

Monday Afternoon, October 18, 2010

Energy Frontiers Topical Conference

Room: Mesilla - Session EN-MoA

Excitonic and Third Generation Solar Cells

Moderator: J.B. Baxter, Drexel University

2:00pm **EN-MoA1 Beyond the Adiabatic Limit: Charge Separation in Organic Photovoltaic Materials**, *R.D. Pensack, J.B. Asbury*, Penn State University **INVITED**

The dynamics of charge separation in photovoltaic polymer blends following photoinduced electron transfer from the conjugated polymer, CN-MEH-PPV, to the electron accepting functionalized fullerene, PCBM, are observed with ultrafast vibrational spectroscopy. The investigators take advantage of a solvatochromic shift of the vibrational frequency of the carbonyl (C=O) stretch of PCBM to directly measure the rate of escape of electrons from their Coulombically bound charge transfer (CT) excitons at donor/acceptor interfaces on ultrafast time scales. The data reveal that the rate of dissociation of CT excitons is temperature independent from 200 to 350 K indicating that excess energy in hot CT excitons plays an important role in mediating charge separation. These observations suggest that conceptual and theoretical descriptions properly taking into account the strong coupling of electronic and nuclear degrees of freedom in organic semiconductors are essential to understand the mechanism of charge separation in organic photovoltaic materials. From a practical stand-point, efforts to develop new low band-gap polymers for organic solar cells should target electron donor and acceptor pairs capable of advantageously redistributing excess energy in hot CT excitons to enable efficient charge separation with minimal donor-acceptor energy level offsets.

2:40pm **EN-MoA3 Third Generation Photovoltaics: Multiple Exciton Generation in Colloidal Quantum Dots, Quantum Dot Arrays, and Quantum Dot Solar Cells**, *A.J. Nozik*, National Renewable Energy Lab and Univ. of Colorado, Boulder, *M.C. Beard, J.M. Luther*, National Renewable Energy Lab, A.G. Midgett, O.E. Semonin, Univ. of Colorado, Boulder, *J.C. Johnson*, National Renewable Energy Lab **INVITED**

One potential, long-term approach to more efficient future generation solar cells is to utilize the unique properties of quantum dot (QD) nanostructures to control the relaxation pathways of excited QD states to produce enhanced conversion efficiency through efficient multiple exciton generation (MEG) in QDs.

We have observed efficient multiple exciton generation (MEG) in PbSe, PbS, PbTe, and Si QDs at threshold photon energies of 2-3 times the HOMO-LUMO transition. We have studied MEG in close-packed QD arrays where the QDs are electronically coupled in the films and thus exhibit good carrier mobility. We have developed simple, all-inorganic QD solar cells that produce large short-circuit photocurrents via both nanocrystalline Schottky junctions and nanocrystalline p-n junctions without the need for QD sintering, superlattice order or separate phases for electron and hole transport. The latter shows an NREL-Certified conversion efficiency of 3%. We have demonstrated that the MEG efficiency in conductive Pb chalcogenide QD films after certain chemical treatments can be comparable to isolated QDs in colloids, but the QY varies greatly depending upon the specific chemical treatment, and subsequent QD surface chemistry.

Selected aspects of this work will be summarized and recent advances will be discussed. Various possible configurations for novel QD solar cells that could produce very high conversion efficiencies will be presented, along with progress in developing such new types of solar cells. Recent controversy about MEG and its application to photovoltaic cells will also be addressed.

3:40pm **EN-MoA6 Solar Cells Based on Semiconductor Quantum Dots and Nanowires**, *K.S. Leschkes*, University of Minnesota **INVITED**

Solar cells based on colloidal semiconductor nanocrystals, or quantum dots (QDs) may have the potential to achieve high power conversion efficiencies at low cost. Quantum confinement of electrons and holes in these nanometer-size crystals endows them with properties that may be advantageous for efficient solar-to-electric energy conversion. For example, varying the QD size changes the electronic energy levels and optical absorption in QDs. This allows the optimization of their optical absorption for maximum overlap with the solar spectrum. In addition, QDs can be prepared in large quantities as stable colloidal solutions under mild conditions and deposited as thin films using inexpensive, high-throughput coating processes to form solar cells.

After a brief review of the literature on QD solar cells, I will focus on a new type of QD solar cell based on heterojunctions between PbSe QDs and thin ZnO films designed to improve on the current state-of-the-art. These QD solar cells were fabricated by depositing thin films of ZnO and PbSe QDs onto a glass substrate coated with conductive indium-tin-oxide (ITO), which forms the bottom contact of the device. Absorption of light produces electron-hole pairs in the QDs that dissociate, either at a QD-electrode interface or within the QD film and generate photocurrent. Specifically, electrons lower their energy by transferring into the ZnO film, which forms a type-II heterojunction with the PbSe QDs. These electrons move across the ZnO film and are collected at the ITO contact while the positive charges are transported to and collected at a top gold electrode.

Under simulated sunlight, the QD solar cells exhibit short-circuit currents as high as 15 mA/cm² and open-circuit voltages up to 0.45 V. The solar cell open-circuit voltage depends on the QD size and increases linearly with the QD effective band gap energy. Charge collection in these devices can be increased further by using nanostructured interfaces between PbSe QDs and ZnO. Specifically, the ZnO film can be replaced with a vertical array of ZnO nanowires, and infiltrating this array with colloidal PbSe QDs. These nanowire-quantum-dot solar cells exhibited power conversion efficiencies of 2%, nearly three times higher than that achieved with thin-film ZnO devices constructed with the same amount of QDs. Supporting experiments using field-effect transistors made from these QDs also show that the QDs' electrical properties are strongly influenced by the presence of nitrogen and oxygen atmospheric gases. Such results have important implications with respect to the assembly, characterization, and exposure of QD-based solar cells to an ambient environment.

4:20pm **EN-MoA8 PbSe and PbS Nanocrystal Solar Cells**, *J.J. Choi, J. Luria, B.-R. Hyun, A.C. Bartnik, L. Sun, Y.-F. Lim, J.A. Marohn, F.W. Wise, T. Hanrath*, Cornell University **INVITED**

Rational progress towards nanocrystal based solar cells demands an improved understanding of electronic and optical interactions of proximate nanocrystals in functional assemblies. We combined transient photoluminescence spectroscopy and electric force microscopy to probe photogenerated exciton dissociation in PbS nanocrystal assemblies. We show that excitons dissociate via charge tunneling between neighboring nanocrystals. Implications in the context of nanocrystal photovoltaic devices will be discussed. We also present the design, fabrication and characterization of excitonic solar cells based on PbSe and PbS nanocrystal active layers. The best performing device shows a 1-sun power conversion efficiency of 4%.

5:00pm **EN-MoA10 Solid-State Quantum Dot Sensitized Solar Cells: Atomic Layer Deposition versus Successive Ionic Layer Adsorption and Reaction**, *P. Ardalan, T.P. Brennan, J.R. Bakke, S.F. Bent*, Stanford University

Narrow band gap nanostructures such as cadmium sulfide quantum dots (QDs) are known to show size quantization effects. In quantum dot sensitized solar cells (QDSSCs), these QDs can be engineered to transfer an electron to a wide band gap semiconductor such as titanium dioxide (TiO₂). However, performance in such devices is reduced by charge recombination at the TiO₂ surface and hence use of organic linkers such as self-assembled monolayers (SAMs) on these devices could provide a means of eliminating recombination sites and lead to increased efficiency. In this study, we investigated the effects of different aliphatic and aromatic SAMs with phosphonic acid headgroups and varied tailgroups on the bonding and performance of cadmium sulfide (CdS) solid-state QDSSCs. TiO₂ was deposited on piranha-cleaned Si or microscope glass via atomic layer deposition (ALD) and the resulting surfaces were characterized by ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Next, different SAMs were attached from solution to either ALD-deposited (planar) or doctor-bladed (nanoporous) TiO₂ substrates, and the effects of chain length, aromaticity, and tailgroup on the quality of the SAMs were investigated. CdS QDs were then grown on the SAM-passivated TiO₂ surfaces by either successive ionic layer adsorption and reaction (SILAR) from solution or by atomic layer deposition (ALD) from the gas phase, and the bonding and performance of the resulting materials were evaluated by UV-visible and other spectroscopic techniques. Our results show that CdS QDs with particle sizes in the range of 2 to 6 nm are grown by SILAR on TiO₂ both with and without SAMs, but more CdS can be deposited on samples with SAMs with the exception of the long-chain methyl-terminated monolayer. Furthermore, it is determined that the SAM chain length affects the SILAR CdS deposition at the TiO₂ surfaces more significantly than does the identity of the tailgroup. ALD also is effective for depositing CdS QDs, but

less CdS is deposited by ALD than by SILAR at TiO₂ surfaces for the same number of cycles. QDSSC devices have been made using both SILAR and ALD, and we will present results on the dependence of solid-state QDSSC performance and efficiency on the deposition technique employed to grow the CdS QDs, as well as on the properties of the SAM. Overall, we observed higher efficiencies in devices with SAMs and we propose that this result can be attributed to the presence of a charge recombination barrier.

5:20pm **EN-MoA11 Synthesis and Application of Branched Titania Nanotubes in Dye-Sensitized Solar Cells**, *G. Butail, P. Gopal, M. Raddiar, R. Teki, N. Ravishankar, G. Ramanath*, Rensselaer Polytechnic Institute

Titania is a promising photocatalyst used in a variety of photovoltaic, optoelectronic and biofiltering applications. There is great interest in synthesizing high surface area titania nanostructures by inexpensive means for low-cost power generation, among which titania nanotubes offer higher efficiencies because of unidirectional charge transport and low scattering losses. Here we demonstrate, for the first time, the formation of branched titania nanotubes using potentiostatic anodization of titanium thin films. The realization of branched titania nanotubes provides a means to tune the electronic properties of titania and to functionalize them with multi-sized quantum dots and other metallic/semiconducting nanostructures.

Experimental analysis show anodization diameter to be a linear function of applied voltage. We exploit the relationship between the anodization voltage and nanotube diameter to obtain and control the extent of branching and tune branch diameters between 30 to 110 nm. Branching achieved through single step voltage induced anodization offers the added advantage of control of point of branching depending on rate of anodization at each voltage. We also evaluate the morphology and the optical properties of branched titania nanotubes and compare their light-harvesting efficiency with unbranched nanotubes in dye-sensitized solar cells. We specifically compare branched titania nanotubes formed by ramping down the voltage from 60 to 33 V and compare the them with titania nanotubes formed at 60 V and 33 V. Preliminary results show a 33% increase in active surface area of branched titania nanotubes as compared to unbranched nanotubes formed at 60 V which is further confirmed through BET analysis.

Application of straight (unbranched) titania nanotubes for fabrication of dye-sensitized solar cells using a ruthenium based dye (N719) results in an efficiency of 0.58±0.2% with short circuit current density of 6.3±1.0 mA/cm² and fill factor of 22.4±0.2. Use of branched titania nanotubes of same thickness under same conditions reports an efficiency of 1.04±0.1% with increase in short circuit current density to 9.1±0.8 mA/cm² and a fill factor of 23.7±0.1%. A two-fold enhancement of photovoltaic efficiency of branched samples as compared to straight nanotubes correlates well to the difference in surface area and optical properties of the two structures.

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