

Tuesday Morning, November 1, 2011

Energy Frontiers Focus Topic

Room: 103 - Session EN+NS-TuM

Ultrafast Charge and Energy Transfer in Nanomaterials

Moderator: J.B. Baxter, Drexel University

8:00am EN+NS-TuM1 **Controlled Deposition of Nanocrystal Quantum Dots on Silicon Surfaces: Demonstration and Application of Forster Resonant Energy Transfer**, *O. Seitz, H.M. Nguyen, Y.N. Gartstein, A.V. Malko*, University of Texas at Dallas, *Y.J. Chabal*, The University of Texas at Dallas

Studying Forster resonant energy transfer (FRET) at semiconductor surfaces has been a challenge because of difficulties in grafting reliably nanocrystal quantum dots (NQDs) onto electronically passivated substrates. Poor control has often resulted in formation of aggregates (3D growth), inhomogeneity, and poor adhesion. In this study, combining IR absorption spectroscopy (IRAS) and X-ray photoelectron spectroscopy (XPS), photoluminescence, atomic force microscopy (AFM) and electrical measurements, we have grafted self-assembled monolayers (SAMs) on both oxidized and oxide-free silicon surfaces with appropriate functionality to obtain dense monolayer of NQDs and to study FRET. SAMs that are directly attached to the silicon via Si-C bonds display a high interface quality with a low density of interface states. This makes it possible to prepare systems with tunable thicknesses necessary for FRET investigation. The time evolution of the fluorescence intensity is in good agreement with the predicted thickness dependence. We are currently developing 3D structures to enhance energy collection for a given surface area. Such hybrid colloidal NQD/Silicon optoelectronic structures could potentially be attractive for both photovoltaic as well as light emitting applications.

8:20am EN+NS-TuM2 **Orbital-dependent Charge Transfer Dynamics in Potential Molecular Wires**, *H. Hamoudi*, Universität Heidelberg, Germany, *S. Nepl*, Technische Universität München, Germany, *P. Kao*, Penn State University, *B. Schüpbach*, Universität Frankfurt, Germany, *P. Feulner*, Technische Universität München, Germany, *A. Terfort*, Universität Frankfurt, Germany, *D.L. Allara*, Penn State University, *M. Zharnikov*, Universität Heidelberg, Germany

Continued progress in technologically important fields such as molecular and organic electronics as well as organic photovoltaics depends on reliable information about the charge transport (CT) through individual molecular groups, above all so-called molecular wires, since these represent important building blocks of a variety of devices. In this context, femtosecond CT dynamics in a series of self-assembled monolayers with oligo(phenyleneethynylene) and oligo(phenyl) backbone, which are prototypes of potential molecule wires, was addressed by resonant Auger spectroscopy using the core hole clock method. The length of the molecular backbone was varied to monitor the respective dependence of the CT time. The CT pathway was unambiguously defined by resonant excitation of the nitrile tailgroup attached to the backbone. Due to the conjugation of the electronic systems of this group and the adjacent terminal phenyl ring of the backbone, a splitting of the degenerated unoccupied molecular orbital (MO) of nitrile occurred, resulting in two different MOs which could be selectively addressed by X-rays and used as the starting points for CT. The characteristic CT times were found to depend strongly on the character of the MO which mediates the CT process. This demonstrates that the efficiency and rate of CT in molecular wires can be controlled by resonant injection of the charge carriers into specific MOs.

8:40am EN+NS-TuM3 **Photophysics of Semiconductor Nanostructures in Relation to Problems of Solar Energy Conversion**, *V.I. Klimov*, Los Alamos National Laboratory

INVITED

This presentation provides a brief overview of research activities in the Center for Advanced Solar Photophysics with focus on spectroscopic properties of semiconductor nanocrystals studied from the prospective of solar energy conversion. One process, which can be used for boosting a photocurrent of solar cells, is carrier multiplication (CM) or multiexciton generation. Our recent activities in this area include the development of reliable methods for efficient screening of CM performance using photon counting with superconducting nanowire detectors, the studies of the impact of "extraneous" processes on CM measurements, and the evaluation of the effects of the nanocrystal composition, dimensions, and shape on CM yields. As part of our effort on controlling excited-state dynamics, we study hot-electron transfer in nanocrystals. We find that the efficiency of this process can approach 10% even with incidental impurity-like acceptors, suggesting that even higher probabilities are possible with engineered

acceptors designed for testing the ideas of hot-electron extraction. We also apply spectroscopic tools for probing the physics of charge transport in nanocrystal assemblies using exploratory devices such as optical field-effect transistors (OFETs). The OFET studies help to understand the nature of conducting states in dark and under illumination and to rationalize many previously unexplained observations including a weak sensitivity of conductance to particles' polydispersity and a significant difference in a photovoltage compared to a nominal band-gap energy. These studies illustrate how key insights into the performance of nanoscale materials are gained through close integration of spectroscopic, materials and device efforts across the Center.

9:20am EN+NS-TuM5 **Hot Electron Transfer from Semiconductor Nanocrystals**, *W.A. Tisdale*, Massachusetts Institute of Technology

INVITED

In conventional semiconductor solar cells, absorption of photons with energies greater than the semiconductor band gap generate "hot" charge carriers that quickly "cool" before all of their energy can be captured – a process that limits device efficiency. Semiconductor nanocrystals (or quantum dots) have been touted as promising materials for photovoltaics because discretization of their electronic energy levels can slow down this cooling process, which might enable the extraction of photogenerated charge carriers before their excess energy is converted to heat.

In this talk, I will demonstrate hot electron transfer from PbSe nanocrystals to delocalized conduction band states of TiO₂ and the concomitant excitation of coherent surface vibrational modes associated with this ultrafast process. In order to make these measurements, we developed the use of optical second harmonic generation (SHG) for femtosecond time-resolved studies of interfacial charge separation. I will discuss the information we obtain from this technique as well as the effect of temperature, nanocrystal size, and surface chemistry, and how these observations inform our understanding of electronic coupling at interfaces between confined states and bulk materials.

10:40am EN+NS-TuM9 **Single Molecule Study of Charge Transfer in 6T-TBPP-Co Molecular Complex**, *Y. Zhang, U.G.E. Perera, S.-W. Hla*, Ohio University

When two molecules having tendency to donate or accept electronic charge are put together, charge transfer between the molecules can take place. By a suitable selection of donor and acceptor molecules, it is possible to engineer an entire class of materials having metallic, semiconducting, insulating, or even superconducting properties [1, 2]. Here, we present a low temperature scanning tunneling microscopy and spectroscopy study of single molecule level charge transfer process between α -sexithiophene(6T) and TBPP-Co molecules on a Cu(111) surface. We form molecular clusters composed of both molecular species on Cu(111). The charge transfer between the molecules is directly evident in the tunneling spectroscopy data, which reveals the shift of 6T HOMO towards the surface Fermi level indicating donation of charge from 6T to TBPP-Co. This work is supported by the US-DOE-DE-FG02-02ER46012 grant.

Reference:

[1] F. Jackel, U. G. E. Perera, V. Iancu, K.-F. Braun, N. Koch, J. P. Rabe, and S.-W. Hla, Phys. Rev. Lett. 100, 126102 (2008).

[2] K. Clark, A. Hassanien, S. Khan, K.-F. Braun, H. Tanaka and S.-W. Hla, Nature Nanotechnology, Vol.5, April, 2010.

11:00am EN+NS-TuM10 **NEGF Quantum Simulation of Nanotip Thermionic Emitters for Direct Energy Conversion**, *T.D. Musho, D.G. Walker*, Vanderbilt University

Wide band-gap diamond nanotip field emission devices have been experimentally shown to have superior performance and lifetime. However, theoretical studies of the electronic emission from these devices using standard Fowler-Nordheim (FN) theory does not fully capture the physics as a result of the fitting parameters inherent to the FN approximation. The following research computationally models wide band-gap nanotip field emission devices from a quantum point of view, using a novel non-equilibrium Green's function (NEGF) approach previously applied to modeling the transport in solid-state electronic devices. In this research the IV characteristics of a single square tip diamond emitter are investigated under several bias conditions. Those bias conditions include both field emission in response to a potential bias and thermionic emission in response to a temperature bias. The NEGF model calculates the ballistic transport using a self-consistent Schrödinger-Poisson solver, calculating the transmission at discrete energy levels which is then used by the Landauer

formalism to determine the total current. Ultimately, this model allows the inherent quantum mechanical transport to be captured without any fitting parameters. Findings from this research have confirmed non-linearities in the FN curve and have demonstrated the experimental transport trends. Additionally, thermionic emission trends suggest that select geometric parameters are target for enhanced emission.

11:20am **EN+NS-TuM11 Mechanisms of Heterogeneous Charge Transfer at the Quantum Dot-Organic Interface**, *A. Morris-Cohen, M. Frederick, L. Cass, E.A. Weiss*, Northwestern University **INVITED**

We examine the rates and mechanisms of electron transfer between colloidal semiconductor quantum dots (QDs) and viologen derivatives using ultrafast transient absorption spectroscopy. Viologens accept electrons from photoexcited QDs on the femtosecond-to-single picosecond timescale. Modifications of the chemistry by which the ligands link to the QD surface, and the density of ligands on the QDs, facilitates control of charge separation and recombination rates, and determination of the operative mechanisms of charge transfer.

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