CHARGE SEPARATION IN HETEROSTRUCTURED SEMICONDUCTOR NANOCRYSTALS.

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ABSTRACT

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Hybrid semiconductor nanocrystals (NCs) consisting of separate donor-acceptor domains are viewed as promising candidates for increasing the efficiency in present-day photovoltaic and photocatalytic applications. Properties of colloidal heterostructured nanocrystals are largely determined by the spatial distribution of photogenerated carriers across the junction of semiconductor materials that form the heterostructure. The two known types of carrier distributions are identified based on whether both carriers reside within the same (type I) or opposite (type II) sides of the heterojunction. Herein, we report on organometallic synthesis of semiconductor heterostructured nanocrystals (nanorods, core/shell nanocrystals, Alloy nanocrystals and nanobarbells) that produce a number of unique properties including enhanced magnitude of quantum confined Stark effect, efficient spatial separation of carriers in between acceptor and donor, and subnanosecond switching of absorption energies that can find practical applications in electroabsorption switches, solar cell and ultrasensitive charge detectors.
To my family: wife, Erandi; father, Simon and mother, Banduwathi; for their encouragement, motivation, and support given throughout my entire life.
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CHAPTER 1
INTRODUCTION

1.1 Background

A quantum dot is a semiconductor whose excitons are confined in all three spatial dimensions. As a result, they have properties that are between those of bulk semiconductors and those of discrete molecules\(^1\).

Researchers have used quantum dots in diodes, transistors, solar cells, LEDs, and diode lasers because, they have longer life time, better charge separation, extensive absorption and different band gap devices are produced using same material (tunable geometry of the semiconductor-metal), without difficulty. Quantum dots have been investigated as agents for medical imaging, bio-labeling and live cell imaging because, they are soluble in water and have longer life time.

Semiconductors are one of the major factors of modern technology. In view of the fact that the properties of semiconductors can be manipulated easily, they are widely used in electronic devices. Modern electronic devices require faster, more accurate, and smaller devices, with a low operating power consumption. As a result, one of the most rapidly expanding fields of research is the synthesis and study of electronic, physical and optical properties of semiconductors.

There are several ways to confine excitons in semiconductors, resulting from different methods of fabricating quantum nanocrystals. In general, quantum rods, barbells and dots are grown by advanced epitaxial techniques in nanocrystals produced, by chemical methods, by ion
implantation, by etching or by state-of-the-art lithographic techniques. We use colloidal synthesis to fabricate semiconductor nanocrystals.

1.1.1 Colloidal synthesis

Colloidal semiconductor quantum dots are synthesized from precursor compounds dissolved in solution, as conventional chemical processes. This colloidal synthesis is based on precursors, organic surfactants, and solvents. When heating a reaction mixture to a sufficiently high temperature, the precursors chemically transform into monomers, and when these monomers reach a high enough supersaturation level, the nanocrystal growth starts with a nucleation process. Temperature and correct monomer concentration are critical factors in determining optimal conditions for nanocrystal growth.

1.1.2 Semiconductor band structure

Semiconductor heterostructured nanocrystals can be divided into two major groups, type-I and type-II. Upon excitation, when the electron and hole stay in same material, the semiconductor is called a type-I material. On the other hand, when the excited electron and hole stay in different materials (hole stays in one material and electron stays in another material), the semiconductor is called a type-II material. Many devices, such as electronic components and solar cells are based on the optical properties of semiconductors. Band gap energy represents the relation between the electron energy and the electron wave vector. Electrons in semiconductors have an energy of the form \( \frac{\hbar^2 k^2}{2m} \), where \( \hbar \) is Planck's constant divided by \( 2\pi \), \( m \) is electron mass, and \( k \) is wave vector.
Figure 1.1 - Semiconductor nanocrystals band structure.

Figure 1.2 - Fluorescence in a bulk semiconductor. Upon excitation, an electron moves to the lowest energy level in the conduction band and the hole moves to the highest energy level in the valence band. After recombination of the electron and the hole, fluorescence occurs.
The electron energy (E) as a function of wave vector (k) has a parabolic shape and the highest completely filled valance band of the semiconductor is separated from the lowest completely empty conduction band by an energy gap or band gap, as in Figure 1.1 and Figure 1.2.

For semiconductor nanocrystals, this band gap energy (E) is typically $0 < E < 6.0 \text{ eV}$ (Band gap energies of a few semiconductor materials are shown in Figure 1.3). Semiconductor nanocrystals can be divided into three groups according to their band gap energies. They are:

- $0 < E < 0.5 \text{ eV}$, narrow band gap semiconductors
- $0.5 \text{ eV} < E < 2.0 \text{ eV}$, standard semiconductors
- $2.0 \text{ eV} < E < 6.0 \text{ eV}$, wide band gap semiconductors

Figure 1.3 - Band gaps of several semiconductors.
Also semiconductor nanocrystals can be classified as direct band gap semiconductors and indirect band gap semiconductors. A direct band gap semiconductor, the local maximum energy in the valence band and the local minimum energy in the conduction band, both occur at the origin of the \( k \) space (Figure 1.1). Therefore, in this type of semiconductor, both the energy and the momentum are conserved. By contrast, in an indirect band gap semiconductor, the conduction band minimum is shifted by a \( k \) vector (Figure 1.4) relative to the valence band maximum resulting in non-conservation of momentum.

Figure 1.4 - Indirect band gap semiconductor nanocrystals.

### 1.2 Nanocrystal Devices

Many modern electronic devices, such as LEDs, solar cells, photo detectors, transistors, and memory elements, are based on quantum dot nanocrystals (NC).
1.2.1 Light-Emitting Devices

Heterostructured NCs have been explored as the emitters for light-emitting diodes (LEDs). LEDs utilizing CdSe colloidal NCs were first reported by Colvin et al. in 1994\(^2\). Performance of NC based LEDs (Quantum Dot (QD)-LEDs) has remarkably improved over the past decade. In a typical LED, a thin layer of light-emitting heterostructured NCs, for example, CdSe/CdS core-shells or CdSe (Figure 1.5 and Table 1.1) are sandwiched between the electron transport layer (ETL) and hole transport layer (HTL), which provide injection of carriers into the NCs through the ETL and HTL layers (Figure 1.5). These NC based LEDs have lower operation power, tunability of emission color from UV to near-IR, longer lifetime and higher emission than other LEDs.

![Figure 1.5 - Structure of a LED utilizing semiconductor QDs\(^3\).](image)

Scientists investigated different types of quantum dot semiconductor materials to develop QD-LEDs (Table 1.1).
Table 1.1 - Device structure and luminance ($L_v$) of reported quantum dot LEDs.

<table>
<thead>
<tr>
<th>QD material</th>
<th>device structure</th>
<th>$L_v$ (cd/m²)</th>
<th>EL color</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe</td>
<td>ITO/QDs/PPV/Mg</td>
<td>600</td>
<td>green to red</td>
</tr>
<tr>
<td>CdSe/CdS</td>
<td>ITO/PPV/QDs/Mg/Ag</td>
<td>2000</td>
<td>green to red</td>
</tr>
<tr>
<td>CdSe/ZnS</td>
<td>ITO/TPD/QDs/Alq3/Mg:Ag</td>
<td>7000</td>
<td>red</td>
</tr>
<tr>
<td>CdSe/ZnS</td>
<td>ITO/TPD/QD(monomer)/Alq3/Mg:Ag/mQD/TPBi/Ag</td>
<td>100</td>
<td>green</td>
</tr>
<tr>
<td>CdSe/CdS/ZnS</td>
<td>ITO/PS-TPD-PFCA/mQD/TPBi/Ag</td>
<td>1000 (max)</td>
<td>red</td>
</tr>
<tr>
<td>CdSe/CdS</td>
<td>ITO/PEDOT/poly-TPD-QD/Alq3/Ca/Al</td>
<td>9064</td>
<td>red</td>
</tr>
<tr>
<td>CdSe/CdS/ZnS</td>
<td>ITO/PEDOT/poly-TPD-QD/Alq3/Ca/Al</td>
<td>3200</td>
<td>orange</td>
</tr>
<tr>
<td>ZnCdSe</td>
<td>ITO/NiO/QDs/ZnO:SnO2/Ag</td>
<td>4470</td>
<td>yellow</td>
</tr>
<tr>
<td>CdSe/ZnS</td>
<td>ITO/NiO/QDs/Alq3/Mg:Ag</td>
<td>3700</td>
<td>green</td>
</tr>
<tr>
<td>CdSe/ZnS</td>
<td>ITO/PEDOT/PFPE/MEH/QDs/Alq3/Ca/Al</td>
<td>1950</td>
<td>red</td>
</tr>
<tr>
<td>CdSe/ZnS</td>
<td>ITO/PEDOT/PFMEH/QDs/Alq3/Ca/Al</td>
<td>3000</td>
<td>white</td>
</tr>
<tr>
<td>CdSe/ZnS</td>
<td>ITO/PEDOT:PSS/TPD/QD(monomer)TAZ/Alq3/Mg:Ag</td>
<td>100</td>
<td>white</td>
</tr>
<tr>
<td>CdSe/ZnS</td>
<td>Saphire/p-GaN/QDs/m-GaN/In</td>
<td>15</td>
<td>blue</td>
</tr>
<tr>
<td>ZnCdS</td>
<td>ITO/PEDOT:PSS/spiroTPD/TPB/Ag/Ag</td>
<td>28</td>
<td>green</td>
</tr>
<tr>
<td>ZnCdS</td>
<td>ITO/PEDOT/PSS/spiroTPD/TPB/Ag/Ag</td>
<td>7</td>
<td>red</td>
</tr>
<tr>
<td>CdSe/ZnS</td>
<td>ITO/PEDOT/PSS/TFB/Ag</td>
<td>13</td>
<td>orange</td>
</tr>
<tr>
<td>CdSe/CdS/ZnS</td>
<td>ITO/PEDOT/PSS/TFB/Ag</td>
<td>12380</td>
<td>red</td>
</tr>
</tbody>
</table>

Abbreviations: PPV (poly(p-phenylenevinylene)), TPD (N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine), TAZ (3-(4-biphenylyl)-4-phenyl-5-t-butylphenyl-1,2,4-triazole), Alq3 (tris(8-hydroxyquinoline) aluminum), TPBI (1,3,5-tri(N-phenylbenzimidazol-2-yl)benzene), HTL (hole transport layer), ETL (electron transport layer), HBL (hole blocking layer), TPBi (2,2',2''-(1,3,5-benzenetriyl)-tris(L-phenyl-1H-benzimidazole), spiroTPD (spiro-N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine), TFB (poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-sec-butylphenyl)) diphenylamine)], CBP (4,4'-N,N'-dicarbazolyl-biphenyl).

### 1.2.2 Photodetectors

Nanocrystal based photodetectors change their electrical conductivity under illumination of light due to the generation of additional mobile charge carriers. These photodetectors have higher sensitivity, less internal noise current, shorter response time and lower frequency operation than other photodetectors. Structure of a photodetector is depicted in Figure 1.6.
Figure 1.6 - (a) Structure of a thin film photoconductive photodetector. (b) Photodetector geometry that is typically used for NC-based devices\(^3\). Au is used as a metal contact material.

1.2.3 Nanocrystals in Solar Cells

The intensifying demand for renewable energy requires significant effort to be invested in the development of efficient and inexpensive photovoltaic materials. As a result, scientists have developed new generation solar cells (Intermediate-band gap solar cell shown in Figure 1.7 and Figure 1.8) using quantum dot semiconductors, which is approximately two times more efficient and cheaper and lighter than any state-of-the-art devices available today.

Figure 1.7 - A sketch of a quantum dot synthesis solar cell\(^3\).
Following the absorption of photons by the nanocrystal-sensitized solar cell (Figure 1.8), the photogenerated electrons are injected into ITO (Indium tin oxide) through TiO$_2$ nanocrystals and collected by the external circuit. Subsequently, positively charged holes are collected into platinum (Pt) counter electrode electrochemically by redox of electrolytes.

![Schematics of the structure (top) and energy diagram (bottom) of a nanocrystal-sensitized solar cell](image)

Figure 1.8 - Schematics of the structure (top) and energy diagram (bottom) of a nanocrystal-sensitized solar cell$^3$.

Researchers have developed quantum dot based solar cells using different types of quantum dot semiconductor materials. Same solar cell materials and their properties are shown below (Table 1.2).
Table 1.2 - Nanocrystal-based photovoltaic devices and devices properties\(^3\).

<table>
<thead>
<tr>
<th>NC materials</th>
<th>active layer design, electrodes</th>
<th>(I_{SC}) (mA/cm(^2))</th>
<th>(V_{OC}) (V)</th>
<th>(\eta)%</th>
<th>(FF)</th>
<th>(\eta), illumination</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe NCs/P3HT</td>
<td>Al/BH/PEDOT:PSS/ITO</td>
<td>5.7</td>
<td>0.7</td>
<td>0.4</td>
<td>1.7%</td>
<td>(AM1.5)</td>
</tr>
<tr>
<td>CdSe NCs/PPV</td>
<td>Al/BH/PEDOT:PSS/ITO</td>
<td>7.3</td>
<td>0.65</td>
<td>0.35</td>
<td>1.8%</td>
<td>(AM1.5)</td>
</tr>
<tr>
<td>CdSe NCs, CdTe NCs</td>
<td>Ca/CdTe-CdSe/ITO</td>
<td>13.2</td>
<td>0.45</td>
<td>0.49</td>
<td>2.9%</td>
<td>(AM1.5)</td>
</tr>
<tr>
<td>HgTe NCs/P3HT</td>
<td>Au/BH/TiO(_2)/ITO</td>
<td>2</td>
<td>0.4</td>
<td>0.5</td>
<td>0.4%</td>
<td>(AM1.5)</td>
</tr>
<tr>
<td>PbS NCs</td>
<td>Au/P3HT/PbS/ITO</td>
<td>0.13</td>
<td>0.4</td>
<td>0.38</td>
<td>0.02%</td>
<td>(AM1.5)</td>
</tr>
<tr>
<td>CdSe hyperbranched NCs/P3HT</td>
<td>Al/BH/ITO</td>
<td>3.5</td>
<td>0.4</td>
<td>0.55</td>
<td>2.2%</td>
<td>(AM1.5)</td>
</tr>
<tr>
<td>CdSe NCs</td>
<td>NNSC, Co(II)/Co(III) redox</td>
<td>5.15</td>
<td>0.6</td>
<td>0.6</td>
<td>1%</td>
<td>(AM1.5)</td>
</tr>
<tr>
<td>CuInS(_2) NCs, CdS NCs</td>
<td>Al/CdS/CuInS(_2)/PEDOT:PSS/ITO</td>
<td>5.63</td>
<td>0.6</td>
<td>0.47</td>
<td>1.6%</td>
<td>(AM1.5)</td>
</tr>
<tr>
<td>CuInSe(_2) NCs</td>
<td>Glass/Mo/ CuInSe(_2)/CdS/ZnO/ITO</td>
<td>25.8</td>
<td>0.28</td>
<td>0.39</td>
<td>2.82%</td>
<td>(AM1.5)</td>
</tr>
<tr>
<td>PbSe NCs</td>
<td>Mg/PbSe/ITO</td>
<td>17</td>
<td>0.23</td>
<td>1.1%</td>
<td>(AM1.5)</td>
<td></td>
</tr>
<tr>
<td>PbSe NCs</td>
<td>Al/Ca/PbSe/ITO</td>
<td>24.5</td>
<td>0.24</td>
<td>0.41</td>
<td>2.1%</td>
<td>(AM1.5)</td>
</tr>
<tr>
<td>PbS NCs</td>
<td>Al/PbS/ITO</td>
<td>12.3</td>
<td>0.33</td>
<td>0.49</td>
<td>1.8%</td>
<td>(AM1.5)</td>
</tr>
<tr>
<td>PbS NCs/Si</td>
<td>Al/a-Si/PbS/ITO</td>
<td>9</td>
<td>0.2</td>
<td>0.39</td>
<td>0.7%</td>
<td>(AM1.5)</td>
</tr>
<tr>
<td>PbSe(_2),(_3)-S NCs</td>
<td>Al/PbSe(_2)/S-S/ITO</td>
<td>14.8</td>
<td>0.45</td>
<td>0.5</td>
<td>3.3%</td>
<td>(AM1.5)</td>
</tr>
<tr>
<td>Cu(_2)ZnSnS(_4) NCs</td>
<td>Glass/Al/Cu(_2)ZnSnS(_4)/CdS/ZnO/ITO</td>
<td>1.95</td>
<td>0.321</td>
<td>0.37</td>
<td>0.23%</td>
<td>(AM1.5)</td>
</tr>
</tbody>
</table>

\(I_{SC}\) (short-circuit current), \(V_{OC}\) (open-circuit voltage), \(\eta\)% (power conversion efficiency), \(FF\) (fill factor).

### 1.2.4 Field-Effect Transistors (FETs)

![Structure of nanocrystal based field-effect transistor (FET). (a) Bottom-gated FET, (b) top-gated FET. Terminals are gate (G), drain (D), and source (S). Au is used as a metal contact material.](image)

\(~ 10 ~\)
The first inorganic material based field-effect transistor (FET) fabricated using colloidal semiconductor nanoparticles was reported in 1999 by Jacobson et al. These devices were assembled from pyridine-capped CdSe quantum dot NCs, in addition quantum dot synthesized FET (Figure 1.9) have faster response time and higher break down voltage than other FETs.

1.2.5 Memory Elements

Memory elements are the integral part of computers, ID cards, phones, and various consumer electronics from satellites to toys. Three leading technologies used today are the dynamic random access memory (DRAM), hard-disk drives (HDDs), and flash memory.

![Diagram of floating gate memory devices](image)

Figure 1.10 – Basic configurations of floating gate memory devices. (a) Conventional nonvolatile flash memory. (b) Nanocrystal nonvolatile flash memory. (c) Operation mechanism of flash memory: write, store, and erase conditions.

In addition, many other memory devices are currently under active development.

Applications of these memory elements (figure 1.10) include high data density, high writing and
erasing speeds, long retention time, longer number of erase-rewrite cycles, low power consumption, and low cost per bit of stored information. Each memory cell of quantum dot synthesis memory elements is represented by the metal–oxide-semiconductor-field-effect-transistor (MOSFET) with a modified gate stack structure.
CHAPTER 2

RADIATIVE RECOMBINATION OF SPATIALLY EXTENDED EXCITONS IN (ZnSe/CdS)/CdS HETEROSTRUCTURED NANORODS.

2.1 Introduction

Synthesis of colloidal heterostructured nanocrystals (NCs) or nanorods (NRs) offers an effective route for the integration of multiple nanostructures with different functionalities into a single nanoscale object without the use of organic linkers, setting the basis for the development of a new generation of optoelectronic devices. Over the years, research on hetero-NCs has evolved from the synthesis of spherical core/shell quantum dots\textsuperscript{6-13} to more complex shapes, including branched tetrapods\textsuperscript{14-16}, barbells\textsuperscript{17-19}, and hyper-branched heterostructures\textsuperscript{20, 21}, where the use of band-gap engineering has provided additional means to control the spatial distribution of charge across material junctions. Recently, a great deal of such synthetic work has been focused on the development of so-called type II hetero-NCs or NRs, constructed from two materials for which both the valance and conduction bands of one component lie lower in energy than the corresponding bands of the other component. The resulting staggered alignment of band edges at the material interface leads to spatial separation of the electrons and holes in different parts of the heterostructure. In spatially asymmetric nanostructures, such a separation of charges can be near by complete, which gives rise to unique optical properties associated with an induced electric dipole. Potential areas of applicability for these materials include photovoltaic technology, where spatially separated excitons require less energy for dissociation, anisotropic
light sources, where an induced electric dipole allows a high level of emission polarization, and optical modulators, where separation of carrier wave functions allows for switching of NC emission energies via the quantum confined Stark effect.

Most noncore/shell hetero-NCs that exhibit the type II carrier localization regime have been based on a heterojunction of CdTe and CdSe semiconductors\(^{17-23}\), assembled using one of the two developed approaches: by nucleating the growth of spherical nanoparticles on one or both sides of the rod\(^{17-19}\), which yields linear structures, such as barbells, or by using spherical quantum dots with zinc blende structure to nucleate the growth of multiple extensions\(^{17, 20-23}\), which leads to a branched architecture, such as tetrapods. While the use of spherical NCs as nucleation sites leads to the formation of highly uniform hetero-NCs and hetero-NRs, where the number of branches is controlled by an appropriate surfactant, the synthesis of linear heterostructures, which makes use of highly reactive facets for nucleation of the secondary material often results in a wide distribution of different shapes. For instance, the difference in the number or type of dangling bonds between 001 and 00\(\bar{1}\) facets in wurtzite CdSe NRs used for seeding the growth of linear CdTe/CdSe/CdTe structures causes uncertainty in the nucleation event resulting in formation of either one- or two-sided barbells\(^{18}\). The presence of nonuniform shapes in a macroscopic volume of linear hetero-NRs lowers the degree of long-range order, complicating the controlled assembly of these structures onto a substrate via external fields\(^{24-27}\) or through interparticle interactions\(^{28-30}\). Nonhomogeneous distribution of shapes and the absence of fluorescence (quantum yield < 1\%) in CdTe/CdSe-based heterostructures hampered their utilization in optoelectronic devices, stressing the need for alternative directions in the synthesis of type II hetero-NRs.
Recently, a novel approach to the synthesis of luminescent, type I CdSe/CdS hetero-NRs has been reported in the literature\textsuperscript{31}. This method relies on small wurtzite CdSe NCs to nucleate the growth of CdS rods along the crystalline $c$ axis and yields high quality structures that are easily oriented in close-packed ordered arrays over large areas. The study also showed that the structural composition of the original CdSe seeds was preserved during the synthesis, such that the emission of hetero-NRs was largely determined by the type I recombination of carriers in a CdSe/CdS heterojunction.

Here, we demonstrate that a general method of nucleating the growth of nanorods from spherical semiconductor NCs can be successfully adapted for the synthesis of hetero-NRs with type II carrier confinement. By using ZnSe/CdS core/shell NCs as nucleation sites for the growth of secondary CdS branches we fabricated homogeneously shaped (ZnSe/CdS)/CdS hetero-NRs.
exhibiting strong emission associated with type II relaxation of carriers across the ZnSe/CdS junction (see Figure 2.1). The location of the original ZnSe/CdS seed within the final structure is offset from the center by approximately 1/4-1/3 of the rod length, which results in a spatially asymmetric distribution of carrier wave functions along hetero-NRs. The linear separation of carriers within such structural arrangement can be modulated with amplitudes of nearly one-half the rod’s length, as inferred from the observed magnitude of the quantum confined Stark effect. Finally, shape control of (ZnSe/CdS)/CdS hetero-NRs can be realized in a straightforward manner by varying concentrations of Cd and S precursors during the final stage of synthesis. Indeed, high concentrations of injection precursors lead to formation of pill-like structures, where the seed is fully incorporated within the body of hetero-NRs, while use of dilute Cd and S stock solutions promotes the growth of high-aspect ratio NRs, where the initial nucleation of CdS occurs on one of the facets of the seeding particle, such that the center of the seed was offset from the central axis of CdS rod by as much as 2 nm. An offset of band edges at the interface of ZnSe and CdS materials promotes spatial separation of an electron-hole pair into opposite parts of the structure such that an electron wave function becomes primarily localized within the CdS and a hole within the ZnSe semiconductor materials. The subsequent recombination of spatially separated excitons occurs across the ZnSe/CdS interface, leading to a considerable red shift of the emission peak in (ZnSe/CdS)/CdS hetero-NRs, with respect to the absorption edge in ZnSe (420 nm) and CdS (440 nm) NCs, as evident from the insert plot showing absorption and emission spectra of hetero-NRs.

The seeded-type approach to the synthesis of type II hetero-NRs provides an effective way to fabricate regularly shaped heterostructures with a narrow distribution of lengths. In contrast to type II NRs based on a CdTe/CdSe heterojunction of materials, (ZnSe/CdS)/CdS
hetero-NRs, reported here, are strongly luminescent, which allows for their utilization in both photovoltaic and light-emitting applications.

2.2 Experimental Section

2.2.1 Chemicals

Cadmium oxide (99%, Aldrich), sulfur (99.9%, Aldrich), zinc stearate (99%, Across), 1-octadecene (ODE, 90%, Aldrich), tributylphosphine (TBP, 99%, Aldrich), oleic acid (OA, 90%, Aldrich), trioctylphosphine (TOP, 97%, Strem) trioctylphosphine oxide (TOPO, 99%, Aldrich), hexadecylamine (HPA, 99%, Aldrich), octadecylamine (ODA, 99%, Aldrich), n-octadecylphosphonic acid (ODPA, 99%, Polycarbon), anhydrous hexane (Aldrich), methanol (Aldrich), chloroform (Acros), and toluene (Aldrich) were used as purchased.

All reactions were conducted under argon using standard Schlenk techniques.

2.2.2 Synthesis of ZnSe Seeds

Synthesis of monodisperse wurtzite ZnSe nanocrystals was based on a procedure described in ref 32 as follows. A 0.3794 g (0.6 mmol) amount of zinc stearate was dissolved in 9.5 mL (3.2 g) of octadecane by heating reagents to 300 °C in the 25 mL three-neck flask while stirring. After the mixture became clear, selenium stock solution, prepared by dissolving 0.0474 g (0.6 mmol) of selenium in 1.5 mL of TOP, was swiftly injected into the reaction flask. During the nanocrystal growth, the temperature was kept at 290 °C. The reaction was stopped after 13 min by removing the flask from the heating mantle. After the reaction mixture was allowed to cool to 50 °C, 3-5 mL of hexane was added into the solution to prevent solidification.
Subsequent cleaning of the nanocrystals was done by hexane/methanol extraction. Typically 6-7 mL of methanol was added to the reaction mixture in hexane, which was then centrifuged for 10 min at 3500 rpm. The upper hexane layer containing QDs was taken with a syringe for further purification. The final clear suspension was then placed under argon and stored in the dark for future shell deposition.

### 2.2.3 Synthesis of Small ZnSe/CdS Core/Shell NCs

In the next step, purified and size-selected ZnSe NCs were then overcoated with 1-2 monolayers of CdS using a previously developed procedure. For shell deposition injection stock solutions were prepared at a concentration of 0.04 M in ODE. Cadmium was obtained by dissolving 0.030 g (0.24 mmol) of cadmium oxide in 0.6 mL of OA and 5.4 mL of ODE in a 25 mL flask under argon by heating it to 280 °C while stirring. After the solution became clear it was cooled to 60 °C. The sulfur injection solution was prepared from 0.0077 g (0.24 mmol) of sulfur dissolved in 6 mL of ODE by heating the mixture to 200 °C under argon flow. For continuous shell deposition both precursors were mixed together and injected into the reaction vessel containing previously prepared ZnSe nanocrystals dispersed in 1.5 g of ODA and 6.3 mL of ODE at 240 °C. The injection rate was 2 mL/h. Aliquots of the reaction mixture were taken at 7-10 min intervals for UV-vis and PL spectral characterization.

### 2.2.4 Synthesis of (ZnSe/CdS)/CdS Hetero-NRs

Growth of CdS extensions from ZnSe/CdS seeds was done using a technique adapted from ref. The cadmium injection solution was prepared by combining 0.060 g (0.47 mmol) of
cadmium oxide, 3 g of TOPO, 0.290 g of ODPA, and 0.080 g of hexadecylamine (HPA) in a 25 mL three-neck flask. The mixture was then pumped at 150 °C for 30 min to remove air, switched to argon, and heated to 380 °C while stirring. After the solution became clear, 1.81 mL of TOP was injected and the temperature was recovered to 380 °C.

The sulfur solution was prepared by dissolving 0.120 g (3.74 mmol) of sulfur in 1.81 mL of TOP at 180 °C under argon flow. After cooling to 60 °C, the sulfur solution was combined with 3-8 mL of ZnSe/CdS NC solution in TOP (the increase in the amount of TOP corresponds to the increase in the aspect ratio of final heterorods). The concentration of seed NCs was chosen so that the product of the absorbance at 500 nm and suspension volume was in the range of 30-40 mL. The mixture was stirred for 10 min and injected into the reaction flask. The temperature was recovered to 390 °C in 3 min, and the growth phase took 7-10 min. The reaction mixture was let to cool to 60 °C and purified using hexane/methanol extraction.

2.2.5 Characterization

UV-vis absorption and photoluminescence (PL) spectra were recorded using a CARY 50 Scan spectrophotometer and Jobin Yvon Fluorolog FL3-11 fluorescence spectrophotometer. PL quantum yield of hetero-NCs was determined relative to known quantum yields (QY) of several organic dyes excited at 400-440 nm. High-resolution transmission electron microscopy measurements were carried out using a JEOL 311UHR operated at 300 kV. Specimens were prepared by depositing a drop of nanocrystal hexane solution onto a Formvar-coated copper grid and letting it dry in air. X-ray powder diffraction measurements were carried out on Scintag XDS-2000 X-Ray Powder Diffractometer. Energy dispersive X-ray (EDX) emission spectra were measured using an EDAX X-ray detector located inside a scanning electron microscope.
The electron beam was accelerated at 20 kV. Picosecond transient absorption measurements were performed using a homebuilt laser system comprising a Ti:Sapphire regenerative amplifier and TOPAS-C optical parametric amplifier operating at 1 kHz. Instrument response time was estimated to be less than 1 ps.

2.3 Results and Discussion

Synthesis of (ZnSe/CdS)/CdS NRs is performed at temperatures that exceed the threshold for homogeneous nucleation, allowing for both homogeneous and heterogeneous growth mechanisms to contribute to formation of nanorods. When the concentration of precursors is low, nucleation of CdS occurs primarily at high reactivity facets [000±1] of ZnSe/CdS seed nanoparticles, such that growth of CdS rods is mostly heterogeneous. For high concentrations of precursors, the activation energy for homogeneous nucleation becomes lower and an appreciable isotropic growth occurs. In this work, the competition between homogeneous and heterogeneous nucleation processes is controlled by varying the amount of TOP in the injection solution, such that injections with higher concentrations of precursors yield a lesser fraction of homogeneous nucleation and vice versa.

High-aspect-ratio hetero-NRs, fabricated using low concentrations of precursors (Cd- and S-limited conditions) are shown in Figure 2.2 a-d. An outline of the original ZnSe/CdS seed can be distinguished in most of the fabricated hetero-NRs, while its presence within the rod structure is confirmed by energy-dispersive X-ray measurements (Figure 2.2-i) that show traces of both Zn and Se elements. The location of the seed appears to be offset from the center of the heterostructure by approximately 1/4-1/3 of the rod’s length. The average seed diameter in the
final structure is just slightly greater than the size of core/shell NCs prior to synthesis of CdS extensions, which indicates that NC growth occurs predominantly via heterogeneous nucleation.

Figure 2. 2 - Transmission electron microscope images of (ZnSe/CdS)/CdS hetero-NRs fabricated using low (a-d) and high (e-h) concentrations of precursors. The location of ZnSe/CdS seeds within high-aspect-ratio hetero-NRs can be distinguished in c and d. Scale bars are as follows: (a-c, e) 20 nm, (f and g) 5 nm, (d and h) 1 nm. (i). Energy-dispersive X-ray spectrum of high-aspect-ratio (ZnSe/CdS)/CdS hetero-NRs. (j) Length distribution of high-aspect-ratio (ZnSe/CdS)/CdS hetero-NRs.
The two images shown in Figure 2.2-c and 2.2-d reveal that in addition to an asymmetric placement of ZnSe/CdS NCs along the nanorod axis some of the seeds may also exhibit a lateral shift, such that the center of ZnSe/CdS NC is offset from the main axis of the rod by as much as 2 nm. A cause of this structural effect can be seen in the high-resolution TEM images, showing that the direction of nanorod growth is not always parallel to the $c$ axis of ZnSe/CdS seeds, such that the center of the seeding NCs is shifted from the 00±1 nucleation cite. By examining 35 specimens under 300 000× magnification we determined the average length of high-aspect-ratio hetero-NRs, such as the ones shown in Figure 2.2a-d, to be 106 nm (Figure 2.2a). The standard deviation of the length distribution was 13.2 nm or 12%.

CdS hetero-NRs fabricated with high concentrations of precursors are shown in Figure 2.2e-h. Most of the structures exhibit symmetric pill-like shapes with an average aspect ratio of 2.5. High-magnification analysis (Figure 2.2h) reveals that original ZnSe/CdS seeds are fully incorporated within the nanoparticle body, indicating that significant homogeneous growth occurs during the synthesis, leading to an isotropic enhancement of hetero-NRs in the direction perpendicular to the crystalline $c$ axis. Despite a mixed growth mechanism the length distribution of pill-like structures (10%) was found to be lower than that of high-aspect-ratio hetero-NRs.

X-ray powder diffraction (XPD) measurements were performed to verify the wurtzite lattice structure of fabricated materials. The experimental diffraction pattern, obtained for high-aspect-ratio (ZnSe/CdS)/CdS hetero-NRs, is shown in Figure 2.3b. As evident from comparison of diffraction patterns for bulk wurtzite CdS (Figure 2.3c) and ZnSe (Figure 2.3d) lattices, the observed set of Bragg peaks corresponds to the wurtzite phase of CdS. The absence of a XPD signal from ZnSe lattice is consistent with a prevailing amount of CdS material in the final
hetero-NR structure (approximately 97% by volume) as well as with the core/shell arrangement of ZnSe/CdS NCs\textsuperscript{31} that enhances the XPD intensity of the shell material.

Figure 2.3 - X-ray powder diffraction spectra of (ZnSe/CdS)/CdS hetero-NRs along with diffraction patterns of bulk wurtzite CdS (b) and ZnSe (c).

Figure 2.4 summarizes the optical properties of the nanostructures obtained after each of the three fabrication stages involved in the synthesis of (ZnSe/CdS)/CdS hetero-NRs. Spectral characteristics of ZnSe NCs fabricated in the first step (Figure 2.4a) are consistent with typical features of monodispersed binary NCs exhibiting a sharp absorption edge and a narrow emission bandwidth. A small amount of trap state emission, distinguishable in fluorescent (FL) spectra as a broad, structureless, tail, centered at 490 nm (see Figure 2.4d, spectrum 1), is caused by the interaction of the solvent with the surface of the ZnSe NCs, which is passivated only by organic
ligands. The contribution of these trap states to the emission in ZnSe NCs becomes particularly evident when the capping layer of TOP is thermally perturbed at the beginning of the second fabrication stage, as seen in spectrum 2 of Figure 2.4d. Here, these traps are referred to as deep due to the core localization of these states in the layered hetero-NR assembly.

Deposition of a thin CdS shell onto ZnSe NCs results in the development of a low-energy tail in the absorption profile (Figure 2.4b), which extends over the visible range due to an onset of the type II localization regime. This process is accompanied by the quenching of type I violet emission in ZnSe NCs and the appearance of the new emission feature in the visible range. Deep trap FL associated with the original ZnSe cores can be still observed around 490 nm, as seen in Figure 2.4d, spectrum 3; however, it does not match the emission peak at 540 nm corresponding to carrier recombination in type II ZnSe/CdS NCs. This excludes the possibility that deposition of the shell simply quenches the band edge FL of ZnSe NCs while the deep trap emission remains. The longer FL lifetime of ZnSe/CdS core/shell NCs relative to that of binary ZnSe NCs (Figure 2.4e) serves as additional evidence that the contribution of deep traps in ZnSe is reduced upon deposition of CdS shell. According to the emission profile in Figure 2.4d, spectrum 3, formation of the ZnSe/CdS interface gives rise to another type of trap state, whose emission is red shifted from the position of the spatially indirect FL (1S_e(CdS)-1S_h(ZnSe)) in core/shell NCs. The intensity of this emission peak is gradually reduced with increasing thickness of the CdS shell, indicating that its origin is likely to be related to electron or hole traps at the ZnSe/CdS interface rather than dangling bonds on the surface of CdS. Growth of short, 1-2 nm CdS extensions at the final stage of the synthesis leads to a near by complete quenching of both deep and interfacial trap emissions as well as further red shifting of the spatially indirect FL, as shown in spectrum 5 of Figure 2.4d. The diminishing contribution of traps to carrier relaxation for these
structures is also evidenced by the increasing lifetime of the FL intensity decay (Figure 2.4e, blue curve).

Optical characteristics of high-aspect-ratio (ZnSe/CdS)/CdS hetero-NRs are shown in Figure 2.4c. Due to the delocalization of electronic wave functions over the increased volume of CdS the emission of 106 nm hetero-NRs undergoes a 10-15 nm red shift from the peak position in short-branched (ZnSe/CdS)/CdS heterostructures (spectrum 5 in Figure 2.4d). Growth of linear CdS extensions is also accompanied by the 10-20 nm decrease in the spectral width of the emission, which is consistent with further quenching of trap state emission as well as the increase of CdS shell beyond the “saturation” value associated with the onset of type II localization regime. The FL quantum yield (QY) of as-prepared high-aspect-ratio hetero-NRs diluted in chloroform is typically in the range of 8-18% and further improved to 14-25% after purification by hexane-50% + chloroform-50%/methanol extraction.

The FL intensity decay of 106 nm (ZnSe/CdS)/CdS hetero-NRs is shown by a black curve in Figure 2.4e. It is expected that radiative relaxation of spatially separated excitons may exhibit unique relaxation times that arise from intrinsically different carrier decay mechanisms associated with a weak-confinement regime. Owing to a nonzero quantum yield and the spatial separation of charges, fabricated hetero-NRs provide a model system for testing such a hypothesis. According to traces 5 and 6 in Figure 2.4e both short- and long-branch NRs exhibit nonexponential radiative relaxation of excited carriers, which is generally anticipated in semiconductor quantum systems due to the mixing of the contributions from different single-exponential lifetimes corresponding to “on” and “off” blinking cycles. The FL lifetime of high-aspect-ratio hetero-NRs appears to be longer than in short-branched heterostructures (blue curve), which could be the result of fewer carrier traps being present at the ZnSe/CdS interface.
or a smaller overlap between electron and hole wave functions brought by the delocalization of electrons in CdS. The overall character of carrier relaxation in high-aspect-ratio hetero-NRs, however, appears to be similar to that of short hetero-NRs or even core/shell NCs, indicating that a mechanism of radiative recombination across the ZnSe/CdS heterojunction is specifically independent of the degree of charge separation.

Figure 2.4 - Optical characteristics of NC and NR colloids. UV-vis absorption and steady-state fluorescence spectra for: (a) 5 nm diameter ZnSe NCs, (b) ZnSe/CdS core/shell NCs, fabricated by depositing 2-3 monolayers of CdS, and (c) high-aspect ratio (ZnSe/CdS)/CdS hetero-NRs. (d) Evolution of the FL spectra during the three-stage synthesis, showing the trap state emission. Deep traps contribute to the...
emission near 490 nm as evidenced by the broad emission tail in passivated (spectrum 1) and unpassivated (spectrum 2) ZnSe NCs. ZnSe/CdS core/shell NCs with ca. 1 monolayer of CdS exhibit both deep and interfacial trap emission (spectrum 3). The former becomes quenched in thick-shell ZnSe/CdS NCs (spectrum 4), while the latter is reduced in large-size (oblong) core/shell structures (spectrum 5) and becomes fully quenched in long (ZnSe/CdS)/CdS hetero-NRs (spectrum 6). (e). FL intensity decay for ZnSe (red), thin-shell ZnSe/CdS NCs (green), thick-shell ZnSe/CdS NCs (blue), and (ZnSe/CdS)/CdS hetero-NRs (black), measured by means of TCSPC technique.

The dynamics of optical excitations in (ZnSe/CdS)/CdS hetero-NRs was further investigated using time-resolved transient absorption spectroscopy. This technique relies on measurements of excitation-induced changes in the absorption spectra (ΔA) and provides information on the relative population of excited states in the system. By using 1 ps of minimal delay between excitation and probe pulses we ensure that most carriers occupying high-energy states (nS, nP, ..., n > 1) relax to band edges such that the primary contribution to the bleaching signal comes from 1S(e, h) states. Figure 5a shows temporal changes in the absorption of hexane-suspended hetero-NRs excited with 420 nm monochromatic light. The spectrum contains three main areas of bleaching corresponding to spectral markers at 461, 482, and 557 nm. By comparing bleach positions with the absorption spectrum of hetero-NRs (Figure 2.4c) we were able to classify the origin of the observed intervals of bleaching at 461 and 557 nm as due to 1S(e)-1S(h) transitions in the CdS shell and the ZnSe/CdS heterojunction, respectively. Meanwhile, the origin of the smaller signal at 482 nm was attributed to excitations of carriers in branch portions of hetero-NRs, where spatial delocalization of the electronic wave function results in a shift of the CdS absorption edge below the energy of the 1S(e)-1S(h) transition in the CdS shell. Similarities in the character of the 461 and 482 nm excitations residing within the same semiconductor material are evidenced by the proximity of corresponding bleach recovery.
times, as shown in Figure 2.5c. Both relaxation trends exhibit an apparent correlation in the
initial fast decay slopes as well as in the following slower bleach recovery time dependences.

A unique type of bleach recovery was observed for the 557 nm signal, corresponding to
$1S_e$ (CdS)-$1S_h$ (ZnSe) excitations in (ZnSe/CdS)/CdS hetero-NRs. As seen in the insert of Figure
2.5a, the spectral position of the $\Delta A$ minimum gradually red shifts from 552 to 590 nm over a
period of 300 ps. This process is sufficiently slow for high-energy carriers to decay to the bottom
of the band$^{38,39}$, indicating that the change in the energy of the bleaching signal cannot be
associated with either $2S_{3/2}(h)-1S_{3/2}(h)$ or $1P(e)-1S(e)$ carrier relaxation pathways. The observed
shift of the $\Delta A$ minimum, on the other hand, can be linked to the decrease in the spatial
confinement of electronic wave functions associated with a charge-separated state in
(ZnSe/CdS)/CdS hetero-NRs. Indeed, the energy of e-h interaction in NCs is inversely
proportional to the square of the confinement length, $a$, such that $\Delta E = - (h^2/8m_e a^2)$, where $m_t =
(m_e^{-1} + m_h^{-1})^{-1}$. If we assume that an electron-hole pair is brought to a separation of 1/3 of the rod
length (approximately 10 nm) from its initial confinement within ZnSe/CdS core/shell NCs ($a \approx
2.5$ nm) then the associated decrease in the energy of the $1S(e)-1S(h)$ transition, $\Delta E (t = 1100$ ps)
to $\Delta E (t = 0)$, will be 0.14 eV, which corresponds to a 37 nm red shift of the emission. This value
is consistent with the 38 nm red shift observed in TA measurements (Figure 2.5a and 2.5b). The
assumption that carriers are initially confined within the spherical core/shell NC is consistent
with the larger amplitude of the bleaching signal originating from the CdS shell (461 nm) in
comparison with the signal forming in the branch portion of hetero-NRs (482 nm). Additional
support of the proposed delocalization-induced shift in the 557 nm signal is provided by the TA
dynamics of ZnSe/CdS seeds (see the insert in Figure 2.5b) that confirms the absence of the
spectral shift of the ZnSe/CdS bleach (denoted by an arrow) when excitons are restricted to a
small volume of core/shell NCs. The temporal dynamics of the charge separation process is shown in Figure 2.5b, where the change in the position of the bleaching signal is plotted versus the pump-probe delay. By fitting the initial evolution of the wavelength with a single exponent we obtain the characteristic time scale for the separation process to be 54 ps.

The effect of external electric field on energy levels in a semiconductor heterostructure can be dramatically enhanced by the quantum confinement of carrier wave functions, causing sizable modulation of the position and width of the emission peak. This phenomenon, also known as quantum confined Stark effect (QCSE), has been demonstrated to produce detectable spectral changes in single, type II CdSe/CdS hetero-NRs, where an efficient red shifting of the emission peak was possible due to a sizable spatial separation of charges\textsuperscript{40, 41}. The value of the type II energy offset in (ZnSe/CdS)/CdS hetero-NRs exceeds that of CdSe/CdS combination of materials, which should produce a more complete separation of charges and thus more extensive QCSE-induced spectral changes.

To study the effect of electric field on the emission properties of (ZnSe/CdS)/CdS hetero-NRs a dilute nanorod suspension in hexane was injected into a sealed cuvette comprising two conducting windows separated by 40 μm. A direct voltage in the range from -120 to 120 V was then applied to the inner walls of the cuvette, creating electric fields of up to 30 kV/cm. The potential difference across (ZnSe/CdS)/CdS hetero-NRs, whose axes are parallel to the direction of the field, is determined as

\[ \Delta V \approx Ed \left( \varepsilon_{\text{hexane}} / \varepsilon_{\text{rod}} \right) \quad \text{(1)} \]

where \( E \) is the electric field, \( d \) is the nanorod’s length, and \( \varepsilon_{\text{hexane}} = 2.0 \) and \( \varepsilon_{\text{rod}} = 9.5 \) are dielectric constants of the surrounding matrix and hetero-NRs, respectively. According to this equation the potential difference across a 100 nm hetero-NR, oriented along the field, is 0.06 V.
Figure 2.5 - Measurements of the state-filling dynamics in (ZnSe/CdS)/CdS hetero-NRs performed with picosecond transient absorption. (a) Absorbance changes (ΔA) of hexane-suspended nanorods excited with 420 nm monochromatic light. Three main areas of photobleaching, corresponding to spectral markers at 461, 482, and 557 nm, were indentified. The insert provides a more detailed representation of absorbance changes in the 557 nm region showing time-dependent shifting of the 557 nm peak toward longer wavelengths. (b) Temporal evolution of the spectral position for the 557 nm bleach is shown. The insert shows the temporal evolution of ΔA for ZnSe/CdS core/shell NCs. (c) Bleach recovery dynamics for the three areas of photobleaching (461, 482, and 557 nm).

The corresponding magnitude of the Stark shift is determined by the change in the electron-hole interaction energy, ΔE_{e-h}, associated with the increased charge separation and the change of the electric potential energy along the NR axis ΔE_V

\[ \sim 30 \]
\[ \Delta E_{\text{Stark}} = \Delta E_{e-h} + \Delta E_V = \left( \frac{\hbar^2}{8m_r} \left( \frac{1}{a_f^2} - \frac{1}{a_i^2} \right) \right) - E(a_f - a_i) \left( \frac{\epsilon_{\text{matrix}}}{\epsilon_{\text{rod}}} \right) \]  

where \(a_i\) and \(a_f\) are the initial and the final electron-hole separations in hetero-NRs, respectively.

Figure 2.6 - Quantum confined Stark effect in (ZnSe/CdS)/CdS hetero-NRs. (a) Schematic representation of field-induced changes in the nanocrystal potential and carrier localization pattern. (b) Observed red shifting, \(\Delta \lambda\), of the FL peak in colloidal (ZnSe/CdS)/CdS hetero-NRs caused by external electric field. (c) Effect of electric field on the spectral width of the emission. (d) Expected amplitudes of the Stark shift for different sets of the initial (\(a_i\)) and final (\(a_f\)) electron-hole separation in (ZnSe/CdS)/CdS hetero-NRs.

The contour plot in Figure 2.6d shows the expected values of \(\Delta E_{\text{Stark}}\) for a NR oriented parallel to the 30 kV/cm electric field, while Figure 2.6b shows the observed spectral changes in the emission of (ZnSe/CdS)/CdS hetero-NRs when the electric field is increased from 0 to 30 kV/cm. As expected, the position of the FL peak red shifts with increasing voltage, reaching a ~ 31 ~
maximum offset of 4.0 nm. The observed modulation of the emission wavelength is considerably larger than previously reported values for CdS/CdSe nanorods\textsuperscript{42}, which is expected to be due to a greater type II band gap offset at the interface of ZnSe and CdS materials that creates a stronger confinement of the hole wave function on one side of the structure. The distribution of nanorod orientations is believed to be responsible for the field-induced inhomogeneous broadening of the emission peak, as shown in Figure 2.6c, caused by contributions from hetero-NRs aligned perpendicular to the field, whose emission is not affected by the applied voltage, and hetero-NRs oriented along the field, which emission undergoes a red shift in excess of 4 nm.

2.3 Conclusions

The present synthesis demonstrates a number of potential benefits associated with the use of ZnSe/CdS heterojunctions for development of type II heterostructured nanorods. First, the large offset of band edges between the ZnSe and CdS semiconductors promotes a more complete spatial separation of photogenerated carriers than can be expected from heterostructures utilizing CdSe/CdTe combination of materials. Second, the observation of strong, spatially indirect, emission in (ZnSe/CdS)/CdS hetero-NRs indicates that a significant portion of charge-separated states in ZnSe/CdS-based heterostructures can recombine radiatively, which has not been observed previously in other type II noncore/shell semiconductor nanomaterials. Finally, the combination of an efficient charge separation and excellent emissive properties in (ZnSe/CdS)/CdS hetero-NRs enhances the magnitude of the quantum confined Stark effect such that application of even small electric fields can produce detectable spectral modulation of the emission.
CHAPTER 3
THE EFFECT OF DIELECTRIC FRICTION ON THE RATE OF CHARGE SEPARATION IN TYPE II ZnSe/CdS SEMICONDUCTOR.

3.1 Introduction

The spatial separation of photogenerated charges is a key requirement for an efficient generation of electrical energy from light in a variety of optoelectronic devices. For semiconductor nanocrystals (NCs), such charge separation is achieved via a two-component heterojunction with a type II or staggered energy alignment at the interface for which both the valance and conduction bands of one component lie lower in energy than the corresponding bands of the other component. The inorganic coupling of materials in such a heterostructure realized either in a symmetric core/shell\textsuperscript{6, 8, 11, 33}, a asymmetric dot-rod\textsuperscript{19}, or a branched\textsuperscript{21} assembly ensures an efficient and rapid separation of excited carriers, which, should stimulate the incorporation of these materials into emerging photovoltaic and photocatalytic technologies when combined with a low-cost organometallic synthesis.

To date several combinations of II-VI semiconductors, including CdS/CdSe\textsuperscript{43, 44}, CdSe/CdTe\textsuperscript{19}, and ZnSe/CdS\textsuperscript{45, 46} have been considered to enhance the photoinduced charge separation in heterostructured NCs. Thus far, the most encouraging characteristics both in terms of electron-hole separation\textsuperscript{47} and low spatial overlap of the corresponding wave functions was demonstrated for ZnSe-seeded CdS nanorods (NRs). In addition, unlike CdSe/CdTe or CdSe/CdS-based heterostructures, ZnSe/CdS NRs also exhibit strong fluorescence associated with type II relaxation of carriers across the ZnSe/CdS junction, with lifetimes on the order of
200–300 ns\textsuperscript{45,46}, which is sufficient for the excited carriers to be transferred to an electrode or metal nanoparticle during a photovoltaic and photocatalytic conversion.

The amount of time required for a complete separation of charges plays an important role in many optoelectronic applications of type II heterostructures, including electroabsorption modulators\textsuperscript{48} where the rate of device operation depends on the speed with which charges are brought into a separated state or multiple exciton generation-based photovoltaic devices\textsuperscript{49}, where electron-hole separation should be fast enough to precede exciton-exciton annihilation\textsuperscript{50}. For structures with a spatially asymmetric charge distribution, such as ZnSe/CdS NRs, the rate of charge separation depends on the surrounding media, through a phenomenon known as dielectric friction (DF), which results from the work necessary to orient external dipoles in response to the motion of charges within the NR. Since the orientational response of the medium is not instantaneous, it affects the charge separation time. Previous research has identified the central role of DF in ionic mobility and dipolar orientational relaxation\textsuperscript{51} and also in charge transfer dynamics\textsuperscript{52} and dipole isomerizations; on the other hand, its effect on carrier mobility in colloidal NCs is majorly unknown.

Here we investigate the effect of DF on the dynamics of charge separation in ZnSe/CdS NRs by measuring the bleach recovery times of band edge excitons. The dielectric media were introduced by dispersing NRs in solvents with different polarities. Temporal evolution of the excited state population was measured using the transient absorption (TA) technique. Present measurements confirm an apparent negative correlation between the solvent polarity and the charge separation rate, which is explained as due to the effectd DF on carrier mobility.
3.2 Experimental section

Colloidal ZnSe/CdS NRs were fabricated via organometallic routes, according to a previously developed three-step procedure that involves the synthesis of ZnSe NCs, deposition of a thin CdS shell\textsuperscript{33}, and subsequent growth of CdS extensions (experimental section in chapter 2). After precipitating from the growth solution, NRs were thoroughly cleaned and redispersed in several solvents with different polarities. In this work we have chosen CCl\textsubscript{4} (\(\varepsilon = 2.2\)), CHCl\textsubscript{3} (\(\varepsilon = 4.8\)), and dichloromethane (DCM, \(\varepsilon = 9.1\)) solvents that allow for NR concentrations to be within the linear Beer–Lambert regime.

3.2.1 Picosecond transient absorption measurements.

The ultrafast pump-probe instrument is based on a regeneratively amplified Ti:sapphire laser system (Hurricane, Spectra Physics) that generates 1-kHz / 90-fs (fwhm) 800-nm laser pulses. The output is split using a 50:50 beam splitter to create pump and probe beams. In the reported spectra, the pump beam is delivered to a TOPAS-C “pump” amplifier to produce 420-nm light pulses used for sample excitation. The typical excitation pulse energy is \(\sim 2 \ \mu\text{J}\), focused into a \(\sim 300 \ \mu\text{m}\) diameter spot at the sample position. The probe beam is attenuated, and focused onto a 3-mm CaF\textsubscript{2} window to produce a white light continuum probe light in the 350-800 nm range. The pump-probe cross-correlation function (150 ± 15 fs, fwhm) is determined using the simultaneous absorption of two (pump and probe) photons in methanol. All transient absorption data were corrected for the group velocity dispersion of the white-light continuum with an accuracy ± 25 fs by using the non-resonant \(\Delta A\) signals from the pure solvents. The incident excitation pulse was attenuated before the sample position using appropriate neutral density filters.
filters to ensure the absence of solvent contribution due to non-linear pump absorption to the measured transient absorption $\Delta A$ spectra at time delays equal to or longer than $\Delta \tau = 200$ fs.

Linearity of the $\Delta A$ data from the samples *versus* excitation pulse energy (400 nm pump, 0.4 - 4 $\mu$J range, A$\approx$ ~ 0.4 at excitation wavelength) and independence of the spectra and kinetic $\Delta A$ traces *vs.* concentration of the samples (up to double the reported concentrations) were verified.

### 3.2.2 Model calculations of zero-angular momentum excited states.

Here, we have used known solutions to the envelope-function Schrödinger equation for noninteracting carriers$^{53}$ in order to find the energies and the associated wave functions for carriers in ZnSe/CdS core/shell nanocrystals. In the present calculations, only the lowest-energy, zero angular momentum, conduction and valence band 1S states were considered.

In present calculations, the band structure parameters of bulk semiconductors, including effective masses ($m_c=0.14$, $m_h = 0.53$ for ZnSe, and $m_c=0.18$, $m_h = 0.6$ for CdS), offset energies ($U_c=0.8$eV and $U_h=0.52$eV), and band gap energies ($E_g=2.72$eV for ZnSe and $E_g=2.45$eV for CdS) were taken from Refs$^{31,53}$.

### 3.3 Characterization

Figure 3.1 shows a type II alignment of the band edges in ZnSe/CdS NRs, which favors electron localization along the CdS branches and holes within the ZnSe NCs. Such a spatially separated arrangement of charges has been experimentally confirmed for ZnSe/CdS NRs using scanning tunneling microscopy (Ref. 47) and TA (Ref. 46) techniques, as well as through observation of the quantum-confined Stark effect in NRs, in which the axes are parallel to the
direction of the electric field. In the present study, changes in the degree of charge separation along the rod axis were monitored by measuring the corresponding change in the energy of the $1S_e(CdS) - 1S_h(ZnSe)$ transition through an empirical equation that relates the position of the absorption peak to the effective electron-hole separation, $l_{eff}$. Model calculations based on known solutions to the envelope-function Schrödinger equation for noninteracting carriers were also employed to estimate the effect of the CdS length on the maximum value of $l_{eff}$ and the corresponding recombination energy.

Figure 3.1 - (a) Relative positions of the conduction and valence band edges in a ZnSe/CdS heterostructure, along with corresponding electron ($1S_e$) and hole ($1S_{3/2}h$) excited state wave functions. (b) The dependence of zero angular momentum state energies on the length of CdS branch. (c) Expected spatial separation of an electron-hole pair vs the length of CdS branch.

Results of these calculations, shown in Figure 3.1(b) and 3.1(c), provided guidance in selecting a suitable range of NR lengths that ensures a large value of $l_{eff}$, and simultaneously
allows for a sufficient separation-induced changes in the $1S_{e}(\text{CdS})-1S_{h}(\text{ZnSe})$ transition energies that can be discriminated via TA measurements. Based on this analysis we have chosen 90-nm-long NRs for which the value of $l_{\text{eff}}$ is approximately 20 nm [Figure 3.1(c)].

![TEM images of ZnSe/CdS NRs](image)

Figure 3.2 – (Color online) [(a) and (b)] TEM images of ZnSe/CdS NRs. (c) Steady-state absorption and emission spectra of ZnSe/CdS NRs in CCl$_4$, CHCl$_3$, and DCM (CH$_2$Cl$_2$) solvents.

Typical transmission electron microscope (TEM) images of as-prepared NRs are shown in Figure 3.2(a) and 3.2(b). The difference in growth rates of CdS in each of the two directions results in the off-center position of the ZnSe/CdS seeds in the final structure, as seen in Figure 3.2(b).
Steady-state absorption and emission spectra of ZnSe/CdS NRs suspended in the three solvents are shown in Figure 3.2(c). Previous reports\textsuperscript{45,46} have identified the origin of the main absorption edge at 500 nm as the $1S(e) - 1S_{3/2}(h)$ transition in the CdS portion of the rod, while the low-energy tail (550–620 nm) was assigned to the $1S_e$(CdS) – $1S_h$(ZnSe) transition in the interfacial area. Comparison of the absorption spectra in Figure 3.2(c) reveals a negligible effect of the solvent polarity on the position of the main absorption edge. Indeed, spectral differences between CCl$_4$- and CHCl$_3$-suspended NRs are minimal, while the increased low-energy absorption of DCM-suspended NRs is likely the result of the inferior solubility of the NR in DCM, which is consistent with a lower emission quantum yield for that case. Similarly, comparison of NR emission spectra also did not show significant solvent effects. As seen in Figure 3.2(c), both the position and the width of FL peaks arising from the $1S_e$(CdS) – $1S_h$(ZnSe) carrier recombination remain the same in all three solvents, indicating that the energies of the $1S_e$(CdS) and $1S_h$(ZnSe) states are not screened by the surrounding dielectric media.

The dynamics of charge separation in ZnSe/CdS NRs was investigated using picosecond TA spectroscopy. The experimental setup was based on the Ti:sapphire laser operating at a repetition rate of 1 kHz, which output was split into two components: one was directed through the TOPAS OPA to produce excitation pulses at 420 nm, and the second one was focused onto a CaF$_2$ plate to generate a white-light-continuum for broadband probe pulses. All TA data were corrected for the group velocity dispersion of the white-light continuum by using the nonresonant signals of pure solvents. The incident excitation pulse was attenuated before the sample position to minimize the solvent contribution due to nonlinear pump absorption.

Figure 3.3(a) shows a typical TA spectrum of CCl$_4$-suspended NRs that contains two primary intervals of bleaching ($\Delta \alpha$ minima) at 455 and 540 nm, corresponding to the

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$1S(e) - 1S_{3/2}(h)$ transitions in the CdS branch and ZnSe/CdS heterojunction, respectively. By using 1 ps of minimal delay between excitation and probe pulses we ensure that most carriers occupying high-energy states ($nS, nP, \ldots, n > 1$) relax to the band edges\textsuperscript{36,37}, such that the primary contribution to the bleaching signal comes from the $1S(e, h)$ states. The recovery of the 540 nm bleach for ZnSe/CdS NRs suspended in CCl\textsubscript{4}, CHCl\textsubscript{3}, and DCM solvents are shown in Figure 3.3(d). In contrast to the adiabatic recovery of the 455 nm signal from the $1S_e1S_h$(CdS) excitons, the spectral position of the 540 nm bleach, corresponding to interfacial relaxation, gradually red-shifts from 525 to 550 nm over the period of 200 ps. This process is sufficiently slower than the decay of high-energy carriers to the bottom of the band, indicating that the change in the energy of the $\Delta\alpha$ minimum cannot be associated with either the $2S_{3/2}(h) - 1S_{3/2}(h)$ or the $1P(e) - 1S(e)$ carrier relaxation pathways. Instead, the observed shift in the 540 nm bleach can be linked to the decrease in the spatial confinement of electronic wave functions associated with a charge separated state, as predicted by the model calculations shown in Figure 3.1(b). This explanation is also consistent with the absence of a spectral shift in the $\Delta\alpha$ minimum for core/shell ZnSe/CdS NCs, where electrons are restricted to a small volume of the CdS shell [Figure 3.3(e)].

Temporal changes in the spectral position of the $\Delta\alpha$ minima for the three solvents are compared in Figure 3.3(c). The fastest shift was observed for NRs suspended in nonpolar CCl\textsubscript{4} (red curve), while the most polar, DCM-suspended NR (blue curve) produced the slowest change in the $\Delta\alpha$ position. Overall, during the 1 ns scan, $\Delta\alpha$ minima for NR in CCl\textsubscript{4}, CHCl\textsubscript{3}, and DCM red-shifted by 50, 60, and 70 nm, respectively, which confirms a sizeable effect of the solvent polarity on the interfacial carrier relaxation rate. In particular, for NRs suspended in nonpolar CCl\textsubscript{4}, the energy of the $1S$ exciton approaches the steady-state limit of the absorption energy (2.1
eV), which indicates near by complete electron-hole separation along the NR axis. In DCM-suspended NR, however, even after 1ns, the exciton energy still remains 0.4 eV above the corresponding band gap value, which, according to Figure 3.1(b), corresponds to an effective electron-hole separation of 2 nm. This is significantly smaller than the 18 nm delocalization of electronic wave functions along the 70 nm CdS branch expected from the model calculations [see Figure 3.1(c)].

Figure 3.3 – (Color online) (a) Steady-state absorption $\alpha$ of ZnSe/CdS NRs dispersed in CCl$_4$. (b) Absorbance changes $\Delta\alpha$ in CCl$_4$-suspended NRs excited with 420 nm monochromatic light. The area highlighted with a dashed rectangle is shown in more detail in (c) Temporal evolution of the bleach shift for all three solvents. (d) for CCl$_4$-, CHCl$_3$-, and DCM-suspended NRs. (e) $\Delta\alpha$ of core/shell ZnSe/CdS NCs suspended in nonpolar hexane.
The effect of solvent polarity on the charge separation rate in NRs can be understood in term of the energy exchange with the surrounding dielectric media (DF) that impedes the delocalization of electrons into CdS. Indeed, polar solvent molecules require more energy to orient along the direction of the electric field, causing some of the energy absorbed by NRs to be dissipated into the surrounding dielectric media. Such energy exchange is consistent with the observation of nearly identical rates in CCl$_4$ and DCM for the initial increase in the $\Delta \alpha$ position from 525 to 540 nm, since the corresponding spatial shift in the electronic wave function for this case is expected to be less than 1 nm. On the other hand, when the $\Delta \alpha$ minimum redshifts from 540 to 550 nm, electron penetration into CdS increases to 10 nm thus causing more energy to be dissipated into the solvent, which is manifested by the difference of charge separation rates for this interval [Figure 3.3(c)]. Based on the proportional delay of charge separation rates in CCl$_4$, CHCl$_3$, and DCM-suspended NRs, as well as the positive correlation of the friction effect with the expected delocalization of electrons along CdS branch, we attribute the observed changes in bleach recovery to DF in the solvent.

In conclusion, we shown have that the solvent polarity has a considerable effect on the rate of charge separation in semiconductor heterostructures and should be considered in the development of NR caging materials, including polymer matrices, solvents, and substrates.
CHAPTER 4
ULTRAFAST CARRIER DYNAMICS IN TYPE II ZnSe/CdS/ZnSe NANO-BARBELLS.

4.1 Introduction

Colloidal synthesis of heterostructured semiconductor nanocrystals (NCs) offers a facile route for integrating multiple materials with different properties into a single nanoscale object, where the spatial localization of carriers can be precisely controlled by manipulating the shapes and sizes of individual components. Recently, a great deal of work on the synthesis of composite semiconductor NCs has been focused on type II heterostructures, constructed from the two materials for which both the valence and conduction bands of one component lie lower in energy than the corresponding bands of the other component. The resulting staggered alignment of band edges at the heterostructure interface leads to an efficient spatial separation of electrons and holes, which presents attractive opportunities for utilization of these materials as charge-separating units in photovoltaic and photocatalytic applications.

To date, compelling evidence of photoinduced charge separation in semiconductor nanocomposites has been provided for a large number of heterostructures including symmetric core/shell as well as more complex dot-on-a-rod barbells, heterodimers, tetrapods and multi-branched structures. While, the core/shell geometry is not fully optimized for photovoltaic applications due to the fact that one of the carriers is always confined to the core of the nanoparticle, asymmetric heterostructures are highly suitable for photochemical conversion of light, as both nanocrystalline domains are exposed to the external environment.
allowing the photogenerated carriers to undergo a charge transfer reaction with an electrolyte or a substrate. Within this group of materials, the carrier separation efficiency is primarily determined by the rate of photoinduced charge transfer across the heterostructure interface, which depends on a number of system-specific parameters, such as the quality of the epitaxial interface, the carrier momentum in each nanocrystalline domain, the degree of band bending, and the amount of carrier trapping at the interface. Since most of these variables are \textit{a priori} unknown, real time spectroscopic investigations of carrier dynamics in heterostructure nanocrystals are exceedingly important for understanding the ensuing charge transfer properties and ultimately the material’s potential for light harvesting applications.

The dynamics of charge carriers in type II heterostructured NCs utilizing an asymmetric arrangement of the two domains has been extensively investigated in recent years by means of ultrafast pump-probe spectroscopies\textsuperscript{46, 61-63}. For instance, Peng et.al.\textsuperscript{22} have used femtosecond transient absorption (TA) spectroscopy to study electron processes in CdSe/CdTe nanotetrapods and have identified carrier cooling dynamics for interband, band-edge and intraband transitions. CdSe/CdTe heterostructures in a barbell-like arrangement were subsequently studied by the Fiebig group\textsuperscript{62}, where evidence of fast, sub-picosecond carrier transfer between CdSe and CdTe domains was presented. Finally, a recent report by Lupo et.al.\textsuperscript{63} has identified an ultrafast (650 fs) localization of holes in quasitype II CdSe/CdS heterostructures, which was attributed to a reduced electron-hole Coulomb interaction associated with spatially separated excitons.

Here we investigate the ultrafast dynamics of charge carriers in type II ZnSe/CdS heterostructures comprising a barbell-like arrangement of ZnSe spheres and CdS nanorods\textsuperscript{58}, fabricated via colloidal routes. Excited state population ratios for both materials were obtained from femtosecond transient absorption measurements through a careful evaluation of the Stark
effect and state-filling contributions into observed bleach recovery traces. We found that selective excitation of the ZnSe “tips” results in an ultrafast transfer (<0.35 ps) of excited carriers into CdS domains, whereas resonant pumping of the CdS portions of the barbells leads to a relatively slow injection of photoinduced holes into ZnSe domains ($\tau_h = 95$ ps). The observed interfacial electron transfer occurring under resonant pumping conditions is faster than previously reported for CdSe/CdTe$^{62}$ and CdSe/CdS$^{63}$ heterostructures, despite the large spatial delocalization of the corresponding wavefunctions across the ZnSe/CdS heterojunction. This phenomenon is attributed to the near-epitaxial relationship between ZnSe and CdS crystalline domains, which is expected due to a relatively small (2.7%) lattice mismatch between merging lattices that helps relieve the interfacial strain, and consequently reduces the number of interfacial defects.

Fast spatial separation of photoinduced charges along the main axis of the ZnSe/CdS barbells, as well as the availability of both carriers for a chemical reaction with external media can be utilized by a number of optoelectronic applications. For instance, the ZnSe/CdS combinations of materials are particularly well suited for photocatalytic water splitting since the electrochemical potentials of electrons and holes in ZnSe/CdS barbells straddle the $\text{H}_2/\text{H}_2\text{O}$ and $\text{O}_2/\text{H}_2\text{O}$ redox potentials.$^{64}$ In addition, fast charge transfer between the ZnSe and CdS domains can be harnessed in applications that rely on a photoinduced electric dipoles to modulate the spectral response of the material (e.g. electroabsorption switching and modulation$^{65}$), as was previously demonstrated for ZnSe/CdS nanorods exhibiting a photoinduced shift of the emission wavelength due to the quantum confined Stark effect$^{46}$. In the case of ZnSe/CdS barbells, the observed sub-picosecond electron transfer can enable switching rates of up to 1-2 terahertz,
which exceed the present day characteristics of Ge-based electroabsorption modulators by an order of magnitude$^{66}$. 

4.2 Experimental section

4.2.1 Synthesis of ZnSe/CdS barbells

ZnSe/CdS barbells were fabricated by growing ZnSe tips onto previously prepared CdS nanorods (NRs). To achieve a moderate dispersion of NR widths, CdS NRs were synthesized using a seeded-type approach by introducing small-diameter CdS NCs into the reaction mixture for nucleating the growth of linear CdS extensions, according to the procedure adapted from Ref. 31. The original CdS seeds were not distinguishable in fabricated CdS NRs.

The number of CdS seeds for the synthesis of CdS NRs, fabricated according to Ref. 67, was calculated using an empirical approach, whereby the product of the particle absorption at 400 nm (excitonic feature) and the volume of the colloidal suspension (in mL) was set to be in the range of 5 to 15. In a typical synthesis of CdS NRs, CdS seed powder was dispersed in 1.8 mL of TOP and subsequently introduced (at 60°C) into the sulfur injection solution, previously prepared by dissolving sulfur (0.120 g) in TOP (1.81 mL) at 200°C. Separately, a mixture of cadmium oxide (0.060 g), TOPO (3.0 g), ODPA (0.290), and HPA (0.080 g) in a 50 mL 3-neck flask was exposed to vacuum at 150°C for ca. 30 min. Subsequently, the system was switched to Ar flow and heated above 350°C until the solution turned optically clear and colorless. At this point, TOP (1.81 mL) was added to the flask as the Cd precursor coordinating solvent. The nanorod growth was initiated by a quick injection of the seed/sulfur solution at 380°C. After the
temperature recovered to 350°C the nanorods were allowed to grow for an additional 7-9 min. Purification of CdS NRs was similar to those of CdS seeds.

In a typical synthesis of ZnSe/CdS barbells, 0.5 mL of hexane-suspended CdS NRs (60 times the diluted injection solution showed an excitonic absorption peak of 0.75, which corresponds to approximately 12 mg of dry nanorods) were injected into a degassed mixture of ODE (6.0 mL) and ODA (1.5 g) at 80°C and pumped for about 20 min to remove hexane and any residual air from the system. At this point, the system was switched to Ar flow and heated to 250°C before injecting the precursors. Zinc injection solution was prepared by heating zinc oxide (0.0350 g), OA (1.2 mL), and TOP (1.5 mL) to above 250°C until the solution was clear. Subsequently, it was allowed to cool to about 60°C and mixed with the Se: TOP precursor (0.0340 g of selenium and 0.7 mL of TOP). During the nano-barbell growth the precursor solution was added via syringe to the reaction flask kept at 245°C in 0.1 mL amounts every 2 min. After 10-20 min, the reaction was stopped by cooling the flask to ca. 50°C and adding excess toluene. Subsequent cleaning was done using hexane/methanol extraction.

4.2.2 Characterization

UV-vis absorption and photoluminescence spectra were recorded using a CARY 50 Scan spectrophotometer and Jobin Yvon Fluorolog FL3-11 fluorescence spectrophotometer. High resolution transmission electron microscopy measurements were carried out using a JEOL 3011UHR operated at 300 kV.
4.2.3 Transient Absorption Spectroscopy

The experimental setup was based on the Ti: sapphire amplified laser system operating at a repetition rate of 1 kHz, which output was split into two components: one was directed to the TOPAS optical parametric amplifier to produce excitation pulses, and the second one was focused onto a CaF$_2$ plate to generate a white-light-continuum for broad-band probe pulses. All transient absorption data were corrected for the group velocity dispersion of the white-light continuum by using the non-resonant signals of pure solvents. The incident excitation beam was attenuated before searching the sample (0.2 mm flow cell) to ensure that the average number of excitations per nanocrystal is less than unity, $\langle N \rangle = j \sigma < 1$, where $j$ is the pump fluence and $\sigma$ is the absorption cross section at the pump wavelength, estimated using known extinction coefficients of CdS colloids$^{68}$ (e.g. for $\lambda_{\text{exc}} = 445$ nm, $\sigma = 2 \times 10^{-14}$ cm$^2$). The typical excitation pulse power was 1.5 $\mu$J per pulse at the sample position with an average beam diameter of 300 $\mu$m. The pump-probe cross correlation width was 200 fs FWHM.

4.3 Results and Discussion.

The motion of excitons in the ZnSe and CdS domains of a barbell structure is confined in three and two dimensions, respectively, with a corresponding degree of confinement being determined by the size of the ZnSe tips and width of the CdS NRs. Accurate determination of these parameters prior to spectroscopic characterization of the system is thus critical for establishing the expected carrier energies in both materials. The average sizes of the ZnSe and CdS domains are first estimated from high-resolution (HR) transmission electron microscopy (TEM) measurements. Figure 4.1(a) and (b) shows typical HR-TEM images of several ZnSe/CdS...
heterostructures, where the barbell-like arrangement of the materials can be distinguished by the unique direction of lattice planes in the ZnSe tips relative to those in the CdS NRs. Statistical analysis of approximately one hundred of such barbells shows a 5.7-nm elongation of these structures along the 001 axis in comparison with CdS NRs used for seeding the growth of the ZnSe tips. Subtracting the mean length of the CdS NRs from that of the ZnSe/CdS barbells yields an average ZnSe diameter of 2.85 nm, which is consistent with the 2.89-nm average tip size determined from the measurement of individual heterostructures. The average width of the barbells was found to be 4.1 nm, with a standard deviation of 0.34 nm (8%).

Figure 4.1 - Structural analysis of ZnSe/CdS barbells. (a). High resolution Transmission Electron Microscope (TEM) images of ZnSe/CdS heterostructures. (b). A typical ZnSe/CdS barbell showing unique directions of lattice planes for each of the material domains. (c) and (d)Statistical distributions of barbell widths and diameters of ZnSe tips.
Steady-state absorption measurements confirm the narrow distribution of barbell widths, as evident from the well-pronounced excitonic features corresponding to the $1S(e)-1S_{3/2}(h)$ and $1P(e)-1P_{3/2}(h)$ transitions in CdS (Figure 4.2a). The band edge absorption in the ZnSe portion of the barbells, which spectral position is expected\textsuperscript{69} to peak at 384 nm is not resolved, possibly due to the relatively small volume fraction of the ZnSe phase in the barbell structure. Nevertheless, evidence of carrier absorption across the band gap of ZnSe is provided by a noticeable change in the slope of the absorption curve below 380 nm and the apparent bleaching of the band edge transition in time-resolved TA measurements (Figure 4.3c).

![Figure 4.2](image.png)

Figure 4.2 - Determination of excited state energies in ZnSe/CdS heterostructures. (a). Steady-state absorption and emission ($\lambda_{\text{excitation}}= 420$ nm) spectra of ZnSe/CdS barbells (red) and CdS NRs (blue). Four lowest-energy excited state transitions are identified in the absorption spectra. (b). Calculated excited state energies for ZnSe/CdS heterostructures comprising 4.1-nm-wide CdS NRs and 2.85-nm ZnSe tips.

The relative alignment of $n = 1$ excited state energies in each component of the ZnSe/CdS heterostructure was calculated using known carrier effective masses\textsuperscript{69, 70} and optical absorption.
measurements, and TEM analysis of average domain sizes, as illustrated in Figure 4.2b. Further splitting of excitonic levels due to the exchange interaction was not considered in this work since the overlap of the electron and hole wavefunctions, which is proportional to the exchange term, is small in type II systems. According to Figure 4.2b, excited electrons find the minimum of the conduction band in the 1S(e) state of the CdS NRs, which is positioned 0.80 eV lower than the 1S(e) energy of ZnSe tips, meanwhile photoinduced holes are expected to localize in the 1S$^{3/2}$(h) level of the ZnSe domain, which lies 0.53 eV above the valence band edge of CdS NRs. The energy of the spatially indirect transition associated with the recombination of carriers across the ZnSe/CdS interface is thus lower than the band gap of either ZnSe or CdS materials, which is consistent with the red-shifted emission of ZnSe/CdS heterostructures ($\hbar \omega = 2.1$ eV), as shown in Figure 4.2a.

The photoinduced filling of excited states in NCs leads to bleaching of the interband optical transitions, such that absorption changes are proportional to the number of excited carriers:

$$\Delta A(\hbar \omega) = - \sum_i A_{0,i}(\hbar \omega - \hbar \omega_i)(n^e_i + n^h_i) ,$$

where $A_{0,i}$ is the absorption profile of the $i$th transition, and $n^e_i$ and $n^h_i$ are the occupation numbers of electron and hole states involved in the transition. Since the effective masses of the holes in CdS and ZnSe materials are approximately 4-5 times greater than those of the electrons, their room-temperature occupation probabilities are small. As a result, the state-filling-induced absorption changes are dominated by electrons. The contribution of holes to the bleaching is further reduced due to exchange interaction that splits the 1S exciton into two different hole...
states\textsuperscript{71,72} such that the higher energy absorbing transition stays unoccupied until the lower energy hole state is completely filled, which occurs only when $\langle N \rangle \gg 1$.

Another possible contribution to the bleaching of NC optical transitions is due to local fields that modify the transient spectra via the stark effect\textsuperscript{73}. This leads to a spectral shift of the absorbing transitions as well as changes in the corresponding oscillator strengths resulting from modifications in the selection rules. For systems exhibiting the spatial separation of charges, such as the barbell nanostructures investigated here, the contribution of the Stark effect can be particularly significant, and its evaluation is important in retrieving the state filling dynamics. As a semi-empirical approach to predicting the spectral changes in the TA measurements of ZnSe/CdS barbells resulting from the Stark effect, we rely on the previously reported formalism\textsuperscript{74,75} that correlates the effect of carrier-induced local fields in semiconductor NCs with a repulsion between close-spaced transitions, such that the Stark effect contribution into $\Delta A$ is approximately equal to the second derivative of the absorption profile.

The transient absorption spectroscopy of hexane-suspended ZnSe/CdS barbells was performed using two excitation regimes that correspond to the resonant pumping of the $n = 1$ transitions in the CdS and ZnSe domains of the structure. TA spectra resulting from the quasi-resonant excitation of ZnSe tips are analyzed in Figure 4.3. The wavelength of the pump beam, in this case, was set to 345 nm, which allows access to the two low energy transitions in the ZnSe domain: $1S(e)-1S_{3/2}(h)$ and $1P(e)-1P_{3/2}(h)$, denoted as $1S_{\text{ZnSe}}$ and $1P_{\text{ZnSe}}$, respectively, as well as three lowest transitions in CdS NRs: $1S(e)-1S_{3/2}(h)$, $1P(e) - 1P_{3/2}(h)$, and $1S(e)-3S_{1/2}(h)$, as shown in the energy diagram (Figure 4.3d). Bleaching of band edge transitions in both materials was observed within 200 fs after excitation (Figure 4.3c) with spectral positions of the bleach signals near the predicted energies of the $1S_{\text{ZnSe}}$ and $1S_{\text{CdS}}$ excitons (Figure 4.2).
The contribution of the Stark effect to the observed TA bleach signals is estimated by comparing the second derivative of the absorption spectra (Figure 4.3a) with the early-time transient spectra (Figure 4.3c), revealing, at first glance, a similarity in corresponding slopes both in the case of the CdS (450 – 465 nm) and the ZnSe (385-405 nm) transitions. However, if the early-time bleach has a significant contribution from the local fields, then the two maxima of \( \frac{d^2A}{dt^2} \) would coincide with the photoinduced absorption (\( \Delta A > 0 \)) in the TA spectra, which is not observed here, as \( \Delta A \) remains negative throughout the entire spectral window of the probe beam. Furthermore, the initial modification of transition energies associated with the Stark effect typically recovers within a few picoseconds, causing a noticeable shift of the bleach minima. Yet, in the present measurements, the spectral positions of the 1S\textsubscript{CdS} (450 – 465 nm) and 1S\textsubscript{ZnSe} (370 – 395 nm) transitions are constant within the entire nanosecond delay range (Figure 4.3b). In view of these observations, we conclude that the Stark effect on the TA spectra is negligible, as can be expected from the low pump intensities (\( \langle N \rangle \approx 0.4 \), see the Experimental section), and the observed TA bleach is attributed primarily to state filling in the ZnSe and CdS domains.

The sub-picosecond bleach recovery resulting from the 345-nm excitation (Figure 4.3c) shows an interesting trend. In contrast to the rapid decay of carrier population occupying the lowest-energy 1S excitons of ZnSe, the bleach signal of the two CdS transitions increases during the 0.2 to 0.5 ps time window, as indicated by grey arrows in Figure 4.3c. The observed rise in the populations of the 1S\textsubscript{CdS} and 1P\textsubscript{CdS} excitons cannot be attributed to the relaxation of “hot” electrons from high-\( n \) states, since the energy of the pump photons is not sufficient to induce absorption in transitions with energies above those of 1S(e)-3S\textsubscript{1/2}(h). The only electronic state that has a sufficient electron population at \( \Delta t > 200 \) fs and is energetically allowed to feed 1S(e) and 1P(e) levels of CdS, is the conduction band edge of the ZnSe domain (see Figure 4.3d).
Indeed, under resonant pumping conditions, valence electrons are selectively channeled into the 1S(e) state of ZnSe, which causes immediate bleaching of the 1S\textsubscript{ZnSe} transition. These carriers can then undergo relaxation into the lower-lying 1S(e) and 1P(e) states of CdS, leading to a rapid recovery of the 1S\textsubscript{ZnSe} bleach (since the remaining holes in ZnSe do not contribute significantly to $\Delta A$), and the simultaneous rise in the 1S\textsubscript{CdS} and 1P\textsubscript{CdS} bleach signals. Such ultrafast electron

Figure 4. 3 - TA measurements of ZnSe/CdS barbells resulting from resonant excitation of ZnSe domains ($\lambda_{\text{pump}} = 345$ nm). (a). Second derivative of the absorption profile. (b) and (c). TA spectra, $\Delta A = A(\text{pump} + \text{probe}) - A(\text{probe})$, corresponding to long (b) and short (c) delay times. (d) Energy diagram of electronic states showing the maximum energy of pump photons (blue arrows) under resonant excitation of ZnSe domains. (e). Temporal dynamics of the TA bleach recovery measured for band-edge excitons in CdS (red) and ZnSe (black) materials.
transfer is consistent with a significant driving force at the interface of ZnSe and CdS domains (total Gibbs free energy $^{52}$, $\Delta G^0 > 1 \text{ eV}$), matching electron momenta at the conduction band edges of both crystal phases, and a relatively low mismatch of lattice parameters at the interface (2.7%). The characteristic transition time corresponding to the transfer of more than half of the electron population that initially resides in the ZnSe domain into CdS NRs was calculated by comparing the temporal evolution of the integrated bleach signals for the $1S_{\text{ZnSe}}$ and $1S_{\text{CdS}}$ transitions (Figure 4.3e), and was found to be less than 350 fs.

Selective excitation of carriers into the CdS domain of the ZnSe/CdS barbells was performed using 420-nm pump pulses, for which photon energies fall below the band gap of the ZnSe tips. According to the energy diagram in Figure 4.4b, these photons can only be absorbed through the excitation of 1S and 1P excitonic transitions in CdS, while excited states of the ZnSe component remain essentially unoccupied. Experimental evidence of selective carrier injection into the CdS portion of the barbells is seen in the TA spectra, where an early-time bleach occurs primarily in the spectral range of the lower-energy $1S_{\text{CdS}}$ transition. In addition to a strong bleach of CdS, a weak negative signal was also observed in the wavelength range of the $1S_{\text{ZnSe}}$ transition, which energy lies 0.3 eV above those of the excitation photons (Figure 4.4d). Such an above-the-threshold bleach is attributed to the energy-independent effect of the local field (Stark effect) and not to the state filling, as can be inferred by the nearly-identical behavior of the earlytime TA curve and the second derivative of the absorption profile (Figure 4.4c). Indeed, due to relatively high excitation fluences used in the case of the $\lambda = 420$ excitation beam, the contribution of the Stark effect to TA bleaching becomes more noticeable than in the case of $\lambda = 345 \text{ nm}$ pumping. For instance, the effect of the local field on the $1S_{\text{ZnSe}}$ and $1S_{\text{CdS}}$ bleaching signals can be easily identified in early time traces ($\Delta t < 1 \text{ ps}$) as spectral shifts of both peaks by
several nanometers from their longer-delay position ($\Delta t > 100$ ps), as indicated by the offsets of the blue and grey lines in Figure 4d. A sizeable contribution of the stark effect to TA is also manifested by a remarkable similarity between the $\Delta A$ ($\Delta t < 1$ ps) and $d^2A/d\lambda^2$ slopes throughout the most of the spectral range.

Figure 4.4 - TA measurements of ZnSe/CdS barbells resulting from selective excitation of CdS domains ($\lambda_{\text{pump}} = 420$ nm). (a). Temporal dynamics of the TA bleach recovery for 1S(e)-1S$_{3/2}$ (h) excitons in ZnSe (black), 1P(e)-1P$_{3/2}$ (h) excitons in CdS (red), and 1S(e)-1S$_{3/2}$ (h) excitons in CdS (blue). (b). Energy diagram of electronic states showing the maximum energy of pump photons (blue arrows) under selective excitation of CdS domains. Note that the average photon energy is not sufficient to induce absorption in ZnSe. (c) Second derivative of the absorption profile. (d) TA spectra of ZnSe/CdS barbells resulting from $\lambda_{\text{pump}} = 420$ nm excitation pulses.
The contribution of the Stark effect to the band edge signals decreases with the time, $\Delta t$, such that the bleach signals corresponding to delays longer than 100 ps are primarily due to state filling. Compelling evidence of the diminishing role of the Stark effect is seen in the bleach recovery of the $1S_{\text{CdS}}$ transition, where the spectral position of the $\Delta A$ minimum is gradually red-shifted towards the steady state value of $\lambda = 455$ nm. The subsequent decay of these excitons is then driven by carrier relaxation through radiative and Auger processes. The early-time recovery of the $1S$ bleach in the ZnSe material is similar to that of the $1S_{\text{CdS}}$ excitons and is manifested by the gradual shift of the $\Delta A$ minimum towards the steady-state value of 384 nm, as expected due to the diminishing contribution of the Stark effect. The subsequent decay of this transition, however, occurs at a surprisingly slow rate, which cannot be attributed to carrier relaxation alone. Indeed, the initial bleach of $1S_{\text{ZnSe}}$ occurs primarily due to the stark effect and not to state filling since the energy of the pump photons is not sufficient to reach across the band gap of ZnSe. Nevertheless, the state filling component is clearly present in the longer-delay spectra. Moreover, the intensity of this band remains nearly constant in the 100 – 500 ps time interval, which strongly suggests re-population of the $1S$ states even after all the high lying levels in ZnSe are clearly depleted.

According to the energy diagram in Figure 4.4, the only excited state that has sufficient energy to inject carriers into $1S_{\text{ZnSe}}$ and remain populated at times longer than 100 ps is a valence band edge in the CdS portion of the barbell. The transition of holes from the $1S_h(\text{CdS})$ to the $1S_h(\text{ZnSe})$ levels is exothermic and is expected to produce a delayed re-population of ZnSe, manifested by the $1S_{\text{ZnSe}}$ bleach. Such a hole transfer scenario is also consistent with the increasing ratio of $1S_{\text{ZnSe}}$ to $1S_{\text{CdS}}$ signals with the pump probe delay (Figure 4.5), which corroborates with a connection between the onset of excited state bleach in the ZnSe domain and
a decrease of carrier population in CdS NRs. Considering the fact that the $1S_{\text{ZnSe}}$ states are initially not occupied and that the delayed bleaching of these transitions correlates well with the recovery of the CdS bleach, we conclude that resonant pumping of the CdS NRs results in the transfer of photoinduced holes into the ZnSe domain. The characteristic time for this process is 95 ps, which is much slower than transfer of electrons from ZnSe into CdS observed under resonant pumping of the $1S_{\text{ZnSe}}$ transitions.

![Figure 4.5](image)

Figure 4.5 - The ratio of $1S_{\text{ZnSe}}$ to $1S_{\text{CdS}}$ excitons $f$ as a function of pump-probe delay. The increase of $f$ supports the assumption that the delayed bleaching of $1S_{\text{ZnSe}}$ transitions occurs due to hole transfer from the band edge of CdS into that of ZnSe.

To better understand the mechanism of charge transfer in ZnSe/CdS barbells we evaluate the basic thermodynamic parameters for this system within the framework of Marcus theory\textsuperscript{52}. This approach can provide an intuitive picture of the photoinduced electron transfer (ET) through the interplay of the free energy difference between the reactants and products, $\Delta G^0$, and the extent of reorganization that the environment must undergo to accommodate the change in charge distribution, $\lambda$ (reorganize energy). Depending on these parameters, Marcus theory identifies three distinct regimes of ET that include normal ($-\Delta G^0 < \lambda$), for which the ET rate increases with increasing driving free energy for the reaction, barrierless ($-\Delta G^0 = \lambda$), for which a
maximum rate is observed, and inverted (-ΔG° > λ), for which the ET rate decreases despite increasing exothermicity driving the reaction.

The main idea of our analysis is to identify a specific ET regime occurring in the fabricated barbells by constructing free energy curves that represent different states of the system as quadratic functions of bath polarization\textsuperscript{76}. As was recently demonstrated by Scholes \textit{et al.}\textsuperscript{77}, such a qualitative description of the electronic processes in heterostructured NCs can be derived from the steady-state emission and absorption spectra provided that the signature of the charge transfer bands can be identified in optical measurements. Within this approach, the reorganization energy associated with an interfacial electron transfer is given approximately as half the Stokes shift between the spatially indirect absorption and the emission energy, which, in this study, corresponds to spectral values of 535 and 583 nm, respectively (Figure 4.6b). Using this information, we can plot the free energy curves (Figure 4.6c) for electronic states in ZnSe, CdS and charge transfer (CT) bands relative to the ground state, calculated as quadratic functions of coordinate x:\textsuperscript{78}

$$G_i(x) = \frac{1}{2}(x - \sqrt{2\lambda_i})^2 + \Delta G_i^0,$$

Where the harmonic force constant is set to unity, and ΔG° \textsubscript{i} is the free energy difference between the ground state and the excited state \textit{i}, given by the energy of the absorption peak E\textsubscript{i} minus the reorganization energy λ\textsubscript{i}.

In order to determine the Stokes shift for all three excitation bands we have assumed that the inhomogeneous broadening of absorption and emission lines corresponds to a Gaussian shape, which represents the case of weakly correlated transitions\textsuperscript{79}. By fitting the absorption and emission CT bands in Figure 4.6b, we find that the reorganization energy required for the
electron transfer from ZnSe to CdS is 94 meV. Based on the fact that the free energy difference, \( \Delta G_0 \), for this band is -1.03 eV, we conclude that the charge transfer reaction occurs in the Marcus inverted region, \((-\Delta G_0 > \lambda)\). Similar results were also found for the case of CdSe/CdTe nano-barbells, where the inverted regime of ET was attributed to the weak exciton-phonon coupling in semiconductor NCs.

Figure 4.6 - Modeling free energy curves associated with the charge transfer in ZnSe/CdS barbells. (a) A fragment of the TA spectrum showing the energy of the ZnSe band edge transition. (b). Analysis of the emission and absorption transitions in ZnSe/CdS barbells. (c). Free energy curves for the ZnSe, CdS, and charge transfer (CT) bands versus bath polarization obtained from the analysis of barbell spectra.

In conclusion, we have used transient absorption spectroscopy to study the dynamics of photoinduced charge transfer in type II heterostructured nanocrystals comprising a barbell-like arrangement of ZnSe and CdS semiconductors. Experimental data provides strong evidence for photoinduced charge transfer between the two nanocrystalline domains, which can be
controllably performed in either direction by modulating the excitation wavelength, such that the resonant excitation of carriers in the ZnSe material leads to 350 fs injection of electrons into CdS, and the excitation of carriers in the CdS portion of barbells results in a slower transfer of holes into ZnSe. A qualitative thermodynamic description of observed electron processes within the classical limit of Marcus theory was subsequently used to show that the charge transfer reaction between ZnSe into CdS domains occurs in the Marcus inverted region.
CHAPTER 5

COMPOSITION-TUNABLE PROPERTIES OF CdS$_x$Te$_{1-x}$ ALLOY NANOCRYSTALS

5.1 Introduction

Semiconductor alloy nanocrystals (AB$_x$C$_{1-x}$)$_{80-83}$ are becoming increasingly important in many areas of nanoscale engineering because of the continuous tunability of their physical and optical properties through the gradual variation of the composition variable $x$. This added degree of freedom allows tuning an exciton energy of alloy nanoparticles independently of their size, which can be used to extend the nanocrystal (NC) emission range into parts of the spectrum that are not easily accessible with binary quantum dots (QDs), or to achieve a wide range of fluorescence colors from nanoparticles of the same diameter. Further optimization of nanocrystal properties is also possible by varying the ratio of alloying elements throughout the quantum dot, such that either homogeneous or gradient nanocrystal composition, often with distinctly different properties, can be formed. Owing to their superior luminescent properties that are on par with binary nanocrystals, ternary alloys are now well suited for many practical realizations, including quantum dot-based LEDs$^{84}$, where emission at a specific wavelength is often required; in vivo imaging$^{81,85-87}$, where small diameter infrared fluorescence labels are preferred; and solar cells$^{23,88}$, where a wide range of absorption and the small size of NC sensitizers are an advantage.

To date, several II-IV semiconductor alloy nanocrystals have been synthesized: CdS$_x$Se$_{1-x}$$_{80}$, Cd$_x$Zn$_{1-x}$S$_{89}$, Cd$_x$Zn$_{1-x}$Se$_{82,90}$, CdSe$_x$Te$_{1-x}$$_{91}$, and HgSe$_x$S$_{1-x}$$_{83}$. These compounds can be classified into two groups according to the type of the two elements, whose stoichiometric ratio
is varied in the resulting ternary alloy, such that nanocrystals of the first group consist of two chalcogen atoms and one transition-metal element (CdS\(_x\)Se\(_{1-x}\), CdSe\(_x\)Te\(_{1-x}\), and HgSe\(_x\)S\(_{1-x}\)), and nanocrystals of the second type are made of two transition-metal elements and one chalcogen atom (Cd\(_x\)Zn\(_{1-x}\)S, Cd\(_x\)Zn\(_{1-x}\)Se). Recent work\(^80,92\) has demonstrated that, in contrast to the second group alloys, whose properties change quasi-linearly with their composition, the properties of nanocrystals in the first group have a pronounced nonlinear dependence on the ratio of the two chalcogens in the alloy and thus could be difficult to predict. For instance, it was found\(^81\) that the emission energies of CdSe\(_x\)Te\(_{1-x}\) NCs are well outside the range of the transition energies of contributing CdSe and CdTe binary QDs, such that \(E(\text{CdSe}_{x}\text{Te}_{1-x}) < xE(\text{CdSe}) + (1 - x)E(\text{CdTe})\).

These nonlinear effects, also known as “optical bowing”, have been observed previously in bulk semiconductors and were subsequently explained in a work by Bernard and Zunger\(^93\) that identified three structural and electronic factors leading to the nonlinearity of ternary compounds: (i) different ions in the alloy have different atomic sizes, (ii) these ions have different electronegativity values, and (iii) the binary structures have different lattice constants. Thus far, the bowing effect has been confirmed for ternary quantum dots that were based on S/Se and Se/Te combinations of chalcogen atoms. Meanwhile, no reports of S/Te composed ternary nanocrystals have been made, which according to Bernard and Zunger should exhibit more extensive nonlinearity, resulting from the large differences in S and Te atomic radii and their electronegativities. In this work, we thus aim to explore such a combination of chalcogens by studying the optoelectronic properties of CdS\(_x\)Te\(_{1-x}\) alloy nanocrystals. The use of Cd as a transition metal was inspired by substantial lattice mismatch (11%) between the binary semiconductor quantum dots CdS and CdTe, which should further enhance nonlinear effects.
In this work, both homogeneous and gradient ternary CdS$_x$Te$_{1-x}$ semiconductor nanocrystals were synthesized via traditional pyrolysis of organometallic precursors. Strong optical bowing was verified for the case of homogeneous alloy NCs, where the emission peak was red-shifted with respect to those of the CdS and CdTe binary subcompounds, extending into the near infrared region. In contrast to homogeneous CdS$_x$Te$_{1-x}$ alloy NCs, nanoparticles with a graded composition of S and Te ions did not exhibit significant nonlinear effects. Nonetheless, their optical properties were found to be different from those of binary or core/shell nanocrystals and to a certain extent from those reported for other ternary heterostructures. For instance, the observed Stokes shifts were in the range of 80-100 nm, which is considerably larger than that for most semiconductor nanocrystals. This property of gradient ternary CdS$_x$Te$_{1-x}$ NCs can be of interest in applications that require a small degree of spectral overlap between the emission and absorption profiles such as in Forster resonance energy transfer-based sensors\textsuperscript{94-96} or when reduced self-absorption of colloids is an advantage.

### 5.2 Experimental section

#### 5.2.1 Synthesis of CdS$_x$Te$_{1-x}$ NCs with Homogeneous Composition

All reactions were conducted under argon atmosphere using standard Schlenk techniques. Cadmium solution was prepared by dissolving 0.0128 g of cadmium oxide in 0.2 mL of oleic acid and 4 mL of 1-octadecene (ODE) in a 25-mL flask while heating the mixture to 300 °C. The sulfur injection stock solution was prepared by mixing 0.0016 g of sulfur in 1.5 mL of ODE and heating to 180 °C followed by cooling of the final (clear) solution to room temperature. The tellurium solution was prepared by dissolving 0.0095 g of tellurium in 0.5 mL of
tributylphosphine and then further diluting the mixture with 2 mL of ODE. To ensure the simultaneous injection of the precursors during the synthesis of homogeneous alloy NCs, epimolar amounts of tellurium and sulfur solutions were mixed together. The mixture was then injected into the cadmium solution at a rate of 0.02-0.05 mL/min while being stirred. The reaction was stopped after 20 min by removing the flask from the heating mantle.

### 5.2.2 Synthesis of CdS$_x$Te$_{1-x}$ NCs with Gradient Composition

The same procedure was carried out to prepare the cadmium, sulfur, and tellurium stock solutions. During the synthesis, the sulfur solution was injected into the reaction flask where a dissolved cadmium solution was kept at 300 °C. The temperature was then lowered to 250 °C, and 0.01-0.04 mL of tellurium was added to the mixture 1-6 min following the S injection. The reaction was stopped after 30-40 min by removing the flask from the heating mantle.

### 5.2.3 Purification of CdS/CdTe QDs

After the reaction mixtures were allowed to cool to 50 °C, 3-5 mL of hexane was added to the solution to prevent solidification. The subsequent cleaning of nanocrystals was done by hexane/methanol extraction. Typically, 6-7 mL of methanol was slowly added to the reaction mixture in hexane, which was then centrifuged for 10 min at 3500 rpm. The upper hexane layer containing QDs was taken out with a syringe for further purification. We found that at least 3-4 extraction cycles were necessary to ensure that the quantum yield of NC colloids was maximized.
5.2.4 Characterization

UV-vis absorption and photoluminescence (PL) spectra were recorded using a CARY 50 scan spectrometer and a Jobin Yvon Flurolog FL3-11 fluorescence spectrophotometer. The PL quantum yield of sufficiently dilute nanocrystal suspensions was determined relative to that of quinine sulfate, Cy3, and Cy5 dyes that were excited at 360-420 nm. For energy-dispersive X-ray (EDX) measurements, purified nanocrystals were deposited onto carbon substrates and loaded into a Hitachi (S-2700) scanning electron microscope (SEM) equipped with an EDAX detector. High-resolution transmission electron microscopy (TEM) measurements were carried out using JEOL 311UHR operated at 300 kV. Specimens were prepared by depositing a drop of nanocrystal hexane solution onto a Formvar-coated copper grid and letting it dry in air. X-ray powder diffraction (XPD) measurements were carried out on a Scintag XDS-2000 X-ray powder diffractometer.

5.3 Results and Discussion

5.3.1 Homogeneous CdS\textsubscript{x}Te\textsubscript{1-x} Alloy Nanocrystals

Previous work on the synthesis of alloy NCs showed that a highly homogeneous spatial distribution of elements within a quantum dot can be achieved if the amount of both precursors is in great excess of the amount of the transition metal\textsuperscript{97,98}. This approach minimizes the influence of uneven reactivities of the participating chalcogens, such as in the case of S and Te, which can lead to a gradient-like composition. Accordingly, homogeneous CdS\textsubscript{x}Te\textsubscript{1-x} nanocrystals were synthesized under Cd limited conditions by the gradual injection of S/Te precursors with a
carefully controlled molar ratio. The as-synthesized nanocrystals were investigated by means of transmission electron microscopy and X-ray powder diffraction to collect statistically reliable data for nanocrystal size, shape, and crystallinity. Typical TEM images of large-diameter CdS$_x$Te$_{1-x}$ nanocrystals are shown in Figure 5.1. The shape of most of the nanoparticles appeared to be elongated, indicating a faster nanocrystal growth along one of its axes. By examining 30-40 isolated specimens under high magnification (up to ×600 K), we estimated the average width and the length of nanoparticles to be 5.1 ± 0.2 and 6.3 ± 0.4, respectively. Considering the size of nanoparticles, the distribution of their diameters was relatively narrow (SD: 7%).

The crystal structure of the homogeneous CdS$_x$Te$_{1-x}$ nanocrystals with a 1:1 stoichiometric ratio of S and Te precursors was investigated using X-ray powder diffraction. By comparing the experimental pattern, shown in Figure 5.2, with the peak positions expected from the cubic phases of bulk CdS and CdTe crystals, we conclude that the lattice structure is
predominantly cubic sphalerite with no evidence of the hexagonal phase. The two reflection peaks (220) and (311) at 42° and 48° appear to incorporate the diffraction patterns of both the CdS and CdTe bulk crystal structure, which is consistent with a linear dependence of the lattice spacing of the homogeneous alloy structure on its composition. The mixture of the CdS and CdTe phases is skewed toward CdTe, as is evidenced by the asymmetric intensity profiles of the (220) and (311) Bragg peaks, which indicates that ternary alloys prepared with an equal amount of chalcogen precursors contain more Te than S ions. This result is also consistent with the EDX analysis showing that the final ratio of Te to S in the homogeneous alloy NCs is 1.5.

Figure 5.2 - X-ray powder diffraction spectra of homogeneous CdS$_x$Te$_{1-x}$ nanocrystals along with XPD patterns of CdTe and CdS bulk cubic phases. Broadening of reflection peaks is attributed to an alloying effect, which alters binary lattice parameters.

The growth kinetics of the reaction mixture is summarized in Figure 5.3, where the evolution of fluorescence (FL) and absorption spectra measured at different times after the
injection of S and Te precursors is shown. Because of a considerable mismatch of band gap energies between the CdS and CdTe binary nanocrystals, the resulting absorption profile of CdS$_x$Te$_{1-x}$ is relatively broad with no clear indication of the band edge peak. Such a wide absorption spectrum seems to be unique to the S/Te combination of elements as it is largely different from the spectral shapes observed in previously studied CdS$_x$Se$_{1-x}$ and CdSe$_x$Te$_{1-x}$ nanocrystals, where distinct absorption features centered near band edge energies were reported. The possibility of inhomogeneous broadening of the CdS$_x$Te$_{1-x}$ absorption profile caused by large variations in nanocrystal diameters should be discarded because of the relatively narrow widths of the observed-

Figure 5.3 - Evolution of the UV-vis absorption and room-temperature fluorescence spectra of homogeneous CdS$_x$Te$_{1-x}$ alloy NCs. During nanoparticle growth, the FL peak gradually shifts from 690 nm (1 min) to 745 nm (45 min).
fluorescence emission, which indicates quasi-monodispersity of the nanoparticles. We therefore believe that a monotonous absorption spectrum is an intrinsic feature of the fabricated CdS$_x$Te$_{1-x}$ alloys. As shown in Figure 5.3, the nanocrystal growth is accompanied by a steady evolution of the fluorescence peak in the spectral window of 690-745 nm, corresponding to nanoparticle sizes of 2.8-6 nm. The quantum yield of the as-fabricated samples in chloroform steadily increases during nanocrystal growth, reaching 6-7%, and is further improved to 14% after coating the purified nanoparticles with a thin ZnS shell in a separate procedure.

![Figure 5.4](image)

Figure 5.4 - Energy dispersive X-ray emission spectrum of homogeneous (a) and gradient (b) CdS$_x$Te$_{1-x}$ alloy nanocrystals.

Energy dispersive X-ray emission spectra were measured to study the elemental composition of the fabricated alloys. For this purpose, a hexane suspension of purified CdS$_x$Te$_{1-x}$ nanocrystals
(FL peak at 745 nm) was evaporated onto a carbon substrate and loaded into an SEM equipped with an X-ray detector. Figure 5.4a shows a typical X-ray spectrum obtained at 20 kV, along with peak assignments for elemental Cd, S, and Te. After integrating the peak area, we converted the X-ray count into the elemental weight percentages using quantification software (EDAX Genesis). The resulting stoichiometric ratio of elements Cd/S/Te was found to be 29:11:17. The amount of Cd in the sample was approximately balanced by the combined amounts of S and Te, which indicates that most of the unreacted ions were removed during purification. From the ratio of S to Te, we determine the stoichiometry of the homogeneous alloy NCs, fabricated by using equal portions of the chalcogen precursors, to be CdS$_{0.4}$Te$_{0.6}$.

In order to understand how the observed emission energies of the CdS$_{x}$Te$_{1-x}$ alloy NCs relate to the emission range of CdS and CdTe binary QDs, we measured the fluorescence of ca. 3.9-nm-diameter CdS and CdTe QDs and compared their spectra to the emission of 3.9-nm CdS$_{x}$Te$_{1-x}$ NCs. As can be seen from the positions of the three peaks in Figure 5.5, the FL peak of the alloy NC is well outside the wavelength range defined by binary CdS and CdTe QDs, with a corresponding interval between CdTe and CdS$_{x}$Te$_{1-x}$ peaks of 125 nm, which indicates that the band gap of a ternary CdS$_{x}$Te$_{1-x}$ NC is smaller than that of CdS or CdTe QDs. This result is consistent with Vegard’s Law for bulk semiconductors, which states that, while the lattice constant changes linearly with composition, other properties, such as band gap, have a more complex dependence on the stoichiometric ratio of binary subcompounds. In the quadratic approximation, the value of the band gap becomes:

$$E_g(CdS_xTe_{1-x}) = xE_g(CdS) + (1 - x)E_g(CdTe) - bx(1 - x)$$  \hspace{1cm} (1)
Where, $b$ is the bowing constant that describes the extent of nonlinearity and $0 < x < 1$.

To estimate $b$ for the CdS$_x$Te$_{1-x}$ alloys fabricated here, we substituted the band gap values of the bulk semiconductor materials, $E_g$, in eq 1, with the measured emission energies of equal-sized CdS, CdTe, and CdS$_x$Te$_{1-x}$ nanocrystals. The strongest nonlinear effects were realized for 3.9-nm-diameter nanoparticles (shown in Figure 5.5), corresponding to a bowing constant of 3.17. This result is somewhat greater than previously reported values of $b$ for other ternary compounds (Table 5.1), which is not surprising if we consider the main factors that contribute to nonlinear behavior in alloys. According to a model proposed in ref 16, the bowing effect is associated with a large lattice mismatch between binary subcompounds, and differences in atomic radii and electronegativities of alloying elements. For CdS$_x$Te$_{1-x}$ nanocrystals, all of these factors are
substantial. First, the lattice mismatch between CdS and CdTe quantum dots (11% for zinc blende structure) is the largest among the possible combinations of binary nanocrystals that form alloys that have been previously reported. Second, the difference in electronegativities and atomic radii (bond length) of S and Te chalcogens is the greatest in group IV elements.

Table 5. 1 - Comparison of the Bowing Constants for Ternary Nanocrystals

<table>
<thead>
<tr>
<th>ternary nanocrystal</th>
<th>bowing constant, $b$</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS$<em>{0.55}$Se$</em>{0.47}$</td>
<td>0.3</td>
<td>ref 1</td>
</tr>
<tr>
<td>CdS$<em>{0.34}$Te$</em>{0.66}$</td>
<td>1.19</td>
<td>calculated from ref 2</td>
</tr>
<tr>
<td>CdS$<em>{0.55}$Te$</em>{0.50}$</td>
<td>3.17</td>
<td>present work</td>
</tr>
</tbody>
</table>

5.3.2 Gradient Cd$_x$Te$_{1-x}$ Alloy Nanocrystals

In contrast to homogeneous alloys, gradient ternary nanocrystals have a continuously changing composition in the form of Cd$_x$Te$_{1-x}$, where $x$ can vary from 0 to 1 within a single quantum dot. These compounds were grown by creating a 1-6 min delay between consecutive injections of the two chalcogen precursors into the Cd solution. In this work, we mainly focus on the synthesis of gradient alloys containing a CdS core, which was motivated by earlier reported$^{91}$ difficulties in the fabrication of fluorescent CdS/CdTe core/shells nanocrystals, via a traditional two-step overcoating procedure. We anticipate that a gradual change of the composition at the CdS/CdTe interface can help minimize lattice stress, which is partially responsible for the absence of FL emission in CdS/CdTe core/shell NCs. The evolution of optical spectra during nanocrystal growth is shown in Figure 5.6. The initial formation of a CdS core is seen in the bottom spectrum, which shows the optical characteristics of a sample that taken was taken 4 min...
after the sulfur injection. Upon the first addition of Te precursor into the reaction flask, the growth solution turned dark red, which was accompanied by appearance of the FL feature near 670 nm. During the subsequent growth, this peak gradually red-shifted until reaching a “saturation” value of 695 nm. The quantum yield of the as-prepared nanocrystals was somewhat lower than that of homogeneous alloys, reaching a maximum value of only 4%. Yet this is the first evidence of CdS/CdTe-like arrangement with a nonzero emission yield.

Figure 5.6 - Evolution of emission (red) and absorption (black) spectra for gradient CdS$_x$Te$_{1-x}$ nanocrystals during their synthesis. The bottom panel shows spectral features of CdS QDs that form in the reaction flask before the injection of Te precursor.

Figure 5.7 shows several TEM images of gradient CdS$_x$Te$_{1-x}$ nanocrystals fabricated by introducing a 6 min delay between the injection of S and Te precursors into the reaction flask. A nearly spherical shape was observed for most of the nanoparticles examined. The average
diameter, determined by studying several specimens under 300 000 magnification (Figure 5.7b), was found to be 5.2 nm, with a somewhat wider distribution of sizes than was observed for homogeneous alloys. The inferior monodispersity of gradient nanocrystals is also reflected in their emission spectra, where the values of the corresponding FL peak widths are almost twice as large as those obtained for homogeneous nanocrystals.

![High-resolution TEM images of CdS\textsubscript{x}Te\textsubscript{1-x} nanocrystals with the gradient composition of S and Te. The scale bars are (a) 20 and (b) 5 nm. (c) Ultrahigh resolution image of the 5.0-nm nanoparticle showing the crystal lattice planes.](image)

The elemental composition of gradient CdS\textsubscript{x}Te\textsubscript{1-x} nanocrystals was investigated using EDX. A typical X-ray scan of purified samples is shown in Figure 5.4b. After converting the integrated peak area into elemental weight percentages, we found the stoichiometric ratio for the three elements Cd, S, and Te to be 1.00:0.35:0.47. X-ray powder diffraction analysis was conducted to further investigate the structure of gradient CdS\textsubscript{x}Te\textsubscript{1-x} alloy NCs. Figure 8 shows an experimental diffraction pattern of nanoparticles that were fabricated by introducing a 4 min delay between the injection of S and Te solutions. By comparison with the peak positions of bulk CdTe and CdS, we identify both cubic and wurtzite lattice structure in our samples. In contrast to the broad spectral features that were observed for homogeneous CdS\textsubscript{x}Te\textsubscript{1-x}, the major reflection...
peaks associated with the CdTe and CdS phases in gradient alloy NCs are easily distinguishable, indicating the formation of separate CdTe and CdS lattice structures. Such a pattern cannot be produced in a pure alloy crystal structure, where a unique ternary lattice is formed, indicating that the composition of the gradient CdS\textsubscript{x}Te\textsubscript{1-x} nanoparticles is more comparable to a core/shell arrangement. In this case, nonlinear effects that arise in homogeneously alloyed CdS\textsubscript{x}Te\textsubscript{1-x} NCs may not be as strong in gradient NCs because of the lower volume of the ternary crystalline phase.

Figure 5.8 - XPD spectra of gradient CdS\textsubscript{x}Te\textsubscript{1-x} alloy NCs along with XPD patterns of relevant bulk phases. Major reflection peaks associated with CdTe and CdS crystal structure are well separated, which is consistent with a core/shell arrangement.

To understand if optical bowing is significant in gradient alloys, we calculated the positions of the 1S\textsubscript{c} and 1S\textsubscript{h} energy levels for a CdS/CdTe core/shell nanoparticle, where a sharp
interface between the two semiconductor materials was assumed. The size of the core CdS nanocrystals in our calculations was set to be equal to that of the CdS seeds that form in the growth solution before the Te injection. It was estimated from the known relation between the FL peak and nanocrystal diameter to be 3.9 nm.

Figure 5.9 shows the relative alignment of zero-angular momentum states for the two different thicknesses (H) of the CdTe shell. When \( H = 0.4 \) monolaye (Figure 9a), the conduction band edge of CdS is situated lower than that of CdTe, causing an electron to localize primarily in the core of the heterocrystal, whereas the higher positioned valence band edge in CdTe results in the shell localization of an excited hole. For this type II interfacial band alignment, the recombination of carriers occurs via a spatially indirect transition, characterized by emission energies that are lower than the ones corresponding to carrier recombination in isolated CdS and CdTe QDs. As shown by the energy diagram in Figure 5.9a, the transition wavelength for this case is expected to be around 595 nm. The experimental value of the FL peak, measured for a sample of thin-shell CdS/CdS\(_x\)Te\(_{1-x}\) nanocrystals, was 670 nm (Figure 5.6). While this difference indicates that some degree of optical bowing could be present, the exact value of \( b \) cannot be determined for this case because of insufficient data on the composition of the gradient alloy. For instance, it is not certain if the shell itself is a gradient mix of S and Te or if it is primarily formed by Te ions as should follow from the stoichiometric ratio of the precursors. For larger gradient nanocrystals such compositional analysis, however, becomes possible through a combination of UHR TEM and EDX measurements, which determine an approximate percentage of Te in the shell. By comparing the average diameter of the quasi-spherical ternary nanocrystals obtained from the TEM study with the size of the CdS seeds that are formed in the flask by the time of Te injection, we can estimate the thickness of the CdS\(_x\)Te\(_{1-x}\) shell. For the 5.2-nm alloy
nanoparticles shown in Figure 5.7, the diameter of the CdS QDs, determined from their emission spectra, was 4 nm, which corresponds to a 2-nm-thick layer of overgrown CdS$_x$Te$_{1-x}$ material. According to the EDX scan of these nanocrystals, the ratio of tellurium to sulfur in a gradient alloy is 1.5. If we assume that the penetration of Te into the CdS core is negligible, then the average ratio of Te to S in the shell of 5.2-nm-diameter gradient CdS$_x$Te$_{1-x}$ NC is approximately 10. This provides additional support to our conclusion that the composition of the gradient alloy NCs is very similar to the CdS/CdTe core/shell arrangement.

Figure 5.9 - Energy diagram showing positions of the zero-angular momentum states in CdS and CdTe binary NCs. Expected optical transitions for a CdS/CdTe core/shell NC containing 0.4 monolayers (a) and three monolayers (b) of CdTe in the shell.

We now would like to address whether any degree of optical bowing is present in large-diameter gradient alloys by comparing their experimental emission energies with that of the CdS/CdTe core/shell structure shown in Figure 5.9b. We first consider the CdTe shell, where the physical properties are linearly dependent on the composition, such that the positions of its zero-angular momentum energy levels, 1$S_e$ and 1$S_h$, are defined by the $x$ to 1 - $x$ ratio of the
corresponding levels in CdS and CdTe nanocrystals. For this arrangement, an excited e-h pair in a 5.2-nm nanocrystal shown (Figure 5.9b) is expected to localize entirely within the shell, which should lead to a transition wavelength of 682 nm. An experimentally observed value for this transition (698 nm, Figure 5.5, top panel) is slightly redshifted, indicating that some extent of bowing could be present. Even if the actual portion of Te in the shell is different from the estimated value of 90%, the transition wavelength in CdS/CdS$_x$Te$_{1-x}$ nanocrystals with linear composition dependence would still be less than the experimental value of $\lambda$ ) 698 nm. We therefore conclude that, for gradient CdS$_x$Te$_{1-x}$ NCs, $b$ is greater than zero. It is also apparent that the bowing effect in gradient alloys is less extensive than that in homogeneous nanocrystals, where red-shifting in the range of 100-130 nm was observed.

5.3 Conclusions

In conclusion, we report on the colloidal synthesis of novel CdS$_x$Te$_{1-x}$ alloy NCs with both homogeneous and gradient compositions of S and Te chalcogens. Our results demonstrate the existence of strong nonlinear effects in homogeneously alloyed nanoparticles, evidenced by a significant red-shift of the emission of ternary compounds relative to FL peaks of binary CdS and CdTe quantum dots, which corresponded to a bowing constant of 3.17. Optical spectra of gradient CdS$_x$Te$_{1-x}$ alloy nanocrystals, fabricated by overcoating small CdS seeds with CdTe-rich shell in a one-pot synthesis, differed from those of homogeneous ternary alloys. In addition to a smaller extent of optical bowing observed for these nanoparticles, their absorption profile was dominated by a CdS $1S_e$-$1S_h$ peak with almost vanishing absorbance for lower photon energies, which gives rise to large Stokes shifts with values of up to 150 nm.

~ 79 ~
Overall, the optical properties of fabricated CdS$_x$Te$_{1-x}$ were found to be markedly different from those of binary or core/shell nanocrystals and to a certain extent from those reported for other ternary heterostructures, making these materials of potential interest in biomedical imaging and photovoltaics.
CHAPTER 6
BLUE-SHIFTED EMISSION IN CdTe/ZnSe HETEROSTRUCTURED NANOCRYSTALS

6.1 Introduction

Conjoining different semiconductor nanostructures in a single quantum dot (QD) provides a synthetic means for the development of novel optoelectronic materials. Indeed, through an appropriate selection of their nanoscale components, such heteronanocrystals (NCs) offer superior control over the spatial distribution of carriers across material interfaces, which determines the overall functionality of the quantum system. Conventionally, a heterojunction of two semiconductor materials can be classified as either type I, where both carriers are confined within the same semiconductor, or type II, where an electron and a hole are spatially separated in two different parts of the heterostructure. Because of the highly stable emission of NCs in the first group\textsuperscript{100-102}, their properties are readily utilized in applications that require the coupling of a QD to organic moieties, such as in hybrid light-emitting diodes (LEDs)\textsuperscript{84, 103} or in vivo imaging\textsuperscript{104, 105}, where the use of binary QDs can lead to an irreversible loss of fluorescence\textsuperscript{106-109}, or severe blinking\textsuperscript{107-109}. Heterostructures of the second group, on the other hand, benefit from an efficient separation of charges between the core and the shell, which makes them useful in photovoltaic applications\textsuperscript{23, 33, 88, 110, 111}, where spatial charge separation reduces the exciton dissociation potential, or QD-based lasers\textsuperscript{112}, where an electric dipole of a photogenerated pair Stark-shifts the biexciton level resulting in a desirable linear light amplification regime.
One common feature, characteristic of the above-mentioned carrier localization types is the straightforward correspondence between a QD emission range and the energy spacing between the two closest band edges the semiconductor materials that form a heterostructure. Indeed, for both type I and type II hetero-NCs, the energy of the emitted photons is determined by the energy difference between the closest zero-angular momentum states, $1S(e)$ and $1S_{3/2}(h)$, of the adjoining materials.

Here we show that II-VI semiconductor hetero-NCs can also emit in a wavelength range that does not correspond to any of the electronic transitions that can be expected from the band structure of their core- or shell-located materials, such that the localization of carriers in these structures can no longer be classified as type I or type II. This behavior was demonstrated in novel CdTe/ZnSe core/shell hetero-NCs fabricated via organometallic routes. In addition to a weak infrared fluorescence that was expected due to a type I band alignment in a CdTe/ZnSe NC arrangement, we observed a blue-shifted emission peak, with an associated quantum yield (QY) of up to 24%. The present study shows that the emission in the CdTe/ZnSe hetero-NCs arises from the recombination of carriers within an interfacial layer, which is formed along the core/shell interface due to the interdiffusion of Se and Zn ions into the CdTe lattice during shell deposition. This type of electron-hole localization has been observed previously in CdTe/ZnSe quantum wells, where atomic interdiffusion at the junction of the two semiconductor thin films leads to the formation of an alloy layer emitting in the 520-600-nm range.

Besides answering related fundamental questions, the demonstrated emission in CdTe/ZnSe hetero-NCs could be of interest in a number of applications, including the development of sensors utilizing Förster resonance energy transfer (FRET$^{94-96}$), where the interfacial localization of excitons can help reduce the effective distance between donor and
acceptor moieties. Biological sensor applications of CdTe/ZnSe materials should also benefit from the fact that only a few monolayers (MLs) of ZnSe shell efficiently decouple the electronic wave functions in CdTe/ZnSe hetero-NCs from the surface environment, which permits a simultaneous realization of the near-surface excitations and improved emission stability.

6.2 Experimental section

6.2.1 Chemicals

Cadmium oxide (99%, Aldrich), Se powder (99.5%, Aldrich), Te powder (99.99%, Aldrich), 1-octadecene (ODE, 90%, Aldrich) tributylphosphine (TBP, 99%, Aldrich), oleic acid (OA, 90%, Aldrich), trioctylphosphine (TOP, 97%, Strem), trioctylphosphine oxide (TOPO, 99%, Aldrich), hexadecylamine (HDA, 99%, Aldrich), ZnEt₂ (97% pure, 10% by weight in hexane, Strem), benzoyl peroxide (BPO, 97%, Aldrich), benzylamine (BzNH₂, 99%, Acros), anhydrous hexane (Aldrich), methanol (Aldrich), chloroform (Acros), and toluene (Aldrich) were used as purchased.

6.2.2 Synthesis of CdTe Nanocrystals

All reactions were conducted under an argon atmosphere using standard Schlenk techniques. The synthesis of monodisperse zinc blende CdTe nanocrystals was based on the procedure described previously⁶⁸. Namely, 0.0128 g (0.1 mmol) of cadmium oxide was dissolved in 0.2 mL (0.63 mmol) of oleic acid and 4.9 mL (3.87 g) of ODE by heating reagents to 280 °C in the 25-mL three-neck flask while stirring. After the mixture became clear, tellurium stock
solution, prepared by dissolving 0.0064 g (0.05 mmol) of tellurium in 0.07 mL of TBP and 1.25 mL (0.986 g) of ODE was swiftly injected into the reaction flask. During the nanocrystal growth, the temperature was kept at 270 °C. The reaction was stopped after 0.5-5 min, depending on the desired nanocrystal size, by removing the flask from the heating mantle.

### 6.2.3 Purification of CdTe Nanocrystals

After the reaction mixture was allowed to cool down to 50 °C, 3-5 mL of hexane was added into the solution to prevent solidification. The subsequent cleaning of the nanocrystals was done by hexane/methanol extraction. Typically 6-7 mL of methanol was slowly added to the reaction mixture in hexane, which was then centrifuged for 10 min at 3500 rpm. The upper hexane layer containing CdTe NCs was taken with a syringe for further purification. Eventually a clear solution of nanoparticles in hexane was obtained. The suspension was then placed under argon and stored in the dark for future shell deposition.

### 6.2.4 Overcoating with ZnSe

A mixture of 1.7 g (4.4 mmol) of TOPO and 1.5 g (6.6 mmol) of HDA in a 25-mL three-neck flask was degassed at 140 °C for 1 h under vacuum. The solution was then allowed to cool down and transferred to argon gas. At this stage, 1.8 mL (1.5 g) of TOP and all of the previously prepared CdTe nanocrystals were added to the flask and heated to 240 °C. The Se solution was prepared by dissolving 0.032 g (0.4 mmol) of Se powder in 1.8 mL (1.5 g) of TOP. The Zn injection solution was prepared by mixing 1.5 mL of 10% diethylzinc with 1.8 mL (1.5 g) of TOP and heating the mixture to 75 °C for 2 h while stirring in order to form TOP-Zn complexes.
During the overcoating procedure a mixture of Zn/Se stock solutions was injected into the reaction flask with CdTe NCs at 240 °C at a rate of 0.015 mL per minute. Aliquots of the growth solution were taken at 5-min intervals for UV-vis and photoluminescence (PL) spectral characterization. The reaction was stopped after approximately 40 min, and the mixture was cooled down to 70 °C. For the shell deposition via successive ion layer adsorption reaction (SILAR), 0.1 mL injections of Zn and Se stock solutions were made sequentially every 5-8 min starting with Zn ions. A total of 5 monolayers were grown.

6.2.5 Synthesis of Ternary (Cd$_x$Te$_y$Zn$_{1-x}$, Cd$_x$Te$_x$Se$_{1-x}$, Zn$_y$Te$_x$Se$_{1-x}$) and Quarternary (Zn$_x$Cd$_{1-x}$Se$_y$Te$_{1-y}$) Nanocrystals.

A unified approach to the synthesis of ternary and quaternary alloy nanocrystals was based on procedures adapted from previous studies $^{82,90,91}$. In the first step, CdO was decomposed in the reaction flask by dissolving 0.0128 g (0.1 mmol) of cadmium oxide in 0.2 mL (0.63 mmol) of oleic acid and 4.9 mL (3.87 g) of ODE at 260-290 °C. In separate vials, tellurium, zinc, and selenium stock solutions were made by dissolving 0.05 mmol of the corresponding source (Te powder, diethylzinc, Se powder, respectively) in 1.8 mL of TOP. During the synthesis of the alloy nanocrystals, appropriate stock solutions were combined and injected into the reaction flask at 260 °C. The injection rate was 0.02 mL per minute.

6.1.6 Etching with BPO

The controlled etching of the nanocrystals with BPO was done following the technique described previously $^{68,113}$. Prior to the etching of the nanocrystals with BPO, their surface
ligands were exchanged to shorter benzylamine by placing 0.5 mL of purified CdTe/ZnSe NCs in hexane with a concentration in about 2 mL of benzylamine. The mixture was then sonicated for approximately 15-20 min or until the nanocrystals were totally dispersed yielding a clear solution. 1.0 mL of this suspension was added to 5.0 mL of a 3:1 toluene/methanol mixture. To initiate the etching process, a solution of benzoyl peroxide (0.165 M in 1:1 toluene/methanol) was quickly injected into the nanocrystal suspension. The etching process was monitored using a home-built confocal microscope fiber coupled to a spectrometer.

6.1.7 Characterization

UV-vis absorption and PL spectra were recorded using a CARY 50 scan spectrophotometer and Jobin Yvon Fluorolog FL3-11 fluorescence spectrophotometer. The PL quantum yield of CdTe/ZnSe nanocrystals was determined relative to known QYs of several organic dyes excited at 400-440 nm. High resolution transmission electron microscopy measurements were carried out using a JEOL 311UHR operated at 300 kV. Specimens were prepared by depositing a drop of nanocrystal hexane solution onto a Formvar-coated copper grid and letting it dry in air. X-ray powder diffraction measurements were carried out on Scintag XDS-2000 X-Ray Powder Diffractometer. The picosecond transient absorption (TA) technique utilized a Ti: Sapphire regenerative amplifier TOPAS-C combination and operated at 1 kHz. The instrument response time was estimated to be less than 1 ps. Further details about the TA system can be found in previous work\textsuperscript{114}.
6.2.8 Fluorescence Lifetime Measurements

Fluorescence lifetime measurements were performed using a time correlated single photon counting setup utilizing a SPC-630 single photon counting PCI card (Becker & Hickle GmbH), with a picosecond diode laser operating at 400 nm as an excitation source (Picoquant), and an id50 avalanche photodiode (Quantique). The repletion rate of the laser was chosen to allow for a 360 nm time window, and the pulse fluence was adjusted to produce about 1 emission photon per 100 excitation pulses.

6.3 Results and Discussion

The energy diagram of zero-angular momentum states in a CdTe/ZnSe core/shell system, estimated from known NC sizes and bulk band gap values for CdTe and ZnSe materials, is shown in Figure 6.1. Both conduction and valence band edges of CdTe are located within the energy gap of ZnSe, which is consistent with the type I localization regime, where an excited electron-hole pair resides primarily in the core of the heterostructure. The corresponding transition energy for such a spatial arrangement of charges is expected to be somewhat lower than the transition energy of binary CdTe NCs due to the increased delocalization of carriers caused by the tunneling of electronic wave functions into the ZnSe layer\textsuperscript{102}. Contrary to these expectations, the observed emission in CdTe/ZnSe hetero-NCs is shifted toward higher energies with respect to the position of the FL peak in CdTe, as shown in Figure 6.1b. This is an unusual result, since the recombination of 1S(e)-1S\textsubscript{3/2}(h) carriers in either the type I or type II structure should not result in photon energies that exceed the band gap values of the either the core or the
shell material. Consequently, the blue-shifting of the emission upon the deposition of ZnSe shell indicates that the heterojunction in CdTe/ZnSe hetero-NCs is likely to have a more complex composition than that of conventional core/shell NCs.

Figure 6.1 - (a) Energy diagram showing a type I band edge alignment in CdTe/ZnSe core/shell NCs. (b) Spectral analysis of nanocrystal emission. The position of the FL peak in CdTe/ZnSe hetero-NCs is blue-shifted with respect to the emission of CdTe NC cores, which does not correspond to type I carrier confinement expected from the energy diagram in part a.

The shape and size distribution of the CdTe/ZnSe hetero-NCs were analyzed using transmission electron microscopy (TEM). Figure 6.2a shows the structure of CdTe NCs prior to the deposition of the ZnSe shell. Most NCs appear to have a tetrapod-like shape with an average size of 7 nm (see Figure 6.2b), which is calculated by measuring the length of one of its branches (extensions). The mean width of the tetrapod branches as well as the average diameter of the central apex were found to be 50-60% of the extension length. The subsequent growth of the ZnSe shell resulted in a 2-nm increase in the average length of the structure, is evident from the
comparison of size distributions for CdTe and CdTe/ZnSe nanoparticles in parts b and c of Figure 6.2. The deposition of ZnSe also led to an increase in the average width of the tetrapod branch (6-7 nm) as well as the standard deviation of the length distribution from 7 to 11%.

![Figure 6.2 - (a) High-resolution TEM images of CdTe NCs. (b and c) Statistical distributions of lengths for tetrapod-shaped CdTe and CdTe/ZnSe NCs, respectively. (d) High-resolution TEM images of CdTe/ZnSe hetero-NCs. (e) High-magnification images of CdTe/ZnSe hetero-NCs showing the lattice structure. Scale bars are (a) 20 nm, (d) 20 nm, and (e) 1 nm.](image)

Changes in the crystal structure and composition of the CdTe NCs caused by the deposition of the ZnSe shell were investigated using a combination of X-ray powder diffraction (XPD) and energy dispersive X-ray (EDX) techniques. The experimental diffraction pattern of
the original CdTe NCs is shown in Figure 6.3c, where the three main peaks corresponding to the cubic phase of bulk CdTe lattice are clearly identified. CdTe/ZnSe hetero-NCs, prepared by depositing a maximum of 2-3 ML of ZnSe (as calculated from the amount of Zn and Se elements in the injection solutions), exhibit a second set of Bragg peaks that are shifted toward higher diffraction angles with respect to those in CdTe (see Figure 6.3b), as expected due to the smaller lattice spacing in ZnSe. The profile of the observed Bragg peaks in CdTe/ZnSe hetero-NCs, however, appears to-

![Figure 6.3 - XPD and EDX analysis of CdTe/ZnSe hetero-NCs](image)

Figure 6.3 - XPD and EDX analysis of CdTe/ZnSe hetero-NCs (a) EDX spectrum of CdTe/ZnSe hetero-NCs, obtained at 20 keV. XPD spectra of CdTe/ZnSe (b) and CdTe (c) NCs along with diffraction patterns of bulk cubic CdTe (d), CdSe (e), and ZnSe (f).
be unusually broad. Despite a substantial difference in the lattice constants of CdTe and ZnSe, their individual phases cannot be resolved in the experimental pattern, indicating the possible formation of a ternary alloy composition, similar to the CdSe crystal phase (Figure 6.3e) that contributes to the diffraction signal at intermediate angles and leads to inhomogeneous broadening of the Bragg peaks. This transitional crystal structure is likely to take up a sizable portion of the synthesized nanoparticles, as can be inferred from near-equal XPD intensities corresponding to diffraction angles of binary CdTe, CdSe, and ZnSe, as well as intermediate ternary alloy structures. Additional experimental evidence supporting the existence of a crystalline phase different from that of CdTe and ZnSe is provided by EDX analysis of the elemental composition, shown in Figure 6.3a. The molar ratio of elements derived from the raw X-ray count, Cd:Se:Zn:Te ; 1:0.68:0.46:0.35, indicates that the amount of Cd in the fabricated material could be in excess of either chalcogen, which is consistent with the simultaneous formation of both Cd-Se and Cd-Te crystalline bonds.

The growth kinetics of the reaction mixture is summarized in Figure 6.4a, where the evolution of fluorescence and absorption spectra is shown for different stages of ZnSe shell deposition. Upon the initial injection of Zn and Se precursors into the reaction flask, emission intensity of the original CdTe NCs (bottom panel) subsides, while a new FL feature appears at 565 nm. During the subsequent shell growth, this high-energy peak gradually red-shifts, reaching a saturation value of 595-600 nm. The nanoparticle growth is also accompanied by a steady increase in the quantum yield, which, for the as-prepared samples in chloroform, was approaching 24%. Changes in the absorption spectrum of CdTe NCs, associated with the deposition of the ZnSe shell, are investigated in Figure 6.4b. The first injection of Zn and Se precursors into the growth solution red-shifts the absorption edge in CdTe NCs (blue arrow)
leading to the formation of a monotonic tail, which extends into the infrared region. The increase in absorption

Figure 6.4 - (a) Changes in the UV-vis absorption and room-temperature fluorescence spectra of CdTe and CdTe/ZnSe hetero-NCs during shell deposition. The bottom panel corresponds to the original CdTe core NCs, while top panels show the temporal evolution of spectral features of the growth solution. (b) Comparison of the absorption spectra of CdTe (blue) and CdTe/ZnSe (green) NCs. An absorption edge in CdTe NCs, located near 725 nm (blue arrow) is red-shifted upon deposition of ZnSe shell, giving rise to a monotonous tail, which extends into the infrared region. This process is accompanied by the appearance of the two peaks at higher energies,
corresponding to a band gap absorption in ZnSe (green arrow 1) and the absorption of interdiffusion layer states (green arrow 2). (c) Changes in the emission of CdTe NCs (blue curve) produced by the deposition of a thin ZnSe layer. In addition to the primary peak at 600 nm, the emission spectrum of CdTe/ZnSe hetero-NCs contains the residual emission in CdTe cores (green arrow), which is red-shifted with respect to the position of the FL peak in binary CdTe NCs.

at energies below the CdTe band gap (green arrow 3) is likely the result of a type I delocalization of $1S(e)1S_{3/2}(h)$ excitons in the CdTe cores, caused by the tunneling of excited carriers into an interfacial layer or ZnSe shell (see Supporting Information for details). It appears that while most excitations in CdTe/ZnSe hetero-NCs recombine through a 600-nm decay channel, a small portion of excitons lacks sufficient energy to undergo such a transition and can channel through the low-energy band gap of the CdTe cores. This leads to broadening of the absorption edge near 725 nm and produces weak infrared emission, which is shown in Figure 6.4c (green arrow), along with the main emission peak at 600 nm. Red-shifting of such residual emission in the CdTe NCs (green arrow) upon shell deposition provides additional support to the fact that the decrease in the absorption energy of the CdTe NCs (Figure 6.4b, blue arrow) is caused by tunneling of the $1S(e)1S_{3/2}(h)$ excitons into a wider band gap layer surrounding the core.

As expected from the XPD measurements that indicate the existence of at least three distinct crystalline phases, the absorption profile of CdTe/ZnSe hetero-NCs contains three separate peaks, denoted as 1, 2, and 3 in Figure 6.4b, which, in view of the above discussion, were attributed to the $1S(e)-1S_{3/2}(h)$ transitions in ZnSe, interfacial layer, and CdTe materials, respectively. Such an arrangement, however, poses a nonconforming issue concerning the long-lived localization of carriers within the interfacial layer, as manifested by a strong emission around 600 nm. Indeed, since the band gap of the interfacial crystalline phase is wider than that
of CdTe, at least one of the carriers should be transferred into the core material promptly upon excitation. This should result in the strengthening of the infrared emission at 780-800 nm, which, in the present experiments, however, is relatively weak.

To understand the temporal dynamics of carrier relaxation in CdTe/ZnSe hetero-NCs we have employed the time-resolved picosecond transient absorption (TA) technique, which allows measuring the excited state population ratios (state filling factors) in real time. Bleaching of the lowest energy absorption feature (1S) in the NCs occurs primarily as a result of the photoexcited electrons residing in 1S(e) state\textsuperscript{38}. The contribution of the holes to the bleach is insignificant because the valence band state involved in the absorbing transition remains unoccupied until the lower-energy emitting hole state is completely filled, which only occurs at high excitation levels\textsuperscript{50}. The contribution of holes to the 1S bleach is further reduced due to the high spectral density of the valence states, which results in the spread of hole populations across many adjacent states, not all of which are optically coupled to 1S(e). This also reduces the contribution of the stimulation emission to the TA signal.

Figure 5c shows the time dependence of absorbance changes in CdTe/ZnSe hetero-NCs, excited with 420-nm monochromatic light. The spectrum contains two main areas of bleaching, corresponding to spectral markers at 470 and 595 nm. By comparison of the observed bleach positions with the absorption spectrum in Figure 6.4b, we were able to classify the origin of the bleaching signals at 470 and 595 nm as due to the 1S(e)-1S\textsubscript{3/2}(h) transitions in the ZnSe shell and the CdTe/ZnSe interfacial layer, respectively. Both 470- and 595-nm bands are quickly bleached upon excitation due to the injection of carriers into corresponding electronic states. The excited carrier population then undergoes an initial fast recovery via nonradiative processes, which is followed by a slower radiative decay. Changes in the absorption of the 595-nm band at negative
absorption, associated with the emission of hetero-NCs, are sufficiently slow in comparison with nonradiative processes and do not alter the observed relaxation trend. Figure 6.5b shows two decay traces that correspond to the temporal bleach recovery for 470- and 595-nm excitations. At early times, changes in the absorption of 470-nm band occur at a faster rate than those of the 595

Figure 6. 5 - (a) PL and PL excitation (PLE) spectra of CdTe/ZnSe hetero-NCs. The detection wavelength was set at the primary emission maximum, and the excitation source was tuned from 400 to 600 nm. (b) Bleach recovery (inverted) of the two primary absorption bands in CdTe/ZnSe hetero-NCs associated with 1S(e)-1S_{3/2}(h) transitions in ZnSe shell and the interfacial alloy, respectively. (c) Temporal evolution of absorbance changes in CdTe/ZnSe hetero-NCs, calculated by taking the difference of absorption spectra before and after the excitation pulse. The dotted line represents the contribution from NC emission.
nm band, indicating a more robust migration of carriers through nonradiative channels in ZnSe. While the observed behavior could simply indicate the difference in nonradiative decay rates associated with the 470-nm and 595-nm bands, it might also be the result of a correlation between the two excitations. More specifically, the transfer of carriers from excited states in the ZnSe shell to unoccupied potential minimum states in the CdTe/ZnSe hetero-NCs is allowed energetically and could explain the observed difference in the initial fast bleach recovery.

The PLE scan, shown in Figure 5a, provides further evidence supporting the migration of excited carriers from the ZnSe shell into the interfacial layer of the CdTe/ZnSe hetero-NCs. In these measurements, the detection wavelength was set at the primary emission maximum, and the excitation source was tuned from 400 to 600 nm. The observed PLE profile exhibits two emission maxima corresponding to excitation wavelengths of 470 and 595 nm attributed to the $1S(e)$-$1S_{3/2}(h)$ transitions in the ZnSe shell and the interfacial layer, respectively. The observed contribution of the 470-nm absorption peak to the PLE emission at 600 nm is consistent with the proposed picosecond transfer of excitations from the shell into the interfacial layer.

One possible mechanism for the formation of the proposed interfacial layer in the CdTe/ZnSe hetero-NCs is via the replacement of Te ions in CdTe NCs with Se, whereby creating an intermediate alloy on which the now better lattice-matched ZnSe can subsequently grow. Cd to Zn cation exchange is another possibility that may lead to a blue-shifted emission in the CdTe/ZnSe hetero-NCs. To test these hypotheses, we have looked for similarities between the optical properties of the fabricated CdTe/ZnSe hetero-NCs and several alloy nanoparticles, which composition may resemble the interfacial layer, including ternary (Cd$_x$Te$_y$Zn$_{1-x}$, Cd$_x$Te$_y$Se$_{1-x}$, Zn$_x$Te$_y$Se$_{1-x}$) and quaternary (Zn$_x$Cd$_{1-x}$Se$_y$Te$_{1-y}$) NCs. While the final stoichiometric ratios of elements in the fabricated alloy NCs cannot be determined precisely, our main focus is
on learning about the emission properties of the nanoparticles that grow when certain elements, in proportions similar to those used for CdTe/ZnSe hetero-NCs synthesis, are allowed to react. First, Cd$_x$Te$_y$Zn$_{1-x}$ alloy NCs were fabricated by simultaneous injection of Te and Zn precursors into a hot reaction mixture containing Cd solution in oleic acid/ODE. The formation of a small amount of binary ZnTe and CdTe NCs in the reaction flask was confirmed by FL peaks at 480 and 690 nm, as shown by the green curve in Figure 6.6a. The emission corresponding to the ternary crystalline phase, the presence of which was verified by XPD measurements, however, could not be distinguished in the emission spectra. A similar trend was also observed for Zn$_x$Te$_y$Se$_{1-x}$ NCs, where the optical spectra contained characteristic FL peaks of binary QDs but showed no indication of alloy nanoparticles, possibly due to the intrinsically low QY for a ternary phase. A somewhat stronger FL signal corresponding to a ternary alloy structure was observed for Cd$_y$Te$_x$Se$_{1-x}$ NCs, along with the less prominent CdSe binary peak, as shown by the blue curve in Figure 6.6a. The position of the FL peak was found to be at 720 nm, which is outside the range of emission of CdTe and CdSe NCs, as expected due to significant optical bowing$^{93}$ in Cd$_y$Te$_x$Se$_{1-x}$ alloys. This effect is known to reduce the energy of the ternary band gap below the corresponding binary values such that $E_g$(CdSe$_x$Te$_{1-x}$) = $xE_g$(CdSe) + $(1-x)E_g$(CdTe) - $bx(1-x)$. Finally, we have attempted the synthesis of quaternary alloy NCs by combining all three precursors, Zn, Te, and Se, with the Cd solution in the reaction flask. The emission spectrum of the resulting nanoparticle suspension (see the red curve in Figure 6.6a) in hexane shows high-intensity FL peak near 600 nm, along with low intensity peaks corresponding to binary NCs.

On the basis of the observed emission ranges of ternary and quaternary NCs as well as the results of TA, PLE, EDX, XPD, PL, and steady-state absorption measurements, we propose that the interfacial layer in fabricated hetero-NCs has a gradient composition such that the inner
CdTe core is overcoated with a strongly emissive Zn$_{x}$Cd$_{1-x}$Se$_{y}$Te$_{1-y}$ alloy, formed via Se/Te and Zn/Cd exchange, followed by a ZnSe shell layer. This idea is illustrated in Figure 6.6b. The presence of CdTe material within CdTe/ZnSe hetero-NCs has been confirmed by XPD, FL, and steady-state absorption measurement, while the presence of a ZnSe shell is supported by XPD, absorption, TA, and PLE techniques. Formation of the CdSe-like Zn$_{x}$Cd$_{1-x}$Se$_{y}$Te$_{1-y}$ emissive layer ($x \ll y < 1$) is consistent with the broadening of the (220) and (311) Bragg peaks in the XPD spectra, which is caused by the development of an intermediate lattice spacing. Such quaternary interfacial composition can also explain the excessive amount of Cd and Se in the CdTe/ZnSe hetero-NCs observed in EDX measurements. Finally, a CdSe-rich Zn$_{x}$Cd$_{1-x}$Se$_{y}$Te$_{1-y}$ alloy appears to be the only composition with an intermediate lattice spacing that produces a strong emission in the 600-nm range.

Within the proposed scheme, photogenerated electrons are believed to be localized at the interface of CdTe and ZnSe, where the energy of CdSe-like conduction band edge dips lower than the corresponding levels in CdTe and ZnSe NCs (Figure 6.6b). Meanwhile, the highest energy hole states are located in the CdTe cores, which should favor the 1S$_{e}$(Zn$_{x}$Cd$_{1-x}$Se$_{y}$Te$_{1-y}$)-1S$_{h}$(CdTe) carrier relaxation pathway, yet the radiative decay of the carriers is observed through both CdTe and Zn$_{x}$Cd$_{1-x}$Se$_{y}$Te$_{1-y}$ hole states. This can be attributed to the existence of two competing decay channels that exhibit very little hole exchange. The reason for such hole confinement within the Zn$_{x}$Cd$_{1-x}$Se$_{y}$Te$_{1-y}$ layer is difficult to determine in the present study due to a lack of information on the precise interfacial stoichiometry and could be interesting to explore in future work.

Fluorescence lifetime measurements can provide a viable tool for distinguishing between different types of excitations that exist in a quantum system. From this perspective, excitons that
are localized at the interface of CdTe/ZnSe hetero-NCs represent a unique class of electronic
excitations, the recombination mechanism of which is intrinsically different from that of the
volumetric excitons in CdTe NCs. As a result, the FL lifetime of the 600-nm emission peak
should be distinguishable from the lifetime of the band-edge FL in CdTe NCs. To test this
hypothesis, we have measured decay traces of CdTe and CdTe/ZnSe NCs using the standard
time-correlated single photon counting technique.

Figure 6. 6 - (a) Emission spectra of ternary Cd$_x$Te$_y$Zn$_{1-x}$ (green curve), Cd$_y$Te$_x$Se$_{1-x}$ (blue curve),
and quaternary Zn$_x$Cd$_{1-x}$Se$_y$Te$_{1-y}$ (red curve) alloy nanocrystals. The strongest
emission is observed in quaternary NCs, which composition is believed to be the
closest to the composition of the emissive interfacial layer in CdTe/ZnSe hetero-
NCs. (b) Proposed radial dependence of 1S(e) and 1S$_{3/2}$(h) state energies in
CdTe/ZnSe hetero-NCs.

~ 99 ~
Figure 6.7 shows temporal changes in the intensity of the FL emission for these nanostructures. Significant differences can be seen both in the character and the lifetime of the observed decay curves. CdTe core NCs (blue curve) exhibit a nonexponential relaxation of fluorescence, which is generally expected for semiconductor QDs. The FL decay of the CdTe/ZnSe hetero-NCs (green curve), on the other hand, is nearly single exponential ($R^2 = 0.997$), which demonstrates the unique character of the optical excitations in CdTe/ZnSe hetero-NCs. Indeed, the simple addition of a wide-band gap semiconductor shell onto a CdTe core should result in a minor increase in the FL lifetime without a significant change in the decay character. Contrary to these expectations the deposition of a ZnSe shell causes dramatic changes in the relaxation character and leads to slightly shorter decay times. Both of these changes are consistent with increased carrier confinement in CdTe/ZnSe hetero-NCs corresponding to the interfacial character of these excitations.

The ZnSe shell in CdTe/ZnSe hetero-NCs serves as a barrier, which separates electronic excitations at the core/shell interface from the nanocrystal surroundings. The resulting structure, therefore, is self-passivating, and its optical properties are expected to be less susceptible to the
surface environment than those of binary QDs. Given the CdSe-like composition of the emissive layer in the fabricated CdTe/ZnSe hetero-NCs, their emission stability is evaluated in comparison with that of CdSe NCs. Such measurements can provide additional proof that the outside layer of wide-band gap ZnSe material is, in fact, present in the fabricated structures. The effect of surface environment is introduced via mild etching with BPO, which allows for the controlled removal of the outer layers from the nanocrystals. This approach simulates the contamination of the NC lattice with ions and structural defects that typically lead to the irreversible loss of band gap

Figure 6. 8 - (a) Comparison of FL quenching kinetics during etching with BPO for CdSe and CdTe/ZnSe NCs. FL spectra of CdTe/ZnSe (b) and CdSe (c) NCs prior to etching (black curve) and after 12 s of etching (red curve).
fluorescence due to carrier trapping. Figure 6.8 shows the kinetics of FL quenching during the etching process for both CdTe/ZnSe and CdSe suspensions with equal concentrations of nanoparticles in hexane. As seen by the reaction traces, the emission of CdSe NCs becomes fully quenched within 10-12 s following the addition of BPO, while the emission of CdTe/ZnSe hetero-NCs is reduced only by 50% over the same time period. A similar trend has been consistently observed in subsequent measurements utilizing different concentrations of BPO and longer etching times, which indicates an overall greater stability of CdTe/ZnSe emission in comparison with that of CdSe NCs.

### 6.4 Conclusions

In conclusion, we report on the organometallic synthesis of CdTe/ZnSe semiconductor heterostructure nanocrystals, exhibiting a mixed type of carrier confinement. It is demonstrated that CdTe/ZnSe emission arises from the recombination of carriers within an interfacial layer, which is formed due to cation/anion exchange in the merging of the ZnSe and CdTe lattices. The fabricated nanocrystals show enhanced emission stability against etching and could be of potential use as fluorescence energy donors in FRET-based sensors, where the effective donor-acceptor distance is reduced due to the interfacial localization of the photogenerated carriers.
CHAPTER 7
LINKER-FREE MODIFICATION OF TiO₂ NANORODS WITH PbSe NANOCRYSTALS

7.1 Introduction

Titanium dioxide is an important photovoltaic and photocatalytic material\textsuperscript{115}, which utilization in dye-sensitized solar cells\textsuperscript{116}, and hydrogen production\textsuperscript{117} is encouraged by its low fabrication costs and minimal environmental hazards. Efficient harvesting of solar radiation within TiO₂ generally requires extending its absorption range into the visible and near-infrared range by introducing an appropriate sensitizer that engages in an electron-transfer reaction with an oxide material upon receiving a photon of light. To date, the most common strategy for the sensitization of TiO₂ involves modification of its surface with organic-based transition-metal complexes, such as porphyrins\textsuperscript{118} or Ru complexes\textsuperscript{116}. However, the incorporation of semiconductor nanocrystals (NC) as sensitizers is now being actively explored\textsuperscript{119-131} because of a number of advantages offered by inorganic NCs, including a wider absorption profile, superior resistance to photobleaching, and continuous tunability of the NC conduction levels.

As shown in recent reports, successful modification of anatase TiO₂ or amorphous TiOₓ with colloidal CdSe\textsuperscript{124}, InAs\textsuperscript{127}, PbSe\textsuperscript{132}, and PbS\textsuperscript{133} NCs can be achieved in a reproducible manner, leading to heterostructures that exhibit photoinduced charge separation. In this work, however, the deposition of colloidal nanocrystals onto the oxide material still relies on organic linkers or nonepitaxial contacts with NC ligands\textsuperscript{132}, which makes it difficult to extract photoinduced carriers from the NC domains, leading to a decrease in electron-transfer rates and
carrier trapping at the hybrid interfaces. For instance, surprisingly slow photoinduced electron transfer has been reported in organically coupled PbS-TiO$_2$ systems\textsuperscript{133}. To avoid these problems, several groups have attempted in situ growth of CdS\textsuperscript{121,134,135} NCs onto mesoporous TiO$_2$ films in ionic solutions. Although the observation of a 2-3-fold increase in the solar conversion efficiency of such films is encouraging, the quality and size distribution of the NCs fabricated using this approach are inferior to those synthesized through colloidal techniques, making it difficult to control the relative positions of the electron energy levels in a donor-acceptor system. Here we demonstrate a colloidal route to the synthesis of PbSe/TiO$_2$ hetero-nanocrystals (HNCs), comprising 2-5 nm PbSe NCs grown directly on the surface of TiO$_2$ nanorods (NRs). As a main benefit of colloidal injection techniques, the present approach allows for a controlled adjustment of the sensitizer electronic levels via tuning of the average NC diameter during synthesis, which is critical for the experimental realization of a desired type II (staggered) offset of donor and acceptor conduction band edges. Moreover, formation of a near-epitaxial interface between the PbSe and TiO$_2$ domains enables a rapid injection of photoinduced carriers into the oxide material, which was demonstrated via a 50-fold increase in the photoinduced electron-transfer rate between the PbSe and TiO$_2$ domains, as compared to organically linked lead chalcogenide-TiO$_2$ assemblies\textsuperscript{133}.

### 7.2 Experimental section

#### 7.2.1 Chemicals

1-Octadecene (ODE, 90\%, Aldrich), oleylamine (OLAM, 70\%, Aldrich), oleic acid (OA, 90\%, Aldrich), titanium tetrachloride (TiCl$_4$, 99.9\%, Aldrich), lead(II) oxide powder (PbO, 99\%, Aldrich), phenylphosphonic dichloride (PhPOCl$_2$, 99\%, Aldrich), toluene (Acros Organics).
99.999%, Aldrich), selenium powder (Se, 99.5%, Acros), sulfur (99.999%, Acros), ODE(tech., 90%, Aldrich), trin-octylphosphine oxide (TOPO, 99%, Aldrich), selenium (99.5+%, Acros), hexane (anhydrous, 95%, Aldrich), methanol (anhydrous, EMD), toluene (anhydrous, 99.8%, Aldrich), and chloroform (anhydrous, 99+%, Aldrich) were all used as received without any further purification. All reactions were performed under an argon atmosphere using the standard Schlenk technique.

7.2.2 Preparation of Injection Precursors

The lead precursor was prepared by dissolving 0.45 g (2.0 mmol) of lead oxide in a mixture of 1.6 g of OA and 4 g of ODE by heating the flask to 200 °C for 30 min. Prior to the injection the temperature of the Pb solution was lowered to 140 °C. One molar TOPSe solution was prepared by dissolving 0.21 g of Se in 2.7 mL of TOP at room temperature and heated up to 100 °C prior to injection. Two different approaches were used to prepare a sulfur stock solution (see Supporting Information for PbS/TiO$_2$ heterostructures). As a low-reactive precursor, 0.04 g of sulfur was combined with 3 mL of ODE and subsequently heated to 200 °C to form a clear solution. Prior to the injection, the mixture was cooled down to room temperature. As a more reactive source of sulfur, 0.3 mL of hexamethyldisilthiane was combined with 3 mL of degassed ODE at room temperature.

7.2.3 Synthesis of PbSe/TiO$_2$ Heterostructures

A one-pot synthesis of PbSe/TiO$_2$ proceeded via the initial growth of TiO$_2$ nanorods onto which PbSe NCs were subsequently grown by injecting lead selenide precursors at lower
Typically, 6.5 mmol of OLAM and 1 mmol of OLAC were mixed in a three-neck flask and degassed using a mechanical vacuum pump at 120 °C for 30 min. The mixture was subsequently switched to argon and 1 mmol of TiCl$_4$ was injected into the flask at 40 °C. The reaction flask was then heated to 300 °C and maintained at that temperature for 30 min. To initiate the growth of PbSe NCs, the temperature of the reaction mixture was lowered to 190 °C and warm precursors of Pb ($T = 100 °C$) and Se ($T = 80 °C$) were injected simultaneously. Typically 3-5 mL of lead and 1.3-3 mL of Se stock solutions were used during the first injection. Subsequent injection(s) were made 4 min after the first (or previous). The grown nanostructures were purified using several toluene/ethanol extractions.

### 7.2.4 Characterization

UV-vis absorption and photoluminescence spectra were recorded using a CARY 50 Scan spectrophotometer and a Jobin Yvon Fluorolog FL3-11 fluorescence spectrophotometer. High-resolution transmission electron microscopy measurements were carried out using a JEOL 3011UHR operated at 300 kV. Specimens were prepared by depositing a drop of nanocrystal hexane solution onto a Formvar-coated copper grid and allowing it dry in air. X-ray powder diffraction measurements were carried out on a Scintag XDS-2000 X-ray powder diffractometer. Energy-dispersive X-ray (EDX) emission spectra were measured using an EDAX X-ray detector located inside a scanning electron microscope. The electron beam was accelerated at 20 kV.
7.2.5 Fluorescence Lifetime Measurements

FL lifetime measurements were performed using a time-correlated single photon counting setup utilizing a SPC-630 single-photon counting PCI card (Becker & Hickle GmbH), picosecond diode laser operating at 400 nm, as an excitation source (Picoquant), and an id50 avalanche photodiode (Quantique). The repetition rate of the laser was chosen to allow for a 1000 ns time window, whereas the pulse fluence was adjusted to produce about 1 emission photon per 100 excitation pulses (excitation power was 100 $\mu$W).

7.3 Results and Discussion

In the case of colloidal heterostructures, the type of inorganic interface that forms at the boundary of the two material domains is determined by the relationship between the total surface energy of the composite nanoparticle and the solid-solid interfacial energy related to the mismatch-induced strain between the two lattices. If the interfacial strain exceeds the surface tension of either material, such a structure may undergo a spatial rearrangement that eliminates some of the interfacial region by increasing the overall surface area. This scenario is clearly observed for PbSe/TiO$_2$ heterostructures, where a large lattice mismatch of either 6.7\% or 18\% corresponding to merging of the 010 and 110 (Figure 7.3b) or the 001 and 100 faces of anatase TiO$_2$ and rock-salt PbSe crystal lattices leads to Volmer-Weber growth of the PbSe material, characterized by the formation of small PbSe islands throughout the surface of TiO$_2$ (Figure 7.1b). One potential benefit associated with such a growth mode is the possibility of increasing the optical extinction coefficient of these nanoparticles by sintering several PbSe sensitizers per
single TiO$_2$ NR. Since the light-absorption cross section of 2 nm PbSe NCs is generally small ($\sim 2 \times 10^{-15}$ cm$^2$, $\lambda = 400$)\textsuperscript{136}, the maximum number of electron-hole pairs generated in a single PbSe/TiO$_2$ structure, under ambient illumination (photon flux $\approx 3 \times 10^{21}$ m$^{-2}$s$^{-1}$) is less than 1, which is not expected to produce nonlinear charging effects\textsuperscript{73}. As a result, increasing the number of PbSe sites in the PbSe/TiO$_2$ heterostructure should result in a linear increase of the power conversion efficiency in NC sensitized solar cells.

Another benefit of the Volmer-Weber growth regime is the thermodynamically stable formation of small-diameter PbSe NCs, which is critical for the realization of a type II heterojunction between PbSe and TiO$_2$. Indeed, according to the energy diagram of electronic states in PbSe NCs (Figure 7.1a), calculated from electron injection studies\textsuperscript{137,138} and empirical scaling of band edge absorption, the transfer of photoinduced electrons from PbSe to TiO$_2$ is energetically permissible only if the size of PbSe is less than 5 nm.

Schematics of the one-pot approach to the synthesis of PbSe/TiO$_2$ HNCs are illustrated in Figure 7.2a. Growth of TiO$_2$ NRs was performed according to a method adapted from ref 139 by heating TiCl$_4$ to 300 °C in the presence of OA and OLAM. This approach makes use of a high concentration of Ti precursor in the reaction mixture to yield high-aspect ratio anatase nanorods elongated along the $\langle 001 \rangle$ crystallographic direction. Upon formation of the TiO$_2$ NRs, the temperature of the reaction mixture was lowered to 180 °C for the growth of PbSe NCs. Typically, a single injection of Pb and Se precursors leads to the formation of 2-3 nm PbSe islands on the surface of the nanorods. A small amount of isolated PbSe NCs (<10% of nanoparticles) was also observed in the as-prepared reaction mixture and was subsequently reduced to less than 2% after the purification stage (Figure 7.3a). Additional injections of precursors were needed to fuel the growth of PbSe islands beyond 3 nm in size.
Transmission electron microscopy (TEM) analysis of the PbSe/TiO$_2$ HNCs reveals a qualitative difference between the shapes of PbSe NCs forming on the surface of TiO$_2$ NRs as a result of single and multiple injections of Pb and Se precursors. The initial injection leads to the formation of several small-diameter PbSe sites per single NR (Figures 7.2b, c), with an average site diameter of 1.8-3.0 nm and a size dispersion of 10-14\% (see Figure S1 for the statistical distribution of diameters). We estimate that the number of PbSe NCs per single TiO$_2$ NR is 21 ±
where the dispersion in the number of dots is mainly determined by the dispersion of the NR surface area.

Figure 7.2 - a, b) PbSe/TiO$_2$ heterostructure fabricated using a secondary injection of precursors. The effect of precursor concentration on the average NC diameter is illustrated by two exemplary distributions. c, d) TEM images of PbS/TiO$_2$ heterostructures fabricated using a single injection of precursors.

Doubling the concentration of precursors for the first injection was found to produce a 10-15% increase in the density of PbSe dots on the surface of TiO$_2$, but did not affect the average dot size. According to the high-resolution TEM image of a typical PbSe/TiO$_2$ HNC in Figure 7.2c, the PbSe dots appear to be uniformly scattered over the entire NR surface and exhibit a moderate dispersion of sizes. A near-symmetric placement of PbSe dots on the surface of TiO$_2$ can be explained in terms of the fundamental energy requirements on the deposition of secondary material in heteroepitaxial growth. Namely, spatially isotropic addition of PbSe monomers onto
TiO$_2$ NRs initially results in the formation of a thin PbSe shell. Subsequent lateral expansion of the shell is associated with the mismatch-induced increase of the interfacial energy, which promotes the collapse of the PbSe layer into segregated islands.

Figure 7.3 - (a) Low-magnification transmission electron microscopy (TEM) image of PbSe/TiO$_2$ HNCs. (b) High-resolution TEM image of the PbSe/TiO$_2$ interface, showing quasimatching of crystal lattices along the 110 and 010 faces of PbSe and TiO$_2$, respectively.

Secondary injections of precursors were used to induce the growth of larger PbSe NCs on the TiO$_2$ surfaces, (Figure 7.2d, e). The amount of PbSe sites per single NR in this case is reduced to 1 (Figure 7.2e) or 2 (Figure 7.3a), which indicates that some of the smaller islands can coalesce into bigger nanoparticles, as evident in the transitional heterostructure (Figure 7.3a). Such a transformation is thermodynamically favorable since the combined surface area of the PbSe NCs is reduced during aggregation, causing a reduction in the total surface energy of the heterostructure. A high-resolution TEM image of a PbSe/TiO$_2$ HNC comprising a single 5 nm PbSe NC (Figure 7.2e) confirms that the surface of a NR is virtually free of small PbSe sites,
which supports the coalescence-induced formation of large PbSe NCs. For these structures the volume of the PbSe crystal phase is approximately equal to that of TiO₂, as can be deduced from the near-equal amplitudes of elemental peaks in the EDX spectra (Figure 7.6d).

Figure 7.4 Distribution of PbSe diameters in PbSe/TiO₂ heterostructures fabricated using a single injection of precursors. The effect of precursor concentration on the average NC diameter is illustrated by two exemplary distributions.

The optical properties of PbSe/TiO₂ HNCs incorporating 1.9 nm PbSe NCs are analyzed in Figure 7.6. The absorption profile of PbSe/TiO₂ is characteristic of a type II heterostructure with nonzero photon absorption in the spectral range below the band gap of both the PbSe and TiO₂ materials. This is expected because of the excitations of intermediate states that exist at the junction of both materials.⁴⁶ The highest energy excitonic feature, corresponding to band edge absorption in the PbSe NCs, can also be identified near 700 nm. Its spectral position correlates well³⁴ with an estimation from the TEM average PbSe size of 1.9 nm (Figure 7.5).
As-prepared PbSe/TiO$_2$ HNCs, comprising small-diameter PbSe NCs, show a weak emission feature (emission quantum yield <0.5%) in the 650-900 nm range, as shown in Figure 7.6a. Both the position and the width of the FL peak are consistent with the expected 1S(e)-1S(h) recombination of carriers in the 1.9 nm PbSe NCs, implicating the band-edge origin of the emission.$^{140}$ Surprisingly, the contribution of trap states to the FL signal, expected because of a large surface area of PbSe NCs and the possible formation of electron-trapping defects along the strained interface of the PbSe and TiO$_2$ domains, was not significant, as evident by the lack of emission originating from below the PbSe band gap.
The dynamics of carrier decay was further investigated using FL lifetime measurements (Figure 7.6b). The observed emission lifetime of 2.1 ns is substantially shorter than expected for the 1S(e)-1S(h) excitons in PbSe NCs, for which room-temperature values in excess of 500 ns were reported\textsuperscript{141}. We also note that, for small-diameter PbSe NCs, FL lifetimes are expected to increase because of the inverse correlation of the radiative rate and NC band gap\textsuperscript{1}. In general, there are two main factors that can potentially lead to such a dramatic decrease of the FL lifetimes in PbSe/TiO\textsubscript{2} HNCs: electron trapping at defects and oxidation of PbSe NCs via carrier transfer to TiO\textsubscript{2}. As mentioned above, the signature of the trap state emission was not observed in the FL spectra. Likewise, the FL relaxation trend is not typical of carrier traps that generally contribute a long-lived component with decay constant in excess of 1 \(\mu\)s. Therefore, the observed rapid quenching of FL is attributed to the transfer of photoinduced electrons from the PbSe NCs to the TiO\textsubscript{2} NRs. On the basis of the observed excited-state lifetime, we conclude that the characteristic time scale for photoinduced electron transfer is 2.1 ns, which is significantly faster than the 100 ns electron-transfer times observed for organically linked PbS-TiO\textsubscript{2} systems\textsuperscript{133}.

7.4 Conclusions

We report on the solution-phase synthesis of PbSe/TiO\textsubscript{2} heterostructures, comprising small-diameter PbSe nanocrystals grown on the surface of TiO\textsubscript{2} nanorods. Fabricated materials exhibit the efficient conversion of visible light energy via a rapid transfer of photoinduced electrons into the TiO\textsubscript{2} domains. From a general perspective, the present synthesis demonstrates an all-inorganic modification of the TiO\textsubscript{2} surfaces with semiconductor NCs and could be extended to other nanocrystalline systems, as shown in the Supporting Information for PbS-
sensitized TiO$_2$ NRs. Moreover, the heteroepitaxial growth of lead chalcogenides is not limited to TiO$_2$ NRs and can be adapted to other nanostructure forms of TiO$_2$ including porous films and nanotubes, thereby introducing a colloidal route to the sensitization of TiO$_2$ surfaces without organic-molecular bridging.
APPENDIX

8.1 List of publications


03. N. N. Hewa-Kasararage, P. Z. El-Khoury, M. Kirsanova, A. Nemchinov, A. N.
Tarnovsky, M. Zamkov, “Ultrafast carrier dynamics in type II ZnSe/CdS/ZnSe nano-
barbells.” ACS Nano. 2010, 4, 1837–1844

04. K. P. Acharya, T. R. Alabi, N. E. Schmall, N. N. Hewa-Kasararage, M. Kirsanova, M. A

05. M. Kirsanova, A. Nemchinov, N. N. Hewa-Kasararage, N. Schmall, M. Zamkov,
“Synthesis of ZnSe/CdS/ZnSe nano-barbells showing photoinduced charge separation.”

06. N. N. Hewa-Kasararage, P. Z. El-Khoury, N. Schmall, M. Kirsanova, A. Nemchinov, A.
N. Tarnovsky, A. Bezryadin, M. Zamkov, “The effect of dielectric friction on the rate of
charge separation in type II ZnSe/CdS semiconductor nanorods.” App. Phys. Lett. 2009,
94, 133113-133115.


8.2 References


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