

Formation and Characterization of Semiconductor Nanorod/Oxide Nanoparticle Hybrid Materials: Toward Vectorial Electron Transport in Hybrid Materials

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Objectives

We are developing new photoelectrocatalytic systems based on semiconductor nanocrystalline materials, ultimately intended to be the active layers in solar fuel forming systems. Photoactive nanocrystals are decorated with electron-rich ligands, and captured into asymmetric matrices that ensure efficient energy capture and vectorial photoelectrochemical energy conversion. New materials are being designed in parallel with unique spectroscopic and electrochemical characterization of their frontier orbital energies, to ensure highest possible rates of charge transfer in the critical energy conversion steps.

Technical Barriers

- There are significant challenges to the formation of stable low bandgap semiconductor nanocrystalline “dots” and “rods;”
- There are even greater challenges to the alignment of semiconductor nanorods into asymmetric arrays, which ensure electron transport in one direction (vectorial), and keep oxidation and reduction processes spatially separated;
- The frontier orbital energy levels of these nanocrystalline materials are difficult to characterize in photoelectrochemically-relevant environments; addition of protective ligands or polymer hosts can further alter these energies; nanocrystal-nanocrystal interactions also alter these energies, and need to be studied for isolated crystals, small aggregates and full assemblies.

Abstract

Our DOE Solar Photochemistry supported research (DE-FG03-02ER15753) has focused on the development and characterization of new semiconductor nanorod (SC-NR) materials coupled asymmetrically to conducting

polymer hosts, or either metal or metal oxide supports, and the development of new nanocrystalline materials decorated with both metallic catalytic sites and metal oxide nanoparticles. The asymmetric structure of these nanomaterials is designed to ensure vectorial electron transfer in photoelectrochemical processes which may ultimately provide pathways for the formation of chemical fuels from sunlight. Recent activities have been centered on: (i) the formation of new nanomaterials and nanocrystals (NCs); (ii) the demonstration of photoelectrochemical processes with SC-NCs tethered to the surface of a conducting polymer; (iii) the characterization of the energetic of these materials by unique protocols involving photoemission spectroscopies of monolayer-tethered SC-NCs; and (iv) the spectroelectrochemical characterization of charge injection into surface-tethered SC-NCs on unique waveguide platforms.

Progress Report

Recent efforts (Fig. 1) have focused on the creation of functional nanocrystalline monolayers and ensemble materials, e.g. CdSe SC-NCs capped with ligands terminated with the monomer of CPs such as (poly(ethylenedioxythiophene) – PEDOT, and its ProDOT and di-ethylProDOT derivatives. New electrochemical protocols were developed to capture close packed monolayers of these NCs on the surface of the CP, following which we interrogated the relative rates of photoelectrochemical reduction of a solution electron acceptor by the CP, using the CdSe NC as the photosensitizer. Electron donation to the photoexcited NC by the CP ($r_{c,2}$) is the rate limiting step and is exponentially related to the excess free energy controlled by the quasi-Fermi level in the CP, and by the NC diameter, which controls E_{VB} . These results demonstrate an enabling method for the capture of SC-NCs in a functional format, which can be used to tailor the architecture of new materials where compositional and energetic asymmetry is required. For photoelectrochemical systems such as this both the electronic coupling and the excess free energy at each heterojunction (e.g. $E_{HOMO}^{MOx} - E_{LUMO}^{SC-NC}$; $E_{HOMO} \approx E_{VB}$; $E_{LUMO} \approx E_{CB}$) control the photovoltage of the complete system, and rates of ET for the redox reactions coupled to this structure.

We have recently developed new ways of characterizing frontier orbital energies of the NC in both high vacuum and solution environments. We demonstrated the successful capture of sub-monolayers of pyridine-capped CdSe NCs (pyr-CdSe) on Au surfaces modified with a short dithiol modifier, and characterized their composition and frontier orbital energies (ionization potential (IP), E_{VB}) for the bare

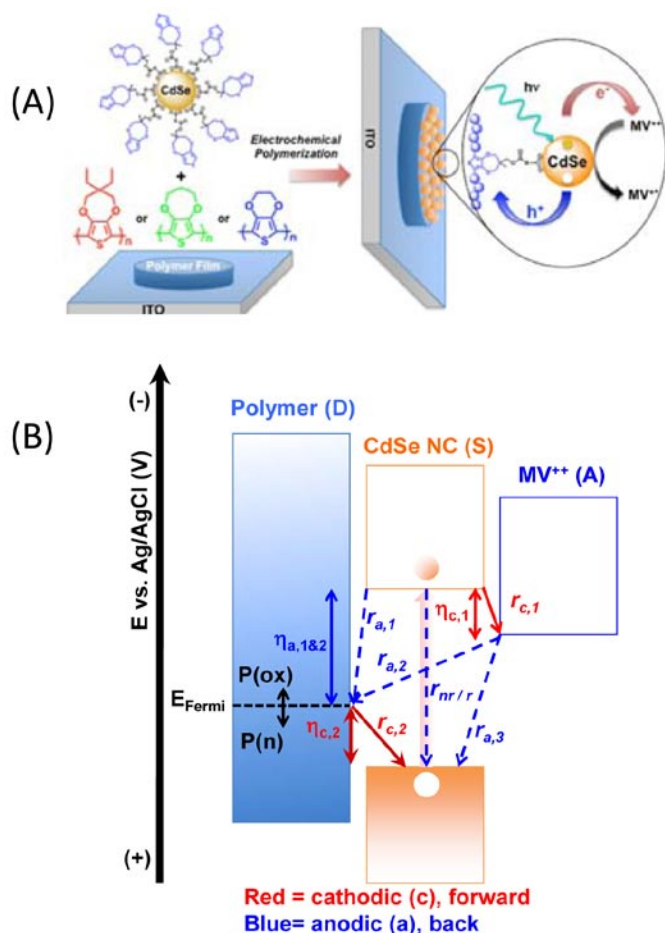


FIGURE 1. (A) Schematic view of the capping of CdSe NCs with ProDot-terminated ligands, followed by the electrochemical capture of the NCs at the surface of CPs based on PEDOT, ProDOT or di-ethylProDOT. A compositionally and energetically asymmetric material combination results, which can reduce a solution electron acceptor, with the CdSe NC acting as the photosensitizer; (B) The overall rate of MV^{++} reduction is determined by a complex series of ET events, and for this first generation of materials the slow step appears to be electron capture from the CP by the photoexcited NC. Excess free energy relationships summarized in Fig. 3 show that $r_{c,2}$ (for cathodic photocurrents) is determined by the free energy difference between the quasi-Fermi potential in the CP and E_{VB} of the NC.

NC, and for NCs modified with short dipolar ligands that vary in their polarizability. We were able to account for the large (up to 1.0 eV) shift in vacuum level caused by even 15% of a monolayer of CdSe NCs adsorbed via dithiols to Au, and the additional increases or decreases in vacuum level caused by dipolar capping ligands.

We developed an alternative approach to characterization of frontier orbital energies of tethered NCs using spectroelectrochemical methods on waveguide substrates. Monolayers of thiol functional carboxylic acids are adsorbed to indium-tin oxide (ITO) substrates (the electroactive component of an ATR/waveguide element),

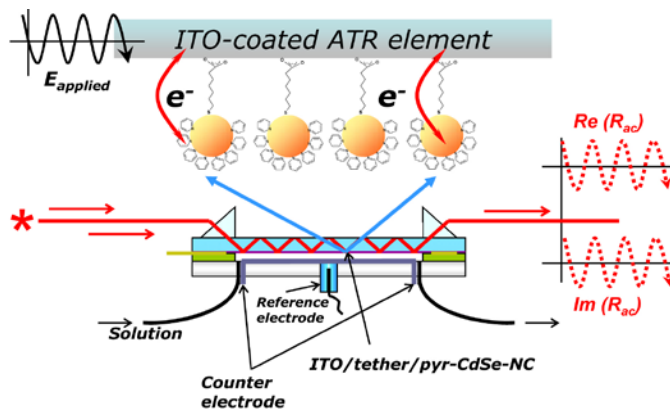


FIGURE 2. Schematic view of the spectroelectrochemical characterization of CdSe NCs, tethered at sub-monolayer coverages to ITO/ATR waveguide platforms. The potential (versus N.H.E. and vacuum) at which full bleaching of the lowest energy excitonic feature (at λ_{ex}) is used to estimate E_{CB} in solution environments. Modulation of the potential then provides in-phase and out-of-phase optical responses, which are used to estimate switching rates, related to k_{ET} to/from the NC.

which can then act as a capture surface for solution pyr-CdSe NCs. The lowest energy excitonic feature is reversibly bleached at a midpoint potential which leads to an estimate of $E_{\text{CB}} \approx -3.5$ eV versus vacuum. Subsequent modulation of the electrode potential around this midpoint potential while measuring both in-phase and out-of-phase components of the ATR/reflectance signal allows for estimation of rates of bleaching/recovery of the monolayer tethered NC (k_s).

We have recently demonstrated the synthesis of p-type cobalt oxide nanowires and heterostructured $\text{Au-Co}_3\text{O}_4$ nanowires via *Colloidal Polymerization*. In these systems, metallic cobalt nanoparticles assemble into 1-D mesostructured “wires” in solution via magnetic dipolar interactions, and are subsequently converted into hollow oxide nanowires via oxidation reactions. Hollow Co_3O_4 nanowire networks were formed on ITO and were shown to be electrochemically active. UPS measurements provided an estimate of $E_{\text{VB}} \approx 5.3 \pm 0.2$ eV for the as-deposited oxide nanowires, which appears to be close to the valence band energy required to drive OER in a photoelectrochemical energy conversion system, without external bias. As discussed further below, these band edge energies will provide large driving forces for photoelectrochemical processes when the oxide NP is married to semiconductor NCs or NRs, such as CdSe, forming true “Type II” heterojunctions. To enhance their catalytic properties these cobalt oxide nanowires were subsequently modified with noble metal inclusions. We demonstrated the ability to insert Au or Pt nanoparticles into the interior or exterior of the cobalt oxide nanowires. We saw a significant enhancement of the electrochemical activity associated with the change of redox states of the cobalt oxide as a consequence of noble metal inclusions.

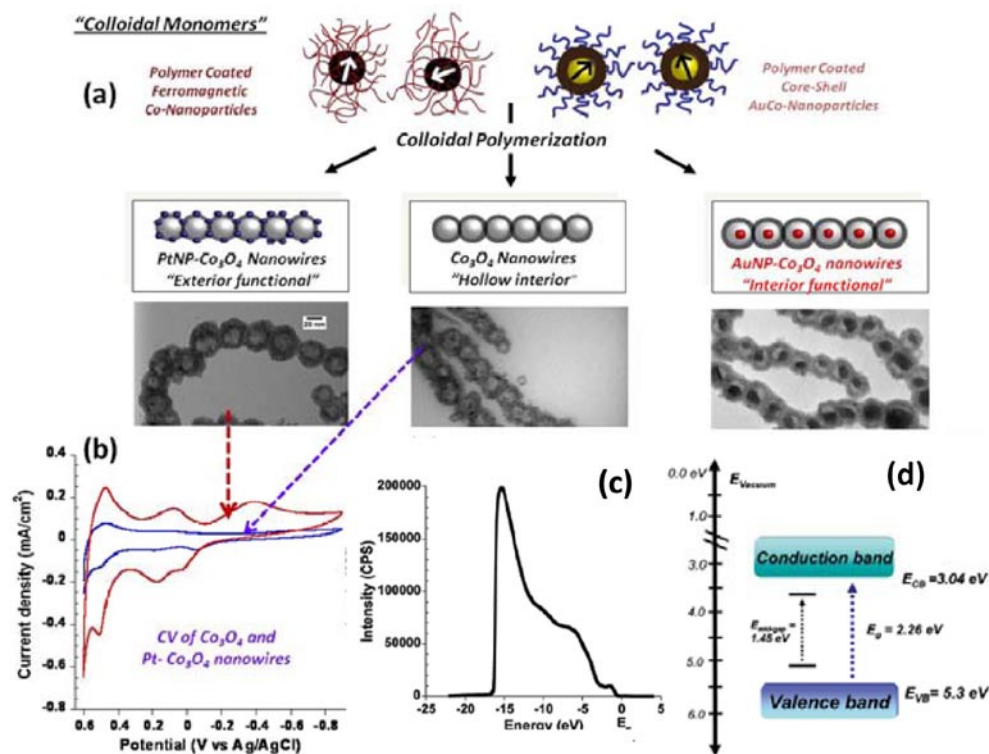


FIGURE 7. (a) Schematic for preparation of hollow Co₃O₄ nanowires, Au-Co₃O₄ nanowires with Au inclusions on the interior of nanowires and Pt-Co₃O₄ nanowires with Pt inclusions on exterior of nanowire. (b) CV of hollow Co₃O₄ vs. Pt-Co₃O₄ nanowires indicates a 7-fold enhancement of electroactivity as a consequence of Pt inclusions (c) UV-photoemission spectroscopy (He(I) UPS) of hollow Co₃O₄ nanowires and (d) estimated band edge energies of Co₃O₄ nanowires constructed from UPS and optical absorption data.

Future Directions

1. We will develop ligand-capped SC-NCs and SC-NRs providing for selective and asymmetric addition of metallic and oxide (e.g. cobalt oxide) catalytic sites, with control over their placement, electronic coupling, and catalytic activity.
2. We will explore directed self-assembly of rod-like molecular objects into vertically aligned arrays.
3. We will characterize band edge energies of monolayer-supported NCs and NRs using photoemission spectroscopies (UPS/XPS), characterizing E_{VB} and vacuum level changes as a function of NC coverage and capping ligand. We will probe NC-NC and NR-NR interactions and extend these studies to either randomly adsorbed or aligned NRs which have been modified with oxide or metallic catalytic sites.
4. We will extend our protocols for spectroelectrochemical study of SC-NCs on electroactive waveguides, to study NC-NC and NR-NR interactions which influence E_{CB} as a function of surface coverage, types of capping ligands, the introduction of asymmetric nanorods, and nanorods modified with catalytic sites.

5. We will develop the first prototypes of membrane encapsulated ensembles of these asymmetric, modified SC-NCs and the first demonstration of proton pumping in response to photoelectrochemical events on either side of the membrane.

Selected Recent Publications

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3. Araci, Z.O.; Shallcross, C.R.; Armstrong, N.R.; Saavedra, S.S., Potential-Modulated Attenuated Total Reflectance Characterization of Charge Injection Processes in Monolayer-Tethered CdSe Nanocrystals. *Journal of Physical Chemistry Letters* **2010**, *1* (12), 1900-1905.

4. Kim, B.Y.; Shim, I.B.; Araci, Z.O.; Saavedra, S.S.; Monti, O.L.A.; Armstrong, N.R.; Sahoo, R.; Srivastava, D.N.; Pyun, J., Synthesis and Colloidal Polymerization of Ferromagnetic Au-Co Nanoparticles into Au-Co₃O₄ Nanowires. *Journal of the American Chemical Society* **2010**, *132* (10), 3234-+.

5. Kim, B.; Keng, P.; Shim, I.-B.; Sahoo, R.; Oskan, Z.; Saavedra, S.S.; Armstrong, N.R.; Pyun, J., Synthesis and Colloidal Polymerization of Dipolar Au-Co Core-Shell Nanoparticles into Au-Co₃O₄ Nanowires *J. Am. Chem. Soc.* **2010**, *132*, 3234-3235.