INVESTIGATION OF OPTICAL GAIN IN COLLOIDAL HETEROSTRUCTURED SEMICONDUCTOR NANOCRYSTALS

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INVESTIGATION OF OPTICAL GAIN IN COLLOIDAL HETEROSTRUCTURED SEMICONDUCTOR NANOCRYSTALS

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DECLARATION

I hereby declare that this thesis is my original work and it has been written by me in its entirety, under the supervision of Asst. Prof. Chan Yin Thai, (in CHAN LABORATORY (S7-04-04)), Chemistry Department, National University of Singapore, between Aug, 2009 and Aug, 2013.

I have duly acknowledged all the sources of information which have been used in the thesis.

This thesis has also not been submitted form any degree in any university previously.

The content of the thesis has been partly published in:


Name ____________________ Signature ____________________ Date ____________________
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SUMMARY

Due to quantum confinement effect, in semiconductor nanocrystals (NCs) the spacing between the electronic states is much greater than the thermal energy, preventing thermal depopulation of the first few excited states. This should result in a lasing threshold independent of operating temperature, thus circumventing one of the major drawbacks of conventional bulk semiconductor lasers. Along with solution processability, emission wavelength tunability and flexible surface chemistry, there have been numerous efforts to try to achieve stimulated emission in wet-chemically synthesized semiconductor NCs and develop them into lasers. This thesis summarizes our present understanding of the lasing properties of semiconductor NCs in different structure and component based on sol-gel fabricated matrix. Chapter 2 describes the exploration of CdSe/CdS nanotetrapod as high performance silica matrix based optical amplifiers. It has been proven in this chapter that by varying the physical dimensions of the tetrapods allowed for room temperature amplified spontaneous emission (ASE) at wavelengths corresponding to either the CdSe core or CdS arms. In Chapter 3, two-photon pumped amplified spontaneous emission (2ASE) in CdSe/CdS nanorod is demonstrated. A micrometer sized silica sphere is coupled with the nanorod to act as a microresonator exhibiting whispering-gallery-mode lasing. Chapter 4 elaborates a novel group of materials which is alloyed NCs. As one of the examples, CdZnS NCs are studied. The composition dependent emission wavelength, narrow emission spectra and slow Auger process indicate their potential as light emission devices or gain material which emits in blue region. Optical gain study of this alloy CdZnS NCs is discussed in Chapter 5. It is for the first time ASE is discovered from alloyed NCs, and on top of which, all liquid, dynamic laser device was established by adopting microfluidic technology.
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<tr>
<th>Abbreviation</th>
<th>Actual name</th>
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<tr>
<td>HDA</td>
<td>1-hexadecylamine</td>
</tr>
<tr>
<td>ODE</td>
<td>1-octadecene</td>
</tr>
<tr>
<td>HDDO</td>
<td>1,2-hexadecanediol</td>
</tr>
<tr>
<td>APS</td>
<td>3-aminopropyltriethoxysilane</td>
</tr>
<tr>
<td>TEOS</td>
<td>tetraethyl orthosilicate</td>
</tr>
<tr>
<td>AP</td>
<td>1-amino-3-propanol</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction Band</td>
</tr>
<tr>
<td>°C</td>
<td>degree centigrade</td>
</tr>
<tr>
<td>DIPA</td>
<td>Diisooctylphosphinic acid</td>
</tr>
<tr>
<td>DDA</td>
<td>Dodecylamine</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>e</td>
<td>electron</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>eV</td>
<td>Electronvolts</td>
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<tr>
<td>EFTEM</td>
<td>Energy-Filtered Transmission Electron Microscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full with half maximum</td>
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<tr>
<td>GM</td>
<td>Goeppert-Mayer</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>HAADF-STEM</td>
<td>High Angle Annular Dark Field-Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>h⁺</td>
<td>hole</td>
</tr>
<tr>
<td>KHz</td>
<td>Kilo Hertz</td>
</tr>
<tr>
<td>kV</td>
<td>Kilovolts</td>
</tr>
<tr>
<td>LA</td>
<td>Lauric aldehyde</td>
</tr>
<tr>
<td>LED</td>
<td>Light Emitting Diodes</td>
</tr>
<tr>
<td>µ-CP</td>
<td>micro-contact printing</td>
</tr>
<tr>
<td>µM</td>
<td>Micro molar</td>
</tr>
<tr>
<td>µL</td>
<td>Micro litre</td>
</tr>
<tr>
<td>MPA</td>
<td>Multi-photon absorption</td>
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<tr>
<td>MAS</td>
<td>Magic-angle-spin</td>
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<tr>
<td>NCs</td>
<td>Nanocrystals</td>
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<tr>
<td>nm</td>
<td>nanometer</td>
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<td>NRs</td>
<td>Nanorods</td>
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<tr>
<td>NIR</td>
<td>Near Infra Red</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>DDAB</td>
<td>n-dodecylammonium bromide</td>
</tr>
<tr>
<td>HPA</td>
<td>n-hexylphosphonic acid</td>
</tr>
<tr>
<td>ODPA</td>
<td>n-Octadecylphosphonic acid</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>QDs</td>
<td>Quantum Dots</td>
</tr>
<tr>
<td>QYs</td>
<td>Quantum Yields</td>
</tr>
<tr>
<td>RBF</td>
<td>Round ottom flask</td>
</tr>
<tr>
<td>TOAB</td>
<td>Tetraoctylammonium bromide</td>
</tr>
<tr>
<td>TRPL</td>
<td>Time Resolved Photoluminescence</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>TOP</td>
<td>Trioctylphosphine</td>
</tr>
<tr>
<td>TOPO</td>
<td>Trioctylphosphine oxide</td>
</tr>
<tr>
<td>2PA</td>
<td>Two-photon absorption</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>UPL</td>
<td>Upconversion Photoluminescence</td>
</tr>
<tr>
<td>VB</td>
<td>Valence Band</td>
</tr>
<tr>
<td>WGM</td>
<td>Whispering Gallery Mode</td>
</tr>
<tr>
<td>w-</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>zb-</td>
<td>Zinc blende</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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CHAPTER 1

General Introduction
1.1 A General Introduction on Semiconductor Nanocrystals

Colloidal semiconductor nanocrystals (NCs) are a unique class of mesoscopic, inorganic materials that generally lie in the size range of ~1-10 nm, and are composed of between a few hundred to a few thousand atoms.

![Figure 1.1](image)

Figure 1.1. NCs are stabilized in the solvent by long carbon chain capping groups, i.e. octadecylphosphonic acid, trioctylphosphine and trioctylphosphine oxide.

From early studies conducted by Brus at AT&T Bell laboratories and Ekimov at Ioffe Physicotechnical Institute in the early 1980's, these nano-sized particles have now become ubiquitous in nanoscience.1-3 While many methods have since been developed for the synthesis of semiconductor NCs,2,4,5 the hot injection method first introduced by Murray et. al. in 1993 is perhaps the most widely adopted for the production of high quality NCs.6 One of the most striking properties of semiconductor NCs is their exhibition of strong quantum confinement effects which result in size-dependent wavelengths of absorption and emission.7-9 These strong quantum confinement effects, which arise due to the fact that the size of these semiconductor NCs are comparable to or even smaller than their bulk exciton Bohr radius, also result in the NC possessing discrete electronic states at its band edge.10,11 For this reason, these semiconductor NCs have been labelled as “artificial atoms”. In addition, they are capable of exhibiting high quantum yields5 and emission of narrow linewidths,6 as well as high photostability6-9 relative to organic dyes.
Additionally, QDs possess extinction coefficient of $X \times 10^5 \text{ cm}^2\text{M}^{-1}$ at the first absorption maximum, resulting in potentially large absorption cross-sections and therefore excellent luminosity.\textsuperscript{12-15} Owing to their many desirable and intriguing photophysical properties, semiconductor NCs have been intensively investigated over the past two decades, and have in recent years shown great promise in technological applications in areas as diverse as light-emitting diodes (LEDs), photovoltaics, lasers and biological imaging.\textsuperscript{12-15}

1.1 Electronic and Optical Properties of Semiconductor Nanocrystals

Electronic states in bulk semiconductors are usually denoted as bands. The band gap is the energy gap which separates the valence band where the electrons are bound locally to atoms in the crystal from the conduction band where an electron moves through the crystal lattice. When a semiconductor absorbs a photon whose energy is equal to or higher than its band-gap, one electron in the valence band is promoted into the conduction band and leaves behind a net positive charge called a “hole”, thus generating an electron-hole pair or “exciton”.

![Figure 1.2. Simplified illustration of semiconductor band structure and exciton generation process.](image)

It is important to realize that in any material, substantial variation of fundamental electrical properties with reduction in size will be observed when the electronic energy level spacing exceeds $kT$. In semiconductors, this transition occurs for a given temperature at a relatively large size compared to metals, insulators or molecular crystals. This difference can be understood by considering that the bands of solid are centered about atomic energy levels, with the width of the band related to the strength of nearest neighbour
interactions. As cluster size increases, the centre of a band develops first. In metals, where the Fermi level lies inside the band, the relevant energy level spacing is small, the electrical states follows a continuum manner even at nano sizes.\textsuperscript{16} However, in semiconductors, the Fermi level lies in between two bands, such that the edges of the bands dominate the low-energy optical or electronic behaviour and result in size dependent absorption and emission as shown in Figure 1.3.

![Figure 1.3](image.png)

\textit{Figure 1.3.} Schematic illustration of the density of states in metal and semiconductor. Reprinted from ref. 17.

In a semiconductor crystal whose diameter becomes comparable to its exciton Bohr radius (e.g. \(\sim 5.6\) nm for CdSe NC), the exciton is affected by the potential of the external environment leading to significant quantum confinement effects and results in discrete electronic energy levels in all three dimensions.\textsuperscript{11,17} The evolution of electronic states with respect to decreasing size from bulk to a zero dimensional structure is illustrated in Figure 1.4. In the case of a bulk semiconductor, the density of states is continuous; in a one-dimension confined quantum well, more discrete transitions are seen; and in a two-dimension confined quantum wire the trend becomes more prominent. When the quantum structure is further reduced to a three-dimensionally
confined crystal called a quantum dot (QD) this culminates in discrete, atom-like electronic states.

![Figure 1.4](image.png)

**Figure 1.4.** Density of states in one band of semiconductor as a function of dimension. Reprinted from ref. 16.

The discrete electronic states for semiconductor QDs result in their size-dependent absorption and emission\(^6\) that can qualitatively be understood by considering a "particle-in-a-sphere" model in which the carriers are confined to a potential that is infinite at the boundaries as illustrated in Figure 1.5. (a). Solving the energy for the first excited state gives

\[
E_{1s} = \frac{\hbar^2}{8m_{\text{eff}}} a^2
\]

Where \(m_{\text{eff}}\) is the effective mass and \(a\) is the radius of the sphere. It is readily seen that the energy shifts to the red with increasing size (see Figure 1.5 (b)). The energy of the photon emitted from a nanocrystal within the quantum confinement regime is then a direct function of the size of the nanocrystals. Although this simple effective mass model provides an intuitive description on the size dependent optical transitions in QDs, it does not explain the observed long emission lifetimes, luminescence Stokes shifts and strong magnetic field dependence. More elaborate theoretical descriptions that explain these phenomena are described elsewhere.\(^{18}\)
Figure 1.5. (a) Particle in a box model. (b) The size dependent optical properties of NCs.

By simply tuning the size of the NC, which is relatively straightforward via chemical means, emission across a large spectral window may be achieved. For example, in the case of CdSe, emission across most of the visible range (480 - 680 nm) may be achieved by using CdSe NCs of diameters ranging from 3.8 to 13 nm in diameter.\(^6\)
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Figure 1.6. Representative fluorescence spectra of various semiconductor NCs as a function of their size: (a) CdSe, (b) CdTe, (c) InAs and (d) PbSe. For (b) and (c), the corresponding absorption spectra is shown as well. (a) is reprinted with permission from ref. 9, (b) from ref. 19, (c) from ref. 23 and (d) from ref. 26
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Emission at wavelengths beyond the visible range may be achieved by the use of NCs of different materials composition with different band gap energies. Thus emission in the near infrared region can be obtained via the use of CdTe\textsuperscript{19} and InP NCs,\textsuperscript{20-22} near to mid-infrared emission via the use of InAs\textsuperscript{23} and PbS NCs,\textsuperscript{24} and mid-infrared to far-infrared emission via the use of PbSe NCs.\textsuperscript{25,26} A summary of the emission spectra from various semiconductor NCs is given in Figure 1.6.

As shown in Figure 1.6 (b), (c), the absorption profile of NCs is nearly continuous at energies much higher than their band-edge transition. This allows multiple NCs of different emission colour to be excited simultaneously with a single wavelength source. Figure 1.7 is a photograph of CdSe NCs of different sizes in hexane under a single excitation source (\textasciitilde360nm) but showing emission from blue to red.

![Figure 1.7. Photograph of CdSe NCs of different sizes in hexane under a single excitation source.](image)

1.1.2 Synthesis of NCs

From early studies conducted by Brus et al at AT&T Bell laboratories and Ekimov et al at Ioffe Physicotechnical Institute in the early 1980's,\textsuperscript{1}, these nano-sized particles have now become ubiquitous in nanoscience. While many methods have since been developed for the synthesis of semiconductor NCs,\textsuperscript{2-5} the hot injection method first introduced by Murray et. al. in 1993 is perhaps the most widely adopted for the production of high quality NCs.\textsuperscript{6} The synthesis begins with the rapid injection of organometallic reagents into a hot coordinating solvent to produce a temporally discrete homogeneous nucleation event as shown in Figure 1.8 (a). Upon the injection of reagents into the hot reaction pot, the metal organic precursors undergo pyrolysis to form
monomers which subsequently undergo nucleation. The depletion of reagents through the nucleation event and the sudden temperature drop associated with the introduction of the precursors prevents further nucleation from taking place. The reaction then enters the growth phase where the precursors add monomers to the existing nuclei at a lower temperature. Different growth times result in NCs of different sizes. Figure 1.8 (b) is a representative TEM image of size-monodisperse CdSe dots.

Recent developments in the wet-chemical synthesis of various NCs have obviated the use of highly toxic organometallic precursors and hazardous sulphur compounds like Cd(CH$_3$) and (TMS)$_2$S. The non-organometallic synthesis of high-quality NCs uses air-stable cadmium salts such as CdO or Cd(ac)$_2$. These new methods allow for enhanced quantum yields and narrow size distribution for the resulting nanocrystals. In this thesis, cadmium acetylacetonate (Cd(acac)$_2$) was employed to synthesize most of the core CdSe NCs while elemental sulphur as was used as the sulphur source in the case of CdS.

Figure 1.8. (a) an image of the experimental setup for synthesis of CdSe NCs, (b) represented TEM image of monodisperse CdSe NCs, reprinted from ref. 27.

In most cases, wet-synthesized colloidal NCs suffer from poor surface passivation and possess surface trap states. These surface trap states result in fast non-radiative relaxation pathways for photogenerated charge carriers, thus leading to reduced fluorescence quantum yields (QY) typically on the order of ~10-20%. Much experimental work has been devoted to surface modification
in order to improve the luminescence efficiency\textsuperscript{29} colloidal stability of the particles or to develop a reliable processing chemistry.\textsuperscript{30,31} However, it is generally difficult to simultaneously passivate both anionic and cationic surface sites by organic ligands, and dangling bonds will to some extent remain on the surface\textsuperscript{32,33}. In order to improve the fluorescence efficiency as well as the photostability of semiconductor NCs, growth of an inorganic shell (typically a wider bandgap semiconductor) is generally adopted. In particular, for CdSe-NCs the particles are typically overcoated with either CdS\textsuperscript{33,34} or with ZnS\textsuperscript{33,35} to establish a core/shell structure. In such a structure, photogenerated excitons are confined inside the CdSe core whose band gap lies within the band gap of the shell material.

One of the earliest and most widely used techniques for the overcoating of semiconductor NCs to this day was introduced by Hines et. al,\textsuperscript{35} where precursors of the semiconductor shell material are added dropwise to a relatively dilute solution of NC cores at temperatures sufficiently low to prevent homogeneous nucleation of the precursors or Ostwald ripening of the NC cores. Growth of the semiconductor shell can lead to effective surface passivation of the core NC, leading to near unity QYs in the case of CdSe/CdS core-shell NCs,\textsuperscript{36} although QYs in the range of 50-70\% are more common.

\textbf{1.2 Anisotropic hybrid semiconductor Nanocrystals}

Starting with the inception of spherical, single component NCs almost two decades ago, the field of quantum dots has since moved towards more complicated structures ranging from different shapes to multicomponent structures.\textsuperscript{37} The enhancement of current applications and the emergence of newfound ones are expected to take place with the increase in the complexity of NCs that can be fabricated. For example, hybrid NCs based on semiconductor materials of different composition located at specific regions within the same nanostructure would be useful for optoelectronic and photovoltaic applications. Appropriately chosen band offsets of adjacent domains of semiconductors could either trap electron–hole pairs in specific regions of the NCs, thus forcing them to recombine with high efficiency, or facilitate the separation of electrons from holes via a staggered band
alignment. \cite{37} Another application of such complex nanostructures may be in the field of photocatalysis, where the semiconductor moiety may be combined with metals or metal oxides to allow the photogenerated charge carriers to perform redox reactions with high efficiency. \cite{37, 38-41}

In contrast with bulk semiconductors, NCs are dominated by facets that expose different crystallographic planes. Due to the selective adhesion of surfactant molecules to specific facets, the growth kinetics at various crystal facets can be very different, facilitating the growth of highly anisotropic structures such as cubes, wires and star shaped structures (Figure 1.9). \cite{42, 43, 44, 45}

This is usually achieved by mixtures of different surfactant molecules which have different binding affinities for different facets of an initially isotropic crystal. Growth is suppressed on facets where binding affinity with the surfactant is strong and takes place primarily on facets where the binding affinity of the surfactant is weak. In terms of synthesis, it has been discovered that a lot of experimental parameters are important in controlling the size as well as the morphology of the nanoparticles such as the choice of metal precursors, pH, growth temperature, catalysts and capping molecules. The different growth mechanisms of anisotropic NCs via wet-chemical synthetic methods can be summarized as follows:

1) The use of hard templates, which physically confine the size and shape of the growing nanoparticles. \cite{44, 46, 47}

2) The use of capping agents during nanoparticle growth to control its direction and dimension. \cite{44, 48-54}

4) The seeded growth method where unidirectional NC growth can be easily achieved by a seed-mediated reaction mechanism.

5) Oriented attachment where individual nanoparticles attach and fuse along identical crystal faces forming oriented chains. \cite{55-61}
6) The vapor–liquid–solid (VLS) growth. In this mechanism, a solid rod-like nanocrystal grows out of a catalyst particle on a substrate has been exploited in the growth of one-dimensional nanostructures. 62–66

![Figure 1.9. Examples of anisotropic NCs with different shapes: TEM images of (a) CuO nano cubes, (b) PbSe nano wires, (c) PbS nano stars and (d) branched CdSe. (a) is eprinted from ref. 44, (b) from 67, (c) from 45 and (d) from 68.](image)

It is noteworthy that in order to synthesize anisotropic hybrid NCs which is made of more than one material, the lattice constants of the two components should not differ significantly and the interfacial strain should be kept low during the reaction. The formation of a large interface between two materials frequently results in the formation of core–shell NCs in which the symmetry of the inner nanocrystal core is retained upon coverage by a layer of another material. 37 In this thesis, we will focus on semiconductor CdSe CdS core–shell hybrid nanorods and nanotetrapods synthesized via the seeded growth approach.

**1.2.1 CdSe seeded CdS nanorod and tetrapod**

The seeded growth approach is arguably the most widely used method to fabricate monodisperse colloidal semiconductor CdSe seeded CdS nanorods and nanotetrapods. In this method, preformed spherical CdSe NCs serve as
Chapter 1: General Introduction

seeds on which a CdS shell is grown via a second hot injection. Through the use of CdSe seeds of hexagonal (wurtzite) and cubic (zinc blende) structure (as shown in Figure 1.10), nanorods and tetrapods may be obtained respectively.

Wurtzite CdSe can be obtained by reacting cadmium and selenium precursors in the presence of the stabilizing agents trioctylphosphine oxide (TOPO), trioctylphosphine (TOP), and hexadecylamine (HDA) at high temperatures, typically above 300°C. On the other hand, zinc blende CdSe NCs are normally synthesized by reacting cadmium myristate with elemental selenium dissolved in 1-octadecene. The zb-CdSe nanocrystals are allowed to nucleate at ~170 °C and grown at 240°C in the presence of oleic acid and oleylamine as the capping ligands. In the shell-growing process, CdS grows along the (001)-axis of wurtzite CdSe, giving rise to a rod-like structure. In case of zinc blende CdSe seeds, CdS grows simultaneously on all four (111) facets of zb-CdSe, giving rise to a four arm tetrapod-like structure.

Figure 1.10. Cartoon illustration of wurtzite and zinc blende polytypes of CdSe determine the morphology of CdSe/CdS nano-heterostructures. Figure reprinted from Ref. 72.
1.2.2 Optical properties of CdSe seeded CdS nanorod and tetrapod

Typical absorption and emission spectra of CdSe seeded CdS nanorods and tetrapods are displayed in Figure 1.11, where it is readily observed that the absorption is dominated by the CdS shell. The emission on the other hand, originates from radiative transitions within the CdSe core. As such, the CdS shell effectively acts as an “antenna”, capturing photons and transferring its generated excitons to the CdSe core.

Figure 1.11. Absorption (black) and normalized emission spectra (red) of nanorod (left) and tetrapod (right). Insets are typical TEM images of CdSe/CdS nanorod and nanotetrapod.

This process is highly efficient, with holes being transferred at sub picosecond scale from CdS to CdSe.\textsuperscript{73} The large CdS shell dramatically increases the molar absorptivity. Tetrapods of CdSe/CdS can possess extremely large linear absorption cross-sections of $\sim 1.5 \times 10^8 \text{ M}^{-1} \text{ cm}^{-1}$ at 350 nm.\textsuperscript{74} Indeed, due to their unique tetrahedral-like arrangement, the tetrapod arms can capture photons from a wide range of incident angles and polarization more effectively than nanorods of the same volume, thus leading to a very large absorption cross section of the entire nanostructure.\textsuperscript{74}

The band gap of CdSe relative to CdS generally results in a Type I band alignment in which the band gap of CdSe is encompassed within that of CdS. In such a case, both electrons and holes generated in CdS at the vicinity of the core would have a tendency to energetically relax into the CdSe core states provided they are not fully occupied. In several reported cases for nanorod and nanotetrapod, however, quasi Type II band alignment was observed if the core...
is sufficiently small such that the conduction band offset between the core and arm-like shell is minimal as illustrated in Figure 1.12. In this condition, the electron wavefunction is delocalized over the whole arm volume but the hole wavefunction is confined to the CdSe core.

**Figure 1.12.** Quazi-Type II band alignment of a tetrapod with small core size.

The unusual architecture of these CdSe seeded CdS shell heterostructures has provide new possibilities for wave function engineering and tailoring optical properties of semiconductor nanocrystals. For example it was reported by Kraus et. al. that in the presence of an electric field, the excitons of CdSe/CdS nanorods can be stored for up to 105 times their natural lifetime, which has implications for optical memory applications.\(^7\) The relative band alignment between the conduction bands of CdSe and CdS was initially a subject of debate which warranted further detailed studies. But it has been proven that the band alignment is extremely important for semiconductor NCs laser applications which will be elaborated later in this thesis.

### 1.3 Alloy Nanocrystals

As described in part 1.2, it is essential to engineer the band gap of semiconductor NCs in order to utilize their unique optoelectronic properties. In this respect, anisotropic structures have shown to be prominent candidate for band gap engineering. Another means of tailoring the semiconductor band gap is by changing the particle composition via control of constituent
stoichiometries. This can be achieved by creating an alloy of two semiconductors with different energy gaps. An increase in band gap energy is generally observed with increasing content of the wider band gap semiconductor even at a constant size. This technique should not be confused with doping (i.e., the intentional introduction of impurity atoms into a semiconductor). While impurity doping is a process chemically related to alloying, it does not really shift the band gap of the host semiconductor but modifies the band structure by creating electronic energy levels (dopant states) within the band gap that allows for lower energy light emission.

Based on distribution of different semiconductor components, alloyed semiconductor nanocrystals can be classified as (1) a homogeneous alloy with a uniform internal structure or (2) a gradient alloy with a gradient internal structure, where the alloy composition varies in different parts of the nanocrystal. These are different from the core-shell structure mentioned earlier, where a layer of another semiconductor is grown on the surface of a core semiconductor. Figure 1.13 schematically shows the difference between nanocrystals having a homogeneous, gradient, and core-shell structure.

Depending on the number of component elements that constitute the alloy, they can be classified as either ternary (3 elements) or quaternary (4 elements). Ternary alloys are formed when the parent composition are two binary systems with either a common anion or cation. For instance, alloying of MA and M'A produces M\textsubscript{x}M'\textsubscript{1-x}A, where M and M' are two different cations and A is the common anion. Examples are Zn\textsubscript{x}Cd\textsubscript{1-x}S, Zn\textsubscript{x}Cd\textsubscript{1-x}Se where sulphur or selenium is the common anion. Common cation alloyed composition, MA\textsubscript{x}A'\textsubscript{1-x}, is formed through alloying of MA and MA', where M is the common cation while A and A' are two different anions. Examples of common cation alloys are CdSe\textsubscript{x}Te\textsubscript{1-x}, CdS\textsubscript{x}Se\textsubscript{1-x}, CdS\textsubscript{x}Te\textsubscript{1-x} and PbS\textsubscript{x}Se\textsubscript{1-x}.

Alloying of two binary systems with no common elements gives rise to quaternary alloys. Due to lattice mismatch of two different semiconductors, examples of quaternary alloys formed by the wet-chemistry method are very limited. Although this unique class of semiconductor materials have the potential to replace conventional NCs in specific application areas, there is
little known in the literature on their structure-property relationship. In this thesis, we attempt to characterize the structural and optical properties of Zn\textsubscript{x}Cd\textsubscript{1-x}S alloy NCs. Their superiority as optical gain materials in comparison to conventional NCs is described in Chapter 4.

![Figure 1.13.](image)

1.3.1 Synthesis and Property

Most of the wet-chemistry synthesis of alloy NCs is based on a hot-injection method similar to the formation of wurzite CdSe. For example, in the case of CdAA’ (i.e. CdS\textsubscript{x}Se\textsubscript{1-x}\textsuperscript{78}, CdS\textsubscript{x}Te\textsubscript{1-x}\textsuperscript{79} and CdSe\textsubscript{x}Te\textsubscript{1-x}\textsuperscript{76}) NCs, the synthetic procedure involves the rapid injection of a premixed solution containing stoichiometric amounts of the chalcogenide precursors into a solution of Cd(II) precursor (usually CdO) in high-boiling coordinating and noncoordinating solvents at \(\sim 300\) °C followed by growth at a lower temperature. Depending on the amount of Cd used in the reaction, NCs can either have a homogeneous or gradient structure. In order to form high quality, monodispersed alloyed NCs, a two-pot hot-injection method was introduced. In the synthesis of Zn\textsubscript{x}Cd\textsubscript{1-x}Se, for example, pre-formed CdSe NCs are dispersed in a coordinating solvent, upon which ZnEt\textsubscript{2} and TOPSe are swiftly injected at high temperature.\textsuperscript{81} The Cd to Zn ratio may be tuned by varying the molar ratio of the corresponding precursors.

It is easy to understand that hot-injection-based synthetic methods are not suitable for large-scale production of high quality QDs with narrow size
distribution. In order to separate the nucleation and growth stages for tight size distribution, the hot-injection approach requires rapid injection of a precursor solution, fast decrease of the reaction temperature right after the injection, and strong stirring for efficient mass transfer; the realization of these requirements is not easy at large-scale production. Accordingly, the development of non-injection synthetic route is in demand. Gradient ZnCdS NCs has been reported by Quyang et.al. using a one-pot approach. In this method Zn(St)₂ and Cd(OA)₂ are mixed together in ODE and heated up slowly to 240°C upon which the NCs starts to nucleate and grow.

Alloyed nanocrystals can exhibit unusual optical properties as compared to their binary counterparts; In particular, without changing their size, they can exhibit various emission wavelengths via modification of their internal composition. As in the case of the widely studied CdSe NCs, it is always difficult to obtain blue emission since the particle size required is extremely small (< 2nm). NCs with such small sizes are not stable and undergo Ostwald ripening easily. This consequently leads to a broad emission FWHM and low quantum efficiency. In contrast, alloying CdSe with ZnSe produces CdₓZn₁₋ₓSe NCs whose emission can be tuned to cover the whole blue to green emission window with high quantum yield and narrow emission FWHM.

It is known that the Vegard’s Law for bulk and thin film alloy materials is a linear function: \[ E_{\text{alloy}} = xE_A + (1 - x)E_B \], where \( x \) is the mole fraction, \( E_A \), \( E_B \), and \( E_{\text{alloy}} \) are the band gap energies of pure A, pure B, and the alloy \( A_xB_{1-x} \), respectively. However, this linear relationship is not necessarily obeyed in several classes of semiconductor alloys. It is observed that homogeneously alloyed CdTeSe nanocrystals emit at considerably lower energies than similarly sized binary CdSe and CdTe. This nonlinear relationship between the band gap energy and the composition is known as “optical bowing”. Similar observations are also reported for other alloy NCs like ZnₓCd₁₋ₓS.
Figure 1.4. (a) Plots of the absorption onset energy (in eV) as a function of tellurium content, (b) PL spectra of CdSe, CdTe and CdSeTe showing the prominent optical bowing effect. Figure reprinted from ref. 77.

1.4 NCs as optical gain material

Bulk semiconductor lasers were first developed in 1962 by Robert N. Hall, and this landmark achievement was followed years later by the inception of lasers based on molecular beam epitaxy (MBE) or chemical vapour deposition (CVD) grown semiconductor quantum wells, quantum wires and quantum dots. Efforts to fabricate semiconductor gain media with lower dimensionality were fuelled by theoretical predictions suggesting lower and temperature insensitive thresholds, higher peak gains and narrow spectral gain profiles.85,86

As mentioned in the previous section, in the case of zero dimensional semiconductor NCs whose physical size is comparable to or smaller than its bulk Bohr exciton radius, the induction of strong quantum confinement effects
causes its density of states to be more discrete and the energy levels spaced further apart, with the oscillator strength concentrated into just a few transitions. \(^\text{16}\) In such a system, the spacing between the electronic states is much greater than the thermal energy, preventing thermal depopulation of the first few excited states. This should result in a lasing threshold even less temperature sensitive than what was observed in quantum well lasers, \(^\text{87}\) thus circumventing one of the major drawbacks of conventional bulk semiconductor lasers. Moreover, it is anticipated that the discrete, delta function-like density of states yields a much higher peak gain and narrower gain profile compared with a bulk semiconductor as illustrated in Figure 1.15. \(^\text{85}\)

![Gain spectra](image)

**Figure 1.15.** Gain spectra calculated for a Ga\(_{0.47}\)In\(_{0.53}\)As/InP 10x10 x10 nm\(^3\) cubic quantum box, 10x10 nm\(^2\) quantum wire, 10 nm thick quantum well film, and bulk crystal at T = 300 K. The quantum box exhibits the narrowest gain profile and highest peak gain. Re-print with permission of reference 85.

Added benefits of an NC-based optical gain medium include solution processability, flexible surface chemistry which allows for convenient incorporation into a wide variety of optical cavities, and ease of emission wavelength tunability by simply varying the size of the NCs. These advantageous properties motivated efforts in the field to try to achieve
stimulated emission in wet-chemically synthesized semiconductor NCs and develop them into lasers.

![Diagram of stimulated emission and gain conditions in colloidal semiconductor NCs.](image)

**Figure 1.16.** Cartoon illustration of the transparent and optical gain conditions in colloidal semiconductor NCs.

Unfortunately, many of the predicted advantages of colloidal NCs as gain media, such as low pump thresholds, were not realized due to their short-lived gain state. Owing to its doubly-degenerate first excited state, gain in NCs such as CdSe can only be achieved when two photons are absorbed to yield two electron-hole pairs, commonly known as a biexciton (as illustrated in **Figure 1.16**). This results in a condition in which an incoming photon resonant with the excited state transition does not get absorbed but rather stimulates the emission of an additional photon, thus giving rise to optical amplification. Despite the recognition that biexcitons were needed to produce gain in quantum confined NCs, efforts to utilize NCs as optical gain material
were unsuccessful until 2000, when Amplified Spontaneous Emission (ASE) was first demonstrated in a close-packed film of CdSe NCs at 80K, as depicted in Figure 1.17 (a).\cite{8} The difficulty in achieving light amplification in NCs was attributed to an unanticipated non-radiative Auger recombination process which essentially dominated the recombination dynamics of the biexciton. Unlike in bulk semiconductors, the Auger recombination process in strongly quantum confined NCs is highly efficient and can briefly be described as follows: in a strongly quantum confined system such as NCs, coulombic interaction between the two excitons is strong. This causes non-radiative recombination of one of the excitons and the energy is transferred to the other exciton, thus annihilating the gain condition.\cite{8} (as shown in Figure 1.17 (b))

![Figure 1.17. (a) ASE demonstrated from close pack CdSe film at 80K for the first time. Reprinted from ref. 88. (b) Non-radiative Auger recombination process in a strongly quantum confined NC due to coulombic interactions between the two excited carriers. One of the excitons recombines non-radiatively and transfers its energy to another exciton, thereby promoting it to a higher energy level.](image)

A comprehensive account of the Auger recombination processes and optical gain dynamics arising from multie excitons in NCs may be found in a number of recent reviews\cite{89, 90} and will not be described in detail here. The seminal work in 2000 showed that to overcome the non-radiative Auger recombination process and achieve optically pumped stimulated emission in NCs, it is important to have a sufficiently high volume fraction of NCs of ~ 1 % and a pulsed excitation source that is able to generate a large number of biexcitons within their extremely short lifetime, which for CdSe NCs is on the order of
The realization of these requirements led to the demonstration of ASE and lasing in a number of other semiconductor NC systems, such as CdSe/ZnS, CdSe/CdZnS, CdSe/CdS, CdS/ZnS, ZnSe/CdSe, PbS, and PbSe.

1.5 Brief introduction of sol-gel chemistry

Sol-gel science may be defined as the study of colloidal particulates or monolithic structures of metal oxides formed from the hydrolysis and subsequent condensation of metal alkoxides or salts. The term "sol-gel" essentially alludes to the process of transitioning from a solution to gel-like phase which describes well the formation of metal oxides from metal alkoxides.

\[
\text{RO-M-OR + H}_2\text{O} \rightleftharpoons \text{RO-M-OR} + \text{OH}^- + \text{ROH}^- \quad (1)
\]

\[
\text{RO-M-OR + HO-M-OR} \rightleftharpoons \text{RO-M-O-M-OR} + \text{ROH}^- \quad (2)
\]

\[
\text{RO-M-OH + HO-M-OR} \rightleftharpoons \text{RO-M-O-M-OR} + \text{H}_2\text{O} \quad (3)
\]

**Scheme 1.1.** Generalized scheme of the sol-gel process. The formation of the M-OH bond takes place via a hydrolysis reaction whereas the formation of the metal oxide bond takes place via a condensation reaction.

The “sol” is a colloidal suspension of clusters in a liquid, upon which a gel is formed when these clusters grow into macroscopic dimensions such that it physically extends throughout the solution. A general reaction scheme for
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the chemical synthesis of sol-gel derived compounds is shown in Scheme 1.1, where the mechanism of formation of a metal oxide bond from metal alkoxide precursors takes place via hydrolysis of the alkoxide moiety followed by a condensation reaction which eliminates an H$_2$O or ROH group. These reactions typically take place in a solution containing trace amounts of water and an alcohol, such as ethanol or methanol. While such reactions are typically carried out at room temperature, annealing at elevated temperatures is often used to drive the reactions to completion and obtain a higher degree of crystallinity.\textsuperscript{117,118}

Owing to the fact that many sol-gel derived metal oxides (such as silica or titania) have low absorption in the visible range, are relatively chemically inert, can be synthesized under mild conditions and possess the flexibility of being shaped into various geometries, it was quickly realized that such metal oxides could be exploited as host matrices for chromophores to isolate them from the external chemical environment. For example, morphologically smooth silica films have been exploited as optical waveguides,\textsuperscript{119} while size-monodisperse silica microspheres obtained via the well-known Stöber process have been utilized for photonic applications\textsuperscript{120} or in biomedical diagnostics, as will be discussed below. The formation of either microspheres or thin films depend strongly on the kinetics of the reaction, which in the case of silica was found to be highly influenced by factors such as pH.\textsuperscript{121} It is thus imperative that the optical properties and colloidal stability of the semiconductor NCs that are to be incorporated into these matrices are not drastically affected by the specific pH requirements of the different sol-gel derived structures.

1.6 Incorporation of semiconductor NCs into sol-gel derived optical microcavities

Although the close-packed film of CdSe NCs had volume fractions as high as 20%, which was more than sufficient to establish light amplification, they were thermally and structurally unstable towards the intense pulsed excitation needed to generate biexcitons. This may be understood from the fact that the NCs in close-packed films are held together by relatively weak Van der Waals
interactions and cannot undergo moderate to large pump fluences, which is not pragmatic for use as an optical gain medium. A much more robust route to NC-based optical amplifiers was first introduced by Sundar et al., who managed to incorporate CdSe/ZnS NCs into a sol-gel derived titania waveguide with volume fractions of 10-12%. This allowed for ASE to be readily achieved at room temperature, since higher pump intensities did not result in noticeable damage to the NC-titania film. Because the NCs were well-embedded within the titania matrix, additional layers of titania containing NCs with different wavelengths of emission could be successively deposited without significantly perturbing the previous layers. This would certainly not be possible in the case of close-packed films, since the deposition of a secondary layer would inevitably expose the underlying NC film to a non-polar solvent, thereby dissolving its structural framework.

Figure 1.18. A diagrammatic representation of a multilayer structure comprising of green and red-emitting CdSe/ZnS NCs in titanium dioxide layers (Upper image), and multi-wavelength ASE spectra at 80K from the multilayer structure. Reprinted from ref. 92.
Figure 1.19. Lasing spectra from a multilayered NC-titania film bearing a distributed feedback structure in each active (green and red-emitting) layer. Reprinted from ref. 94.

**Figure 1.18** illustrates how the consecutive deposition of NC-titania layers (with a buffer layer in between) can lead to a device capable of supporting ASE at two distinct wavelengths. It was found that the sol-gel matrix was also amenable to pattern transfer via imprinting with a pre-patterned surface. By using soft-lithography techniques to emboss the individual NC-titania active layers with a distributed feedback (DFB) structure, lasing at two distinct wavelengths could be achieved,94 as shown in **Figure 1.19**. The flexibility of the deposition process with NC-titania sols could also be extended to 3D optical microcavities such as polymer or silica microspheres. Snee et al. employed methods similar to the deposition of NC-titania on planar substrates and developed a spin-coating procedure which involved both microspheres and the NC-titania sol.100 This facile technique was able to yield hundreds of NC-titania coated microspheres (and hence optical resonators) on a substrate with a single spin-coat process, as depicted in **Figure 1.20 (a)**. **Figure 1.20 (b)** illustrates the Whispering Gallery Mode (WGM) lasing which results from optically pumping an individual NC-titania coated microsphere. These various
NC-titania optical resonators showcase the utility of sol-gel titania as a host matrix to interface the NCs with a microcavity feedback structure.

The chemistry of the NC incorporation process into sol-gel derived matrices is critical to the success of achieving ASE or lasing in these composites and deserves elaboration. In the method described by Sundar et al., the native ligands from hydrophobic as-synthesized CdSe/ZnS NCs are replaced with tris-hydroxypropylphosphine (THPP), which confers the NCs with hydroxyl functional groups. These functional groups serve two purposes: (i) to disperse the NCs in ethanol for the sol-gel process to take place, and (ii) to form covalent linkages with the titania network via condensation reactions between the OH and Ti-OH chemical groups. The incorporation of CdSe/CdZnS NCs into the titania matrix was carried out by the use of both 5-amino-1-pentanol (AP) and THPP as surface ligands for the NCs to render them compatible with the sol-gel process. In general, the use of different NCs would require modifications to the sol-gel incorporation procedure. From our own experience, the surface chemistry of the as-synthesized NCs is critical to the successful application of the protocols detailed in these reports. For example, a CdSe NC which is synthesized using trioctylphosphine oxide

Figure 1.20. (a) Fluorescence optical microscope image of NC-titania coated silica microspheres about 6.85 μm in diameter. (b) Fluorescence (blue solid line) and lasing (red solid line) spectra from an individual sphere in (a). reprinted from ref. 100.
(TOPO) and trioctylphosphine (TOP) is more likely to be compatible with these protocols than a CdSe NC which is synthesized using octadecene (ODE), TOP and oleylamine (OA). This may be attributed to differences in the efficacy of ligand exchange between the native ligands of the as-synthesized NCs and the surface ligands required for compatibility with the sol-gel process. Thus even NCs of the same composition which were synthesized using different solvents and surfactants would yield contrasting results when subjected to the same sol-gel incorporation process. It is noteworthy that a method was developed by Petruska et al. which circumvents the ligand exchange process by introducing an amphiphilic polymer around the as-synthesized NCs. The hydrophobic interior of the amphiphilic shell interacts with the native hydrophobic ligands of the NC while the hydrophilic exterior of the polymer allows the particle to be dispersed easily in ethanol, thus making it compatible with sol-gel processes. This approach is appealing in that it can potentially be used to incorporate hydrophobic NCs of different composition into a sol-gel matrix.

The structural and thermal stability of the NC-titania matrix towards very large pump fluences was aptly demonstrated by the achievement of ASE from multiexcitonic states higher in energy than that of the biexciton state. In the case of CdSe under pump intensities high enough to produce an average of 4 electron-hole (e-h) pairs per NC per pulse, multiexciton ASE from both the 1S3/2 – 1Se and 1P3/2 – 1Pe transitions were observed, as illustrated in Figure 1.2. This important observation soon led to the development of a dual wavelength NC-based laser by integrating the NC-titania matrix with a DFB structure, and it was demonstrated that room temperature lasing at two distinct wavelengths from a single active NC layer could be achieved, as exemplified in Figure 1.22. Aside from being able to withstand high peak intensities from an ultrafast pulsed pump source, the thermal resilience NCs in sol-gel derived titania matrices is also fairly remarkable, with minimal declines in lasing intensity despite being continuously pumped for more than 1 hour. This is certainly an important attribute if such composites are to be utilized as operational gain media.
Figure 1.21. Dual wavelength ASE (stars) and photoluminescence (squares) spectral of an optically pumped 5.2 nm radius CdSe/ZnS NC doped titania thin film. Reprinted from ref. 95.

Figure 1.22. Lasing spectra of a DFB CdSe/ZnS NC-titania laser when the grating stop band is matched with the biexcitonic ASE peaks. Lasing from the 1Pe electronic state (right) at a different detection angle than the peak at 673 nm which originates from the 1Se electronic state (left). Reprinted from ref. 96.

Further improvements to the performance of NCs as optical gain materials were made by employing different sol-gel derived materials as the
host matrix. For example, it was discovered that the NC-titania composites suffered from structural and photophysical degradation when exposed to polar solvents due to the unavoidable presence of unreacted titanium alkoxide moieties.\textsuperscript{101} By incorporating the NCs in high volume fraction into a silica matrix, it was demonstrated that lasing in the presence of water or methanol could be achieved,\textsuperscript{101} thus suggesting that silica may be a more suitable host matrix than titania for NC-based lasers operating under ambient conditions. Jasieniak et al. also showed that sol-gel derived zirconia can serve as a more robust waveguide for NCs due to its retention of more of the original NC quantum yield and its exhibition of a longer term photostability than that of titania.\textsuperscript{105}

1.7 Thesis Outline

Chapter 2 describes the exploration of CdSe/CdS nanotetrapod as high performance silica matrix based optical amplifiers. It has been proven in this chapter that by varying the physical dimensions of the tetrapods allowed for room temperature amplified spontaneous emission (ASE) at wavelengths corresponding to either the CdSe core or CdS arms. In Chapter 3, two-photon pumped amplified spontaneous emission (2ASE) in CdSe/CdS nanorod is demonstrated. A micrometer sized silica sphere is coupled with the nanorod to act as a microresonator exhibiting whispering-gallery-mode lasing. Chapter 4 elaborates on the structural and optical properties of a novel group of materials, namely CdZnS alloyed NCs. The composition dependent emission wavelength, narrow emission spectra and slow Auger recombination processes indicate their potential as light emission devices or gain material which emits in the blue. Optical gain study of the alloyed CdZnS NCs is discussed in Chapter 5. It is shown for the first time ASE from these alloyed NCs, with thresholds sufficiently low to be incorporated into an optofluidic laser device.
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1.8 References

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CHAPTER 2

Amplified Spontaneous Emission from CdSe seeded CdS Nanotetrapods Incorporated Sol-gel Matrix
Chapter 2: Amplified Spontaneous Emission from CdSe seeded CdS Nanotetrapods Incorporated So-gel Matrix

2.1 Introduction

Wet-chemically synthesized colloidal semiconductor nanocrystals (NCs) are desirable as optical gain media due to their size dependent emission wavelengths, ease of fabrication and flexible surface chemistry which facilitates incorporation into an optical feedback device of various configurations.\textsuperscript{1–3} Early attempts to achieve stimulated emission via close-packed films of NCs required low temperature and high pump fluences since such films generally suffer from low optical quality, poor heat dissipation, and consequently short operational device lifetimes.\textsuperscript{4,5}

On the other hand, the incorporation of spherical core-shell colloidal NCs such as CdS/ZnS and CdSe/CdZnS into sol-gel derived matrices facilitated room temperature amplified spontaneous emission (ASE) and lasing with continuous operability over a time scale of hours, thus providing a more pragmatic route to NC-based optical amplifiers.\textsuperscript{1,6} Despite the enhanced thermal resilience afforded by the sol-gel derived host matrix, however, the excitation pump intensities and volume fraction of NCs required to attain ASE remained expectedly high since the thresholds are dominated by the Auger recombination processes stemming from the intrinsic optoelectronic properties of the NCs.\textsuperscript{5,7,8} In order to further enhance the performance of NC-based sol-gel derived composites for optical gain applications it is clear that NCs with more salient optical properties and reduced Auger recombination rates need to be employed.

Recent studies on CdSe seeded CdS nanotetrapods synthesized via seeded growth techniques have shown that they can possess extremely large linear absorption cross-sections ($\varepsilon \approx 1.5 \times 10^8$ M$^{-1}$cm$^{-1}$ at 350 nm) and relatively high quantum yields of up to $\approx 60\%$.\textsuperscript{9} Indeed, due to their unique tetrahedral like arrangement, the tetrapod arms can capture photons from a wide range of incident angles and polarization more effectively than nanorods of the same volume, thus leading to a very large absorption cross-section of the entire nanostructure. Radiative recombination typically takes place at the CdSe core at the centre of four rod-like CdS arms, and extensive leakage of the CdSe electron wavefunction into the CdS shell results in a dramatic redshift in its optical spectra relative to the original CdSe NC seed.\textsuperscript{9} The
ensuing reduced spatial overlap between the CdSe electron and hole wavefunctions is expected to yield suppressed Auger recombination rates, as was previously observed in a related system of CdSe seeded CdS nanorods exhibiting relatively long biexciton lifetimes of ~ 300 ps.\textsuperscript{10} While it has been suggested that CdSe seeded CdS nanotetrapods hold promise as good NC-based optical gain materials,\textsuperscript{9,11} however, ASE from such structures has to the best of our knowledge not yet been demonstrated. In this work we synthesize and incorporate ZnS overcoated CdSe seeded CdS nanotetrapods into a solvent resistant and thermally stable sol-gel derived silica matrix, and demonstrate room temperature ASE from the resulting nanotetrapod-silica composites.

\section{2.2 Experimental}

\subsection{General methods}

Unless stated otherwise, all the reactions were conducted in oven-dried glassware under nitrogen atmosphere using standard Schlenk line techniques. All the chemicals were used as received without further purification. All solvents were used as received.

The CdSe seeded CdS tetrapods used in this study were synthesized using the seeded growth approach of Manna et. al.\textsuperscript{12}

\subsection{Chemicals}

Cadmium oxide (CdO, 99.99%), oleic acid(OA, 99%), n-hexylphosphonic acid (HPA, 99%), 1-octadecene (ODE, 90%), trioctylphosphine oxide (TOPO, 99%), trioctylphosphine oxide (TOPO, 90%), sulfur (S reagent grade, powder), di-ethylzinc (99%), bis(trimethylsilyl) sulfide ((TMS)\textsubscript{2}S, 99%), 3-aminopropyltrimethoxysilane (APS, 99%), tetraethoxysilane (TEOS) were purchased from Sigma Aldrich, trioctylphosphine (TOP, 97%), 5-amino-1-pentanol (AP, 97%) was purchased from Alfa Aesar.

\subsection{Synthesis of spherical zb-CdSe seeds}

Monodispersed zb-CdSe was synthesized according to previously reported methods.\textsuperscript{21} In a 50 mL three-neck round bottom flask 0.3 mmol CdO, 0.6 mmol myristic acid and 5 mL of 1-ODE were degassed at 90 °C for about 1 hr. The solution was then heated to 250 °C for ~10-15 min to yield a clear
solution, followed by the addition of 12 mL of ODE before cooling to 90 °C to degas for another 1 hr. Upon cooling to room temperature, 0.012 g (0.15 mmol) of 100 mesh Se powder (99%) was added to the reaction mixture and degassed at 50 °C for ~20 min. Upon heating to 240 °C under N₂, a color change from colorless to yellow at ~150 °C and then to orange-red color upon reaching 240 °C were observed, signifying the formation of zb-CdSe nuclei. A degassed mixture of 0.5 mL oleic acid and 0.5 mL oleylamine in 2 mL of 1-ODE was subsequently added dropwise to the reaction mixture. As-synthesized zb-CdSe NCs were precipitated out from the growth solution by adding acetone, and were subsequently allowed to undergo two more cycles of re-dispersion and precipitation in toluene and methanol respectively.

The processed CdSe seeds were dissolve in minimum amount of toluene and the concentration was determined by measuring the absorption at 350 nm, whose molar absorptivity is known.

**Synthesis of CdSe seeded CdS nanotetrapods**

2.65 g TOPO (99%), 0.05175 g CdO, and a mixture of OA, HPA were degassed at 150 °C for about 1.5 hr in a 50 mL three-neck round bottom flask. The reaction mixture was then heated to 350 °C under N₂, whereupon the solution turned from reddish brown to colorless. Separately, a mixture of S, TOP and CdSe seeds was derived by first dissolving a predetermined amount of S in TOP at 50 °C before adding $2 \times 10^{-8}$ mol CdSe. Upon reaching 350 °C, an additional 1.8 mL of TOP was added, and the temperature was allowed to recover to 350 °C before the mixture of S, TOP and CdSe was swiftly injected. The temperature was again allowed to recover to 350 °C and the anisotropic CdS arm was grown at this temperature for 8 minutes. The heating mantle was then removed and the solution was allowed to cool to 80 °C. As synthesized CdSe seeded CdS nanotetrapods were then processed by repeated cycles of precipitation in methanol and re-dispersion in toluene.

**Surface coating of CdSe seeded CdS nanotetrapod**

10g TOPO (90%) and 0.1g HPA were degassed at 150°C for 1hr. The mixture was allowed to cool down to 80°C under nitrogen before tetrapod-toluene solution was added. Toluene was evaporated under vacuum at the same temperature before increase the temperature to 140°C, upon which a mixture
of 0.065g diethylzinc, 0.114g (TMS)$_2$S and 1mL TOP was dripped into the 3-neck RBF slowly under N$_2$ within 30min. The temperature was then cooled down to 100°C and maintained at that temperature for overnight. Overcoated CdSe seeded CdS nanotetrapods were then processed by repeated cycles of precipitation in methanol and re-dispersion in hexane.

**Nanotetrapod sol-gel film fabrication**

The route employing 3-aminopropyltrimethoxysilane (APS) as silica precursor was adopted from a previously reported method with slight modifications.\(^6\) Processed ZnS overcoated CdSe seeded CdS tetrapods (80 mg) were dissolved with 100μL amino pentanol (AP) and 200 μL ethanol. This afforded a clear solution of NCs into which 40 μL APS and 10 μL TEOS was added and stirred vigorously for ~1 min. The resultant viscous liquid was allowed to pass through a 0.2 μm syringe filter and spin-coated onto a pre-cleaned glass substrate, yielding a clear, smooth film. The film was subsequently annealed on a hotplate for 5 min at 150°C, upon which no cracking or obvious degradation of the film quality was observed.

**TEM characterization**

JEOL JEM 1220F (100 kV accelerating voltage) microscope was used to obtain bright field TEM images of the nanoparticles. For TEM sample preparation, the processed nanoparticle solution was dropped onto a 300 mesh size copper grid covered with a continuous carbon film. Excess solution was absorbed by a filter paper underneath and the copper grid was dried under ambient condition.

**Optical characterization**

Room temperature UV-visible absorption spectra were measured with an Agilent 8453 UV-Visible spectrophotometer. Photoluminescence (PL) spectra were collected with a Shimadzu RF-5301PC Spectrofluorophotometer.

For the ASE measurement, the excitation source was a Coherent Legend regenerative amplifier (150 fs, 1 kHz, 800 nm) that was seeded by a Coherent Mira oscillator (100 fs, 80 MHz). 400 nm wavelength laser pulses were obtained by using a beta barium borate (BBO) doubling crystal and focused by a cylindrical lens (with focal length f = 20 cm) to a stripe (with dimensions of ~5.5 mm × 0.5 mm). The sample slides were aligned perpendicular to the
excitation stripe. The emission from the film edge was collected in a lateral configuration by a pair of lenses focused onto an optical fiber coupled to a spectrometer (Acton, Spectra Pro 2500i) and detected by a charge coupled device (Princeton Instruments, Pixis 400B CCD camera).

The time-resolved photoluminescence (TRPL) was detected by an Optronis Optoscope streak camera system which has an ultimate temporal resolution of ~10 ps when operated at the shortest time window of 330 ps. The TRPL measurements were typically performed with a time window of ~10 ns and a time resolution of ~300 ps.

Room temperature modal gain measurements were carried out using a standard Variable Stripe Length (VSL) method. The excitation stripe and emission collection set-up was the same as described above. The sample is optically excited by an intense laser beam, which is focused by a cylindrical lens to form a narrow stripe on the sample film. The length of the stripe was varied through an adjustable slit actuated by a micrometer which was placed at the focal line of the cylindrical lens.

2.3 Results and Discussion

The CdSe seeded CdS tetrapods used in this study were synthesized using the seeded growth approach of Manna et. al.,\textsuperscript{12} with the distinction that a mixture of OA and HPA was used as surfactants instead of octadecylphosphonic acid (ODPA) and HPA. As illustrated in the Transmission Electron Microscope (TEM) images in Figure 2.1 this allowed for monodisperse tetrapods of various arm dimensions with yields as high as 90% (with respect to nanorod, bipod and tripod by-products) to be obtained, which may be attributed to the stabilization of the zinc blende phase of CdSe by OA.\textsuperscript{13} Initial attempts to directly incorporate the as-synthesized CdSe seeded CdS tetrapods into sol-gel derived silica films proved futile as the tetrapods could not be ligand-exchanged at elevated temperatures with hydrophilic molecules such as AP and be rendered dispersible in ethanol. This may be understood from the high binding affinity of alkylphosphonic acids to Cd in cadmium chalcogenide NCs,\textsuperscript{14} making the surface intractable to ligand-exchange processes under mild conditions. In order to circumvent this issue, the tetrapods were overcoated
with ZnS in the presence of trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO) at a relatively low temperature of ~130 °C since it was often observed that a significant fraction of tetrapod arms had broken off at temperatures in excess of ~180°C. Subsequent incorporation of the processed ZnS overcoated CdSe seeded CdS tetrapods into sol-gel derived silica via slight modifications of a published method was successful, attesting to the need for the surface chemical modification afforded by the ZnS overcoating process.

**Figure 2.1.** Representative TEM image of monodispersed ZnS overcoated CdSe seeded CdS tetrapods featuring a CdSe core diameter of ~3.1 nm with CdS arms of ~21 nm in length and ~5 nm in diameter.

Atomic Force Microscope (AFM) measurements on the resulting tetrapod-silica composite film, as exemplified in **Figure 2.2**, yielded a smooth morphology with a typical surface roughness (RMS) of about ~7.5 nm, over a 1 μm² scan area, suggesting a uniform incorporation of tetrapods into the sol-gel derived silica matrix.
Absorbance measurements, profilometry analysis of the film thickness and the molar absorptivity of CdSe seeded CdS tetrapods determined via a previously reported method\textsuperscript{9} provided an estimate of the volume fraction of tetrapods in the silica film, which was about ~6-10\% for all the films presented in this work. It is important, however, to note that the volume fraction with respect to the CdSe core is less than 1\% given the dominant contribution of CdS to the overall volume of the CdSe seeded CdS tetrapod structure.

Optical excitation of the tetrapod-silica films proceeded via a frequency-doubled Ti:Sapph with a pulse duration of 150 fs at a repetition rate of 1 kHz. The laser pulses were focused into a ~5.5 mm × 0.5 mm stripe using a cylindrical lens and the resulting emission was collected via an optical fiber coupled to a spectrometer and detected by a charge coupled device (CCD) camera.
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**Figure 2.3.** Room temperature ASE spectra from CdSe seeded CdS tetrapod-silica film with CdS arm dimensions of ~21 nm in length and ~5 nm in diameter with a CdSe core size of ~5.4 nm diameter. Inset compares the ASE (red) and PL (black) emission of the CdSe seeded CdS tetrapod-silica film.

**Figure 2.3** illustrates the room temperature photoluminescence (PL) spectra at different excitation pump intensities of tetrapod-silica composite films comprising of 5.4 nm CdSe cores with CdS arms approximately 21 nm long and 5 nm in diameter. A narrowing of the emission profile from ~38 nm to ~11 nm is readily observed at higher pump powers, signifying the onset of ASE. A low threshold of ~68 μJcm⁻² was derived from a plot of the integrated PL intensity against pump power (Figure 2.4) using the equation as follows:

\[
\text{ASE Threshold (μJcm}^{-2}\text{)} = \frac{\text{Pump Power (1.9 mW)/1000 s}^{-1}}{\text{Excitation Area (0.0275cm}^2\text{)}}
\]

(2.1)
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Figure 2.4. The corresponding integrated PL intensity versus pump power spectra of the ASE transition, with the inset depicting the intensity of the ASE transition as a function of the number of laser shots from the pump source.

This obtained threshold is 5 and 50 times lower than the best ASE thresholds previously reported in CdSe/CdS/ZnS based zirconia films,\textsuperscript{15} and CdS/ZnS based silica films respectively.\textsuperscript{6} It is possible that further reduction in the threshold may be achieved using state-resolved optical pumping, which was demonstrated recently in CdSe NC-based films.\textsuperscript{16,17} The photostability of the ASE in CdSe/CdS tetrapod-silica film was evaluated by continuously exciting the sample with $4.5 \times 10^6$ laser shots over a duration of 75 minutes, as shown in the inset of Figure 2.4. No obvious decrease in the ASE intensity was observed within the time window of our measurements, indicative of the optical robustness of the tetrapod-silica composites. A slight increase in the ASE intensity may be seen during the first 25 min of excitation, which may either be due to a thermally-mediated densification of the silica matrix or photo-annealing of the incorporated semiconductor tetrapods. The exact nature of the photo-brightening of the tetrapods in such sol-gel derived films is presently unclear, although such a process has also previously been observed in spherical CdSe nanocrystals under above-gap illumination.\textsuperscript{18,19}

When CdSe cores of smaller diameter (~3.1 nm) but with similar CdS arm dimensions were employed, excitation at moderate intensities yielded dual fluorescence emission from the CdS arms and CdSe core, as shown in Figure 2.5. A similar observation was made by Lutich et. al, except that in their case
the CdS arm length was varied instead of the size of the CdSe core.\textsuperscript{20} Their measurements did not show any discernible manifestation of ASE despite excitation pump fluencies of up to \~600 Jcm\textsuperscript{-2} however, presumably because of the low volume fractions associated with particles dispersed in solution.\textsuperscript{20} In the case of tetrapod-silica films, higher pump intensities resulted in ASE that was not from the CdSe core but rather from the CdS arms, yielding an ASE threshold of \~120 Jcm\textsuperscript{-2}, as seen in Figure 2.5. In contrast with the ASE from the CdSe core, the ASE intensity from the CdS shell as a function of time, as depicted in the inset of Figure 2.6, showed considerable photo-brightening and decay that may be attributed to a less passivated surface and a resulting higher tendency to trap photoexcited carriers.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure25.png}
\caption{Room temperature ASE spectra from CdSe seeded CdS tetrapod-silica film with similar CdS arm dimensions (\~21 nm in length and \~5 nm in diameter) but with a CdSe core size of \~3.1 nm diameter. Inset illustrates the PL spectra at low (black) and high excitation intensities (red).}
\end{figure}
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**Figure 2.6.** The integrated PL intensity of CdSe seeded CdS tetrapod-silica film (black dotted line) with similar CdS arm dimensions (~21 nm in length and ~5 nm in diameter) and a CdSe core size of ~3.1 nm diameter plotted against pump power. The red dotted line reflects the increase in emission intensity of CdSe core as a function of pump power. The inset depicts the intensity of the ASE transition as a function of the number of laser shots from the pump source. The initial decrease in intensity of the ASE transition as a function of the number of laser shots is attributed to excitation pump instability.

The intriguing omission of ASE in small CdSe core seeded CdS tetrapods cannot be ascribed to a volume-based, defect mediated photoinduced absorption process that was previously used to explicate the absence and presence of ASE in short and long CdSe seeded CdS nanorods respectively, given that in our case the dimensions of the CdS arms in both small and large core tetrapods as well as their volume fractions in the film are comparable. One plausible explanation would be to consider an exciton blocking effect in which the small CdSe core is populated with a high density of excitons at sufficiently large excitation intensities such that the electrons and holes photogenerated in CdS do not experience a strong driving force for relaxing into the CdSe core, thus recombining radiatively. This effect is further accentuated by the quasi-Type II band alignment between the small CdSe core and the CdS arms which results in slower single exciton CdSe recombination rates, therefore affording less opportunity for excitons in CdS to relax into
the CdSe core. It is also likely that although the extensive leakage of the CdSe electron wavefunction into the CdS shell should result in reduced CdSe Auger recombination rates and thus lower ASE thresholds, a concurrent reduction in the oscillator strength can also diminish the optical gain cross section in such quasi-Type II structures.

Conversely, for larger CdSe cores possessing a Type I band alignment with the CdS arms, stimulated emission in the CdSe core rapidly depletes the population of excitons photogenerated in CdS since both stimulated emission and CdS carrier relaxation into the CdSe core are extremely fast processes. Given that the achievement of stimulated emission in the CdSe core occurs at the expense of exciton buildup in the CdS shell, simultaneous ASE from both moieties is decidedly difficult, and our many attempts to achieve concurrent dual wavelength ASE from both the core and arms were without success. While an independent detailed study of the complex exciton dynamics of many-body interactions between multiple excitons generated in the CdSe core and CdS arms is clearly warranted here, it is foreseeable that large-core CdSe seeded CdS tetrapods with sufficiently long arms such that exciton relaxation to the CdSe core does not extend across a significant fraction of the arm length may exhibit dual wavelength ASE from both the core and its arms, provided other requirements on parameters such as quantum yield and volume fraction are satisfied.

**Figure 2.7 (a)** illustrates the room temperature modal gain of the tetrapod-silica composites which was evaluated by using the standard VSL method as in the optical characterization section. A linear fit was used to account for the change in PL intensity as a function of excitation stripe length prior to optical amplification while the onset and subsequent saturation of the ASE intensity was fitted with a previously reported 1-D amplifier model:

$$I \propto g l_{\alpha} \left(1 - e^{-(z-z_0)/l_{\alpha}}\right)$$

(2.2)

where $I$, $g$, and $z$ are the ASE intensity, modal gain coefficient and excitation stripe length respectively and $z_0$ accommodates for possible pump beam
inhomogeneity and delayed ASE onset. The parameter $l_{\alpha}$ is defined as the modal gain lifetime of the NCs in the film multiplied by the speed of light within the gain medium and accounts for saturation in the ASE intensity.\textsuperscript{6} Extraction of the parameters $g$ and $l_{\alpha}$ from the fit yielded values of $\sim151$ cm$^{-1}$ and 0.05 cm respectively, the latter of which translates to a modal gain lifetime of $\sim3$ ps. While the VSL obtained gain value is not appreciably higher than previous reports on NC-based composites,\textsuperscript{15,24} presumably due to the extremely low volume fraction of CdSe cores in the film, the fitted gain lifetime is unlikely due to fast Auger recombination processes as ascribed to by previous studies\textsuperscript{6} on spherical CdS/ZnS NCs since it is expected that the CdSe core electron wavefunction can delocalize extensively into the four CdS arms, thereby reducing the Auger recombination rate. This supposition was experimentally verified by biexciton lifetime measurements as illustrated in Figure 2.7 (b), where a remarkably long average biexciton lifetime of $\sim1.6$ ns was determined, though comparatively smaller than the 10 ns biexciton lifetime of spherical “giant” shell CdSe/CdS NCs previously reported by Klimov \textit{et. al.}.\textsuperscript{25} The observed short modal gain lifetimes is therefore attributed to depletion of electron-hole pair density due to stimulated emission, which is a well-known mechanism in VSL measurements on semiconductors. Since the threshold condition for ASE in NCs is inversely proportional to their Auger-dominated biexciton lifetime,\textsuperscript{5} the long-lived biexcitonic lifetimes in tetrapods, indicative of a suppressed Auger recombination rate, should allow ASE to be more readily achieved. Indeed, this is consistent with our observed low thresholds for the biexcitonic ASE transitions in the tetrapod-silica composite films.
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Figure 2.7. (a) Room temperature Variable Stripe Length (VSL) measurements of the same CdSe seeded CdS tetrapod-silica film from Figure 2.2. The dotted lines are a fit using a 1-D amplifier model which takes into account saturation due to Auger recombination processes. (b) Lifetime measurements of a dilute solution of CdSe seeded CdS tetrapods with a CdSe core diameter of ~5.4 nm and a CdS arm length of ~21 nm under excitation intensities corresponding to an average of 1 e-h pair (black), 2 e-h pairs (red) and 3 e-h pairs (green) per particle. A single exciton and biexciton lifetime of ~15.7 ns and ~1.6 ns were extracted from the lifetime measurements respectively.

Given the structural robustness of the nanotetrapod-silica composites, we examined their capacity to exhibit multiexcitonic ASE, which can only take place under sufficiently intense optical excitation such that the excited energy states higher than 1S e are simultaneously populated.26,27 As shown in Figure 2.8, a second narrow emission peak at 619 nm emerges at larger pump intensities, which may be contrasted with the lower energy biexcitonic ASE transition centered at 661 nm. Nearly identical energy spacings between the two ASE transitions were found in films of the same tetrapods but with different thicknesses, thus excluding the possibility that the higher energy
ASE transition is due to a broad gain profile coupled to different waveguide modes.\textsuperscript{24}

**Figure 2.8.** PL intensity of a CdSe seeded CdS tetrapod-silica film under relatively high excitation pump intensities. Inset: zoom in on the spectral region featuring a higher energy ASE peak.
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Figure 2.9. (a) PL intensity of a CdSe seeded CdS nanorod-silica film under high excitation pump intensities. (b) Summary of the thresholds obtained for ASE from the biexcitonic (XX) and multiexcitonic (MX) transitions in tetrapods and rods respectively.

An analysis of its PL intensity as a function of pump power revealed that the threshold for the higher energy ASE transition was approximately two times that of the biexcitonic ASE. A similar observation was previously reported for CdSe/ZnS NCs in titania matrices where a higher energy ASE peak at large pump intensities was ascribed to stimulated emission originating from a non-degenerate CdSe 1P_e-1P_h transition.\(^ {27}\) Taken together, these findings suggest that the higher energy ASE transition is due to multiexcitonic states in the CdSe core of the tetrapod with a threshold sufficiently low (~ 171 \( \mu \text{Jcm}^{-2} \)) to warrant dual wavelength optical amplification in a practical device. As a comparison with our nanotetrapod silica slabguide, we evaluated the optical gain performance of CdSe seeded CdS nanorods with core and rod-like shell dimensions similar to those of the tetrapods and their arms. The nanorods were incorporated into a thin film silica matrix using the same synthetic procedures developed for tetrapods, and it was ensured that key parameters such as NC volume fraction, film thickness and roughness were comparable between both rod- and tetrapod-silica composites. As shown in Figure 2.9(a), both biexcitonic and multiexcitonic ASE were observed at higher pump intensities, with an energy difference of ~ 0.15 eV and an approximate two-fold difference in thresholds between the two ASE transitions, consistent with those of the tetrapods in Figure 2.8. The room temperature ASE thresholds of the two heterostructured semiconductor-silica composite films are summarized in Figure 2.9. (b). It is readily seen that the tetrapods have a significantly lower threshold than those of their nanorod counterparts, which is likely attributed to a larger absorption cross-section and a longer-lived multiexcitonic lifetime due to the more extensive leakage of the electron wavefunction to four CdS arms as compared with a single rod-like CdS shell in the case of nanorods.

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2.4 Conclusion
To summarize, we have presented the fabrication of heterostructured nanotetrapod-silica composite films via the incorporation of monodisperse colloidal CdSe seeded CdS tetrapods into a sol-gel derived silica matrix using a relatively facile process. These tetrapod-silica composites were found to exhibit very low threshold, highly stable room temperature biexcitonic and multiexcitonic ASE from the CdSe core for Type I tetrapods while ASE at blue wavelengths from the CdS arms were evident for tetrapods of Type II configuration. Preliminary comparisons with CdSe seeded CdS nanorods in silica films suggest that within the device parameters explored, the tetrapod-silica composite films are more promising as NC optical amplifiers. Further optimization of the core/arm dimensions, NC volume fraction and film optical quality may well allow for the development of low threshold, heterostructured NC lasers capable of simultaneously emitting at multiple wavelengths over a large spectral range from a single active layer, thus representing a unique class of solution processable optical gain media.

2.5 References
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CHAPTER 3

Two-Photon Pumped Amplified Spontaneous Emission and Lasing from CdSe Seeded CdS Nanorods

![Image showing CdSe Seeded CdS Nanorods]

![Graph showing PL Intensity vs Wavelength]
3.1 Introduction

Colloidal semiconductor nanocrystals (NCs) are desirable as optical gain media due to their excellent photostability, continuous tunability over a wide spectral range, and easy chemical processability.\textsuperscript{1-17} These advantageous physicochemical properties make NCs highly suited for optical applications such as multiwavelength on-chip microcavity lasers and as miniaturized light sources in lab-on-a-chip diagnostics.\textsuperscript{1-16} To date, optically pumped Amplified Spontaneous Emission (ASE) and lasing in colloidal semiconductor NCs have largely been demonstrated using one-photon excitation (1PE) with ultraviolet/visible light sources.\textsuperscript{1-12} However, it is foreseeable that in many of the applications for which NC lasers are relevant the use of UV-vis excitation wavelengths risks the high possibility of photodamage to the sample and substrate or unwanted excitation of fluorescent contaminants present in the application setup. A promising route to the derivation of ASE and lasing in NCs while circumventing the above issues is optical pumping via two-photon excitation (2PE) at infrared (IR) wavelengths.\textsuperscript{12-16} 2PE is achieved through the simultaneous absorption of two photons, which induces an electronic transition from the ground state to an excited state via virtual states. In contrast to 1PE, 2PE possesses several unique features such as higher spatial resolution and longer penetration depth when operating in the semitransparent infrared window of biological media and has thus been exploited for bioimaging.\textsuperscript{12-16,18-21} Additionally, for the generation and wavelength tuning of coherent light, the absence of a phase matching requirement in the 2PE process makes it highly attractive over other nonlinear frequency conversion techniques (e.g., optical harmonic generation), as this permits its application to a much wider range of resonator designs and gain media (other than birefringent crystalline materials).\textsuperscript{12-16} Given the advent of robust, low cost, versatile, and compact IR laser sources (e.g., fiber lasers), 2PE has become a viable technique for the generation of coherent light via the attainment of optical gain in colloidal semiconductor NCs.

One major impediment to the development of practical two-photon pumped colloidal semiconductor NC lasers is the small two-photon absorption (2PA) cross-section (typically $\sigma_2 \approx 10^{-46}$ cm$^4$/photon) for most spherical core-
(thin) shell II-VI semiconductor NCs that necessitate the use of high laser excitation fluences to derive optical gain. Thus, prior efforts to achieve two-photon induced stimulated emission in NCs typically resulted in very high thresholds of over 10 mJ/cm$^2$.

For 2PE, the average number of electron-hole (e-h) pairs created by each laser pulse is given as $< N_2 > = f^2 \sigma_2 / \tau_p$, where $f$ is the fluence and $\tau_p$ is the pulse duration. For a fixed $\tau_p$, it is desirable to increase $\sigma_2$ and reduce $f$ for the same $< N_2 >$ in order to reduce the likelihood of photodamage to the gain media. While simply increasing the volume of strongly confined NCs to increase $\sigma_2$ appears to be a straightforward solution, an increase in size for these strongly quantum-confined NCs inevitably red shifts their band edge fluorescence, thereby imposing severe limitations on their spectral tunability. For the fabrication of devices with wavelength-specific requirements such as lasers, this presents a formidable challenge.

Herein we demonstrate that these issues may be simultaneously addressed using seeded CdSe/CdS nanorod (NR) heterostructures, which comprise a spherical CdSe core that is encapsulated by a rod-like CdS shell as the optical gain media. While the CdS shell functions as an antenna in light harvesting, emission from the rod originates primarily from the quantum-confined CdSe core. This unique optical configuration thus allows for $\sigma_2$ and the emission wavelength to be varied independently by adjusting the physical dimensions of the rod-like shell and spherical core, respectively.

We then show that via the use of highly monodisperse CdSe-seeded CdS NRs, room-temperature ASE via 2PE at 800 nm can be obtained with thresholds as low as 1.5 mJ/cm$^2$. The NRs were subsequently incorporated into a silica matrix and coupled to a microspherical cavity, where single-mode lasing at a threshold of 0.99 mJ/cm$^2$ was derived. At such low pump intensities, lasing from the NRs via 2PE was stable over the course of $6 \times 10^6$ laser shots under ambient conditions, thus making these NC laser devices plausible for use in practical applications. Ultrafast optical spectroscopy (UOS) also revealed that while the nonradiative Auger recombination processes ($\tau_{\text{Auger}} \approx 200-300$ ps) are indeed suppressed in these NR heterostructures, the ASE could still be strongly affected by the ultrafast hole trapping to the NR surface.
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3.2 Experimental

General methods

Unless stated otherwise, all the reactions were conducted in oven-dried glassware under nitrogen atmosphere using standard Schlenk line techniques. All the chemicals were used as received without further purification. All solvents were used as received.

The CdSe seeded CdS nanorods used in this study were synthesized using the seeded growth approach as described in Chapter 2.

Chemicals

Trioctylphosphine oxide (TOPO (90%)), 1-hexadecylamine (HDA), diisoocylphosphinic acid (DIPA), cadmium acetylacetonate (Cd(acac)$_2$), 1,2-hexadecanediol (HDDO), trioctylphosphine selenide (TOP-Se), diisoocylphosphinic acid (DIPA), 1-octadecene (ODE, 90%), trioctylphosphine oxide (TOPO (99%)), cadmium oxide (CdO, 99.99%), n-octadecylphosphonic acid (ODPA), n-hexylphosphonic acid (HPA), sulfur (S reagent grade, powder), di-ethylzinc (99%), bis(trimethylsilyl) sulfide ((TMS)$_2$S, 99%), 3-aminopropyltrimethoxysilane (APS), tetraethoxysilane (TEOS) were purchased from Sigma Aldrich. Trioctylphosphine (TOP, 97%), 5-amino-1-pentanol (AP), was purchased from Alfa Aesar.

Synthesis of spherical wurzite CdSe core

Synthesis of monodispersed wurzite CdSe NCs proceeded based on a previously reported procedure with slight modifications.$^{16}$ A mixture of 8.5 g TOPO (90%), 6 g HDA and 0.3 ml of DIPA was degassed in a 3-neck RBF at 100 °C for 1.5 hr. Separately a precursor solution comprising of 0.317 g Cd(acac)$_2$ and 0.567 g HDDO in 8 mL ODE was degassed at 120 °C for 1.5 hr 2 mL of 1.5 M TOP-Se was added in the precursor solution at room temperature under N$_2$. The precursor solution was then swiftly injected into the 3-neck RBF at 360 °C and allowed to cool to 80 °C. As-synthesized wurzite CdSe NCs were subsequently processed by 2-3 cycles of precipitation in methanol and re-dispersion in toluene for further use.

Processed CdSe QDs was dispersed in a minimum amount of toluene and their concentration was determined by measuring their absorbance at 350 nm, whose molar absorptivity is known.$^{17}$
Synthesis of CdSe seeded CdS nanorods
CdSe/CdS nanorods were prepared according to the method of Manna.\(^{18}\) 3 g TOPO (99%), 0.07 g cadmium oxide (CdO), 0.29 g n-Octadecylphosphonic acid (ODPA) and 0.08 mg n-hexylphosphonic acid (HPA) are mixed in a 100 mL three neck RBF and degassed at 150 °C for about 1.5 h. The reaction mixture was then heated up to 360 °C under N\(_2\). The solution turned from reddish brown to colorless around 270 °C, indicating the formation of the Cd-ODPA complex. Separately, 0.11 g sulfur was dissolved in 1.8 mL TOP at 50 °C upon which 1.5×10\(^{-7}\) mol of the CdSe was added. Before hot injection, 1.8 mL TOP was added to the 3-neck RBF, and the temperature was allowed to recover to 360 °C before the mixture of S, TOP and CdSe was injected. The temperature was again allowed to rise to 360 °C and the anisotropic CdS shell was grown at this temperature for about 6-8 minutes. The heating mantle was then removed and the reacting solution was allowed to cool down to 80 °C. As-synthesized CdSe/CdS nanorods (NRs) were then processed by the same repeated cycles of precipitation in methanol and re-dispersion in toluene.

Surface coating of CdSe seeded CdS nanorod
10 g TOPO (90%) and 0.1 g HPA were degassed at 150 °C for 1 hr. The mixture was switched to N\(_2\) and allowed to cool down to 80 °C before rod-toluene solution was added. Toluene was evaporated under vacuum at the same temperature before increase the temperature to 140 °C, upon which a mixture of 0.065 g Diethylzinc, 0.114 g \((\text{TMS})_2\)S and 1mL TOP was dripped into the 3-neck RBF slowly under N\(_2\) within 30 min. The temperature was then cooled down to 100 °C and maintained at that temperature for overnight. Overcoated CdSe seeded CdS nanotetrapods were then processed by repeated cycles of precipitation in methanol and re-dispersion in hexane.

Surface coating of CdSe seeded CdS nanorod
12 g TOPO (90%) and 0.1 g HPA were degassed at 150 °C for 1 hr. The mixture was switched to N\(_2\) and allowed to cool down to 80 °C before tetrapod-toluene solution was added. Toluene was evaporated under vacuum at the same temperature before increase the temperature to 220 °C, upon which a mixture of 0.032 g diethylzinc, 0.05 mL \((\text{TMS})_2\)S and 2 mL TOP was dripped into the 3-neck RBF slowly under N\(_2\) within 30 min. The temperature was then
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cooled down to 100°C and maintained at that temperature for overnight. Overcoated CdSe seeded CdS nanorods were then processed by repeated cycles of precipitation in methanol and re-dispersion in toluene.

**Nanorod coated silica sphere fabrication**
The route employing 3-aminopropyltrimethoxysilane (APS) as silica precursor was adopted from a previously reported method with slight modifications. Processed ZnS overcoated CdSe seeded CdS nanorods (80 mg) were cap-exchanged with 100 μL AP in 200 μL ethanol. This afforded a clear solution of NCs into which 40 μL APS and 10 μL TEOS was added and stirred vigorously for ~1 min. The resultant viscous liquid was allowed to pass through a 0.2 μm syringe filter and mix with commercially available silica microspheres with a diameter of 5.0 ± 0.3 μm. The resultant suspension of silica microsphere and nanorod was spin coated on a pre-cleaned glass slide followed by thermal annealing at 120 °C for 6 min.

**TEM characterization**
JEOL JEM 1220F (100 kV accelerating voltage) microscope was used to obtain bright field TEM images of the nanoparticles. For TEM sample preparation, the processed nanoparticle solution was dropped onto a 300 mesh size copper grid covered with a continuous carbon film. Excess solution was absorbed by a filter paper underneath and the copper grid was dried under ambient condition.

**Optical characterization**
Room temperature UV-visible absorption spectra were measured with an Agilent 8453 UV-Visible spectrophotometer. Photoluminescence (PL) spectra were collected with a Shimadzu RF-5301PC Spectrofluorophotometer.

For femtosecond optical spectroscopy, the laser source was a Coherent Legend regenerative amplifier (150 fs, 1 kHz, 800 nm) that was seeded by a Coherent Mira oscillator (100 fs, 80 MHz). Laser pulses of 800 nm wavelength were from the regenerative amplifier's output, while 400 nm wavelength laser pulses were frequency doubled with a BBO crystal.

For Z-scan measurements, the incident laser pulses were focused onto the sample by a lens with 30 cm focal length. The NR heterostructures in
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toluene solution were placed in a 2 mm thick quartz cell, which was traversed across the focal point along the beam propagation axis.

For femtosecond TA experiments, the samples were pumped at 3.1 eV and probed with a white-light continuum. The probe pulses (400-750 nm) were generated by focusing a small portion (~5 μJ) of the fundamental 800 nm laser pulses into a 1 mm thick sapphire plate. The linear polarization of the pump pulse was adjusted to be perpendicular to that of the probe pulse with a polarizer and a half-wave plate. The cross-polarization will help eliminate any contribution from coherent artifacts at early times. Pump-induced changes of transmission (Δ T/T) of the probe beam were monitored using a monochromator/PMT configuration with lock-in detection. The pump beam was chopped at 83 Hz, and this was used as the reference frequency for the lock-in amplifier.

For 2ASE experiments, the 800 nm laser pulses were focused by a cylindrical lens (with focal length f = 20 cm) to a stripe (of dimensions ~0.1 mm×6 mm) on the films coated on the sample slides, which were aligned perpendicular to the excitation stripe. The emission from the film edge was collected in a lateral configuration by a pair of lenses focused onto an optical fiber coupled to a spectrometer (Acton, Spectra Pro 2500i) and detected by a charge-coupled device (Princeton Instruments, PIXIS 400B CCD).

The two-photon pumped time-resolved PL was detected by an Optronis Optoscope streak camera system, which has an ultimate temporal resolution of ~6 ps when operated at the shortest time window of 330 ps. Lastly, lasing from a single microsphere was observed using a home-built confocal microscope with both the excitation pulses and emission light being coupled and collected through the same long working distance 50 × microscope objective (NA = 0.55) and spectrally resolved by the above-mentioned spectrometer and CCD detector.

For nanosecond TA experiments, a laser flash photolysis spectrometer (LKS.60, Applied Photophysics), equipped with a Q-switched Nd:YAG laser (Brilliant B, Quantel), a 150 W pulsed Xe lamp, and a R928 photomultiplier, was used to record nanosecond-difference absorption spectra. Samples were
excited at 440 nm, and each time-resolved trace was acquired by averaging 10 laser shots at a repetition rate of 1 Hz.

3.3 Results and Discussion
In this work, seeded CdSe/CdS NR heterostructures of three different rod lengths (i.e., 15, 34, and 39 nm) with the same CdSe core (~2.4 nm) were investigated. The size of the CdSe core (< 2.8 nm) indicates that these rods are expected to exhibit a quasi-type II core-shell energy profile. The photoluminescence (PL) quantum yield (QY) of these NRs in toluene were measured to be 0.75, 0.61, and 0.56, respectively. Their structure and basic optical properties are shown in Figure 3.1.

Figure 3.1. (a-c) Normalized UV-visible absorption spectra (solid line) and its magnified (×10) region (dashed line), 400 nm excited PL spectra for 15 (red), 34 (green), and 39 (blue) nm CdSe/CdS nanodot/nanorod heterostructures, respectively. (d-f) Corresponding TEM images for 15, 34, and 39 nm CdSe/CdS nanodot/nanorod heterostructures respectively; scale bars are 50 nm.
These NR samples in toluene were spin casted onto glass slides to form close-packed thin films of NRs, with thicknesses of ~500 nm. The surface roughness of these films was characterized using tapping mode atomic force microscopy, which yielded typical rootmean square roughness values of ~ 6 nm measured over a 2 \( \mu \text{m} \times 1 \ \mu \text{m} \) scan area. The resultant film and optical set-up were shown in Figure 3.2.

**Figure 3.2.** (a) Digital photograph of frequency-upconverted stimulated emission from a CdSe/CdS heterostructure film, pumped by 2PA at 800 nm. Inset shows the pumping configuration. (b) Tapping mode AFM image of the typical surface profile of the close-packed CdSe/CdS heterostructures films.
Optical gain in type-I colloidal semiconductor NCs is generally achieved with the generation of multiexcitons due to the spin degeneracy in its first excited state. For example, due to a 2-fold degeneracy in the $1S^e_{\text{e}}-1S^h_{\text{h}}$ transition of CdSe NCs, biexcitons are required in order to derive optical gain.\textsuperscript{1,26} The 2PA cross-section $\sigma_2$ thus becomes an important metric in determining the photon flux required to generate biexcitons via 2PE and subsequently achieve stimulated emission. In the case of ASE from NC-based waveguides, it is fairly obvious that increasing $\sigma_2$ without exacerbating other key parameters such as NC volume fraction, Auger recombination rates, and waveguide Q factors would result in lower threshold fluences. The relationship between the PLQY and the ASE threshold, however, can be rather complex. On one hand, the PLQY may not be as important a factor compared to the extremely fast Auger recombination rates if its nonradiative contribution is comparatively slower. On the other hand, the PLQY is a reflection of the degree of passivation of the NC surface, which has been shown by several reports to be strongly related to Auger recombination processes in the NC.\textsuperscript{27,28} Furthermore, given that the carriers are generated primarily in the CdS shell and then undergo charge transfer to the CdSe core in these NR heterostructures, carrier trapping processes to the NR surface states can also be a highly efficient nonradiative pathway that competes effectively with both ASE and Auger recombination processes. Finally, the single-exciton PLQY is likely to play a role in the provision of seed photons for the photon cascade that occurs in ASE. Hence, to take into account the contributions from these factors, we use the two-photon action cross-section (i.e., $\sigma \times \eta$) of the NC sample as a basis for analyzing the relationship between the threshold fluence and $\sigma_2$.

**Determination of 2PA Cross-Sections**

As the two-photon pumped ASE of the NR films is strongly dependent on the nonlinear absorption properties of the CdS-seeded CdS NRs, we first determined the 2PA cross-sections ($\sigma_2$) of these NR heterostructures using the open-aperture Z-scan technique with 150 fs laser pulses (1 kHz) at a
wavelength of 800 nm. Table 3.1 lists the $\sigma_2$ values measured for samples with different rod lengths, which can ostensibly be described as exhibiting a linear dependence.

**Table 3.1.** Average Length, Quantum Yield ($\eta$), 2PA Cross-Section ($\sigma_2$), Two-Electron-Hold Pair Decay Time ($\tau_2$), and 2ASE Threshold of CdSe/CdS Nanodot/Nanorod Heterostructures

<table>
<thead>
<tr>
<th>Length (nm)</th>
<th>$\eta$ [%]</th>
<th>$\sigma_2$ [GM]</th>
<th>$\tau_2$ [ps]</th>
<th>Threshold [mJ/cm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>75</td>
<td>70 000</td>
<td>190</td>
<td>3.4</td>
</tr>
<tr>
<td>34</td>
<td>61</td>
<td>190 000</td>
<td>260</td>
<td>1.8</td>
</tr>
<tr>
<td>39</td>
<td>56</td>
<td>230 000</td>
<td>300</td>
<td>1.5</td>
</tr>
</tbody>
</table>

*Experimental uncertainty: ±20%*

Elucidating the physical origins of this linear dependence is nontrivial, though it is likely due to the local field effects on the nanostructure size and the density of states. For 39 nm long NRs, a $\sigma_2$ value of $2.3 \times 10^5$ GM (where 1 GM = $10^{-50}$ cm$^4$ s/photon) was measured, which is 2 to 4 orders of magnitude larger than that previously reported for spherical semiconductor QDs and about 4 orders of magnitude larger than that of typical organic dyes. Importantly, $\sigma_2$ can be varied independently of the CdSe core, whose size primarily determines the emission wavelength. The advantages of size-dependent emission afforded by the quantum-confined CdSe core are therefore preserved in these heterostructures.

**Two-Photon Pumped Amplified Spontaneous Emission**

Figure 3.3 (a)-(c) show the normalized room-temperature emission spectra below and above the two-photonpumped ASE (2ASE) threshold for 15, 34, and 39 nm long CdSe-seeded CdS NRs with a CdSe core size of ~2.4 nm, respectively. Following 2PA, which is dominated by the CdS shell, electron-hole pairs are formed and undergo ultrafast charge localization to the CdSe core within ~1 ps, where radiative recombination occurs. Below the threshold fluence, the twophoton pumped spontaneous emission (SE) of the heterostructures dominates the light output with a bandwidth of ~40 nm (i.e., full width at half-maximum (fwhm)). These spectra are indistinguishable from
the 1PE PL spectra shown in Figure 3.1. Above this threshold, the emission bandwidth reduced to less than 12 nm for all the samples, as a result of gain-induced narrowing.

![Graph](image)

**Figure 3.3.** 2ASE spectra (red) obtained from the films with 15 nm (a), 34 nm (b), and 39 nm (c) CdSe/CdS heterostructures at an 800 nm pump wavelength. The 2PA-induced SE spectra (black) are also shown for each corresponding sample.

Notably, the 2ASE peaks of all the samples are blue shifted with respect to the exciton peak with energy separations of 10, 29, and 47 meV for the 15, 34, and 39 nm NR heterostructures, respectively. The origins of this blue shift may be attributed to the quasi-type-II band alignment between the CdSe core and CdS shell (valid for CdSe core sizes < 2.8 nm\textsuperscript{22-25}), which results in a negative biexciton binding energy (repulsive exciton -exciton interaction) that causes its radiative recombination to occur at a higher energy than that of the single exciton.\textsuperscript{1,4,7,26} This repulsive interaction increases with the length of the NR and stems from a decreased overlap of the electron\_hole wave functions due to an increased electron wave function delocalization into the rod-like shell. The resulting reduced attractive electron\_hole interaction is subsequently commensurate with a stronger repulsive interaction between charges in the core and shell.\textsuperscript{1,4,7,26} It should be noted that it is unlikely that single-exciton 2ASE from these heterostructures was obtained since the
biexciton repulsion energy is much smaller than the ensemble line width of the single-exciton emission (i.e., ~130 meV).\textsuperscript{7} Within quasi-type-II band alignment of the CdSe/CdS heterostructure, the 2ASE peak should be tunable between ~550 and ~600 nm by tailoring the CdSe core and CdS shell size.\textsuperscript{11,22,24}

\textbf{Figure 3.4.} (a) Variable fluence measurements show the 2ASE thresholds of the CdSe/CdS heterostructures. (b) Plot of 2ASE vs 2PA action cross-section ($\sigma\eta$). The experimental results were taken from present work (■), ref 14 (●), and ref 15 (▲). The red line is a power-law fitting.
Figure 3.4 (a) shows the dependence of the integrated PL intensity on the pump fluence. At relatively low pump intensities (i.e., <1.2 mJ/cm²), the PL emission shows a near quadratic pump intensity dependence for all the samples, which validates the 2PA process at 800 nm.²⁰,²⁹ At higher pump intensities, an abrupt change of the slope occurs, indicating a threshold behavior that is characteristic of 2ASE. The 2ASE threshold pump intensities for the 15, 34, and 39 nm CdSe/CdS heterostructures were found to be 3.4, 1.8, and 1.5 mJ/cm², respectively, for samples with comparable film thicknesses (~500 nm) and loading fraction (~30%).¹⁵ It is evident that the 2ASE threshold pump fluence decreases with increasing rod length, which may be attributed to the increased \( \sigma_2 \). The 2ASE threshold pump intensities as a function of the heterostructures' 2PA action cross-section (\( \sigma_2 \eta \)) are presented in Figure 3.4 (b). The plot summarizes the experimental results from this study as well as those collated from the literature.¹⁴,¹⁵ From the fit, the 2ASE threshold pump intensities exhibit a power-law dependence of -0.5 ± 0.1 to \( \sigma_2 \eta \). It shows that the 2ASE threshold is nearly inversely proportional to \( \sigma_2 \eta \) (i.e., a near reciprocal relation), which is consistent with the notion that the enhanced 2PA cross-section at 800 nm due to the CdS rod-like shell would effectively lower the pump intensities needed to achieve ASE. Within our range of samples measured, the 39 nm long CdSe-seeded CdS NRs have the largest 2PA action cross-section and yielded, to the best of our knowledge, the lowest 2ASE threshold to date (i.e., ~1.5 mJ/cm²) for a colloidal NC system. Comparatively, this value is as much as 1 order less than that obtained for spherical quantum dots.¹⁴,¹⁵ We emphasize that this comparison is based on the achievement of ASE in a waveguide geometry, where unlike in the case of lasing in optical cavities, the thresholds obtained are less strongly dependent on cavity Q factors and modal volumes. On the basis of the 2PA cross-sections measured with the Z-scan technique, the number of electron-hole pairs generated per NC at threshold pump fluence are estimated to be approximately 1.3, 1.1, and 1.0 for 15, 34, and 39 nm long CdSe-seeded CdS NRs, respectively. This result is consistent with previous observations that the NR optical gain derives primarily from the generation of biexcitons.¹⁻¹⁶
Chapter 3: Two-Photon Pumped Amplified Spontaneous Emission and Lasing from CdSe Seeded CdS Nanorods

Transient Optical Spectroscopy

Time-resolved two-photon excited PL experiments at room temperature were also performed on the NR films in order to investigate the biexciton modal gain dynamics in these heterostructures. Typical time-resolved three-dimensional (3D) plots of the 2PA-induced SE and ASE spectra for the 15 nm CdSe/CdS heterostructures are shown in Figure 3.5 (a) and (b), respectively, while the emission decay curves for all the samples and their corresponding decay fits are shown in Figure 3.5 (c) (i.e., extracted at the peak of the excitonic emission and photoexcited with a pump fluence of ~ 0.1 mJ/cm²).

**Figure 3.5.** Typical 3D time-resolved 2PA induced SE (a) and ASE (b) spectra for 15 nm CdSe/CdS heterostructures film. (c) 2PA induced SE (integrated ± 5 nm around the emission peak) decay curves and the single-exponential fittings for 15 nm (black), 34 nm (red) and 39 nm (green) heterostructure films. (d) Typical time-resolved PL traces with 2PA excitation fluence just below (black) and above (red) the ASE threshold for the 15 nm heterostructure film.
Chapter 3: Two-Photon Pumped Amplified Spontaneous Emission and Lasing from CdSe Seeded CdS Nanorods

It is readily seen that the time dynamics of 2PA-induced SE are similar to that of 1PE and the intensity decays with time via a single-exponential function, with fitted decay lifetimes for the 15, 34, and 39 nm rods at 10, 12, and 14 ns, respectively. These fitted lifetimes show that the exciton PL lifetimes increase with increasing rod length, in accordance with the decrease in the CdSe electron-hole wave function overlap due to more extensive delocalization of the electron wave function in the longer rods. However, compared to an ensemble of relatively isolated NRs in a dilute solution (i.e., in a solvent - $\tau_{\text{solution}} \approx 20 \text{ ns}$), the lifetimes obtained for these close-packed films are slightly shorter, likely due to dipole-mediated energy transfer processes between neighboring rods. \(^{30}\) The energy transfer time ($\tau_{\text{ET}}$) is estimated to be around tens of nanoseconds with $1/\tau_{\text{film}} = 1/\tau_{\text{solution}} + 1/\tau_{\text{ET}}$. Therefore, the dipole-dipole interaction between neighboring rods in our film is not expected to have any significant effect on the 2ASE threshold. (2ASE occurs on a much faster time scale as shown below).

At pump fluencies above threshold for the 15 nm rod sample, a short-lived, spectrally narrow emission band emerges at energies higher than that of the 2PA induced SE peak, as shown in Figure 3.5 (b). Figure 3.5 (d) shows its luminescence decay profile at the peak wavelength of the ASE transition for pump fluencies below (i.e., $\sim 3 \text{ mJ/cm}^2$) and above threshold (i.e., $\sim 3.5 \text{ mJ/cm}^2$). Although the pump fluence of $\sim 3 \text{ mJ/cm}^2$ is just below the threshold needed for ASE, it is important to highlight that such high pump fluence is in the regime of multie exciton generation. Therefore, the PL decay dynamics exhibit a short lifetime component of $\sim 200 \text{ ps}$, which is much shorter than the typical $\sim 10 \text{ ns}$ excitonic recombination lifetimes for these NRs. This 200 ps relaxation time closely matches the Auger limited biexciton recombination lifetimes in these CdSe/CdS heterostructures, which were probed using ultrafast transient absorption (TA) spectroscopy, and these results will be presented in the next paragraph. Beyond the threshold fluence of $\sim 3.5 \text{ mJ/cm}^2$, an even shorter fitted lifetime component of $\sim 7 \text{ ps}$ dominates the radiative recombination dynamics, in addition to the $\sim 200 \text{ ps}$ Auger-limited biexciton recombination lifetime. This even faster lifetime component is due to the ASE resulting from an avalanche of biexcitonic recombination, where its lifetime
measurements are limited by the system temporal response of the streak camera.

Optical gain in semiconductor NCs is strongly dependent on the competition between radiative and nonradiative processes (i.e., multiexciton Auger recombination, fast charge carrier trapping, etc.). Therefore, it is very important to elucidate and gain a clear understanding of the dynamic interplay between the various carrier relaxation channels through TA spectroscopy. Figure 3.6 (a) shows representative differential transmittance (DT) spectra of these CdSe/CdS heterostructures (in toluene) at probe delay of 2 ps following 3.1 eV photoexcitation.

![Figure 3.6](image)

Figure 3.6. (a) Differential transmission spectra for the nano heterostructures in toluene solution at a probe delay of 2 ps. The bleaching peaks corresponding to the
lowest lying energy levels in CdS and CdSe are labeled as $Y_0$ and $X_0$, respectively. **(b)** Pump fluence-dependent decay transients of $X_0$ normalized to their long-lived decay component for the 15 nm CdSe/CdS nanorods. The inset show the decay transients of the two electron-hole pair states for the NRs with different lengths, fitted with a single exponential decay function (line).

The photobleaching (PB) peaks (i.e., $\Delta T/T > 0$) evident in the DT spectra arise from the state filling of the hole states in the CdSe core and the electron states in the CdS shell. These correspond to the lowest lying energy levels in the CdSe and CdS system and are labelled as $X_0$ and $Y_0$, respectively.\(^8,23,25\)

With increasing NR length, the amplitude ratio of $X_0$ to $Y_0$ decreases, consistent with an increased absorption from the larger rod-like shell. Pump-power dependent bleaching kinetics at $X_0$ was performed to elucidate the biexciton Auger recombination lifetimes in these NR heterostructures. **Figure 3.6 (b)** shows the representative decay transients for the 15 nm NRs for different pump powers (expressed in term of the average number of electron-hole pairs generated by the pump). Using a procedure previously reported by Klimov et al.,\(^26\) the biexciton Auger recombination lifetimes were extracted and are shown in the inset of **Figure 3.6 (b)**. These were fitted to be 190, 260, and 300 ps for the 15, 34, and 39 nm rods, respectively, which are much longer than the biexciton lifetime (i.e., $\sim$ 45 ps) for 2.3 nm CdSe spherical dots.\(^26\) Hence, it may be inferred that the biexcitonic Auger recombination rates are indeed greatly suppressed in these NR heterostructures. The slower rates found in the longer rods are consistent with the decrease in the CdSe electron- hole wave function overlap caused by the more extensive delocalization of the electron wave function in the longer rods. However, compared to CdSe NRs of similar volume, the biexciton Auger rate is slightly faster in these heterostructures. We attribute this to the strong confinement of the holes in the CdSe core (in our heterostructures) and a more weakly confined electron that delocalizes into the CdS shell. Hence, it is understandable that the Auger dynamics in this system of mixed dimensionality are in-between the case of a zero-dimensional quantum dot and that of a one dimensional quantum rod.\(^26\) Further experimental investigations and theoretical modelling are under way to gain a clearer understanding of the Auger processes that occur in these heterostructures of mixed dimensionalities.
In these CdSe/CdS NR heterostructures where the Auger rates are suppressed, the optical gain buildup time compares favorably with the nonradiative Auger processes.

In light of the fact that the suppressed Auger processes may not play a dominant role in the ultrafast multiexciton dynamics of our 2PE-derived ASE from CdSe/CdS NRs, we examined the dynamics of other possible nonradiative processes, in particular ultrafast charge trapping to surface states and their impact on the ASE process. As discussed previously, the relationship between PLQY and the ASE threshold is complicated. If the PLQY is limited by the ultrafast nonradiative surface-trapping processes, it will play a bigger role than previously envisaged for these mixed-dimensionality heterostructures, and this provides a strong justification for our use of $\sigma_2 \eta_1$ as a basis for analyzing the relationship between threshold fluence and $\sigma_2$. Furthermore, our ASE threshold measurements show that the 2ASE threshold is nearly inversely proportional to $\sigma_2 \eta_1$ in the CdSe/CdS NR heterostructures, which indicates that the PLQY (dependent on the NR length) is indeed limited by some ultrafast nonradiative processes (i.e., other than Auger recombination). The presence of the ultrafast nonradiative surface-trapping processes can be confirmed through TA spectroscopy.

**Figure 3.7 (a)** shows the representative normalized bleaching kinetics at $X_0$ and $Y_0$ with femtosecond time resolution for the 39 nm NRs upon photoexcitation with a pump fluence of approximately 1 electron-hole (e-h) pair per rod. Following 1PA at 3.1 eV (or 2PA at 1.55 eV), e-h pairs are primarily generated in the CdS shell. This results in an ultrafast buildup of the PB transients (at $Y_0$) that occurs on a time scale comparable to the pulse width of the femtosecond laser (i.e., ~150 fs). Following fast hole localization from the CdS shell to the CdSe core, the fast buildup of the PB transient at $X_0$ is simultaneously matched with an equally fast PB decay at $Y_0$ occurring within 1 ps. The ensuing PL emission originates from the radiative recombination between the strongly localized hole in the core and delocalized electron in the NR shell.\textsuperscript{8, 22-25} Due to the limitations in temporal resolution (i.e., ~150 fs) of our femtosecond laser and that of the delay line of the fs-TAS setup (i.e., a
maximum of $\sim 6$ ns, though $\sim 3$ ns is typically used), it may be difficult to elucidate the evidence of such surface/trap states from fs-TAS alone.

**Figure 3.7.** Normalized PB transients at $X_0$ and $Y_0$ shown with fs time resolution (a) and ns time resolution (b) for the 39 nm nano rod with an excitation fluence that
produces ~ 1 e-h pair per rod. The inset shows the rod length dependent surface trapped hole decay lifetime for the heterostructures.

A complementary approach to validating the presence of such nonradiative surface/trap states in the CdS shell would be to examine the recovery of the system back to the equilibrium condition (on a much longer time scale, i.e., tens of ns to μs), with nanosecond (ns-) TA spectroscopy. Figure 3.7 (b) shows the ns-TA kinetics at Y₀ and X₀, where the PB dynamics clearly show a prolonged recovery of the PB signals back to the equilibrium for Y₀ (i.e., CdS shell), while those of X₀ have already decayed. The lifetime of the fast PB decay component for both Y₀ and X₀ coincides with the PL lifetime of the heterostructures in toluene. Hence, we attribute this long PB lifetime in Y₀ to arise from the nonrecovery of the electrons in the lowest CdS energy levels back to the equilibrium. This can be attributed to the presence of some holes still being trapped at the CdS surface states. Considering the high PLQY for these heterostructures (i.e., > 50%), we can further infer that the trapping to these surface hole states would have occurred on a time scale slightly longer than the hole relaxing to the CdSe core (i.e., within a few ps), which is comparable to surface hole-trapping lifetimes reported in the literature for other NCs and NRs.31-33 This assignment is consistent with the rod length-dependent PLQY measurements, where the PLQY decreases with increasing rod length. The longer the NR, the higher the possibility of the holes being trapped at the surface states as they migrate to the CdSe core. The long decay of Y₀ represents the slow recombination between the surface-localized holes with delocalized electrons in the NR. Due to the reduced wave function overlap between localized hole and the delocalized electron in the longer NR, one would expect that the recombination lifetimes would increase as the NR length increases. This is indeed validated by the results in the inset of Figure 3.7(b). Nevertheless, despite that the fast surface hole-trapping time is comparable with the time scales of the biexcitonic recombination avalanche that triggers the ASE, low ASE thresholds can still be achieved due to the large cross-sections and high PLQY (i.e., action cross-sections) of these NR heterostructures.
Lasing from a Spherical Cavity

We demonstrate the potential of these CdSe/CdS NRs as a gain medium for two-photon pumped lasing using a spherical optical cavity. Such optical cavities can potentially possess extremely high Q factors because of the strong confinement of photons within a given modal volume. The CdSe/CdS NRs described above were chemically functionalized and incorporated into a sol-gel-derived silica matrix to permit the adhesion of a thin layer of NRs-silica onto the exterior of commercially available silica microspheres (with a diameter of 5.0 (0.3 μm). The motivation to put NRs-silica composites over a silica sphere instead of NRs directly attached to spheres is to increase the damage tolerance of samples to continuous pulsed excitation. Figure 3.8 (a) shows an optical image of a typical NR-coated microsphere under optical excitation. Under two photon (800 nm) pumping, single-mode threshold lasing from the NR-coated microsphere was achieved as shown in Figure 3.8 (b).

![Figure 3.8](image)

**Figure 3.8.** (a) A microscopic image of a 5 μm silica micro-sphere coated with a CdSe/CdS NRs silica film. (b) The spectra of a single 5 μm microsphere below laser threshold (800 μJ/cm², black) and above laser threshold (990 μJ/cm², red) laser with...
two-photon pumping. The photoluminescence intensity as a function of pump intensity for one- (blue) (c) and two-photon (red) (d) pumping, respectively. Shot dependent lasing intensity of a microsphere under one- (e) and two-photon (f) pumping.

The laser line exhibits a fwhm of ~ 0.75 nm with a Q factor of ~ 800 (i.e., the Q factor is defined as $\lambda / \Delta \lambda$, where $\lambda$ and $\Delta \lambda$ are the wavelength and the fwhm of the laser emission). This value is consistent with previously reported values in similar cavities under one-photon pumping and may be attributed to the self-absorption of NRs, scattering from structural defects within the film and surface roughness.\textsuperscript{6} Figure 3.8 (c) and (d) show the threshold behaviour for two photon pumped lasing in comparison to one-photon pumped lasing. The threshold fluences are 910 ± 50 and 12 ± 2 $\mu$J/cm$^2$ for two-photon and one photon pumped lasing, respectively. The ratio of their threshold fluence is ~ 100, which is typical of those for two-photon to one-photon pumped lasing.\textsuperscript{12-16} While slightly lower 2PA lasing thresholds for NCs in spherical optical resonators have previously been reported,\textsuperscript{16} it should be recognized that such thresholds are a strong function of the cavity Q factor, which is likely to differ significantly from our setup. It should be noted that increasing the size of the NR shell increases not only $\sigma_2$ but also that of the one-photon absorption cross-section. Nonetheless, compared to spherical semiconductor QDs under similar experimental conditions, both the one-photon and two photon pumped lasing thresholds are dramatically lowered in these NRs.\textsuperscript{12-16} Lastly, the photostability of our prototype microsphere laser was evaluated by monitoring the lasing intensity as a function of time under a continuous irradiation at a 1 kHz repetition rate under ambient conditions. Figure 3.8 (e) and (f) show the variation in lasing intensity over 5×10$^6$ laser shots under one-photon and two-photon pumping, respectively. Following such a large number of laser pulse excitation events, the near invariance of the output intensity for both cases bears testimony to the excellent optical stability of the microsphere laser with the CdSe/CdS nanodot/nanorod heterostructures as gain media.
3.4 Conclusion

In summary, ultralow-threshold two-photon pumped ASE and lasing with CdSe/CdS nanodot/nanorod heterostructures was demonstrated for the first time. Essentially, these NR heterostructures afford us the means to independently tune the 2PA cross-section using the CdS shell and the quantum-confined emission wavelengths using the CdSe core. Using these NRs as the gain media, the greatly enhanced $\sigma_2$ allows us to achieve 2ASE in thin film samples with an ultralow threshold pump fluence of 1.5 mJ/cm$^2$ for the 39 nm NRs, which is as much as one order less than that needed for 2ASE of spherical quantum dots. Importantly, by exploiting the unique property of the seeded NRs to exhibit strong quantum confinement even at relatively large rod sizes, a near inverse proportional dependence of the 2ASE threshold on the $\sigma_2 \eta$ was found and validated over a wide volume range for II-VI semiconductor nanostructures. New insight into the charge dynamics of these NR heterostructures was also uncovered through ultrafast optical spectroscopy techniques. Our investigations revealed that while the 2ASE ($\tau \leq 7$ps) can effectively compete with the suppressed Auger process ($\tau_{\text{Auger}} \approx 200$ ps) in these NR heterostructures, the 2ASE could be strongly affected by the competition between hole localization to the CdSe core ($\tau \approx 1$ ps) and to CdS surface states ($\tau > 1$ ps). Lastly, to demonstrate the potential of these NR heterostructures as a viable gain media for achieving 2PE lasing, a high stability prototypical microsphere laser with ultralow pump threshold was showcased.

3.5 References


Chapter 3: Two-Photon Pumped Amplified Spontaneous Emission and Lasing from CdSe Seeded CdS Nanorods

CHAPTER 4

Synthesis and Characterization of Zn$_x$Cd$_{1-x}$S/ZnS Alloy Nanocrystals
4.1 Introduction
Among II-VI colloidal semiconductor NCs, CdSe NCs are probably the most extensively investigated with respect to the development of synthetic routes and applications, including surface passivation with organic or inorganic layers, ligand dynamics, together with photophysical studies and modeling.\textsuperscript{1-7} Although the size dependent emission of CdSe covers a broad range within the visible light spectrum, it is very difficult to obtain blue emission from CdSe NCs since the particle size required is extremely small (< 2 nm). NCs of such a small size are not stable and this leads to Ostwald ripening at relatively low temperature, resulting in a broad emission profile and low quantum efficiency.\textsuperscript{8} In order to overcome this issue, ternary wide band-gap semiconductors can be used instead. One such example is that of Zn\textsubscript{x}Cd\textsubscript{1-x}S. The use of ternary semiconductors is also appealing as the band gap can be tuned by the alloy composition in addition to changing the particle size, thus affording an extra dimension of tunability with respect to particle emission and absorption.

In order to synthesize high quality Zn\textsubscript{x}Cd\textsubscript{1-x}S NCs, different wet-chemistry methods were reported during the last decade. Zn\textsubscript{x}Cd\textsubscript{1-x}S NCs with blue band gap emission and narrow emission peak was first synthesized in 2003 by Zhong and co-workers.\textsuperscript{8} These NCs were synthesized via a hot-injection approach and demonstrated with variable compositions the ability to obtain uniform sizes, as well as extremely narrow emission FWHM (14-18nm).\textsuperscript{8} The hot injection approach requires fast recovery of reaction temperature after injection which is not easy for large scale production.\textsuperscript{8,9} Accordingly, a noninjection based approach was developed by Ouyang et al. in 2008.\textsuperscript{10} In contrast to the homogeneous alloys usually reported previously, they observed a gradient distribution of Cd and Zn components by using solid-state magic-angle-spin (MAS) nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS). In the same year, Bae et al. reported a one-pot synthesis of highly luminescent blue emitting Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS core/shell structured NCs through the second injection of S precursors directly into the reaction vessel with existing Zn\textsubscript{x}Cd\textsubscript{1-x}S NCs without purification.\textsuperscript{10}
Due to the thick ZnS shell passivation on top of the alloyed core, the quantum efficiency was able to reach up to 80%.

However, aside from synthetic milestones, there is limited literature on the detailed investigation of the chemical structures and physical properties of these Zn$_x$Cd$_{1-x}$S/ZnS NCs. Also, information on their synthesis-structure-property relationships is still very much lacking. In this chapter, we focus on the synthesis of highly luminescent Zn$_x$Cd$_{1-x}$S/ZnS core/shell NCs together with detailed characterization of their chemical structures and optical properties by using HRTEM, EDX, PL and absorption measurements.

4.2 Experimental

General methods

Unless stated otherwise, all the reactions were conducted in oven-dried glassware under nitrogen atmosphere using standard Schlenk line techniques. All of the chemicals used are commercially available and were used as received. All solvents were used as received without further purification.

Chemicals

Cadmium oxide (CdO, 99.99%), zinc acetate (99.9%), sulfur (S reagent grade, powder), 1-octadecene (ODE, 90%), oleic acid (OA, 90%) were purchased from Sigma Aldrich. Trioctylphosphine (TOP, 97%) was purchased from Alfa Aesar.

Synthesis of Zn$_x$Cd$_{1-x}$S/ZnS Core/Shell Structured Nanocrystals

The synthetic procedure is similar with Bae et. al.³ 0.0256 g CdO (0.2 mmol), 0.367 g zinc acetate (2 mmol), and 1.4 mL Oleic acid were mixed in a 100 mL 3-neck RBF and degassed 30 min at 100 °C. The temperature was increased to 150 °C and degassed for another 30 min, filled with N$_2$ gas, added 0.6 mL ODE into the mixture and degassed again at 100 °C for about 1 hr. The reaction mixture was then heated to 300 °C under N$_2$ atmosphere to form a clear solution of Cd(OA)$_2$ and Zn(OA)$_2$. A degassed mixture of 0.0128 g S (0.4 mmol) and 0.6 mL ODE was quickly injected into the reaction flask. The reacting temperature was elevated to 310 °C upon the S precursor injection for further growth of Zn$_x$Cd$_{1-x}$S particles. After 8 min of the reaction, aliquot of the reaction mixture was taken to monitor the fluorescence. The temperature
was allowed to maintain at 310 °C for 30 min before 0.0257 g S (0.8mmol) dissolved in TOP introduced into the 3-neck RBF to overcoat the existing ZnₙCd₁₋ₙS cores with ZnS shell without any purification step. After the reaction was completed, the temperature was cooled down to 80 °C and acetone was added to precipitate out the nanocrystals. The as-synthesized ZnₙCd₁₋ₙS were then processed by repeated cycles of precipitation in methanol and re-dispersion in chloroform. Using the same synthetic procedure, we were able to scale up the reaction at least five times by scaling up all the amounts of chemicals with slightly adjusted ratio of Cd(OA) and Zn(OA).

**TEM characterization**

JEOL JEM 1220F (100 kV accelerating voltage) microscope was used to obtain bright field TEM images of the nanoparticles. For TEM sample preparation, the processed nanoparticle solution was dropped onto a 300 mesh size copper grid covered with a continuous carbon film. Excess solution was absorbed by a filter paper underneath and the copper grid was dried under ambient condition.

The High-Angle Annular Dark Field Scanning-TEM (HAADF-STEM) studies and detailed elemental analysis were carried out on a FEI Titan 80-300 electron microscope operated at 200 kV, which is equipped with an electron beam monochromator, an energy dispersive X-ray spectroscopy (EDX) and a Gatan electron energy loss spectrometer. EDX line scan across the spherical particle used scan steps of 0.3 nm with a dwell time of 5 seconds.

**Optical characterization**

Room temperature UV-visible absorption spectra were measured with an Agilent 8453 UV-Visible spectrophotometer. Photoluminescence (PL) spectra were collected with a Shimadzu RF-5301PC Spectrofluorophotometer.

**Time resolved PL**

The time-resolved PL was detected by an Optronis Optoscope streak camera system, which has an ultimate temporal resolution of ~6 ps when operated at the shortest time window of 330 ps. Lastly, lasing from a single microsphere was observed using a home-built confocal microscope with both the excitation pulses and emission light being coupled and collected through the same long
working distance 50× microscope objective (NA = 0.55) and spectrally resolved by the above-mentioned spectrometer and CCD detector.

**Pump-probe experiment**

For femtosecond TAS, the laser source was a Coherent Legend™ regenerative amplifier (150 fs, 1 KHz, 800 nm) that was seeded by a Coherent Vitesse™ oscillator (100 fs, 80 MHz). The 800 nm wavelength laser pulses were from the regen’s output while 400 nm pump pulses were frequency doubled with a BBO crystal. Broadband probe pulses (400-800 nm) were generated by focusing a small portion (~5 μJ) of the fundamental 800 nm laser pulses into a 2 mm-thick sapphire plate. The pump and probe pulses were cross-polarized to eliminate any contribution from coherent artifacts at early times. Pump-induced changes in transmission (ΔT/T) of the probe beam were monitored using a standard monochromator/PMT configuration with lock-in detection. The pump beam was chopped at 83 Hz and this was used as the reference frequency for the lock-in amplifier.

**4.3 Results and Discussion**

**Preparation and TEM characterization of ZnₓCd₁₋ₓS/ZnS core/shell NCs**

ZnₓCd₁₋ₓS/ZnS core/shell structured NCs were prepared through a one pot, two-step hot injection method similar to a previously reported method.¹⁰ CdO and Zn(acet)_₂ are mixed with OA and this forms Cd-Oleate and Zn-Oleate at high temperatures. After injection of the sulfur precursor (S-ODE), Cd and Zn nucleate and form ZnₓCd₁₋ₓS cores. In this reaction, the Zn to Cd molar ratio was as large as 10 to 1. Thus, with the second injection of another sulfur precursor (S-TOP), ZnS shell forms and increases the fluorescence efficiency dramatically as the shell grows. The relatively narrow emission spectrum indicates that the resultant ZnₓCd₁₋ₓS and ZnₓCd₁₋ₓS/ZnS nanoparticles are fairly homogeneous in term of size and composition. **Figures 4.1 (a), (b)** are representative TEM and HRTEM images of ZnₓCd₁₋ₓS cores. The particles are uniform spheres of ~6 nm in diameter. EDX (**Figure 4.1 (c)**) measurements gave a Cd:Zn composition of around 3.4:1 (Zn₀.2Cd₀.8S) indicating a Cd dominated alloy.
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Figure 4.1. (a) TEM image of Zn\textsubscript{0.2}Cd\textsubscript{0.8}S NCs. (b) HRTEM image shows zinc-blende structure of Zn\textsubscript{0.2}Cd\textsubscript{0.8}S NCs. (c) EDX data of the same sample.

As observed from TEM images, the diameter of the NCs increased from \~6 nm to \~9 nm in diameter upon growth of ZnS. This increase in size corresponds to 4-5 layers of ZnS shell formation which is further confirmed by STEM and EDX analysis of the Cd to Zn ratio. It is known that in the weak quantum confinement regime, where the particle radius is close to or larger than the Bohr exciton radius, the size distribution results in a relatively small variation in the band gap energy. The width of the emission spectra width thus becomes dependent mainly on the composition of the NCs rather than their size distribution. The typical exciton Bohr radii of ZnS and CdS are 2.2 nm and 3.0 nm respectively. Hence the \~2.5 nm particle radius of the particles obtained in this work is comparable to the average Bohr radius and thus no
significant red shift of the emission was observed (< 5nm) with the 4 nm increase in diameter after the ZnS shell growth. **Figures 4.2 (a)-(c)** represent the TEM, HRTEM and EDX of NCs after second injection of sulfur precursor respectively.

**Figure 4.2.** (a) TEM image of Zn_{0.2}Cd_{0.8}S/ZnS core/shell structured NCs obtained after 15min of reaction from the second sulfur injection. (b) Representative HRTEM of Zn_{0.2}Cd_{0.8}S/ZnS (c) EDX data of the same sample.

**Figure 4.3** reflects the PL spectra of the Zn_{x}Cd_{1-x}S core and Zn_{x}Cd_{1-x}S/ZnS core/shell NCs at different reaction times. Upon injection of the first sulfur precursor (S-ODE), the band edge emission of Zn_{x}Cd_{1-x}S NCs can be measured after 1 min of reaction time. The broad emission hump centered at 640 nm originates from surface trap states. The thermal annealing process
slowly reduces the original deep-trap emission by removing crystalline defects. At ~ 15 min after injection, the band edge emission had already become prominent. With the shell formation from the addition of the second sulfur precursor, S-TOP, the surface trap emission was completely suppressed, showing only the strong band edge emission with a relatively narrow spectral band width (FWHM ~23 nm).

![Figure 4.3. PL spectra of a Zn$_x$Cd$_{1-x}$S core and Zn$_x$Cd$_{1-x}$S/ZnS core/shell NCs at different reaction times.](image)

By changing the feed ratio of Cd to Zn and keeping all other reaction parameters constant, the emission wavelength of Zn$_x$Cd$_{1-x}$S/ZnS NCs can be tuned from ~420 nm to ~480 nm as shown in Figure 4.4. However, TEM images of these Zn$_x$Cd$_{1-x}$S/ZnS NCs show no obvious difference in particle size. Thus we believe that the emission wavelength shifts are not attributed to quantum-size effect, but mainly due to continuous shift of the band gap energy of the NCs with a change in their composition.
Figure 4.4. Tunable PL spectra of Zn$_x$Cd$_{1-x}$S/ZnS NCs.

Although the spherical shape and size of Zn$_x$Cd$_{1-x}$S is highly reproducible at the same metal precursors’ ratio, the shelled structures tended to be irregular from batch to batch. Some of the resultant particles have been observed to have pyramid-like branched structures as shown in Figure 4.5. The lattice constant determined (as shown in Figure 4.1 (b)) showed a zinc blende cubic structure for the Zn$_x$Cd$_{1-x}$S nanocrystals. We surmised that the zinc blende Zn$_x$Cd$_{1-x}$S cores produced at the nucleation stage supported the formation of wurzite ZnS arms during the kinetically controlled shell growth process, resulting in branched core-shell structures similar to those of CdSe seeded CdS nanotetrapods.$^{11}$

Figure 4.5. TEM image of a representative flower shaped Zn$_x$Cd$_{1-x}$S/ZnS NCs. Inset is the zoom in image.
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It is of fundamental interest to study the extent of alloying in these ternary NCs alloys prepared using a one pot reaction scheme. Although the chemical composition of these ternary NCs and their relative elemental ratio can be readily determined by using XRD and EDX analyses, it is challenging and not straightforward to determine whether alloying in these ternary NCs is homogeneous. Therefore, High-Angle Annular Dark Field Scanning-TEM (HAADF-STEM) and EDX line scan were carried out to monitor the Cd and Zn distribution over a single Zn$_x$Cd$_{1-x}$S/ZnS particle, as illustrated in Figure 4.6 (a). The elemental intensity v.s. position plot exemplifies the pure ZnS shell at the outer part of the particle and gradient alloy core. The center of Zn$_x$Cd$_{1-x}$S is Cd rich but the Zn content increases continuously along the growth direction.

![Figure 4.6](image)

**Figure 4.6.** (a) STEM image of Zn$_x$Cd$_{1-x}$S/ZnS NCs showing the core shell structure of the particle. The yellow line illustrates the position of EDX line scan across the spherical particle (b) EDX line scan of the spherical particle in the direction of arrow showing in (a).

To quantitatively examine the chemical composition of a single Zn$_x$Cd$_{1-x}$S NC, the probe beam was separately focused onto the center and border of the particle as depicted in Figure 4.7 (a). The red spots represent the locations used to obtain the EDX spectra. The Cd to Zn ratio calculated at position 1 is 4.4 : 1 and 1.9 : 1 at position 2. This gradient Cd and Zn distribution can be explained as follows: Since Cd$^{2+}$ has a weaker binding energy with oleic acid compared with Zn$^{2+},^{10,12}$ Cd(OA)$_2$ reacts with sulfur precursor faster than Zn(OA)$_2$, and thus Cd$^{2+}$ and S$^{2-}$ nucleate first forming the gradient Zn$_x$Cd$_{1-x}$S alloyed particles even though the initial Cd to Zn feed ratio is about 1 to 10.
Temperature dependent PL

To further characterize the fluorescence properties from solution prepared Zn$_x$Cd$_{1-x}$S/ZnS NCs, additional experimental studies at different temperatures were conducted on NCs of a certain composition. Similar to the PL observed at room temperature (Figure 4.4), these NCs always showed a dominant sharp, near band-edge PL with a weak broad trap-state related emission at low temperature. We will focus on the properties of the band edge PL. According to previous publications, the emission intensity of an ideal Type I core/shell semiconductor quantum dot is near temperature independent as a result of strong spatial localization of the exciton in the core and large energy level separations. The room temperature thermal energy is not large enough to change the charge carrier population among different energy levels.$^{13,14}$ However, Figure 4.8 clearly shows that the emission intensity quickly decreases with increasing temperature, which indicates that the electronic properties of the above synthesized Zn$_x$Cd$_{1-x}$S/ZnS NCs are different from those of ideal Type I quantum dots.

Figure 4.7. (a) STEM image of a Zn$_x$Cd$_{1-x}$S NCs paritcle. The red spots 1 and 2 are the locations used to obtain the EDX spectra depicted in (b) and (c) separately.
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Figure 4.8. PL spectra of Zn<sub>x</sub>Cd<sub>1-x</sub>S/ZnS NCs film at various temperatures after photoexcitation with 400 nm, 150 fs and 1 KHz laser pulses at a pump fluence of 0.2 μJ/cm<sup>2</sup>.

The temperature-dependent integrated band edge emission intensity was extracted and presented in Figure 4.9. It is well-fitted by an Arrhenius plot with two thermal activation processes:

\[ I(T) = \frac{I_0}{1 + A_1 \exp(-E_1 / (k_B T)) + A_2 \exp(-E_2 / k_B T)} \]  

(4.1)

where \( E_1 \) and \( E_2 \) denote different activation energies for the two different thermal activation processes; and \( A_1 \) and \( A_2 \) are the relative ratios of the two non-radiative recombination processes. From the fit, we obtained the activation energies of \( E_1 = 32 \) meV and \( E_2 = 315 \) meV. Based on magnitude of the activation energies determined, we deduce that \( E_1 \) is likely to be related to the thermal energy required for changing the population between the lowest energy level and the second energy level in the NCs; while \( E_2 \) would correspond to the thermal-assisted capture of carriers at some defect states in the NCs.
Chapter 4: Synthesis and Characterization of $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{ZnS}$ Alloy Nanocrystals

**Figure 4.9.** The dependence of the integrated PL intensity as a function of $T$ for $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{ZnS}$ NCs film. The solid curve is an Arrhenius fit with two activation energies. Excited with 400 nm, 150 fs and 1 KHz laser pulses at a pump fluence of 0.2 $\mu$J/cm$^2$.

**Figure 4.8** also shows that these NCs emit at 478 nm at room temperature. However, the emission peak energy monotonically increases with decreasing temperature. This is usually caused by the thermal expansion of the crystal lattice and the presence of exciton-phonon interactions in semiconductors. **Figure 4.10** shows a plot of the emission peak energy as a function of temperature. The open circles denote experimental data and the solid line indicates a theoretical fit using the Bose-Einstein equation:

$$E(T) = E(0) - \frac{\lambda}{\exp(h\omega/(k_B T)) - 1} \quad (4.2)$$

where $E(0)$ is the band gap at 0 K, $\hbar\omega$ is the effective phonon energy, and $\lambda$ is the proportionality constant. Figure 4.10 clearly shows that the temperature dependent evolution of the emission peak can be well-fitted with Equation 4.2. The fitting parameters obtained are $E(0) = 2.66$ eV, $\lambda = 53$ meV, and $\hbar\omega = 16$ meV. This fitted effective phonon energy is much smaller than the longitudinal optical (LO) phonon energy (i.e., $\sim 42$ meV) – indicating that the acoustic phonons have a significant contribution to the shrinking of the band gap in this NC. The values of band gap determined under the present...
experimental conditions are 2.66 eV at 0 K and 2.59 eV at 300 K for the NC investigated here.

\[ \Gamma = \Gamma_{inh} + \gamma_{LA} T + \frac{\Gamma_{LO}}{\exp(h\omega_{LO}/k_B T) - 1} \]  

(4.3)

where \( \Gamma_{inh} \) is the inhomogeneous broadening factor, \( \gamma_{LA} \) is the exciton-LA phonon coupling strength, \( \Gamma_{LO} \) is carrier-LO phonon coupling strength, and \( h\omega_{LO} \) is the LO phonon energy (used with 42 meV here).
Chapter 4: Synthesis and Characterization of Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS Alloy Nanocrystals

**Figure 4.11.** Temperature dependence of the PL peak width (FWHM). The solid curve is a fit based on Equation 4.3. The dashed line (Green) shows the contribution from the LA phonon scattering alone; while the dotted line (Blue) indicates the contribution from the LO phonon alone. In both cases the inhomogeneous broadening is also added. Excited with 400 nm, 150 fs and 1 KHz laser pulses at a pump fluence of 0.2 μJ/cm\textsuperscript{2}.

The experimental data can be well-fitted with Equation 4.3 and the fitting parameters obtained are $\Gamma_{inh} = 102$ meV, $\gamma_{LA} = 36.6$ μeV/K, and $\Gamma_{LO} = 13.11$ meV (Figure 4.11). If compared with bulk semiconductors, the inhomogeneous broadening is greatly enhanced in the NCs as a result of larger size and shape distributions.\textsuperscript{15-19} To better appreciate the effects of LA phonon scattering (i.e., term 2 of Equation 4.3) or LO phonon scattering (i.e., term 3 of Equation 4.3) to the band broadening, we consider the cases where either contribution is disregarded. In Figure 4.11, the dashed line shows the case where the contributions from LA phonon scattering and inhomogeneous broadening are considered; while the dotted line shows the case where LO phonon scattering and inhomogeneous broadening are considered. Note the crossover at ~ 200 K where the LA phonon broadening initially dominates over the LO phonon broadening, but is rapidly superseded by the LO phonon broadening that increases quickly with the lattice temperature. Nonetheless, we note that the LO phonon coupling strength obtained here is smaller than the values obtained for other wide band gap semiconductors.\textsuperscript{15-21}
Chapter 4: Synthesis and Characterization of Zn$_x$Cd$_{1-x}$S/ZnS Alloy Nanocrystals

Time-Resolved PL

It is of crucial importance to get a clear understanding of the charge carrier dynamics inside the ZnCdS/ZnS NCs for all potential optoelectronic applications. Therefore, pump power dependent time-resolved (TR) PL measurements were performed. The emission decay curves and their corresponding decay fits at three typical pump fluences are shown in Figure 4.12. Here, the pump fluences were converted to the average number of excitons per particle generated per pulse in the ensemble by:

\[ <N_{e-h}> = \frac{F \cdot \sigma}{\hbar \omega} \]  

(4.4)

where \( F \) is the pump fluence (uJ/cm$^2$), \( \hbar \omega \) is the photon energy at 400 nm.

![Figure 4.12](image.png)

*Figure 4.12.* Lifetime measurements of the Zn$_x$Cd$_{1-x}$S/ZnS NCs under pump fluences corresponding to an average of 1 e-h pair (Black), 2 e-h pairs (Red) and 3 e-h pairs (Green) per particle.
Chapter 4: Synthesis and Characterization of Zn$_x$Cd$_{1-x}$S/ZnS Alloy Nanocrystals

Figure 4.13. Decay transient of the two electron-hole pair states for the Zn$_x$Cd$_{1-x}$S/ZnS NCs. A biexciton lifetime of ~ 1 ns was extracted from fitting with a single exponential decay function (line).

Figure 4.12 shows that the decay curves can be well fitted by two- or three-exponentials with the system response of the streak camera deconvoluted. At low pump fluence level (the photo-generated excitons per particle are less than unity), the decay transients are almost invariant with the pump fluence. However, these emission decays already show multi-exponential behavior at this fluence level. This indicates that trap states can effectively compete with the radiative recombination in ZnCdS/ZnS NCs, which is consistent with the relative low quantum yield observed at room temperature. At a higher pump fluence level (the photo-generated excitons per particle are more than unity), the multi-particle interaction induced non-radiative Auger recombination is clearly observed as additional fast decay processes (Figure 4.12). Following the procedure previously reported by Klimov et. al., the biexciton Auger recombination lifetime was extracted and shown in Figure 4.13. It was fitted to be 1 ns, which is much longer than the biexciton lifetime (i.e., ~ few tens of ps) for small CdSe spherical dots which emit photons at a similar wavelength. Hence, it may be inferred that the biexcitonic Auger recombination rates are indeed greatly suppressed in these gradient alloyed...
semiconductor NCs. The optical gain build-up time compares favourably with the non-radiative Auger processes.

**Transient Absorption**

To characterize the potential coherent light emission properties of the ZnCdS/ZnS NCs, pump fluence dependent transient absorption (TA) experiments were conducted.

*Figure 4.14.* (a)-(d) Differential transmission spectra clearly show blue shifting of the photobleaching (developing of gain) peak with increasing pump fluence. The CdZnS/ZnS quantum dot solution was contained in 1 mm quartz cell following excitation at 400 nm (1 KHz, 150 fs). Red spectrum (1 ps), Green spectrum (5 ps), Blue spectrum (2 ps), Cyan spectrum (100 ps), Magenta spectrum (1 ns).

In the gradient-alloyed ZnCdS/ZnS NCs, as a result of the "V" shaped distribution of Zn atoms across the NC diameter, the lowest energy exciton is strongly localized in the central part of the NC. Further from the center region, exciton energy increases and spatial localization of the exciton decreases. Therefore, the density of states increases much quicker with the energy for ZnCdS/ZnS NCs when compared to NCs with perfect type I band alignment.
This is evidenced in the differential transmission spectra (Figure 4.14), which clearly shows that the photobleaching amplitude (development of optical gain) increases quickly with increasing the probe photon energy around the band edge. Figure 4.14 shows that the development of gain presumably due to biexcitons occurs at energies higher than that of the single exciton peak. Additionally, it is seen that multie exciton states can last over hundred ps.

**Inner structure and band alignment simulation**

In order to understand the blue shift of the optical gain, we consider the charge separation in the nanocrystal. Compositional analysis of isolated particles reveals that the alloy cores are inhomogeneous. According to STEM-EDX results above, at the center of the core, the composition was found to be Cd$_{0.8}$Zn$_{0.2}$S, while further from the center the composition was measured to be Cd$_{0.5}$Zn$_{0.5}$S. This implies that a compositional gradient developed in the core, as illustrated in Figure 4.15. We model the compositional inhomogeneity by the core itself exhibiting a core/shell structure, with an inner core radius of $R_i$.

![Figure 4.15](image)

*Figure 4.15. Model of the compositional inhomogeneity of Cd$_x$Zn$_{1-x}$S particle. The Cd$_x$Zn$_{1-x}$S core itself exhibits a core/shell structure with an inner core radius of $R_i$.*

Under the effective mass approximation, the core may be studied using the simple two band/two effective mass model described by Piryatski *et al.* The computed Schrödinger equation for the radially symmetric potential is shown in Figure 4.16 (a). Because the band offset for the quasi-electrons ($\Delta U_e$) is
much larger than that of the holes ($\Delta U_h$), a quasi-Type II situation exists in which the electron is localized in the defect but the hole is delocalized over the entire core. We have further found that as the size of the inner core radius shrinks, the quasi electron-hole overlap likewise diminishes. This should allow for exciton-exciton repulsion and a corresponding blue shift, consistent with observations in “giant” CdSe/CdS core/shell nanocrystals with very thick shells as demonstrated in Figure 4.16(b).23

Figure 4.16. (a) Band alignment of Cd$_x$Zn$_{1-x}$S. $\Delta U_e$ and $\Delta U_h$ are energy offsets of electron and hole at the interface of Cd rich inner core and Zn rich outer shell. (b) shows a contour plot of the calculated electron-hole overlap integral. Two grey lines are boundaries between regions of (R, H)-space that correspond to different localization regimes. These two lines are calculated from the condition that the probabilities of finding an electron (left) or a hole (right) in the core and the shell are equal to each other.

4.4. Conclusion

In this chapter, we successfully synthesized high quality, blue emissive Zn$_x$Cd$_{1-x}$S/ZnS NCs. Based on the single particle “point” EDX and STEM line scan, the Zn$_x$Cd$_{1-x}$S core is found to be inhomogeneous in which the center of the particle is Cd rich but the outer part is Zn rich. Optical properties of this kind of alloy NCs are fully studied. Temperature dependent position of band edge emission implies that the band structure of the synthesized Zn$_x$Cd$_{1-x}$S/ZnS NCs are different from those of perfect type I quantum dots. According to TRPL experiment, the biexciton lifetime is determined to be as
long as 1 ns, indicating that the Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS NCs are good optical gain material. Interestingly, the biexciton gain is observed at the higher energy side of the spontaneous emission spectrum during transient absorption measurement. The temperature dependent PL, long-lived biexciton lifetime and blue side gain build-up illustrated the unique optical properties of Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS NCs unlike those of CdSe or CdSe/CdS type of NCs. In order to understand these phenomena, charge separation in the nanocrystal is considered. We model the compositional inhomogeneity by the Zn\textsubscript{x}Cd\textsubscript{1-x}S core itself exhibiting a core/shell structure with a type II like energy band alignment at the core/shell interface. Based on high quantum yield, weak quantum confinement and type II band alignment induced charge separation, ultra-low threshold stimulated emission at blue wavelengths is expected from Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS NCs.

4.5 References

Chapter 4: Synthesis and Characterization of Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS Alloy Nanocrystals

CHAPTER 5

Amplified Spontaneous Emission from Zn$_x$Cd$_{1-x}$S Alloy
Semiconductor Nanocrystals and its Optofluidics Application
Chapter 5: Amplified Spontaneous Emission from Zn\textsubscript{x}Cd\textsubscript{1-x}S Alloy Semiconductor Nanocrystals and its Optofluidics Application

5.1 Introduction

Wet-chemically synthesized colloidal semiconductor nanocrystals (NCs) are desirable materials as optical gain media due to their size-dependent emission wavelengths, ease of fabrication and facile incorporation into a plethora of optical microcavities. Since ASE was first measured from a film of close packed CdSe NCs in 2000,\(^1\) room temperature stimulated emission and lasing over the entire visible range and even with low pump thresholds were demonstrated for solid state NCs which are mainly comprised of close-packed films or NCs incorporated sol-gel derived matrices. Such solid structures are important to ensure a sufficiently high volume fraction which is required to overcome the fast Auger recombination rates intrinsic to strongly quantum confined NCs as mentioned in Chapter 1. This requirement limits the lasing establishment in NCs and restricts most of the semiconductor NCs lasing devices to solid film.

To better its lasing performance, optimization of solid NC film is often challenging because a myriad of inter-connected factors such as quantum yield of NCs, volume fraction and surface morphology of NC film are involved. In addition, influence of each factor on the lasing performance is even more difficult to establish as the variation from film to film is too large. Efforts thus far in this field have not addressed two important issues: 1) The lack of a clear picture on the build-up of ASE and how much amplification is expected in an ensemble of NCs; 2) NCs gain media has not been demonstrated for any practical application.

Herein we employed Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS alloyed core/shell semiconductor NCs as optical gain media and showed that these NCs have sufficiently low pump threshold which allows them to be studied in an optofluidic device. This unprecedented achievement of room temperature ASE in a stable NC-based optofluidic device allowed us to provide a quantitative description of the ASE amplification process in a given NCs gain media and examine several factors such as quantum yield and volume fraction of NCs. Moreover, a potential application of the optofluidic NCs ASE device as a nonlinear optical detection platform for metal-ion sensing is demonstrated.
5.2 Experimental

General methods

Unless stated otherwise, all the reactions were conducted in oven-dried glassware under nitrogen atmosphere using standard Schlenk line techniques. All of the chemicals used are commercially available and were used as received. All solvents were used as received without further purification.

Chemicals

Cadmium oxide (CdO, 99.99%), zinc acetate (99.9%), sulfur (S reagent grade, powder), 1-octadecene (ODE, 90%), oleic acid (OA, 90%) were purchased from Sigma Aldrich. Trioctylphosphine (TOP, 97%) was purchased from Alfa Aesar.

Synthesis of ZnₓCd₁₋ₓS/ZnS Core/Shell Structured Nanocrystals

The synthetic procedure is similar with Bae at al.² 0.0256 g CdO (0.2mmol), 0.367 g zinc acetate (2 mmol), and 1.4 mL oleic acid is mixed in a 100 mL 3-neck RBF and degassed 30 min at 100 °C. Increase the temperature to 150 °C and degassed for another 30 min, filled with N₂ gas, added 0.6 mL ODE into the mixture and degas again at 100 °C for about 1hr. The reaction mixture was then heated to 300 °C under N₂ atmosphere to form a clear solution of Cd(OA)₂ and Zn(OA)₂. A degassed mixture of 0.0128 g S (0.4 mmol) and 0.6 mL ODE was quickly injected into the reaction flask. The reacting temperature was elevated to 310 °C upon the S precursor injection for further growth of ZnₓCd₁₋ₓS particles. After 8 min of the reaction, aliquot of the reaction mixture was taken to monitor the fluorescence. The temperature was allowed to maintain at 310 °C for 30 min before 0.0257 g S (0.8 mmol) dissolved in TOP introduced into the 3-neck RBF to overcoat the existing ZnₓCd₁₋ₓS cores with ZnS shell without any purification step. After the reaction was completed, the temperature was cooled down to 80 °C and acetone was added to precipitate out the nanocrystals. The as-synthesized ZnₓCd₁₋ₓS/ZnS were then processed by repeated cycles of precipitation in methanol and re-dispersion in chloroform. Using the same synthetic procedure, we were able to scale up the reaction at least 5times by scaling up all the amounts of chemicals with slightly adjusted ratio of Cd(OA) and Zn(OA).
Surface modification of Zn$_x$Cd$_{1-x}$S/ZnS Nanocrystals
6 g TOPO (90%) were degassed at 150 °C for 1 hr. The mixture was switched to N$_2$ and allowed to cool down to 80 °C before Zn$_x$Cd$_{1-x}$S/ZnS-chloroform solution was added. Chloroform was evaporated under vacuum at the same temperature before increase the temperature to 140 °C, upon which a mixture of 0.1 g diethylzinc, 0.15 g (TMS)$_2$S and 1 mL TOP was dripped into the 3-neck RBF slowly under N$_2$ within 30 min. The temperature was then cooled down to 100 °C and maintained at that temperature for 1 hr. The surface coated NCs were then processed by repeated cycles of precipitation in methanol and re-dispersion in chloroform.

Zn$_x$Cd$_{1-x}$S/ZnS sol-gel film fabrication
The route employing 3-aminopropyltrimethoxysilane (APS) as silica precursor was adopted from a previously reported method$^3$ with slight modifications. Processed Zn$_x$Cd$_{1-x}$S/ZnS (50 mg) were cap-exchanged with 100 μL AP in 100 μL ethanol. This afforded a clear solution of NCs into which 20 μL APS and 10 μL TEOS was added and stirred vigorously for ~1 min. The resultant viscous liquid was allowed to pass through a 0.2 μm syringe filter and spin-coated onto a pre-cleaned glass substrate, yielding a clear, smooth film. The film was subsequently annealed on a hotplate for 5 min at 100 °C, and at 150 °C for 2 min. Transparent, smooth films were formed without cracking observed.

Zn$_x$Cd$_{1-x}$S/ZnS-AP solution preparation
Zn$_x$Cd$_{1-x}$S/ZnS NCs were process 3 cycles of precipitation in acetone and re-dispersion in chloroform and another 3 cycles of precipitation in methanol and re-dispersion in hexane. The resultant NCs (~250 mg) are leaving dry under N$_2$ followed by adding 2 mL AP. The NCs-AP mixture is sonicated for 1 hr to allow the NCs to dissolve completely and gives rise in a clear, slightly viscous solution.

Optofluidic chip fabrication
A general procedure$^4$ for replica molding and rapid prototyping is outlined on Figure 5.1. A patterned silicon mold is fabricated by typical photo lithography process including UV exposure and selective wash-off of the photoresist. The micro features of the mold are examined by microscope and profilometer. Soft
lithography starts with the production of a polydimethylsiloxane (PDMS) replica of the pre-prepared mold. The PDMS used in our experiment is supplied in two components, a base and a curing agent. To produce a replica, we mix the two parts together (10:1, base: curing agent) pour the liquid pre-polymer over the mold that has been silanized with Perfluoro (methyldecalin) before hand. The liquid pre-polymer conforms to the shape of the mold with high fidelity. After being baked in oven at 80 °C for 30 min, the polymer cross-linked into solid, rubber like PDMS and could be peeled off without damaging the pattern on the mold. Opening of the channels are made by hole puncher under a microscope. While baking the PDMS replica, same liquid pre-polymer mixture are spincoated onto a glass slide and baked at 80 °C for five minutes. PDMS replica is then attached to the glass substrate to enclose the channel and bake in oven overnight in order to form irreversible seal.

![Scheme 5.1. Simplified outline of photolithography silicon molding and soft lithography optofluidic chip fabrication process.](image-url)
Optical characterization

Room temperature UV-visible absorption spectra were measured with an Agilent 8453 UV-Visible spectrophotometer. Photoluminescence (PL) spectra were collected with a Shimadzu RF-5301PC Spectrofluorophotometer.

For the ASE measurements, the excitation source was a Coherent Legend regenerative amplifier (150 fs, 1 kHz, 800 nm) that was seeded by a Coherent Mira oscillator (100 fs, 80 MHz). 400 nm wavelength laser pulses were obtained with a BBO doubling crystal and focused by a cylindrical lens (with focal length f = 20 cm) to a stripe (of dimensions (~1 mm × 7.5 mm). The sample slides were aligned perpendicular to the excitation stripe. The emission from the film edge was collected in a lateral configuration by a pair of lenses focused onto an optical fiber coupled to a spectrometer (Acton, Spectra Pro 2500i) and detected by a charge coupled device (Princeton Instruments, Pixis 400B CCD camera).

Room temperature modal gain measurements were carried out using a standard VSL method. The excitation stripe and emission collection set-up was the same as described above. The excitation stripe length was varied through an adjustable slit actuated by a micrometer which was placed at the focal line of the cylindrical lens.

5.3 Results and Discussion

As discussed in chapter 4, optoelectronic properties such as high quantum yield, weak quantum efficiency as well as type II band alignment suggests that Zn$_x$Cd$_{1-x}$S/ZnS NCs can be a good optical gain medium. In this work we first synthesized Zn$_x$Cd$_{1-x}$S/ZnS NCs and incorporated them into a sol-gel derived silica matrix. Then we demonstrated ultra-low pump threshold ASE from the resulting Zn$_x$Cd$_{1-x}$S/ZnS-silica composites at room temperature.

As discussed in Chapter 2, direct incorporation of as-synthesized NCs into sol-gel derived silica matrix is futile. Due to the presence of OA as capping ligands on the surface of NCs, serious aggregation of NCs occurs during the exchange of capping ligands with APS. In order to circumvent this problem, the Zn$_x$Cd$_{1-x}$S/ZnS alloyed core/shell NCs were further coated with an additional shell of ZnS in the presence trioctylphosphine oxide (TOPO) at
140 °C. This additional ZnS shell provides surface passivation and prevents aggregation of NCs during the ligand exchange process which involved repeated cycles of precipitation and re-dispersion. Subsequent incorporation of the ZnS overcoated Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS NCs into the sol-gel derived silica via slight modifications of a published method\textsuperscript{3} was successful. This attests the need for the surface modification of the Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS NCs afforded by the additional ZnS overcoating step.

Atomic Force Microscope (AFM) measurements on the resulting Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS silica composite film, as exemplified in Figure 5.1, yielded a smooth morphology with a typical surface roughness (RMS) of about ~5 nm, over a 1 μm\textsuperscript{2} scan area, suggesting a uniform incorporation of NCs into the sol-gel derived silica matrix.

![AFM Image](image.png)

**Figure 5.1.** Representative AFM image of a typical Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS-silica film spin-coated onto a glass substrate.

Optical excitation of the alloy-silica films proceeded via a frequency-doubled Ti:Sapph with a pulse duration of 150 fs at a repetition rate of 1 kHz. The laser pulses were focused into a ~1 mm × 7.5 mm stripe using a cylindrical lens and the resulting emission was collected via an optical fiber coupled to a spectrometer and detected by a charge coupled device (CCD) camera. **Figure 5.2** illustrates the room temperature photoluminescence (PL) spectra at different excitation pump intensities of Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS-silica
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Figure 5.2. Room temperature ASE spectra from Zn$_x$Cd$_{1-x}$S/ZnS-silica film with Zn$_x$Cd$_{1-x}$S core dimensions of ~5 nm and ~9 nm in diameter with ZnS shell.

Composite films. A narrowing of the emission profile from ~24 nm to ~12 nm is readily observed at higher pump powers, signifying the onset of ASE. A low threshold of ~75 Jcm$^{-2}$ was derived from a plot of the integrated PL intensity against pump power as depicted in Figure 5.3. This is comparable to the lowest threshold value we reported for CdSe/CdS tetrapod which is 5 and 50 times lower than the best ASE thresholds previously reported in CdSe/CdS/ZnS based zirconia films, and CdS/ZnS based silica films respectively.

Figure 5.3. The corresponding integrated PL intensity versus pump power spectra of the ASE transition.
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From Figure 5.2, we obtained that the ASE peak shows up from the higher energy side of the single exciton PL peak. This indicates that the gain buildup at the blue side of the spontaneous emission and agrees well with the transient absorption experiments as discussed in Chapter 4. The repulsion of biexciton recombination energy and the ultra-low threshold obtained further confirm our earlier assumption that the alloyed core of the NCs has a type II band-alignment.

The room temperature modal gain of the Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS-silica composites was evaluated using Variable Stripe Length measurements, as illustrated in Figure 5.4. A linear fit was used to account for the change in PL intensity as a function of excitation stripe length prior to optical amplification\textsuperscript{5} while the onset and subsequent saturation of the ASE intensity was fitted with a previously reported 1-D amplifier model\textsuperscript{6,7}:

\[
I \propto e^{g l_\alpha \left(1 - e^{-\frac{-(z-z_0)}{l_\alpha}}\right)}
\]  

Figure 5.4. Room temperature Variable Stripe Length (VSL) measurements of the same Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS-silica film from Figure 5.2. The dotted lines are a fit using a 1-D amplifier model which takes into account saturation due to Auger recombination processes.
where \( I, g, \) and \( z \) are the ASE intensity, modal gain coefficient and excitation stripe length respectively and \( z_0 \) accommodates for possible pump beam inhomogeneity and delayed ASE onset. The parameter \( l_\alpha \) is defined as the modal gain lifetime of the NCs in the film multiplied by the speed of light within the gain medium and accounts for saturation in the ASE intensity.\(^6\) Extraction of the parameters \( g \) from the fit yielded value of \( \sim 100 \text{ cm}^{-1} \) which is comparable with what is reported for CdSe/CdS tetrapod. But the \( 100 \text{ cm}^{-1} \) gain is unlikely due to big absorption cross-section as the particle size is significant smaller than that of the tetrapod which contains four giant CdS arms. Thereby we believe the reduced Auger lifetime caused by the type II band structure is the major contribution to the VSL gain.

Given the structural robustness of the Zn\(_x\)Cd\(_{1-x}\)S/ZnS-silica composites, we examined their capacity to exhibit multiexcitonic ASE, which can only take place under sufficiently intense optical excitation such that the excited energy states higher than 1S\(_e\) are simultaneously populated.\(^8,9\) As shown in Figure 5.5, a second emission peak emerges at \( \sim 445 \text{ nm} \) when larger pump intensities are used and this peak is very close to the biexcitonic ASE emission peak centered at \( 455 \text{ nm} \).

![Figure 5.5. PL intensity of a Zn\(_x\)Cd\(_{1-x}\)S/ZnS-silica film under relatively high excitation pump intensities.](image)

Under higher excitation pump intensities, this second emission peak was also observed for other Zn\(_x\)Cd\(_{1-x}\)S/ZnS NCs films with different alloy composition
(i.e. different values of $x$) and film thickness. Thus we can exclude the possibility that the 445 nm emission shoulder is due to a broad gain profile coupled to different waveguide mode.\textsuperscript{10} Based our understanding on multiexcitonic ASE of binary NCs such as CdSe, this higher energy ASE peak at large pump intensities can be ascribed to $1P_e$-$1P_h$ transition which becomes efficient when the $1S_e$-$1S_h$ transition becomes saturated. But the energy difference between the two transitions is so close that the ASE peak appears continuous over the range of wavelengths, 440 nm – 455 nm. This interesting behavior may due to increased density of states created by alloying of two kinds of semiconductor materials. Extensive computational work and quantitative measurements are needed to gain more insights into the energy states and band structure of this alloyed core/shell NCs.

Since an ultra-low blue color ASE was readily measured from the Zn$_x$Cd$_{1-x}$S/ZnS-silica composite, we subsequently attempted to incorporate these Zn$_x$Cd$_{1-x}$S/ZnS NCs into an optofluidic device to achieve a dynamic, liquid phase ASE.

\textbf{Figure 5.6.} Photo illustration of optofluidic PDMS chip. NCs solution is driven through the channel from inlet opening and excited at the three outlet channels. The chip is thoroughly rinsed before measuring a different sample.
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The optofluidic chip design is illustrated in Figure 5.6. The chip is sealed on a glass substrate, with two solution inlets and three parallel outlets. Figure 5.7 shows the microscope image of the micro-channels of the optofluidic chip. PDMS was used to form the highly optical transparent micro-channels which also function as emission waveguide. According to the working principle of a waveguide, the fluid passing through the micro-channel must have a higher refractive index than that of the material forming the micro-channel (which is PDMS in our case) in order to have total internal reflection. Moreover, the fluid must be chemically compatible with PDMS and have desirable dissolvability for the semiconductor NCs. Therefore, the most appropriate fluid for the optofluidic device has to be chosen. Commonly used solvents for dispersing semiconductor NCs such as toluene are not acceptable because these hydrophobic solvents will cause PDMS to swell and damage the integrity of the micro-channel. AP is a transparent liquid with a refractive index of 1.46 which is slightly higher than that of PDMS (n = 1.4) and was tested to be compatible with PDMS. The hydrophobic capping ligands on \( \text{Zn}_x\text{Cd}_{1-x}\text{S/ZnS} \) NCs are thus exchanged with AP and rendered to dissolve in excess AP. As AP serves as both surface ligand and solvent, a solution with extremely high concentration of \( \text{Zn}_x\text{Cd}_{1-x}\text{S/ZnS} \) NCs can be prepared.

Figure 5.7. Microscopic image of the optofluidic PDMS chip features. Outlet/inlet channels are 200 um in width, connecting channel is 400 um in width and the height of the channels is 45 um.
For the ASE measurements, $\text{Zn}_x\text{Cd}_{1-x}\text{S}$/$\text{ZnS}$-AP solutions are injected from one end of the waveguiding micro-channel to the outlet via a syringe pump. Pump laser is then focused onto the outlet channel vertically as a stripe and the emission is collected at the end of the waveguide as shown in Figure 5.8. Three outlet channels are designed for triplicate measurements to allow consistency check.

![Image](image_url)

**Figure 5.8.** The optofluidic chip is aligned vertically to the cylindrical lens. $\text{Zn}_x\text{Cd}_{1-x}\text{S}$/$\text{ZnS}$-AP solutions are injected from one end of the waveguide and flow through the channel to the outlet waveguides via a syringe pump. Pump laser is focused into a $\sim 7.5 \text{ mm} \times 1 \text{ mm}$ stripe onto one of the outlets and the emission is collected at the end of the waveguide.

Stable, optofluidic room-temperature ASE was obtained as illustrated in Figure 5.9. Narrowing of PL peak with increased intensity is readily observed at $\sim 200 \mu\text{J/cm}^2$. Given the volume fraction of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$/$\text{ZnS}$ NCs dispersed in AP is much smaller than that of a solid film, a slightly higher threshold value is expected and indicates the good optical waveguiding property of the PDMS micro-channels.
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Figure 5.9. Room temperature optofluidic ASE spectra from Zn_{x}Cd_{1-x}S/ZnS-silica film with ZnCdS core dimensions of ~5 nm and ZnS shell thickness of ~2 nm. Single exciton peak centers at 469 nm, as increasing of the pump power, a sharp, narrow ASE peak centers at 450 nm starts to dominate. Inset shows the corresponding integrated PL intensity versus pump power spectra of the ASE transition.

By keeping all other parameters such as dimensions of micro-channels, particle size of Zn_{x}Cd_{1-x}S/ZnS NCs constant, the dependence of ASE on volume fraction of NCs can be elucidated by using the optofluidic device. Different concentrations of Zn_{x}Cd_{1-x}S/ZnS NCs in APS are introduced to the same wave-guiding optofluidic device to examine their ASE threshold separately. Integrated PL intensity versus pump power curve is obtained for each sample to extract the threshold values as plotted in Figure 5.10. It is interesting to note that the threshold did not decrease linearly with increasing NCs’ volume fraction. When the volume fraction reaches a certain value, it no longer plays an important factor in determining the ASE threshold. From Figure 5.10, it is summarized that the region above the curve is where the ASE is readily to be expected which suggests the exact boundary condition of the onset of light amplification regarding to a sample with known volume fraction.
Fluorescence sensors are one of the most widely used detection technologies. Sensitivity of such sensors remains big challenge. To meet this challenge, increasing emphasis in analytical science has been directed towards materials and devices having highly nonlinear feedback properties. For a nonlinear optical sensor, a large change in fluorescence signal is expected corresponding to small fluctuations in analytes’ concentration. This unique metric will lead to dramatically increase in sensitivity. For example, attenuated lasing in optically pumped semiconducting organic polymers thin film displays sensitivity to vapours of explosives more than 30 times higher than is observed from spontaneous emission. However, organic polymers are easily self-quenched and have no resistance to photobleaching. Also the film based detector requires saturated vapour pressure of explosives in order to efficiently defuse through and interact with the embedded polymers.

Many works have shown that some metal ions quench the emission of NCs through charge/energy transfer process.\textsuperscript{11-18} In this work, we found that stimulated emission of Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS NCs rapidly declines in the presence of certain amounts of Ag ions. Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS NCs \textendash{} AP solutions are pre-mixed with different amount of Ag ions and injected into the optofluidic device to

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**Figure 5.10.** Summary of threshold values obtained from sample Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS NCs solution of different concentrations.
examine their emission spectra under an excitation pump power higher than
the ASE threshold.

![Emission spectra of the Zn$_x$Cd$_{1-x}$S/ZnS NCs–AP solution exposed to
different amount of Ag ions pumped at a same excitation power (higher than ASE
threshold).](image)

**Figure 5.11.** Emission spectra of the Zn$_x$Cd$_{1-x}$S/ZnS NCs–AP solution exposed to
different amount of Ag ions pumped at a same excitation power (higher than ASE
threshold).

As illustrated in **Figure 5.11**, different intensity changes are observed at
stimulated emission regime and spontaneous emission regime to the same
amount of Ag. Approximately two folds increase of silver concentration
(from 0.2 to 0.37) almost diminished the strong ASE emission peak but the
spontaneous emission remains comparable in intensity. If we plot the
integrated output emission intensity change with Ag ion amount, a steep
decline of emission intensity is observed at low Ag concentration causing by
exponentially decayed ASE regime as depicted in **Figure 5.12.** At high Ag
concentrations, where the ASE emission already vanished, the emission
intensity is no longer sensitive to the Ag concentration.
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Figure 5.12. Integrated emission intensity of Zn$_x$Cd$_{1-x}$S/ZnS NCs–AP solution pumped at a same excitation power (higher than ASE threshold) v.s. relative Ag ion concentration contains in the solution.

To validate the ASE enhanced sensitivity of this detection method, sensitivities of both spontaneous emission and ASE of Zn$_x$Cd$_{1-x}$S/ZnS NCs to the addition of Ag ions were compared as shown in Figure 5.13.

Figure 5.13. Change in the output emission intensity v.s. relative Ag ion concentration at pump excitation above (Red) and below (Blue) threshold.

The differential sensitivity is apparent at pump excitation power above and below threshold. At pump excitation below threshold, spontaneous emission
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decreases linearly when relative Ag concentration increases from 0 to ~27. On the other hand, at pump excitation above threshold, detection of low relative Ag concentrations (0 to ~5) is about 12 fold more sensitive by using change in ASE intensity when compared to the attenuation in the spontaneous emission. At relative Ag concentration higher than five, the sensitivity remains the same at pump power below or above the threshold, proving ASE induced sensitivity enhancement instead of excitation power.

It was been found by Alivisato’s group that CdSe reacts with Ag ions to yield Ag$_2$Se nanocrystals by the forward cation exchange reaction, and vice versa for the reverse cation exchange reaction. Cd$^{2+}$ ions can be completely replaced by Ag$^+$ at ambient temperature.$^{19,20}$ Thus, a rapid change of quantum dot solution color and disappearance of fluorescence is observed within a second. Subsequently, CdSe can be recovered from the Ag$_2$Se NCs by adding excess amount of Cd$^{2+}$. Original fluorescence was also recovered over a period of 1min. The cation exchange followed by reverse exchange process is illustrated in Figure 5.14 (a). Figure 5.14 (b) shows the CdSe PL before Ag$^+$ cation exchange and after Cd$^{2+}$ back-exchange. Also, the broad emission hump centred at 700 nm is explained due to the increased surface trap.$^{19}$

![Figure 5.14](image_url)

*Figure 5.14.* (a) Cartoon illustration of CdSe transforms to Ag$_2$Se from the forward cation exchange reaction, and Ag$_2$Se recovers to CdSe from the reverse cation exchange reaction. (b) PL emission of original CdSe (Red) and recovered CdSe (Green). The additional broad emission centered at 700nm is due to increased surface trap after reverse cation exchange. Reprinted from ref. 19.
This reversible ion exchange reaction was similarly observed for Zn$_{x}$Cd$_{1-x}$S/ZnS NCs in our work. With the addition of Ag$^+$ ions, they partially replace the Zn$^{2+}$ and Cd$^{2+}$ ions and quench the PL of Zn$_{x}$Cd$_{1-x}$S/ZnS NCs in several seconds. With the introduction of excess Cd$^{2+}$ ions, the reverse cation exchange process occurred and emission was recovered in a few minutes. The PL spectra of Zn$_{x}$Cd$_{1-x}$S/ZnS NCs before forward cation exchange process and after reverse cation exchange reaction are shown in Figure 5.15.

**Figure 5.15.** PL emissions of the original Zn$_{x}$Cd$_{1-x}$S/ZnS (Black) and recovered Zn$_{x}$Cd$_{1-x}$S/ZnS (Red) NCs.

Base on this reversible cation exchange mechanism, we demonstrate a turn-on signal nonlinear optical sensor which selectively detects Cd$^{2+}$. Exposure of NCs which have already been quenched with Ag$^+$ to controlled amounts of Cd$^{2+}$ under conditions of stimulated emission yielded exponential gains in intensity as a function of Cd$^{2+}$ concentration. Dramatic enhancement of sensitivity comparing with spontaneous emission is obtained. Comparisons of the sensory responses of the spontaneous emission and stimulated emission of Ag$^+$ quenched Zn$_{x}$Cd$_{1-x}$S/ZnS well validate the ASE recovery enhanced sensing principle. According to differential sensitivity plot depicted in Figure 5.16, we demonstrated 11-fold increase in detection sensitivity when operating above the lasing threshold.
5.4 Conclusion

In this chapter, we proved ultralow threshold blue color ASE based on Zn$_x$Cd$_{1-x}$S/ZnS semiconductor NCs. Their type II band alignment reduced Auger process is sufficiently weak to be incorporated in an opticalfluidic device. It is successfully demonstrated stable, room temperature ASE in an NC-based optofluidic device for the first time. Unlike in NCs films whose lasing behavior is significantly affected by cavity morphology and concentration fluctuation, the consistency of the optofluidic ASE allows one quantitatively examine volume fraction dependent gain build up. Last but not the least, the optofluidic NCs ASE device is demonstrated as a robust platform for non-linear optical sensing. The exponential decrease/increase nature of stimulated emission dramatically enhanced the sensitivity: 12-fold more sensitive than spontaneous emission based Ag$^+$ sensor and 11-fold more sensitive Cd$^{2+}$.

5.5 References


CHAPTER 6

Conclusion and Future Outlook
This thesis broadly introduced the chemistry and physics of wet-synthesized semiconductor NCs and emphasized on employing them as optical gain materials. It was shown in Chapter 2 that CdSe seeded CdS tetrapod NCs were incorporated into sol-gel derived silica matrix. Due to extremely large absorption cross-sections, high quantum yield, reduced spatial overlap between electron and hole wavefunctions, remarkably low threshold and high gain was observed from CdSe/CdS tetrapod incorporated silica film. Moreover, the biexcitonic ASE was found to originate from either the CdSe core or CdS arms depending on the CdSe core size while higher excitation intensities facilitated the exhibition of multiexcitonic ASE from the CdSe core under ambient conditions. These findings proved that heterostructured NC lasers are capable of simultaneously emitting at multiple wavelengths over a large spectral range from a single active layer, thus representing a unique class of solution processable optical gain media.

In order to avoid the use of UV-Vis excitation wavelengths which risk the high possibility of photo-damage, two photon absorption property of CdSe seeded CdS nanorods was explored in Chapter 3. Large two-photon absorption cross section of CdSe/CdS nanorods leads to ultra low room temperature ASE via 800nm excitation. Subsequently, incorporation of CdSe/CdS nanorods into a silica based microspherical optical cavity demonstrated a single mode lasing device. The robustness and thermal resistance of the optical cavity make the CdSe/CdS nanorods based laser plausible for practical applications.

The application of semiconductor NCs as optical gain media is always faced by the challenge of Auger dominated fast biexciton lifetime. Although CdSe/CdS core-shell heterostructured NCs reduce the Auger recombination process, it is still extremely difficult to achieve blue ASE from CdSe based NCs. This is because the particle size of CdSe must be less than ~ 2nm to have blue emission and Auger process dominates for small particle size. To address this problem, we have demonstrated that Zn$_x$Cd$_{1-x}$S alloyed semiconductor can be a good substitute for CdSe NCs as a potential blue emitter ternary. Unlike those binary NCs, studies in this class of ternary NCs are still lacking in terms of syntheses and optoelectronic properties. Thus our investigation in the
structures, chemical compositions and optical properties of Zn\textsubscript{x}Cd\textsubscript{1-x}S alloy in Chapter 4 is very important. In Chapter 5, we demonstrated a blue ASE with ultra-low threshold from Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS semiconductor NCs. Due to the unique band structures of these alloyed NCs, the highly efficient gain build up process allows the utilization of Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS NCs in an optofluidic device. This unprecedented achievement of stable, room temperature ASE from a NCs-based optofluidic device makes it possible to understand the stimulated emission amplification process quantitatively, without complications such as cavity morphology and sample concentration fluctuation faced with NCs film. Eventually, the optofluidic device was used as a signal turn-off/turn-on non-linear optical sensor for heavy metal ions. At least ten-fold increase in sensitivity was obtained for the novel optofluidic device with simple working principle.

Sol-gel process provides a feasible method to incorporate semiconductor NCs into a matrix film. However, this method has a major challenge which remained largely unaddressed; the incorporated NCs typically suffer from significant loss of quantum yield upon covalent attachment to the sol-gel network. This is most likely caused by the incomplete ligand exchange process which is required to ensure that these NCs are chemically compatible with the sol-gel reaction. Thus new methodologies to incorporate NCs into sol-gel derived matrices with negligible loss in quantum yield need to be developed in future work. At the same, in order to enhance the lasing performance of NCs incorporated matrix film, it is necessary to explore other types of sol gel derived matrices such as titania and zirconia to be used in conjugation with semiconductor NCs.

The observation of dynamic liquid phase ASE from the Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS NCs in an optofluidic device with wave-guiding property presents many interesting results and possible future studies. As research on these ternary NCs is still in the infant stage, many of the materials properties and potential uses are yet to be discovered.\footnote{1} The structure analyses and optical characterization of Zn\textsubscript{x}Cd\textsubscript{1-x}S/ZnS alloyed core/shell NCs in Chapter 4 is a good example of an in-depth study of this new class of ternary NCs.
The optofluidic non-linear optical sensor shown in Chapter 5 is a proof-of-concept type sensing experiment. It is promising that the nonlinear optical sensor is able to break the sensitivity limit of conventional linear ones. Based on this platform, the sensitivity and detection limit can be strikingly improved by coupling a suitable lasing cavity to the optofluidic device in future. A mixing component can also be added to fabricate microfluidic chips with multifunction integration.

As a better understanding of the surface chemistry of NCs emerges, synthetic procedures to couple various NCs to an expanded set of sol-gel derived materials will be made available, thus allowing for possibilities to expand the lasing wavelength range, like IR laser. Similarly, the continued development of NCs with optical properties superior to those of the current generation will undoubtedly enhance the performance of these composites and the applications. As the field of semiconductor NCs continues to evolve, the outlook for NC/sol-gel composites promises to be a bright one.

6.1 References
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