. Progress in Photovoltaics: Research and Applications, January 1, 2016.

[2] Yu, Xuelian, Alexey Shavel, Xiaoqiang An, Zhishan Luo, Maria Ibáñez, and Andreu Cabot. Journal of the American Chemical Society 136, no. 26 (July 2, 2014): 9236–39.

[3] Exarhos, Stephen. eScholarship, January 1, 2015. http://escholarship.org/uc/item/1pw1t81k.

11:00am **EM+NS-WeM10 Designer Nanomaterials by Magnetron Sputtering and Ion Soft Landing**, ***Grant Johnson***, *V. Prabhakaran,* Pacific Northwest National Laboratory*; T. Moser,* Michigan Technological University*; M.H. Engelhard, N. Browning, J. Laskin,* Pacific Northwest National Laboratory

Clusters and nanoparticles comprised of controlled amounts of different atoms are of interest for applications in optics, magnetics, catalysis, sensors, and biotheraputics. Alloy nanoparticles, in particular, may possess enhanced properties compared to single-metal species due to the additional interplay between their different elemental components. By reducing the quantity of precious metals in alloys by substitution with cheaper base metals, it is possible to achieve equivalent or superior performance to noble metal nanoparticles at reduced material cost. In addition, alloying of elements that are immiscible in the bulk is possible at the nanoscale because the enthalpy of mixing decreases and becomes negative at small particle sizes. As a result, a broad array of alloy species may be generated in the form of clusters and nanoparticles. Magnetron sputtering of multiple targets in the same region of gas aggregation is demonstrated to produce ionic alloy clusters and nanoparticles with defined composition and morphology that are not obtainable through solution synthesis. Introduction of reactive gases into the sputtering and aggregation region is shown to result in the formation of complex morphologies. A suite of characterization techniques including atomic force microscopy, scanning and transmission electron microscopy, and x-ray photoelectron spectroscopy is utilized to determine how the size, shape, and elemental composition of soft landed particles may be tuned through variations in source parameters. The electrochemical activity of the soft landed nanomaterials toward the oxygen reduction reaction, a critical process occurring in proton exchange membrane fuel cells, is evaluated ex-situ using cyclic voltammetry in solution and in-situ using an ionic liquid membrane in vacuum.

11:20am **EM+NS-WeM11 A Facile Electrodeposition Method for Vertically Standing Plasmonic Nanorods for Surface Enhanced Photoelectrochemical Catalysis***, **Jue Wang**, S. Pan,* The University of Alabama

A facile template-free electrodeposition technique is developed for large-scale fabrication of vertically standing plasmonically active silver nanorods (NRs). The diameter, length, and surface coverage of Ag NRs are dependent on the electrodeposition time. The growth mechanism of the vertically standing Ag NRs is investigated by tracking their morphology evolution as a function of deposition time. Because of their large specific surface area, oriented alignment, broad range light scattering, and light absorption tunability, these NRs are ideal substrates for thin layer photocatalysts for enhancing light absorption and charge collection. The Preliminary tests on plasmon-induced photocurrent of bare Ag NRs, Ag NR converted to Ag_2S NRs, and coated with CdS nanoparticles (NPs) are presented to demonstrate surface enhancement characteristics. This simple NR fabrication method can be extended to other conductive substrates and other materials for obtaining vertically standing NR structures.

11:40am **EM+NS-WeM12 Influence of Surface Reaction on the Infrared Localized Surface Plasmon Resonance of Indium Tin Oxide Nanocrystals***, **Weize Hu**, M.A. Filler,* Georgia Institute of Technology

Heavily doped oxide nanocrystals exhibit a tunable plasmonic response in the infrared, a capability that is promising for future photonic, spectroscopic, and energy harvesting/transport technologies. Nanocrystal carrier density, and thus spectral response, is adjustable via chemical reaction; however, the fundamental processes governing this behavior are poorly understood. Here, we study the oxidation and reduction of indium tin oxide (ITO) nanocrystals with O_2 and H_2, respectively, with in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). We show that the main absorption feature redshifts upon oxidation more than 1000 cm^{-1} and blueshifts to its original position upon reduction. The same magnitude spectral shift is observed over many cycles of oxidation and reduction. A kinetic model, which includes surface reaction and bulk diffusion, allows us to quantitatively rationalize the process, revealing that surface reaction is rate limiting under the conditions studied. Our experiments provide a deeper understanding of the connection between surface reaction and carrier density in oxide nanocrystals, and open the door to a priori control of plasmonic response.

12:00pm **EM+NS-WeM13 Electrochemical Synthesis of Nanostructured Cu and Cu_xO Electrodes for the Reduction of CO_2 to Usable Fuels***, **Nelly Kaneza**, S. Pan,* The University of Alabama

In effort to controlling carbon dioxide (CO_2) levels in the atmosphere, the conversion of CO_2 into useful products, although very challenging, has emerged as a very attractive area of research. In this work, a series of Cu based nanostructures are synthesized and characterized to demonstrate a low cost approach to reduce CO_2 electrochemically to specific fuel products at low overpotential. The synthesized Cu and Cu_xO nanostructures are characterized with X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) and their performance evaluated in terms of their activity, selectivity and stability using cyclic voltammetry (CV), gas chromatography (GC) equipped with a mass spectrometry (MS).

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