Chapter 1: Introduction

1.1 Semiconductor Quantum Dots

Semiconductor quantum dots (QDs), or nanocrystals, represent nanometer-sized materials that exist between molecular and bulk forms.\textsuperscript{1-3} Generally, as the number of atoms in a material increases, discrete molecular orbitals evolve into continuous energy bands. However, QDs (with \textasciitilde100–100,000 atoms) do not attain this continuous distribution of the bulk energy bands because they are the intermediate state between molecules and bulk materials.

The separation between the valence band maximum and the conduction band minimum becomes smaller when the QD size increases. Consequently, one important advantage of semiconductor QDs is the tunability of the emission wavelength, simply by changing the QD size. The origin of the energy gap of QDs (reported by Brus\textsuperscript{4}) is described primarily as a perturbation that results from the Coulombic interaction between the electron and the hole and the confinement of this exciton. Therefore, quantum confinement effects of quantum dots can be described as:\textsuperscript{4}

\[
E \sim E_g + \frac{\hbar^2 \pi^2}{2 R^2} \left[ \frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8 e^2}{\varepsilon R} \quad (1.1)
\]

where $E$ is the energy gap of quantum dots, $E_g$ is the bulk band gap, $R$ is the radius of QDs, $m_e$ and $m_h$ are the effective masses of the electron and hole, respectively, and $\varepsilon$ is the semiconductor dielectric constant. The quantum confinement terms follow $R^{-2}$ and shift $E$ to higher energy as the radius decreases; oppositely, the Coulomb term
shifts $E$ to lower energy as $R$ decreases. In this equation, the correlation between electron and hole positions induced by the Coulomb interaction is not strong, and the major effect is the electron and hole confinement energy. Therefore, the QD energy gap increases as the particle size is reduced.

The Bohr radius is the natural length scale of the electron and hole. Nanometer-sized semiconductor QDs confine electrons and holes in all three dimensions. QDs will show size-dependent properties when the radius of QDs is smaller than the Bohr radius ($a_0$), which is calculated by:

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu_{e,h}e^2} \quad (1.2)$$

$\varepsilon_0$ is the semiconductor dielectric constant, $\hbar$ is the reduced Planck’s constant, $\mu_{e,h}$ is the reduced mass of the exciton, and $e$ is the elementary charge. Cadmium selenide (CdSe), lead sulfide (PbS) and lead selenide (PbSe) are the semiconductors investigated in this thesis. The Bohr radii for these semiconductors are 5.6, 18, and 46 nm for CdSe, PbS, and PbSe, respectively. The radii of quantum dots investigated in this thesis are much smaller than their Bohr radii, and thus they exhibit strong size-dependent properties.

1.2 Synthesis of Colloidal Semiconductor Quantum Dots

Colloidal luminescent semiconductor QDs have become the subject of great interest both for fundamental research and industrial development in recent years. Colloidal semiconductor QDs are prepared via a chemical synthetic route that
produces high quality, nearly monodisperse nanometer-sized particles.\textsuperscript{6} The synthesis derives from classical chemistry; the formation of monodisperse colloids requires a rapid nucleation event followed by slower controlled growth of the nuclei.\textsuperscript{7} In the growth of semiconductor QDs, the nucleation event is triggered by a rapid injection of precursors into a flask containing hot organic solvents. A combination of phosphines, phosphine oxides, phosphonic acids, fatty acids, ethers, and alkenes is used as the blend of organic solvents for the QD synthesis. Different-sized QDs can be obtained by using different growth times, changing reaction temperatures, and using different reaction solvents.

Following synthesis, the addition of hexane, methanol, and butanol to the reaction mixture will flocculate the QDs. Next, centrifugation and precipitation isolate the QDs from the reaction solvent. The purified QDs can then be redispersed into a variety of organic solvents for further experiments. The surfaces of these colloidal QDs are passivated with a monolayer of organic molecules which makes them hydrophobic and soluble in nonpolar or slightly polar organic solvents.

The QD surface plays an important role in determining its structural and optical properties due to the high surface-to-volume ratio. For a CdSe QD with a diameter of 4 nm, \(\sim30\%\) of its atoms reside on the surface and are thus missing one or more of their four (tetrahedral) bonds to neighboring atoms. Unsaturated surface atoms, or dangling bonds, that result from incomplete passivation can lead to the development of surface trap states. These states which influence the photoluminescence properties of QDs such as quantum yield, spectral shape, and spectral dynamics.\textsuperscript{2}
Therefore, control of the surface is the key to highly luminescent quantum dots. A major improvement in QD optical properties takes place when a semiconductor shell grows around the core, chemically passivating the QD surface atoms much more efficiently than simple organic surface capping ligands. Overcoating CdSe QDs with epitaxial layers of ZnS increased photoluminescence quantum efficiencies by an order of magnitude (~50%) over QDs without such a shell (~5%), resulting from enhanced coordination of surface dangling bonds.

With a bulk band gap of 1.7 eV, II-VI semiconductor CdSe QDs can be synthesized in various sizes with tunable emission across the visible range (due to quantum confinement effect). These QDs can be used advantageously in technical applications including light-emitting diodes, lasers, biological fluorescence labeling. IV-VI materials such as PbS ($E_g = 0.41$ eV) and PbSe ($E_g = 0.28$ eV) have relatively large Bohr radii (46 nm for PbSe and 18 nm for PbS), which permit the optical properties of several nanometer sized PbS and PbSe QDs to be evaluated in the regime of extremely strong quantum confinement with absorption and emission tuned through the near-infrared region. These properties indicate the potential use of PbS and PbSe QDs in telecommunications, NIR lasers, solar cells, and biological sensing applications.

1.3 Characterization of Colloidal Semiconductor Quantum Dots

The spectroscopic and structural properties of colloidal quantum dots are characterized using a variety of techniques. In this thesis, absorption and
photoluminescence spectra are the most frequently used optical characterization techniques for colloidal semiconductor QDs. A Perkin-Elmer Lambda-19 UV/vis/NIR spectrometer and an Acton Research Corporation SpectraPro spectrometer were used to measure the absorption and photoluminescence properties of the QDs, respectively. QD sizes were estimated by comparing the lowest electronic transition (first exciton peak) in the absorption spectra with those reported in the literature.\textsuperscript{21,27} QD quantum yields were calculated by comparing the optical density and integrated emission of QDs to a standard dye.\textsuperscript{28}

Transmission electron microscopy (TEM) is also a powerful technique for characterizing QDs and their assemblies. TEM studies permit a statistical description of the size and shape of QDs, and the individual QD shape and internal structure can be revealed by high resolution TEM images. In addition, electron energy loss spectroscopy (EELS) is an important tool for the study of a material’s electronic structure and chemical distribution.\textsuperscript{29} When fast electrons in the beam of an electron microscope penetrate a thin specimen, some will lose their energy to inner-shell electrons. The amount of energy that is lost depends on the atomic number of the specific atom being imaged, thereby allowing for a determination of the chemical composition of an individual QD using EELS.

X-ray diffraction (XRD) is one of the most important characterization tools used in solid state chemistry and materials science. Each crystalline solid has a unique characteristic x-ray powder pattern. To determine how the atoms are packed together in nanometer-sized QDs, x-ray radiation emitted by copper is used to strike a
powder QD sample. The resulting diffraction is collected and analyzed to determine the crystal structure of QDs. Energy dispersive x-ray spectroscopy (EDX) is the analytical tool used to characterize the chemical composition of a QD ensemble sample. This technique utilizes x-rays, that are emitted from the QD sample during bombardment by the electron beam, to determine the elements presented in the QD sample.

1.4 Dipolar Interactions in Close-packed Solid Quantum Dot Films

Most colloidal semiconductor quantum dot research is carried out in dilute samples where the distance between QDs is large and the nanocrystals behave like individual entities. By decreasing the distance between QDs, it becomes possible to observe inter-dot coupling between resonant transitions between different excited and ground state QDs. Therefore, close-packed quantum dot solids present opportunities to explore not only the unique properties of individual semiconductor QD materials, but also the cooperative physical phenomena resulting from the interaction of proximal QDs.

The coupling between QDs causes the excitation in the excited QD (donor) to be transferred to the ground state QD (acceptor), a process also known as fluorescence resonance (or Förster) energy transfer (FRET). For FRET to occur, the acceptor must fulfill two requirements. It must have a transition energy that is in resonance with the energy of donor emission and it must also possess a lower energy
state in which to trap the transferred excitation. The donor typically emits at a shorter wavelength that overlaps with the absorption spectrum of the acceptor. Due to the quantum confinement effect, small-sized quantum dots emit at shorter wavelength thus acting as the donors and large sized quantum dots are the acceptors during the energy transfer process. The use of inter-QD energy transfer to enhance the performance of integrated QD photonic systems is expected to take on increasing importance, in a similar manner to what has taken place for all-organic devices.\textsuperscript{32}

1.5 Thesis Outline

This thesis describes the synthesis and characterization of II-VI (CdSe) and IV-VI (PbS and PbSe) colloidal semiconductor QDs. In Chapter 2, different-sized colloidal CdSe core and core/shell CdSe/ZnS QDs were synthesized. By collecting localized core/edge EELS spectra on the sub-nanometer scale, the distribution of core and shell material for CdSe/ZnS QDs was determined. The Cd signal of the CdSe core and the S signal of ZnS shell were obtained and used to determine whether the core and core shell QDs were spherically shaped.

Chapter 3 describes different-sized PbSe QDs that were prepared using different reaction solvents and precursors. The optical spectra of these PbSe QDs exhibit two emission peaks corresponding to the existence of two different sizes of QDs. The small-sized particles were determined to be magic sized clusters, which can be separated from regular sized PbSe QDs by careful size selective precipitation. Magic sized PbSe clusters can be prepared at low reaction temperatures, producing a
well-defined exciton absorption peak, emission at ~900 nm, and a remarkably high photoluminescence QY, typically >50%. Organic dyes emit poorly\textsuperscript{34} between 700–1000 nm, where there is reduced absorption by biological fluids. This provides magic sized PbSe quantum dot clusters with enormous potential as superior fluorophores for biological imaging applications at near infrared (NIR) wavelengths between 700–1000 nm. Chapter 3 also describes how PbSe MSCs are unusually photostable for their size and can be easily transferred from organic to aqueous solutions while maintaining their high fluorescence efficiency. Thus, they could potentially serve as ideal fluorophores for a range of fluorescence-based bioanalyses.

Chapter 4 describes the synthesis and characterization of colloidal PbSe/SrSe core/shell QDs. EDX spectra from a dense cluster of purified PbSe/SrSe core/shell QDs show a strong strontium signal in addition to lead and selenium signals. However, the photoluminescence spectra of these core/shell QDs show a significant blue shift when compared to the PbSe core QDs, indicating the etching of PbSe core QDs. In general, the effect of different solvents and precursors on the photoluminescence properties of PbSe QDshad not been thoroughly and systematically investigated previously, and such studies are especially necessary for research using colloidal PbSe QDs in biological applications. Chapter 4 also presents studies examining the influence of the immediate surroundings on photoluminescence properties of PbSe QDs.

In chapter 5, we describe the energy transfer between different-sized PbSe/PbSe QDs and PbS/PbSe QDs by comparing the photoluminescence spectra of
a mixture of donor–acceptor QDs in solution and as solid films. A comparison of luminescence spectra in solution and solid films reveals an increase in the ratio of large to small QD photoluminescence intensity for solid films, which is due to the fluorescence resonance energy transfer from small QDs to large QDs in the solid films of mixed QDs. Different energy transfer efficiency was obtained by studying the PL spectra of mixed PbS/PbSe QDs in spun coated films with different spin speed and different spin coated layers. In Chapter 5, we also present the study of energy transfer between small- and large-sized CdSe/ZnS colloidal QDs in a Fabry-Perot microcavity formed between two distributed Bragg reflectors (DBRs). The fluorescence intensity from the larger (acceptor) QDs in a microcavity is substantially enhanced compared with purely large QDs in free space. This substantial fluorescence intensity enhancement arises from both an increase in the electric field inside the optical cavity and from significant energy transfer to the larger QDs from the smaller QDs. The output from the optical cavity is also very spectrally pure. The understanding of and the ability to manipulate energy transfer between QDs inside of optical cavities will positively impact future applications in nanophotonics.

1.6 Foreword

STEM and EELS measurements in Chapter 2 were performed by Dr. Zhiheng Yu. STEM images in Chapter 3 were obtained by Sara E. Maccagnano. In Chapter 3, the transfer of magic-sized PbSe clusters from organic solvent to water and the measurement of hydrodynamic diameters and optical stability were carried out by
Christopher M. Evans. The microcavity structures used in Chapter 5 were provided by Carl B. Poitras. Part of chapter 2 is published in *nano letters*, 5, 565-570. Part of chapter 5 is published in *applied physics letters*, 89, 061104.
1.7 References


Chapter 2: Shell distribution on colloidal CdSe/ZnS quantum dots

2.1 Introduction

Colloidal luminescent semiconductor quantum dots (QDs) have become of great interest for both fundamental research and industrial development in recent years.\(^1\) Nanometer-sized QDs show size dependent optical and electrical properties due to the quantum confinement effect, when the radii of semiconductor QDs are smaller than the bulk exciton Bohr radius. Thus, one important advantage of semiconductor QDs is the tunability of the emission wavelength simply by changing the QD size. Future technical applications of QDs include light-emitting diodes,\(^2\) lasers,\(^5\) and biomedical tags.\(^6\),\(^7\)

Considerable progress has been made to control the synthesis of colloidal II-VI semiconductor QDs;\(^8\) cadmium selenide (CdSe) QDs have become the most well studied system in terms of the control over the size,\(^8\),\(^9\) shape,\(^10\) and optical quality.\(^11\) Murray et al.\(^8\) first reported the synthesis of CdSe QDs using dimethyl cadmium (Cd(CH\(_3\)_2)) as the cadmium precursor, but dimethyl cadmium is extremely toxic, unstable at room temperature, and air sensitive. Peng et al.\(^12\) reported that hazardous dimethyl cadmium could be successfully replaced by cadmium oxide (CdO), a safer cadmium precursor.

Due to the high surface-to-volume ratio of small QDs, the surface plays a key role in the structural, optical, and solubility properties of QDs. Colloidal CdSe QDs
are capped with a monolayer of organic ligand molecules. Triocetylphosphine oxide (TOPO) and triocetylphosphine (TOP) molecules coordinate the Cd and Se surface QD atoms, respectively. The TOPO and TOP molecules surround the CdSe QDs and keep the coloidal QDs soluble, stable, and unaggregated in organic solvents; however, organic ligand coated QDs still fall victim to photooxidation. Under exposure to light, the surface Se atoms oxidize to form selenate.\(^\text{13}\) Overcoating, or capping, QDs with a higher band gap inorganic material has been shown to improve the robustness, luminescence quantum yield, and photostability. The successful inorganic capping of CdSe QDs with several wide band semiconductors (ZnS,\(^\text{14, 15}\) CdS,\(^\text{16}\) ZnSe,\(^\text{17}\) CdS/ZnS and ZnSe/ZnS double shells\(^\text{18}\)) has been reported.

The growth of a ZnS semiconductor shell around CdSe core QDs improved the optical properties of the QDs by chemically passivating the QD surface atoms more efficiently than simple organic surface capping ligands.\(^\text{14}\) As we observed in the experiments and found in the literature,\(^\text{14, 15}\) these core/shell CdSe/ZnS QDs showed increased PL quantum efficiencies (QY) by an order of magnitude (QY \(\sim 50\%\)) over CdSe QDs without such a shell (QY \(\sim 5\%\)). Also, studies of luminescence from single CdSe/ZnS QDs show reduced effects of surface defects compared to QDs capped with only organic ligands.\(^\text{19}\) Although capping the QD with a semiconductor shell showed significant improvement in surface passivation over organic molecules, significant evidence exists that the surface passivation provided by the semiconductor shell is not perfect: (1) photoluminescence QYs are typically only \(\sim 50\%\), and a significant percentage of QDs are permanently non-emissive (dark),\(^\text{20}\) (2) core/shell
samples still suffer from rapid photooxidative processes, and (3) single CdSe/ZnS QD PL exhibits fluctuations (albeit reduced in frequency compared to CdSe QDs) in intensity and spectra attributed to trapping of carriers or charges in surface trap-states. On the other hand, fluorescence from individual self-assembled semiconductor QDs with uniformly well-passivated surfaces do not suffer nearly as much from such surface induced imperfections, suggesting that the semiconductor shell for colloidal core/shell QDs is incomplete or ill formed. In order to improve the surface capping quality for CdSe QDs, it is clear that careful studies of shell material distributions around the core of CdSe/ZnS QDs are essential.

Electron energy loss spectroscopy (EELS) is an important tool for the study of a material’s electronic structure and chemical distribution. When fast electrons in the beam of an electron microscope (EM) penetrate a thin specimen, some will lose their energy to inner-shell electrons. The amount of energy lost is dependent on the atomic number of the specific atom being imaged, which allows for a determination of chemical composition using EELS.

In this chapter, the synthetic procedure used to create CdSe QDs followed a modified procedure published by Peng and Murray. Modified synthetic methods from Hines et al. and Dabbousi et al. for CdSe/ZnS core/shell QDs were used. In this study, we have used EELS to study the shell distribution properties of core/shell CdSe/ZnS QDs by collecting localized core-edge EELS spectra on the sub-nm scale.
2.2 Synthesis Experiment for CdSe and CdSe/ZnS QDs

2.2.1 Materials

Triocetylphosphine oxide (TOPO; \((CH_3(CH_2)_7)3PO\), 99% pure and 90% technical grade), cadmium oxide (CdO, 99.99+%), diethylzinc ((C_2H_5)_2Zn, Zn 52.0 wt.% (minimum)), hexamethyldisilathiane \(((CH_3)_3Si)2S\), synthesis grade), stearic acid (SA; CH_3(CH_2)_16COOH, 98%), and selenium pellets (Se, ~2 mm, 99.999+%), were purchased from Aldrich. Diethylzinc and hexamethyldisilathiane were stored in a dry inert nitrogen environment due to their high reactivity in air. Triocetylphosphine (TOP; \((CH_3(CH_2)_7)3P\), 90% technical grade) was purchased from Fluka. Tetradecylphosphonic acid (TDPA; \((CH_3(CH_2)13)P(O)(OH)2\), 98%) was purchased from Alfa Aesar. Methanol and toluene were received from Mallinckrodt Chemicals, hexanes from Fisher Scientific, and acetone from J.T. Baker. All reagents were used without further purification. Triocetylphosphine selenide (TOPSe) was prepared in the glovebox by dissolving 0.66 g (8.4 mmol) of selenium pellets in 20 mL of TOP, forming a 0.41 M TOPSe solution.

2.2.2 Synthesis of CdSe QDs: Method 1

CdSe QDs were synthesized in coordinating solvents according to a modified version of literature methods.\(^8,12\) The entire synthesis was performed using a vacuum gas manifold system (Schlenk line). In a typical synthesis experiment, 0.05 g (~0.4 mmol) of CdO, 0.1625 g (~0.6 mmol) of TDPA, 1.3 g (~4.6 mmol) of SA, and 7 g of 99% TOPO were loaded into a 3-neck reaction flask (Figure 2.1 (a)). The mixture was then dried and degassed by heating to 190 °C under vacuum for about an hour.
while flushing periodically with nitrogen. The temperature was then raised to 320 °C for selenium injection; a syringe containing 2.5 mL 0.41 M TOPSe was removed from the glove box and immediately injected into the vigorously stirring reaction flask in a single shot through a silicone rubber septum. The temperature of the reaction flask dropped to 270 °C with the rapid injection of TOPSe, and then was gradually raised to a temperature between 280 - 290 °C. The solution turned from yellow to orange then to red indicating the formation and growth of CdSe QDs. Aliquots of the reaction solution were removed and stored in equal amounts of hexane at regular intervals of 1 minute, for the first 6 minutes to monitor the growth of the QDs. QDs prepared using this method have a first exciton peak wavelength between 500 and 570 nm.

2.2.3 Synthesis of CdSe QDs: Method 2
A modified version of the synthesis of large sized CdSe QDs\(^9\) was used as method 2. The experimental setup is the same as that used in method 1 (Figure 2.1 (a)). In a typical synthesis, 0.05 g (~0.4 mmol) of CdO and 2 g (~7 mmol) of SA were loaded into a 3-neck flask. The mixture was evacuated to ~170 °C with periodic nitrogen flushes until CdO was dissolved and all reagents became optically transparent. Then the flask was cooled down to room temperature and 2 g of 99% TOPO was added to mixture. The flask was resealed and reheated to 190 °C for an hour under vacuum. Next, the temperature was increased to 320 °C and 2.5 mL of 0.41 M TOPSe was quickly injected into the reaction flask; the heat was removed immediately after injection and the reaction flask was cooled down to room
temperature. The position of the first exciton peak from the measured absorption spectra is found between 590 and 630 nm.

2.2.4 Determination of Shelling Material for CdSe QDs

After CdSe QDs were synthesized, they were capped with an inorganic semiconductor shell. In this experiment, ZnS was used as the shell material. Diethylzinc and hexamethyldisilathiane were used as the Zn and S precursors, respectively. There are several reasons why ZnS is a good choice for capping CdSe QDs. First, ZnS has a wider bulk band gap (3.7 eV) than CdSe (1.7 eV), which confines electrons and holes to the CdSe core. Second, both CdSe and ZnS can form wurtzite or zincblende crystal structure with a lattice mismatch of 12%. Finally, ZnS forms at lower temperatures than CdSe; therefore, the procedure for capping CdSe QDs with ZnS can take place at lower temperature, which minimizes separate ZnS QD nucleation and avoids further growth of the CdSe core QDs themselves.

2.2.5 Calculation of the Precursor Amount for Shell Growth

The amount of precursor materials to prepare 2 ~ 4 monolayers was used. A monolayer of thickness is the distance between consecutive planes along the [002] axis in bulk wurtzite ZnS, which equals 3.1 Å. First, the average size of a CdSe QDs was estimated from the first exciton position measured by absorption spectroscopy. The amount of ZnS needed for each CdSe QD can be calculated by multiplying the density of ZnS (4.1 g/cm³) by the volume difference between the CdSe core and CdSe/ZnS core/shell sphere.
Second, the concentration (C) of CdSe QDs can be calculated using the Beer-Lambert law:

\[ A = \varepsilon CL \]  

(2.1)

where \( A \) is the absorbance at the first exciton peak, which can be determined from measured absorption spectra; \( L \) is the distance (cm) light travels through the sample cell, which is 1 cm for our experiments; and \( \varepsilon \) is the extinction coefficient per mole of CdSe QDs, which can be obtained from literature.\(^8,^{25}\)

The total amount of precursors required to grow the desired shell thickness was then determined using the calculated CdSe QD solution concentration, the volume of CdSe QD solution used for the capping experiment, and the amount of ZnS needed per QD.

### 2.2.6 Synthesis of CdSe/ZnS Core/Shell QDs

The precursor solution was prepared by dissolving equal mole amount of diethylzinc and hexamethyldisilathiane in 4 mL of TOP inside the glovebox. The experimental setup used for capping procedure is shown in Figure 2.1 (b). A 3-neck reaction flask containing 6 g of 90% technical grade TOPO was heated under vacuum at 190 °C for an hour. Then the flask was cooled to 90 °C under nitrogen flow. Next, 2 mL of TOP and 0.1 mmol of CdSe QDs in hexane solvent were injected into the reaction flask; hexane was pumped off under evacuation. After all of the hexane was removed (no more bubbles escaped from solution), the evacuation was stopped and the temperature was increased to 130 °C. Once 130 °C was reached, the prepared ZnS precursor solution (diethylzinc and hexamethyldisilathiane in 4 mL of TOP) was
transferred out of the glovebox and added drop-wise into the vigorously stirring reaction mixture over a period of 40 minutes. The rate of adding precursors at 6 mL per hour was controlled by a KD Scientific syringe pump.

2.2.7 Purification of CdSe and CdSe/ZnS Core and Core/Shell QDs

After a synthesis reaction was completed, the reaction solution was removed and placed in a vial containing equal amounts of hexane. Butanol and methanol were then added to remove excess TOP, TOPO, and other reagents. The QDs were isolated by precipitation, centrifugation, and decantation. After that, the CdSe and CdSe/ZnS QDs were redispersed in several milliliters of hexane and stored in the dark under ambient conditions for future use.

2.3 Optical Characterization

2.3.1 Optical Properties of CdSe QDs

Optical absorption spectra of colloidal CdSe QDs were collected at room temperature using a Perkin-Elmer Lamda 19 UV/VIS/IR spectrometer. The synthesis presented above produces CdSe QDs with a range of core and core/shell sizes. For example, Figure 2.2 shows absorption spectra of CdSe QDs, from the same batch prepared using method 1 at 270 °C, with different growth times. The measured first exciton peak red shifted from 509 to 564 nm as the growth time increased.

Absorption and photoluminescence (PL) spectra of colloidal CdSe QDs were taken at room temperature and typical results are shown in Figure 2.3. PL spectra of
CdSe QDs were measured using a modular Acton Research fluorometer with a Si detector. A Hg lamp was used to excite samples for optical absorption spectroscopy measurements and a Xe lamp was used for PL measurements. Fluorescence quantum yields of CdSe QDs were measured relative to rhodamine (quantum yield ~ 90%) and were typically around 5%. The full width at half maximum of the photoluminescence spectra for CdSe QDs is about 25 to 30 nm, which is due to both homogeneous and inhomogeneous broadening. The evolution of the absorption and PL spectra in Figure 2.3 is a result of the increase in CdSe QD sizes.

2.3.2 Optical Properties of CdSe/ZnS Core/Shell QDs

The CdSe/ZnS core/shell QDs can be produced with a range of sizes by using different CdSe core sizes. The absorption and PL spectra were measured using the same instruments described in section 2.3.1. Figure 2.4 represents the absorption and PL spectra of two different sizes of CdSe core QDs and the corresponding CdSe/ZnS core/shell QDs. The spectra of CdSe/ZnS core/shell QDs show a slight red shift when compared to the same CdSe core QDs before the capping process. This shift to a lower energy is due to the leakage of the exciton into the ZnS shell. The redshift is more significant in smaller CdSe core QDs where the ZnS shell has less confinement when compared to larger CdSe core QDs. The spectra lineshapes and linewidths of core and core/shell QDs are similar, which indicates that the CdSe core QDs were not modified significantly. The core/shell CdSe/ZnS QDs also showed an increase in the PL QY by an order of magnitude (QY ~ 50%) over QDs without such
a shell (QY ~ 5%). The PL intensity is stable for years with no reduction in the quantum yield.

A typical EDX (Energy Dispersive X-Ray) spectrum from a dense cluster of core-shell CdSe/ZnS QDs is shown in Figure 2.5. All the major peaks are labeled in the figure. Zinc and sulfur (shell material) signals are detected in addition to the cadmium and selenium signals (the core material). The vertical solid line indicates the Zn K-edge. P and O signals are from organic ligands (TOPO). The Cu signal arises from the copper grid and the C signal primarily comes from the support film.

2.4 Shell Distribution on Colloidal CdSe/ZnS QDs

2.4.1 Scanning Transmission Electron Microscopy (STEM) Characterization of the CdSe/ZnS Core/Shell QDs

The average size of well-formed CdSe/ZnS QDs increased to 4.3 nm as determined with STEM (Figure 2.6) from the average size of 3.4 nm for the CdSe QD core as determined from optical spectroscopy. EM samples were prepared by depositing ~ 0.1 mL of the QD suspension in hexane onto a copper grid covered by a thin carbon film, which was subsequently loaded into the Cornell VG HB501 100kV UHV STEM.
2.4.2 Shell Material Distribution for an Ideal Spherical Core/Shell QD

For an ideal core/shell QD with a spherical core and shell as shown in Figure 2.7 (a), the EELS signal from the shell material should be higher closer to both edges than at the center, reflecting the change of shell thickness across the dot. For an inner radius of \( R_c \) and an outer radius of \( R_s \) the shell thickness \( t \) at a position \( x \) relative to the center of the QD is

\[
t(x) = \begin{cases} 
2\sqrt{R_s^2 - x^2} & \text{when } -R_s < x < -R_c \text{ or } R_c < x < R_s \\
2\sqrt{R_s^2 - x^2} - 2\sqrt{R_c^2 - x^2} & \text{when } -R_c < x < R_c 
\end{cases}
\]

To a first approximation, the EELS signal of the shell material is proportional to the thickness of the shell in the \( z \) direction. Figure 2.7 (b) is a calculation of the thickness of the shell when \( R_c = 2 \) nm and \( R_s = 3 \) nm. While this simple calculation does not include convolutions with the probe shape (FWHM ~ 0.2 nm), it is clear that the EELS signal of the shell material from an ideal core-shell QD should be higher closer to either edge than at the center.

2.4.3 CdSe Core Materials Distribution on CdSe/ZnS Core/Shell QD Measured by STEM

To collect localized EELS spectra, the convergent electron probe in the STEM was focused to a spot size as small as 0.2 nm and then fixed on a particular location of the QD. For each probe location, an annular dark field (ADF) signal was obtained simultaneously with the EELS spectrum. In addition, a high-resolution (0.2 nm) ADF image was taken immediately before and after the EELS spectrum to check for specimen drift during the data collection. It is very challenging to collect localized...
EELS spectra from a sub-nm area on a single colloidal QD sitting on a supporting film, since the signal from the film could easily overwhelm the signal from the individual QD. In order to get suitable EELS data, care was taken to find very thin regions of support film and to minimize contamination from organics.\textsuperscript{26} Care was also taken to acquire spectra from QDs that were clearly in single monolayers to avoid possible misinterpretations in the EELS data.

Figure 2.6 shows an ADF-STEM image of some typical isolated CdSe/ZnS core/shell QDs. Sub-nm EELS measurements were carried out on the QD labeled “A”. Figure 2.8 (a) shows an ADF image of the same QD with five probe positions labeled from which corresponding EELS spectra were collected. Figure 2.8 (b) shows EELS spectra of the Cd M-edge taken from the five probe locations indicated in Figure 2.8 (a). The intensity of the Cd M-edge changes with position, indicating that the quantity of Cd at those probe locations changes. Figure 2.8 (c) shows the integrated cadmium signal from the five probe locations by integrating the Cd M-edge in Figure 2.8 (b). Also shown in Figure 2.8 (c) are the ADF intensities collected simultaneously with the EELS spectra at those positions. Clearly the Cd signal closely follows the ADF intensity. For example, at approximately the center of the QD (position 4) the QD is thicker, and there is a correspondingly larger Cd signal in EELS as well. This larger signal is expected because Cd is the core material and a spherically-shaped object is thicker at the center, causing the ADF signal to be stronger.
2.4.4 ZnS Shell Materials Distribution on CdSe/ZnS Core/Shell QD Measured by STEM

Figure 2.9 (b) shows EELS spectra of the S L-edge from six different probe locations (shown in Figure 2.9 (a) on the same QD described in Figure 2.8). Figure 2.9 (c) shows the integrated sulfur signals together with the ADF intensities at those probe locations obtained simultaneously with the EELS spectra. Whereas the spatial distribution of the EELS Cd signal closely follows the ADF intensity, the spatial distribution of the sulfur signal is clearly offset from the ADF intensity signal. The ADF intensity is higher around the center of the QD (positions 3 and 4); however, the S signal is higher closer to the top edge of the QD (position 5) rather than at the center of the QD (positions 3 and 4), as expected for an ideal spherical shell. Furthermore, the bottom edge of the QD has less S (position 2) than either the center or the top edge, suggesting a highly anisotropic distribution of ZnS around the CdSe QD core.

As exemplified in Figure 2.9 (c), we have found that the ZnS capping layer is not uniformly distributed around the QD core. For example the detected S signal in Figure 2.9 (c) is higher on one side of the QD, lower in the center, and still lower on the other side. Figure 2.10 shows another example of a nonuniform distribution of S on a single core-shell CdSe/ZnS QD. Again the EELS data shows the distribution of sulfur is higher close to one edge of the QD and lower close to the other edge. The distribution of Cd is higher at the center of the QD, following the ADF intensity signal closely.
Our studies of seventeen randomly selected CdSe/ZnS QDs in detail using localized EELS indicate that the nonuniform shell distribution is a common phenomenon, suggesting that the anisotropic shell of ZnS arises during the "typical" shell growth process. The distribution and magnitude of the anisotropy changes from QD to QD indicating that the shell anisotropy is not a manifestation of the direction the EELS spectra are taken or of any other electron beam effects. Relative to the EELS sequence, some QDs have more S on the farther end and some QDs have more S on the nearer end. Some QDs even have higher S signal in the center than both edges. Since the measured EELS signal is a projection of the material along the optical axis (the z direction) of the microscope, when the ZnS is mainly distributed on the surfaces perpendicular to the z axis, the center of the QD appears to have more S signal than both edges. Conversely, when the ZnS is mainly distributed on one of the sides, that side appears to have more S than the center. Our results did not depend on whether a particular QD was completely isolated on the TEM grid or had close neighbors: all still showed an anisotropy of the shell distribution. Altogether, the random distribution of the peak sulfur signal suggests that the ZnS shell material forms nonuniform patches on the QD core and in general does not surround the core uniformly.

The CdSe/ZnS QDs studied here are comparable to other high-quality core/shell QD in the literature\textsuperscript{14, 15, 21} in every respect, such as fluorescence QY, QD size, and narrowness of the size distribution. Thus the anisotropic distribution of the ZnS shell is not due to poor growth or poor quality QDs. The anisotropic growth of
the ZnS shell on the CdSe core may reflect the large difference in lattice constant (a = 3.81 Å and c = 6.26 Å for ZnS versus a = 4.30 Å and c = 7.01 Å for CdSe) between the two materials. Indeed, for CdSe quantum rods (QR; where interfacial strain between a core and a shell is a more serious concern than for QDs) capping with pure ZnS can result in a highly anisotropic tail of ZnS from one end of the QR. A middle shell (CdS, ZnSe), which has the lattice parameter between CdSe and ZnS, is introduced between CdSe core and ZnS shell in an article reported by Talapin, et, al.. Comparing with CdSe/ZnS core-shell QDs, these core shell QDs may provide a better shell material distribution. However, to our knowledge, no other EELS study has been reported on core shell QDs. Another explanation for the anisotropy in the shell coverage is the anisotropic chemical reactivity on various faces of the core. It was recently calculated that the binding of phosphine oxide (this ligands is present on the CdSe core surface) was stronger for some crystal faces relative to others. This variation in ligand binding energy implies that ZnS shell formation will not be isotropic, since crystal faces that bind ligands more weakly will be more chemically reactive. It is thus reasonable to speculate that this anisotropy of shell nucleation, combined with the large difference in lattice constant between CdSe and ZnS, can result in a nonuniform ZnS shell around the entire particle.
2.4.5 Comparison of ZnS Shell Distribution along Two Perpendicular Directions on One QD

As mentioned earlier, it is very difficult to collect EELS spectra from individual QDs due to contamination and radiation damage. Most of the EELS measurements were carried out along a single line across a single QD in order to reduce exposure of the sample to the electron beam, which helped to mitigate the effects of radiation damage and contamination. However, in one particular case we collected EELS data along two perpendicular directions on the same QD. Figure 2.11 (a) shows an ADF image of a QD with some regions of weaker signal stretching out from the QD along the vertical axis. The STEM probe was placed along the horizontal axis at fifteen probe locations as indicated in the figure (labeled as H1-H15). EELS spectra of the S L-edge were taken from these probe locations and Figure 2.11 (b) shows some of the spectra. The quality of the EELS spectra is very good and the S L-edges can be clearly seen. After the horizontal EELS scan was done, an ADF image of the QD was taken as shown in Figure 2.11 (c). A comparison with Figure 2.11 (a) suggests that no serious contamination or radiation damage occurred during the process of collecting EELS spectra in Figure 2.11 (b). Figure 2.11 (c) shows fifteen probe locations along the vertical axis (labeled as V1-V15). EELS spectra of S L-edges were collected from these positions and some spectra are shown in Figure 2.11 (d).

Figure 2.12 shows the integrated S signals at various positions along the horizontal axis and the vertical axis, respectively. Clearly the S signal is higher close to the center of the QD than the edges along both directions, suggesting that there are
thick shell patches on surfaces perpendicular to the electron beam direction. However, the S distribution in the dimmer region on the top of the QD along the vertical axis (positions V2-V5) contains more sulfur than other edge regions, suggesting that the extended regions along the vertical axis are primarily ZnS.

One characteristic of ADF STEM imaging is Z contrast (Z refers to atomic number). Materials with a larger Z appear brighter than those with a smaller Z. In all our ADF images we found that the sulfur rich regions (enclosed by the ellipse in Figure 2.10 (a)) appear darker than the sulfur-deficient regions. Thus, the simplest reasoning suggests that the dimmer regions in an ADF image of a CdSe/ZnS QD correspond to the shell material because Zn has a smaller Z than Cd. However, a direct conclusion based on only the ADF image that this darker region consists of ZnS is not completely correct. ADF imaging is sensitive to thickness contrast as well as Z contrast, and the shell region alone may appear dimmer in an ADF image simply because it is thinner than the combined thickness of the shell plus the core. Therefore, extreme care must be taken when using the ADF image alone to check the distribution of the shell material around the core. A more conclusive methodology is that in tandem with ADF-STEM imaging EELS is used to determine the chemical composition of such dimmer regions in order to verify that they arise from the shell material.
2.5 Conclusion

Nearly monodisperse colloidal CdSe core and CdSe/ZnS core/shell QDs with a range of sizes were prepared using a slightly modified method from literature.\textsuperscript{8, 9, 12, 14, 15} The quantum yield of CdSe core QDs is around 5%. The quantum yield of CdSe/ZnS core/shell QDs is increased by nearly an order of magnitude, to 30% to 50%. The QDs were stored under air in dark environment without reduction of the QY over several years.

Our studies have also shown that growth of a simple shell of ZnS on the surface of a CdSe core QD will not lead to a complete and uniform spherical shell. Although capping with such a shell does improve the optical properties considerably, it is likely that further significant improvements can be made by improving the shell quality.
2.6 Figure Captions

**Figure 2.1** CdSe and CdSe/ZnS synthesis setup schematics. (a) Experimental setup used in CdSe core QD synthesis. TDPA, TOPO and SA were used as the coordinating solvents in method 1, SA and TOPO was used in method 2. (b) Experimental setup used in CdSe/ZnS core/shell QD synthesis.

**Figure 2.2** Evolution of CdSe optical absorption spectra with different growth times. CdSe QDs were grown using method 1 with growth times of 0 (Right after TOPSe injection, black), 1 (red), 2 (green), 3 (blue), 4 (light blue), 5 (purple), and 6 (yellow) minutes. Exciton peak evolved from 509 nm to 564 nm corresponding to CdSe QDs diameter changing from 2.5 nm to 3.5 nm.

**Figure 2.3** Absorption and photoluminescence spectra of different sized CdSe QDs. Solid lines represent absorption spectra and same colored dashed lines represent photoluminescence spectra from the same sample. Different colored lines represent different sized CdSe QDs with exciton peaks of 518 nm (black solid line), 528 nm (red solid line), 536 nm (green solid line), 553 nm (navy solid line), 602 nm (dark yellow solid line), 621 nm (dark cyan solid line), 633 nm (yellow solid line).

**Figure 2.4** Absorption and photoluminescence spectra of CdSe core and CdSe/ZnS core/shell QDs. The absorption and PL spectra for CdSe core (solid) and the
corresponding CdSe/ZnS core/shell (dashed) QDs. The CdSe core QD sizes are 2.7 nm (red) and 4.8 nm (blue), respectively.

**Figure 2.5** EDX (Energy Dispersive X-Ray) spectrum from a dense cluster of core-shell CdSe/ZnS QDs. Cd and Se signals indicate the presence of QD cores, and Zn and S signals indicate presence of QD shells. The vertical solid line indicates the Zn K-edge. P and O signals arise from the presence of organic surface ligands, TOPO. The Cu signal arises from the copper grid and the C signal primarily comes from the support film.

**Figure 2.6** ADF-STEM image of typical CdSe/ZnS core/shell QDs. Sub-nm EELS measurements were carried out on the QD labeled “A”.

**Figure 2.7** Shell material distribution for an ideal spherical core-shell QD. (a) Diagram of an ideal CdSe/ZnS core/shell structured QD: a shell of uniform thickness distributed over a spherical core. The inner radius is $R_c$ and the outer radius is $R_s$. (b) The profile of the shell thickness across the QD when $R_c = 2$ nm and $R_s = 3$ nm.

**Figure 2.8** CdSe core materials distribution on CdSe/ZnS core/shell QD measured by STEM. (a) ADF image of the QD labeled as “A” in Figure 2.6 with five positions labeled to locate the STEM probe to take localized EELS spectra. (b) EELS spectra of Cd M-edge from the five probe locations in (a). (c) Integrated Cd signals at the
five probe locations by integrating the EELS spectra in (b) over energy range. Also shown are the ADF intensities at the five probe locations obtained simultaneously as the EELS spectra.

**Figure 2.9** ZnS shell materials distribution on CdSe/ZnS core/shell QD measured by STEM. (a) ADF image of the same QD as shown in Figure 2.8 (a) with six new positions labeled to identify the STEM probe location at which localized EELS spectra were taken. (b) EELS spectra of S L-edge from the six probe locations in (a). (c) Integrated sulfur signals and the ADF intensities at the six probe locations obtained simultaneously with the EELS spectra.

**Figure 2.10** Another example of a nonuniform distribution of shell material on a single core-shell CdSe/ZnS QD. (a) An ADF image of a QD with eleven probe locations labeled. (b) S signals from these locations by EELS and ADF intensities obtained simultaneously. (c) Cd signals from these locations by EELS and ADF intensities obtained simultaneously. The dimmer region enclosed by the ellipse is the S rich region. Positions 8, 9, and 10 contain more S than position 3, even though the ADF intensities at positions 8, 9, and 10 are much lower than that at position 3.

**Figure 2.11** ZnS shell materials distribution along two perpendicular directions on one QD. (a) ADF image of a core/shell CdSe/ZnS QD before EELS spectra were taken. The circles labeled as H1-H15 indicate STEM probe positions to collect EELS
data in the horizontal direction. (b) Some EELS spectra of the S L-edge taken from probe locations H1-H15. The quality of the spectra is very good. (c) An ADF image of the same QD taken after EELS spectra in (b) were taken. The circles labeled as V1-V15 indicate STEM probe positions to collect EELS data in the vertical direction. (d) Some EELS spectra of the S L-edge taken from probe locations V1-V15.

**Figure 2.12** Integrated ZnS shell materials distribution along two perpendicular directions on one QD. Profiles of S distributions for the QD in Figure 2.11 along both the horizontal direction and the vertical direction by integrating the EELS spectra from positions H1-H15 and V1-V15 in Figure 2.11.
2.7 Figures

Figure 2.1
Figure 2.3

Absorption and Photoluminescence (a.u.)

Wavelength (nm)

400 450 500 550 600 650 700
Figure 2.4
Figure 2.5

A graph showing the X-ray energy spectrum with various elements labeled:
- Cu Kα
- Cu Kβ
- Zn Kα
- Se L
- O K
- P K
- S K
- Cd Lα & Lβ

The graph plots count against X-ray energy (KeV) with peaks corresponding to different elements.
Figure 2.6
Figure 2.7
Figure 2.8
Figure 2.9

(a)

(b)

(c)
Figure 2.10

(a)

(b)

(c)
Figure 2.11
Figure 2.12
2.8 References


(22) Empedocles, S. A.; Bawendi, M. G. *Science* 1997, 278, 2114-2117.


Chapter 3: Growth of magic-sized PbSe quantum dot nanoclusters

3.1 Introduction

Colloidal IV–VI lead chalcogenide quantum dots (QDs) have received much attention in both fundamental studies and technical applications owing to their size-dependent electronic and optical properties in the near infrared. High quality colloidal PbSe QDs have been synthesized using different precursors and reaction conditions.\textsuperscript{1-6} PbSe quantum rods, cubes, nanowires, and nanorings have also been reported by several groups.\textsuperscript{7-10} Although much effort has aimed to control the particle shape of PbSe QDs and to improve their photoluminescence properties, the study of initial nucleation and growth of PbSe QDs is very limited.

Between molecules and several nanometer-sized particles, clusters have received attention regarding their formation mechanism, nucleation, and growth.\textsuperscript{11} The term “magic sized clusters” has been used for particularly stable structures containing well-defined numbers of atoms. For example, CdSe magic sized clusters have been observed during the growth of colloidal quantum dots,\textsuperscript{12} and a controlled method for sequential growth of CdSe magic sized clusters in solution was reported by Kudera et al.\textsuperscript{13}

In this chapter, we show that PbSe magic sized clusters (MSCs) or quantum dot nanoclusters (QDNCs) coexist with nanometer-sized PbSe QDs during synthesis. These clusters can be separated from regular-sized QDs with careful size selective
precipitation. Room temperature synthesis of extremely small (diameter < 2 nm) PbSe QDs produce nanoclusters that emit in the NIR with a well-defined exciton absorption peak, emission at ~900 nm with remarkably high fluorescence QYs, typically >50%. These QDNCs are unusually photostable for their size and can be easily transferred from organic to aqueous solutions while maintaining high fluorescence efficiency. Thus, magic sized PbSe quantum dots clusters have enormous potential to be superior fluorophores for biological imaging applications at near infrared (NIR) wavelengths.

Organic dyes emit poorly between 700 and 1000 nm, a window of reduced absorption by biological fluids due to a local minimum in the absorption spectrum of water in this range. Indeed, demonstrations of in vivo NIR fluorescence imaging using QDs composed of CdTe, InAs, and InAs_xP_{1-x} have been reported. However, the synthesis of these and most other semiconductor QDs requires high temperatures (~300 °C), air-free techniques, and careful handling to ensure QDs with high brightness and a well-controlled size. Thus, semiconductor QD syntheses are generally limited to small scales, severely restricting their general utility and availability.

A fundamental weakness of incorporating QDs into biological imaging applications is their relatively large size. Biocompatible QDs are approximately 10–15 nm in diameter, with a hydrodynamic diameter typically exceeding 25 nm. As such, it is essentially impossible for QDs to enter a cell through carrier-mediated mechanisms, whereas smaller fluorescent dye molecules can be carried easily into a
cell and its nucleus.\textsuperscript{19} QDs can be directly injected into cells,\textsuperscript{20} but such methods typically destroy the cell membrane and/or are highly inefficient. The use of QDs as fluorescent reporters of intracellular biophysical and biochemical processes is therefore restricted to fixed cells with permeable membranes due to difficulty in traversing the cell membrane.\textsuperscript{21} Small InAs QDs (diameter < 2 nm) were recently synthesized, but the synthesis is complex, involves extremely pyrophoric arsenic precursors (As(SiMe$_3$)$_3$), and produces QDs that are relatively unstable to air or water and have low QYs (<10%).

### 3.2 Preparation of PbSe QDs

#### 3.2.1 Materials.

All reagents were used as received unless otherwise indicated: lead (II) acetate anhydrate (99.9+\%, Aldrich), phenyl ether (99\%, Aldrich), lead (II) oxide (PbO, 99.999\%, Aldrich), oleic acid (OA, Tech. grade 90\%, Aldrich), selenium pellets (2 mm, 99.999+\%, Aldrich), trioctylphosphine (TOP, 90\%, Fluka), 1-octadecene (ODE, Tech. 90\%, Aldrich), tetrachloroethylene (TCE, 99\%, Aldrich). A solution of 1.0 M trioctyl phosphine-selenium (TOPSe) was prepared by dissolving selenium pellets in TOP in a glove box under N$_2$. Methanol and toluene were received from Mallinckrodt Chemicals, hexanes from Fisher Scientific, and acetone from J.T. Baker.
3.2.2 Synthesis Procedure for PbSe QDs

Method 1: The experimental setup is the same used for the CdSe synthesis (Figure 2.1 (a)), except that the reaction mixture was loaded into a four neck flask (instead of three neck flask) to let nitrogen flow through. In a typical synthesis, 0.67 g of PbO, 4.75 mL of OA, and 9.35 mL of ODE were combined. The reaction flask was heated to 150 °C for ~1h under N₂ to dissolve PbO and form lead oleate. Six milliliters of 1M TOPSe were quickly injected, in one shot, into the vigorously stirred reaction flask. The heat was removed after 5–60 seconds according to the desired PbSe size, and the reaction was cooled with an ice water bath to ~50 °C.

Method 2: In this synthesis, 0.76 g of lead acetate, 3.2 mL of OA, and 16 mL of phenyl ether were combined and heated at 150 °C in a four neck flask for 1 h under N₂. Next, 6 mL of 1M TOPSe was injected into the vigorously stirred flask. The color of the reaction solution turned from yellow–brown to dark. The heat was removed after 5-60 seconds according to the desired PbSe size, and the reaction was cooled to ~50 °C with ice water bath.

Method 3: Using a method slightly modified from the literature, 1, 22 0.58 g of lead acetate, 1.9 mL of OA, and 10 mL of trioctyolphosphine were mixed and heated in a flask at 150 °C. The mixture was stirred under N₂ for 1 hour. The temperature of the reaction mixture was lowered to 140 °C and 4.5 mL of 1M TOPSe was injected into the reaction flask. The QDs were grown between 15 seconds and 1 minute to obtain different sizes. The flask was quickly cooled to ~50 °C using an ice water bath.
3.2.3 Purification of PbSe QDs and Size Selective Precipitation

The octadecene, oleic acid, trioctylphosphine, and phenyl ether show strong NIR absorption. Therefore, these chemicals must be removed before absorbance measurements. After cooling, the reaction mixture was removed and quenched with room-temperature hexane. Butanol and methanol were added to the mixture until it became cloudy, but not separated into layers. The PbSe QDs were extracted by centrifugation and dissolved in TCE.

Quantum dots are stabilized by hydrophobic interactions between the solvent and organic surfactant molecules that coat the QD. The solubility of surfactant-coated QDs in a non-polar solvent can be disrupted by gradually adding a polar solvent. When a certain threshold of solvent polarity is reached, the QDs begin aggregating, with larger-sized QDs precipitating first. This is the mechanism behind size selective precipitation, a technique that is widely used to isolate different-sized monodisperse nanocrystals from the same batch.¹³

To isolate different-sized quantum dots, the original solution of PbSe QDs was mixed with hexane and butanol. Methanol was slowly added to the mixture until the solution became cloudy. Upon centrifugation, the larger QDs settled to the bottom of the centrifuge tube and the smaller QDs remained in the supernatant. The precipitate was dissolved in TCE. If the color of top supernatant remained yellow–brown, the same procedure could be repeated for the top supernatant to extract different-sized QDs from the same batch.
3.3 Optical Characterization of PbSe QDs

3.3.1 Absorbance and Photoluminescence Spectra of Typical PbSe QDs

Optical absorbance spectra of colloidal PbSe quantum dots were collected with a Perkin–Elmer Lambda-19 UV/vis/NIR spectrometer. Photoluminescence fluorescence experiments were performed using an Acton Research modular fluorescence system. Fluorescence was collected at a right angle to the excitation with a N₂ cooled Ge detector. Samples were prepared by dispersing washed PbSe QDs in TCE. The laser dye IR 125 (QY ~ 13% in dimethyl sulfoxide) was used as a standard for determining the quantum yield of the PbSe QDs. PbSe quantum dots with a range of different sizes were produced via the synthesis methods presented previously. Figure 3.1 shows typical absorbance and photoluminescence spectra of different-sized PbSe quantum dots.

3.3.2 PbSe QD Photoluminescence Spectra with No Size Selection

Excess methanol was used to precipitate all sizes of PbSe QDs produced during the synthesis process. To precipitate all QDs, the reaction mixture is taken into a 1:1 ratio with hexane. Next, butanol is added in an amount equal to the total volume of the reaction mixture and hexane. Finally, excess methanol is added until the solution turns so cloudy that more methanol does not cause precipitation. The supernatant is colorless and transparent for samples prepared this way. Without size selective precipitation, typical photoluminescence spectra from one batch of PbSe
dots usually show two emission peaks: one peak at ~900 nm and the other varying between 1100 and 1600 nm, as shown in Figure 3.2.

### 3.3.3 PbSe QD Photoluminescence Spectra with Size Selective Precipitation

To determine whether two emission peaks in PL spectra result from different sized PbSe QDs in solution, careful size selective experiments were performed. First, several drops of butanol were added to the original reaction mixture, which had been mixed with hexane in a 1:1 ratio. Then, methanol was added into the mixture slowly until the mixture appeared cloudy. By centrifugation, the larger sized dots were precipitated and the yellow–brown supernatant was moved to a second centrifuge tube. After adding more butanol and methanol, the solution turned cloudy, and centrifugation was used again to extract the second precipitate. The precipitates were dissolved in TCE for spectrum measurements. Figure 3.3 (a) shows PL spectra of the first and second precipitations from the same batch of PbSe QDs. The PL spectrum for the first precipitation (sample 1) shows only one emission peak at 1488 nm; however, the PL spectrum for the second precipitation (sample 2) shows two emission peaks, one at 1488 nm and the other around 900 nm.

Transmission electron microscope (TEM) images for sample 1 and sample 2 are shown in Figures 3.3 (b) and (c). For sample 1 with one emission peak at 1488 nm (first exciton absorbance peak at 1457 nm), 5-nm regular sized PbSe QDs predominate in the TEM image, with only a few small particles present. Based on a theoretical size prediction according to the PbSe QD energy band gap, the 1488 nm
emission peak arises from 5-nm sized PbSe QDs.\textsuperscript{23} For sample 2 with two emission peaks (Figure 3.3 (c)), TEM images show not only 5-nm regular sized PbSe QDs, but also many much smaller sized particles. These measurements confirm that the two peaks observed in Figure 3.2 are due to the presence of two different sized QDs produced during synthesis, in which the small sized particles contribute to the emission peak at 900 nm.

Figure 3.4 provides a second example of the evolution of two PL peaks from one batch of PbSe QDs by size selective precipitation. The scheme in Figure 3.4 (a) outlines the evolution of PL spectra from two sizes of PbSe QDs obtained by size selective precipitation. The method is the same as described above (i.e., two samples were obtained from one batch of PbSe QDs using size selective precipitation with hexane, methanol and butanol). The first precipitation is labeled as PbSe-a and the second precipitation is labeled as PbSe-b. Both PbSe-a and PbSe-b were dissolved in TCE. A small amount of methanol was added to PbSe-a and PbSe-b to further refine the separation of different sized QDs. PbSe-a\textsubscript{1}, PbSe-a\textsubscript{2}, and PbSe-a\textsubscript{3} were prepared from PbSe-a as the first, second and third precipitations, respectively. PbSe-b\textsubscript{1}, PbSe-b\textsubscript{2}, and PbSe-b\textsubscript{3} were prepared similarly from PbSe-b. As shown in Figure 3.4, the two emission peaks from small PbSe QDs and large PbSe QDs can be separated completely. The evolution of the relative intensity changes of these two PL peaks through the size selection process is also reported in Figures 3.4 (b) and (c).

The complete isolation of small sized PbSe QDs from the regular sized PbSe QDs is possible in principle, but laborious (Figure 3.4). Also as shown in Figure 3.3,
the small sized PbSe QD emission peak does not appear in PL spectra (black line in Figure 3.3 (a)); however, TEM image of this sample still shows a small percentage of small sized PbSe QDs existing with the regular sized PbSe QDs (Figure 3.3 (b)).

3.4 Preparation of Pure Small Sized PbSe Clusters

3.4.1 Introduction

Small sized PbSe QDs coexist with regular sized PbSe QDs when produced by any of the three synthesis methods described in the experimental section. These small particles repeatedly observed at the same emission peak with regular sized PbSe QDs are termed “magic sized PbSe clusters”, similar to those reported for CdSe QDs.12, 13 Because large QDs are contaminated with small dots, even when purified by size selective precipitation, a method for producing pure, small sized PbSe QDs is desirable. Toward that end, a lower temperature was used for the nucleation and growth of magic sized PbSe clusters.

3.4.2 Synthesis of Magic Sized Clusters

Lead oxide (0.892 g, 4mmol), oleic acid (3 mL, 9.5mmol), and ODE (12 mL) were loaded into a four-neck flask and heated to 150 °C under N₂ flow for 1 h. After one hour, the temperature was lowered to 75 °C and 8 mL of 1.0 M TOPSe was injected into the reaction flask. After 45 seconds, the flask was removed from the heating mantle and N₂ source. The reaction solution was moved to a vial using a syringe and was mixed with an equal amount of hexane. The mixture was left in air
at room temperature for 1~3 hours. During this time, the color of the mixture changed from nearly transparent to dark brown, indicating the formation of PbSe QDs. Unreacted precursors and excess ligands were removed by adding methanol and butanol to a portion of the reaction solution until the QDs flocculated. PbSe QDs were isolated by centrifugation and dispersed in TCE for further spectral characterization.

3.4.3 Optical Characterization

Typical absorbance and photoluminescence spectra of magic sized PbSe clusters are presented in Figure 3.5. The sample was prepared by diluting PbSe QDs in TCE. An exciton peak at 680 nm is clearly visible in the absorption spectrum and the fluorescence peaks is at ~900 nm. Unlike PbSe QDs grown at higher temperatures, the absorption and emission maxima of these PbSe QDNCs are not strongly dependent on growth time. QDNCs isolated with 1 h of growth time show nearly identical absorption and emission maxima as those with 3 h growth times.

Fluorescence QYs, measured relative to the dye IR125, are extremely high (40–84%). Such high QYs are quite unexpected because the QDNC synthesis takes place at relatively low temperatures and under ambient conditions. Indeed, the conventional thinking is that any potential for surface oxide formation, especially for a QD with such a high surface-to-volume ratio, leads to poor fluorescence properties. High temperatures are necessary for high QYs because defects are expelled to the QD surface, where they are removed during growth. It is unclear why these PbSe QDNCs are so bright.
We believe these QDNCs to be "magic-sized" clusters (MSCs) of PbSe QDs, which explains their unusual growth behavior and size stability. MSCs have been reported for several Cd-based nanoparticles, and are < 2 nm in diameter, are remarkably size stable due to the presence of a closed-shell structure, and are identified by persistent and isolated peaks in the absorption spectra, all of which we observe in these PbSe QDNCs. In addition, during the synthesis of larger-sized PbSe QDs (at 150 °C), PbSe QDNCs are simultaneously produced, with similar absorption and fluorescence properties as those synthesized here at 300 K, supporting the notion that these QDNCs are incredibly size stable. Indeed, the diameter of the second closed-shell MSC (Pb$_{19}$Se$_{44}$) is estimated to be 1.2 nm, in reasonable agreement with the measured diameters of the PbSe QDNCs shown below.

3.4.4 STEM Characterization

Scanning transmission electron microscopy (STEM) was used to determine the size of QDNCs. STEM samples were prepared by depositing ~ 0.1 mL of the QD suspension in TCE onto a thin carbon film covered copper grid, which was subsequently loaded into the Cornell VG HB501 100kV UHV STEM. STEM of 1-nm MSCs is notoriously difficult, as the clusters are believed to aggregate and coalesce into larger particles at even the lowest electron beam applications. This behavior is evident in the STEM images of Figure 3.6 (a), in which the ~1 nm MSCs weakly contrast against the dark background and the larger ~5 nm aggregates are more easily observed.
In order to overcome difficulties associated with visually determining the QD diameter, we employed a non-biased TEM analysis software package (Digital Micrograph, Gatan Inc.). The analysis program employs a user-defined threshold intensity to define all QD perimeters in the STEM image. After applying a smoothing function, the diameters of all particles were calculated, assuming a spherical shape. A histogram of all the measured QD diameters (43 total) determined from 6 different areas is shown in Figure 3.6 (b). Two peaks are observed, the first corresponding to MSCs with an average diameter of 1.6 ± 1.0 nm and the second corresponding to the agglomerates with an average diameter of 5.1 ± 1.0 nm. The QDNC size from the STEM analysis agrees very well with the ~1.5 nm diameter predicted from absorption spectra and extrapolations of PbSe QD sizing curves.23

3.4.5 Elemental Analysis
Elemental analysis was determined by energy dispersive x-ray spectroscopy (EDX). EDX was performed using a Zeiss-Leo DSM 982 scanning electron microscope equipped with an EDAX Phoenix system. The samples were prepared by drying a drop of PbSe MSC solution onto a carbon substrate. As shown in Figure 3.7, the MSCs are composed of Pb and Se, as the EDX shows that these elements are predominant. Small oxygen and phosphorous peaks are present, which likely come from organic ligands.
3.4.6 Crystal Structure

The crystal structure of PbSe QDs was determined by x-ray diffraction (XRD). Powder x-ray diffraction was performed at room temperature using a Philips multipurpose diffractometer with Cu \( K\alpha_1 \) radiation (0.154056 nm). Samples were prepared by evaporating several drops of the PbSe QD sample onto a low-background x-ray sample plate. As expected for a 1-nm particle, the XRD peaks of the MSCs are weak in comparison to a 4.2-nm PbSe QD (Figure 3.8). Nonetheless, some peaks (e.g., (200), (311) and (222)) are observed, which confirm that the PbSe QDNCs are crystalline, with the expected rock salt crystal structure.

3.5 Magic Sized PbSe QD Nanoclusters for Biological Applications

3.5.1 PbSe QDNC Aqueous Solubilization

As synthesized, PbSe QDNCs have hydrophobic surfaces and require appropriate chemical processing to achieve the aqueous solubility necessary for biological applications. PbSe QDNCs were made hydrophilic through lipid encapsulation and direct ligand exchange with 2-aminoethanethiol, mercaptoundecanoic acid, and (1-mercaptoundec-11-yl)tetra(ethylene glycol) (MTPEG). In terms of colloidal stability, fluorescence QY, and photostability, MTPEG produced the best results.

One hundred microliters of MTPEG were added to 500 \( \mu \)L of a 20 mM aqueous HEPES buffer solution. The aqueous solution contained a 100-fold molar
excess of MTPEG relative to PbSe QDNCs, and was added dropwise to a suspension of PbSe QDNCs in TCE. The mixture was vortexed briefly and centrifuged at 13,000 rpm for 15 minutes. The water-soluble QDNCs could be removed simply by decanting the aqueous layer. When performing quantitative spectroscopic measurements, deuterated water was used to limit solvent absorption in the NIR. We found that both the QY and colloidal stability were strong functions of the ligand concentration. At low MTPEG concentration (5-fold excess), the QY was quite low and the optical clarity was poor; at high MTPEG concentration (100-fold excess), QYs were measured as high as 29% and the optical clarity is excellent.

3.5.2 Optical Characterization of PbSe QDNCs in Water.

Absorption and fluorescence spectra for PbSe QDNCs in water are shown in Figure 3.9 (a). The absorption and fluorescence spectra red shift for QDNCs in water as reported in other literature.\textsuperscript{24} The spectrum redshift for QDNCs in water may result from a solvatochromatic shift, which depends on the solvent polarity. The polarities of ground and excited state of a QD are different; therefore, a change in the solvent polarity can lead to differential stabilization of the ground and excited states, and thus a change in the energy gap between these states. The large dielectric constant for TCE (~ 2.5) and for water (~ 80) may lead to the redshift of PbSe QDNCs in water. This effect has been measured before for CdSe\textsuperscript{25}, and the spectrum red shifts when QDs are placed in an environment with a higher dielectric.

Also, the QY dropped from 75% in TCE to 29% in water. However, even when exposed to air, the aqueous QDNC solution was stable and remained so over
several weeks (Figure 3.9 (b)). The aqueous QDNCs also show excellent photostability (Figure 3.9 (c)), as the fluorescence intensity decreases only 40% over 6 hours under continuous photoexcitation. Although the aqueous QDNC photostability is not vastly superior to the dye IR 125 (with a QY of 13%), the higher initial QY means that the QDNC is at least 2.5 times brighter overall at all times under irradiation.

3.5.3 Hydrodynamic Diameter

The hydrodynamic diameter was determined by dynamic light scattering (DLS) measurements using a Malvern ZetaSizer Nano ZS. The sample was placed into an ultra low volume cuvette and irradiated with a 633 nm HeNe laser during the measurement. The solvent viscosity, index of refraction, and solute absorption were taken into account by the ZetaSizer software package for the hydrodynamic diameter calculations.

An average hydrodynamic radius of 2.4 ± 0.6 nm was measured for the MTPEG-solubilized PbSe QDNCs by DLS (Figure 3.10). Such a small QD diameter is very significant, as these highly fluorescent QDNCs are potentially small enough to be transported through the cell membrane or into the nucleus through carrier-mediated mechanisms. Further enhancing their utility as a superior in vivo fluorescent probe is that the synthesis of these QDs is extremely straightforward. By simply mixing together the relatively benign Pb and Se molecular precursors in an organic solvent under ambient conditions, large amounts of QDs can easily be
synthesized on demand within hours with no need for air-sensitive chemical techniques.

3.6 Conclusions

In this chapter, we have reported the formation of magic sized PbSe nanoclusters together with regular sized PbSe QDs. The magic sized PbSe MSCs can be separated from regular sized PbSe QDs using size selective precipitation. A method of preparing pure PbSe MSCs at low reaction temperature under ambient conditions is also reported. In comparison to other semiconductor QDs, these small sized MSCs show high fluorescence efficiency. The optical properties of PbSe MSCs provides them with enormous potential as superior fluorophores for biological imaging applications at NIR wavelengths between 700 and 1000 nm. Other semiconductor MSCs suffer from poor fluorescence or photostability characteristics, and larger QDs involve complicated syntheses and are too large to penetrate cell membranes. In contrast, PbSe MSCs retain their remarkable optical properties in water, suggesting that they are ideally suited to potentially enable significant breakthroughs for in vivo biological imaging.
3.7 Figures Captions

**Figure 3.1** Absorbance and photoluminescence spectra of different sized PbSe QDs (blue lines represent QDs with smallest size, and green lines represent QDs with largest sizes).

**Figure 3.2** PL spectra of PbSe QDs show two emission peaks. One emission peak ranges from 1100 to 1600 nm depending on growth time and the other peak at ~900 nm is independent of reaction growth time. The two curves represent the PL from two batches of PbSe QDs with different growth time.

**Figure 3.3** PL spectra of PbSe QDs using size selective precipitation and corresponding TEM images. (a) PL spectra from the first precipitation (sample 1, black line) and the second precipitation (sample 2, red line). (b) TEM image of PbSe QDs from sample 1. (c) TEM image of PbSe QDs from sample 2.

**Figure 3.4** Evolution of two PL emission peaks’ relative intensity change with size selective precipitation. (a) Scheme used to separate different sized QDs using size selective precipitation. (b) PbSe-a and (c) PbSe-b were first and second precipitations of PbSe QDs from the same synthesis, respectively.
Figure 3.5 Typical absorption and photoluminescence spectra of PbSe QDNCs. An exciton peak at 680 nm is clearly visible in the absorption spectrum and the fluorescence peaks is at ~900 nm.

Figure 3.6 STEM of PbSe quantum dots nanoclusters and their size distribution. (a) STEM images of MSC PbSe QDs, showing both ~1-nm MSCs and larger ~5-nm aggregates. 10-nm scale bars are shown in each image. (b) Histogram of all particle diameters from STEM characterization.

Figure 3.7 EDX spectra of magic sized clusters of PbSe QDs. Peaks are labeled by their elemental identity.

Figure 3.8 XRD spectra of 1-nm PbSe quantum dots nanoclusters and 4.2-nm PbSe quantum dots (red line) with (h k l) peak indices. XRD spectrum of 1-nm PbSe quantum dots nanoclusters (red line). XRD spectrum from 4.2-nm PbSe QDs produced in a separate synthesis (black line). The peak positions of the bulk solution (solid vertical lines) are shown for reference.

Figure 3.9 Optical properties of PbSe quantum dot nanoclusters in tetrachloroethylene and in water. (a) Absorbance and fluorescence spectra of isolated QDNCs in TCE (red) and water (blue). (b) Picture of OA- (left) and MTPEG-terminated (right) PbSe QDNCs in organic (upper) and aqueous (lower) solvents,
demonstrating excellent overall optical clarity. (c) The fluorescence intensity of an aqueous solution of PbSe MSCs under continuous laser excitation.

**Figure 3. 10** Hydrodynamic diameter for PbSe QD MSCs with size distribution centered at 4.8 nm.
3.8 Figures

Figure 3.1
Figure 3.2
Figure 3.3 

(a) Photoluminescence intensity (a.u.) vs. Wavelength (nm)

(b) and (c) Images with scale bars of 25 nm
Figure 3.4
Figure 3.5
Figure 3.6
Figure 3.7
Figure 3.8
Figure 3.9

![Graph showing absorbance and fluorescence intensity over wavelength.](a)

![Image of two vials containing a liquid.](b)

![Graph showing normalized intensity over time.](c)
Figure 3.10

![Bar chart showing the distribution of hydrodynamic diameter (nm) with corresponding fraction (%) values. The peak is centered around 6 nm with a significant drop-off for larger diameters.]
3.9 References


Chapter 4: Synthesis of PbSe/SrSe core/shell nanocrystals

4.1 Introduction

Colloidal semiconductor nanocrystals, or quantum dots (QDs), exhibit size-dependent optical and electronic properties due to the quantum confinement effect. The large Bohr radius for PbSe (46 nm) and other lead chalcogenide (PbS and PbTe) permit optical properties of nanometer sized PbSe particles to be evaluated in the regime of extremely strong quantum confinement. The band gaps of lead selenide is small (0.28 eV); however, due to strong quantum confinement, the absorption and emission of PbSe QDs can be tuned through the near-infrared region, which provides potential use in opto-electronic and biophysical applications. The synthesis of high quality colloidal PbSe QDs has been reported by several groups.

A major improvement in optical properties usually takes place when an inorganic shell grows around the core, which chemically passivates the QD surface atoms much more efficiently than simple organic surface capping ligands. Overcoating QDs with a higher band gap inorganic material has been shown to improve the robustness, luminescence quantum yield, and photostability. Moreover, PbSe QDs has enormous potential for biological imaging applications at near infrared (NIR) wavelengths between 700–1000 nm, where there is reduced absorption by biological fluids and where organic dyes emit poorly. As synthesized, QDs are soluble in nonpolar solvents; however, this original hydrophobic layer must be
replaced or adapted with a hydrophilic ligand in order to be used in aqueous solutions for biological studies. Successful ligand exchange has so far mostly been achieved on core shell QDs, such as CdSe/ZnS QDs.\textsuperscript{12,13}

The successful inorganic capping of CdSe QDs with several wide band semiconductors (ZnS,\textsuperscript{14,15} CdS,\textsuperscript{16} ZnSe,\textsuperscript{17} CdS/ZnS and ZnSe/ZnS double shells\textsuperscript{18}) has been reported. The inorganic shelling of PbSe QDs has received little attention. Lifshitz reported the successful coating of PbSe QDs with PbS using a two-injection process with the formation of PbSe core QDs followed by the injection of Pb and S precursors into the solvent containing PbSe core QDs.\textsuperscript{19} However, these PbSe/PbS core shell QDs showed a significant spectrum redshift (~150 meV), which is due to the relatively small potential barrier (~0.1 eV) provided by the PbS shell. A following study by Stouwdam et al. reported that these PbSe/PbS core shell did not show an increased stability in solution excited with a xenon lamp when compared with Pbse core QDs.\textsuperscript{20}

The choice of capping material is guided by the need for a semiconductor with a wider bandgap than the core, which confines the excitons in the core, and the same crystal structure as the core with low lattice mismatch, which provides the possibility of a well grown shell. Although a lot of semiconductor materials have wider bandgaps than PbSe, an appropriate shell is hard to find for PbSe QDs due to the reason that most colloidal semiconductors (CdS, CdSe, ZnS, et al.) studied are wurtzite or zinc blende crystal structure, while PbSe forms rock-salt crystal structure. In this chapter, SrSe is used as the shell material for PbSe QDs. PbSe and SrSe share
a rock-salt crystal structure with lattice constants of 6.12 and 6.25 Å, respectively. Although the lattice constants differ by only 2%, the bulk energy gap of SrSe is 3.81 eV, much higher than that of bulk PbSe, 0.28 eV, which provides good confinement for PbSe core QDs.

In this chapter, we studied the coating of PbSe QDs with SrSe. The resulting core-shell QDs have high room temperature quantum yields. Also, the core-shell quantum dots exhibit an unusual blue shift in emission spectra in comparison with the PbSe core. Further studies of the reaction solvent and precursors are carried out to investigate the effect of each of them on the spectrum blueshift.

4.2 Experimental section

4.2.1. Materials and experimental setup.

All chemicals were used as purchased without further processing or purification. Lead oxide (PbO, 99.999% from Aldrich), oleic acid (OA, Tech. grade 90% from Aldrich), selenium pellets (2 mm, 99.999+% from Aldrich), trioctylphosphine (TOP, 90% from Fluka), 1-octadecene (ODE, Tech. 90% from Aldrich), diphenylphosphine (DPP, 98% from Aldrich), tetrachloroethylene (TCE, 99% from Aldrich), and strontium oxide (SrO, 99.9% from Aldrich) were used in the QD synthesis. A solution of 1.0 M trioctylphosphine-selenium (TOPSe) was prepared by dissolving selenium pellets in TOP in a glove box under N₂. Methanol and toluene were received from Mallinckrodt Chemicals, hexanes from Fisher Scientific, and acetone from J.T. Baker. All synthesis experiments were performed in
a 125 mL 4-neck flask equipped with a temperature controller, magnetic stirrer, and heating mantle with N₂ flow.

4.2.2. Synthesis of PbSe core QDs.

First, highly fluorescent PbSe QDs were prepared based on a modified version of literature methods.⁷,⁹ Typically, 0.892 g (4.00 mmol) of PbO, 5 mL of OA, and 12 mL of ODE were mixed together in a 4-neck flask and heated to 150 °C under N₂ flow for an hour. A clear, colorless solution was obtained. The temperature of the reaction flask was then decreased to 110 °C. Inject 8 mL of 1 M trioctylphosphine selenide (TOPSe, 8 mmol) mixed with 150 µL of DPP quickly into the reaction flask at 110 °C. The reaction lasted for about one minute and the solution turned dark. Using an ice bath, the reaction flask was cooled to about 50 °C. Hexane, methanol, and butanol were added to the reaction solvent to precipitate the PbSe QDs. The QDs were separated from the solution by centrifugation. Approximately 75% of the precipitated PbSe QDs were redissolved in 4 mL of hexane for use in capping experiments, and the remaining 25% was redispersed into TCE for use in spectroscopic measurements.

4.2.3 Synthesis of PbSe/SrSe core/shell QDs

SrSe was used as the capping material for PbSe QDs. Strontium oxide and TOPSe were used as precursors for Sr and Se in shelling experiments, respectively. To make the SrSe shell, SrO (0.31 g, 3 mmol), OA (5 mL), and ODE (12 mL) were loaded into a 4-neck flask and heated to 200 °C with N₂ flow for an hour under rapid stirring to ensure the complete dissolution of all SrO. The temperature was reduced
to 75 °C and the reaction solution was evenly divided into two different flasks held at 75 °C. To each flask was added 2 mL of PbSe QDs in hexane prepared using the procedure in experiment section 4.2.2. After waiting 10 minutes for the hexane to evaporate, 1.8 mL of 1 M TOPSe was injected into each of the flasks. The reaction was kept at 75 °C under N₂ for 6 hours.

4.2.4. Synthesis of different sized PbSe QDs.

The preparation of different sized PbSe QDs was based on a similar procedure in part 4.2.2, except 3 mL OA was used instead of 5 mL. 8 mL of 1M TOPSe (without DPP) was injected into the reaction flask at 75 °C. The temperature of the reaction mixture was kept at 75 °C with N₂ flow as the growth of PbSe QDs occurred. Aliquots of 1~2 mL were extracted from the reaction flask at different time intervals and mixed with an equal amount of hexane. Six samples were prepared with growth times of 1.75, 6.75, 16, 32, 65, and 130 minutes. Half of each extracted aliquot was washed or purified immediately using methanol and butanol, and the other half was left in air at room temperature for 2.5 hours before being purified with methanol and butanol. The low synthesis temperature ensured slow nucleation and growth; therefore, different sized PbSe QDs were obtained by removing aliquots after different growth times.

4.2.5 Effect of different precursors on photoluminescence spectra.

PbSe QDs were prepared using a method similar to that used in chapter 4.2.2, except 3 mL OA was used instead of 5 mL and 8 mL 1M TOPSe without DPP was injected into the reaction flask at 150 °C. The heat was removed after about 1.5
minutes, and the flask was cooled down using an ice bath. PbSe QDs were purified by adding hexane, methanol, and butanol to precipitate the QDs from any organics. PbSe QDs were then redissolved in 10 mL of hexane, which was subsequently divided into 6 vials. To each vial, a different precursor solution was added: 0.5 mL of OA, 2 mL of ODE, 3.5 mL of Pb precursor with 2.5 mL of original Pb precursor and 1 mL hexane, and 1.4 mL 1 M TOPSe. The original lead precursor was prepared by dissolving 4 mmol PbO in 3 mL of OA and 12 mL of ODE. No precursor was added to the fifth vial, which was used as reference for other samples. PbSe QDs in the sixth vial were washed and stored in TCE for storage. The first five samples were left in air for about 3 hours. Methanol and butanol were then added to precipitate the PbSe QDs, and the resulting precipitant was redissolved in TCE for further measurements.

4.2.6 Preparation of PbSe QD samples exposed to O₂ for different time intervals.

PbSe QDs were prepared using the same method as in experimental section 4.2.5. After synthesis, PbSe QDs in original solution were mixed with an equal amount of hexane, immediately transferred to the glove box, and stirred continuously. Aliquots were taken out of the glove box after 1.5, 2.5, and 3.5 hours. After removal from the glove box, these QDs were purified immediately using a mixture of methanol and butanol and redispersed in TCE for spectroscopic measurements.
4.3 Characterization.

4.3.1 Optical characterization.
Absorption spectra were recorded using a Perkin-Elmer UV/vis/NIR spectrometer (Lambda 19). Fluorescence experiments were performed using a modular research fluorescence system from Acton Research. Fluorescence was collected at a right angle to the excitation and detected with a N₂ cooled Ge detector. Samples were prepared by dispersing precipitated PbSe QDs in TCE or hexane. The laser dye IR 125 (QY = 13% in dimethyl sulfoxide) was used as a standard for determining the quantum yield of the PbSe QDs.

4.3.2 Energy Dispersive X-ray.
Energy dispersive X-ray was performed using a Zeiss-Leo DSM 982 scanning electron microscope equipped with EDAX Phoenix system. The samples were prepared by drying a drop of QD solution onto a carbon substrate

4.4 Results and Discussion

4.4.1 Synthesis of core/shell PbSe/SrSe.
PbSe/SrSe core/shell QDs were synthesized in a two-step procedure. In the first step, PbSe core QDs were synthesized using OA and ODE as described in experiment section 4.2.2. In the second step, the core QDs were coated with SrSe. SrO was used as the Sr source by dissolving 3 mmol in 5 mL of OA and 12 mL ODE, the same solvent used for PbSe core QDs synthesis. SrO dissolves much slower than
PbO. It is very important that all Sr was dissolved before the shelling experiments proceeded; unreacted SrO at the bottom of the reaction flask resulted in unsuccessful shelling experiments due to the formation of dark, undissolved particles. 1M TOPSe was used as the Se source of the shell. During the core shell synthesis, if the reaction was carried out in one flask instead of distributing the reagents evenly into two flasks, the reaction was unsuccessful. Therefore, the concentration and distribution of chemicals used in the capping process is very critical.

4.4.2 Optical characterization.

The synthetic procedure in experimental section 4.2.3 produced PbSe/SrSe core/shell QDs using a range of core sizes. A significant blue shift (higher energy) in the PL spectrum was observed after shelling (Figure 4.1), which is unusual for semiconductor core/shell QDs. Quantum yields of 40% - 90% were obtained for PbSe core QDs and comparable values were measured for PbSe/SrSe core/shell QDs.

To check for the existence of SrSe shell materials in core and core/shell QD samples, EDX was used to survey samples for the presence of Sr. Figure 4.2 shows a representative EDX spectrum from a dense cluster of purified PbSe core QDs and the corresponding PbSe/SrSe core/shell QDs. Lead and selenide signals were detected in the PbSe core QDs, while strong strontium signals were present, in addition to lead and selenium, in the core/shell QD sample.
4.4.3 STEM images and optical stability of PbSe core and PbSe/SrSe core/shell QDs

The QD sizes were examined by STEM. The following figure 4.3 shows typical STEM images of PbSe core QDs (PL spectrum of these PbSe core QDs was shown as blue solid line in Figure 4.1) and corresponding PbSe/SrSe core/shell QDs (PL spectrum was shown as blue dash line in Figure 4.1). Also shown are their size histograms collected from several images. The average size of PbSe core QDs is around 3.5 nm and the average size of the corresponding core shell QDs is around 3.2 nm. The size distribution is narrower for PbSe core QDs than for the corresponding core shell QDs, which agrees with the fact PL spectrum for core shell QDs is broader than core QDs (Figure 4.1 blue lines). The reason for this is probably due to the size instability of PbSe core QDs, which grow to larger or smaller sizes during the core shell experiment.

The photostability of the same core and core shell QDs is shown in Figure 4.4. The experiments were performed under continuous excitation from 633 nm He:Ne laser. We didn’t observe improved photostability for core shell QDs comparing with the core QDs.

The PL spectrum blueshift and the slight smaller sizes for PbSe/SrSe core shell QDs comparing with PbSe core QDs indicate that overall a thick shell is not formed around the core QDs, which helps explain why the optical stability of core shell QDs is not increased. What might have happened is that Pb atoms in the outer layer of PbSe core QDs were replaced by Sr atoms, forming PbSe/SrSe core shell
QDs; therefore, the spectrum is slightly blueshifted for the core shell QDs and their sizes were not increased.

4.4.4 Etching of different sized PbSe QDs:

Usually, a red shift is expected after shelling of QDs with an inorganic layer due to partial leakage of the exciton wave function into the shell material. Our explanation for this remarkable PL blue shift is that PbSe core QDs were etched by the chemicals in the shelling reaction solution; therefore, a blue shift in the optical spectra is caused by the shrinking of the PbSe core. To test if the PbSe core particles are being etched by the organics in the reaction solvents, we did the following experiment: (1) prepare different sized PbSe QDs, isolate half of these QDs from the reaction organics and redissolve them in hexane, and leave the other half of these same QDs with the reaction solvent for a certain time period before isolating them from the reaction organics, which is 2.5 hours for our experiment. (2) Single sized PbSe core QDs are prepared and left with the original reaction solvent. PbSe QDs are then isolated from the reaction organics at different time length, followed by spectrum measurement to observe the change in QDs emission with time. (3) If the spectra of PbSe QDs blueshift when left with reaction solvents, experiment to study the effect of each organic used in the synthesis is going to be performed.

PbSe QDs with a range of sizes from the same batch were prepared according to the methods in experimental section 4.2.4. Figure 4.5 shows the evolution of absorption and PL spectra of PbSe QDs extracted after different time lengths and purified immediately using methanol, butanol, and hexane to get rid of unreacted
precursors and organics. Both absorption and PL spectra red shifted with longer reaction and growth times due to the increasing particle size. The PL maxima for PbSe QDs that were purified immediately after synthesis with growth times of 1.75 minutes, 6.75 minutes, 16 minutes, 32 minutes, 65 minutes, 130 minutes, and 265 minutes growth times are at 802 nm, 1006 nm, 1168 nm, 1242 nm, 1312 nm, and 1366 nm, respectively.

As described in experimental section 4.2.4, when various sized PbSe QDs were prepared by removing aliquots from the reaction flask, while half of the solution was washed immediately, the other half was mixed with hexane at an equal volume of reaction solution and left in the air for 2.5 hours before being washed or purified to get rid of unreacted precursors and organics. Hexane was added to keep the mixture soluble, otherwise it solidified in about 30 minutes. The optical properties of PbSe QDs reacted in the flask for the same time length but washed 2.5 half hours later were significantly different from the samples that were washed immediately (Figure 4.6). Comparing PL spectra of PbSe QDs purified 2.5 hours later with the same PbSe QDs purified immediately after synthesis, five samples exhibit significant blue shifts, except the first sample red shifted to about 900 nm. The PL signal that appears around 900 nm corresponds to magic sized PbSe clusters, which are very stable. Magic sized QDs form because unlike other larger sized PbSe QDs, these small PbSe QDs are both very stable and can form at room temperature.21

For the formation of magic sized clusters, PL peak redshifted by 114 nm for the first sample (802 nm to 916nm). For the other five samples, the PL peaks
blueshifted by: 66 nm (1006 nm to 940 nm), 122 nm (1168 nm to 1046 nm), 120 nm (1242 nm to 1122 nm), 146 nm (1312 nm to 1148 nm), and 188 nm (1366 nm to 1178 nm), respectively. Figure 4.6 (b) shows quantum yields of PbSe QDs purified immediately are similar to those purified 2.5 hours later with a value of ~60%.

4.4.5 Time-dependent PL spectra evolution of single sized PbSe QDs when left in original reaction solution with an equal volume of hexane.

To study time dependent spectra change of PbSe QDs, single sized PbSe QDs were prepared and mixed with equal amount of hexane without any purification. The mixture was left under ambient condition at room temperature. Small aliquots were removed from the mixture and washed with methanol and butanol to isolate PbSe QDs from the excess precursors and additional organics after different time lengths: 0 minute (immediately after synthesis), 1.5 hours, 2.5 hours, 3.5 hours, 5 hours, 6.5 hours, 8 hours and 22 hours. Figure 4.5 shows the evolution of PbSe QDs PL spectra washed at these different time lengths. A larger PL blue shift occurs as the solution sits longer before being washed. A PL peak around 900 nm with strong intensity appears as the QDs are allowed to sit undisturbed in hexane. This peak is found in almost the same position as first sample washed after 2.5 hours after synthesis in Figure 4.6. The PL signal that appears around 900 nm corresponds to magic sized PbSe clusters. These small PbSe QDs clusters are both very stable and can form at room temperature. Despite the change of photoluminescence spectra with longer sitting time, the quantum yields of PbSe QDs stay stable, with a value of ~70%, as shown in figure 4.7 (b).
4.4.6 Study of the effect of different precursors and solvents on the PL blue shift of PbSe QDs.

Based on quantum confinement theory, PL spectra blue shift for PbSe QDs in original reaction solution indicate that the effective size of PbSe QDs were shrinking. To study the etching of PbSe quantum dots, the effects of different precursors and solvents on the PL blue shifts are studied. As described in experimental section 4.2.5, PbSe QDs were synthesized, purified, and redistributed in hexane. Different precursors and solvents were then added with these QDs under ambient condition at room temperature. The amount of precursors and solvent used was one sixth of the amount used in the synthesis reaction due to the fact that six samples were prepared. After three hours left in air with different precursors and solvent, these QDs were purified using methanol and butanol, and redispersed in TCE for spectra measurement. From Figure 4.8, PbSe QDs mixed with TOPSe for three hours show almost identical PL spectra when compared to the reference spectrum of PbSe QDs in hexane. PL spectra of PbSe QDs mixed with ODE, OA, and Pb precursor blue shifted 22, 40, and 122 nm, respectively (Figure 4.8). These experiments conclude that OA and ODE, especially OA, both contribute to the PL blue shift or the etching of PbSe QDs.

4.4.7 The effect of O₂ and solvent (hexane, TCE) on PbSe QD PL blue shift.

To determine the role of O₂ in the blue shift of PbSe QD spectra, experiments were carried out by transferring the PbSe QDs in original solvent to the glove box filled with N₂. Figure 4.9 shows the evolution of the spectra in N₂. The PL spectra do not show significant changes in a N₂ atmosphere for 3.5 hours. When PbSe QDs
were left in the original reaction solvents in an O\textsubscript{2} environment, their PL properties behaved very differently compared to the behavior under inert atmosphere (N\textsubscript{2}). Therefore, the presence of oxygen plays a role and greatly affects the PL spectra of PbSe core QDs when mixed with original reaction solvent.

After PbSe QDs were purified, they were stored in hexane or TCE. To determine whether hexane and/or TCE also factors into the PL blue shift, PbSe QDs diluted in hexane or TCE were left in air for several days. No significant change was observed from the PL spectra in 48 hours (Figure 4.10), which leads to the conclusion that hexane and TCE solvents do not contribute to the significant PL blue shift reported here.

4.5 Conclusion

Highly fluorescent PbSe/SrSe core/shell QDs were prepared via a two-step process. The PL spectra of these QDs show a significant blue shift when compared to PbSe core QDs. The etching of PbSe QDs were studied by adding different precursors into the QD solution and under different environments. From the experimental results, we conclude that the influence of O\textsubscript{2} and precursors, especially oleic acid, in the solution play a decisive role in the etching of PbSe QDs, which leads to the PL blue shift. The mechanism for this phenomenon is under investigation. A possible explanation is that the outer layer of PbSe QDs oxidizes first to form PbO. Subsequently, dissolution of PbO in oleic acid removes the oxidized layer, which leads to further oxidation and dissolution of PbSe core QDs.
The etching of PbSe core QDs by reaction solvent, such as oleic acid, and O₂ can not fully explain the PL blueshift of PbSe/SrSe core/shell QDs due to the fact that the shelling experiments were carried out under continuous N₂ flow. Without Sr precursors present, PbSe QDs cores will continue growing under the shelling experiment conditions (i.e., the method for preparing different sized PbSe QDs); therefore, Sr precursor is closely involved in the PL blue shift of PbSe/SrSe core/shell QDs. Future experiments will investigate this mechanism.
4.6 Figure captions.

**Figure 4.1** PL spectra of PbSe core QDs (solid lines) and the corresponding PbSe/SrSe core/shell QDs (same colored dashed lines).

**Figure 4.2** A representative energy dispersive analysis of X-ray (EDX)spectrum of PbSe core QDs (top) and PbSe/SrSe core/shell QDs (bottom). A Sr signal appears in PbSe/SrSe core/shell QD sample.

**Figure 4.3** STEM of PbSe, PbSe/SrSe quantum dots and their size distribution. (a) typical STEM images of PbSe QDs. (b) STEM images of PbSe/SrSe core/shell QDs. (c) Histogram of PbSe (from 3 images) and (d) PbSe/SrSe core/shell particle diameters from STEM characterization.

**Figure 4.4** Normalized integrated PL intensity of PbSe core (black line) and PbSe/SrSe core/shell (red line) QDs under continuous laser excitation.

**Figure 4.5** Absorption and PL spectra evolution of PbSe core QDs washed immediately after different growth lengths from same initial solution: 1.75 (black), 6.75 (red), 16 (green) 32 (dark blue), 65 (light blue) and 130 (purple) minutes, corresponding to PL maxima at: 802, 1006, 1168, 1242, 1312, and 1366 nm, respectively.
**Figure 4.6** (a) PL spectra of different sized PbSe core QDs washed immediately (solid line) and washed 2.5 hours (dashed lines) after removing from the reaction flask. Samples were removed after 1.75 (black), 6.75 (red), 16 (green) 32 (dark blue), 65 (light blue) and 130 (purple) minutes. (b) Quantum yield measurements of different sized PbSe QDs washed immediately (black squares) and 2.5 hours (red circles) after synthesis.

**Figure 4.7** Time dependent blue shift of single sized PbSe QDs PL. (a) PbSe QDs were synthesized, and then added to an equal volume of hexane. PL was measured of aliquots removed from this solution after 0 (immediately after synthesis) (black), 1.5 (red), 2.5 (green), 3.5 (blue), 5 (light blue), 6.5 (pink), 8 (yellow), and 22 (brown) hours. (b) Quantum yield measurements of same aliquots from top figure portion.

**Figure 4.8** Etching of PbSe QDs using different precursors. PbSe QDs stored in hexane in the presence of different precursors for 3 hours in air: TCE (immediately redissolved, black), OA (red), ODE (green), Pb precursor (blue), and Se precursor (pink).

**Figure 4.9** O$_2$ effect on the PL blue shift of PbSe QDs. PbSe QDs were synthesized and immediately stored in the glovebox under N$_2$. PL spectra were obtained after
removing aliquots after 0 hours (washed immediately after synthesis, black), 1.5 (red), 2.5 (green), and 3.5 (blue) hours.

**Figure 4.10** PL spectra change of PbSe QDs in hexane after two days left in ambient environment. (a) black solid line represents PbSe QDs in hexane in day 1, and black line with open triangle represents PbSe QDs in hexane in day 3 (48 hours later). (b) black solid line represents PbSe QDs in TCE in day 1, and black line with open triangle represents PbSe QDs in TCE in day 3 (48 hours later).
4.7 Figures

Figure 4.1
Figure 4.2

![Graph showing X-ray energy spectra for PbSe and PbSe/SrSe]
Figure 4.3
Figure 4.4

[Graph showing the normalized integrated PL intensity over time for PbSe core QDs and PbSe/SrSe core/shell QDs.]
Figure 4.5

![Graph showing absorbance and photoluminescence](image)

- Absorbance and Photoluminescence (a.u.) vs Wavelength (nm)
- Various time points indicated: 130 min, 65 min, 32 min, 16 min, 6.75 min, 1.75 min
Figure 4.6

(a) Photoluminescence (a.u.) vs. Wavelength (nm)

(b) Quantum Yield (%) vs. PbSe QDs samples
Figure 4.7

Photoluminescence intensity (a.u.)

Wavelength (nm)

Quantum yield (%)
Figure 4.8
Figure 4.9
Figure 4.10
4.8 Reference


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Chapter 5: Energy transfer between PbSe-PbSe and PbS-PbSe semiconductor quantum dots (QDs), and energy transfer between CdSe/ZnS-CdSe/ZnS QDs in an optical microcavity

5.1 Introduction

Colloidal II-VI and IV-VI semiconductor quantum dots (QDs) exhibit size dependent optical and electronic properties\(^1\) as a result of quantum confinement effects. The emission wavelength for II-VI QDs (such as CdSe) can be tuned through the visible range and the emission wavelength for IV-VI QDs (such as PbS and PbSe) can be tuned through near infrared range by changing the particle sizes. Several attempts to modify the luminescence of semiconductor QDs using photonic structures have been described, including QDs embedded in polymer spheres,\(^2\)\(^-\)\(^3\) one-dimensional optical microcavities,\(^4\)\(^-\)\(^5\) and opal photonic crystals.\(^6\)\(^-\)\(^8\) The use of inter-QD energy transfer to enhance the performance of integrated QD-photonic systems is expected to take on increasing importance in a similar manner to what has taken place for all-organic devices.\(^9\) Whereas cavity-induced enhancement of the spontaneous emission of colloidal QDs was recently demonstrated,\(^5\) the study of the nonradiative energy transfer process between two different size populations of colloidal semiconductor QDs in an optical microcavity has not been reported.

Förster (fluorescence) resonance energy transfer (FRET) is the transfer of the excited state energy from the excited donor to an acceptor.\(^10\) The donor typically
emits at a shorter wavelength which overlaps with the absorption spectrum of the acceptor. Due to the quantum confinement effect, small QDs have higher energy levels, thus acting as donors; and large QDs have lower energy levels acting as acceptors during the energy transfer process. Since FRET arises when interdot separations are $\leq 10$ nm, solid films of QDs were prepared to observe energy transfer from the donor to the acceptor QDs. The use of inter-QD energy transfer to enhance the performance of integrated QD-photonic systems is also expected to take on increasing importance in a similar manner to what has taken place for all-organic devices.\textsuperscript{9} Indeed, nonradiative energy transfer involving semiconductor QDs has been studied in QD assemblies\textsuperscript{11} and QD-organic dye systems,\textsuperscript{4,12} with applications in biological sensing\textsuperscript{12} and nanophotonics.\textsuperscript{13}

In this chapter, energy transfer in two different samples, a mixture of small and large diameter PbSe core QDs and a PbS-PbSe core QD mixture, is studied. We also present the study of CdSe/ZnS core/shell colloidal QDs in a Fabry-Perot (1-D) microcavity formed between two distributed Bragg reflectors (DBRs) and studies of energy transfer between semiconductor QDs placed in microcavities.

5.2 Fluorescence Resonance Energy Transfer (FRET)

For a FRET process, spectral overlap between the donor emission and the acceptor absorption determines the strength of the resonant dipole-dipole interactions (RDDI) for a given separation of the donor and acceptor.\textsuperscript{14} Accordingly, for a given spectral overlap, a critical donor-acceptor distance $R_0$ can be defined as the distance
where the rate of energy transfer \( k_{ET} \) equals the sum of all other radiative \( (k_r) \) and nonradiative \( (k_{nr}) \) rates. The critical distance \( R_0 \) can be calculated according to\(^{10}\)

\[
R_0 = 9.78 \times 10^3 \left[ \kappa^2 n^{-4} Q_D J(\lambda) \right]^{1/6}
\]  

(5.1)

where \( \kappa^2 \) is the relative orientation of the donor and acceptor and has the value 2/3 for two randomly oriented transition dipoles, \( n \) is the refractive index of the QD solid film, \( Q_D \) is the luminescence quantum yield of the donor, and \( J(\lambda) \) is the spectral overlap of donor emission and acceptor absorption. Using this value of \( R_0 \), the expected energy transfer efficiency \( E \) is:\(^{10}\)

\[
E = mR_0^6 / (mR_0^6 + R_{DA}^6)
\]  

(5.2)

where \( m \) is the number of acceptors per donor, and \( R_{DA} \) is the actual donor acceptor distance.

5.3 Energy Transfer between PbSe Core QD Populations with Different Diameters

5.3.1 Experiment

Colloidal PbSe core QDs were synthesized following a procedure described in Chapter 3, purified using a hexane-methanol-butanol mixture, and redispersed in tetrachloroethylene (TCE). A QD mixture was prepared by combining two core QD populations with different diameters in TCE, precipitating the QDs with methanol, and redissolving them into toluene with 1% polymethyl methacrylate (PMMA). Solid
samples used to study energy transfer were prepared by drying a drop of the QD mixture solution onto a glass substrate.

5.3.2 Optical Characterization

Absorption spectra were recorded using a Perkin-Elmer UV/Vis/NIR spectrometer (Lambda 19). Fluorescence experiments were performed using a modular research fluorescence system from Acton Research with an excitation wavelength of 730 nm. Fluorescence spectra were collected and detected with a N₂ cooled Ge detector.

Figure 5.1 shows the absorption and fluorescence spectra of a dilute solution of small and large sized PbSe core QDs in TCE. The smaller PbSe QDs show excitonic emission at a maximum at 1062 nm and have a diameter of about 2 nm. The larger PbSe QDs show excitonic emission at a maximum of 1522 nm and have a diameter of about 5.2 nm. The donors (smaller PbSe QDs) emit at a shorter wavelength which overlaps with the absorption spectrum of the acceptors (larger PbSe QDs).

5.3.3 Energy Transfer between PbSe Core QD Populations with Diameters of 2 and 5.2 nm

Figure 5.2 represent typical normalized spectra of the 2 and 5.2 nm PbSe core QD mixture in solution and deposited as a solid film. The PL measurement for the solid films was performed at a 45° angle. A comparison of luminescence spectra in solution and solid films reveals an increase in the ratio of large to small dot PL intensity for solid films. The quenching of the luminescence of small PbSe QDs accompanied by enhancement of the large PbSe QDs luminescence intensity are
consistent with FRET from the small to the large PbSe QDs in the solid films. We also observed that PL spectrum for QDs in the solid film slightly redshifed relative to the PL spectrum for QDs in solution. This is due to the unavoidable size inhomogeneity between the same kinds of (“small” or “large”) PbSe QDs. The inhomogeneous size distribution is about 10% for PbSe QDs prepared in a given batch of synthesis. In a film, this size difference causes energy to be transferred from QDs emitting on the blue side of PL spectrum to the QDs emitting on the red side of PL spectrum, which leads to the overall spectrum redshift for QDs in solid films.

5.4 Energy Transfer between PbS and PbSe Core QDs

5.4.1 Experiment

PbSe core QDs were prepared using the same procedure as in section 5.3 described in chapter 3. PbS core QDs were synthesized according to the method reported by Hines et al.\textsuperscript{16} In a typical experiment, 0.22 g lead (II) oxide, 2 mL oleic acid, and 8 mL 1-octadecene were heated at 150 °C for an hour under N\textsubscript{2} flow. The reaction flask was then cooled to 90 °C and then 5 mL 0.1 M hexamethyldisilathiane (0.5 mmol) dissolved in ODE was quickly injected into the reaction flask. The color of the reaction solution turned dark almost immediately, indicating the formation of PbS QDs. The heat was removed and the flask was cooled using an ice bath. The PbS QDs were isolated by precipitation with hexane, methanol, and butanol and redissolved in TCE.
5.4.2 Optical Properties

Figure 5.3 shows the absorption and PL spectra of PbS and PbSe core QDs in TCE. PbS QDs emit at 1040 nm and have a size of about 3.2 nm\textsuperscript{17} and PbSe QDs emit at 1490 nm and have a size at about 5 nm\textsuperscript{15}. The overlapping of PbS luminescence and PbSe absorption spectrum suggests the possibility of efficient energy transfer from PbS to PbSe QDs.

5.4.3 Energy Transfer between 3.2 nm PbS and 5.0 nm PbSe Core QDs

To study energy transfer between PbSe and PbS core QDs, PL spectra were measured for a PbS-PbSe core QD mixture in solution and deposited as solid films. The solid films were prepared by drop casting the mixture onto glass substrates. Figure 5.4 shows the PL spectra of PbS-PbSe QD mixture in solution and in solid film. Energy transfer was observed from PbS to PbSe QDs according to the increase of PbS luminescence intensity with the quenching of PbSe luminescence intensity in QD solid films. After the measurement, the solid film of PbS-PbSe QD mixture was redissovled into TCE and luminescence spectrum was remeasured. Figure 5.4 shows that the PL spectrum of the mixture in TCE recovered the spectrum of the mixture in original TCE solution, which confirms that the relative PL intensity increase for PbS and decrease for PbSe QDs is not due to quantum yield changes during the experiment, but rather to the energy transfer process.
5.4.4 Film Thickness Dependent Energy Transfer Efficiency between PbS and PbSe Core QDs

To observe the change in energy transfer efficiency, solid films were prepared by both spin coating at different speeds and spin coating multilayer films. Figure 5.5 (a) reported normalized solid films fluorescence spectra with different spin speeds. Lower spin speeds provided higher energy transfer efficiencies corresponding to the relative luminescence intensity increase observed for PbSe QDs acceptor. Figure 5.5 (b) shows the normalized PL spectra change of PbS-PbSe QD mixture solid films with a different number of layers. The number of layers is defined by how many times things are put down on the substrate. A single layer sample was prepared by spin coating one drop of mixture solution onto the substrate at a spin speed of 3000 rpm for 40 seconds, subsequently the PL was measured for this sample. Another layer was spin coated on top of first layer to form a two layer film sample, followed by a PL measurement. The procedure was repeated until a film sample with 5 layers was prepared. A single layer of spin coated film did not show any obvious energy transfer when compared to the PL spectrum of the mixture in solution in 5.4. The PL spectra showed an increase in energy transfer efficiency as more layers were added to the solid film. Lowering the spin speed\(^{18}\) and depositing more layers leads to an increase in the thickness of the solid film. Regardless of the sample preparation, the critical distance \((R_0)\) remains the constant for the mixed QD samples, as calculated from equation 5-1 and 5-2. The increase in energy transfer efficiency by either decreasing the spin speed or increasing the spin coat layers indicates that the effective distance between donor and acceptor \((R_{DA})\) is reduced.
5.5 FRET Observed in Solid Film Samples between CdSe/ZnS Core/Shell QDs with Different CdSe Core Diameters

5.5.1 Experiment

CdSe/ZnS core/shell QDs were synthesized according to the published method\textsuperscript{19-21} described in detail in Chapter 2.2. Purified CdSe/ZnS core/shell QDs were stabilized by an organic (TOPO, TOP) monolayer and redispersed in hexane for further experiments. A CdSe/ZnS core/shell QD mixture with two different CdSe core diameters was prepared by combining small and large sized CdSe/ZnS core/shell QDs in their original hexane solution.

5.5.2 Optical Properties of CdSe/ZnS Core/Shell QDs

Figure 5.6 shows the optical absorption and PL spectra of two populations of CdSe/ZnS core/shell QDs with different CdSe core diameters in solution. The calculated CdSe core diameter is 3.6 and 4.6 nm for the small and large CdSe/ZnS core/shell QDs, as determined using absorption spectroscopy. The emission of smaller QDs overlaps with the absorption spectrum of the larger sized QDs. Fluorescence quantum yields of the smaller and larger QDs (after capping with ZnS) were 27\% and 10\% respectively, relative to Rhodamine 590 and Rhodamine 640, respectively. Fluorescence lifetimes were measured using a time-correlated single photon counting apparatus with excitation at 420 nm.
5.5.3 Langmuir Blodgett Films

Energy transfer experiments between a CdSe/ZnS core/shell QD mixture with CdSe core diameters of 3.6 and 4.6 nm were conducted using Langmuir-Blodgett (LB) solid films because the LB technique provides a uniform film required for energy transfer studies in microcavity devices. LB experiments were preformed using a KSV 3000 instrument. Nanopure water with a resistivity of 18.2 MΩ-cm was used for all the experiments. Glass substrates were cleaned using methanol and acetone in an ultrasonic tank and dried under a stream of nitrogen. Plasma etching was employed to clean the surface for 2 minutes to remove surface contaminants and to enhance adhesive strength.

The CdSe/ZnS core/shell QD mixture was filtered through 0.2 um filter to get rid of big aggregates and dusts prior to the LB experiments. The CdSe/ZnS QDs were dissolved in hexane at concentrations between 1 and 10 mg/mL and deposited as a thin film on the surface of water. Then, the QD films were compressed in the Langmuir trough until a close packed monolayer was formed at a surface tension of 36 mN/m, at which point the monolayer of QDs was transferred onto the glass substrate using conventional vertical dipping methods.

5.5.4 Surface Topography and Optical Properties of CdSe/ZnS Core/Shell QD LB Films

Atomic force microscopy (AFM) topographic images of LB films were obtained using a Digital Instruments Nanoscope IIIa AFM. Figure 5.7 (a) represents a typical AFM image LB films created using CdSe/ZnS QDs. The LB film did not form an ideal monolayer of QDs, possibly due to the hydrophobic TOPO capping around the
QDs; however, small QD islands with an average thickness of 10 nm were observed without the presence of any large aggregates. Absorption and PL spectra of the LB films were measured at different positions across the 2.5 cm x 7.5 cm glass slide substrate as shown in Figure 5.7 (b). The spectra show spectroscopic uniformity across the LB film with no significant difference observed in the spectra at different positions.

5.5.5 Energy Transfer in LB Films between CdSe/ZnS Core/shell QDs with CdSe Core Diameters of 3.6 and 4.6 nm

Using equation 5-1, a $R_0$ of 5 nm was calculated for optimal energy transfer between CdSe/ZnS core/shell QDs with CdSe cores of 3.6 and 4.6 nm diameter (shown in Figure 5.6). This agrees with earlier calculations for similarly sized QDs. A colloidal suspension of small and large CdSe/ZnS QDs with a molar ratio of 4:3 is used for the experiment. Using the value of $R_0$, we can estimate the expected energy transfer efficiency ($E$) according to:

$$E = \frac{mR_0^6}{(mR_0^6 + R_{DA}^6)}$$

(5.2)

where $m$ is the number of acceptors per donor ($3/4$) and $R_{DA}$ is the actual donor acceptor distance. Given the diameters of the CdSe core QDs (3.6 nm and 4.6 nm) and the thickness of the ZnS shell (0.45 nm), and assuming a separation of 1.1 nm due to the organic surface capping molecule (TOPO), we calculate 6.1 nm for $R_{DA}$ and an energy transfer efficiency of 36%. Thus, we expect the possibility of significant excitation of the larger QDs through nonradiative energy transfer from the smaller QDs.
The PL spectrum measured from a colloidal suspension of small and large CdSe/ZnS core/shell QDs with a molar ratio of 4:3 is shown in Figure 5.8 (a). Also shown in Figure 5.8 (a) is the PL from the same suspension cast into a single monolayer. Relative to the colloidal suspension, in the thin QD film the PL intensity from the smaller QDs is decreased while that from the larger QDs is increased. For comparison, the PL spectrum of a monolayer of purely large QDs is also shown in Figure 5.8 (a). This spectrum is normalized such that it represents PL from the same number of large QDs as the spectrum from the mixed QD monolayer. QDs were photoexcited with the 514 nm line from an argon ion laser. Fitting the PL data in Figure 5.8 (a) with a sum of two Gaussian functions each centered at the fluorescence maxima of the smaller and larger QDs, respectively, allows for a quantitative determination of the contribution of each sized QD to the mixed QD fluorescence spectrum and thus a determination of the relative increase in photoluminescence intensity (per large QD) in the mixed size films. We determine that the relative integrated emission is increased by a factor of 2.0±0.3 for the mixed QD film compared to the purely large QD film.

PL lifetime measurements taken at the emission maxima, which are 556 nm and 620 nm for the smaller and larger QDs, respectively, are shown in Figure 5.8 (b). The fluorescence decay for the solid films is multiexponential, as expected. The fluorescence lifetime of the small QDs is decreased in the mixed sized film relative to a monolayer of just small QDs (weighted lifetime 5.7 ns versus 16.1 ns). On the other hand, the PL lifetime of the larger QDs is increased in the mixed size monolayer,
relative to a monolayer of solely large QDs (weighted lifetime 2.1 ns versus 4.1 ns). Such an increase in the fluorescence lifetime of an acceptor and a decrease in the lifetime of a donor are consistent with a FRET process from the donor QDs to acceptor QDs.\textsuperscript{11, 23-25} Thus, we conclude that the observed increase in fluorescence intensity of the larger QDs in the mixed sized QD monolayer results from FRET processes.

5.6 Energy Transfer Observed in an Optical Microcavity between CdSe/ZnS Core/Shell QDs with Different CdSe Core Diameters

5.6.1 Microcavity

Periodic photonic structures\textsuperscript{26} can confine and enhance the electromagnetic field by orders of magnitude. Many properties have been predicted for structures such as microcavities and photonic crystals, including the ability to enhance and inhibit light emission.

In our experiments, the optical microcavity structure was formed between two distributed Bragg reflectors (DBRs) as shown in Figure 5.9. Each DBR consisted of six periods of quarter-wavelength thick alternating TiO\textsubscript{2}-SiO\textsubscript{2} layers. Rf sputtering was used to deposit the SiO\textsubscript{2} and reactive dc sputtering was used to deposit the TiO\textsubscript{2} layers. The distribution of electric field throughout a structure of a λ/2\textsubscript{n} microcavity formed between two DBRs is shown in Figure 5.9 (d).\textsuperscript{27} The intensity is strongest at
the center of the device, which suggests that the active material should be placed as close as possible to that region inside the microcavity.

To place a monolayer of QDs inside the optical cavity, Langmuir-Blodgett thin-film deposition techniques were used. Briefly, CdSe/ZnS core/shell QDs were dissolved in hexane at concentrations between 1 and 10 mg/mL and deposited as a thin film on the surface of water. Then, the QD films were compressed in the Langmuir trough until a close packed monolayer was formed at a surface tension of 36 mN/m, at which point the QD monolayer was deposited onto the substrate (consisting of a SiO₂ spacer layer and one DBR). After drying, more SiO₂ and the second DBR were deposited to complete the cavity. A reference sample consisting of a monolayer of QDs on a glass slide was similarly prepared but capped with a layer of 75-nm thick SiO₂. A typical transmission spectrum of microcavity with QDs is shown in Figure 5.9 (c) with a cavity mode at ~620 nm (FWHM: ~ 4 nm).

5.6.2 CdSe/ZnS Core/Shell QDs in an Optical Microcavity.

Most demonstrations of enhancement and inhibition of spontaneous emission rely on the construction of the photonic structure on the substrate of the active layer itself, which limits the application to a specific set of materials. Examples include self-assembled QDs in photonic crystals, single QDs embedded in pillar microcavities and epitaxially grown quantum wells in planar microcavities. In the case of self-assembled QDs, the nature of the growth technique also makes it difficult to control the number of QDs interacting with the optical field. Here, we will study
CdSe colloidal QDs in a microcavity formed between two distributed Bragg reflectors (DBRs).

The diagram of the fluorometer used for the fluorescence measurement is shown in Figure 5.10. The 514 nm line of an argon laser is used as the excitation source. Figure 5.10 also shows the fluorescence spectrum for a monolayer of large QDs (blue spectra in Figure 5.6) inside the 1-D optical microcavity when their free space fluorescence maximum is in resonance with the cavity mode. Also shown is the fluorescence spectrum from the corresponding reference sample. The spectrally integrated fluorescence in the forward direction (numerical aperture = 0.2) from the QDs in the cavity is enhanced by a factor of $4.8 \pm 0.6$ compared to the reference sample. The full width at half maximum (FWHM) of the QD fluorescence spectrum narrows considerably from 33 nm to 5.5 nm for the QDs inside the microcavity. This narrow luminescence line width is also very close to the FWHM of the cavity mode (4 nm) as measured with transmission spectroscopy, and is due to coupling between the cavity mode and the QD emission.$^5$

Previously, it was observed that in addition to emission from the cavity mode, a weaker background emission was present that corresponded to the free-space fluorescence spectrum from NCs not coupled to the cavity mode.$^5$ As seen in Figure 5.10, this background has been totally eliminated due to the more uniform deposition process afforded by LB methods relative to a simple spin casting of the colloidal suspension.
5.6.3 Energy Transfer between CdSe/ZnS Core/Shell QDs in an Optical Microcavity.

Figure 5.11 also shows the fluorescence spectrum of a thin film monolayer made using a CdSe/ZnS core/shell QD mixture with CdSe core diameters of 3.6 and 4.6 nm consisting of a 4:3 molar ratio of small to large QDs (shown in Figure 5.6) inside the 1-D optical microcavity, where the free space fluorescence maximum of the larger QDs (620 nm) is tuned in resonance with the cavity mode. For comparison, this spectrum is normalized such that it represents fluorescence from the same number of large QDs as would be present in a monolayer of only large QDs. On a per QD basis, the spectrally integrated fluorescence for the mixed QD film is more intense by a factor of $2.7^{+0.4}$ compared to the film consisting of purely large QDs. The increase in the cavity-mode emission arising from the large QDs in the mixed QD layer is clearly due to energy transfer from the smaller QDs to the larger QDs. The increase in fluorescence intensity from placing QDs in the cavity (4.8 fold) combined with the increase in intensity seen due to energy transfer (2.7 fold) results in an overall factor of 13 increase in fluorescence intensity for the mixed QD monolayer inside the microcavity compared to a monolayer of purely large QDs in free space. Also note that we observed no fluorescence from the smaller QDs (fluorescence spectrum in Figure 5.6) when the cavity mode is not resonant with the smaller QD fluorescence spectrum (Figure 5.11). Thus, the smaller QDs are also completely coupled to the cavity.

Another interesting effect that can be observed is the shift to higher energy of the cavity’s resonance mode as the collection angle is increased.$^{27}$ The angle is
measured with respect to the normal of the surface of the sample. Figure 5.12 shows this change in the cavity’s resonance position as a function of the collection angle. Calculations of the angle dependence of the transmission give excellent agreement with the experimental results. In our experiments the fluorescence is collected at the normal direction of sample surface, and the half angle of the cone of light that enters the lens is 11°. Therefore, the fluorescence intensity enhancement we observed in the microcavity is in the forward direction.

The microcavity greatly increases the overall fluorescence from the larger QDs in several ways. First, as was demonstrated in Ref. 9, the enhanced electric field inside the cavity causes an increase in overall QD absorption. In particular, the increase in absorption by the smaller QDs causes a direct increase in emission by the larger QDs due to energy transfer. Second, the increased electric field inside the cavity also causes an intensity increase in the fluorescence from the larger QDs even with no smaller QDs present. Third, the smaller QDs are prevented from radiating into cavity modes that are directed perpendicular to the cavity, although we expect that the smaller QDs can radiate into modes emitting out the sides of the cavity.

The integrated emission enhancement ($\frac{\Gamma}{\Gamma_0}$) in a 1D cavity is given by:

$$\frac{\Gamma}{\Gamma_0} = \frac{2F}{\sqrt{2\pi}} \xi$$

(5-3)

where the finesse $F = \lambda_0 Q/(2 \pi d)$ ($d = 310$ nm is the cavity length) and $\xi = |E_{dots}|^2 / |E_{max}|^2$. For the case of the cavity in resonance with the peak in the fluorescence spectrum of the large QDs, the quality factor $Q$ in $F$ is given by $\lambda_0/\Delta\lambda_{PL} = 20$, since
\[ \Delta \lambda_{\text{PL}} \gg \Delta \lambda_{\text{cav}} \] (\( \Delta \lambda_{\text{PL}} \) is the QD photoluminescence line width and \( \Delta \lambda_{\text{cav}} \) is the cavity mode line width). The enhancement factor \( \xi \) corresponds to the ratio of the intensity of the optical field at the QD layer to the peak value of that intensity in the cavity region. We assume \( \xi \sim 1 \) since the monolayer of QDs is deposited in the center of the cavity, exactly where the field intensity is maximum, and thus calculate an expected value for the luminescence enhancement \( \Gamma/\Gamma_0 = 10.9 \). Including energy transfer processes but neglecting the effect of the cavity on the energy transfer rate adds an additional factor of \( \sim 2 \) (Figure 5.8 (a)) for a total enhancement per QD of 22, which reasonably agrees with the measured value of 13. The major contribution to the difference between the measured and calculated enhancement likely lies in our assumption of \( \xi \sim 1 \), since the QD monolayer is probably not in the exact center of the cavity. An additional contribution may come from the fact that for emitters with very high (unit) QY, the enhancement due to the microcavity is predicted to be relatively independent of the local optical mode density.\(^{33}\) In this case, we would expect a lower experimental value than what is calculated based on a simple comparison of the optical mode densities of the microcavity and the reference.

### 5.7 Concluson

In summary, we have studied energy transfer between a mixture of PbSe core QDs with different diameters and a PbS-PbSe core QD mixture. Enhanced energy transfer efficiency was obtained by studying PL spectra of mixed PbS-PbSe QDs in spin coated films with lower spin speed and more spin coated layers, which is due to
the decreased effective donor acceptor distance. We also studied the PL of colloidal semiconductor QDs embedded inside a SiO$_2$–TiO$_2$ microcavity structure. When the cavity mode is in resonance with the PL maxima of the QDs, we measure a spectrally integrated PL enhancement of 4.8.

Furthermore, we have measured the optical emission characteristics from a microcavity containing a monolayer of two distinct semiconductor QD sizes. The fluorescence intensity from the larger (acceptor) QDs in the monolayer is enhanced by over a factor of 13 (per QD) compared with a monolayer of purely large QDs in free space. This substantial fluorescence intensity enhancement arises from both an increase in the electric field inside the optical cavity and from significant energy transfer to the larger QDs from the smaller QDs. In addition to the considerable fluorescence enhancement seen in the larger QDs, it is significant to note that the fluorescence from the smaller QDs is completely quenched. Thus, the output from the optical cavity is spectrally very pure. The understanding of and the ability to manipulate energy transfer between QDs inside of optical cavities will positively impact future applications in nanophotonics.
5.8 Figures Captions

**Figure 5.1** Absorption (dashed) and PL (solid) spectra of 2 (blue) and 5.4 nm (red) PbSe core QDs. The vertical line at 1062 nm highlights the overlap between the 2 nm PbSe QD donor emission and 5.4 nm PbSe QD acceptor absorption which is necessary for FRET.

**Figure 5.2** The PL spectra of a 2 and 5.2 nm PbSe core QD mixture in TCE (black) and dried into a thin film (red).

**Figure 5.3** Absorption (dashed) and PL (solid) spectra of PbS (blue) and PbSe (red) QDs used for the energy transfer experiments. The vertical line at 1040 nm highlights the overlap between the PbS QD donor emission and PbSe QD acceptor absorption which is necessary for FRET.

**Figure 5.4** PL spectra of PbS/PbSe QD mixture in TCE (black), of PbS/PbSe QD mixture dried into a thin film (red), and of the redissolved QDs from the thin film into TCE (green).

**Figure 5.5** Energy transfer between PbS and PbSe QDs with different efficiencies (a) PL spectra of PbS-PbSe QD mixture thin film samples spin-coated at different spin speeds (in rpm). (b) PL spectra of PbS-PbSe QD mixture thin films spin coated with
one (black), two (red), three (green), four (blue), and five layers (light blue). All spectra are normalized to the emission wavelength maximum of the PbS core QD donors.

**Figure 5.6** Absorption (dashed) and emission (solid) spectra of CdSe/ZnS core/shell QDs with a CdSe core diameter of 3.6 (blue) and 4.6 nm (red). The vertical line at ~560 nm highlights the overlap between the donor emission and acceptor absorption, which is necessary for FRET.

**Figure 5.7** Surface and optical properties of LB films created using CdSe/ZnS core/shell QDs. (a) Typical AFM image of a LB film. (b) Absorption (dashed) and PL (solid) spectra of LB film using a CdSe/ZnS core/shell QD mixture at different positions across the film surface.

**Figure 5.8** Energy transfer between CdSe/ZnS core/shell QDs with a CdSe core diameter of 3.6 and 4.6 nm in LB films. (a) PL spectra in free space from: a colloidal suspension of mixed-sized QDs (black line), a single monolayer of mixed sized QDs (open circles), and a monolayer of large QDs (filled circles). The red and blue dashed lines are Gaussian fits indicating the contributions of each sized QD to the mixed and large QD fluorescence spectra, respectively. (b) Fluorescence decay measured at 556 nm of the smaller QDs in: a monolayer of small QDs (black solid line), and a
monolayer of mixed sized QDs (black dashed line). Fluorescence decay measured at
620 nm of the larger QDs in: a monolayer of large QDs (red dashed line), and a
monolayer of mixed sized QDs (red solid line).

Figure 5.9 (a) Schematic of the microcavity device formed by sandwiching a LB QD
film between two distributed Bragg reflectors. (b) Cross section of the microcavity
device showing the alternating TiO$_2$ and SiO$_2$ layers of the Bragg reflectors. (c)
Transmission spectrum of microcavity with cavity mode at ~ 620 nm with QDs
embedded in the middle. (d) The electric field intensity throughout the microcavity.
The light grey regions (TiO$_2$) represent a material with higher index of refraction than
the dark grey regions (SiO$_2$).

Figure 5.10 Top image: block diagram of the fluorometer used to measure
microcavity fluorescence. Bottom image: normalized fluorescence spectra measured
from a monolayer of 4.6 nm CdSe core diameter CdSe/ZnS core/shell QDs in free
space (open circles) and in the optical cavity (solid line). The spectrum representing
the monolayer in free space is scaled by a factor of 10.

Figure 5.11 Normalized fluorescence spectra measured from monolayers of
CdSe/ZnS core/shell QDs in an optical microcavity. The solid and dashed lines
correspond to a monolayer of large QDs in the optical cavity and mixed sized QDs in
the optical cavity, respectively. The spectrum of the large QD monolayer in the
microcavity is scaled by a factor of 3. Inset shows the comparison of normalized fluorescence spectra corresponding to a monolayer of large QDs in free space, large QDs in the optical cavity, and mixed sized QDs in the optical cavity, respectively.

Figure 5.12 Position of the cavity’s resonance as a function of the collection angle. The squares show the experimental measurements, the triangles represent the transfer matrix method simulations, and the dashed line is a calculation from reference.27
5.9 Figures

Figure 5.1

![Graph showing absorbance and fluorescence over wavelength (nm).](image)
Figure 5.2

[Graph showing fluorescence intensity against wavelength]
Figure 5.3
Figure 5.6
Figure 5.7
Figure 5.8

(a) Intensity (arb. units) vs. wavelength (nm)

(b) Intensity (arb. units) vs. Time (ns)
Figure 5.9
Figure 5.11
Figure 5.12
5.10 Reference


(27) Poitras, C; Dissertation titled “Light emitting materials and control of their emission properties for applications in integrated optics”, 2006.


Chapter 6: Conclusions

6.1 Summary

In this thesis we reported synthesis and characterization of colloidal luminescent semiconductor quantum dots (QDs), which have become of great interest for both fundamental research and industrial development in recent years. We studied the shell material distribution around core QDs in chapter 2; the synthesis and biological application of PbSe magic sized clusters were discussed in chapter 3; a method of capping PbSe QDs was reported in chapter 4; the study of energy transfer between QDs in free space and in optical microcavity was presented in chapter 5.

In chapter 2, CdSe and CdSe/ZnS, core and core/shell QDs, were prepared. The capping of CdSe QDs with a ZnS shell improves PL QY by a factor of 10 due to a better surface passivation by reducing surface dangling bonds. Using EELS to study the shell distribution around the core has shown that growth of a simple shell of ZnS on the surface of a CdSe core QD will not lead to a complete and uniform spherical shell, although it does improve the optical properties considerably. The anisotropic growth of the ZnS shell on the CdSe core may reflect the large difference in lattice constant between the core and shell materials. Another explanation for the anisotropy is the anisotropic chemical reactivity on various faces of the core.

Colloidal IV–VI lead chalcogenide, especially lead selenide, quantum dots have also received much attention in recent years owing to their size-dependent electronic and optical properties in the infrared. During the synthesis of regular sized
PbSe QDs, small PbSe magic sized clusters (MSCs) were found to exist as well. These clusters can be separated from regular-sized QDs with careful size selective precipitation. Pure magic sized PbSe clusters were prepared at low reaction temperatures, producing a well-defined exciton absorption peak, emission at ~900 nm, and a remarkable high photoluminescence QY, typically >50%. PbSe MSCs emit within the biological window (between 700 to 1000 nm), where the absorption by biological fluids was reduced and organic dyes emit poorly.\(^1\) Thus, magic sized PbSe quantum dots clusters have enormous potential to be superior fluorophores for biological imaging applications at these near infrared (NIR) wavelengths. An average hydrodynamic radius of \(2.4 \pm 0.6\ \text{nm}\) was measured for the (1-mercaptoundec-11-yl)tetra(ethylene glycol) -solubilized PbSe MSCs by dynamic light scattering. Such a small QD diameter is very significant, as these highly fluorescent MSCs are potentially small enough to be transported through the cell membrane or into the nucleus through carrier-mediated mechanisms.

The significant increase of scientific and technological interest in PbSe QDs stimulates development of synthesizing high quality PbSe core shell QDs. Highly fluorescent PbSe/SrSe core/shell QDs were prepared via a two-step process. Energy dispersive x-ray (EDX) spectra from a dense cluster of purified PbSe/SrSe core/shell QDs shows strong Sr signal, in addition to lead and selenium signals, indicating the presence of Sr around the PbSe core. The photoluminescence spectra of these core/shell QDs also show a significant blue shift when comparing to the PbSe core QDs indicating the etching of PbSe core QDs. Previous investigations performed on
PbSe QDs have shown evidence for the important roles of O\textsubscript{2} on the PL spectrum blueshift of lead calcogenide QDs in thin films\textsuperscript{2,3}. Our studies showed that oleic acid, octadecene, and O\textsubscript{2} all played a role in the PbSe QD PL spectrum blueshift in solution?.

The use of inter-QD energy transfer to enhance the performance of integrated QD-photonic systems is expected to take on increasing importance in a similar manner to what has taken place for all-organic devices\textsuperscript{4}. In chapter 5, we studied energy transfer between different sized PbSe-PbSe QDs and PbS-PbSe QDs by studying photoluminescence spectra of donor acceptor mixture of QDs in solution and solid films. A comparison of luminescence spectra in solution and solid films reveals an increase in the ratio of large to small dot photoluminescence intensity for solid films. The quenching of the luminescence of small PbSe (PbS) QDs accompanied by enhancement of the large PbSe QDs luminescence intensity are consistent with fluorescence resonance energy transfer from small PbSe (PbS) QDs to the large PbSe QDs in the mixed solid films. Enhanced energy transfer efficiency was obtained by studying PL spectra of mixed PbS/PbSe QDs in spun coated films with lower spin speed and more spun coated layers, which is due to the decreased effective donor acceptor distance.

In chapter 5, we also present the study of CdSe/ZnS colloidal QDs in a Fabry-Perot (1-D) microcavity formed between two distributed Bragg reflectors (DBRs) and studies of energy transfer between semiconductor QDs placed in microcavities. The fluorescence intensity from the larger (acceptor) QDs in the monolayer is enhanced
by over a factor of 13 (per QD) compared with a monolayer of purely large QDs in
free space. This substantial fluorescence intensity enhancement arises from both an
increase in the electric field inside the optical cavity (4.8) and from significant energy
transfer to the larger QDs from the smaller QDs (2.7). In addition to the considerable
fluorescence enhancement seen in the larger QDs, it is significant to note that the
fluorescence from the smaller QDs is completely quenched. Thus, the output from
the optical cavity is spectrally very pure. The understanding of and the ability to
manipulate energy transfer between QDs inside of optical cavities will positively
impact future applications in nanophotonics.

6.2 Future Studies

Future studies to complete the understanding of the shell material distribution
around CdSe core QDs includes trying shell material with smaller lattice mismatch
comparing with the core material, such as CdS and ZnSe, followed by applying EELS
measurements on these core shell QDs to measure the shell material distribution to
decide if such shells are more uniform. Further studies about PbSe MSCs are
important as well. Various PbSe clusters family with different magic sizes could
exist as reported in CdSe QD system, where various families of CdSe MSCs were
observed. And the application of these PbSe MSCs in biology is worth further
exploration due to their high QY, small hydrodynamic diameters, and optical stability.
Studies using SrSe material to coat PbSe core QDs is also of great interest in both
fundamental synthesis and potential applications. As we reported in this thesis, we
believe SrSe exists on the shell of PbSe QDs; however, the growth of a SrSe shell with significant thickness was not observed. Using different reaction chemicals, different precursors, and different reaction conditions can possibly lead to better shelling experiment results.
6.3 References


