RICE UNIVERSITY

Chemical Processing of Colloidal Cadmium Selenide Nanoparticles: New Approaches to Dimensional and Morphological Control

By

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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February 2008
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Abstract

Chemical Processing of Colloidal Cadmium Selenide Nanoparticles:
New Approaches to Dimensional and Morphological Control

By
Subashini Asokan

Cadmium selenide (CdSe) quantum dots (QDs) are colloidal semiconductor nanoparticles (NPs) that are nanometer sized fragments of the corresponding bulk crystals. They are being probed as a very interesting system for their applications in LEDs, solar cells and biomedical labeling because of their rich photophysics arising from their size dependent optical and electronic properties and flexible processing chemistry. 1-Octadecene was the only non-coordinating solvent used for the synthesis of CdSe NPs. It was imperative to understand the chemistry of synthesis of CdSe NPs using other non-coordinating solvents. Also, there is a constant search for the greener, cheaper, reproducible and scalable methods for the synthesis of CdSe NPs while not compromising on their quality. Towards the above mentioned goals, the use of heat transfer fluids was successfully demonstrated as cost-effective alternative solvents for quantum dot synthesis. Heat transfer fluids (HTF) are a class of organic liquids commonly used in chemical process industries to transport heat between unit operations. The solvents were found suitable for the hot injection synthesis of QDs while reducing the cost of the raw materials. These solvents were found to slow the growth kinetics of the CdSe NPs, leading to greater control over QD diameter.
Although the chemistry of synthesis of CdSe spherical and rod shaped particles were well understood, the synthesis of tetrapod shaped NPs with uniform size and shape is especially difficult to carry out at a large scale. Post-synthesis separation can be applied though this leads to additional processing steps and reduced particle yields. Cationic surfactant ligands were discovered to lead to the successful formation of tetrapod shaped CdSe NPs with highly uniform arm lengths, arm widths and shape. Typical selectivity values for the tetrapod morphology exceeded 90%, much higher than the previously reported values of 40%. The cationic surfactant ligands were found to induce anisotropy during the growth of the CdSe NPs, with cetyltrimethylammonium bromide (CTAB) and didodecyldimethylammonium bromide (DDAB) leading to the specific tetrapod shape. Optimization of the synthesis procedure led to the control over the range of dimensions of the tetrapod shaped particles. The uniformity of size and shape of the CdSe tetrapodal NPs were found to be very sensitive to the ratio of the surfactants and the precursors. It was also observed that the presence of the cationic surfactants led to the exclusive formation of zinc-blende nuclei which is indispensable for the growth of nuclei into tetrapodal NPs. The growth of CdSe tetrapodal NPs from the preformed zinc-blende CdSe NPs, just by the addition of CTAB, demonstrated the crucial role of the cationic surfactants in inducing anisotropy. These findings were helpful in gaining insight in to the nucleation and growth of the anisotropic nanoparticles.

These new methods should lead to improvements in current synthesis methods of tetrapodal shaped CdSe NPs, enabling the faster development of polymer/tetrapod photovoltaic devices. These results may be applicable to other compositions, leading to opportunities for large-scale application of shaped NPs.
Acknowledgments

This thesis is the essence of five years of hard work and this would not have been possible without the help of many fine people. I take this opportunity to express my heartfelt gratitude towards my thesis mentor Prof. Michael Wong for his invaluable guidance and support throughout my tenure as a graduate student at Rice University. His knowledge, inquisitive nature, infinite energy, attention to the tiniest details, organization in just about anything, written, articulate and presentation skills have been awe inspiring. His quick and detailed response to emails is a rare trait amongst professionals as busy as he is. I thank him for providing a home away from home for many international students like me.

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proud of me and think of me as the daughter/sister that they never had. I could not have asked for better in-laws. This family made me what I am today and I thank god everyday for you people.

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Subashini Asokan

February 2008
# TABLE OF CONTENTS

Abstract.................................................................................................................. (ii)

Acknowledgments.................................................................................................... (v)

Table of Contents.................................................................................................... (ix)

List of Abbreviations and Symbols........................................................................ (xiii)

List of Tables ........................................................................................................... (xx)

List of Figures......................................................................................................... (xxi)

Appendix................................................................................................................... (xxx)

1 Background and Motivation

1.1 Properties and Applications of Nanomaterials ................................................. 1

1.2 Synthetic Methods of Nanoparticles................................................................. 2

1.2.1 LaMer Model of Particle Nucleation and Growth ................................. 4

1.2.2 Thermodynamics of Nucleation and Growth of the Particles ............... 6

1.3 Semiconductor Nanoparticles .......................................................................... 15

1.3.1 Synthesis of Cadmium Selenide Nanoparticles .................................... 19

1.3.2 Synthesis of Bifunctional Core/Shell Nanoparticles ............................ 24

1.3.3 Synthesis of Cadmium Selenide Nanoshapes ...................................... 25

1.4 Outline of Thesis Work.................................................................................... 27

1.5 References........................................................................................................ 30

2 Characterization Techniques

2.1 Characterization of Cadmium Selenide Nanoparticles .................................... 50

2.1.1 UV-Visible Spectroscopy ........................................................................ 50
2.1.2 Fluorescence Spectroscopy ........................................... 52
2.1.3 Fourier Transform Infrared Spectroscopy (FTIR) .............. 55
2.1.4 Thermogravimetric Analysis (TGA) .............................. 56
2.1.5 X-ray Diffraction (XRD) ........................................... 58
2.1.6 Transmission Electron Microscopy (TEM) ..................... 59
2.1.7 X-Ray Photoelectron Spectroscopy (XPS) ....................... 60
2.1.8 X-Ray Dispersive Spectroscopy (EDS) ......................... 62
2.1.9 References .................................................................. 63

3 Heat Transfer fluids in the Synthesis of High-Quality CdSe Quantum Dots,
Core/Shell Quantum Dots, and Quantum Rods

3.1 Introduction ........................................................................ 66
3.2 Materials and Methods ..................................................... 67
  3.2.1 Synthesis of CdSe QDs .................................................. 67
  3.2.2 Synthesis of CdSe/CdS Core/Shell QDs ....................... 69
  3.2.3 Synthesis of CdSe Rod Shaped QDs ............................ 70
3.3 Results and Discussions ................................................... 71
  3.3.1 Synthesis of CdSe QDs ................................................. 71
  3.3.2 Synthesis of Core/Shell and Rod-shaped CdSe QDs ...... 78
  3.3.3 Computational Analysis of the Solvent Effect on CdSe
        QD Growth Kinetics ................................................... 81
3.4 Summary and Conclusions .............................................. 89
3.5 Acknowledgments .......................................................... 89
3.6 References .................................................................... 90
4 Shape-Controlled Synthesis of CdSe Tetrapods Using Cationic Surfactant Ligands

4.1 Introduction ................................................................. 98
4.2 Materials and Methods ..................................................... 99
4.3 Results and Discussions .................................................. 102
4.4 Summary and Conclusions ................................................. 117
4.5 Acknowledgments ......................................................... 118
4.6 References ....................................................................... 119

5 Effects of Synthesis Reaction Parameters on Tetrapodal CdSe Nanoparticles

5.1 Introduction .................................................................... 125
5.2 Experimental Section .......................................................... 126

5.2.1 Single Injection Method .................................................. 126

5.2.2 Multiple Injection Method ............................................... 127

5.2.3 Synthesis of CdSe Tetrapod NPs in Ternary Surfactant System .................................................. 128

5.2.4 Fluorescence Quenching Study ...................................... 128

5.3 Results and Discussions .................................................... 130

5.3.1 Effect of Temperature and Reaction Time .................... 130

5.3.2 Synthesis of CdSe Tetrapodal NPs by Multiple Injection Method .................................................. 137

5.3.3 Nature and Ratio of Surfactants .................................... 141

5.3.4 Stoichiometry of Cd:Se .................................................. 148

5.4 Fluorescence Quenching Study ......................................... 148
6 Study of Formation Mechanism of Cadmium Selenide Nano-Tetrapods

6.1 Introduction ................................................................. 161
6.2 Experimental Section ..................................................... 162
  6.2.1 Seeded Growth of CdSe Tetrapodal NPs ......................... 162
6.3 Results and Discussions .................................................. 163
  6.3.1 Seeded Growth of CdSe Tetrapodal NPs ......................... 163
  6.3.2 Infrared Spectroscopy ................................................. 167
  6.3.3 X-ray Photoelectron Spectroscopy (XPS) ......................... 171
  6.3.4 X-ray Dispersive Spectroscopy (EDS) ............................ 174
  6.3.5 Thermogravimetric Analysis (TGA) ............................... 177
6.4 Summary and Conclusions .............................................. 181
6.5 References .................................................................... 182

7 Conclusions and Recommendations for Future Work

7.1 Recommendations for Future Work .................................. 188
7.2 References .................................................................... 192
# LIST OF ABBREVIATIONS AND SYMBOLS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₂Cd</td>
<td>Dimethylcadmium</td>
</tr>
<tr>
<td>(CH₃COO)₂Cd</td>
<td>Cadmium acetate</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>0D</td>
<td>Zero dimensional</td>
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</tr>
<tr>
<td>AuCl₃</td>
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<tr>
<td>B.E.</td>
<td>Binding energy</td>
</tr>
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<td>BaF₂</td>
<td>Barium fluoride</td>
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<tr>
<td>C_∞</td>
<td>Bulk solubility</td>
</tr>
<tr>
<td>C_b</td>
<td>Bulk monomer concentration</td>
</tr>
<tr>
<td>C_{b,0}</td>
<td>Initial monomer concentration in the bulk</td>
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<tr>
<td>CBDMAC</td>
<td>Cetylbenzyldimethylammonium chloride</td>
</tr>
<tr>
<td>CBEN</td>
<td>Center for Biological and Environmental Nanotechnology</td>
</tr>
<tr>
<td>Cd</td>
<td>Cadmium</td>
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$\text{CdCl}_2$  Cadmium chloride
$\text{CdCO}_3$  Cadmium carbonate
$\text{CdO}$  Cadmium oxide
$\text{CdS}$  Cadmium sulfide
$\text{CdSe}$  Cadmium selenide
$\text{CdTe}$  Cadmium telluride
$C_e$  Monomer concentration at equilibrium
$\text{cm}$  Centimeter
$\text{Co}$  Cobalt
$\text{CoPt}_3$  Cobalt platinide
$cP$  Centi Poise
$\text{CTAB}$  Cetyltrimethylammonium bromide
$\text{CTAC}$  Cetyltrimethylammonium chloride
$\text{Cu}$  Copper
$\text{CV}$  Cyclic voltammetry
$D(E)$  Electron density of state
$D$  Diffusivity
$Da$  Damkohler number
$\text{DDAB}$  Didodecyldimethylammonium bromide
$\text{DMAB}$  Decamethonium bromide
$\text{DTA}$  Dowtherm-A
$\text{EDS}$  X-ray dispersive spectroscopy
$\text{Eqn}$  Equation
<table>
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<td>Et</td>
<td>Ethyl</td>
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<tr>
<td>eV</td>
<td>Electron Volt</td>
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<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>Iron(III)oxide</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
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<tr>
<td>Grad</td>
<td>Gradient</td>
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<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
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<td>hr</td>
<td>Hour</td>
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<td>HRTEM</td>
<td>High resolution transmission electron microscope</td>
</tr>
<tr>
<td>HTF</td>
<td>Heat transfer fluids</td>
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<td>InAs</td>
<td>Indium arsenide</td>
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<td>IR</td>
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</tr>
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<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>Kₜ</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>kₛ</td>
<td>Rate constant</td>
</tr>
<tr>
<td>LaB₆</td>
<td>Lanthanum boride</td>
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<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lower unoccupied molecular orbital</td>
</tr>
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<td>m</td>
<td>Meter</td>
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<td>Me</td>
<td>Methyl</td>
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<td>meV</td>
<td>Millielectron Volt</td>
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<td>Mg</td>
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<td>Nitrogen</td>
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<td>nm</td>
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<td>Nanoparticle</td>
</tr>
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<td>OA</td>
<td>Oleic acid</td>
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<td>ODE</td>
<td>1-Octadecene</td>
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<td>P</td>
<td>Phosphorous</td>
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<td>Lead selenide</td>
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<td>Phenyl</td>
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<td>PL</td>
<td>Photoluminescence</td>
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<td>Pt</td>
<td>Platinum</td>
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<tr>
<td>PV</td>
<td>Photovoltaic</td>
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<td>QD</td>
<td>Quantum dot</td>
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<tr>
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<td>Quantum rod</td>
</tr>
<tr>
<td>Quat</td>
<td>Quaternary ammonium salt</td>
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<td>QY</td>
<td>Quantum yield</td>
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<td>r</td>
<td>Radius</td>
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<td>Rh6G</td>
<td>Rhodamine-6G</td>
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<td>r_{mono}</td>
<td>Precursor radius</td>
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<td>Selenium</td>
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<td>sec</td>
<td>Second</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
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<tr>
<td>SILAR</td>
<td>Successive Ion Layer Adsorption and Reaction</td>
</tr>
<tr>
<td>std</td>
<td>Standard</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
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<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>T66</td>
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<tr>
<td>TBAB</td>
<td>Tetrabutylammonium bromide</td>
</tr>
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<td>TDAB</td>
<td>Tetradecylammonium bromide</td>
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<td>TDPA</td>
<td>Tetradecylphosphonic acid</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
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<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<td>Abbreviation</td>
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<tr>
<td>TMAB</td>
<td>Tetramethylammonium bromide</td>
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<tr>
<td>TOA</td>
<td>Trioctylamine</td>
</tr>
<tr>
<td>TOAB</td>
<td>Tetraoctylammonium bromide</td>
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<td>TOP</td>
<td>Trioctylphosphine</td>
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<td>TOPO</td>
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<td>TOPSe</td>
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<td>V_m</td>
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<td>Wurtzite</td>
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<td>X-ray photoelectron spectroscopy</td>
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<td>Zinc sulfide</td>
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<td>Zinc selenide</td>
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<tr>
<td>γ</td>
<td>Surface free energy</td>
</tr>
<tr>
<td>μ_s</td>
<td>Viscosity of solvent</td>
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# LIST OF TABLES

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<tbody>
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<td>Table 2.1</td>
<td>Wavelength of absorption of first exciton peak and corresponding size of the particles in nm. Reprinted with permission from Peng et al., 1998. Copyright 1998 American Chemical Society.</td>
<td>53</td>
</tr>
<tr>
<td>Table 2.2</td>
<td>Vibrational mode assignments for the FTIR spectrum shown in Figure 2.4.</td>
<td>56</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>Organic solvents used in this study.</td>
<td>68</td>
</tr>
<tr>
<td>Table 3.2</td>
<td>A comparison of ~2.7-nm CdSe QDs synthesized at 220 °C using the different organic solvents.</td>
<td>76</td>
</tr>
<tr>
<td>Table 5.1</td>
<td>Abbreviations and chemical structures of various quaternary ammonium salts used in this study.</td>
<td>127</td>
</tr>
<tr>
<td>Table 5.2</td>
<td>The diameter of Au NPs formed in this study by varying the amounts of reducing agents.</td>
<td>149</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1.1. Schematic diagram illustrating the various stages of nucleation and growth during the synthesis of NPs as proposed by LaMer and Dinegar. Reprinted, with permission, from the Annual Review of Materials Science, Volume 30 © 2000 by Annual Reviews www.annualreviews.org. 5

Figure 1.2. Schematic diagram showing the surface of the particle in a homogeneous medium and the spherical concentration gradient around it. 11

Figure 1.3. Schematic illustration of the density of states of electrons in 0D NPs, 1D nanowires, 2D quantum wells and 3D bulk materials. Reprinted with permission from ASME International. All rights reserved. www.asme.org. 17

Figure 1.4. Schematic picture illustrating the increase in the number of surface atoms with decrease in the size of the particles. Nanoscale Materials in Chemistry, 24, 2001. 18

Figure 1.5. Schematic of the hot-injection method for the synthesis of monodisperse nanoparticles. 20

Figure 1.6. HRTEM image of a CdSe crystallite synthesized by Murray et al. Repinted with permission from Murray et al., 1993. Copyright 1993 American Chemical Society. 21

Figure 1.7. Thermolysis of cadmiumimino-bis(diisopropylphosphine selenide) in the presence of TOP/TOPO. 23

Figure 1.8. Transmission electron micrographs of (a) rice shaped (b) rod shaped (Peng et al., 2003; Copyright Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission.) (c) tear shaped (d) arrow shaped. Reprinted
with permission from Manna et al., 2000. Copyright 2000 American Chemical Society. .......................................................... 27

Figure 2.1. (a) Typical UV-Visible spectrum of spherical shaped CdSe NPs of average diameter 3 nm (b) CdSe NPs of diameter ranging from 2 nm to 4.2 nm disperse in toluene fluorescing in the visible region under UV light. ... 52

Figure 2.2. Typical PL spectra of spherical shaped CdSe NPs of diameter 6.3 nm. 53

Figure 2.3. Calibration curves for the dye Rhodamine-6G at excitation wavelengths 480 nm and 500 nm. The slopes of the curves were $2.99 \times 10^5$ and $2.86 \times 10^5$ respectively. ................................................................. 54

Figure 2.4. Typical FTIR spectra for spherical shaped CdSe NPs with oleic acid capping on the surface. ................................................................. 55

Figure 2.5. Typical thermogram for spherical shaped CdSe NPs with oleic acid capping on the surface. ................................................................. 57

Figure 2.6. XRD patterns of spherical shaped CdSe NPs and the peak assignments to crystal axes (a) Wurtzite phase (b) Zinc-blende phase. ....................... 59

Figure 2.7. Transmission electron micrograph of spherical shaped CdSe NPs. ..... 60

Figure 2.8. Typical XPS survey spectrum of spherical shaped CdSe NPs on Si using Al X-ray source................................................................. 62

Figure 2.9. Typical EDS spectrum for spherical shaped CdSe NPs.................. 63

Figure 3.1. Molecular structures of (a) TOPO, (b) ODE, and the HT fluids (c) DTA and (d) terphenyl in T66. ................................................................. 68
Figure 3.2. UV-vis absorbance and fluorescence spectra of CdSe QDs synthesized in (a) DTA, (b) T66, (c) ODE, and (d) TOPO, as a function of time (injection @ 250 °C and growth @ 220 °C). Each set of spectra was collected at 10 sec, 1 min, 5 min, 30 min, 1 hr, 3 hr, and 5 hr after injection of TOPSe solution. Corresponding spectra for QDs synthesized in (e) T66 and (f) ODE at higher temperatures (injection @ 300 °C and growth @ 280 °C). Each set of spectra was collected at 5 min, 15 min, 30 min, 1 hr, and 2 hr after injection of TOPSe solution. .................................................. 72

Figure 3.3. TEM images of CdSe QDs synthesized for 1 hr in (a) DTA, (b) T66, (c) ODE, and (d) TOPO solvents (injection @ 250 °C and growth @ 220 °C). Scale bars: 20 nm. .......................................................... 73

Figure 3.4. (a) Average particle diameter and (b) particle concentration plotted against synthesis time (log scale), calculated from UV-vis absorbance data of CdSe QDs synthesized in the four different organic solvents (injection @ 250 °C and growth @ 220 °C). The same data plotted on a linear scale (c,d). .......................................................... 75

Figure 3.5. UV-vis absorbance and fluorescence spectra of ~2.7-nm CdSe QDs synthesized in (a) DTA, (b) T66, (c) ODE, and (d) TOPO (injection @ 250 °C and growth @ 220 °C). .................................................. 77

Figure 3.6. UV-vis absorbance and fluorescence spectra of CdSe QDs (a) before heating, (b) after heating at 220 °C for 30 min in presence of Cd and S precursors, and (c) after heating at the same conditions but without the shell precursors. .................................................. 79
Figure 3.7. (a) TEM image, (b) size histograms, and (c) optical spectra of CdSe QRs synthesized in T66 for 30 min (injection @ 300 °C and growth @ 250 °C). Scale bar: 50 nm.............................

Figure 3.8. Simulation results for the dynamics of: (a) the average particle radius normalized by the initial average particle radius, (b) total number of particles, and (c) standard deviation of particle size distribution divided by the initial standard deviation. Solid red lines: Nominal case (Da = 4, χ = 0.6, So = 10). Dotted green lines: ½× nominal viscosity (Da = 2, χ = 0.6, So = 10). Dashed blue lines: ½× nominal viscosity, ½× nominal solubility, and 1.5× nominal surface free energy (Da=3, χ = 0.318, So = 21)........

Figure 3.9. Normalized FWHM (by initial FWHM value)-time profiles for CdSe QD growth (injection @ 250 °C and growth @ 220 °C) in T66 (solid line-open circles) and DTA (dashed line-filled circles)..........................

Figure 4.1. Representative transmission electron microscopy (TEM) images of CdSe tetrapods synthesized with a) CTAB b) DDAB c) spherical CdSe QDs synthesized without any quat ligand and d) TEM image of CdSe tetrapods synthesized with CTAB through the slow-decomposition method, and recovered after 1 h at 300 °C. All scale bars: 20 nm. The particles were recovered 1 min after injection. Insets: higher magnification of individual tetrapod particles (not to scale)..........................

Figure 4.2. Histograms of tetrapod arm width and length distributions for tetrapods synthesized with a,b) CTAB and c,d) DDAB.................................

Figure 4.3. XRD patterns of CdSe tetrapods synthesized with a) CTAB and b) DDAB,and of c) spherical CdSe QDs synthesized without any quat ligand. Diffraction peaks for the wurtzite and zinc-blende crystal structures of CdSe are shown in blue (bottom) and magenta (top) respectively........
Figure 4.4. Possible mechanisms for the a) nonselective and b) selective formation of CdSe tetrapods with CTAB or DDAB ligands. ........................................ 109

Figure 4.5. XRD pattern of CdSe QDs prepared with 1/12th of original Se/CTAB precursor amount used for the tetrapod sample of Figures 1a and 2a. Diffraction peaks for the wurtzite and zinc-blende crystal structures of CdSe are shown in black (top) and magenta (bottom) respectively. ..... 110

Figure 4.6. Representative TEM image of CdSe QDs synthesized with ten times the amount of CTAB used for the tetrapod sample of figure 4.1 a. The particles were recovered 1 min after injection. Inset: higher magnification of an individual tetrapod particle (not to scale). Scale bar: 50 nm. ...... 111

Figure 4.7. XRD pattern of CdSe tetrapods synthesized with ten times the amount of CTAB used for the tetrapod sample of figure 4.1 a. Diffraction peaks for the wurtzite and zinc-blende crystal structures of CdSe are shown in black (bottom) and magenta (top) respectively. ........................................... 112

Figure 4.8. Representative TEM images of shaped CdSe QDs, synthesized with (a) tetradecylammonium bromide and (b) tetrabutylammonium bromide. The particles were recovered 1 min after injection. All scale bars: 20 nm... 113

Figure 4.9. TEM images of ZnSe QDs synthesized a) without and b) with DDAB; PbSe QDs synthesized c) without and d) with DDAB, and CdS QDs synthesized e) without and f) with DDAB. The particles were recovered 1 min after injection. All scale bars: 20 nm..................................... 114

Figure 4.10. Schematic illustration of two modes of thermal decomposition of quaternary ammonium salts. ................................................................. 115
Figure 4.11. UV-vis absorbance (in blue) and photoluminescence spectra (in magenta) of CdSe tetrapods synthesized with (i) CTAB and (ii) DDAB; and (iii) spherical CdSe QDs synthesized without any quat ligand. The particles were recovered 1 min after injection. .................................................. 117

Figure 5.1. (a) Bright orange CdSe tetrapod NPs dispersed in toluene (b) Bright yellow colored gold precursor solution (C) Murky brown solution of hybrid Au-CdSe NPs................................................................. 129

Figure 5.2. Transmission electron micrographs of CdSe tetrapodal NPs formed under various injection and growth temperatures. As the temperature is increased the length of the particles decreases steadily and the width of the same increases steadily. The loss of selectivity with time is drastically reduced with reduction in synthesis temperatures allowing for the observation of growth of particles before the Ostwald ripening. Control experiments where CTAB was excluded yielded spherical particles at all temperatures and times................................................................. 131

Figure 5.3. (a) Variation of QY of CdSe tetrapods with time at various injection temperatures (i) 220 °C (ii) 190 °C (iii) 250 °C (iv) 300 °C (b) Variation of selectivity of the CdSe tetrapods synthesized at various injection temperatures with time (c) Variation of dimension of CdSe tetrapods synthesized at various injection temperatures (i) length (ii) width (d) Variation of QY of CdSe tetrapods with injection temperatures at various time (i) 60 min (ii) 1 min ................................................................. 132

Figure 5.4. Absorption and PL spectra of the CdSe nano-tetrapods synthesized at (a) 300 °C/280 °C (b) 280 °C/250 °C (c) 250 °C/220 °C (d) 220 °C/190 °C (e) 190 °C/160 °C (f) 160 °C/130 °C at various times of synthesis. The red
lines signify the absorbance spectra and the blue lines signify the emission spectra. ................................................................. 135

Figure 5.5. Powder X-ray diffraction patterns of as-synthesized CdSe tetrapods at various injection temperatures (i) 160 °C (ii) 190 °C (iii) 220 °C (iv) 250 °C (v) 280 °C (vi) 300 °C (vii) CdSe nanoparticles synthesized without CTAB at an injection temperature of 300 °C (viii) CdSe nanoparticles synthesized without CTAB at an injection temperature of 190 °C. Diffraction peaks of zinc-blende and wurtzite are shown in magenta (bottom) and black (top) lines respectively. ......................................................... 136

Figure 5.6. TEM images of CdSe tetrapods synthesized by multiple injection after (a) 1st injection (b) 2nd injection (c) 3rd injection (d) 4th injection and (e) 5th injection. All the scale bars equal to 20 nm. The table indicates the average dimensions and the quantum yield of the tetrapodal NPs synthesized after each injection. ................................................................. 138

Figure 5.7. (a) Optical spectra of particles synthesized by multiple injection method after (i) 1st injection (ii) 2nd injection (iii) 3rd injection (iv) 4th injection and (v) 5th injection. (b) Optical spectra of particles including excitation spectra synthesized by multiple injection after (i) 1st injection (ii) 2nd injection (iii) 3rd injection (iv) 4th injection. The magenta lines represent absorbance spectra, the blue lines represent the emission spectra and the red lines represent excitation spectra. ................................................................. 140

Figure 5.8. (a) TEM image of CdSe tetrapods synthesized with CBDMAC as the quat. The system showed occasional six armed structures as shown in the inset (b) QY at various synthesis times for CdSe tetrapod NPs synthesized with (i) CTAB (ii) CTAC........................................................................................................................................ 143
Figure 5.9. TEM images of CdSe tetrapodal NPs synthesized in the ternary surfactant system at various reaction times (a) 1 min (b) 5 min (c) 30 min (d) 1 hr. All scale bars equal 20 nm. ................................................................. 144

Figure 5.10. (a) Optical spectra of CdSe NPs synthesized in ternary surfactant system at various reaction times. (b) The growth profile of the CdSe in (i) binary surfactant system (CTAB and OA) (ii) ternary surfactant system (OA, CTAB, and TOPO). (c) Variation of stokes shift with reaction time for (i) ternary surfactant system (OA, CTAB, and TOPO) and (ii) binary surfactant system (CTAB and OA). ................................................................. 145

Figure 5.11. TEM images of CdSe tetrapodal NPs synthesized at various ratios of oleic acid and CTAB. The injection temperature was 190 °C and growth temperature was 160 °C and the ratio of Cd:Se was 2:1. The aliquots were withdrawn at 1 min after the injection of Se/CTAB solution. Insets show individual particles at higher magnifications (not to scale). ................. 147

Figure 5.12. TEM images of CdSe tetrapods with Au NPs (a) web like structure seen with a 2.2 nm Au NPs (b) web like structures seen with 3.2 nm Au NPs (c) and (d) Au NPs of diameter 4.8 nm arranged along the arms of CdSe tetrapodal NPs (e) XRD of the (i) Au-CdSe hybrid NPs (ii) CdSe tetrapod NPs. The scale bars for (a) equals 50 nm, and for (b), (c), and (d) equal 20 nm. ......................................................................................................... 150

Figure 5.13. (a) Emission spectra of Au-CdSe nanocomposites made with Au NPs of various different diameters. It can be seen that the Au-CdSe NPs show a drastic fall in the PL intensity. Inset (i) shows the Stern-Volmer plot of decrease in the PL intensity with diameter of Au NPs. The inset (ii) shows the magnified area specified by the rectangle. The blue and black line in the inset represents the PL spectrum of Au-CdSe nanocomposite made
with Au NP of 2 nm and 3.2 nm respectively. The red and green represent that of nanocomposites made with Au NPs of 4.8 nm.

Figure 6.1. TEM images of CdSe NPs (a) preformed ZB seeds (b) after 1st secondary injection (c) after 2nd secondary injection (d) after 3rd secondary injection (e) after 4th secondary injection. All the scale bars equal to 20 nm.

Figure 6.2. (a) Optical spectra of CdSe NPs. Magenta lines signify absorbance spectra and the blue lines represent the emission spectra. (i) Preformed ZB seeds (ii) after 1st injection (iii) after 2nd injection (iv) after 3rd injection (v) after 4th injection (b) XRD patterns of CdSe NPs (i) Preformed ZB seeds (ii) after 4th injection.

Figure 6.3. (a) TEM image of preformed WZ CdSe seeds (b) TEM image of rod shaped CdSe NPs after 4th secondary injection (formed from WZ CdSe seeds). All the scale bars equal to 20 nm.

Figure 6.4. Schematic picture showing the formation of tetrapodal NPs and rod shaped NPs from ZB and WZ CdSe seeds respectively.

Figure 6.5. FTIR spectra of (a) pure OA (b) CTAB (c) CdSe tetrapodal NPs capped with OA and CTAB (d) CdSe spherical NPs capped with OA and the peak assignments to corresponding vibrational motions.

Figure 6.6. (a) XPS survey spectrum of CdSe tetrapodal NPs bound to Si using Al X-ray source (b) Close-up surveys for Cd 3d (c) Se 3d (d) C 1S (e) O 1S and (f) Br 3d.

Figure 6.7. (a) EDS spectrum obtained for CdSe tetrapodal NPs (b) Mapping of elements to the emitted X-ray energy on various areas of the NP film on Si surface. (c) Quantification of the atomic percentage of various atoms.
Figure 6.8. Thermograms of CdSe NPs (a) Preformed ZB seeds (b) after 1st secondary injection (c) after 2nd secondary injection (d) after 4th secondary injection (e) Thermogram of pure CTAB (f) Thermogram of pure OA

Figure 6.9. Estimation of percentage of OA on CdSe NPs of different diameters.
Chapter 1

Background and Motivation

“There is plenty of room at the bottom” said Richard Feynman in his famous talk at California Institute of Technology (Caltech) in 1959 and the talk was published in the Caltech journal of Engineering and Science in 1960\(^1\). Ever since his talk the field of manipulating and controlling things on a small scale has been under constant scrutiny and was christened “nanotechnology” in the mid 1980s. It is interesting to note that despite the buzz around the word nanotechnology it does not have a hard and fast definition. In the inaugural issue of the journal Nature Nanotechnology in 2006\(^2\), the pioneers in this field were asked to define nanotechnology. Interestingly enough, no definition was alike. But for all practical purposes, the National Science Foundation defines nanotechnology as “research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1-100 nanometer range”\(^3\) and a nanoparticle as any particle, natural or man-made, that has at least one of its dimensions between 1-100 nm.

1.1 Properties and Applications of Nanomaterials

Intensive studies of physicochemical properties of nanoparticles (NPs) carried out over the past decades have revealed a large number of unusual characteristics such as mechanical, chemical, electrical, optical, magnetic, optoelectronic and magneto-optical properties\(^4\)-\(^7\) of nanomaterials that are significantly different from those observed for bulk materials. These properties of nanoparticles (NPs) are very useful in optoelectronics\(^8\)-\(^9\), catalysis\(^10\)-\(^11\), single electron transistor and light emitting diode\(^12\), nonlinear optical
devices\textsuperscript{12} and photo electro-chemical applications\textsuperscript{13}. Magnetic nanoparticles are being used in memory storage devices\textsuperscript{14}, magnetic resonance image enhancement\textsuperscript{15} and could probably be employed in interesting applications such as magnetic refrigeration\textsuperscript{16}. Semiconductor nanoparticles are very attractive because of their size-dependent optical properties for use in quantum dot lasers\textsuperscript{17}. Other than these, nanomaterials have potential applications in synthesis of advanced materials, energy storage devices, electronic and optical display, chemical and bio- sensors as well as bio-medical devices\textsuperscript{18}. All these applications require preparation of nanoscale materials of desired property and their assembly in required geometry. Therefore, the most fundamental objective of nanotechnology is the controlled synthesis of those building blocks and their subsequent assembly into nanostructures for useful devices. Roughly two kinds of "nanostructure induced effects" can be distinguished:

(a) **Size effect**, in particular the quantum size effects where the normal bulk electronic structure is replaced by a series of discrete electronic levels.

(b) **Surface or interface induced effect**, which is important because of the enormously increased specific surface in particle systems. Both the effects are explained in detail with reference to semiconductor NPs later in this chapter.

1.2 Synthetic Methods of Nanoparticles

The synthesis of NPs is an important component of the rapidly growing research efforts in nanoscale science and engineering. Various methods of synthesis of NPs can be broadly classified into two categories (a) Top – down approach, when the precursors are bulk materials and the synthesis is physical, where in the small particles are chiseled out
of the bulk materials. (b) Bottom–up approach, when the precursors are fundamental molecules and the synthesis is chemical and particles grow by the assembly of atoms or molecules. Any different method of synthesis of NPs, one may come across will definitely fall into one of the above mentioned classes. The bottom-up approach is widely used for the precision in the size and shape control of the resulting NPs. Since the various different methods of synthesis of NPs are overwhelmingly vast, for the sake of simplicity the methods can be broadly classified based on the phase of medium of synthesis as (a) gas-phase synthesis and (b) liquid-phase synthesis, as these two phases of synthesis are the most common and the discussions will be limited to the bottom–up approach.

In the gas-phase NP synthesis, precursors (molecular or bulk) are aerosolized and decomposed into NPs at high temperatures. The literature boasts a plethora of gas phase synthesis techniques like inert gas condensation\textsuperscript{19-23}, pulsed laser ablation\textsuperscript{24-28}, spark discharge generation\textsuperscript{29,30}, ion sputtering\textsuperscript{31}, chemical vapor synthesis\textsuperscript{32-38}, spray pyrolysis\textsuperscript{39,40}, laser pyrolysis\textsuperscript{41-44}, thermal plasma synthesis\textsuperscript{45}, flame spray pyrolysis\textsuperscript{46}, to name a few. Although vapor-phase synthesis methods can produce large quantities of NPs, agglomeration and non-uniformity in particle size and shape are typical problems, especially for NPs on the smaller end of the nanometer range (1–10 nm).

Despite recent developments\textsuperscript{47,48}, these problems can potentially be best avoided by following the liquid-phase synthesis route, since various methods of this type yield unagglomerated and relatively monodisperse (relative standard deviation ($\sigma$)<10\%) NPs. Due to the improved quality of the products, the liquid phase synthesis methods attracted extensive attention and it is indicated by the plethora of reports and reviews on the synthesis of NPs using this technique. The most popular liquid phase synthesis methods
are coprecipitation\textsuperscript{49,50}, sonochemical synthesis\textsuperscript{51-54}, electrochemical synthesis\textsuperscript{55-57}, solvothermal synthesis\textsuperscript{58-60}, sol-gel synthesis\textsuperscript{61-63}, radiolytic synthesis\textsuperscript{64-66}, and microemulsion methods\textsuperscript{67-69}. However, purification of the synthesized NPs from the unreacted precursors, ligands and solvent requires a post preparative treatment be done.

The objective of this thesis is to develop economically and environmentally friendly methods to synthesize NPs of uniform size and shape, high degree of crystallinity and defect free surface.

1.2.1 LaMer Model of Particle Nucleation and Growth

The key to the synthesis of narrow size distribution of resulting NPs is explained by the classic studies by LaMer and Dinsegar which show that the production of monodisperse colloids require a short burst of nucleation event followed by slower controlled growth of the existing nuclei (Figure 1.1)\textsuperscript{70}. Rapid addition of the reagents to the reaction vessel increases the reactive precursor concentration above the nucleation threshold. The reactive precursors are often referred to as monomers\textsuperscript{71-74}. No precipitation is observed while the super-saturation is being built, because the energy barrier for a homogeneous nucleation is very high. When the degree of super-saturation is high enough the energy barrier is overcome resulting in the burst of nucleation. The growth profile of all the nuclei produced would be the same because they were formed simultaneously. The monomer concentration rapidly dwindles, because the rate of consumption of the monomers by the nucleation process is very high compared to the rate of supply of the monomers. When the concentration of monomers falls below the nucleation threshold no new nuclei are formed and the growth stage kicks in. The final size distribution of the
particles is determined by the time beyond which the nuclei are formed and begin to grow. Hence, an ensemble of monodisperse particles is achieved when the nucleation and growth are separated. If the growth of the NPs during nucleation is limited as compared to the subsequent growth, the resulting particle size distribution would be very uniform\textsuperscript{75}. This phenomenon is later referred to as focusing of the size distribution\textsuperscript{71-74}.

![Diagram of monodisperse colloid growth](image)

**Figure 1.1.** Schematic diagram\textsuperscript{76} illustrating the various stages of nucleation and growth during the synthesis of NPs as proposed by LaMer and Dinegar\textsuperscript{70}. Reprinted, with permission, from the *Annual Review of Materials Science*, Volume 30 © 2000 by Annual Reviews [www.annualreviews.org](http://www.annualreviews.org)

Most of the systems exhibit secondary growth, which is very distinct and often called as “Ostwald ripening”\textsuperscript{77,78}. In this process the larger particles grow at the expense of smaller particles. In other words, the larger particles have lower surface energy and the smaller particles have higher surface energy. In their attempt to attain a lower energy
configuration, the small particles dissolve in to their fundamental moieties and deposit themselves on the larger particles. This in turn leads to the decrease in the number of particles and hence to the broadening of the size distribution since the deposition of the molecules on the larger particles is random. This is referred to as defocusing of the size distribution 71-73.

1.2.2 Thermodynamics of Nucleation and Growth of the Particles

The thermodynamics of the nucleation of CdSe NPs is explained as follows 70.

The Gibbs free energy of formation of a spherical NP of radius \( r \) from a solution of super-saturation \( S \) is given by

\[
\Delta G = 4\pi \cdot r^3 \gamma + \frac{4}{3} \pi \cdot r^3 \Delta G_v \quad \text{.......................................... (1)}
\]

Where \( \Delta G \) is Gibbs free energy of formation of NP

\( \gamma \) is the surface free energy per unit area

\( \Delta G_v \) is the change in the free energy between the monomers in the solution and unit volume of bulk crystal \( (r \rightarrow \infty) \) (negative when the formation of NP is spontaneous \( i.e., \) when the solution is super-saturated)

\[
\Delta G_v = \left( -\frac{RT \ln S}{V_m} \right) \quad \text{.......................................... (2)}
\]

Where, \( V_m \) is the molar volume of the bulk crystal.

The value of \( r \) at the maximum \( \Delta G \) is called critical radius and this is the minimum radius of the nucleus that can grow spontaneously in the supersaturated solution.

Differentiating \( \Delta G \) with respect to \( r \),
\[ \frac{d\Delta G}{dr} = 8\pi \gamma r + 4\pi r^3 \Delta G \]  
\quad \quad \quad \quad (3)

Substituting equation 2 in equation 3 and setting \( d\Delta G/dr = 0 \),

We find that critical radius is

\[ r_c = \frac{-2\gamma V_m}{RT \ln S} \]  
\quad \quad \quad \quad (4)

Equation 4 tells that for the radius to be small the supersaturation \( S \) has to be as high as possible for the homogeneous nucleation. The nuclei are supposed to be of the molecular dimensions ~1 nm\(^7\).\(^{80}\)

The critical free energy of formation of a spherical NP of radius \( r_c \) is given by substituting equation 4 in equation 1\(^7\),

\[ \Delta G_c = \frac{16\pi \gamma V_m^2}{3(RT \ln S)^2} \]  
\quad \quad \quad \quad (5)

If rate of nucleation is the rate of increase of number of particles \( N \), it can be written in the Arrhenius equation form\(^7\),\(^{80}\),

\[ \frac{dN}{dt} = A \exp \left[ -\frac{\Delta G_c}{KT} \right] = A \exp \left[ \frac{16\pi \gamma V_m^2}{3K^3 T^3 N^2 (\ln S)^2} \right] \]  
\quad \quad \quad \quad (6)

The critical supersaturation level \( S_c \) at which the nucleation takes place is given by\(^7\)

\[ \ln S_c = \left[ \frac{16\pi \gamma V_m^2}{3K^3 T^3 \ln(A/\dot{N})} \right]^{\frac{1}{2}} \]  
\quad \quad \quad \quad (7)

Where \( \dot{N} = \frac{dN}{dt} \)

It is prudent to be aware of the fact that even while the super-saturation is very high to induce nucleation there is always re-dissolution happening as the system tries to
attain equilibrium\textsuperscript{81}. Equation 7 shows that $S_c$ is the critical supersaturation level where the rate of nucleation is higher than the rate of dissolution. In short, at critical supersaturation the effective number of nuclei increases in spite of the dissolution of the smaller nuclei.

However, the major flaw of the above mentioned thermodynamic model is the assumption that $\gamma$ and $\Delta G_e$ are constants, while these two parameters are strongly influenced by the size of the nuclei. As the size of the particle approaches the molecular dimension, the percentage of the surface atoms increases considerably, leading to the increase in the surface free energy $\gamma$\textsuperscript{82}.

Nucleation is a rapid process that is characterized by the constant number of particles and a maximum particle concentration. To get a complete picture of the nucleation process one would need the particle concentration and the monomer concentration simultaneously. This would require one to characterize the aliquots withdrawn from the hot reaction vessel, after quenching the reaction for room temperature measurements. This limits the time resolution to tens of seconds at the least. A full description of the nucleation process is almost impossible because of the time constraints. Also, an accurate characterization of the particles requires withdrawal of a significant amount of aliquot from the reaction flask, constantly disturbing the equilibrium between the particles and the monomers in the reaction solution.

Qu \textit{et al.} addressed these issues by monitoring the CdSe crystallization systems \textit{in situ}, using the size dependent optical properties of crystals in the transition regime from molecular precursors to NPs\textsuperscript{83}. A series of absorption spectra of CdSe particles were recorded \textit{in situ} at different reaction moments. The size and the concentration of the
particles were calculated using the position of the first exciton peaks of the absorption spectra\textsuperscript{84}. The monomer concentration at a given moment was calculated with the size and concentration of the particles and the initial monomer concentration. The results of the study were in agreement with the classical LaMer theory\textsuperscript{70}.

In 2005 Bullen \textit{et al.} studied the nucleation and growth kinetics of CdSe NPs in octadecene\textsuperscript{71}. The results obtained showed that the nuclei concentrations were constant throughout the reaction within experimental error. They verified that the growth phase proceeds independently of the nucleation phase and the growth kinetics obeys equation 6. The study estimates the radius of the nuclei to be ~1 nm. The authors also showed that the capping agents not only determine the rate of growth but also play an important role in determining the number and size of the nuclei formed during the injection.

The first theoretical studies on the uniform growth of colloidal dispersions was performed by Reiss\textsuperscript{75,79}. His model is known as “growth by diffusion” where in he proposed that the growth rate of the particles depended on the flux of the monomers to the particles (J).

\begin{equation} \label{eq:8}
J = \frac{4\pi r^2}{V_m} \frac{dr}{dt} \end{equation}

Each particle can be assumed to be undisturbed by the neighboring particles if the distance between the particles is large enough. A single particle in a homogeneous medium has a concentration gradient with spherical symmetry (Figure 1.2).

Flux J is given by Fick’s law

\begin{equation} \label{eq:9}
J = 4\pi r^2 D \frac{dC}{dx} \end{equation}
Where,

D is the diffusion coefficient

C is the concentration

x is the distance from the center of the particle to the surface of the sphere enclosing the particle (r+dr in Figure 1.2).

If J is assumed to be constant for x, the integration of C(x) from r to r+dr with respect to x gives,

\[ J = 4\pi D \frac{r(r + dr)}{dr} \left[ C(r + dr) - C(s) \right] \] \hspace{1cm} (10)

When dr is very large \((r<<dr)\),

\[ J = 4\pi r D(C_r - C_x) \] \hspace{1cm} (11)

Where, \(C_r\) is the concentration of the monomer at the surface of the particle

\(C_b\) is the concentration of the monomer in the bulk solution

Substituting equation 11 into equation 8,

\[ \frac{dr}{dt} = \frac{V_n D}{r} (C_b - C_x) \] \hspace{1cm} (12)

This equation tells that the growth rate of the particles is inversely proportional to its radius. Hence, the size distribution of an ensemble of particles always becomes narrow regardless of the initial size distribution as long as the particles are growing and no new nucleation takes place. This is the self-regulating mechanism of the size distribution during the growth process and is referred to as the “focusing” effect\(^\text{72}\). This result is experimentally verified by Bullen and coworkers.\(^\text{71}\).
Figure 1.2. Schematic diagram\textsuperscript{85} showing the surface of the particle in a homogeneous medium and the spherical concentration gradient around it.

The focusing of the particle size distribution is followed by broadening of the size distribution often called as defocusing stage. The Reiss model cannot explain the defocusing stage because it does not take into effect the equilibrium that exists in the system between the growth of the particle (precipitation) and the dissolution of the particle into monomers. The surface energy of the particles change with growth and the kinetics of crystal growth responds to the change, provided the crystallites are small enough that the Gibbs-Thomson effect is significant\textsuperscript{86-88}.

\[ nM^s \xrightleftharpoons{K_p}{K_d} M^c \]

Where $M^s$ and $M^c$ refer to monomers in solution and in the crystal, and $K_p$ and $K_d$ are the reaction rate constants for precipitation and dissolution, respectively. It is assumed
that the precipitation is the first order reaction with respect to $C_s$ and that the dissolution rate is independent of $C_s$. Then at equilibrium, $K_p C_{s,eq} = K_d$

And hence, $C_{s,eq} = \frac{K_d}{K_p}$

The change in the chemical potential $\mu(r)$ of a spherical crystal with radius $r$ with respect to that of $(\mu^0)$ of the bulk crystal arises from the surface free energy of area (A).

$$\Delta \mu = \mu(r) - \mu^0 = \gamma \frac{dA}{dn}$$  \hspace{1cm} (13)

Because, $dA = 8\pi r dr$ and $dn = \frac{4\pi r^2 dr}{V_m}$ equation 13 can be rewritten as Gibbs-Thomson equation, \(\Delta \mu = \frac{2\gamma V_m}{r}\)  \hspace{1cm} (14)

The chemical potential change is related to the precipitation and dissolution as follows,

$$K_p = K_p^0 \exp\left[-\alpha \frac{\Delta \mu}{RT}\right] = K_p^0 \exp\left[-\alpha \frac{2\gamma V_m}{rRT}\right]$$  \hspace{1cm} (15)

$$K_d = K_d^0 \exp\left[(1-\alpha) \frac{\Delta \mu}{RT}\right] = K_d^0 \exp\left[(1-\alpha) \frac{2\gamma V_m}{rRT}\right]$$  \hspace{1cm} (16)

These equations signify that smaller the radius of the particle harder it is to grow but easier it is to dissolve, because of the chemical potential. This is in contrast to the focusing mechanism, where the smaller crystals grow faster.

To combine this effect with that of Reiss model, the assumption that $C_s$ is a constant has to be modified. The fluxes of the monomers towards the surface of the particle by precipitation and dissolution ($J_p$ and $J_d$, respectively) for a particle of radius $r$ are given by,
\[ J_p = 4\pi r^2 K_p^0 C_s \exp\left[-\alpha \frac{2\gamma V_m}{rRT}\right] \] ................................................(17)

\[ J_d = -4\pi r^2 K_d^0 \exp\left[(1 - \alpha) \frac{2\gamma V_m}{rRT}\right] \] ................................................(18)

The net flux of the monomers towards the surface of the particle of radius \( r \) is given by,

\[ J = J_p + J_d = 4\pi r^2 K_p^0 C_s \exp\left[-\alpha \frac{2\gamma V_m}{rRT}\right] - 4\pi r^2 K_d^0 \exp\left[(1 - \alpha) \frac{2\gamma V_m}{rRT}\right] \] ...... (19)

\[ C_s = \frac{K_p^0 r \exp\left[(1 - \alpha) \frac{2\gamma V_m}{rRT}\right] + DC_b}{K_d^0 \exp\left[-\alpha \frac{2\gamma V_m}{rRT}\right] + D} \] ................................................(20)

Substituting equation 20 in equation 12 we get,

\[ \frac{dr}{dt} = V_m DC_{s,eq} = \frac{S \exp\left[\frac{2\gamma V_m}{rRT}\right]}{\left[ \frac{D}{K_p^0} \exp\left[\frac{2\gamma V_m}{rRT}\right] + \frac{r + \frac{D}{\alpha} \exp\left[\frac{2\gamma V_m}{rRT}\right]}{K_p^0} \right]} \] ................................................(21)

Where \( C_{s,eq}^0 \) is the equilibrium surface concentration of the bulk crystal \( (r \to \infty) \), and \( S \) is the degree of supersaturation, which is defined as \( S = \frac{C_p}{C_{s,eq}^0} \). This equation is the modified form of equation 12 where both the mass transport and the reaction kinetics are considered. Hence when the growth is diffusion controlled the focusing effect dominates and when the NP growth is surface reaction-controlled the dissolution dominates the growth of the particle.

For an ensemble of particles, it is very difficult to trace the time evolution of the size distribution, mainly because the concentration of monomers in bulk \( (C_b) \) is not a
constant but dwindles with the increase in size of all the particles in the ensemble. Furthermore the growth rate also depends upon the \( C_b \). This mutual dependence complicates the analysis. Also, the classical descriptions fail to describe the real ensembles of nanosized particles as they use only first two terms of the expansion of the Gibbs-Thompson equation:

\[
C(r) = C_{flat}^0 \exp \left[ \frac{2\gamma V_m}{rRT} \right] \approx C_{flat}^0 \left( 1 + \frac{2\gamma V_m}{rRT} \right) \]

Equation 22 describes the solubility of the colloidal particles of radius larger than 20 nm. However for NPs with \( r = 1-5 \) nm the solubility of the particles ceases to linearly depend on \( r^{-1} \). Also, the chemical potential of the NPs with radius 1-5 nm depends nonlinearly on \( r^{-1} \). Both of these effects were not taken into account by the classical description of the Ostwald ripening.

Talapin et al. performed Monte Carlo simulations of Ostwald ripening of an ensemble of growing NPs, taking into account the size dependence of the activation energies of the growth and the dissolution processes as well as the mass transport of monomer toward the particle surface (equation 21). They simulated a volume of \( 3 \times 10^{-12} \) cm\(^3\) of the colloidal solution containing \( 5 \times 10^3 - 5 \times 10^4 \) NPs. The remaining concentration of monomer and value of monomer oversaturation S were calculated after
each time step instead of keeping them constant as they did in the classical studies. The performed Monte Carlo simulations of the evolution of an ensemble of growing NPs successfully established the conditions leading to either “focusing” or “defocusing” of the particle size distribution. The simulation studies of Talapin proposed two general strategies for improving the NP size distributions:

1) To carry out the process of the NP growth in the diffusion controlled regime, presumably by decreasing the diffusion or mass transfer coefficient of the system.

2) To increase the surface tension at the solvent-NP interface, for example by a proper choice of surfactants.

1.3 Semiconductor Nanoparticles

Semiconductor materials are basic to modern electronics. Macro-crystalline semiconductors are defect free; consist of 3 dimensional networks of ordered atoms. The large number of atoms present in the bulk semiconductors leads to the formation of a continuum of energy levels. At 0 K the lower energy level (highest occupied molecular orbital, \textit{i.e.}, HOMO) is filled with electrons and the lowest unoccupied molecular orbitals (LUMO) are not. The energy gap between HOMO and LUMO is called forbidden energy gap or band gap; the magnitude of which is characteristic of bulk macro-crystalline materials (at a specific temperature). Semiconductors usually have band gaps in the range of 0.3-3.8 eV. Semiconductor NPs has been under the researchers’ constant scrutiny since the 1980’s due to the sensitivity of their optical spectra to size\cite{90,92}. Typically for the 1-20 nm range, semiconductor NPs show optical, electronic and mechanical properties distinct
from those of the corresponding bulk material. The popular semiconductor NPs are materials of II-VI and III-V groups like CdSe, CdS, ZnSe, ZnS and InAs.

The unusual physico-chemical properties of semiconductor NPs stem from two facts:

a) As the size of the particles in study approaches the Bohr-exciton radius (the distance in an electron-hole pair), the energy levels of the NPs become discrete and quantized as opposed to continuous and the laws of classical mechanics cease to operate and the laws of quantum mechanics come into operation. As the characterization dimension of the materials is reduced to be comparable to the wavelength of electrons, the motion carriers (electrons or holes) is confined in one direction leading to a change in the shape of electron density of state D(E). This phenomenon is called as quantum confinement\(^3\), thus the nomenclature of quantum dots (QDs) and quantum wires, depending on their geometry. Figure 1.3 shows D(E) as a function of energy E for 0D NPs, 1D nanowire, 2D superlattice and 3D bulk\(^4\). This drastic change in the energy levels of the NPs as compared to their bulk counter parts lead to interesting optical, luminescent, and redox properties.
Figure 1.3. Schematic illustration of the density of states of electrons in 0D NPs, 1D nanowires, 2D quantum wells and 3D bulk materials\textsuperscript{34}. Reprinted with permission from ASME International. All rights reserved. www.asme.org.

(b) The fraction of surface atoms in the NPs is very high. As the size of the particle decreases, the percentage of number of surface atoms increases (Figure 1.4), leading to interesting thermodynamic properties and structural transitions of NPs. Also the high surface energy of the NPs can lead to interesting catalytic and other surface related properties.

Cadmium Selenide (CdSe) NPs are one of the most studied systems in the past two decades\textsuperscript{90-92} because of the versatile electronic and optical properties, stemming from the quantum confinement of the charge carriers, surface effects and geometrical confinement of phonons\textsuperscript{95-98}. These properties have made CdSe NPs promising material for many applications such as light emitting diodes, lasers, holographic optical memories, photonic band-gap crystals, ultra fast photonic switches, biomedical tags for fluoro-immuno assays and nanosensors\textsuperscript{99-103}. The challenge has been to design a synthetic
method that is reliable, scalable, and green without compromising on the quality of the resulting NPs, *i.e.*, size uniformity, morphology uniformity, crystallinity, and defect-free surface.

<table>
<thead>
<tr>
<th>Full-shell Clusters</th>
<th>Total Number of Atoms</th>
<th>Surface Atoms ($f^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Shell</td>
<td>13</td>
<td>92</td>
</tr>
<tr>
<td>2 Shells</td>
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</tr>
<tr>
<td>7 Shells</td>
<td>1415</td>
<td>35</td>
</tr>
</tbody>
</table>

*Figure 1.4.* Schematic picture illustrating the increase in the number of surface atoms with decrease in the size of the particles.$^{82}$
1.3.1. Synthesis of Cadmium Selenide Nanoparticles

In the late 1980’s Steigerwald and co-workers prepared capped CdSe, ZnS, ZnS/CdSe, and CdSe/ZnS NPs from inverse micellar solutions\textsuperscript{91,104}. Silylchalcogenide reagents were added to micro-emulsions containing the appropriate metal ions.

\[
\begin{align*}
\text{CdCl}_2 + \text{Se(SiMe)}_3 & \rightarrow \text{CdSe} + 2\text{Me}_2\text{SiCl} \\
\text{ZnEt}_2 + \text{Se(SiMe)}_3 & \rightarrow \text{ZnSe} + 2\text{Me}_2\text{SiEt} \\
\text{CdMe}_2 + \text{Te(SiPr(Me)}_2 & \rightarrow \text{CdTe} + 2\text{Me}_2\text{SiPr}
\end{align*}
\]

Where Me, Et and Pr stand for methyl, ethyl and propyl respectively.

The particle surfaces were subsequently capped to prevent agglomeration of the synthesized particles. The surface passivated CdSe NPs were isolated as powders and dispersed in organic solvents like pyridine, chloroform for further characterizations. However the interpretation of sophisticated optical experiments remained difficult due to the polydispersity in size and shape, surface electronic defects due to uneven surface derivatization and poor crystallinity.

In 1993 Murray, Norris and Bawendi reported a very powerful method for the synthesis of CdSe NPs and this synthesis method is one of the most cited articles in nanoscience with over 2000 citations\textsuperscript{105}. This method was the first to reliably produce high quality, crystalline, and monodisperse semiconductor NPs (CdS, CdSe, CdTe) in organic solution. In this method, dimethylcadmium ((CH\textsubscript{3})\textsubscript{2}Cd) and selenium metal (Se) dissolved in trioctylphosphine (TOP) are rapidly injected into hot (300 °C) trioctylphosphine oxide (TOPO) to produce a short burst of homogeneous nucleation.
(Figure 1.5). This method is often referred to as the hot injection method. Besides acting as the solvent for the reaction, TOPO binds to the NP through a coordination bond.

![Schematic diagram](image)

**Figure 1.5.** Schematic of the hot-injection method for the synthesis of monodisperse NPs.

This synthesis results in the formation of monodisperse NPs of diameter varying between 1.2 nm to 11.5 nm, with a quantum yield of 9.6% relative to Rhodamine-640 at room temperature. The synthesized crystallites exhibited a wurtzite crystal structure. High resolution transmission electron micrograph (HRTEM) reveals that these particles were crystalline (Figure 1.6).

Although this method yielded highly monodisperse NPs, this method suffers from the disadvantage of being very dangerous because the cadmium precursor, dimethyl cadmium is extremely toxic, pyrophoric, expensive, and unstable at room temperature and explosive at elevated temperatures by releasing large amount of gas. The synthesis
was also hard to control and not reproducible. This urged the search for the safer synthetic methods.

Figure 1.6. HRTEM image of a CdSe crystallite synthesized by Murray et al.\textsuperscript{105}. Repinted with permission from Murray et al. 1993. Copyright 1993 American Chemical Society.

Peng and co-workers reported synthesis of cadmium chalcogenide NPs\textsuperscript{106-109} using cadmium oxide (CdO), cadmium acetate (CH\textsubscript{3}COO)\textsubscript{2}Cd and cadmium carbonate (CdCO\textsubscript{3}) as the cadmium precursor and demonstrated that the new synthetic schemes worked better than the dimethyl cadmium related ones. In these articles, CdSe NPs were synthesized by heating Cd precursors (CdO, (CH\textsubscript{3}COO)\textsubscript{2}Cd and CdCO\textsubscript{3}) to high temperatures in different solvent systems, such as fatty acids (e.g. oleic acid, stearic acid), amines (e.g. hexadecyl amine, octadecyl amine), phosphine oxides (TOPO), phosphonic acids (e.g. tetradecyl phosphonic acid, octadecyl phosphonic acid) and the mixture of these common chemicals with certain compositions, followed by injection of Se
precursor (typically selenium powder dissolved in trioctyl phosphine (TOP)). The authors showed that they could controllably vary the crystal structure between zinc-blende and wurtzite phases using these synthesis schemes. They also demonstrated the synthesis of CdSe NPs of diameter varying between 1.5 nm to 25 nm, a much broader range than achieved by the original organometallic synthesis. The size distribution was narrow with standard deviation between 5% to 10% and the quantum yield for the CdSe NPs synthesized by Peng and co-workers varied between 20% - 30% although they reported a decrease in the quantum yield with increase in the diameter of the particle\textsuperscript{\textsuperscript{108}}.

Mulvaney and co-workers reported a phosphine free synthesis of CdSe NPs in 2005\textsuperscript{\textsuperscript{110}}, where Se was dissolved in 1-octadecene at 200 °C to give a homogeneous Se stock solution that is stable at room temperature. This method left the Se atoms in the resulting CdSe NPs unpassivated and provided information on the effect of ligands on the growth dynamics and the photophysics of the CdSe NPs.

Yang \textit{et al.} showed a non injection synthesis for making high-quality CdSe NPs, where in they slowly heated the reaction mixture to slightly above the decomposition temperature of cadmium myristate and the melting point of selenium\textsuperscript{\textsuperscript{111}}. The relative standard deviation of the size of the resulting CdSe NPs was found to be less than 5%.

O’Brien and co-workers reported the usage of single molecular precursors for the synthesis of cadmium chalcogenide NPs\textsuperscript{\textsuperscript{112-114}}. This method involves using air stable inorganic molecular clusters like \([M_{10}Se_{4}(SPh)_{16}]^{4+}\), \(M^{n}(Se_{2}CNR^{1}R^{2})_{n}\)\textsuperscript{14} which would act as a precursor for both Cd and Se and would lead to the formation of CdSe NPs during the thermolysis of these precursors in the presence of TOP/TOPO (Figure 1.7). The single molecular precursors were not readily available and they have to be synthesized,
recovered, purified and characterized. Also this method suffered from the disadvantage of poor size and shape selectivity and poor luminescence properties.

![Thermolysis of cadmiumimino-bis(diisopropylphosphine selenide) in the presence of TOP/TOPO.](image)

**Figure 1.7.** Thermolysis of cadmiumimino-bis(diisopropylphosphine selenide) in the presence of TOP/TOPO.

The popular co-ordinating solvents like TOPO and long chain phosphonic acids were replaced by long chain fatty acids\textsuperscript{115,116} and amines\textsuperscript{107} because phosphonic compounds were found to be extremely toxic and difficult to handle. Evidently only a few compounds can act as the coordinating solvents\textsuperscript{108} and this makes it extremely challenging to identify a suitable reaction system for growing high quality NPs in most cases. Yu \textit{et al.}\textsuperscript{115,116} demonstrated that the non-coordinating solvents not only are compatible with the synthesis of semiconductor NPs, but also provide tunable reactivity of the precursors by simply varying the concentration of the ligands.
1.3.2. Synthesis of Bifunctional Core/Shell Nanoparticles

The luminescence efficiency and the colloidal stability of the NPs were found to be strongly influenced by the surface passivation. However, it was found that the simultaneous passivation of anionic and cationic surface sites by organic ligands was difficult. In order to circumvent this problem, inorganic materials were used to passivate the NP surface. The requirements for the ideal core/shell NPs both from a crystallographic and electronic point of view are as follows,

(a) The core and shell materials should have similar lattice parameters such that the shell growth happens in the epitaxial manner without the surface defects.

(b) The shell material should possess a much higher band gap than the core to suppress the tunneling of the electrons and holes from the cores to the newly formed surface atoms of the shell.

In particular, for CdSe NPs the particles were often covered with CdS, ZnS, and ZnSe. The quantum yield for the core/shell NPs were found to be as high as 50-80%, where it varied from 10-40% for bare CdSe NPs. The core/shell NPs were also found to be more chemically and thermally stable than the corresponding plain core NPs.

However, the core/shell NPs were found to have poor size distribution as compared to that of the bare CdSe NPs. This was due to the homogeneous nucleation of shell materials and the irregular thickness of the shell material on the core NPs. Li et al. synthesized CdSe/CdS core/shell NPs with narrow size distribution through successive ion layer adsorption and reaction (SILAR), whereby a CdS shell was grown one monolayer at a time by alternating the injections of the CdO precursor solution and sulfur.
solution into a reaction mixture containing the as-prepared CdSe core NPs\textsuperscript{130}. The resulting core/shell NPs were found to have a quantum yield ranging between 20-40\% and the size distribution of the core/shell NPs were found to be the same as that of the core NPs. The SILAR method was extensively followed for the synthesis of core/shell NPs of different compositions in the later years\textsuperscript{126-130}.

1.3.3. Synthesis of CdSe Nanoshapes

Besides the monodispersity and the photoluminescence of the resulting NPs, the synthesis of anisotropic NPs has also been the focus of the researchers for the past decade. With emergence of complex shapes, improved control over these properties can be achieved and hence robust synthetic routes to produce both size and shape control are of critical importance\textsuperscript{76,131-137}. In 1999, Wang \textit{et al.}\textsuperscript{138} reported the non hot-injection synthesis of CdSe nanorod by using ethylene diamine. The method involved autoclaving CdCl\textsubscript{2}, Se, and Na metal with ethylenediamine, resulting in the formation of CdSe nanorods ranging in diameter from 8 – 20 nm and in length from 150 – 500 nm. Although the nanorods of CdSe were found to be aggregated and polydisperse, this article stirred interest in the shape control of CdSe NPs.

It was the further pioneering work from the group of Alivisatos\textsuperscript{134,139} in 2000, that induced anisotropy in CdSe NPs with a modification to the previous work from Murray and co-workers\textsuperscript{105}. The synthetic variation for inducing anisotropy was the use of phosphonic acid in addition to the previously used TOPO as the coordinating ligand. The nanorods displayed many unique property modifications compared to the nanodots like polarized light emission\textsuperscript{140}. In continuation of this initial success, the research groups of
Peng and Alivisatos were able to synthesize various other morphologies such as arrow, pine trees, tear drops and tetrapods (Figure 1.8), among others\textsuperscript{134,139,106,109,132,141-143}. The precursor concentration, time of synthesis of NPs and the concentration of the capping agents were identified to be the key parameters in defining the morphology of the resulting NPs\textsuperscript{142}.

The formation of all of these morphologies was explained on the basis of the effective monomer model and the selective adsorption of surfactants on different crystallographic faces, because of the difference in binding energy of the surfactants to the various different crystal faces\textsuperscript{144-146}.

One of the most sought-after geometries in the CdSe NP system is the tetrapodal shape. The tetrapod-shaped NPs can potentially exhibit a variety of interesting mechanical, electrical, and optical properties. For example, tetrapods can serve as a very interesting building block for preparing superstructures\textsuperscript{147}. CdSe tetrapods have obvious potential advantages in photovoltaic devices because their shape makes it impossible for them to lie flat within the film, leading to improved packing and increased electron transfer efficiency\textsuperscript{148-150}. Currently CdSe tetrapods are synthesized using toxic and expensive phosphonic ligands\textsuperscript{106,115,132,134,151,152}. This method suffers from the disadvantage of low yield as the tetrapods are typically formed mixed with rods. A postpreparative separation process is needed to get rid of the NPs of undesirable geometry. A synthesis method that would yield CdSe tetrapods in high yield with dimensional uniformity without a separation step would enable scaling up tetrapodal NP synthesis.
Figure 1.8. Transmission electron micrographs of (a) rice shaped\textsuperscript{142} (b) rod shaped\textsuperscript{142} (Peng et al. 2003; Copyright Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission.) (c) tear shaped\textsuperscript{139} (d) arrow shaped\textsuperscript{139}. Reprinted with permission from Manna et al. 2000. Copyright 2000 American Chemical Society.

1.4 Outline of Thesis Work

This thesis describes the synthesis and characterization of CdSe NPs of controllable size and shape. Chapter 2 describes the state-of-the-art characterization techniques which were used for the thorough understanding of the synthesized materials.

The initial focus is on the size controllable and cost effective synthesis methods of CdSe NPs. A limiting step in large-scale production was identified to be the raw materials cost, in which the solvent accounts for 90\% of the materials cost in preparing one batch of CdSe NPs (~15mg of CdSe) using the synthesis method published by Yu and Peng\textsuperscript{15,116}. In an effort to address the cost issue in scaling up, it was discovered in collaboration with several fellow researchers that inexpensive organic liquids known as heat transfer fluids (HT fluids) can be used as solvents for synthesizing QDs. Chapter 3 focuses on the experimental and theoretical findings elucidating the economical and
experimental viability of the new solvents proposed by us. The observations and results of this work were published in 2005 ("The Use of Heat Transfer Fluids in the Synthesis of High-Quality CdSe Quantum Dots, Core/shell Quantum Dots, and Quantum Rods", *Nanotechnology* 2005)\(^\text{153}\).

Shape control of the CdSe NPs forms the core of the rest of this thesis. CdSe tetrapodal NPs were being synthesized in low yield with very low dimensional and morphological uniformity through the existing methods. These methods also suffered from the disadvantage of using toxic and expensive phosphonic acids as ligands. It was imperative to understand the chemistry of anisotropic growth of CdSe NPs to be able to tailor the NPs for specific applications. Chapter 4 addresses this issue, in which it was discovered that a class of cationic surfactants called quaternary ammonium salts ("quats") could be used as ligands for the synthesis of tetrapodal CdSe NPs. These ligands are more environmentally friendly and cost effective, and they lead to the formation of CdSe quantum dots of uniformly-sized tetrapod shapes with minimal formation of other shapes. Anisotropic NPs of other compositions may also be synthesized in similar approach. The observations and results of this work were published recently ("Shape-Controlled Synthesis of CdSe Tetrapods Using Cationic Surfactant Ligands", *Small* 2007)\(^\text{154}\).

Chapter 5 focuses on the optimization of the synthesis of tetrapods of CdSe discussed in Chapter 4, and the resulting dimensional control and optical properties without any post preparative treatment. Synthesis temperature, synthesis time, surfactant ratio ([oleic acid]:[quat]) and the precursor ratio ([cadmium]:[selenium]) were identified to be important parameters in controlling the size, shape and hence the optical properties of the resulting CdSe tetrapodal NPs.
Chapter 6 discusses the formation mechanism of these tetrapodal NPs in greater detail. It was observed that the quats were responsible for the exclusive nucleation of CdSe in zinc-blende phase. The nature of surface capping on the CdSe tetrapodal NPs was analyzed. While oleic acid was observed to be present on the surface of the NPs, the characterization results indicative of the presence of the quats were inconclusive.

My efforts in NP synthesis led to several collaborations and publications in aggregation studies of carboxy fullerene\textsuperscript{155} and gadolinium fullerene\textsuperscript{156} using dynamic light scattering (DLS), synthesis and surface modification of CdSe NPs and the study of their interactions with polymers\textsuperscript{157-159}, and a new method for the synthesis of submicron lead sulfide NPs\textsuperscript{160} which will not be discussed in this thesis. Chapter 7 concludes the future prospects of the findings of my thesis work.
1.5 References


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Chapter 2

Characterization Techniques

2.1 Characterization of the CdSe Nanoparticles

Characterization of nanoparticles is indispensable to understand the behavior and properties of nanoparticles. Characterization contains two main categories: structure analysis and property measurements. Structural analysis of our nanoparticles was performed with extensive electron microscopy (transmission electron microscopy (TEM)), spectroscopy (UV-visible spectroscopy, Fourier transform infra-red spectroscopy (FTIR)), X-ray photoelectron spectroscopy (XPS)) and X-ray diffraction (XRD) and X-ray dispersive spectroscopy (EDS). The properties of our NPs were analyzed by photoluminescence spectroscopy (PL) and thermo gravimetric analysis (TGA).

2.1.1. UV-Visible Spectroscopy

UV-Visible spectroscopy is used extensively for the characterization of the CdSe NPs, since they exhibit strong and unique absorption in the visible region. UV-Visible spectroscopy is highly sensitive to the dimension, morphology and surface modification of the NPs. A distinct red shift is observed with increase in the size of the particles and the features of the exciton peak vary with the morphology and the surface modification of the NPs. The first exciton peak also can be used to calculate the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). This energy difference is referred to as band gap. The concentration of the CdSe NPs was calculated by using the classic Beer-Lambert’s law;
A = ξ \cdot b \cdot C

Where A is absorbance with no units

ξ is molar extinction coefficient in liter mol⁻¹ cm⁻¹

b is the path length in cm

C is concentration in mol liter⁻¹

However, the extinction coefficient of the NPs were found to vary with the size of the NPs. Peng et al. experimentally determined the extinction coefficients for cadmium chalcogenides, i.e., CdSe, CdTe and CdS³ using the wavelength at which the first exciton peak occurred. The concentration of the particles under study was determined by atomic absorption spectroscopy. The experimental results were fitted in to empirical function of diameter of CdSe NPs as follows,

\[ ξ = 5857(D)^{2.65} \]

Where ξ is the extinction coefficient per mole of CdSe NPs in liter mol⁻¹ cm⁻¹

D is the diameter of particles in nm and is given by,

\[ D = (1.6122 \times 10^{-9}) \lambda^4 - (2.6575 \times 10^{-6}) \lambda^3 + (1.6242 \times 10^{-3}) \lambda^2 - (0.4277) \lambda + 41.57 \]

Where λ is the wavelength of first exciton absorption in nm.

These empirical formulas were used for finding the diameter of the spherical shaped CdSe NPs synthesized in this thesis work.
**Figure 2.1. (a)** Typical UV-Vis spectrum of spherical shaped CdSe NPs of average diameter 3 nm (b) CdSe NPs of diameter ranging from 2 nm to 4.2 nm dispersed in toluene fluorescing in the visible region under UV light.

All the UV-Vis spectroscopic measurements were performed on Shimadzu UV-Visible spectrophotometer (UV-2401PC) operated at a resolution of 0.5 nm in absorbance mode at ambient temperature in solution using a clean quartz cell with a path length of 1 cm.

### 2.1.2. Fluorescence Spectroscopy

CdSe NPs when excited emit in the visible region. The quantum yield of the CdSe NPs as a function of the solvent of preparation, size, morphology, synthesis temperature, capping agents was measured by the fluorescence spectroscopy. In the present work, fluorescence measurements were done on a SPEX-Fluoromax-3 at ambient temperature with a slit width of 5 nm for both emission and excitation monochromators. The photoluminescence (PL) spectra were collected between 400 and 750 nm using an excitation wavelength of 380 nm (Figure 2.2).
Figure 2.2. Typical PL spectra of spherical shaped CdSe NPs of diameter 6.3 nm.

<table>
<thead>
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<th>UV-Vis peak (nm)</th>
<th>PL peak (eV)</th>
<th>Size (nm)</th>
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<tr>
<td></td>
<td>2</td>
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</tr>
</tbody>
</table>

Table 2.1. Wavelength of absorption of first exciton peak and corresponding size of the particles in nm. Reprinted with permission from Peng et al. 1998. Copyright 1998 American Chemical Society.

Quantum yield (QY) analysis was done with Rhodamine-6G (Rh6G) in ethanol as standard (QY = 95%). We followed the method described by the Jobin Yvon Ltd⁵, where in we measured the solvent background as the first step. This was followed by the measuring the UV-vis absorbance and fluorescence spectra of increasing concentrations of the standard dye (Rh6G). At least five different concentrations of Rh6G were used. A
series of such measurements was carried out for the chosen sample. A graph of integrated fluorescence intensity and the absorbance was plotted for both Rh6G and the sample and the gradient of each plot was obtained.

![Graph showing calibration curves for Rhodamine-6G at excitation wavelengths 480 nm and 500 nm. The slopes of the curves were $2.99 \times 10^9$ and $2.86 \times 10^9$ respectively.]

**Figure 2.3.** Calibration curves for the dye Rhodamine-6G at excitation wavelengths 480 nm and 500 nm. The slopes of the curves were $2.99 \times 10^9$ and $2.86 \times 10^9$ respectively.

We observed that the quantum yield was independent of the excitation wavelength (Figure 2.3) as was also observed by Karstens and Kobs\textsuperscript{6}. Quantum yield of the sample was obtained by using the following equation,

$$\Phi_x = \Phi_{std} \left[ \frac{Grad_x}{Grad_{std}} \right] \left[ \frac{n_x^2}{n_{std}^2} \right]$$

Where "std" and "x" represent standard dye (Rh6G) and sample under investigation respectively,
\( \Phi \) is quantum yield.

"Grad" is the gradient of the plot of integrated fluorescence intensity versus absorbance

\( \eta \) is the refractive index of the solvent (\( \eta_{\text{chamol}} = 1.36 \) and \( \eta_{\text{solution}} = 1.49 \))

### 2.1.3. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used as a probe to study the nature of the capping agents binding to the surface of CdSe NPs. The IR characterization was carried out on Nicolet-6700 in the transmission mode in the range of 4000 - 700 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\) (Figure 2.4).

Generally a total of 256 scans yielded a good signal to noise ratio of IR spectrum.

**Figure 2.4.** Typical FTIR spectra for spherical shaped CdSe NPs with oleic acid capping on the surface.
<table>
<thead>
<tr>
<th>S. No</th>
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<th>Assignment</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>3608</td>
<td>-O-H stretch</td>
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<tr>
<td>2</td>
<td>3028.74</td>
<td>Olefinic C-H stretch</td>
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<td>3</td>
<td>2930.71</td>
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<td>4</td>
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<td>5</td>
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<tr>
<td>6</td>
<td>1434.12</td>
<td>COO - stretch</td>
</tr>
</tbody>
</table>

**Table 2.2.** Vibrational mode assignments\(^7\) for the FTIR spectrum shown in Figure 2.4.

We used a demountable BaF\(_2\) liquid cell for our analyses. The path length could be very easily varied by changing the Teflon spacers in this versatile demountable cell. But for all our analyses the path length was kept a constant at 0.1 mm. The data obtained was analyzed by using the software OMNIC version 7.3.

### 2.1.4. Thermogravimetric Analysis (TGA)

This technique is very useful for the study of physical properties related to phase transitions like temperature of transition, energy of transition, stability, chemical reaction of materials as a function of temperature. TGA / DTA of the purified nanoparticles powder was done on a TGA-SDT-2960 instrument in the temperature range 25 – 1000 °C at a scan rate of 10 °C /min, in alumina crucible. Argon (Purity 99.9999%) was constantly purged through the furnace while the measurements were performed ensuring a completely inert atmosphere. The data obtained was analyzed by the software TA-
Universal Analysis 2.6d. We used TGA for understanding the nature and number of organic species bound to the surface of the CdSe NPs.

Figure 2.5 shows a typical thermogram for spherical shaped CdSe NPs with oleic acid capping on the surface. The data shows that there is a 39% weight loss between 330 °C and 476 °C, indicating that 39% of total weight of the synthesized CdSe NPs corresponded to the surface capping agent. Since there is only one weight loss it can also be confirmed that there exists only one surface capping species or there are multiple capping agents which undergo thermal decomposition at the same temperature range.

![Typical thermogram for spherical shaped CdSe NPs with oleic acid capping on the surface.](image)

**Figure 2.5.** Typical thermogram for spherical shaped CdSe NPs with oleic acid capping on the surface.
2.1.5 X-Ray Diffraction (XRD)

Powder x-ray diffraction technique has been used to determine phase purity, crystal structure and to roughly estimate the size of the nanocrystallites. X-ray diffraction patterns have been obtained with a Rigaku D/Max Ultima II Powder Diffractometer instrument using monochromatic high intensity CuKα radiation (λ = 1.54056 Å) at 40 KV and 40 mA. A nickel filter is used to eliminate the Kβ lines. Diffraction patterns were collected in continuous scan mode at 0.02 ° step size and ~2.5 second.step⁻¹ scan rate. All the XRD measurements were done with drop coated films of nanoparticles on glass substrate. The average crystallite size of the nanoparticles can be obtained from the XRD pattern using the Debye-Scherrer formula:

\[ d = \frac{0.9 \lambda}{\beta \cos \theta} \]

where \( d \) is the crystallize size, \( \lambda \) is the wavelength of X-ray, \( 2\theta \) is the center of the peak, \( \beta \) is the full width at half maxima (FWHM) of the peak after correcting for instrumental broadening.

\[ \beta^2 = \beta_{obs}^2 - \beta_{ins}^2 \]

Where \( \beta_{obs} \) is the FWHM of the measured peak and \( \beta_{ins} \) is calculated from the FWHM of instrument broadening curve based on a LaB₆ powder standard (NIST 660a). The upper limit of the meaningful crystallite size that can be calculated through Scherrer formula is dictated by the accuracy of the instrument. The instrument used for the study, a crystal size of ~100 nm leads to broadening equal to the instrumental broadening thereby representing the upper limit of meaningful estimates.
Crystal phase identification, peak finding, peak profile analysis, crystallize size were obtained by using MDI Jade 7.5 and the ICDD PDF-2 data base is used for obtaining information on the crystal structure of the CdSe NPs. CdSe NPs exist in two different crystal structures depending upon the reaction conditions, i.e., zinc-blende (cubic) and wurtzite (hexagonal) (Figure 2.6)

![Figure 2.6. XRD patterns of spherical shaped CdSe NPs and the peak assignments to crystal axes (a) Wurtzite phase (b) Zinc-blende phase.](image)

2.1.6. Transmission Electron Microscopy (TEM)

Transmission electron microscopy has been invaluable in the estimation the size and the morphology of the CdSe nanocrystals. TEM samples were prepared by placing a drop of the nanoparticles solution onto a carbon coated copper TEM grid (PELCO® carbon/Formvar/Cu TEM grid). After 5 minutes, the excess amount of the solution was removed using a blotting paper. TEM measurements were performed on a JEOL 2010 FasTEM, high resolution transmission electron microscope operated at an accelerating
voltage of 200 kV with a LaB₆ filament. Images taken with a CCD camera were recorded using Digital Micrograph software. Particle size analysis of TEM images was carried out using ImageJ® (Version 1.33, NIH) software, on at least 500 particles per sample. Exporting the results from ImageJ to Origin (Version 6.1) software, the histograms were plotted. Figure 2.7 shows an example of the transmission electron micrograph of spherical shaped CdSe NPs.

![Transmission electron micrograph of spherical shaped CdSe NPs.](image)

**Figure 2.7.** Transmission electron micrograph of spherical shaped CdSe NPs.

### 2.1.7 X-Ray Photoelectron Spectroscopy (XPS)

The surface of an inorganic NP influences the structural, thermodynamic, optical and transport properties. XPS is a surface characterization technique and useful for characterization of the nanoparticles, multilayer films of nanoparticles and to understand the interaction between nanoparticles and capping agent. The measurements were carried out on a PHI-Quantera. XPS microprobe operates at a pressure of $10^{-9}$ Torr. The general scan of desired core level spectra were recorded with monochromatized Al Kα radiation (photon energy = 1486.7 eV) at a pass energy of 50 eV and electron takeoff angle (angle
between electron emission direction and surface plane) of 60°. The overall resolution was ~1 eV for the XPS measurements. The core level spectra were background corrected using the Shirley algorithm\textsuperscript{10} and the chemically distinct species resolved using a non-linear least squares procedure, automatically by the software Multipak 7. The core level binding energies (BE) were aligned with the adventitious carbon binding energy of 285 eV. We studied the surface composition of CdSe NPs, with a particular attention to the organic groups which cap the NPs and to surface compounds formed after the NPs are synthesized. The samples were prepared by dropping the CdSe NPs dispersed in hexane on clean Si (111) wafers. The Si wafers were cleaned by immersion in a 1:1 solution of methanol (Fisher Scientific – ACS grade) and 1N hydrochloric acid (Fisher Scientific). The wafers were then rinsed with distilled water and dried under a jet of argon gas. Figure 2.8 shows a typical XPS survey of CdSe NPs bound to Silicon using Al X-ray source.
**Figure 2.8.** Typical XPS survey spectrum of spherical shaped CdSe NPs on Si using Al X-ray source.

2.1.8. X-Ray Dispersive Spectroscopy (EDS)

Elemental composition of the CdSe NPs was measured using electron dispersive spectroscopic detectors (EDAX Genesis -2000) attached to a high resolution field emission scanning electron microscope (FEI Quanta 400). The samples were deposited on a clean Si wafer which was then attached to the aluminum stub using a double sided tape. The aluminum stub was then mounted on the sample stage of the scanning electron microscope. Figure 2.9 shows typical EDS spectrum of spherical shaped CdSe NPs. This state of the art equipment can operate in high and low vacuum and wet modes. It also is equipped with a cooling stage.
Figure 2.9. Typical EDS spectrum for spherical shaped CdSe NPs.
2.2. References


Chapter 3
The Use of Heat Transfer Fluids in the Synthesis of High-Quality CdSe Quantum Dots, Core/Shell Quantum Dots, and Quantum Rods

3.1 Introduction
Fluorescent semiconductor nanoparticles (NPs) known as quantum dots (QDs) have generated scientific and commercial interest as a nanomaterial due to their size-dependent optoelectronic properties and their potential uses in electronics, fluorescence imaging, and optical coding. The anticipated advances in QD-based technologies point to the impending requirement of large quantities of inexpensive QDs, but published synthesis methods are optimized for milligram amounts and commercially available QDs are costly. Efforts to develop preparation methods that are cost-effective, scalable, and environmentally friendly are ongoing, such replacing the metal precursors with greener and safer compounds and developing continuous-flow reactors.

As the most well-studied QD material, CdSe NPs are formed from the rapid decomposition of Cd (e.g., dimethylcadmium and cadmium complexes with alkylphosphonic acids, alkylcarboxylic acids, trioctylphosphine, and trioctylphosphine oxide) and Se precursors (e.g., trioctylphosphine selenide and tributylphosphine selenide) in an organic solvent at elevated temperatures (250-350 °C). Trioctylphosphine oxide (TOPO) is most commonly used as the solvent due to its high boiling point and chemical stability, and its ability to prevent particle aggregation via coordination to the NP surface. TOPO can be replaced by octadecene (ODE), a non-coordinating solvent, if another compound such as oleic acid is used as the surface-
binding ligand\textsuperscript{25}. ODE provides several advantages over TOPO: its use allows for particle formation kinetics to be controlled; it is a liquid at room temperature whereas TOPO is a wax; and it is less expensive than TOPO.

Interestingly, ODE accounts for \( \sim 90\% \) of the materials cost in preparing one batch of CdSe NPs (\( \sim 15 \text{ mg} \) of CdSe), using the synthesis method published by Yu and Peng\textsuperscript{25}. In this paper, we demonstrate that inexpensive organic liquids known as heat transfer fluids (HT fluids) can be used as solvents for synthesizing QDs. With high boiling points and chemical stability at high temperatures, HT fluids are used to transport heat between unit processes found in the chemical process industries, but are generally not used as reaction solvents\textsuperscript{30,31}.

3.2 Materials and Methods

3.2.1 Synthesis of CdSe QDs

A synthesis method of Peng and co-workers\textsuperscript{25} was modified by using lower injection and growth temperatures, allowing a comparison of the organic solvents to be done at constant conditions. In a typical batch synthesis of CdSe QDs, a solution of TOPSe is freshly prepared in a glove bag under an argon gas purge. Selenium powder (32 mg, 99.999%, Sigma-Aldrich) was added to a vial containing 1.44 ml of trioctylphosphine (TOP, 90%, Sigma-Aldrich). The vial was parafilm-sealed and the suspension was vortex-mixed for a minimum of 2 minutes until the powder dissolved completely to form a clear and colorless trioctylphosphine selenide (TOPSe) solution. The Cd precursor was prepared by combining 0.102 g of CdO (99.99%, Sigma-Aldrich), 40 ml of a solvent (initial [Cd] = 20 mM), and 4 ml (99.99%, Sigma-Aldrich) of oleic acid as stabilizer in a
three-neck flask (mole ratio of oleic acid to Cd (oleic acid:Cd) = 50; Cd:Se = 2). A total of 4 different solvents were used: TOPO, ODE, DTA, and T66 (Figure 3.1, Table 3.1). DTA (Dowtherm A, Dow Chemical Co.) is a eutectic mixture of biphenyl (26.5 wt%) and diphenyl ether (or biphenyl oxide) (73.5 wt%), and T66 (Therminol 66, Solutia Inc.) is a mixture of terphenyl (~8 mol%, CAS No. [26140-60-3]), partially hydrogenated terphenyls (~74 mol%, [61788-32-7]), and higher polyphenyls/partially hydrogenated polyphenyls (~18 mol%, [68956-74-1]) \(^{30}\). Their molecular structures are shown in figure 3.1.

![Molecular structures of TOPO, ODE, DTA, and T66](image)

**Figure 3.1.** Molecular structures of (a) TOPO, (b) ODE, and the HT fluids (c) DTA and (d) terphenyl in T66.

<table>
<thead>
<tr>
<th>Synthesis solvent</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
<th>Cost ($/l)</th>
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<tr>
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<tr>
<td>Therminol 66 (T66)</td>
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</tbody>
</table>

**Table 3.1.** Organic solvents used in this study.

Under a constant argon purge, the magnetically stirred Cd-oleic acid-containing reaction mixture was heated slowly (2 °C/min) from room temperature to 250 °C, the injection temperature. When the rust-colored Cd-oleic acid-containing reaction mixture
turned colorless and clear at 250 °C, the entire aliquot of TOPSe solution was rapidly injected using a needle syringe (<2 sec). The temperature of the reaction mixture immediately dropped to 240 °C after injection, and was allowed to drop to a steady-state growth temperature of 220 °C. One-ml aliquots of reaction mixture were removed at various times over a course of 10 hrs (i.e., 10 sec, 30 sec, 1 min, 2 min, 5 min, 10 min, 15 min, 30 min, 1 hr and every half hour afterwards), and deposited in vials containing 10 ml of ODE (lowering the temperature to 40 °C in order to quench further particle growth). Final reaction volumes at the end of 10 hrs were 12, 12, 15, and 14 ml for TOPO, ODE, DTA, and T66, respectively. Higher injection and growth temperatures of 300 °C and 280 °C, respectively, were used to compare T66 with ODE. The solvent and unreacted precursors were removed through induced aggregation of the quantum dots with anhydrous methanol (99.8%, Sigma-Aldrich), centrifugation and washing with methanol, and re-suspension in 10 ml of anhydrous hexane (95%, Sigma-Aldrich). The 10-hr synthesis experiments for each of the four solvents were repeated at least three times. There were batch-to-batch variations, as generally known for hot-injection QD synthesis routes\textsuperscript{18,20}. The values reported were somewhat different from the preliminary results reported earlier\textsuperscript{32}, but the general trends remained the same.

3.2.2 Synthesis of CdSe/CdS Core/Shell QDs

The above-procedure for synthesizing CdSe QDs (Sec. 3.2.1) was modified to study the formation of CdSe/CdS core/shell QDs. The TOPSe solution was freshly prepared from Se powder (32 mg) and TOP (1.5 ml). The Cd/oleic acid solution was prepared by combining CdO (0.102 g), T66 (40 ml, initial [Cd] = 20 mM), and oleic acid (4 ml, oleic
acid: Cd = 16; Cd: Se = 2). Under a constant argon purge, the magnetically stirred Cd-oleic acid-containing reaction mixture was heated slowly (2 °C/min) from room temperature to 250 °C, turning clear at 220 °C. The TOPSe solution was rapidly injected using a needle syringe (<2 sec), and toluene (5 ml) was then added drop-wise to lower the reaction temperature to 150 °C.

The cooled reaction mixture was split into two aliquots. One aliquot was slowly heated to 220 °C, to which additional Cd (2 ml, 0.04 M) and sulfur precursors (2 ml, 0.04 M) were injected sequentially. The Cd stock solution was comprised of 0.123 g CdO, 20 ml T66, and 4 ml oleic acid, and the Se stock solution was comprised of 25.6 mg S and 20 ml T66. The reaction temperature was maintained at 220 °C for 30 min, after which toluene (5 ml) was added drop-wise to lower the temperature to 120 °C. The other aliquot was used as a control; T66 solvent (4 ml) was added instead of the Cd and S precursors.

### 3.2.3 Synthesis of CdSe Rod-Shaped QDs

The above-procedure for synthesizing CdSe QDs (Sec. 3.2.1) was modified to study the formation of CdSe quantum rods. The Cd/oleic acid solution was prepared by combining CdO (0.102 g), T66 (40 ml, initial [Cd] = 20 mM), and tetradecylphosphonic acid (TDPA, 0.893 g, 98%, Alfa Aesar; TDPA:Cd = 2; Cd:Se = 0.62), and heating to 320 °C under Ar purge until the mixture became optically clear. The solution was cooled to 300 °C, and the Se precursor (100 mg Se and 2.4 ml TOP) was injected. The reaction temperature was lowered and kept at 250 °C for 30 min.
3.3 Results and Discussions

3.3.1 Synthesis of CdSe QDs

The organic solvents used in the generic synthesis of NPs are much more varied than those used in the synthesis of CdSe QDs. Examples include diphenyl ether for PbSe and Co NPs,\textsuperscript{32,34} and CoPt\textsubscript{3} NPs\textsuperscript{35}; dioctyl ether for FePt NPs\textsuperscript{36} and γ-Fe\textsubscript{2}O\textsubscript{3};\textsuperscript{37} α-dichlorobenzene for disk-shaped Co NPs\textsuperscript{38,39}; ODE for Fe\textsubscript{3}O\textsubscript{4} NPs\textsuperscript{40}; eicosene for mixed-phase iron oxide NPs\textsuperscript{41}; and squalene for CdSe QDs\textsuperscript{18}. T66 and DTA HT fluids used in this study are solvent mixtures, and we are not aware of their use in NP synthesis prior to this work.

CdSe QDs were found to form using the DTA and T66 HT fluids. The particles grow in DTA and T66 with reaction time, as shown by the red-shifting in the distinctive spectral peaks (Figure 3.2). The fine features in the optical spectra are similar to those of QDs synthesized in ODE, indicating that particle formation processes occurring in the HT fluids are also similar to those occurring in ODE. Narrow band-edge PL peaks and no deep trap emissions were observed from the fluorescence spectra. The QDs formed in the HT fluids are approximately spherical, resembling those formed in ODE and TOPO (Figure 3.3). Many faceted NPs can be observed in the TEM images, which we have found to be a common occurrence and which have been observed by others\textsuperscript{25,42,43}. Though TOPO is typically used in conjunction with dimethyleadnium and not with Cd-oleic acid complex\textsuperscript{25}, optical data (Figure 3.2d and 3.3d) indicated that the latter Cd precursor could be used with TOPO to yield CdSe QDs, consistent with the results of Qu \textit{et al.}\textsuperscript{43}. 
Figure 3.2. UV-vis absorbance and fluorescence spectra of CdSe QDs synthesized in (a) DTA, (b) T66, (c) ODE, and (d) TOPO, as a function of time (injection @ 250 °C and growth @ 220 °C). Each set of spectra was collected at 10 sec, 1 min, 5 min, 30 min, 1 hr, 3 hr, and 5 hr after injection of TOPSe solution. Corresponding spectra for QDs synthesized in (e) T66 and (f) ODE at higher temperatures (injection @ 300 °C and growth @ 280 °C). Each set of spectra was collected at 5 min, 15 min, 30 min, 1 hr, and 2 hr after injection of TOPSe solution.
Figure 3.3. TEM images of CdSe QDs synthesized for 1 hr in (a) DTA, (b) T66, (c) ODE, and (d) TOPO solvents (injection @ 250 °C and growth @ 220 °C). Scale bars: 20 nm.

CdSe QDs are usually synthesized at higher injection and growth temperatures but the injection and growth temperatures (250 °C and 220 °C) used in this study were limited by the boiling point of DTA. T66 has a boiling point comparable to that of TOPO and one that is higher than that of ODE, allowing for higher synthesis reaction temperatures to be used. At injection and growth temperatures of 300 °C and 280 °C,
respectively, QDs formed in T66 were smaller than those formed in ODE (Figure 3.2c.i). This difference in growth rates was less apparent at the lower synthesis temperatures.

The average particle diameters and concentrations were estimated from the wavelength location and absorbance of the first exciton peak maximum, respectively, using the correlations published by Yu et al.\textsuperscript{44} Clearly, the QD particle sizes increased with synthesis time (Figure 3.4a and 3.4c). At long synthesis times, larger particle sizes were favored by the solvents in the following order: TOPO > T66 > ODE ~ DTA; at short synthesis times, the solvent order changed slightly: TOPO > ODE > T66 > DTA. The average particle sizes of QDs produced in DTA, T66, ODE, and TOPO after 1 hr were 2.9, 3.1, 3.1, and 4.0 nm, respectively. These values were consistently smaller than the particle sizes derived from TEM (in same order): 3.5, 3.9, 4.5, and 5.2 nm (Figure 3.3). This could likely be an artifact of our TEM image analysis in which smaller particles are more difficult to resolve visually, leading to a bias particle size distribution. In the same order, the relative standard deviations for the various QDs were 18%, 17%, 15%, and 13%. Values as small as 5% have been reported for CdSe QDs, and the size distributions were attributed to uncertainty in TEM measurements to within one lattice plane (\(\sim 0.18\) nm)\textsuperscript{23}. Our wider size distributions could, too, be an artifact of TEM analysis. The particle concentrations were comparable among the different samples, allowing for proper comparison of the particle sizes at similar reaction conversions (Figure 3.4b and 3.4d). TOPO led to the formation of larger particles compared to the other solvents, suggesting that TOPO (with its ability to coordinate to the CdSe particle surface that the other solvents lack) also has the ability to coordinate with the Cd precursor such as to increase its reactivity to form the QDs.
Figure 3.4. (a) Average particle diameter and (b) particle concentration plotted against synthesis time (log scale), calculated from UV-vis absorbance data of CdSe QDs synthesized in the four different organic solvents (injection @ 250 °C and growth @ 220 °C). The same data plotted on a linear scale (c,d).

CdSe QDs synthesized at short times in the different solvents were compared at a common size (Table 3.2). The full-width at half-maximum (FWHM) indicates the sharpness of the PL emission, and indirectly, the particle size distribution. Thus, TOPO- and ODE-derived QDs have lower fluorescence (and particle size distribution) quality than those synthesized using HT fluids. This trend may be correlated to synthesis time.
The FWHM values for QDs prepared in all four solvents tend to decrease with synthesis time, indicating that the longer synthesis times help to sharpen the emission peak (data not shown). This decrease is attributed to a focusing of the particle size distributions, arising from the rapid growth of all particles in the presence of high concentrations of Cd and Se monomers\textsuperscript{1,42,45,46}. We do not make the distinction between “precursor” (e.g., CdO:oleic acid and TOPSe complexes) and “monomer” (reactive intermediate formed from the precursor, which leads to nucleation or adds to a growing particle). We observed an increase in FWHM after \~2 hr of synthesis time in DTA and T66, marking the onset of particle size distribution broadening or defocusing. Defocusing occurred after 1 hr and 1.5 hr using TOPO and ODE solvents, respectively (data not shown). To achieve the same small particle size (<3 nm), longer times were needed with HT fluids than with TOPO and ODE (Figure 3.4a). The difference in growth kinetics is clearly observed, with the results indicating that particle growth can be slowed down and that smaller particles with equal or higher quality (e.g., comparable UV-vis absorbance spectra, comparable particle size distributions, and narrower PL peaks) can be synthesized using HT fluids (Figure 3.5).

<table>
<thead>
<tr>
<th>Synthesis solvent</th>
<th>Particle diameter (nm)</th>
<th>FWHM of PL peak (nm)</th>
<th>Quantum yield (%)</th>
<th>Synthesis time (sec)</th>
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<td>TOPO</td>
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</tr>
</tbody>
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*Table 3.2. A comparison of \~2.7-nm CdSe QDs synthesized at 220 °C using the different organic solvents.*
Figure 3.5. UV-vis absorbance and fluorescence spectra of ~2.7-nm CdSe QDs synthesized in (a) DTA, (b) T66, (c) ODE, and (d) TOPO (injection @ 250 °C and growth @ 220 °C).

For all solvents, the quantum yields of CdSe QDs fluctuated significantly over the course of 10 hr. This observation contrasts the QDs prepared by Talapin et al. using a different method, in which quantum yields dropped with increasing QD particle size or synthesis time\(^{47}\). No extra care was taken to exclude oxygen and moisture during the washing process or the spectroscopy measurements, which likely contributed to the observed quantum yield fluctuations. Quantum yield differences could also result from
surface structure differences, as several research groups have concluded that photoluminescence is very sensitive to surface structure and surface defects\textsuperscript{34,46}.

3.3.2 Synthesis of Core/Shell and Rod-Shaped CdSe QDs

Core/shell QD synthesis using HT fluids was successfully carried out (Figure 3.6). A suspension of CdSe QDs (peak maximum = 541 nm $\rightarrow$ diameter = 2.87 nm) was heated in the presence of Cd and S precursor at 220 °C, which resulted in the red-shifting of the absorbance and PL spectra. This red-shift is similar to earlier observations made by Alivisatos and co-workers\textsuperscript{48}. The QDs grew in size to 4.17 nm (peak maximum = 590 nm), indicating a shell thickness of 0.65 nm or $\sim$2 monolayers of CdS (thickness of a monolayer shell of CdS $\sim$ 0.35 nm\textsuperscript{48}). The formation of a CdS shell corresponded to the observed increase in quantum yield, a hallmark of core/shell QDs\textsuperscript{48,50}. For comparison, the same CdSe starting material was heated in the absence of the Cd and S precursors. The optical spectra of the resultant QDs indicated particle growth, due to the presence of free Cd and Se precursors which remained from the original synthesis (Figure 3.6c). These particles grew to the same size as the core/shell QDs but had a lower quantum yield, further indicating CdSe/CdS core/shell QD formation in HT fluids (Figure 3.6b).
Rod-shaped CdSe QDs, or quantum rods (QRs), were also found to be successfully prepared in HT fluids. Researchers have demonstrated that shape anisotropy could be introduced through the use of alkylphosphonic acids\(^{51-53}\) or different Cd-ligand complexes (ligand = naphthenic acid\(^ {54}\) or alkylphosphonic acid\(^ {55}\)) in TOPO and ODE solvents. Here, QRs were prepared using TDPA and T66 and the average width and length were measured to be 5.0 and 15.7 nm, respectively (Figure 3.7a, b). The absorbance and fluorescence spectra were similar to previous reports of optical properties of CdSe QRs (Figure 3.7c)\(^ {51,56}\). The QRs exhibited a Stokes shift of \(\sim 30\) nm (=660-629 nm) or \(\sim 93\) meV, which is expectedly larger than that for CdSe QDs. For example, QDs prepared in T66 for 30 min (Figure 3.2c) have a Stokes shift of \(\sim 13\) nm (=563-550 nm) or \(\sim 52\) meV. The quantum yield of the QRs was measured to be 0.8\%. 

**Figure 3.6.** UV-vis absorbance and fluorescence spectra of CdSe QDs (a) before heating, (b) after heating at 220 °C for 30 min in presence of Cd and S precursors, and (c) after heating at the same conditions but without the shell precursors.
Figure 3.7. (a) TEM image, (b) size histograms, and (c) optical spectra of CdSe QRs synthesized in T66 for 30 min (injection @ 300 °C and growth @ 250 °C). Scale bar: 50 nm.
3.3.3 Solvent Effect on CdSe QD growth kinetics

The particles were significantly larger using TOPO than the other solvents, and the particles synthesized in T66, DTA, and ODE were close in size. The differences among the diameter-size curves indicated that particle growth depends on the nature of the solvent, e.g., molecular structure or physical property. As discussed earlier, TOPO appears to increase the reactivity of CdO-oleic acid precursor to form the reactive monomer needed for nucleation and growth, and it can be reasoned that T66, DTA, and ODE do not increase the Cd precursor reactivity to the same extent.

We observed that the particle concentration and particle average diameter-time profiles exhibited 3 stages over the course of 10 hr (Figure 3.4). To the first approximation, particle concentrations remained constant while the average diameter increased in the first stage (<0.5 hr). This can be attributed to the growth of all QDs in the synthesis medium in the absence of Ostwald ripening. The particle size distributions became narrower in this stage, based on the FWHM decrease (not shown). In the second stage (between 0.5 and 3 hr), the particle concentration decreased by ~67% for all solvents, while the average diameter continued to increase at a smaller rate than in the first stage. Finally, in the third stage, the particle concentration and average diameter-time profiles became flat. Using Se instead of Cd as the basis for calculation since it was the limiting reagent (Cd:Se = 2), we calculated the percentage of TOPSe that was converted into nanoparticulate form. Based on the average CdSe QD particle size and concentration values at the end of 10 hrs, nearly all the Se reacted to form QDs in TOPO (~99%), whereas 33%, 34%, and 27% of Se reacted to form QDs in DTA, T66, and ODE, respectively. Steady-state average particle sizes were reached even though TOPSe
precursor was in abundance, suggesting the CdSe QDs reached concentration equilibrium with the remaining TOPSe in the latter solvents. We note that the duration of each of the three stages was virtually identical for all four solvents, and larger particle growth rates were favored by the solvents in the following order: TOPO > T66 > ODE ~ DTA.

In order to obtain insight into these experimental findings we utilized the population balance model recently developed by one of us to describe the dynamics of QD growth\(^{57}\). One key advantage offered by this deterministic framework over stochastic models (such as the Monte Carlo simulations of Talapin et al.\(^{58}\)) is the use of dimensionless parameters. This allows one to easily analyze the effects of key parameters on the asymptotic and transient NP growth behavior without having to specify the various synthesis parameters and physical properties especially if these values are not known (e.g., surface free energy and monomer solubility in a given solvent).

We briefly present the basic mathematical formulation (see\(^ {57}\) for details). The time evolution of the particle size distribution is given by the following first-order partial differential equation:

\[
\frac{\partial N(r,t)}{\partial t} + \frac{\partial}{\partial r} \left( r \dot{r}(r,C_b) N(r,t) \right) = 0
\]

\(N(r,t)dr\) denotes the number of particles which have radii between \(r\) and \(r+dr\) at time \(t\);
\(\dot{r}(r,C_b)\) represents the single-particle growth rate, which depends on the particle radius \(r\), and the bulk monomer concentration \(C_b\). Here, the monomer refers to TOPSe, and the equation assumes particles do not interact or aggregate.

To derive the single particle growth rate \(\dot{r}(r,C_b)\) first order kinetics (with a rate constant \(k_s\)) for the surface reaction between the monomer and the particle were assumed.
Moreover, the monomer concentration at equilibrium \((C_e)\) with CdSe particles with the particle radius \(r\) was expressed as a function of the CdSe molar volume \(V_m\) (32.995 mol/cm\(^3\)), the surface free energy \(\gamma\), the temperature \(T\), and the bulk CdSe solubility \((C_x)\) using the Gibbs-Thompson equation \((C_e = C_x \exp\left(\frac{2\gamma V_m}{rRT}\right))\). Finally, monomer molecules diffuse from the bulk to the surface of the particles through a diffusion layer. This is taken to be a pseudo-steady-state process as was also assumed by Talapin et al.\(^{58}\) and Sugimoto\(^{59}\). The thickness of the diffusion layer was assumed to be much bigger than particle radius as was also argued by Peng and Peng\(^{51}\). These assumptions allow the derivation of the following closed-form expression that relates the growth rate law with the particle radius and the monomer concentration in the bulk:

\[
\frac{dr}{dt} = \frac{\frac{V_m k_s}{1 + \frac{k_s r}{D}}}{C_b - C_e \exp\left(\frac{2\gamma V_m}{rRT}\right)}
\]

Lastly, mass conservation requires that the total monomer amount existing either as free monomer or as monomer incorporated in the NPs remains constant and equal to the total initial monomer amount in either form. Thus, for constant reactor volume, we have:

\[
C_{b,0} + \frac{4\pi}{3} V_m \int_0^{r_{\text{max}}} r^2 N_0(r) \, dr = C_b(t) + \frac{4\pi}{3} V_m \int_0^{r_{\text{max}}} r^2 N(r,t) \, dr
\]

where \(C_{b,0}\) is the initial monomer concentration in the bulk and \(N_0(r)\) is the initial particle size distribution.

To simplify the mathematical formulation and identify key systemic parameters, we non-dimensionalized the model (Eqn 1-3) with respect to both radius and time, which
yielded two dimensionless parameters: $\chi$ and Da. Parameter $\chi$ largely controls transient behavior and is defined as:

$$\chi = \frac{S_0}{S_0 + 4 \pi \frac{\eta m^2}{3 V m C_\infty} \int_0^{r_m} r^2 N_o(r) dr}$$

where $S_0 = \frac{C_{b,0} - C_\infty}{C_\infty}$ is the initial supersaturation. Ranging from 0 to 1, this parameter quantifies the magnitude of the initial monomer concentration in the form of free excess monomer (monomer concentration above solubility) relative to the total monomer concentration that exists in the form of both free excess monomer and particles.

The dimensionless Damköhler number Da quantifies the magnitude of surface reaction of monomer relative to monomer diffusion, and is given as

$$Da = \frac{k_c}{D} \frac{2 \gamma V_m}{RT}$$

The system is surface reaction-limited for $Da = 0$, and is monomer-diffusion-limited for $Da \to \infty$. Mantzaris\textsuperscript{57} showed that the model was in excellent agreement with the analytical solutions for the asymptotic, normalized particle size distribution in the diffusion- ($Da \to \infty$) and reaction-limited ($Da = 0$) cases, as derived by Lifshitz and Slyozov\textsuperscript{60} and Wagner\textsuperscript{61}, respectively. We used this computational model to elucidate the salient features of the QD growth process through comparison with our experimental data.

The particle size distribution evolution behavior is fully characterized by the initial conditions $S_0$ and $N_o(r)$ and the two dimensionless parameters Da and $\chi$. To illustrate the typical behavior predicted by the population balance model, we chose the
following dimensionless parameter values as nominal: $Da = 4$, $\chi = 0.6$, $S_o = 10$, and $N_o(\tau)$ = Gaussian distribution. As shown in figure 3.8a (solid red line) the average particle size exhibits a fast increase before the time profile becomes flat at around 35% of its initial value, during which time the particle concentration decreases due to Ostwald ripening (Figure 3.8b). Also, the particle size distribution exhibits focusing-defocusing behavior (Figure 3.8c). We note that the model predictions for the dynamics of average radius and QD concentration are in qualitative agreement with the experimental data for the first two stages of QD growth (compare with Figure 3.4). The steady-state third stage is not predicted by the model, however, as the model indicates further particle growth and decreasing QD concentration (beyond dimensionless time of 5; simulation data not shown). To explain this discrepancy, we suggest that another particle formation mechanism besides growth and Ostwald ripening is responsible for stabilizing the QD particle size and concentration at long synthesis times. Nevertheless, the model appears to capture the dynamics well for the first two stages of the process.

With this observation in mind, we then used the computational model to interpret the experimentally observed differences in the QD growth kinetics for T66 and DTA solvents. To establish a basis for our comparison, we assumed the base case (solid red lines, Figure 3.8) qualitatively matched the particle formation kinetics in T66 (Figure 3.4). The quantifiable difference between T66 and DTA was solvent viscosity $\mu_s$, and thus we were interested in understanding its effect on growth kinetics. Viscosity is related to molecular precursor diffusivity in the solvent via the Stokes-Einstein equation

$$D = \frac{k_B T}{6\pi\mu_r_{monomer}}$$

(where $k_B$ is the Boltzmann constant and $r_{monomer}$ is the precursor radius).
which indicates that the monomer species diffuses more slowly in more viscous solvents than in less viscous ones.

Figure 3.8. Simulation results for the dynamics of: (a) the average particle radius normalized by the initial average particle radius, (b) total number of particles, and (c) standard deviation of particle size distribution divided by the initial standard deviation. Solid red lines: Nominal case (Da = 4, $\chi = 0.6$, $S_n = 10$). Dotted green lines: $\frac{1}{2}$ nominal viscosity (Da = 2, $\chi = 0.6$, $S_n = 10$). Dashed blue lines: $\frac{1}{2}$ nominal viscosity, $\frac{1}{2}$ nominal solubility, and $1.5$ nominal surface free energy (Da = 3, $\chi = 0.318$, $S_n = 21$).
We found the viscosities of T66 and DTA to be 0.72 and 0.35 cP at 220 °C using a HT fluids physical properties program (Thermomol Reference Disk\textsuperscript{[2]}. With an estimated radius of 1 nm for TOPSe, we calculated $D_{T66} = 5 \times 10^{-10}$ m\textsuperscript{2}/s and $D_{DTA} = 1 \times 10^{-9}$ m\textsuperscript{2}/s. Thus, the Da number for DTA is half that of T66.

The dotted green lines in figure 3.8 show the QD growth kinetics obtained for half the Da number of the nominal case. The average radius reaches a plateau value close to that of the nominal case, reaches this plateau slightly faster, and persists for a shorter period of time. However, this particle growth behavior does not match the experimental results for DTA (Figure 3.4a, c). The average particle size in DTA is clearly smaller than that of T66. In addition, the model predicts that the QD concentration drops significantly faster for the less viscous solvent (Figure 3.8b), which contrasts the slightly higher QD concentrations in DTA than in T66 (Figure 3.4b, d).

These discrepancies between model and experimental results indicate that solvent viscosity differences cannot fully explain the experimentally observed patterns. It is thus reasonable to consider other possibilities resulting from the use of different solvents. Specifically, solvents could have different bulk CdSe solubilities $C_x$. Also, it is reasonable that the QD surface is not completely coated by oleate ligands and that the free energy of the QD surface ($\gamma$) could be modified by interactions with solvent molecules at the solid-liquid interface. So, we suggest that the experimentally observed differences in the QD growth kinetics for the different HT fluids could result from the combined differences in their corresponding $\mu_x$, $C_x$, and $\gamma$ values. Through exhaustive numerical simulations, we found that a lower viscosity, smaller solubility and higher surface free energy led to a lower plateau in the average particle radius and higher
particle concentration (Figure 3.8a, b), qualitatively matching the experimental profiles for DTA much better (Figure 3.4).

![Graph](image)

**Figure 3.9.** Normalized FWHM (by initial FWHM value)-time profiles for CdSe QD growth (injection @ 250 °C and growth @ 220 °C) in T66 (solid line-open circles) and DTA (dashed line-filled circles).

This model indicates that lower viscosity, lower solubility and higher surface tension lead to a less pronounced focusing stage and to a broader particle size distribution, relative to the base case (Figure 3.8c). The FWHM data associated with figure 3.4 were of low quality, unfortunately, and were not shown, and so we re-synthesized CdSe QDs in T66 and carefully measured the FWHM values. Due to batch-to-batch variations, the actual particle sizes and concentrations did not exactly correspond to those shown in figure 3.4. Although defocusing occurred at ~5 minutes for these samples instead of the ~2 hr indicated for figure 3.4, we found that the experimentally observed FWHM values still matched the predicted particle size distribution trends.
(Figure 3.9). Specifically, the T66 curve was the base case (solid red line) and the DTA matched the dashed blue line (Figure 3.8c).

3.4. Summary and Conclusions

HT fluids are shown as viable alternatives to the solvents currently used in the synthesis of high-quality CdSe QDs, which will help to eliminate cost as a barrier to large-scale production of QDs and nanoparticles of other compositions. CdSe quantum rods and CdSe/CdS core/shell QDs can also be prepared in the HT fluids. QDs with smaller diameters can be prepared more controllably using T66 and DTA compared to TOPO or octadecene, indicating that QD synthesis chemistry in these fluids can be optimized to yield higher quality materials in the smaller nanometer size range. Only TOPO leads to near complete conversion of TOPSe into CdSe QDs. Detailed simulation studies strongly suggests that the experimentally observed differences in the QD growth kinetics in different HT fluids are the combined result of solvent-dependent differences in viscosity, CdSe bulk solubility, and surface free energy. Further study is needed to reconcile the disagreement between experimental data and the growth model during the last stage of QD growth. The use of different HT fluids could lead to predictive modulation of QD growth kinetics, if CdSe solubility and surface free energy values at elevated temperatures were known.

3.5. Acknowledgments

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3.6. References


Chapter 4
Shape-Controlled Synthesis of CdSe Tetrapods Using Cationic Surfactant Ligands

4.1 Introduction

The search for alternative energy sources has been gathering momentum in the recent years as part of an effort to protect the environment and preserve the natural resources. One of the major threats to the environment is the burning of the fossil fuels that leads to carbon dioxide (CO₂) emission and hence global warming. The debate on alternative energy sources that exploit solar power has been of great relevance with media acting as a bridge between science and technology.

Photovoltaic devices based on solution-processable conjugated polymers are attractive for the production of low-cost solar cells¹. To obtain high efficiencies, it is necessary to have an interpenetrating network of electron-accepting and hole-accepting components within the device. This can be achieved using polymer blends² or mixtures of conjugated polymers with C₆₀ derivatives³,⁴. Nanocrystals of inorganic semiconductors such as CdSe also act as good electron acceptors from conjugated polymers; however, the efficiency of photovoltaic devices made with spherical nanocrystals is limited by the problem of electron extraction through the nanocrystal network⁵,⁶. The use of nanorods instead of spherical nanocrystals has been shown to give significantly higher efficiencies because of the smaller number of inter-particle hops necessary for electrons to leave the device⁷,⁸. However, nanorods have a tendency to lie in the plane of the film, which is not
the optimum arrangement for electron extraction, and Sun et al. showed that the use of branched CdSe to improve the electron extraction problem\textsuperscript{9}

Tetrapod-shaped nanocrystals have been synthesized for a variety of semiconductor compositions, such as ZnO\textsuperscript{10,11}, MnS\textsuperscript{12}, CdS\textsuperscript{12-14}, CdTe\textsuperscript{15,16}, and CdSe\textsuperscript{16-19}. Uniquely, CdTe tetrapods can be synthesized with high shape selectivity (up to 70 % of QDs were tetrapods) and high size uniformity (arm lengths were “within a few percent”) directly without selective precipitation\textsuperscript{15}. However, CdSe based devices were found to be more efficient than the CdTe based ones\textsuperscript{20,21}. But CdSe tetrapods are more difficult to synthesize with high shape selectivity (limited to <40 %) and high size uniformity\textsuperscript{16,19}. Mohamed et al. reported on the synthesis of “tetrapod-like” CdSe NPs with a selectivity of 90 %, with many of the observed NPs not strictly having the tetrapod shape (i.e., with four arms)\textsuperscript{17}. Pang et al. reported the formation of CdSe tetrapods by incorporating acidic aqueous solutions into a variant of the hot-injection method; tetrapod selectivities as high as 80 % were claimed\textsuperscript{18}. In this chapter we report that CdSe tetrapods can be synthesized with surprisingly high shape and dimensional uniformity through the novel use of quaternary ammonium surfactant ligands.

4.2 Materials and Methods

The cadmium precursor solution was prepared by heating CdO (0.103 g, 0.8 mmol, 99.99 %, Sigma-Aldrich) in ODE (20 ml 90 %, Sigma-Aldrich) containing OA (2.825 g, 10 mmol, 90 %, Sigma-Aldrich) to ~140 °C under an argon atmosphere, at which the mixture turned clear and colorless. The Cd solution was then cooled to room temperature. The selenium precursor solution was prepared by combining Se metal (0.032 g,
0.4 mmol, 99.999 %, Sigma-Aldrich) with liquid trioctylphosphine (TOP; 1.5 ml, 90 %, Sigma-Aldrich), and then adding a solution of the quaternary ammonium compound (0.05 mmol) in toluene (2 ml). The quats studied were CTAB (98 %, Sigma-Aldrich), DDAB (98 %, Sigma-Aldrich), tetramethylammonium bromide (99 %, Fluka Chemika), tetrabutylammonium bromide (99 %, Fluka Chemika), tetraoctylammonium bromide (Sigma-Aldrich), and tetradecylammonium bromide (99 %, Fluka Chemika). The Cd solution was heated at a rate of 10 °C min⁻¹ to 300 °C, at which point the Se/quat solution was injected within 6 s. Caution: injecting too rapidly leads to violent boiling of the reaction volume.

In the slow-decomposition method, the Se/CTAB solution was combined with a cooled Cd precursor solution and heated slowly to 300 °C at a rate of 10 °C min⁻¹. The reaction flask was kept at 300 °C for 1 hr once that temperature was reached. In the synthesis of zinc-blende CdSe QDs, one twelfth of the Se/CTAB precursor solution was used in otherwise identical hot-injection synthesis conditions. Withdrawn aliquots were immediately cooled in a room-temperature water bath. The resultant NPs were recovered by precipitation with acetone, centrifuged, and washed with acetone at least three times, and then redispersed in toluene.

In the control experiment using trioctylamine, the ligand (0.05 mmol) was combined with toluene (2 ml) and TOPSe solution (0.032 g of Se metal in 1.5 ml of TOP). In the experiment using HCl, an aqueous solution of HCl (1 ml, 1 N) was added to the Cd precursor solution (0.8 mmol of CdO, 20 ml of ODE, and 2.825 g of OA) in a three-neck flask. This mixture was carefully heated to 300 °C, after which the TOPSe solution (0.032 g of Se metal in 1.5 ml of TOP) was injected. For the HCl/trioctylamine
experiment, the ligand was injected along with the TOPSe into the HCl/Cd precursor mixture. Growth was maintained at 280 °C. Caution: heating of the flask containing HCl leads to violent boiling of the reaction volume.

In the synthesis of ZnSe QDs, the zinc precursor solution was prepared by heating zinc(II) oxide (0.0813 g, 1 mmol, 99.7 %, Strem Chemicals) in ODE (20 ml) containing OA (2.825 g) to ≈250 °C under an argon atmosphere, at which the mixture turned clear and colorless. In the synthesis of PbSe QDs, the lead precursor solution was prepared by heating lead(II) oxide (0.223 g, 1 mmol, 99.99 %, Sigma-Aldrich) in ODE (20 ml) containing OA (2.825 g, 10 mmol) to ≈200 °C under an argon atmosphere, at which the mixture turned clear and colorless. The selenium precursor solution was prepared by combining Se powder (0.039 g, 0.5 mmol) with TOP (1.5 ml), and then with a solution of DDAB (0.05 mmol) in toluene (2 ml). The solution was heated further to 300 °C at a rate of 10 °C min⁻¹, after which the Se/DDAB precursor solution was injected.

In the synthesis of CdS QDs, the cadmium precursor solution was prepared by heating CdO (0.128 g, 1 mmol) in ODE (20 ml) containing OA (2.825 g) to ≈140 °C under an argon atmosphere, whereupon the mixture turned clear and colorless. The sulfur precursor solution was prepared by combining S powder (0.016 g, 0.5 mmol, 99.98 %, Sigma-Aldrich) with TOP (1.5 ml), and then with a solution of DDAB (0.05 mmol) in toluene (2 ml). The solution was heated further to 300 °C at a rate of 10 °C min⁻¹, after which the S/DDAB precursor solution was injected. Withdrawn aliquots were cooled and precipitated with acetone, and washed at least three times with acetone. The precipitated NPs were then re-dispersed in toluene.
4.3 Results and Discussions

We note that nearly all hot-injection syntheses of CdSe nanoshapes, including tetrapods, involve alkylphosphonates (e.g., methyl\textsuperscript{22}, hexyl\textsuperscript{23}, tetradecyl\textsuperscript{15,19,24}, and octadecylphosphonic acids\textsuperscript{25}). These phosphonate ligands bind to certain particle facets preferentially to reduce growth rates of those facets, a property not shown by trioctylphosphine oxide (TOPO), amine, or carboxylate ligands\textsuperscript{15,19,24,26}. Precursor concentration and injection sequence provide other synthesis parameters for shape control\textsuperscript{16,19,24}. The interesting use of metallic NPs as seeds in the colloidal synthesis of CdSe tetrapods and other nanoshapes was recently shown\textsuperscript{27,29}.

The use of quaternary ammonium salt compounds ("quats") in the hot-injection synthesis of QDs (or NPs in general) has not been previously reported. Quats differ substantially from phosphonate and the other electron-rich ligands in that the head group has a cationic NR\textsubscript{4} structure containing an electron-poor nitrogen center and four alkyl groups. Depending on the alkyl substituents, quats are variously used as wetting agents\textsuperscript{30}, emulsifiers, and phase-transfer agents\textsuperscript{31}. In materials chemistry, they are used as structure-directing agents in zeolite\textsuperscript{32} and mesoporous materials synthesis\textsuperscript{33}, in aqueous-phase metal nanorod synthesis\textsuperscript{34}, and in phase-transfer synthesis of metal NPs\textsuperscript{35}. The possibility that quats can bind electrostatically to surface-exposed anionic sites motivated us to study their possible role in particle shape control.

We modified the synthesis method for spherical CdSe QDs\textsuperscript{36,37} in which trioctylphosphine selenide (TOPSe; Se precursor) is injected into an octadecene (ODE) solution of CdO and oleic acid (OA). The quat was introduced into the synthesis by combining it with the Se solution prior to injection at 300 °C. Toluene was used to
solubilize the quat, and so care was needed to avoid uncontrolled boiling of the reaction volume. The particles were grown at 280 °C, and recovered and washed with acetone. Selective precipitation was not carried out.

**Figure 4.1.** Representative transmission electron microscopy (TEM) images of CdSe tetrapods synthesized with a) CTAB b) DDAB c) spherical CdSe QDs synthesized without any quat ligand and d) TEM image of CdSe tetrapods synthesized with CTAB through the slow-decomposition method, and recovered after 1 h at 300 °C. All scale bars: 20 nm. The particles were recovered 1 min after injection. Insets: higher magnification of individual tetrapod particles (not to scale).
Figure 4.2. Histograms of tetrapod arm width and length distributions for tetrapods synthesized with a,b) CTAB and c,d) DDAB.

The CdSe QDs were unexpectedly found to be tetrapod shaped when the synthesis was carried out in the presence of cetyltrimethylammonium bromide (CTAB; Figure 4.1a). Tetrapods accounted for 90% of the 500 particles analyzed, and the balance comprised single rods, bipods, and tripods. Defined as the percentage of all observed NPs identified to be tetrapods, the selectivity was 90%. No spherical particles were detected. The mean average arm length and width were 10.9 nm (relative standard deviation 14.0%) and 3.4 nm (15.0%), respectively (Figure 4.2a, b). The dimensions of the fourth
arm (pointing out of the images and observed as the higher-contrast center) could not be quantified.

On replacing CTAB with didodecyldimethylammonium bromide (DDAB), we found that the resultant QDs were also tetrapodal in shape, with a selectivity of 92% (Figure 4.1b). With assumed Gaussian size distributions, these particles had a mean average arm length and width of 7.4 nm (13.5%) and 3.2 nm (12.0%), respectively (Figure 4.2c, d). Without having to perform selective precipitation, we found that these as-synthesized CdSe tetrapods were also of higher quality (i.e., higher selectivity towards the tetrapod shape and more uniform dimensions) than those described in the early papers of Manna et al.\textsuperscript{38} and Peng and Peng\textsuperscript{19} and in more recent reports\textsuperscript{17,18,28}. For comparison, we carried out the QD synthesis without using any quats but kept the toluene in the Se precursor solution. Spherical QDs with a mean average diameter of 5.6 nm (10.8%) resulted, which indicates that toluene was not responsible for the tetrapod shape (Figure 4.1c). The monodispersity of these particles could be improved by replacing the toluene co-solvent with a higher-boiling-point solvent that can solubilize the quat ligands (thereby allowing for a more rapid injection).

Both tetrapod materials contained the CdSe wurtzite phase as the spherical QDs, according to X-ray diffraction (XRD) analysis (Figure 4.3). The more intense and narrow diffraction peak at 20 \(\approx 25^\circ\) relative to the peaks at 20 \(\approx 24\) and \(\approx 27^\circ\) was consistent with tetrapod arms lengthened in the c-axis direction of the wurtzite phase, as others have found for II-VI tetrapods\textsuperscript{17,18,22,25}. Scherrer analysis of the (002) wurtzite peak indicated grain sizes of \(\approx 7\) and \(\approx 8\) nm, respectively, for the CTAB- and DDAB-derived samples. XRD grain sizes and average TEM particle sizes are volume-weighted and number-
weighted averages, respectively, and so a direct comparison of these values to determine the presence of internal defects (*i.e.*, stacking faults and twinning boundaries) cannot be done. For the spherical QDs (Figure 4.1 c), analysis of the peaks of $2\theta=24, \approx 25$, and $\approx 27^\circ$ indicated (100), (200), and (101) grain sizes of 7.0, 7.7, and 7.9 nm, respectively.
Figure 4.3. XRD patterns of CdSe tetrapods synthesized with a) CTAB and b) DDAB, and of c) spherical CdSe QDs synthesized without any quat ligand. Diffraction peaks for the wurtzite and zinc-blende crystal structures of CdSe are shown in blue (bottom) and magenta (top) respectively.
Through the “slow-decomposition” synthesis approach\textsuperscript{39} to NPs, we found that the Se/quat precursor can be combined in one pot with the Cd precursor solution and carefully heated to generate the tetrapods. By heating to 300 °C at a ramp rate of 10 °C min\textsuperscript{-1} and holding at 300 °C for 1 hr, CdSe tetrapods with longer arms (≈10-40 nm) were synthesized (Figure 4.1d). The tetrapods were less uniform in size and shape however, and spherical QDs were also formed. The selectivity was estimated to be 8 % and the arm width and arm length were in the ranges of 2.1-3.8 and 16-26 nm, respectively. A sudden color change in the reaction medium was observed during the heat ramp at ≈140 °C, which indicates initiation of particle nucleation. Nucleation most likely continued during the heat ramp, thus leading to the non-uniform tetrapods and spherical QDs.

Alivisatos and coworkers theorized that phosphonate-assisted QD tetrapod formation is the result of nucleation of zinc blende particles followed by surface-initiated growth of wurtzite arms. High tetrapod selectivities result from the nucleation of zinc blende-only NPs followed by growth of wurtzite-only arms, as in the case of CdTe tetrapods. The cohesive energy difference between the two polymorphs of CdTe is sufficiently large (≈10 meV) for zinc-blende (and not wurtzite) particles to nucleate, and small enough to allow the wurtzite phase to grow off the zinc blende NP surfaces. By extension, low selectivities result from the nucleation of both zinc-blende and wurtzite phases (Figure 4.4a). The theory thus suggests that it is inherently difficult to synthesize CdSe tetrapods with high selectivities, since CdSe has a smaller energy difference between its two phases (<1 meV).
The high selectivity to CdSe tetrapods with CTAB or DDAB ligands suggested the nucleation of zinc-blende-only CdSe NPs as one possible mode of formation (Figure 4.4 b). To gather evidence for this, we attempted to recover the NP products at very short synthesis times but were unsuccessful. We then sought to separate nucleation from arm growth by significantly reducing the amount of injected Se/quat precursor. The resultant particles had the zinc-blende phase, consistent with CdSe NPs nucleating in the zinc-blende phase (Figure 4.5). The observation that ligands can modify the crystal structure of nuclei is consistent with previous reports\textsuperscript{32,40}.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure44.png}
\caption{Possible mechanisms for the a) nonselective and b) selective formation of CdSe tetrapods with CTAB or DDAB ligands.}
\end{figure}
Figure 4.5. XRD pattern of CdSe QDs prepared with 1/12th of original Se/CTAB precursor amount used for the tetrapod sample of Figures 1a and 2a. Diffraction peaks for the wurtzite and zinc-blende crystal structures of CdSe are shown in black (top) and magenta (bottom) respectively.

To gain insight into the structure-directing role of the quats, we explored the effects of quat concentration and quat molecular structure. Increasing CTAB concentrations led to decreased tetrapod selectivity (down to \(\approx30\%\)) and increased
faceting of all formed particles (Figure 4.6), which indicates that there is some optimum amount of quat that maximizes nucleation of the zinc blende phase and therefore CdSe tetrapod selectivity. XRD analysis showed that these particles were of the wurtzite phase (Figure 4.7). With increased amounts of quat, the tetrapod arms were shaped like petals instead of rods, indicative of the ligand modifying the growth of the arms (Figure 4.6). It is presumed that the mode of ligand-particle interaction is electrostatic, because of the cationic nature of the quat head group.

Figure 4.6. Representative TEM image of CdSe QDs synthesized with ten times the amount of CTAB used for the tetrapod sample of Figure 4.1a. The particles were recovered 1 min after injection. Inset: higher magnification of an individual tetrapod particle (not to scale). Scale bar: 50 nm.
Figure 4.7. XRD pattern of CdSe tetrapods synthesized with ten times the amount of CTAB used for the tetrapod sample of figure 4.1 a. Diffraction peaks for the wurtzite and zinc-blende crystal structures of CdSe are shown in black (bottom) and magenta (top) respectively.

There was also a significant change in particle morphology when symmetric quats (with four equivalent alkyl groups, $R$=methyl, butyl, octyl, or decyl) were tested as ligands. These also led to CdSe tetrapods, but the selectivities decreased significantly.
Irregularly shaped QDs (not classifiable as spheres, rods, bipods, tripods, or tetrapods) made up about 50% of the particle population (Figure 4.8). These quats modified the particle formation pathway to yield nonspherical, nonuniform CdSe QDs, which confirmed the shape-inducing role of the head group and the importance of quat asymmetry (found in CTAB and DDAB) for CdSe tetrapod shape control.

Figure 4.8. Representative TEM images of shaped CdSe QDs, synthesized with (a) tetradeoxlammonium bromide and (b) tetrabutyrammonium bromide. The particles were recovered 1 min after injection. All scale bars: 20 nm.

We explored the synthesis of QDs of other compositions using DDAB, and found that the ligand caused a definite change in particle morphology (Figure 4.9). CTAB induced similar changes in particle morphology. Although the tetrapod shape was not formed, the ZnSe, PbSe, and CdS particles were more faceted relative to particles synthesized without the quat. The faceted shapes were reasonably uniform, which suggests that quats can be optimized for NP shape control for various compositions.
Figure 4.9. TEM images of ZnSe QDs synthesized a) without and b) with DDAB; PbSe QDs synthesized c) without and d) with DDAB, and CdS QDs synthesized e) without and f) with DDAB. The particles were recovered 1 min after injection. All scale bars: 20 nm.
The molecular details of how the quats participate in CdSe zinc blende nucleation and wurtzite arm growth are not yet known and are the subject of ongoing studies. One possibility is that quats are not active for shape control but that quat degradation products are. Unlike other ligands, quats are known to be susceptible to thermal decomposition via a reverse Menschutkin reaction and Hofmann elimination, to yield trialkylamines, HCl, alkenes, and alkyl halides as possible decomposition products\textsuperscript{41} (Figure 4.10).

\textbf{Reverse Menschutkin Reaction}

\[
R_4N^+X^- \xrightarrow{\text{Quat}} RX + R_3N \xrightarrow{\text{Alkyl halide}} \xrightarrow{\text{Trialkyl amine}}
\]

\textbf{Hofmann Elimination}

\[
\begin{array}{c}
\text{Quat} \\
\begin{array}{c}
H \\
\text{C} \\
\text{C} \\
H \\
\text{H}
\end{array}
\end{array}
\xrightarrow{\text{N}^+X^-} \xrightarrow{\text{C} = \text{C}} \xrightarrow{\text{Alkene}} \begin{array}{c}
\text{Quat (with one less alkyl group)} \\
\begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{C}
\end{array}
\end{array}
\]

\textbf{Figure 4.10}. Schematic illustration of two modes of thermal decomposition of quaternary ammonium salts

To determine if such compounds play a role in CdSe tetrapod formation, we carried out QD syntheses using trioctylamine, HCl, and a trioctylamine/HCl mixture. Triocylamine led to spherical CdSe QDs and the other two syntheses led to irregularly shaped particles, which indicates that quat decomposition products can modify particle shape but do not lead to CdSe tetrapod formation.
The electronic structure of tetrapods is more complex than that of their spherical counterpart, which makes interpretation of their optical spectra difficult. The CTAB-derived tetrapods had an absorbance spectrum shape similar to those of the reported spectra of CdSe\textsuperscript{18} and CdTe tetrapods\textsuperscript{15,38}. The first absorption peak was located at 597 nm, and the second peak was at \(\approx 497\) nm. Unusually, the photoluminescence (PL) peak was centered at 595 nm (Figure 4.11a). This may be possible if the shorter-armed fraction of the tetrapod distribution fluoresced and the longer-armed tetrapods did not (while both contributed to the absorbance spectrum). Such particle-size-dependent PL is known for CdSe QDs\textsuperscript{42}. The measured quantum yields of the tetrapods (0.30 and 0.12 % for CTAB- and DDAB-derived samples, respectively) were lower than that of the spherical QDs (15.2 %), consistent with previous reports. The absorbance of DDAB-derived tetrapods was different from that of CTAB-derived tetrapods, in which the first and second absorbance peaks were located close to one another (610 and 574 nm, Figure 4.11b), thus resembling the spectrum reported by Mohamed \textit{et al}\textsuperscript{17}. These authors attributed the higher-wavelength peak to the zinc-blende core diameter and the other peak to arm length. For CdTe tetrapods, Alivisatos and coworkers reported that optical absorbance was dependent on arm width and not arm length\textsuperscript{15}.
Figure 4.11. UV-vis absorbance (in blue) and photoluminescence spectra (in magenta) of CdSe tetrapods synthesized with (i) CTAB and (ii) DDAB; and (iii) spherical CdSe QDs synthesized without any quat ligand. The particles were recovered 1 min after injection.

4.4 Summary and Conclusions

In conclusion, QD shape control through the use of quats is demonstrated for the first time. The surfactant ligands of CTAB and DDAB lead to the formation of CdSe tetrapods with unprecedented high shape selectivity and size uniformity, as established through rigorous TEM analysis. Quats with other structures lead to nonspherical particles, with
faceting the probable result of charge interactions between the quat head group and particle surface. A deeper understanding of these charge interactions and the quat molecular-structure effect would lead to greater shape control for a variety of compositions. The use of quats eliminates both selective precipitation as a purification step and the more costly alkylphosphonate ligands for inducing nonspherical shapes. This new synthesis method offers the important advantages of greener chemistry and scalability, which could further the development of tetrapod-based photovoltaic and electronic devices\textsuperscript{43,44}.

4.5 Acknowledgments

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4.4 References


Chapter 5

Effects of Synthesis Reaction Parameters on Tetrapodal CdSe Nanoparticles

5.1. Introduction

The electronic and optical properties of semiconductor NPs have generated considerable interest in recent years because of the ease of tunability of these properties with size, due to quantum confinement effects\(^{1-17}\). With emergence of complex shapes, improved control over these properties can be achieved and hence robust synthetic routes to produce both size and shape control are of critical importance\(^{18-25}\). The tetrapod-shaped NPs can potentially exhibit a variety of interesting mechanical, electrical, and optical properties. Tetrapods can serve as a very interesting building block for preparing superstructures; especially three dimensional ones\(^{26}\). Three-dimensional CdSe tetrapods have obvious potential advantages in photovoltaic devices because their shape makes it impossible for them to lie flat within the film, leading to improved packing and increased electron capture efficiency\(^{8,9,17}\). Currently CdSe tetrapods are synthesized using phosphonic ligands\(^{19,22,27-30}\). This method suffers from the disadvantage of low yield as the tetrapods are typically formed mixed with rods. Recently we reported the synthesis of CdSe tetrapods with dimensional uniformity, in high yield using the family of ligands called quaternary ammonium salts (quats) without any post-preparative treatment\(^{31}\).

While the optical properties of spherical CdSe NPs are understood in detail, there are very few studies about the optical properties of tetrapodal CdSe NPs. In this chapter, we investigate the morphological and optical properties of CdSe tetrapodal NPs as a
function of various reaction parameters, \textit{i.e.}, reaction temperature, time, precursor ratio (Cd:Se), nature and ratio of surfactants (quat:OA).

5.2. Experimental Section

5.2.1 Single Injection Method

The cadmium precursor solution was prepared by heating CdO (0.128 g, 1 mmol, 99.99\%, Sigma- Aldrich) in ODE (1-octadecene, 20 ml, 90\%, Sigma-Aldrich) containing OA (oleic acid, 1.402 g, 6 mmol, 90\%, Sigma-Aldrich) to 140 °C under an argon atmosphere, at which the mixture turned clear and colorless forming cadmium oleate complex. The selenium precursor solution was prepared by combining Se metal (0.039 g, 0.5 mmol, 99.999\%, Sigma-Aldrich) with liquid trioctylphosphine (TOP, 1.5 ml, 90\%, Sigma-Aldrich), and then adding a solution of cetyltrimethylammonium bromide (CTAB, 0.05 mmol, 98\%, Sigma-Aldrich) in toluene (3 ml). The cadmium oleate complex was brought to the desired injection temperature, at which point the Se/CTAB solution was injected within 6 seconds. The reaction mixture was cooled to the desired growth temperature and aliquots (~1 ml) were withdrawn at regular time intervals. The same procedure was followed when the synthesis was done with other quats. Due caution was taken because injecting too rapidly at high temperatures lead to violent boiling of the reaction mixture. Synthesis of CdSe NPs was also performed with various different quats of different alkyl chain lengths and counter anions (Table 5.1) using the above mentioned method.
<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetyltrimethylammonium bromide</td>
<td>$\text{CH}_3(\text{CH}_2)_4(\text{CH}_3)_3\text{N}^+\text{Br}^-$</td>
<td>CTAB</td>
</tr>
<tr>
<td>Didecyldecyltrimethylammonium bromide</td>
<td>$(\text{C}<em>{12}\text{H}</em>{25})_2(\text{CH}_3)_2\text{N}^+\text{Br}^-$</td>
<td>DDAB</td>
</tr>
<tr>
<td>Tetraoctylammonium bromide</td>
<td>$(\text{C}<em>8\text{H}</em>{17})_4\text{N}^+\text{Br}^-$</td>
<td>TOAB</td>
</tr>
<tr>
<td>Tetradecylammonium bromide</td>
<td>$(\text{C}<em>{10}\text{H}</em>{21})_4\text{N}^+\text{Br}^-$</td>
<td>TDAB</td>
</tr>
<tr>
<td>Cetyltrimethylammonium chloride</td>
<td>$\text{CH}_3(\text{CH}_2)_4(\text{CH}_3)_3\text{N}^+\text{Cl}^-$</td>
<td>CTAC</td>
</tr>
<tr>
<td>Cetylbenzyltrimethylammonium chloride</td>
<td>$\text{C}<em>{16}\text{H}</em>{33}(\text{C}_6\text{H}_5\text{CH}_3)(\text{CH}_3)_3\text{N}^+\text{Cl}^-$</td>
<td>CBDMAC</td>
</tr>
</tbody>
</table>

Table 5.1. Abbreviations and chemical structure of various quats used in this study

5.2.2 Multiple Injection Method

The cadmium precursor solution was prepared by heating CdO (0.128 g, 1 mmol, 99.999%, Sigma-Aldrich) in ODE (1-octadecene, 20 ml, 90%, Sigma-Aldrich) containing OA (oleic acid, 1.402 g, 6 mmol, 90%, Sigma-Aldrich) to 140 °C under an argon atmosphere, at which the mixture turned clear and colorless. The primary selenium precursor solution was prepared by combining Se metal (0.039 g, 0.5 mmol, 99.999%, Sigma-Aldrich) with liquid trioctylphosphine (TOP, 1.5 ml, 90%, Sigma-Aldrich), and then adding a solution of cetyltrimethylammonium bromide (CTAB, 0.05 mmol, 98%, Sigma-Aldrich) in toluene (3 ml). The secondary selenium solution was prepared by combining Se metal (0.078 g, 1 mmol, 99.999%, Sigma-Aldrich) with liquid trioctylphosphine (TOP, 3.0 ml, 90%, Sigma-Aldrich), and then adding a solution of cetyltrimethylammonium bromide (CTAB, 0.1 mmol, 98%, Sigma-Aldrich) in toluene (6 ml). The secondary Se solution was divided into 4 equal parts. The primary injection was done as mentioned in the single injection method. An aliquot was withdrawn after 1 minute of the primary injection. Subsequent injections were done very slowly dropwise and an aliquot was withdrawn after 1 minute of each injection. Each injection differed by
5 minutes. The desired growth temperature was maintained steadily through out the secondary injection process.

5.2.3 Synthesis of CdSe Tetrapod NPs in Ternary Surfactant System

The cadmium precursor solution was prepared by heating CdO (0.128 g, 1 mmol, 99.99%, Sigma-Aldrich) in ODE (1-octadecene, 20 ml, 90%, Sigma-Aldrich) containing OA (oleic acid, 1.402 g, 6 mmol, 90%, Sigma-Aldrich) and Triocetylphosphine oxide (TOPO, 2.6 mmol, 90%, Sigma-Aldrich) to 140 °C under an argon atmosphere, at which the mixture turned clear and colorless forming cadmium oleate complex. The selenium precursor solution was prepared by combining Se metal (0.039 g, 0.5 mmol, 99.999%, Sigma-Aldrich) with liquid trioctylphosphine (TOP, 1.5 ml, 90%, Sigma-Aldrich), and then adding a solution of cetyltrimethylammonium bromide (CTAB, 0.05 mmol, 98%, Sigma-Aldrich) in toluene (3 ml). The cadmium oleate complex was brought to 190 °C, at which point the Se/CTAB solution was injected within 6 seconds. The reaction mixture was cooled to 160 °C and aliquots (~1 ml) were withdrawn at regular time intervals.

5.2.4 Fluorescence Quenching Studies

In a typical reaction of growing Au NPs on the tips of the CdSe tetrapodal NPs, a gold solution was produced with 12 mg of AuCl₃ (0.04 mmol, 99.99%, Aldrich), 20 mg of CTAB (0.05 mmol, 98%, Sigma-Aldrich), 70 mg of dodecylamine (DDA, 0.37 mmol, 99.99%, Sigma-Aldrich) in 3 ml of toluene and was sonicated for 5 minutes at room temperature, during which the solution changed color from brown to bright yellow. DDAB helps dissolve the otherwise insoluble AuCl₃ in toluene. 20 mg of CdSe tetrapod NPs were dissolved in 4 ml of toluene and was taken in a three necked flask. The flask
was purged with Ar gas. The gold precursor solution was added through a syringe into the flask with constant stirring dropwise over a period of 3 minutes, during which Au\(^{3+}\) was reduced \textit{in situ} to form Au NPs. DDA helps prevent the agglomeration of the resulting Au NPs. During the addition of gold precursor solution, the CdSe NP solution changed color from bright orange to murky brown (Figure 5.1). The hybrid Au-CdSe NPs were precipitated with methanol and washed with acetone three times before redispersing in toluene for further characterizations. Au NPs of various diameter were formed \textit{in situ} by varying the amounts of AuCl\(_3\), DDAB and DDA (Table 5.2).

**Figure 5.1.** (a) Bright orange CdSe tetrapod NPs dissolved in toluene (b) Bright yellow colored gold precursor solution (c) Murky brown solution of hybrid Au-CdSe NPs.
5.3. Results and Discussion

5.3.1. Effect of Temperature and Reaction Time

The change in injection and growth temperature had a significant effect on the morphology and the optical properties of the as-prepared CdSe tetrapods. Figure 5.2 shows the series of transmission electron micrographs of the CdSe tetrapods synthesized at various injection and growth temperatures. As the injection temperature decreased steadily from 300 °C, a pronounced improvement in the stability of the particles was observed over the time-frame of the study. At higher temperatures, a loss of selectivity was observed with time and over 60 minutes after the injection the selectivity drastically fell from 90% to 10%, due to Ostwald ripening, which initiates rapidly at higher temperatures (Figure 5.3b).
Figure 5.2. Transmission electron micrographs of CdSe tetrapodal NPs formed under various injection and growth temperatures.

As the injecting temperature decreased to 220 °C and 190 °C, the loss of selectivity became very gradual and the selectivity remained at 60% or greater at 1 hour (Figure 5.3b). Also, since the operating temperatures are lowered, the reaction rate is
decreased thereby promoting the controlled slow growth of particles and allowing us to observe the growth of particles in the high-selectivity range before Ostwald ripening begins.

![Graphs showing the variation of QY, selectivity, and dimension with temperature and time.](image)

**Figure 5.3.** (a) Variation of QY of CdSe tetrapods with time at various injection temperatures (i) 250 °C (ii) 300 °C (iii) 190 °C and (iv) 220 °C (b) Variation of selectivity of the CdSe tetrapods synthesized at various injection temperatures with time (c) Variation of dimension of CdSe tetrapods synthesized at various injection temperatures (i) length (ii) width.

However, at very low injection temperatures 160 °C and 130 °C, the selectivity is very poor, even at short reaction times and the particles are very low in contrast, making their imaging difficult. However, we observe that the selectivity improves with time for very low injection temperatures like 160 °C. This can be explained by the fact that, as the temperature decreases, the concentration of reactive Cd and Se precursors and free
ligands are very low as they remain in the complexed form. Hence there is a low monomer concentration, poor growth and incomplete capping of the few formed particles, leading to surface defects.

Also, we observe that with increase in the injection temperatures, the lengths of the particles decrease and widths of the particles increase gradually (Figure 5.3c). At a particular operating temperature, we observe that the length of the particle increases rapidly as compared to the width. This identifies the facet (002) as the one with the highest interfacial energy, because of the quick growth.

The temporal evolution of absorbance and PL spectra of CdSe tetrapods synthesized at various temperatures are shown in Figure 5.4. Like spherical CdSe NPs, the size dependence of the NPs is observed in the optical spectra of tetrapodal NPs: the absorption band-edge red shifts with increase in the size of the NPs. The absorbance spectra become more resolved and the quantized exciton states are clearly detectable at lower synthesis temperatures. The stokes shift was found to increase with decreasing size, as was observed by Tari et al.\textsuperscript{32} and Norris et al.\textsuperscript{33}. But it was remarkably large in comparison to the spherical particles. For example, stokes shift was $\sim$100 meV for CdSe tetrapod NPs of average length 10 nm and average width 2.5 nm, while it was $\sim$50 meV for spherical CdSe NPs of mean diameter 5 nm. A larger Stokes shift means a smaller overlap area between absorption and emission spectra, which is desirable in applications such as light-emitting diodes, where reabsorption reduces the total efficiency\textsuperscript{34}. The PL spectra exhibit a very narrow FWHM of $\sim$ 29 nm. However the PL quantum yield (QY) of the particles synthesized at lower temperatures were comparable to the ones synthesized at higher temperatures ($\sim$1-3\%) (Figure 5.3). These results are comparable to the published results on the QY of bare CdSe tetrapods\textsuperscript{35}. We believe that the width of
the tetrapods is responsible for the fluorescence rather than the length because of the weaker electron confinement due to the length of the growing arm. An enhanced QY (~60%) was reported by Talapin et al. in their system where they grew CdS arm on ZB CdSe seeds to form tetrapodal NPs. They observed that the QY increased with decrease in the width of the particles and that the length of the arms had little to no effect on the QY. Tari et al. observed that the quantum confinement was stronger due to the diameter of the arms than due to the length of the arms in CdTe tetrapodal NPs. Lowering the injection temperature to 160 °C and below, leads to poor spectral resolution and a huge trap emission in the PL spectra (Figure 5.4f).
Figure 5.4. Absorption and PL spectra of the CdSe nano-tetrapods synthesized at (a) 300 °C/280 °C (b) 280 °C/250 °C (c) 250 °C/220 °C (d) 220 °C/190 °C (e) 190 °C/160 °C (f) 160 °C/130 °C at various times of synthesis. The red lines signify the absorbance spectra and the blue lines signify the emission spectra.
Figure 5.5. Powder X-ray diffraction patterns of as-synthesized CdSe tetrapods at various injection temperatures (i) 160 °C (ii) 190 °C (iii) 220 °C (iv) 250 °C (v) 280 °C (vi) 300 °C (vii) CdSe nanoparticles synthesized without CTAB at an injection temperature of 300 °C (viii) CdSe nanoparticles synthesized without CTAB at an injection temperature of 190 °C. Diffraction peaks of zinc-blende and wurtzite are shown in magenta (bottom) and black (top) lines respectively.
Figure 5.5 shows XRD patterns of CdSe nano-tetrapods synthesized at various injection and growth temperatures. They suggest that the particles crystallize in hexagonal close packed (wurtzite) structure with strongly characteristic (100), (002), (101), (102), (110), (103) and (112) peaks. The sharp peak at 23.5° indicates that the arms of the tetrapods are growing in (002) direction.

Peng and co-workers\textsuperscript{30,37} identified that, for CdSe, formation of a particular crystal structure depends on the processing temperature and noted that a high temperature (>250 °C) reaction always produces wurtzite structure, whereas a low-temperature (<230 °C) reaction favors zinc blende structure.

Control reactions without CTAB at 190 °C produced spherical shaped CdSe nanoparticles with zinc-blende as their native crystal structure – demonstrating the crucial effect of this ligand in the selective generation of tetrapod shapes (Figure 5.5(viii)). Since the rate of supply of the precursors to the nuclei and the rate of growth were optimal at 190 °C, this temperature was used for all our further syntheses and the other reaction parameters were changed keeping the injection temperature constant at 190 °C and the growth temperature at 160 °C. Also, this reduction in the operational temperature removed the risk of vigorous boiling of toluene during injections at higher temperatures.

5.3.2 Synthesis of CdSe Tetrapodal NPs by Multiple Injection Method

Significant growth of the particles could not realized by using a single injection method, because of the quick depletion of the Se precursors (limiting reagent). Hence multiple injection of TOPSe and CTAB solution in toluene was carried out to be able to observe
the growth profile of the tetrapods. Figure 5.6 shows the series of TEM images of CdSe tetrapods synthesized by the multiple injection method performed at 190 °C. The particles glow from green to red under UV lamp and they exhibit very interesting optical properties. We observe that once the basic tetrapod shape is formed, growth of the arms occurs according to the controllable kinetic mechanisms previously observed by for nanorods and CdTe tetrapods\textsuperscript{19,38}. The particles so formed exhibit monodispersity in their dimensions and a very high selectivity.

<table>
<thead>
<tr>
<th>Injection</th>
<th>PL color</th>
<th>Length (nm)</th>
<th>Relative standard deviation (%)</th>
<th>Width (nm)</th>
<th>Relative standard deviation (%)</th>
<th>Quantum Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>17</td>
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<td>8.4</td>
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<td>10</td>
<td>0.41</td>
</tr>
<tr>
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<td>0.41</td>
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<td>0.33</td>
</tr>
<tr>
<td>5</td>
<td>Red</td>
<td>38.5</td>
<td>7.8</td>
<td>6.6</td>
<td>8.2</td>
<td>0.08</td>
</tr>
</tbody>
</table>

**Figure 5.6.** TEM images of CdSe tetrapods synthesized by multiple injection after (a) 1st injection (b) 2nd injection (c) 3rd injection (d) 4th injection and (e) 5th injection. All the scale bars equal to 20 nm. The table indicates the average dimensions and the quantum yield of the tetrapodal NPs synthesized after each injection.

Figure 5.7a shows the variation of the absorption and PL spectra of the CdSe NPs with synthesis times. With the prolonging reaction time and subsequent Se precursor injection we observe little broadening of the absorption peak and red-shift of the absorption edge, which agrees with the growth of the tetrapods. Figure 5.7b shows the
photoluminescence excitation spectra (PLE) of the CdSe tetrapods of various sizes synthesized by multiple injection method, along with the absorbance and PL spectra. PLE was recorded at different emission wavelengths spanning the luminescence band. PLE spectra are obtained by recording the emitted intensity as a function of excitation wavelength. Since the intensity of emitted light is directly proportional to the intensity of absorbed light one would expect PLE spectra to be an exact replica of absorption spectra. Figure 5.7b shows that the luminescence of the particles is due to the same entity because the first exciton peak of the absorbance spectra and that of PLE are right on top of each other. Chergui and co-workers showed similar results to prove that the absorbing and emitting species in their system were one and the same. However we observe an increased offset between the PLE and absorption spectra on the higher energy side of the spectra. This phenomenon was observed by Rumbles et al. in their InP quantum dots. They later explained this by suggesting that excitations to higher energies significantly reduces the carrier relaxation efficiency to the emitting states.
Figure 5.7. (a) Optical spectra of particles synthesized by multiple injection method after (i) 1\textsuperscript{st} injection (ii) 2\textsuperscript{nd} injection (iii) 3\textsuperscript{rd} injection (iv) 4\textsuperscript{th} injection and (v) 5\textsuperscript{th} injection. (b) Optical spectra of particles including excitation spectra synthesized by multiple injection after (i) 1\textsuperscript{st} injection (ii) 2\textsuperscript{nd} injection (iii) 3\textsuperscript{rd} injection (iv) 4\textsuperscript{th} injection. The magenta lines represent absorbance spectra, the blue lines represent the emission spectra and the red lines represent excitation spectra.

Tonti et al. studied the deviation between the PLE and the absorption spectra in detail\textsuperscript{41} and suggested that the deviation could be because of the scattering due to the aggregation of CdSe NPs with organic capping molecules, between themselves and also between the organic capping molecules, thus introducing macroscopic inhomogenities in the sample. We also observed that as the particle size increases the overlap between the two first exciton peaks of the absorbance spectra and PLE decreases, meaning that there are more absorbing species than the luminescing ones, which is in agreement with the decrease of QY\% with the progress of the reaction.
5.3.3 Effect of Nature and Ratio of Surfactants

The effect of the alkyl chain length, symmetry of alkyl chains around the electronegative nitrogen atom and the counter anion on the morphology and dimensions of the resulting CdSe tetrapodal NPs was studied in detail.

The previous chapter summarizes our observations on the growth of tetrapods as a function of different quaternary ammonium salts. We observed that symmetric quats like tetraoctyl ammonium bromide (TOAB), tetrabutyl ammonium bromide (TBAB), tetradecyl ammonium bromide (TDAB) yielded tetrapods with very low selectivity, when the injection temperature was 300 °C and the growth temperature was 280 °C. However with the reduction in the operational temperatures, we observed that the resulting tetrapodal CdSe NPs exhibited improved morphological and dimensional uniformity. But when compared to the asymmetrical quats the symmetrical quats always yielded particles of lower selectivity irrespective of the operational temperatures. Also it was observed that the rate of growth of particles in the presence of symmetric quats was considerably slower as compared to the asymmetric ones. Amongst the symmetric quats, the morphological selectivity suffered drastically with increase in the alkyl chain length. These observations could be explained by the steric effects induced by the alkyl chain lengths around the positively charged nitrogen atom, making it less accessible for the selenium atoms. As observed in the previous paper\textsuperscript{42} we noticed that the aspect ratio of the arms of the resulting CdSe tetrapodal NPs increased with increase in the alkyl chain length.

When the anion was changed no significant changes in the morphology and the dimension was observed. The anion effect was studied with CTAB and CTAC as the quats. But higher selectivities were obtained when the anion was bromide (~90%) as
compared to ~70% with CTAC. This could probably be due to the difference in the
degree of dissociation of the surfactants with different anions\textsuperscript{43} and area occupied per
molecule. Mata et al.\textsuperscript{44} experimentally calculated the area per molecule of CTAB and
CTAC to be 51.7 and 54 Å\textsuperscript{2}. Lesser number of CTAC molecules would bind to the
surface of the CdSe NPs of a given size as compared to CTAB, because of the larger area
per molecule of CTAC. Hence in the presence of CTAC lesser Se atoms would be
capped and this is likely to induce polydispersity in the size and shape of the resulting
particles.

CBDMAC yielded few seemingly six armed structures (Figure 5.8). The dark
center signifies the presence of another arm perpendicular to the plane of the other arms.
Hence the particles have at least seven arms if not eight. This ligand is different from
other quats so far used in this study in that it has three distinct substituents around the
positively charged nitrogen (C\textsubscript{16}H\textsubscript{33}-, C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}- and CH\textsubscript{3}-) and hence exhibits more
asymmetry than other ligands. One could argue that the complexity of the shapes could
be increased by increasing the asymmetry around the electron deficient nitrogen atom.
Figure 5.8. TEM image of CdSe tetrapods synthesized with CBDMAC as the quat. The system showed occasional six armed structures as shown in the inset. The injection and growth temperatures were 190 °C and 160 °C respectively.

So far we studied the growth of CdSe NPs in single and double surfactant systems. The results obtained in the single and binary surfactant systems were drastically different from morphological and crystallographical stand point. In order to study the effect of the number of surfactants on their properties, CdSe tetrapod NPs were synthesized in the ternary surfactant system (oleic acid, TOPO and CTAB) at an injection temperature of 190 °C and a growth temperature of 160 °C. It was observed that the growth of the particles considerably slowed with the introduction of TOPO leading to the formation of small tetrapods fluorescing green under UV light. The growth rate is limited by the concentration of Cd precursor, which is a strong complex between Cd\(^{2+}\) and oleic
acid. The presence of TOPO might be expected to stabilize the complex more, leading to the slow and controlled release of the Cd ions.

**Figure 5.9.** TEM images of CdSe tetrapodal NPs synthesized in the ternary surfactant system at various reaction times (a) 1 min (b) 5 min (c) 30 min (d) 1 hr. All scale bars equal 20 nm. The injection and growth temperatures were 190 °C and 160 °C respectively.

Figure 5.9 shows the TEM images of CdSe tetrapodal NPs synthesized in the ternary surfactant system. The optical spectra shows the particles grow with time by the red shift (Figure 5.10a). We observed that Stokes shift decreased with time unlike the
CdSe NPs synthesized in the binary surfactant system (Figure 5.10c). This interesting phenomena call for a detailed study in this system.

![Figure 5.10](image)

**Figure 5.10.** (a) Optical spectra of CdSe NPs synthesized in ternary surfactant system at various reaction times. (b) The growth profile of the CdSe in (i) binary surfactant system (CTAB and OA) (ii) ternary surfactant system (OA, CTAB, and TOPO). (c) Variation of Stokes shift with reaction time for (i) ternary surfactant system (OA, CTAB, and TOPO) and (ii) binary surfactant system (CTAB and OA).

The ratio of oleic acid to quat plays an important role in determining the aspect ratio of the resulting tetrapodal NPs. It was observed that with increase in the concentration of quat, the width of the particle was found to increase rapidly (Figure 5.11). When excess oleic acid is used in the system the particles have more shorter and rounded arms (Figure 5.11). This might be attributed to the slow and release of Cd$^{2+}$
because cadmium oleate complex is more stable in the presence of excess oleic acid. When the ratio of OA:quat exceeded 400 the resulting particles were spherical irrespective of the presence of quat. It was interesting to note that when the concentration of CTAB exceeded 0.05 mmol, the optical spectra lost all their features and the quantum yields of the resulting particle were reduced drastically and were always found to be less than 0.01%. The electron confinement in the width of the particle weakens with increase in the concentration of quat, leading to a considerable decrease in quantum yield.
Figure 5.11. TEM images of CdSe tetrapodal NPs synthesized at various ratios of oleic acid and CTAB. The aliquots were withdrawn at 1 min after the injection of Se/CTAB solution. Insets show individual particles at higher magnifications (not to scale). The base case ratio of OA:CTAB is shown by the blue rectangle of dashed lines.
5.3.4. Stoichiometry of Cd:Se

The study of variation of Cd:Se was done at an injection temperature of 190 °C and a growth temperature of 160 °C. The OA:CTAB ratio was maintained at 100. Higher Cd/Se ratios result in longer arms whereas more CTAB per Se atom yields larger arm diameters. This observation is in agreement with that of CdTe tetrapods synthesized by Manna and co-workers.\(^{19}\) When the Cd/ Se molar ratio is high, Cd\(^{2+}\) is far excessive as compared to Se\(^{2-}\) so as to achieve the Cd\(^{3+}\) rich nanoparticles surfaces, which is favorable for the formation of a Cd-OA coordination shell on CdSe NP surface. However, at the low precursor molar ratio, the formation of Cd-OA surface layer is baffled possibly due to the increase of Se dangling sites on the surface of CdSe NPs. We found that the selectivity of the resulting tetrapods was very high when the Cd:Se was maintained at 2:1.

5.4. Fluorescence Quenching Study

Semiconductor NPs are known to be very effective as donor fluorophores in various bioassays based on fluorescence resonance energy transfer (FRET)\(^{45-48}\). On the other hand gold NPs were found to effectively quench the fluorescence of the dyes in proximity\(^{49-51}\). This suggested that Au NPs and CdSe NPs could be effective acceptor – donor pairs. A plethora of studies have been performed on the methods to assemble and characterize the Au-CdSe hybrid nanocomposites\(^{52-53}\). The quenching process of fluorescent semiconductor QDs by Au NPs was found to be due to the long – distance dipole-metal interactions\(^ {54}\).

Banin and coworkers\(^ {55}\) showed the selective growth of gold tips on to CdSe nanorods and tetrapods by a simple reaction. This resulting metal – semiconductor hybrid nanostructures were shown to provide natural contact points for self-assembly. We used
this method to understand the origin of fluorescence of the CdSe tetrapods synthesized with quats.

When the tetrapods (average arm length is 24 nm and average arm width is 2.8 nm) with quantum yield of 0.5% were used to make the Au-CdSe hybrid structures, it was observed that the Au NPs were preferentially attached to the tips of the arms of the tetrapods (Figure 5.12), although Au NPs were seen randomly attached along the length of the arms of the tetrapods. We observed that the diameter of the Au NPs was larger at the tips than that of the ones on the arms (Figure 5.12d). We also observed that when the diameter of the Au NPs was comparable to the arm width the tetrapodal NPs were connected to each other through the tips forming a web like structure (Figure 5.12a, b). However such webbing was not observed when the Au NPs was larger than the width of the tetrapodal NPs (Figure 5.12c). The CdSe tetrapodal particles could not be seen clearly in figure 5.12c. However we could see that the Au NPs were attached to CdSe tetrapodal NPs from the way they are oriented with respect to each other (Figure 5.12c, d).

The presence of Au NPs was further confirmed by powder XRD of CdSe tetrapod NPs and Au-CdSe hybrid NPs. The peaks due to cubic crystalline phases ((111), (200) and (220)) of Au NPs were observed in the hybrid material (Figure 5.12c).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nanoparticles (mg)</th>
<th>DDAB (mg)</th>
<th>DDA (mg)</th>
<th>Au(III)Cl (mg)</th>
<th>Size of gold NP (nm)</th>
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<td>10</td>
<td>100</td>
<td>160</td>
<td>33</td>
<td>4.8</td>
</tr>
</tbody>
</table>

Table 5.2. The diameter of Au NPs formed in this study by varying the amounts of reducing agents.
Fluorescence of the particles was dramatically reduced and PL spectrum was observed to have only the noise (Figure 5.13a). Quenching data is usually represented by the Stern-Volmer equation\textsuperscript{56,57},

\[
\frac{\Phi^0}{\Phi_f} = K_Q \tau_0 [Q] + 1 = K_{nQ} [Q] + 1
\]

Where $\Phi^0_f$ and $\Phi_f$ are the quantum yield in the absence and the presence of a quencher respectively,

$K_Q$ is the energy transfer rate from the fluorophore to quencher (liter mol$^{-1}$s$^{-1}$),
\( \tau_0 \) is the lifetime of fluorescence in the absence of quencher,

\([Q]\) is the concentration of quencher,

\( K_{sv} \) is the Stern-Volmer quenching constant.

It was observed that the decrease in the PL intensity was directly proportional to the diameter of Au NPs attached to the tips of the tetrapodal NPs (Figure 5.13). However the signal to noise ratio of the PL spectra of Au-CdSe particles were very low (Figure 5.13 inset (ii)) and hence the QY was not measured for those particles. The increase in the decrease of PL intensity is plotted against the diameter of the Au NPs formed \textit{in-situ} (Stern-Volmer plot, Figure 5.13 inset (i)).

Quenching of the emission by the metal tips is expected via the new non-radiative pathways created by the proximity of the metal, likely leading to the electron transfer to the Au NPs. It could be inferred from these observations that the fluorescence of the tetrapods did not originate only from the core of the particles but the arms of the tetrapods were equally responsible for the high QY exhibited by the CdSe tetrapods. This result suggests that the exciton hole pair could be created and transferred along the lengths of the arms of the tetrapods, making them very attractive for the photovoltaic applications, where electron transfer is very crucial for the efficiency.
Figure 5.13. (a) Emission spectra of Au-CdSe nanocomposites made with Au NPs of various different diameters. Inset (i) shows the Stern-Volmer plot of decrease in the PL intensity with diameter of Au NPs. The inset (ii) shows the magnified area specified by the rectangle. The blue and black line in the inset represents the PL spectrum of Au-CdSe nanocomposite made with Au NP of 2 nm and 3.2 nm respectively. The red and green represent that of nanocomposites made with Au NPs of 4.8 nm.

5.5. Summary

The study enabled us to understand the evolution of morphology and optical properties with respect to various reaction parameters. We synthesized luminescent CdSe tetrapods with a narrow size distribution varying the temperatures, with an optimum operating temperature of 190 ºC/160 ºC, precursor ratio of 2:1, when the quat was CTAB. This study enables one to synthesize tetrapod shaped nanoparticles of CdSe in high yield with dimensional uniformity and resolved optical properties. Also, the quenching of emission
due to the Au NP on the tips of the arms of the tetrapods suggested that the exciton hole pair could be created and transferred along the arms of the tetrapods. This will facilitate further studies on the incorporation of CdSe tetrapods into photovoltaic devices and may open up new avenues for the applications of CdSe tetrapods.
5.6. References


Chapter 6

Study of Formation Mechanism of CdSe Nano-Tetrapods

6.1 Introduction

One of the currently accepted models for the formation of tetrapodal NPs is where the zinc-blende (ZB) nuclei are formed first and wurtzite (WZ) arms develop by the growth from four equivalent (111) facets of ZB nuclei. CdSe exists in two crystalline lattice structures: wurtzite (WZ, hexagonal) and zinc-blende (ZB, cubic). These structures only differ in the stacking sequence of the CdSe hexagonally packed layers. WZ structure has an ABABAB stacking sequence along the (001) direction, while the ZB structure has an ABCABC stacking sequence along the (111) direction. These subtle structural differences and energy difference between these two phases is often referred to as WZ-ZB polytypism.

Recent efforts in the shape control of CdSe, CdTe, CdS, and ZnSe identified that the control of crystal phases and controlled switching between the crystal phases was responsible for achieving the complex and branched structures. Yeh et al. investigated the energy difference between the WZ and ZB crystal phases for various binary semiconductor compositions. They found that when the WZ-ZB energy difference was found to exceed 10 meV per atom the switch between the two crystal phases was observed to be impractical. In case of CdS, CdSe, ZnS, the energy difference was found to be 3.1, 3.3 and 1.86 meV per atom respectively. This energy difference is so small that it is difficult to isolate controllably the growth of one phase exclusively at a time. However, the WZ-ZB energy difference for CdTe was found to be intermediate i.e., the
energy difference between the two crystal structures is just right, exclusive nucleation in ZB phase and further growth in WZ phase is possible. These results were experimentally verified by Manna et al. where in CdTe tetrapodal NPs were synthesized with high selectivity of 70% using alkyl phosphonic acids as ligands\(^3\). However CdSe tetrapod NPs could not be realized at high yield\(^4\).

Another model proposes that the initial nucleus is formed by eight WZ domains connected to each other through (1122) twin boundaries\(^{16,19-24}\). Theoretical studies proposed that the shape inducing surface ligands bound preferentially to (011) crystal facets, encouraging growth in (001) facet inducing anisotropy in the system\(^{25,26}\).

In this chapter we attempt to explain the formation mechanism of the CdSe tetrapodal NPs synthesized by the methods explained in chapters 4 and 5. Also inorder to ascertain the presence of quats on the surface of CdSe tetrapodal NPs, we characterized our samples with FTIR, XPS, EDS and TGA.

### 6.2 Experimental Section

#### 6.2.1 Seeded Growth of CdSe Tetrapodal NPs

The cadmium precursor solution was prepared by heating CdO (0.128 g, 1 mmol, 99.99%, Sigma-Aldrich) in ODE (1-octadecene, 20 ml, 90%, Sigma- Aldrich) containing OA (oleic acid, 1.8 g, 6 mmol, 90%, Sigma-Aldrich) to 140 °C under an argon atmosphere, at which the mixture turned clear and colorless forming cadmium oleate complex. The Cd solution was then cooled to room temperature. The primary selenium precursor solution was prepared by combining Se metal (0.039 g, 0.5 mmol, 99.999%, Sigma-Aldrich) with liquid trioctylphosphine (TOP, 1.5 ml, 90%, Sigma-Aldrich). The
secondary injection solution was prepared by combining Se metal (0.078g, 1mmol, 99.999%, Sigma-Aldrich) with liquid TOP (3.0ml, 90%, Sigma-Aldrich) and then adding a solution of cetyltrimethylammonium bromide (CTAB, 0.1 mmol, 98%, Sigma-Aldrich) in toluene (6 ml). The secondary injection solution was divided into four equal parts. The cadmium oleate complex was heated brought to the 190 °C when the primary injection solution was injected rapidly and an aliquot ~1ml was withdrawn after 1 minute of injection. The reaction temperature was immediately brought to 160 °C. The secondary injections were done dropwise and an aliquot was withdrawn after 1 minute of each injection. Each injection differed by 5 minutes. The growth temperature was maintained steadily at 160 °C through out the secondary injection process. All the aliquots were washed three times with acetone, centrifuged and redispersed in toluene for further characterizations. However, when the preformed CdSe seed NPs were of WZ phase, the primary injection was done at 280 °C and the reaction temperature was reduced to 160 °C before the secondary injections took place.

6.3 Results and Discussions

6.3.1 Seeded Growth of CdSe Tetrapodal NPs

Our discussions in Chapters 4 and 5 revealed that CdSe tetrapodal NPs could be synthesized at high yields (>90%) with controllable dimensions and brilliant optical properties. The formation of tetrapods at such high yield indicated that CdSe nucleated exclusively in ZB phase in the presence of quats. However, it was not possible to isolate the particles in the nucleation stage to verify this fact, because the kinetics of the growth of the tetrapodal CdSe NPs was very rapid. In order to circumvent this problem, we
investigated the growth of the CdSe NPs from preformed ZB CdSe NPs as seeds (seeded growth). Multiple injections of CTAB dissolved in toluene and Se precursor (TOPSe) were performed dropwise to the preformed ZB CdSe seeds. With each injection the degree of anisotropy increased in the system (Figure 6.1a-e), and after 5 injections 90% of the particles were found to have transformed into tetrapods with the remaining 10% comprising of rods, tripods and bipods. Spherical particles were not observed at all after the third injection. Growth of particles was observed by the red shift in the optical spectra of the particles after every injection (Figure 6.2a). Figure 6.2b shows the XRD of the particles before and after the addition of CTAB. Before the addition of CTAB the crystal structure was ZB and after the multiple injections of CTAB and TOPSe, the crystal structure was found to be of WZ phase, indicating the growth of WZ arms. The diffraction pattern of WZ CdSe NPs shows (102) and (103) peaks at 35.1° and 45.8° 20 respectively, characteristic of WZ phase. The peak around 25° in the diffraction pattern of WZ CdSe NPs is a convolution of (100), (002) and (101) peaks.

When the preformed seeds were WZ, the addition of CTAB dissolved in toluene and TOPSe resulted in the formation of anisotropic structures which were predominantly rods, few branched structures but not tetrapods (Figure 6.3a, b). Figure 6.4 shows a schematic diagram of these observations. When CTAB was not added to the preformed ZB and WZ CdSe seeds the particles continued to grow and remain in ZB and WZ phases respectively. As a control experiment, the secondary injection was done just with CTAB without TOPSe. This yielded tetrapodal NPs as well but with a lower selectivity.
Figure 6.1. TEM images of CdSe NPs (a) preformed ZB seeds (b) after 1st secondary injection (c) after 2nd secondary injection (d) after 3rd secondary injection (e) after 4th secondary injection. All the scale bars equal to 20 nm.
Figure 6.2. (a) Optical spectra of CdSe NPs. Magenta lines signify absorbance spectra and the blue lines represent the emission spectra. (i) Preformed ZB seeds (ii) after 1\textsuperscript{st} injection (iii) after 2\textsuperscript{nd} injection (iv) after 3\textsuperscript{rd} injection (v) after 4\textsuperscript{th} injection (b) XRD patterns of CdSe NPs (i) Preformed ZB seeds (ii) after 4\textsuperscript{th} injection.

Figure 6.3. (a) TEM image of preformed WZ CdSe seeds (b) TEM image of rod shaped CdSe NPs after 4\textsuperscript{th} secondary injection (formed from WZ CdSe seeds). All the scale bars equal to 20 nm.
**Figure 6.4.** Schematic picture showing the formation of tetrapod NPs and rod shaped NPs from ZB and WZ CdSe seeds respectively.

### 6.3.2 Infrared Spectroscopy

To better understand the adsorption mechanism of the OA and CTAB on the surface of CdSe NPs, FTIR measurements were carried out on the pure OA and the CdSe NPs capped with oleic acid (spherical) and tetrapodal CdSe NPs (synthesized with OA and CTAB). The particles were synthesized at an injection temperature of 190 °C and growth temperature of 160 °C. All the particles discussed in this section were withdrawn from the reaction flask after 30 minutes of injection of Se precursor solution. Figure 6.6a represents the typical IR spectrum of pure OA and the assignments of peaks.

The broad feature between 3350 cm\(^{-1}\) was undoubtedly due to the O-H stretch of the carboxylic acid. The aliphatic C-H stretches are observed at 3010 cm\(^{-1}\), 2918 cm\(^{-1}\) and 2844 cm\(^{-1}\). The intense peak at 1716 cm\(^{-1}\) was derived from the existence of the C=O
stretch and the band at 1281 cm$^{-1}$ exhibited the presence of C-O stretch. The O-H inplane and out of plane bands appeared at 1470 cm$^{-1}$ and 938 cm$^{-1}$ respectively.

Figure 6.6b reveals the FTIR spectrum obtained from the spherical CdSe NPs coated with OA and the assignment of peaks to various vibrational motions. With the surfactant, the asymmetric CH$_2$ stretch and symmetric CH$_2$ stretch are observed at 2926 cm$^{-1}$ and 2850 cm$^{-1}$ respectively. It is worth noting that the C=O stretch band of the carboxyl group which is present at 1716 cm$^{-1}$ in the IR spectrum of pure oleic acid is absent in that of spherical CdSe NPs. Instead, two new bands at 1538 cm$^{-1}$ and 1434 cm$^{-1}$ are characteristic of the asymmetric vas (COO$^-$) and the symmetric COO$^-$ stretch. This reveals OA is chemisorbed as the carboxylate onto the CdSe NPs and the two oxygen atoms in the carboxylate are coordinated symmetrically to the CdSe molecules. A weak wide band at 3357 cm$^{-1}$ reveals that some OA could be present as free OA physically adsorbed on the surface of CdSe NPs.
Figure 6.5. FTIR spectra of (a) pure OA (b) CTAB (c) CdSe tetrapodal NPs capped with OA and CTAB (d) CdSe spherical NPs capped with OA and the peak assignments to corresponding vibrational motions.

Figure 6.5c reveals the FTIR spectra of the CdSe tetrapodal shaped NPs synthesized with CTAB and OA as surfactants. The presence of OA in the carboxylate form on the surface of the particles is confirmed by the two bands at 1531 cm$^{-1}$ and 1427
cm\(^{-1}\), which are characteristic of asymmetric COO and the symmetric COO\(^-\) stretch. These peaks were observed in the spherical shaped CdSe NPs capped only with OA (Figure 6.5b). The weak peaks at 1427 cm\(^{-1}\) and 1013 cm\(^{-1}\) are assigned to C-N stretch. Since the quaternary ammonium salts do not have N-H bonds, there are no other significant peaks to identify these compounds by other than from the weak C-N peaks. The singlet peak observed for pure CTAB at 956 cm\(^{-1}\) (Figure 6.5d) is attributed to C-N\(^+\)\(^{27}\). However no peak was observed around 956 cm\(^{-1}\) for CdSe tetrapodal NPs (Figure 6.5c). This could be due to the trace quantities of CTAB used in the reaction. But the broad new bands at 1013 cm\(^{-1}\) and 1130 cm\(^{-1}\) are also considered as stretching modes of C-N\(^+\) effected by metal surface, as described by El-Sayed for CTAB capped Au particles\(^{28}\). The characteristic [C-H--metal] vibration, however, has not been observed, indicating the absence of C-H binding to metal surface\(^{29,30}\).

These peaks are not very conclusive to the presence of CTAB because the peaks could also arise from the C-H outplane bending. Even in the FTIR spectrum of pure CTAB the C-N stretch peaks are very weakly observed (Figure 6.5d). Hence FTIR though shows the presence of OA in its carboxylate form unambiguously, it does not offer proof for the presence or absence of CTAB.

### 6.3.3 X-Ray Photoelectron Spectroscopy (XPS)

To further examine the chemical structure of the surfactant coated CdSe tetrapodal NPs, the XPS spectra of C1s, O1s, Cd 3d, and Se 3d were obtained (Figure 6.7). Figure 6.6a shows the survey XPS spectrum of CdSe tetrapodal NPs bound to Si surface. The C1s peak at 285 eV (Figure 6.6b) is used as the internal standard and is
ascribed to the carbon atoms in the aliphatic chain (C-C) and the carboxylate (-COO\(^{-}\)) moiety respectively, which is consistent with the data obtained from the previous literature\(^{31-33}\). No C1s peak corresponding to the carboxylic carbon (-COOH) appeared in the spectrum at 290 eV\(^{34}\), indicating the absence of free acid in the coated CdSe NPs. This is also confirmed by the feature of the O1s peak at 532.2 eV (Figure 6.6c). A single and symmetric O1s peak reveals the presence of two symmetric oxygen atoms in the COO\(^{-}\) moiety and the absence of C=O bond in the coated CdSe NPs. The Cd 3d\(_{5/2}\) and 3d\(_{3/2}\) peaks appear at 404.3 and 411.2 eV respectively (Figure 6.6d). The peaks are sharp and distinct indicating the absence of oxidized Cd on the NP surface. This indicates the Cd atoms are capped by the oleic acid thoroughly. The spin orbit splitting ratio is 2:3 for the Cd 3d\(_{5/2}\) and 3d\(_{3/2}\) peaks as expected for the d levels\(^{34}\). This indicates that the peaks are solely due to Cd. The binding energies of the Se (3d\(_{5/2}\) and 3d\(_{3/2}\)) are observed at 53.2 and 54.2 eV respectively. The peaks are found to be convoluted because of the proximity of the two peaks. They were resolved into two peaks using the non-linear least square method (Figure 6.6c)\(^{35}\). The oxidized peak of Se (SeO\(_2\) 3d\(_{5/2}\)) was observed at 58.5 eV. The peak's position relative to the CdSe peak agrees with the peak position seen for Se oxides on CdSe, as would be expected\(^{36,37}\). While no oxidized Cd peak was observed, the presence of SeO\(_2\) peak indicates the poor coverage of Se atoms by capping agents as compared to that of Cd atoms and hence making them susceptible to oxidation. Cd:Se ratio was calculated by integrating the corresponding peak areas by using the non-linear least square method\(^{35}\). XPS performed on various different samples of CdSe tetrapodal NPs synthesized with various different surfactant ratios (OA: CTAB) was found to have Cd rich surfaces irrespective of the synthesis parameters. The Cd:Se ratio was found to be
consistently 2:1 on the surface of CdSe tetrapodal NPs synthesized using various different reaction parameters.

Figure 6.6. (a) XPS survey spectrum of CdSe tetrapodal NPs bound to Si using Al X-ray source (b) Close-up surveys for Cd 3d (c) Se 3d (d) C 1S (e) O 1S and (f) Br 3d.

Close-up spectra of N 1S region (Figure 6.6b) which overlaps with the Cd 3d region indicate the absence of N on the NPs or the N 1S peak is buried underneath the dominant Cd 3d peaks. However, evidence for the presence of trace quantities of bromine atom was seen in the CdSe tetrapodal NPs by the Br 3d peak occurring at 69 eV (Figure 6.6f). The peak for Br is very noisy because of its presence in trace quantities. The peak at 69 eV is a convoluted peak of Br 3d3/2 (70 eV) and Br 3d5/2 (69 eV)31, because of the proximity of these two peaks.

It is known from the previous investigations31,38,39 when carboxylic acids adsorb from solution to the metal surface, there may exist two different bonding types of carboxylate groups to the metal i.e., either a bidendate bond through two equivalent
oxygen atoms or monodendate bond through inequivalent oxygen atoms. In case of monodendate bond, the C=O would still be present and the acid hydrogen is substituted by metal atoms. In this way, the IR spectrum would have displayed a strong band at 1700 ~1730 cm\(^{-1}\) and the O 1s XPS would have presented another peak at around 533 eV in addition to the one around 532 eV. The present study demonstrates that the IR band at 1700 cm\(^{-1}\) disappears after the oleic acid has been adsorbed on the surface of CdSe NPs. In addition O 1s XPS spectrum from OA coated CdSe NPs illustrates a single symmetrical peak indicating presence of two equivalent oxygen atoms. Hence it is clear that carboxylate group is bound to the surface of CdSe NPs symmetrically through its two oxygen atoms.

### 6.3.4 X-Ray Dispersive Spectroscopy (EDS)

To identify the local chemical composition of tetrapod shaped CdSe NPs, energy-dispersive X-ray (EDS) spectroscopy was also used. The EDS spectra (Figure 6.7a) were taken by sweeping various area of the CdSe NP film formed on Si wafer. The spectrum confirms the presence of Se, Cd at many different spots. EDS did not show the N (K) peak at 0.4 KeV. EDS does not convincingly prove the presence of lighter atoms unless they are present in large quantities. Hence lack of N peak does not necessarily mean the absence of CTAB because of the trace quantities of CTAB used during the synthesis of CdSe tetrapods. Also EDS hints the presence of bromine at various different spots albeit in low percentage. Also based on the quantitative data obtained from EDS, the ratio of Cd to Se ratio remained 1:1 at all spots of focus (Figure 6.7c), as one would expect. However this is in direct contrast to our XPS data where we observed a ratio of Cd:Se on the
surface of the CdSe tetrapodal NPs. Deviations of composition measured by XPS from that determined by independent elemental analysis would indicate the orientation of faceted NPs upon binding to the Si surface.

Unfortunately, the particles were too small to be seen individually under SEM. Hence, EDS could not be performed at the core and the arms of a single tetrapod which could have provided the difference in the elemental profile between the core and the arms, if any. Nevertheless, these results are encouraging because they are hinting towards the presence of Br atom, which might mean that the quats are attached to the surface of CdSe tetrapodal NPs, although in trace quantities. Also mapping of the elements on various different areas on the film indicated that Cd and Se atoms were uniformly distributed on the film (Figure 6.7b).
Figure 6.7. (a) EDS spectrum obtained for CdSe tetrapodal NPs (b) Mapping of elements to the emitted X-ray energy on various areas of the NP film on Si surface. (c) Quantification of the atomic percentage of various atoms.

<table>
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<th>S. No.</th>
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6.3.5 Thermogravimetric Analysis (TGA)

Figure 6.8 shows the corresponding thermograms of the CdSe NPs shown in Figure 6.1. The particles were synthesized as described in the experimental section. Figure 6.8a shows the thermogram of the preformed ZB CdSe seeds. The particles are synthesized only with OA capping and the thermograms show only one weight loss of 49.1% starting at 346 °C. We estimated the percentage coverage of OA on the surface of the CdSe spherical NPs by the method mentioned by Katari and coworkers. First, the number of CdSe units in the CdSe NP of radius R nm was calculated by using the bulk density, which does not change significantly with size. We assumed that the area occupied by a molecule of OA was 0.25 nm² as was assumed by Kumar and coworkers. The percentage of OA per NP was calculated as a function of radius of the NP and it varied between 56% and 11% (Figure 6.9). The mean diameter of the ZB spherical particles (Figure 6.1a) is 3.2 nm. According to the calculation the expected weight loss was 46% and the actual weight loss seen was in good agreement with the estimated values.

However the introduction of CTAB into the system changes the profile of thermogram drastically. Figures 6.8b, 6.8c, 6.8d show the thermograms of the CdSe NPs after 1st, 2nd and 4th secondary injections respectively. The particles are anisotropic as can be seen from Figure 6.1. The thermograms show three weight losses at 300 °C, 460 °C and 630 °C respectively. However, with increase in the concentration of CTAB in the system, the third weight loss seems to get prominent and the second weight loss begins to merge with the first. OA in its unbound state shows one weight loss at 222 °C (Figure 6.8f) and CTAB in its unbound state shows a single weight loss at 222 °C (Figure 6.8e). However the thermal behaviour of these surfactants is dramatically different in their
bound state. In CdTe, the tetrapods are grown by using alkyl phosphonic acids as surface ligands\textsuperscript{43}. These molecules are known to stabilize selectively the non-polar facets of hexagonal CdTe\textsuperscript{3,44,45}. This stabilization considerably reduces the growth rate of these facets\textsuperscript{44,46}. Since OA binds to CdSe NPs uniformly in the absence of CTAB, TGA shows a single weight loss. However, the presence of CTAB induces anisotropy forcing OA to bind differently to different axes of the CdSe NPs. The three weight losses observed in tetrapodal CdSe NPs could be attributed to two different kinds of OA binding and to the presence of CTAB on the surface of the CdSe tetrapodal NPs or to three different kinds of OA binding to CdSe tetrapods. The first weight loss could be attributed to the thermal decomposition of OA weakly binding to the (002) axis, which is the fastest growing facet as was observed in Chapter 5. The percentage weight loss in the first step decreases with increase in the size of the particle. TGA hints to the possibility of more than one organic species present on the surface of the CdSe tetrapod NPs. However, the nature and the identity of the organic species could not be specified with certainty because of the close proximity of decomposition temperatures of pure CTAB and OA (Figure 6.8e, f).
Figure 6.8. Thermograms of CdSe NPs (a) Preformed ZB seeds (b) after 1st secondary injection (c) after 2nd secondary injection (d) after 4th secondary injection (e) Thermogram of pure CTAB (f) Thermogram of pure OA.
Figure 6.9. Estimation of percentage of OA on CdSe NPs of different diameters.

The total weight loss decreases with increase in the size of the particles, as would be expected because of the decrease in the surface area of the particles with increase in size, thereby reducing the percentage of surfactants on the surface (Figure 6.8b-d). However it is very intriguing that the total weight loss of the anisotropic NPs is more than the seed spherical CdSe NPs. One would expect to see more percentage weight loss for the small CdSe spherical NPs, because of the higher surface area. A plausible explanation might be the presence of excess OA (bound to the surface and not by a covalent bond), which might not have been washed away by acetone and methanol. However a thorough understanding of how CTAB binds to the surface, its packing efficiency and how it influences the binding behavior of OA is very vital to explain the discrepancy.
6.4 Summary and Conclusions

In conclusion, we showed that CdSe tetrapodal NPs could be grown from preformed ZB CdSe seeds and it proved that the presence of CTAB (quat) is very vital for the formation of tetrapods, in that CTAB causes exclusive nucleation of CdSe in ZB phase. XPS showed the presence of bromide ion. TGA showed the possibility of CTAB present on the surface by the increase in the number of steps of weight loss. EDS was not useful in detecting nitrogen which is an element of low atomic number. No evidence from FTIR could prove the presence of CTAB conclusively. Thus the results were not conclusive enough to prove the presence of quat on the surface of the NPs beyond doubt. This is because of the difficulty in finding the light nitrogen atom. Elemental analysis using a high resolution TEM to focus specifically on the core and the arms of the tetrapods would yield convincing evidence for the presence of the quat on the surface of the CdSe NPs. These findings are a significant step towards understanding the formation mechanism of the CdSe tetrapods and other branched structures of different compositions.
6.5 References


Chapter 7

Conclusions and Recommendations for Future Work

This dissertation focused on the chemistry of synthesis of CdSe NPs of different shapes and sizes and attempted to answer the following questions:

(a) What are the major impacts of using heat transfer fluids as solvents on the synthesis chemistry of CdSe NPs?

(b) How does an electron deficient surfactant influence the synthesis chemistry of CdSe NPs in contrast to the conventionally used electron rich surfactants (e.g. oleic acid and phosphonic acids)?

One of the major findings of the work is the size controllable and cost effective synthesis of CdSe NPs in HT fluids. This synthesis chemistry was extended for CdSe/CdS core/shell quantum dots and CdSe quantum rods. The effect of different HT fluids on QD growth kinetics in terms of solvent effects, i.e., solvent viscosity, CdSe bulk solubility in the solvent and surface free energy, was understood with the help of population balance model. These findings will facilitate the large scale production of CdSe NPs for various applications.

Another important contribution made was the synthesis of CdSe tetrapodal NPs using cationic surfactant ligands (quats), with high morphological and dimensional uniformity. The interaction between the quats and the CdSe was hypothesized to be electrostatic in nature. The use of quats eliminates both selective precipitation as a purification step and the more costly alkylphosphonate ligands for inducing nonspherical shapes. This new synthesis method offers the important advantages of greener chemistry
and scalability, which could further the development of tetrapod-based photovoltaic and
electronic devices.

7.1 Recommendations for Future Work

One of the most formidable problems faced during this research work was to find
out the presence of quats on the surface of the CdSe NPs. One of the ways to do this
might be to use quats tagged with isotopes of easily recognizable elements. This can also
be accomplished by using quaternary phosphonium salts instead of quaternary
ammonium salts. Because it is relatively easier to find the presence of P atom on the
surface of CdSe NPs than the N atoms and the interaction of phosphonium ligands is
expected to be the same as that of the ammonium ligands.

It is extremely vital to study the exact nature of interaction between quats and the
CdSe NPs. This knowledge would immensely help in manipulating the crystal structure
of various different compositions to synthesize tailor made particles for specific
applications. Once the presence of quats on the surface of CdSe tetrapodal NPs is
ascertained, simple \textit{ab-initio} calculations\textsuperscript{1-3} may be performed to understand the binding
energies of quats to various different crystal facets. These findings would help one
understand the origin of anisotropy in CdSe NPs with the introduction of quats.

The phase transfer of quantum dots from organic to aqueous phase has the serious
limitations of lower quantum yield and the higher hydrodynamic diameter of the phase
transferred particles. The lower quantum yield of the phase transferred particles is due to
the surface corruption that happens during the ligand exchange. Because the simultaneous
passivation of anionic and cationic sites is very difficult. However forming inorganic
shell of higher band gap on the CdSe NPs are known to have boosted the quantum yield\(^8\). Hence studying the synthesis of core/shell CdSe tetrapodal NPs would prove to be useful various applications where high quantum yield could be critical.

Understanding the band-edge (HOMO and LUMO) positions of the NPs is crucial for their applications in optoelectronic devices like NP-polymer hybrid PV devices. This is easily studied by cyclic voltammetry (CV)\(^9,12\). Cyclic voltammetry is a dynamic electrochemical method, where current-potential curves are recorded at well-defined scan rates. The technique measures the oxidation (Ionization potential, \(I_p\)) and reduction potential (Electron affinity, \(E_a\)) of the electroactive substance (equations (1) - (3)).

\[
E_{HOMO} = -I_p = -(E_{ox} + 4.71)eV
\]  
\[
E_{LUMO} = -E_a = -(E_{red} + 4.71)eV
\]  
\[
E_{gap} = (E_{ox} - E_{red})eV
\]

This study would allow one to choose a compatible conducting polymer for the synthesis of hybrid nanocomposite materials.

Hybrid organic-inorganic nanomaterials are of great importance because of the possibility of exploiting the best properties of both the components and the possibility of the hybrid nanomaterials featuring new properties that none of the components have. These are the basic components for the development of new and smart nanocomposite materials. The research efforts of Advincula and co-workers\(^13\) focus on fabricating devices based on polymer–NP nanocomposites for electro-optical applications due to their high electrical and thermal conductivities. They constructed a simple PV device by spin coating polymer–CdSe nanocrystals (spherical) on to Indium tin oxide (ITO) coated glass substrates. The power conversion efficiency was found to be 0.29%. They
concluded in their study that by changing the size and shape of the NPs, the conversion efficiency could be improved drastically. A similar study on the tetrapod shaped CdSe NPs of various arm lengths and widths can be expected to improve the power conversion efficiency of the PV devices.
7.2 References


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