

## II.K.19 “Electronically Wired” Semiconductor Nanoparticles: Toward Vectoral Electron Transport in Hybrid Materials

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### Objectives

This DOE effort is focused on the development of new photoactive semiconductor nanoparticle (SC-NP)-polymer hybrid materials, “wired” to transparent conducting oxide (TCO) substrates to enable the development of new electrical solar energy conversion, and new solar hydrogen producing technologies. Our approach includes: *i*) the use of highly photoactive II-VI semiconductor nanoparticle materials (e.g. 2-8 nm diameter CdSe nanocrystals); *ii*) the development of new electron-rich thiophene-based electroactive ligands which cap these SC-NPs, rendering them solution processable and electroactive; *iii*) development of electrodeposition protocols designed to incorporate these modified SC-NPs into conducting and semiconducting polymer films, or tether them at sub-monolayer to monolayer coverages to oxide supports; *iv*) characterization of the frontier orbital energies of these ligand capped and tethered SC-NPs, as a means of optimizing photo-induced electron transfer, electrical power generation, and photoelectrochemical hydrogen production; *v*) addition of catalytic metal sites to these polymer-tethered SC-NPs to further enhance rates of H<sub>2</sub> production.

### Technical Barriers

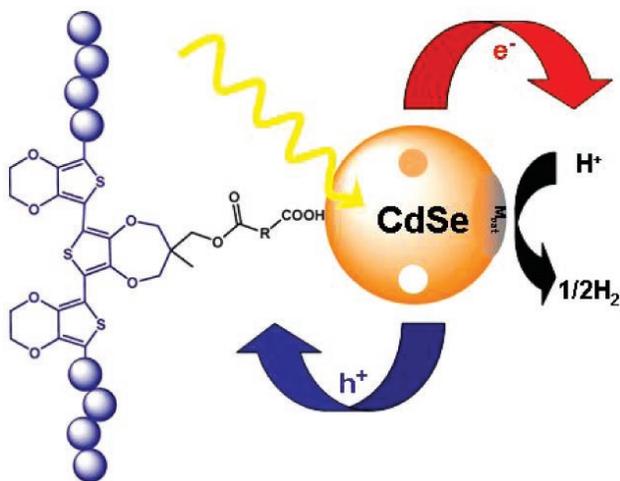
Semiconductor nanoparticles, such as CdSe, are well known to be highly photoactive, and capable of providing the energy to reduce water to hydrogen along with formation of an alternate chemical fuel. They have also been extensively studied as the primary photoactive layer in a number of emerging photovoltaic energy conversion systems. The efficiency of energy conversion in either system, however, is limited by: *i*) the photostability of the NP; *ii*) the frontier orbital energies of the NP, which vary significantly as a function of NP

diameter and the dielectric constant of the surrounding environment; *iii*) the proper “wiring” of the NP into a host material insuring rapid photo-induced electron transfer, efficient charge separation and vectoral electron transport to collection electrodes or the site of photoelectrochemical fuel production. Optimization of all three of these issues is critical to the creation of viable energy conversion technologies based on II-VI SC-NPs, and we believe, all competing nanoparticle and related organic/inorganic hybrid energy conversion technologies.

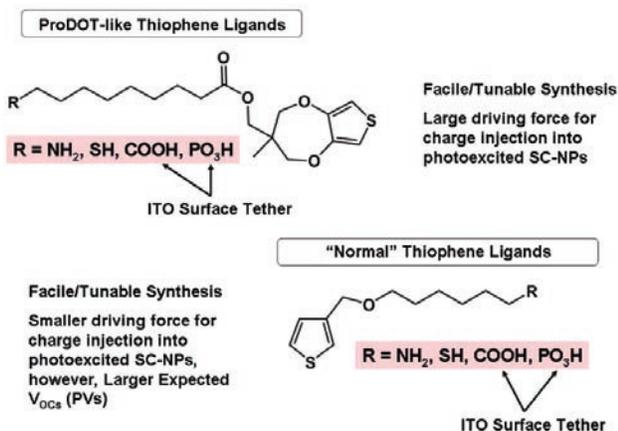
### Abstract, Progress Report and Future Directions

Moderate-to-low bandgap semiconductors have been of interest for solar electric energy conversion and solar fuel (hydrogen) production for decades, mainly because of their high absorptivities, accompanied by a direct gap optical transition, and band edge energies which appear to favor photo-induced electron transfer to protons, and hydrogen production, and/or total water splitting. This photoactivity is accompanied by chemical instabilities of these materials toward oxidative corrosion, often ameliorated by carrying out these photoelectrochemical processes in the presence of excess reducing agents, such as S<sup>-2</sup>, triethanolamine (TEA), etc. Higher bandgap oxide semiconductors, of course, have good photoactivity and stability, but must often be sensitized with adsorbed dyes for use with visible wavelength excitation.

We have adopted a unique approach to solving these problems by developing a series of ligand capping groups, targeted to semiconductor nanoparticles (SC-NPs) such as CdSe, terminated in electron-rich thiophene groups. These capping ligands can be electrochemically cross-linked into a poly(thiophene) host, directly wired to an activated, transparent electrode (Figures 1,2).<sup>1-4,6,7</sup> Photoelectrochemical hydrogen formation occurs with photopotentials of at least 0.5 volts (Fig. 1), when the thiophene host polymer achieves its fully reduced state. Hole-capture from the excited SC-NP, by the host polymer, depends upon capping ligand length, the functional group which binds the ligand to the NP (e.g. -COOH versus, -SH, versus -NH<sub>2</sub>, etc.) and the applied field. We are currently evaluating two different routes to capture of the SC-NP: *i*) the ligand-capped SC-NP is cross-linked in solution phase into a growing poly(thiophene) film, created by pulsed potential-step (PPS) electrodeposition protocols;<sup>2</sup> *ii*) an SC-NP with easily displaced ligands (e.g. pyridine) is incubated with a poly(thiophene) co-polymer, where a -COOH-terminated thiophene ligand is co-deposited



**FIGURE 1.** Schematic view of the electrochemically “wired” semiconductor nanoparticle (SC-NP). Upon photoexcitation, and separation of the electron/hole pair on the NP, hole-capture occurs from the electron-rich polymer host, while electron capture occurs with either a solution acceptor (such as  $H^+$ ) or a condensed phase acceptor (e.g. a fullerene) for PV applications. Rates of electron transfer to the photoexcited NP depend upon NP diameter and surface composition, the type and length of ligand, the ionization potential of the ligand terminal group and the polymer host, and the applied field.<sup>1,2</sup>



**FIGURE 2.** Capping ligands which have been developed for II-VI (CdSe) SC-NPs. ProDOT-terminated ligands are electron-rich, with significant driving forces for hole injection into the photoexcited SC-NP. Thiophene-terminated ligands have a lower driving force for charge injection into the SC-NP, however, when cross-linked into a poly-(thiophene) matrix, e.g. poly-3-hexylthiophene (P3HT) they provide for a hybrid solar cell with potentially larger open-circuit voltages ( $V_{oc}$ ).<sup>6</sup>

into a high surface area (PPS-deposited) film. Both approaches appear to provide high surface area matrices, with photoactive CdSe terminations.

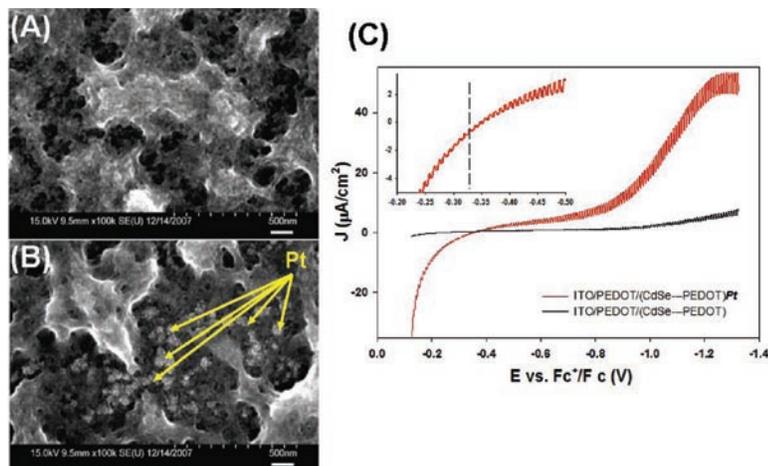
In parallel with our optimization of SC-NP incorporation into electroactive polymer films, we have

initiated the decoration of the most photoactive NP sites with Pt catalytic deposits, designed to enhance rates of  $H_2$ -evolution (Fig. 3). Once these Pt sites are added to the NP surface, the photoelectrochemical activity in protic solvents is significantly enhanced, suggesting that once NP coverage are optimized we can begin evaluating relative rates of  $H_2$ -evolution, as a function of type of ligand, NP diameter, etc.

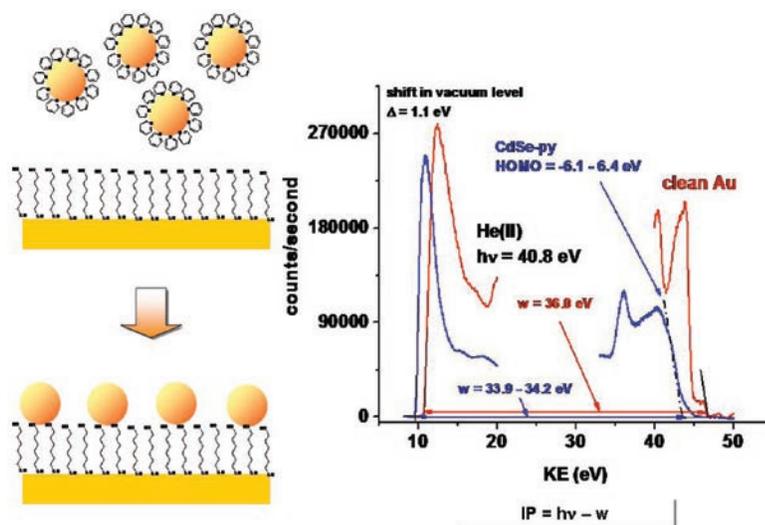
One of the key issues to be resolved in these studies is the assessment of the frontier orbital energies for the SC-NP, with no capping ligands, and for SC-NPs with various  $-COOH$ ,  $-SH$ ,  $-NH_2$  and  $-PO_3$  capping ligands, and polymer host environments. It has been observed that for monolayer tethered “bare” SC-NPs such as CdSe the HOMO energy (ionization potential, IP) may be as high as 6.4 eV, versus vacuum, with substantial shifts in this energy as NP diameter increases.<sup>5</sup> Our recent studies, and electrochemical studies of charge injection into CdSe NP films, suggest that in the presence of capping ligands, high dielectric constant solvent environments, etc. that these IP values may be reduced by 0.5 to 1.0 eV, which may strongly affect the driving force for proton reduction, or electron injection into a condensed phase electron acceptor (photovoltaic applications). We are therefore devoting considerable effort into the characterization of frontier orbital energies of monolayer-tethered CdSe NPs, using primarily He(I) ultra-violet photoelectron spectroscopy (UPS). Results of these initial studies will be summarized in this presentation as well.

## Publications from DOE Support

- Shallcross, R. C. D’Ambruoso, G.D., Korth, B.D., Hall Jr., H.K., Zheng, Z., Pyun, J., Armstrong, N.R., Poly(3,4-ethylenedioxythiophene) - Semiconductor nanoparticle composite thin films tethered to indium tin oxide substrates via electropolymerization. *Journal of the American Chemical Society* **129**, 11310-+ (2007).
- Shallcross, R.C.; Bowles, S.E.; Pyun, J.; Armstrong, N.R., Nanocomposite Thin Films of Semiconductor Nanoparticles in Polythiophene Thin Films: Electrodeposition Conditions Which Optimize Uptake of Ligand-capped CdSe Nanoparticles; *Chemistry of Materials*, **2008**, in preparation.
- Marrikar, F.S. et al. Modification of indium-tin oxide electrodes with thiophene copolymer thin films: Optimizing electron transfer to solution probe molecules. *Langmuir* **23**, 1530-1542 (2007).
- Marrikar, F.S. et al. Conducting polymer diffraction gratings on gold surfaces created by microcontact printing and electropolymerization at submicron length scales. *Langmuir* **23**, 10395-10402 (2007).
- Graham, A., Shallcross, R.C., Armstrong, N.R., UV- and X-ray Photoelectron spectroscopic characterization of ultra-thin films of semiconductor nanoparticles: effect of ligand addition on frontier orbital energies, *manuscript in preparation*.



**FIGURE 3.** FE-SEM views of A) textured electrodeposited PEDOT films with captured CdSe SC-NPs and B) the same type film following photoelectrochemical deposition of Pt sites associated with the most photoactive SC-NPs. The photoelectrochemical response of such a thin film is shown in (C) before and after the Pt-metallization process, showing the enhanced photocatalytic activity provided by the metallization process. As discussed in the text, optimization of the photoelectrochemical activity of these hybrid materials requires a highly textured, electron-rich polymer host (which our pulsed-potential step deposition protocols provide), and efficient wiring of each SC-NP to this polymer host, assuring hole-capture and suppression of NP corrosion. The addition of the Pt-nanoparticle sites enhances the rate of  $\text{H}_2$  evolution, however its coverage must be optimized to avoid short-circuiting of these cells, and enhanced recombination.



**FIGURE 4.** Schematic view of the capture of pyridine-capped CdSe NPs in solution, on an alkanedithiol modified Au surface. The pyridine ligands are easily displaced during the adsorption process, and are completely removed upon introduction into the high vacuum environment. He(I) (21.2 eV) and He(II) (40.8 eV) excitation of these tethered monolayers can be used to characterize IP values as a function of NP diameter, but must be corrected for local vacuum level shifts (interface dipole shifts) of up to 1.1 eV.<sup>5</sup> Once the initial characterization has been completed, these NP monolayers can be incubated in solutions of alternative ligands, which bind to these robust monolayers, and then provide a means for characterization of the effect of ligand attachment on frontier orbital energies of the NP.

6. Ratcliff, E., Jenkins, J., Shallcross, R.C., Armstrong, N.R., Photovoltaic performance of electrodeposited/nanotextured, P3HT thin films, *manuscript in preparation*.

7. Brumbach, M., Veneman, P. Alex, Marrikar, F. Saneeha, Schulmeyer, Thomas, Simmonds, Adam, Xia, Wei, Lee, P.A. Armstrong, Neal R., Surface Composition, Electrical and Electrochemical Properties of Freshly Deposited and Acid-Etched Indium-Tin Oxide Electrodes, *Langmuir*, **23**, 11089-11099.

8. Brumbach, M., Armstrong, N.R., Modification of Transparent Conducting Oxide (TCO) Electrodes Through Silanization and Chemisorption of Small Molecules, in *Encyclopedia of Electrochemistry, Volume 10 - Modified Electrodes*, M. Fujihira, I. Rubenstein, J. Rusling, (Volume 10 editors.), A.J. Bard, M. Stratmann, eds. Wiley-VCH, pp. 15-29 (2007).