BES001 Semiconductor Nanorod/Metal(Metal Oxide) Hybrid Materials: Characterization of Frontier Orbital Energies and Charge Injection Processes Using Unique Combinations of Photoemission Spectroscopies and Waveguide Spectroelectrochemistries

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Objectives

We are focused on the development of new semiconductor nanomaterials which are prototypical for systems that may be ultimately used to photoelectrochemically produce fuels from sunlight, and in understanding how the introduction of catalytic sites (e.g. metallic tips on a semiconductor nanorod) can alter the band edge energies (E_{VB}/E_{CB}) and the dynamics of electron transfer to/from these nanomaterials.

Technical Barriers

Producing rod-like semiconductor materials, tipped with catalysts at nanometer length scales, with good control over composition, size and energetic dispersity, is extremely challenging. Arranging these materials in interconnected assemblies without loss of function is even more challenging. We also need (and are developing) new ways of characterizing band edge energies of these materials, and rates of electron transfer, in motifs that apply to their use in energy conversion platforms – even more challenging! A key target and technical question is whether the conjugation of cobalt oxide nanoparticles onto semiconductor nanorods offers a route to preparing photosensitized cobalt oxide NPs for OER.

Abstract

This talk will review our multi-PI study of the formation of unique semiconductor nanorods (NRs) and NRs decorated with metallic or oxide catalytic sites, and the characterization of their band edge energies as catalytic sites are introduced.[1-5] We demonstrate new approaches to a) the characterization of valence band energies using photoemission spectroscopies, which for the first time fully take into account local vacuum level shifts (due to the dipolar nature of the NR), and b) conduction band energies (E_{CB}) using waveguide-based spectroelectrochemical approaches to determine the potentials (versus vacuum) for electron injection into the NC or NR. Both approaches show significant shifts in band edge energies, and the rates of electron transfer (ET), when NCs and NRs are decorated with metallic and oxide catalytic sites at the NR tip. Even small Au nano-tips on CdSe NRs, where the metallic component is less than 1% of the total atomic content of the NR, introduces shifts in E_{VB} and E_{CB} which are predicted to alter efficiencies of photoelectrochemically driven water splitting and related formation pathways toward solar fuels. This work underpins the rational design of new photocatalytic materials, and is a necessary step toward a complete understanding of the effects of modification and interconnection of NR assemblies on both energetics and dynamics of ET in these materials.

Progress Report

1. Formation of new semiconductor nanorods with metallic and oxide catalytic tips:

We have created a series of new semiconductor NR materials which have been tipped at both end, or one end, with catalytic sites, either metallic in nature (Pt, Au) or oxides such as Co_xO_y. The synthetic methods developed under this project allow the installation of a photosensitizing semiconductor nanorod (either CdSe@CdS, CdS, CdSe) with metallic (Au, Pt), or metal oxide (Co_xO_y) NP tips. The modularity of this approach enables spatial and energetic control in this photoactive nanocomposite. Heterostructured nanorods based on CdSe@CdS have served as model systems to develop these synthetic methods, with an emphasis on installing one, or two NP tips per nanorod. To facilitate spectroelectrochemical measurements, we have also prepared

heterostructured CdSe nanorods that incorporate Au, Co and Co_xO_y tips. Our work has focused on these CdSe NRs which have high bandgap energies and afford ease of synthesis and tuning of the NR size, shape and functionalization in ways which leads to insights about their energetics which we think will be generalizable across a number of material platforms. Figure 1 at right shows a recent TEM characterization ofi individual NRs, Au-tipped NRs and Au-NR fused assemblies which show intriguing linkages between NRs which, if controlled, might lead to vectoral charge transport – a perquisite for photoelectrocatalytic assemblies.

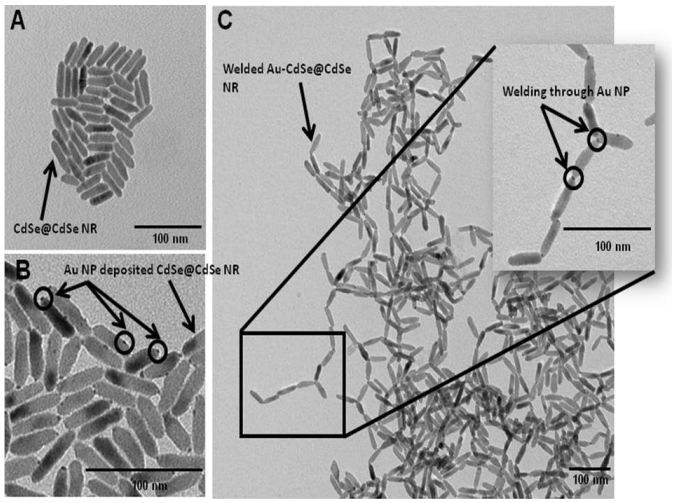

FIGURE 1. TEM images of (A) synthesized CdSe@CdSe nanorod heterostructures (L = 40.1 ± 4.1 nm; D = 9.6 ± 1.2 nm). (B) Au-CdSe@CdSe heterostructures exhibiting matchstick and dumbbell morphologies, with some lateral deposition of AuNP observed. (C) Fused Au-CdSe@CdSe nanorod networks formed by coalescence of AuNP tips. Fusion of CdSe@CdSe NRs occurs through Au NPs.

2. Characterization of valence band energies in NCs and NRs using photoemission spectroscopies, effect of metallic tips on E_{VB}:

We have recently developed a unique approach to the characterization of NC and NR band edge energies (E_{VB} directly, E_{CB} from E_{VB} and the optical band gap), using UV-photoemission spectroscopies (He I and He II UPS) for NC and NR thin films on highly ordered pryolitic graphite (HOPG), accompanied by removal of He satellite emission lines and secondary electron background, and correction for local shifts in vacuum levels due to the dipolar nature of these NC and NRs. This approach gives us for the first time good accuracy for determination of E_{VB}, and confidence in the shifts we see in E_{VB} as NRs are modified with metallic and oxide catalytic sites. Figure 2 shows, for example, that there are significant decreases in E_{VB} (and E_{CB})for Au-tipping of CdSe NRs, and even larger decreases in E_{VB}/E_{CB} when these NRs are fused through their tips, both effects are predicted to increase the driving force for proton reduction on these assemblies, and will factor into the design of new semiconductor nanomaterials.

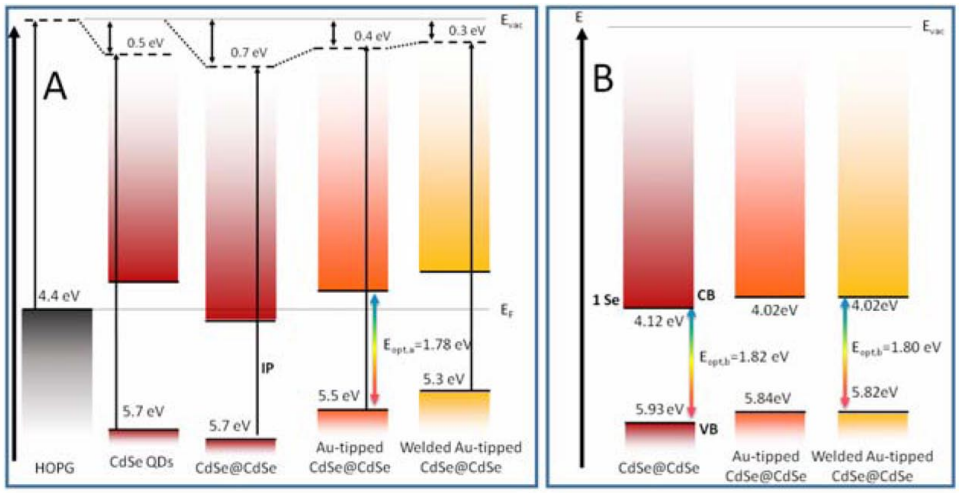

FIGURE 2. Estimates of EVB and ECB from UV-photoemission studies (UPS) of NC and NR thin films on HOPG (A) and waveguide spectroelectrochemical studies of electron injection (B). In the UPS studies we were able to uniquely correct for shifts in local vacuum levels (critical) and show that addition of Au tips to the NR, and NR fusion through the Au tpis, lead to demonstrable decreases in E_{VB}/E_{CB}. These changes in band energies are confirmed in the spectroelectrochemical studies of electron injection into E_{CB}, in contact with electrolyte solutions.

3. Characterization of conduction band energies and rates of heterogeneous ET in NCs and NRs using waveguide-based spectroelectrochemistries:

We have also recently demonstrated that waveguide-based spectroelectrochemical techniques can be used to monitor injection of electrons into the conduction band of both NCs and NRs, at coverages on the waveguide that ensure isolation of the NR or NC, or at coverages where strong interactions exist between these nano-objects, this time in contact with electrolyte solutions. As shown in Figure 3A, we can uniquely monitor the bleaching of the lowest energy excitonic features in these NRs, as electron injection proceeds, at potentials which can be translated to the vacuum scale and compared with PES measurements in Figure 2. Furthermore, by modulating the potential applied to the NR assembly and poising at the excitonic wavelength, we obtain estimates of rates of electron injection/extraction from optical impedance data (Figure 3B) which show that electronic coupling to the substrate electrode, and rates of ET, are greatly improved by introduction of Au tips and fusion of NRs through these tips.

Future Directions

We are in the process of expanding the scope of this work by: *i)* varying tip composition of the semiconductor NR, adding catalytic sites that function for both hydrogen evolution (HER) and oxygen evolution (OER), with both symmetric (dumbbell) and asymmetric (matchstick) motives; *ii)* interconnecting the asymmetric assemblies to create a network which retains the asymmetry (critical for photoelectrochemical water splitting and related processes), iii) systematic characterization of the energetics and dynamics of electron transfer to/from these NR materials, as isolated nano-objects, and as a function of tip modification and interconnection, using both photoemission and spectroelectrochemical protocols.

Recent publications

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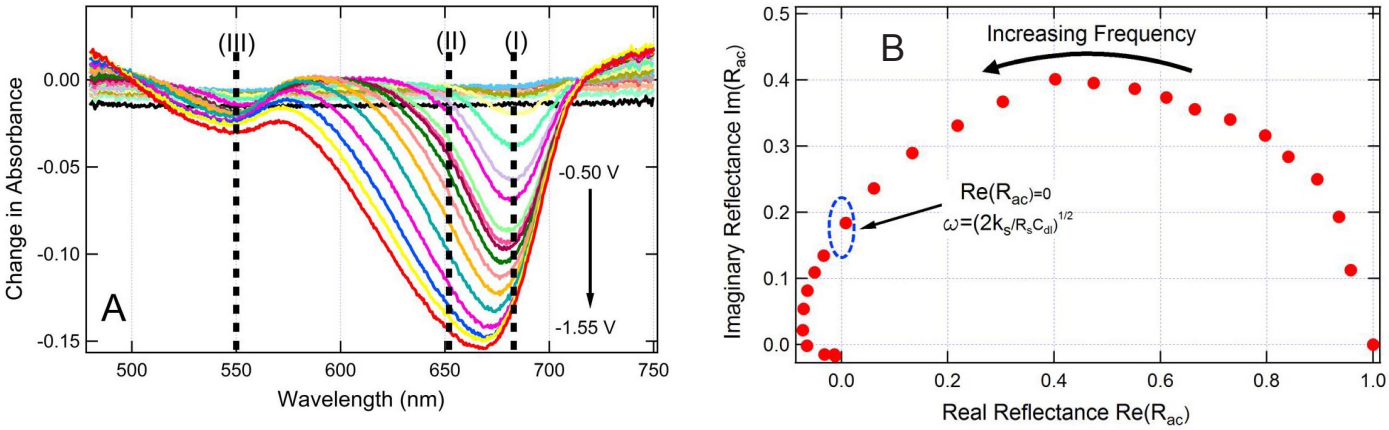

FIGURE 3. (A) Bleaching spectra for CdSe NRs on a waveguide spectroelectrochemical substrate, showing the loss of the excitonic band feature as electrons are injected into the conduction band, the potential for this process defines E_{CB}; (B) PM-ATR optical impedance data (imaginary versus real components of the optical bleach) as a function of frequency, which can be used to estimate the rate of electron injection/extraction ($k_{s,app}$) for these NR assemblies.

7. Hill, L.J.; Pyun, J. Colloidal Polymers via Dipolar Assembly of Magnetic Nanoparticle Monomers. *ACS Applied Interfaces* **2014**, *ASAP*, DOI: 10.1021/am405786u http://dx.doi.org/10.1021/am405786u

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