Nanocrystals Research for Energy Efficient and Clean Energy Technologies: DOE-BES Final Report

The following summarizes projects completed or in the process of being completed during the final year of funding in 2008. Efforts centered on: nanocrystal photovoltaic fabrication, ultrafast dynamics and aberration-corrected STEM characterization of II-VI core, core/shell and alloyed nanocrystals, and fundamental investigation and applications of ultrasmall white light-emitting CdSe nanocrystal.

Photovoltaic Cells fabricated by electrophoretic deposition of CdSe nanocrystals

Electrophoretic deposition (EPD) was investigated as a method for depositing nanocrystals onto counter electrodes for photovoltaic devices.¹ The deposition current followed an exponential decay, consistent with the current being comprised of charge transfer from charged nanocrystals to the electrodes. Rutherford backscattering spectroscopy indicated the composition of the deposited films depended on the polarity of the electrode on which the film formed. EPD deposition was used to construct a simple device, which exhibited a photovoltaic response from the region in which nanocrystals were deposited, with an efficiency of $\sim 10^{-6}\%$. The low efficiency was likely due to the planar geometry employed for the TiO_2 substrate.

Figure 1. Fabrication of nanocrystal photovoltaic using EPD. Left: current vs. voltage curve showing photovoltaic response. Right: Rutherford backscattering spectra showing electrode deposition dependence.¹

Band Edge Dynamics in CdSe Nanocrystals Observed by Ultrafast Fluorescence Upconversion

The change in carrier dynamics of cadmium chalcogenide nanocrystals associated with varying ligands and surface composition has been explored through femtosecond fluorescence upconversion.² Exploring fluorescence lifetime at the band edge for CdSe nanocrystals, it was revealed that both the short- and long-lived components (τ_1 and τ_2 , respectively) are size dependent (Figure 2a). Specifically, it was shown that an increase in nanocrystal size is accompanied by an increase in τ_1 . The change in CdSe carrier dynamics associated with the addition of hexadecylamine (HDA) as a cosolvent was also examined. Compared to tri-n-octylphosphine oxide (TOPO) only synthesized nanocrystals, τ_1 was shown to increase, indicating a reduction in the number of available surface traps with the addition of HDA. Based on surface stoichiometry, TOPO only CdSe nanocrystals are Cd-rich, indicating the presence of Se dangling bonds. These Se dangling bonds can then act as hole traps on the surface. Although an amine binding to selenium is not likely, due to the tilting of the HDA chain, it is possible that the methylene protons on HDA interact with the dangling selenium bonds on the surface. This is a plausible interaction, as it is doubtful that there is any coupling between the amine hydrogen atoms and the dangling selenium bonds on the surface. These results were corroborated through molecular modeling (Figure 2b).

Figure 2. (a) Graph of τ_1 and τ_2 vs nanocrystal diameter. The increase in τ_1 corresponds to the reduction in surface-to-volume ratio, resulting in a reduction in the overlap of the electron and hole wave functions with the nanocrystal surface. The increase in τ_2 is attributed to the decrease in relaxation from a triplet state to the ground state and the increase in recombination through the transition from the singlet to the ground state as nanocrystal size increases. (b) GaussView3.09 model of a single surface slice of wurtzite CdSe. The calculated distance between the amine hydrogen and the selenium atom was found to be 3.87 Å, whereas the characteristic bond length in free molecules for H-Se is 1.47 Å. Consequentially, it is unlikely that there is any binding or coupling between the amine hydrogen and the selenium atoms. (Inset) CdSe wurtzite unit cell, where cations are represented as the small shaded circles.

It has also been shown that photo-oxidation of the selenium surfaces of the nanocrystal leads to an increase in radiative decay efficiency from both the band edge and deep trap emission states (Figures 3a and 3b). It has been further demonstrated that CdSe/ZnSe core/shell nanocrystals are not immune from contributions from surface states because of the alignment of the band structures of the core and shell materials due to the band offsets (Figures 3c and 3d).³ This property of preferentially confining charges could possibly be exploited in tailoring a material for use in electronic devices such as photovoltaics.

Figure 3. Bandedge emission (A) and deep trap emission (B) monitored as a function of oxygen exposure time. (C) Ultrafast fluorescence upconversion spectra of nanocrystals of all surface treatments studied with a 560 nm band edge absorption feature. Washed CdSe/ZnSe core/shells (circles), unwashed CdSe/ZnSe (squares), TOPO/HDA CdSe nanocrystals (triangles), and TOPO only CdSe nanocrystals (inverted triangles). (D) Band offsets between different sized CdSe core nanocrystals and the ZnSe shell.

Band Edge Recombination in CdSe, CdS and CdS_xSe_{1-x} Alloy Nanocrystals Observed by Ultrafast Fluorescence Upconversion: The Effect of Surface Trap States

The effect of surface trap states on band edge recombination in CdSe, CdS and CdS_xSe_{1-x} alloy nanocrystals has been determined using fluorescence upconversion spectroscopy.⁴ These measurements revealed both a size and composition dependence of the short-lived

(τ_1) and long-lived (τ_2) components of fluorescence lifetime at the band edge. Increasing the nanocrystal diameter, (2.3 to 6.0 nm), increases τ_1 . This is explained by the decrease in accessible trap sites through a reduction in surface-to-volume ratio. τ_2 is found to also increase with increasing nanocrystal diameter. However, increasing the sulfur concentration in alloy nanocrystals, results in both a reduction in the magnitude of τ_1 and a reversal in the trend for τ_2 . These changes in lifetimes associated with the addition of sulfur are explained by increased surface trapping. These results indicate that carrier dynamics may be controlled not only through size, but also through composition of the nanocrystals. Additionally, an increase in the Stokes shift is observed for $\text{CdS}_x\text{Se}_{1-x}$ alloy nanocrystals as compared to CdSe and CdS nanocrystals. This indicates that the Stokes shift is highly influenced by the nonlinear effects of alloying.

Figure 4. (a) Z-STEM image of $\text{CdS}_{0.50}\text{Se}_{0.50}$ 51 Å alloy nanocrystals taken on a VG Microscopes' model HB603U, operating at 300 kV and fitted with a Cs corrector from Nion, located at Oak Ridge National Laboratory. (b) It can be seen that there is no core/shell structure, as the nanocrystal is uniform in intensity. Right: Graph of τ_2 versus nanocrystal composition for a series of 44 Å ((5%) alloy nanocrystals. It can be seen that τ_2 begins to decrease in the $\text{CdS}_x\text{Se}_{1-x}$ alloy material. The decrease in τ_2 with increasing sulfur contribution is attributed to increased trapping at the nanocrystal surface.

Pinned Emission in Ultrasmall Nanocrystals.

The emission spectrum for ultrasmall CdSe nanocrystals, passivated with alkyl phosphonic acids, with a diameter of 1.7 nm and smaller is shown to be pinned at 440 nm.⁵ When the surface ligand is changed from a phosphonic acid to either dodecanethiol, oleic acid or pyridine, the emission at 440 nm is quenched. However, the positions of the remaining features are preserved, except in the case of the 550 nm emission for

dodecanethiol. This indicates the pinning of the 440 nm emission peak is due to a surface state introduced by the phosphonic acid ligand binding to the surface of the nanocrystal.

Figure 5. The position of the first emission feature is plotted against the position of the first absorption feature for CdSe nanocrystals passivated with (a) octylphosphonic acid, (b) dodecylphosphonic acid, and (c) hexadecylphosphonic acid. In all cases, when the band edge absorption wavelength is below 420 nm, corresponding to nanocrystals less than 1.72 nm in diameter, the first emission feature is pinned at approximately 440 nm. The line on each graph represents the trend of blue-shifting emission with a blue-shift in the absorption. The emission spectrum remains broad and unchanged at nanocrystal sizes below 2 nm.

Control of Surface State Emission via Phosphonic Acid Modulation in Ultrasmall CdSe Nanocrystals: The Role of Ligand Electronegativity

In addition to showing that the emission for CdSe nanocrystals becomes pinned at ultrasmall size, we have also demonstrated the ability to modify this pinned emission from 2.79 to 2.91 eV by changing the phosphonic acid ligand.⁶ A blue shifting emission

is observed and is attributed to the increased electronegativity of shorter chain length ligands. Additionally, the quantum yield of these nanocrystals increases with increasing ligand chain length. This data further solidifies the critical role surface ligands play on the emission properties of ultrasmall nanocrystals.

Figure 6. Modulation of white light CdSe surface-emission via ligand electronegativity.⁶

Encapsulated White-light CdSe Nanocrystals as Nanophosphors for Solid-state Lighting

In order to utilize ultrasmall nanocrystals in devices, a suitable encapsulant needed to be determined that did not cause them to aggregate and that does not alter the emission color. Ultrasmall CdSe nanocrystals were encapsulated in a variety of polymers.⁷ A correlation between the Hildebrand parameter and the Hildebrand solubility parameters of the encapsulants and their effectiveness was found, which was also dependent on the nanocrystal ligands BP-PFCB was found to offer a practical option for encapsulation, creating a rugged, color-stable environment for the white-light nanocrystals. This encapsulation in BP-PFCB allowed the nanocrystals to be combined with UV LEDs to create a potentially viable, solid-state white-light source. Initial attempts at coating UV LEDs exhibited CIE chromaticity coordinates (0.324, 0.322) and a CRI of 93.

Figure 7. Identification of a suitable encapsulant for ultrasmall CdSe nanocrystals for white light applications.⁷

White Light-emitting Diodes Based on Ultrasmall CdSe Nanocrystal Electroluminescence

Prototypical electroluminescent devices were fabricated utilizing the native white-light emission for ultrasmall nanocrystals to produce a white light LED.⁸ This was the first electroluminescent device produce using nanocrystals with diameters less than 2 nm. The LEDs had excellent color characteristics, with CIE color coordinates (0.333, 0.333), correlated color temperatures of 5461-6007 K, and color rendering indexes as high as 96.6.

Figure 8. White light from electroluminescent device based off of ultrasmall CdSe nanocrystals.⁸

Structure and Ultrafast Dynamics of White Light-emitting CdSe Nanocrystals

We obtained the first atomic resolution images as well as the first ultrafast fluorescence upconversion spectra of ultrasmall CdSe nanocrystals.⁹ The aberration-corrected STEM

image indicated that they are crystalline, and consist of approximately four lattice planes with defects. The different ultrafast decay rates measured indicate that a variety of trap-mediated pathways are responsible for the radiative recombination and involve both the electron and the hole.

Figure 9. Ultrafast dynamics of ultrasmall CdSe nanocrystals. (A) Absorption and emission of a typical sample exhibiting a narrow band-edge absorption (light-gray line) and white-light emission (black line). The colored arrows indicate the wavelengths probed during the ultrafast experiment. (B-F) ultrafast data traces acquired at (B) 459, (C) 488, (D) 535, (E) 552, and (F) 585 nm. (G) Comparison of the early time dynamics at 459 and 552 nm. The fast decay at 459 nm (blue circles) coincides with the rise occurring at 552 nm (red triangles), indicating that the state emitting at 585 nm is being populated by the state emitting at 459 nm.

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