

Chemically Functional Semiconductor Nanocrystals: Electrochemistry and Self-Assembly on Surfaces

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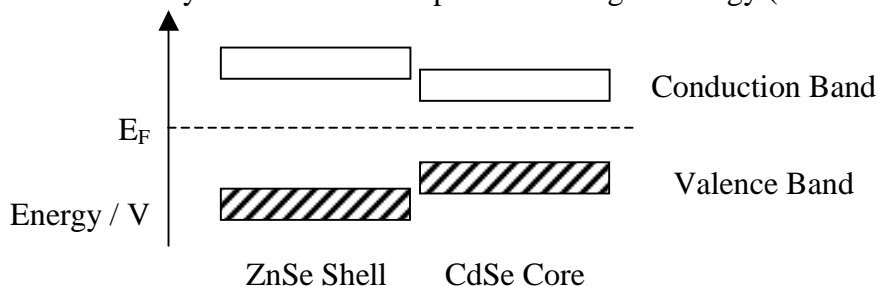
ABSTRACT

Semiconductor nanocrystals (*i.e.*, Quantum Dots, QDs) exhibit size-dependent emission properties and have synthetically adjustable ligand shells, making them interesting materials for applications ranging from luminescent displays to biomolecular tags. In this paper, the electrochemical properties of two types of nanocrystal are studied with an emphasis on the effect of core/shell vs core structures. The band gap energy of CdSe particles, measured using optical spectroscopy, was shown to increase slightly with the application of a ZnSe shell, as expected based on the increased energy required to transfer an electron through the shell material. The electrochemically determined band gaps are overestimated in the case of CdSe/ZnSe core/shell nanoparticles, reflecting the band gap of the ZnSe shell. Finally, QDs were self-assembled onto gold surfaces by electrostatic and covalent attachment, and their presence confirmed by fluorescence spectroscopy. The high intensity of emitted light shows that the QDs can be self-assembly onto metallic surfaces, without energy transfer quenching of the luminescence.

INTRODUCTION

The electronic properties of semiconductor nanocrystals (known as quantum dots, QDs) have been extensively examined over the past decade.¹⁻³ Their size- and composition-dependent band gap energies provide a near continuous spectrum of narrow line-width emission sources. Only recently, however, have their bulk properties been investigated using electrochemical methods.⁴⁻⁶ Using cyclic voltammetry (CV), the bulk electronic properties of CdSe and CdS QDs have been examined and compared to well-understood UV-Visible absorption spectra; the difference in potential between the anodic and cathodic peak currents has been shown to correspond to the average band gap (*i.e.*, the separation of the lowest unoccupied and highest occupied (LUMO and HOMO) energy levels) of the sample.⁶ This previous work showed that the electrochemically determined band gaps may slightly overestimate those determined spectroscopically.

Application of an electrical potential to an electrode surface shifts the Fermi level of the electrode and thus that of any surface-adsorbed particles to higher energy (reduction) or lower



Scheme 1. Energy level diagram depicting the relative energies of the valence and conduction bands of two semiconductors, ZnSe and CdSe, versus the experimentally adjustable Fermi level (E_F) of the electrode.

energy (oxidation), as shown in Scheme 1. During voltammetry of semiconductors, when the Fermi potential reaches the semiconductor band edge, an electron can be transferred between the particle and the electrode, causing current to flow. A current peak in the cyclic voltammogram thus corresponds to the band energy of the appropriate (conduction or valence) band, and the separation between the anodic and cathodic peaks is a measure of the band gap energy. This effect is expected for any semiconducting material; however the size and surface effects on the band gaps properties of QDs make them potentially very interesting electrochemical systems that have not been extensively examined.

While the band gap of a QD composed of a single type of semiconductor is typically characterized by the absorption of a photon corresponding to the excitation of an electron from the HOMO to LUMO energy levels, this does not necessarily accurately describe photoexcitation in semiconductor nanoparticles with more complex structure, such as core/shell particles. For example, when a semiconductor is coated with a shell of a different semiconductor with larger band gap, the emission properties are determined by the lower energy (core semiconductor) transition due to ultrafast hole and electron transport to the interior of the nanocrystal. The electrochemical properties of core/shell semiconductor nanocrystals have not been explored, and key questions remain regarding electron transfers to and from the particle. Understanding the control of electron and hole transport in semiconductors, and how these relate to photoemission, has substantive implications for QD use in novel nanoscale light-emitting devices.

In addition, to enable use in device applications, the semiconductor nanoparticles must be chemically derivatized to enable their attachment to a conductive surface. However, attachment of semiconductors to metal surfaces can lead to spontaneous electron transfer to the metal and quench fluorescence emission. This paper presents our approach for the synthesis of functionalized core/shell semiconductor nanoparticles and our preliminary electrochemical investigations on these complex systems. Finally, we have developed a strategy to prevent fluorescence emission quenching and to electrostatically bind the nanocrystals to Au surfaces, and confirmed by steady-state fluorescence emission spectroscopy that the QDs retain their emissive properties.

EXPERIMENTAL METHODS

Methylene chloride was purified by distillation. Tetrabutylammonium hexafluorophosphate (Fluka) was recrystallized from ethyl acetate. All other chemicals were used as received.

CdSe nanocrystals were synthesized by a modified literature method.⁷ Briefly, 51 mg (0.4 mmol) cadmium oxide (CdO, Aldrich), 2.3 g (9.35 mmol) hexadecylamine (HDA, Aldrich), and 0.98 g (2.52 mmol) trioctylphosphine oxide (TOPO, Fluka) were heated to melting (~100°C) under vacuum for *ca.* 1 hour. The solution was then heated to 270°C and 0.20 g (0.8 mmol) dodecylphosphonic acid (DPA, PolyCarbon Industries, Inc.) was added. The temperature was reduced to 250°C, and 2.5 mL of a 0.2 M (0.5 mmol) Se (Alfa Aesar) in trioctylphosphine (TOP, Fluka) solution were rapidly injected. The temperature was maintained at 250°C and particle growth monitored by UV-Visible absorption spectroscopy on a Cary 500 UV-Vis spectrophotometer. Nanocrystals were isolated by flocculation in a mixed butanol/methanol solvent mixture.

Some of the CdSe nanocrystals were passivated with a ZnSe shell according to published procedures.⁷ In a typical preparation, ~20 mg of purified nanocrystals in 4mL of heptane were

added to 2.1 g (5.5 mmol) TOPO and 1.2 g (5.0 mmol) HDA, and heated to 100°C under vacuum for 20 minutes. The vessel was back-filled with argon and heated to 190°C. A solution of 316 mg (0.5 mmol) zinc stearate (Zn(St), Fisher) in 2.5 mL toluene was added to 2.5 mL of 0.2M Se(TOP), and the resulting solution added dropwise to the CdSe/HDA/TOPO reaction vessel in 1 hr. The solution was heated for an additional 1.5 hrs at 190°C to anneal the shell, and purified by the same method as above.

Electrochemical measurements were performed using a CH Instruments Model 660A Electrochemical workstation with computer data acquisition and control. All voltammetric experiments were performed on thoroughly degassed solutions, and employed a Pt disk working electrode, Pt wire counter electrode, and Ag wire pseudo-reference electrode. Solutions were placed into the electrochemical cell, purged with Ar, and tightly sealed to prevent oxygen contamination.

Gold slides were prepared by sequential evaporative deposition of a 10 nm thick adhesion layer of Cr and 25 nm thick film of Au onto freshly cleaned glass using a Edwards Auto306 Evaporator. The Au surfaces were then modified with a monolayer of mercaptoundecanoic acid (MUA) by exposure of the metal surface to a 2 mM solution mercaptoundecanoic acid in ethanol overnight.

CdSe nanocrystals were self-assembled onto the MUA-modified Au slides by one of two methods. The modified Au slides were in a stirred solution of TOPO/HDA/TOP coated CdSe nanoparticles in heptane for 12 hrs. The slides were removed from the solution, rinsed with heptane, and dried under a stream of Ar. Alternatively, the TOPO/HDA/TOP ligands on the CdSe QDs were exchanged by stirring the particles in pyridine at 60°C for 12 hrs. MUA-containing Au slides were placed in the solution containing pyridine-coated nanocrystals for a minimum of 30 minutes. The films were rinsed with heptane, dichloromethane, and acetone, and then placed in an ethanolic solution of undecanoic acid (UDA, Aldrich) for 30 minutes. The slides were then rinsed with ethanol and acetone, and dried under a stream of nitrogen.

The presence of adsorbed nanoparticles was confirmed with reflective mode steady state fluorimetry; emission spectra were collected with a PTI steady state fluorescence spectrometer. In all cases, the excitation wavelength was 350 nm, and the fluorescence emission detected in a front-face/reflection geometry. To minimize reflected and scattered source radiation in the signal, the emission beam was passed through a 2 nm slit and a low pass filter.

RESULTS

In this presentation, comparison of optical and electrochemical properties is made between samples of CdSe nanocrystals and CdSe cores (with the same diameter as the pure CdSe particles) surrounded by thin, concentric ZnSe shells. To test our ability to prepare and characterize these materials versus previously published procedures, we use UV-Visible absorption and emission spectroscopies to monitor their optical behavior. Figure 1 shows typical absorption spectra obtained for CdSe and CdSe@ZnSe nanoparticles in chloroform solutions. From the energy of the peak absorption of the nanoparticles, the optical band gaps are determined to be 2.16 eV and 2.14eV for CdSe and CdSe@ZnSe, respectively. Emission spectra for the same samples are shown in the inset to Figure 1; a slight red shift (*vs.* the absorption peak) in the peak emission energy was observed, an effect which has been previously attributed

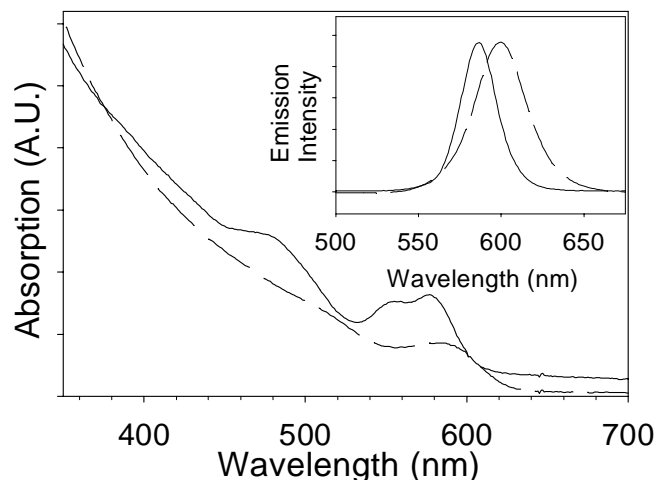


Figure 1. Absorption spectra of TOPO/HDA passivated CdSe (—) and CdSe@ZnSe (- - -) nanoparticles in CH_2Cl_2 . Inset: Fluorescence spectra of same particles.

to partial exciton leakage into the shell lattice.⁸⁻¹⁰ The narrow line widths in the emission spectra are indicative of the high level of monodispersity of the nanocrystal samples.

As part of our efforts to understand and manipulate electronic properties of semiconductor nanocrystals, we utilize electrochemical methods to interrogate these materials. We first performed cyclic voltammetry on solutions of CdSe nanoparticles to confirm previous reports⁶ that the optically determined band gap corresponds with the difference between oxidative and reductive peak potentials. A typical voltammogram of the CdSe nanoparticles is shown in Figure 2, together with a cyclic voltammogram of the core/shell CdSe/ZnSe nanocrystals. The lack of current when the potential scan is reversed (for both the oxidative and reductive peaks) is indicative of a chemically irreversible process, and has been described previously⁶ for CdSe

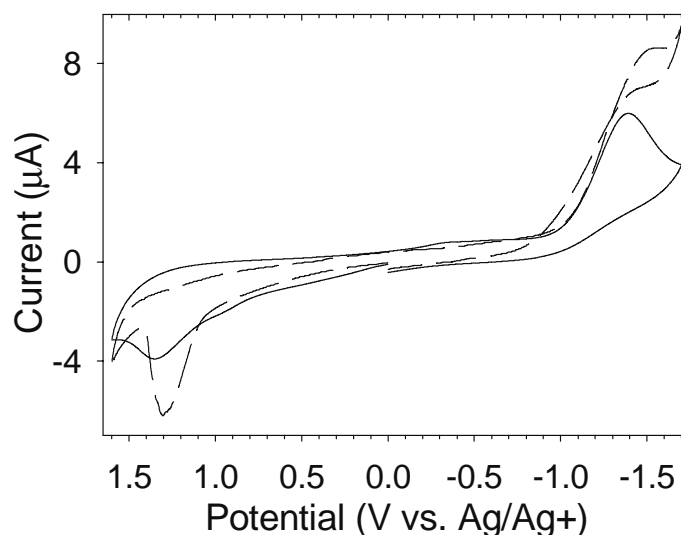


Figure 2. Cyclic voltammetry of CdSe (—) and CdSe@ZnSe (- - -) nanocrystals in CH_2Cl_2 with 0.1 M tetrabutyl ammonium perchlorate supporting electrolyte. The working electrode was a 6 mm diameter Pt disk electrode, and the potential scan rate was 50 mV/s.

nanoparticles. The difference in peak potentials (ΔE_p) for the CdSe nanocrystals is 2.3 eV, in reasonable agreement with the (above) optically determined band gap. In contrast, the voltammogram of the CdSe@ZnSe nanocrystals exhibits a ΔE_p of 2.8 eV, which is significantly larger than the optically measured band gap (2.14 eV, above). This difference is attributed to charge injection into the outer ZnSe shell, which has a larger band gap. We note that both the oxidative and reductive peaks are more well defined for the CdSe@ZnSe nanocrystals, but there is again an absence of signal in the reverse scan direction. Our continuing studies are aimed toward understanding the origin of this observation, since it may be attributed to chemical instability (as in the CdSe nanocrystals) or by charge transfer and trapping to the CdSe core.

In addition to their solution phase electrochemical behavior, we are investigating the electronic properties of functionalized semiconductor nanocrystals adsorbed onto conductive electrode surfaces. Our preliminary experiments therefore have focused on the attachment of quantum dots onto gold coated glass slides which contain a carboxylic acid terminated self-assembled monolayer. The acid groups have been used to either electrostatically bind the nanocrystals or to covalently link the CdSe nanoparticles to the surface. Figure 3 shows examples of fluorescence emission spectra obtained on slides containing each of these types of quantum dot films. The emission maxima at 550 nm is consistent with the wavelength expected for emission from the CdSe nanocrystals based on their above solution-phase spectra, confirming the presence of surface adsorbed nanoparticles. The emission peak is somewhat broadened compared to the spectra shown in Figure 1, which is most likely a result of particle-particle interactions on the surface. Comparison of the two spectra in Figure 3 shows that the signal for the pyridine-exchanged particles is greater than the electrostatically bound particles. We are in the process of conducting additional experiments to determine if the difference between the two samples is a result of either greater surface coverage of the pyridine-containing particles or

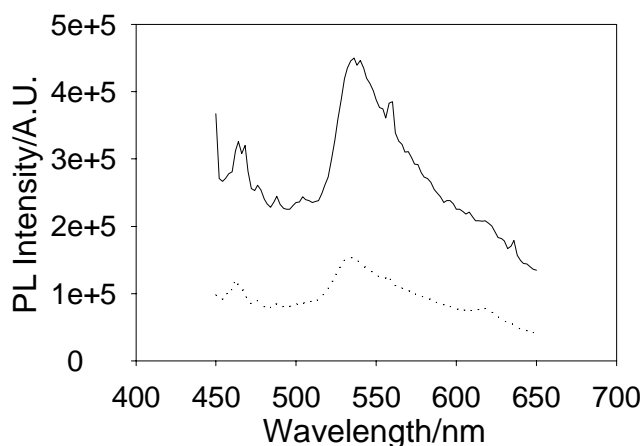


Figure 3. Fluorescence emission spectra CdSe nanocrystals attached to Au surfaces containing a self-assembled monolayer of mercaptoundecanoic acid. The lower spectrum (.....) is for CdSe nanoparticles containing TOPO/HDA ligands electrostatically bound to the MUA; top spectrum (—) is for pyridine-modified CdSe nanoparticles covalently attached to MUA. The excitation wavelength was 350 nm.

greater quantum yield for that sample. In both cases, however, the amount of fluorescence emission is large and the signal easily discernible above the background signal, demonstrating that despite the close proximity of the quantum dots to the Au metal surface, fluorescence

emission is not quenched. We hypothesize that the organic capping ligands on the nanocrystals and the MUA monolayers prevent direct contact and energy transfer quenching.

CONCLUSIONS

The electrochemical properties of core/shell CdSe/ZnSe nanoparticles are compared to CdSe semiconductor nanocrystals. The differences in peak potentials for the oxidation and reduction reactions of the nanoparticles estimate the band gaps, and these values are compared to those obtained from optical spectra. The core/shell nanoparticles have voltammetry consistent with the band gap of the outer ZnSe shell even though fluorescence emission arises from hole-electron recombination within the core CdSe. The chemically modified surfaces of the CdSe quantum dots were used to self-assemble the particles onto Au slides, and their presence confirmed with fluorescence emission spectroscopy. Intense fluorescence emission is observed despite the close proximity of the quantum dots to the metallic surface, confirming that the organic ligands prevent energy transfer quenching of luminescence.

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