



## Users Meeting

Advanced Photon Source  
Center for Nanoscale Materials  
Electron Microscopy Center

**APS/CNM/EMC Users Meeting, May 2-5, 2011**

**CNM Workshop Summary: Photoinduced Charge Transfer in Nanostructures**

*Workshop held on May 4, 2011*

**Organizers:** Gary Wiederrecht and Matthew Pelton (CNM)

Photoinduced charge-transfer processes underlie emerging energy technologies, particularly photovoltaic devices that convert sunlight into electricity. Nanometer-scale structure in these devices strongly influences charge-transfer processes, and engineered nanomaterials provide a unique opportunity to understand and control the physics and chemistry of charge transfer. This full-day workshop explored the fundamental science of photoinduced charge transfer in organic, inorganic, and hybrid materials and applications in solar energy conversion. The collection of eight invited speakers included senior and early-career researchers approaching the problem from different directions and in different systems, engendering extensive discussion and drawing new connections between the work that was represented. There were 42 registered attendees for this workshop, with many more walk-ins, and feedback from the attendees was overwhelmingly positive.

The workshop began with a talk by the CNM Division Director, Amanda Petford-Long, which introduced the CNM user program, capabilities, scientific directions, and management structure. This talk resulted in many inquiries from potential users throughout the day. Stephen Forrest from the University of Michigan opened the scientific talks with an overview of his recent research in organic photovoltaics (OPV). Organic thin films are under investigation as a substitute for inorganic materials such as silicon in solar cells because of their strong optical absorption, wide availability, and compatibility with low-cost fabrication techniques. The performance of OPV, however, has been limited by the ability to efficiently separate and extract charges that are produced through absorption of a photon. Prof. Forrest showed how the nanometer-scale organization of donor and acceptor molecules in an organic thin film controls charge separation processes, paying particular attention to the formation of a charge-transfer state at the donor-acceptor interface, or heterojunction. The physical understanding developed through the experimental studies was used to develop a model for the fundamental efficiency limit in OPV. The relationship between nanoscale structure and charge extraction in OPV was revisited by Russell Holmes from the University of Minnesota. Prof. Holmes described his recent work on OPV with graded compositions. Most previous OPV have used uniform mixtures of donor and acceptor species, which limits charge mobility, whereas a graded composition provides a compromise between the need to separate charges at donor-acceptor interfaces and the need for continuous donor and acceptor paths to transport the separated charges to the electrodes, and thus increases device efficiency. Prof. Holmes also showed that exciton transport by energy transfer, and not just diffusion of excitons and carriers, can be of critical importance in the operation of an organic photovoltaic device.

As well as organic molecules, the workshop involved extensive discussion of photoinduced charge separation in semiconductor nanocrystals, or quantum dots. Greg Scholes from the University of Toronto provided a wide-ranging overview of charge separation in these model systems, focusing in particular on type-II nanocrystal heterostructures. These structures consist

of two different semiconductor materials with staggered offsets between the conduction band and valence band. When these structures absorb a photon, the resulting exciton is rapidly separated, with the electron going into one material and the hole going into the other. Prof. Scholes expanded on the similarities and differences between this process and exciton dissociation at donor-acceptor interfaces in organic materials. In particular, he discussed the importance of solvent effects, and he asked whether a single-carrier picture was sufficient to describe the charge-separation process, or whether it is important to include electron-correlation effects, as is the case in organics. A related inorganic heterostructure was discussed by Bruce Parkinson from the University of Wyoming – CdSe nanocrystals on a titanium dioxide surface. This interface is of particular interest for quantum-dot-sensitized solar cells, the all-inorganic version of the widely studied dye-sensitized solar cell. Conversion of sunlight into electricity in this system involves absorption of a photon by the nanocrystal and electron transfer into a network of titania nanoparticles. However, the complex, inhomogeneous morphology of this device makes quantitative studies difficult, if not impossible. Prof. Parkinson has developed the ability to make measurements on monolayers of isolated quantum dots on a well-defined single-crystal titania surface. His quantitative studies indicate that a single photon absorbed by a nanocrystal can lead to the injection of more than one electron into the titania crystal, supporting the controversial concept of multiple exciton generation, or exciton multiplication, in the nanocrystals.

A single layer of nanocrystals on a single-crystal titania surface would be an ideal solar-cell system, except that the monolayer does not absorb nearly enough light to be useful. Dr. Alex Martinson, a CNM user from Argonne's Materials Science Division, proposed a solution to this limited absorption, which could also have important implications for other systems such as OPV. As demonstrated in the previous talks, carrier transport limits the efficiency of these devices, and a thinner layer of organic material would have correspondingly less carrier loss. Dr. Martinson's solution is to couple light into surface plasmon polaritons that travel along a metal surface parallel to the light-absorbing layer. His experimental results show that the incident photon-to-current conversion efficiency could be greatly improved in this way. Noel Giebink of the CNM discussed another method to reduce the amount of photovoltaic material required for energy conversion: luminescent solar concentrators that absorb sunlight over a large area and re-emit lower-energy photons into a waveguide, so that the emitted light is coupled into a small-area solar cell. The performance of luminescent solar concentrators has so far been limited by re-absorption of emitted light by the luminescent material itself, and Dr. Giebink demonstrated a novel method to overcome this reabsorption. Rather than simply using a uniform layer of emitting material on top of the light guide, this method uses a layer with varying thickness, which supports different guided modes along its length. Light from molecules at a particular location along the guide can be efficiently coupled into the slab; however, by the time this light returns to the absorbing material, the mode resonance has shifted and can no longer be re-absorbed.

The two previous systems – semiconductor nanocrystals and organic molecules – can be combined into a charge-transfer system, providing an ideal model for photoinduced charge transfer at the organic / inorganic interface. Tianquan Lian from Emory University discussed his group's measurements of charge transfer from nanocrystals to electron-accepting molecules chemically bound to the nanocrystal surface. He showed that the transfer rate depends on the free-energy difference in a way that cannot be simply explained by Marcus theory, and proposed a new mechanism of Auger-assisted electron transfer to explain the results. Emily Weiss from Northwestern University pointed out that interpretation of the transient-absorption measurements used to infer electron-transfer rates in these systems depends critically on knowing the number of molecules attached to each nanocrystal, but that this number is very difficult to measure independently. She demonstrated a solution to this problem through careful analysis of the transient-absorption data itself.