

Thursday Morning, October 21, 2010

Energy Frontiers Topical Conference
Room: Mesilla - Session EN+NS-ThM

Nanostructures for Energy Conversion & Storage II
Moderator: K.S. Leschkie, Applied Materials

8:00am **EN+NS-ThM1 Rare Earth Oxide Nanocavity Upconversion**,
V.D. Jankovic, J. Hoang, J.P. Chang, UCLA

Rare-earth (RE) oxides represent an important class of photonic materials owing to their nonlinear optical and upconversion (UC) properties which find applications in high power lasers, remote sensing, optical communications and photovoltaics. In the context of solar cells, these materials could increase cell efficiencies by upconverting photons with energies below and near the silicon bandgap (1.1eV) which are poorly absorbed by the indirect band-gap semiconductor to higher energy photons that can be absorbed more efficiently. Unfortunately, up-conversion efficiencies in rare-earth ions are usually low due to non-radiative processes such as concentration quenching. One strategy to address this problem is to couple RE ions with metal nanoparticles. Noble metal nanoparticles exhibit localized surface plasmon resonances which can readily be tuned to a particular spectral range of interest by means of size, shape and local dielectric environment. By coupling metal nanoparticles' plasmon resonances to rare earth ion energy transitions, the absorption cross sections of rare earth ions can be significantly improved.

In this work, we designed and synthesized Au|Yb:Er:Y₂O₃ core|shell nanorods as a potential route to improve solar cell efficiencies in the near infrared regime. A modified Mie scattering algorithm determined the optimum theoretical Au nanorod aspect ratio to be 9, for a resonance close to the Yb 980-nm energy transition. The Au nanorods were synthesized using a surfactant mediated growth technique, in which cetyltrimethylammoniumbromide micelles were used to direct the growth of Au nanoparticles in the [111] direction while suppressing the growth in [100] and [110] directions. Au nanorods with aspect ratios from 6 to 12 have been synthesized by varying the concentration of the reducing agent, ascorbic acid. Spatially and compositional controlled Yb:Er Y₂O₃ shells were deposited using sequential radical enhanced atomic layer deposition process. The plasmon-Er color center and plasmon-Yb sensitizer distance was systematically varied by controlling the thickness of the Y₂O₃ spacer layer from 1nm to 10nm. The length, aspect ratio, nanorod monodispersity and shell thickness were verified using transmission electron microscopy, while the shell composition was verified by energy dispersive X-Ray spectroscopy. Photoluminescence and radiative lifetime measurements with 980 nm excitation were used to investigate the distance dependence effects of the noble metal-emitter coupling on the optical properties of the core|shell nanorods. Quantitative measurements of the absorption cross section are underway and will also be presented

8:20am **EN+NS-ThM2 Thermal Transport Property of SiGe Nanowire**, *E.K. Lee*, Samsung Advanced Institute of Technology, Republic of Korea, *J.W. Lee*, Sungkyunkwan University, Republic of Korea, *L. Yin*, Texas A&M University, *B.L. Choi, S.J. Lee*, Samsung Advanced Institute of Technology, Republic of Korea, *D.M. Whang*, Sungkyunkwan University, Republic of Korea, *C.H. Yu*, Texas A&M University, *J.M. Kim*, Samsung Advanced Institute of Technology, Republic of Korea

8:40am **EN+NS-ThM3 Hydrogen Storage in Metal Organic Frameworks (MOFs)**, *N. Nijem, J.-F. Veyan*, University of Texas at Dallas, *L. Kong, K. Li, J. Li, D.C. Langreth*, Rutgers University, *Y.J. Chabal*, University of Texas at Dallas

Hydrogen storage is one of the most challenging problems in hydrogen-based energy technologies. One of the goals of hydrogen storage is the ability to store a high volumetric density of hydrogen at room temperature. As a result, studies exploring molecular hydrogen interaction in storage materials are important to facilitate further development of materials. Metal-organic Frameworks are promising candidates for hydrogen storage because their high surface area and porosity facilitate high hydrogen physisorption on specific sites of the structures and because many options are possible to enhance the interaction of molecular hydrogen with the host.

This work explores the incorporation of hydrogen into various MOFs using infrared (IR) absorption spectroscopy to characterize its interaction. IR spectroscopy can distinguish possible H₂ binding sites based on the perturbation of the internal H₂ stretch mode. IR measurements are performed on saturated metal center MOFs varying the ligand and/or the

metal center and on unsaturated metal center MOF-74-M (M=Zn, Mg and Ni). We combine room temperature, high pressure with low temperature (20-100K) measurements and theoretical van der Waals density functional (vdW-DF) calculations to derive quantitative information from IR shifts and dipole moment strengths.

Our results show that, in contrast to the current understanding, IR shifts are independent of binding energies and depend instead on the chemical environment of the molecule, including effects such as H₂-H₂ interactions. For example, we see little difference in IR shifts between saturated MOFs with low binding energy (~4kJ/mol), and unsaturated MOFs with higher binding energy (~10kJ/mol) sites at room temperature. Furthermore, we show that dipole moments of adsorbed H₂ depends greatly on parameters such as geometry of adsorption site and H₂-H₂ interactions. Measurements performed at low temperatures on MOF-74 show that IR shifts of H₂ is greatly red shifted (an additional ~30 cm⁻¹) due to H₂-H₂ interactions on close proximity adsorption sites, and that dipole moments of adsorbed H₂ can appreciably vary with loading.

Our analysis indicate that the intensity of H₂ IR band cannot always be a measure of the amount of H₂ adsorbed, therefore methods such as variable temperature IR (VTIR) used to deduce binding energies cannot always be implemented.

9:00am **EN+NS-ThM4 The Influence of Acid Treatment of TiO₂ Film Prepared by FFCVD on the Performance of Dye-Sensitized Solar Cell**, *B.R. Chen, Y.J. Chen*, National Dong Hwa University, Taiwan, Republic of China

In this study, we use the acid treatment to enhance the dye-sensitized solar cell (DSSC) efficiency from 4.58% to 5.87%. Comparing with the untreated films, the photocurrent and efficiency both largely increase ~28%. We also found that the use of acetic acid, as well as hydrochloric acid, can easily enhance the performance of DSSCs. The untreated film was prepared using a one-step method by the flat-flame chemical vapor deposition (FFCVD) system which deposits the nanoporous TiO₂ film directly as working electrode used in the DSSC. The TiO₂ film was grown on ITO substrate at the temperature of 400°C and the pressure of 20 torr. The efficiency of DSSC using as-synthesized TiO₂ electrode approaches 4.58% with the film thickness about 11~13 nm with proper tuning of carrier gas flow rate in the TiO₂ deposition process. We know that the DSSCs with best efficiency about 11% were prepared exclusively by hydrothermal method. The efficiency we have is among the highest for DSSCs prepared through non-hydrothermal process. The influence of acid treatment increase conversion efficiency was largely attributed to the short circuit current increase. In previous studies, some group improved the acid treatment to make the dye absorption increase effectively. However, most of them performed the treatment during hydrothermal process for the powder synthesis, which cannot be incorporated with the direct film preparation process. Therefore, we take the dipping method to treat our nanoporous TiO₂ film, and try to determine if the treatment can enhance the dye absorption as well. The crystalline quality and morphologies of surface modified TiO₂ electrodes were characterized by using XRD and FESEM. FT-IR and XPS were used to perform the surface characterization. The dye absorption of the DSSCs was also characterizes by UV-vis spectrophotometer. The efficiency of DSSCs using these working electrodes were measured under AM 1.5G 100 mW/cm² by Keithley 2400 sourcemeter. The optimized cell efficiency is 5.87% with the short-circuit photocurrent density of 14.50 mA/cm² and open-circuit voltage of 0.60 V at 0.1M hydrochloric acid solution and half-an-hour soaking.

9:20am **EN+NS-ThM5 Development of Novel Nanomaterials as the Building Blocks for Next-Generation Solar Cells**, *J.M. Pietryga, D.C. Lee, I. Robel, V.I. Klimov*, Los Alamos National Laboratory **INVITED**

The use of colloiddally synthesized nanomaterials in devices is attractive not only because of the low-cost and scalability of solution-based fabrication methods, but because of the facile control over electronic and optical properties of these materials made possible by structural fine-tuning. As the range of applications-of-interest has become more sophisticated, such tuning has progressed beyond simple control over effective band gap using quantum size effects to include much more fundamental modification of electronic structure and dynamics. Design and synthesis of novel nanomaterials that exploit such effects to create unique materials for use in next-generation solar cells are an important part of the ongoing effort within the Center for Advanced Solar Photophysics, a DOE Energy Frontier Research Center. I will examine a number of specific examples from this work, including germanium nanocrystals with partial direct-gap behavior and unique infrared-active heterostructures with extremely long-lived charge-separated excited states, and how such materials may be incorporated into devices.

10:40am **EN+NS-ThM9 CdSe-Coated ZnO Nanowires for Extremely Thin Absorber Solar Cells**, *H. Majidi, J.B. Baxter*, Drexel University

Solar cells can provide an abundant, clean, and sustainable source of electricity, but high costs have limited their implementation. Extremely thin absorber (ETA) cells are robust solid state cells that utilize low cost processing while promising potential efficiencies above 15%. However, the highest reported efficiency of ETA cells is only 2.5%. Improving this efficiency will require fundamental understanding and control of the charge transfer in materials and interfaces within the cell.

We report on materials synthesis and photovoltaic response of ETA cells consisting of a vertical array of *n*-type ZnO nanowires coated with CdSe absorber and with the pores between nanowires filled with *p*-type CuSCN. CdSe absorbs visible light and injects photoexcited electrons into the ZnO nanowires. The architecture of the ETA cell enables use of absorbers with smaller carrier lifetimes than those used in thicker planar films, and elimination of liquid electrolytes renders them more robust than conventional dye sensitized solar cells. However, CdSe deposition must be carefully controlled to obtain highly crystalline, uniform, and conformal coatings with an optimal thickness to achieve maximum light harvesting and charge injection efficiency.

We have deposited CdSe coatings at room temperature using electrodeposition with precise control over morphology and material properties. Detailed information about nucleation, crystal growth, and morphology of the coating on both planar ZnO films and ZnO nanowire arrays was obtained by electrochemical probes and electron microscopy at the early stages of deposition. Under potentiostatic deposition, applied potential of ~ -1.25 V resulted in instantaneous nucleation and high areal density of nuclei and, hence, conformal coatings. Smaller applied potentials ~ -1.05 V resulted in sparse and progressive nucleation and non-uniform coatings. However, deposition at potentials larger than -1.6 V resulted in precipitation in electrolyte solution. After annealing, x-ray diffraction and transmission electron microscopy show nanocrystalline CdSe in both hexagonal and cubic phases. Using the optimal potential range determined from the potentiostatic studies, we investigated galvanostatic deposition of CdSe coatings on ZnO nanowire arrays. The thickness of CdSe coating is precisely controlled by electrodeposition charge density, and the deposition is conformal and uniform, which is ideal for ETA cells. UV-Vis transmission spectroscopy and photoelectrochemical solar cell measurements demonstrate that CdSe coatings effectively sensitize ZnO nanowires to visible light.

11:00am **EN+NS-ThM10 Titanium Dioxide Nanowires for Dye-Sensitized Solar Cells, Lithium Ion Batteries and Photocatalysis**, *E.S. Aydil, B. Liu, A. Khare*, University of Minnesota

One-dimensional titanium dioxide nanowires find applications ranging from photocatalysis to lithium ion batteries and dye sensitized solar cells. A simple and environmentally benign method was developed for growing oriented single-crystalline TiO₂-B and/or anatase TiO₂ nanowire arrays on titanium foil over large areas. These nanowire arrays are suitable for use as the anode in lithium-ion-batteries; they exhibit specific capacities ranging from 200-250 mAh/g and retention of these capacities at high charge-discharge rates and over as many as 200 charging-discharging cycles. These promising properties are attributed to both the nanometer size of the nanowires and their oriented alignment. The comparable electrochemical performance to existing technology, improved safety, and the ability to roll titanium foils into compact three-dimensional structures without additional substrates, binders or additives suggest that these TiO₂ nanowires on titanium foil are promising anode materials for large scale energy storage. Another application of these nanowires is in photocatalysis. Ideally, after photogeneration, electrons and holes must be segregated to different parts of the photocatalyst to take part in separate oxidation and reduction reactions. One way to achieve spatial control of electron-hole separation is by building junctions into the catalyst with built-in electric fields that tend to separate the electron and the hole into two different regions of the catalyst. We sought to accomplish this by controllably forming junctions between different phases of TiO₂. A solution method followed by a subsequent heating process has been developed to prepare core-shell TiO₂ nanowires made of TiO₂-B core and anatase shell. We control the anatase phase surface coverage on the TiO₂-B phase and show that the maximum photocatalytic activity is obtained when the solution containing the reactants can contact both the anatase and TiO₂-B phases. The photocatalytic activity drops both with bare TiO₂-B nanowires and with completely anatase covered TiO₂-B nanowires. In contrast, nanowires partially covered with anatase phase gives the highest photocatalytic activity. The improved photocatalytic activity is attributed to the effective electron-hole separation at the junction between the anatase and TiO₂-B phases, which reduces charge recombination and increases the electron and hole lifetimes. Finally, we have developed a method to grow rutile TiO₂ nanowires on transparent conducting oxide substrates for use in dye-sensitized solar cells (DSSC). A light-to-electricity conversion efficiency of

3% could be achieved by using 4 mm-long TiO₂ nanorod films as the photoanode in a DSSC.

11:20am **EN+NS-ThM11 Device Characteristics of Dye Sensitized Solar Cells Based on Evaporated TiO₂ Nanowire Photoanodes**, *S.M. Pursel, S.H.A. Lee, T.E. Mallouk, M.W. Horn*, The Pennsylvania State University

11:40am **EN+NS-ThM12 Dye Sensitized Solar Cells with Aerogel-Templated Nanostructured Photoanodes Fabricated using Atomic Layer Deposition**, *A. Yanguas-Gil, J.W. Elam*, Argonne National Laboratory, *V.O. Williams*, Northwestern University, *M. Mushfiq, D.M. Hess, R. Winter, U. Sampathkumaran*, Innosense LLC, *M.J. Pellin*, Argonne National Laboratory, *J.T. Hupp*, Northwestern University

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