FROM FLASKS TO APPLICATIONS: DESIGN AND OPTIMIZATION OF GIANT QUANTUM DOTS USING TRADITIONAL AND AUTOMATED SYNTHETIC METHODS

Christina J. Hanson

University of New Mexico

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Dr. Han. Htoon

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Prof. Andrew P. Shreve
FROM FLASKS TO APPLICATIONS: DESIGN AND OPTIMIZATION OF
GIANT QUANTUM DOTS USING TRADITIONAL AND AUTOMATED
SYNTHETIC METHODS

BY

CHRISTINA J. HANSON

B.S., Chemical Physics, University of California at San Diego, 2008
S.M., Inorganic Chemistry, Massachusetts Institute of Technology, 2013

DISSERTATION

Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy

Nanoscience and Microsystems Engineering

University of New Mexico
Albuquerque, New Mexico

May, 2018
DEDICATION

For my family:

My husband, who never let me give up and has loved me unconditionally

My Father who instilled in me at a young age enthusiasm for science

My Mother who taught me to be generous and more independent than I probably should be most days

The cats, Malinky and Lotus, who tried to help write this thesis by sitting on my keyboard
ACKNOWLEDGEMENTS

“Success is going from failure to failure without loss of enthusiasm”
-Winston Churchill

Graduate school, all the many years of them, has been a time of personal and professional growth for me, and a journey I could not have done alone. I have been so unbelievably fortunate for those I have met along the way, and as a result have looked forward to trying to express my gratitude here as best as possible.

First and foremost I am so thankful to Dr. Jennifer Hollingsworth and Dr. Han Htoon at Los Alamos National Laboratory who decided to take a chance on a post-masters student to tackle some device work in their labs. I arrived back at LANL feeling discouraged and not a “good enough” scientist to be able to do important work, but through their guidance and encouragement, I was able to realize that I did in fact love doing science; I'd just forgotten this along the way. I am indebted to them for their encouragement to reapply to graduate school to finish my doctorate, and am so grateful I got the opportunity to do that in their laboratories at the Center for Integrated Nanotechnologies (CINT). Jen's enthusiasm for scientific results, tough love when we didn’t work as hard as we should have, motivation to produce the most thorough and accurate science we possibly could, and friendship have shaped me as a member of the scientific community. I can’t thank her enough for the time and effort she’s put into my education.

First and a half, I have to thank John Grey at the University of New Mexico who agreed to take me on as his satellite graduate student. Every discussion I’ve had with him has been extremely helpful both scientifically when I’ve looked at solving problems, and on a professional level when we’ve discussed the highs and lows of being a professor at UNM. John has always been available to answer any questions I may have about research, given me extremely helpful feedback on presentations and scientific discussions, and has never blinked an eye when I’ve needed help navigating the UNM system. I’m so thankful for his positivity and enthusiasm every time we’ve met. Additionally I must thank Diane Lidke and Andrew Shreve from UNM. Diane has been on my comprehensive exam committee and now my thesis committee and has always offered extremely helpful and insightful comments on our science. I have thoroughly enjoyed having her as a committee member. Andrew Shreve stepped in at the last minute to fill a committee spot for this thesis, and I couldn’t have asked for a better fit. His willingness to meet with me before hand to learn about my work before my defense, and his extensive knowledge and wealth of information on experimental design of high-throughput synthesis has been extremely helpful, and I am so grateful for his enthusiasm and guidance.

I have had the good fortune to work with some fantastic post-docs and other students while in Jennifer and Han’s labs in CINT. Nimai Mishra, Krishna Acharya, Niladri Karan, Aaron Keller, Farah Daewed, and Matthew Buck were all post docs in Jen’s lab when I arrived, and made sure I immediately felt welcome and were willing to answer any questions I had or help me with anything I needed. Allison Dennis, a former student, provided some fantastic guidance to me through email (until she visited and I got to meet her in person!) about fixing our wonderful Horiba fluorometer. William DeBenedetti was a fabulous student visiting from UT Dallas during my time there, and not only provided some
great scientific discussions, but was a great bike riding buddy and beer drinking friend. Many other post-docs who have come and gone in Jen’s lab have provided valuable input and support along the way, and I am extremely thankful for them. In Han’s lab, I had the pleasure of working with Xuedan Ma, Feng Wang, Noah Orfield, Nicolai Hartmann, and Zhongjian Hu on various projects. Xuedan took beautiful measurements of the IR dots for me, and was a fabulous office mate for the first couple of years I was at CINT. Feng, Noah and Zhongjian have all helped me at one point or another with blinking measurements or blinking set ups. Their patience, knowledge, and willingness to answer questions at any time are unsurpassed. Nicolai took beautiful measurements of the single IR dots in Steve Doorn’s laboratory. His attention to detail and dedication to quality work are very much appreciated.

I’ve had the unique chance to work and mentor some fantastic young scientists. Sarah Bouquin and Matt Ticknor were high schoolers when they started working in our lab, and I enjoyed watching them grow as scientists while they ran experiments. Sarah and Matt both had an enthusiasm for the work they were doing like I’ve never seen, and I know they’ll both go on to do great things. Sophie Click came to us as an undergraduate, then a post-bac, and has a personality that could light up a room. She was always excited to learn new things and to try out different experiments, and was a fun person to work with. Current high schoolers Radhika Iyer and Sophia Jeffrey are both wickedly smart and get work done faster than any high schooler I’ve seen. Working with them has been a fantastic experience, and I am sure they will go on to be fantastic scientists.

I’ve also had the pleasure of working with many other great scientists and staff members in CINT. Quinn McCullouch, Chris Sheehan, Kevin Baldwin, and Darrick Williams, technologists in CINT, have been fantastic whenever I’ve needed help with something. Quinn has been a great graduate school confidant, as he’s started his PhD in the same program at UNM. His patience, kindness, and friendship have been very appreciated, and I’ve greatly enjoyed our walks for coffee. Chris Sheehan has been a fabulous office mate (and knee surgery friend) for the past couple of years. His SEM and STEM images are always of the highest quality, and I am so thankful for his time and thoughts on my samples. Kevin Baldwin has always been willing to help me when I’ve needed any sort of deposition. He completed some beautiful work that is not presented in this thesis of some co-metal deposition for a small side project. Darrick Williams has done some beautiful XRD work for me, and has been extremely helpful in getting supplies and chemicals ordered. Antonya Sanders, once a communications officer for CINT, has been a fantastic friend and hiking buddy since we met. Her insights into LANL as a whole, and life as a whole are very much appreciated. Jen Martinez, a CINT scientist, has provided many insightful discussions about professional decisions and paths of which I’ve very much appreciated. Gabe Montano and Stacy Copp have done amazing work with my gQD samples using micelles, and I’m excited to see how that project evolves. Stacy has been a fantastic friend while I’ve been working with her as well, and her enthusiasm is greatly appreciated.

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to hang out. Henrik Sandin and Chris Carr, both from the P-21 crew have been amazing
friends all these years, and have always encouraged me to keep pressing on, even when it
seems like things aren’t going anywhere.

Last in the list but far away from last in importance is my friends and family, without
whom I would not have made it to this point. Their unwavering and unending support has
meant the world to me, especially when I couldn’t see the path ahead clearly. My husband,
David Carlson, has been instrumental in reminding me not to sweat the small stuff, and to
keep pressing on when things seem impossible. He’s been the most supportive and patient
person through all of this, and the not so quiet voice of reason when I start to waver from
sanity. His support and love has been a driving factor in the completion of this work. My
father, a scientist himself, instilled in me the importance of scientific discovery and curiosity
to understand the world from a very young age. Although we’ve had many arguments about
experiment vs theory, he’s been a strong supporter of pressing on to figure out the answer,
and I’m so thankful for his love and guidance. My mother supported me in whatever I
wanted to do, whether that be a history teacher, a special education teacher, a scientist, or
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life was infectious, and I hope to one day become half as patient and kind as she was. She
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Machuca-Grebe, Melissa Garren, John Goeltz, Erin Preston, Robert Radford, Tony Zukaitis,
Laura Martin, Laura Kelley, Jen Olsen, and the Los Alamos Slow Pitch Softball crew. Thank
you for everything.
FROM FLASKS TO APPLICATIONS: DESIGN AND OPTIMIZATION OF GIANT QUANTUM DOTS USING TRADITIONAL AND AUTOMATED SYNTHETIC METHODS

By

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ABSTRACT

Semiconducting nanocrystals, also known as quantum dots (QDs), that emit light with near-unity quantum yield and are extremely photostable are attractive options as down-conversion and direct electricity-to-light materials for a variety of applications including solid-state lighting, display technologies, bio-imaging and optical tracking. Standard QDs with a core/thin shell structure display fluorescence intermittency (blinking) and photobleaching when exposed to prolonged room temperature excitation for single dot measurements, as well as significant reabsorption and energy transfer when densely packed into polymers or at high solution concentrations.

We have developed thick shell “giant” QDs (gQDs), ultra-stable photon sources both at the ensemble and single-QD level, i.e., yielding 100% blinking suppression and no photobleaching when exposed at room-temperature to high-power laser excitation for extended periods (at least 1 hour) as “bare” solid-state nanocrystals. gQDs further exhibit significantly suppressed non-radiative Auger recombination and minimal self-reabsorption, where the latter is due to a large effective Stokes shift between absorption (primarily in the
shell) and emission (from the core). Previously we developed, red emitting CdSe/CdS core/thick shell (15-20 monolayers) gQDs. These materials are nearly ideal red downconverters for solid state lighting applications (which primarily use blue light emitting diodes (LEDs) and a phosphor to generate white light). Presented herein are the results we obtained when gQDs were densely packed into polymer blocks and placed directly on an LED chip and tested for stability and downconversion efficiency. Additionally, for potential utilization of any nanoparticles in commercial applications that demand large volumes of consistent materials, fast methods for materials discovery and optimization are needed. Thus, the ability to scale-up benchtop chemistry is also critical, as is maintaining batch-to-batch and within-batch consistency. To undertake this challenge in our laboratory, we developed a customized fully automated batch reactor system (FABRS) that allows for high throughput synthesis and material scale up. Within are some of the first results we have obtained from our FABRS system for a multidimensional synthetic phase space analysis, where automation affords rapid correlation between synthetic parameters and gQD material properties. We are also interested in the development of new materials, and so a novel gQD material will be discussed, IR emitting PbSe/CdSe/CdSe gQDs. These gQDs allow, for the first time with any lead chalcogenide IR emissive QD, observation at a single dot level using standard detection methods.
# TABLE OF CONTENTS

LIST OF FIGURES...........................................................................xii

LIST OF SCHEMES AND TABLES..................................................xiv

LIST OF ABBREVIATIONS..............................................................xv

CHAPTER 1: INTRODUCTION.........................................................1

1.1 Quantum Confinement.........................................................1

1.2 Quantum Dot Synthesis.......................................................4

1.2.1 Nanoparticle Growth Mechanisms.............4

1.2.2 Synthesis of Core Materials Using Hot Injection
       Methods...........................................................................5

1.3 Surface Passivation and Shell Growth.......................8

1.3.1 Surface Passivation of QDs.........................8

1.3.2 Band Alignment and Emission Tuning..........10

1.3.3 Traditional Shell Growth.........................12

1.3.4 Thick-Shell Growth for Giant-Quantum Dot
       Synthesis.................................................................14

1.3.5 gQD Initial Studies...........................................17

1.4 Further Optimization and Materials Development......21

1.4.1 Optimization of CdSe/CdS System............21

1.4.2 Materials Development...............................22

1.5 Outline of Thesis and Specific Acknowledgements.....22

1.6 References...........................................................................24
4.1 Introduction .........................................................................................80
4.2 High-Throughput Combinatorial Chemistry Design ......82
  4.2.1 Combinatorial Chemistry ........................................83
4.3 Automated High-Throughput Synthesis with FABRS ……85
  4.3.1 FABRS System Design ..............................................85
  4.3.2 Optimal Coverage Algorithm for gQDs .................86
  4.3.3 CdSe Core Synthesis for Reactions ....................92
  4.3.4 General Procedure for SILAR in FABRS ……93
4.4 CdSe/CdS 9ML Shell Results from FABRS …………………94
  4.4.1 Optimal Coverage Results .................................94
4.5 Conclusions ....................................................................................97
4.6 References .....................................................................................98
## LIST OF FIGURES

**Figure 1.1:** Band structures for Metals, Semiconductors, and Insulators .............2

**Figure 1.2:** Band gaps and emission of QDs across visible spectrum .................3

**Figure 1.3:** CdSe core quantum dots absorption and emission .......................4

**Figure 1.4:** LaMer diagram showing process of growth for nanoparticles grown by burst nucleation .................................................................5

**Figure 1.5:** Band diagrams for common core/shell systems ..........................11

**Figure 1.6:** Optical properties and TEM of gQDs with 16ML shell ...............15

**Figure 2.1:** Device Structures for gQDs as downconverters on LEDs ............32

**Figure 2.2:** Emission spectra and downconversion efficiency for standard QDs and gQDs directly on chip .................................................................34

**Figure 2.3:** Temperature effects on emission, PL lifetime of gQDs, comparison of power vs intensity for gQDs vs other downconverters ...............................36

**Figure 2.4:** Current vs Emission measurements for QDs and gQDs on chip with and without spacers .................................................................41

**Figure 2.5:** Transmittance of different Aerogel Samples .............................42

**Figure 3.1:** Synthesis controlled structure and optical properties of PbSe/CdSe/CdSe gQDs .................................................................59

**Figure 3.2:** TEM and XRD of PbSe/CdSe/CdSe samples .............................61
Figure 3.3: Emission as a function of shell growth of PbSe/CdSe/CdSe gQDs synthesized with SeODE………………………………………………………………63

Figure 3.4: Theoretical calculations of band structure of IR gQDs………………64

Figure 3.5: Cluster stability of IR gQDs with different shell thickesseses over an hour of observation time, lifetime measurements……………………………………65

Figure 3.6: Single dot images of IR gQDs using standard detection techniques, blinking statistics…………………………………………………………………………68

Figure 4.1: Traditional vs Automated gQD synthetic timescales………………82

Figure 4.2: Optimal Coverage Algorithm for High Throughput FABRS Synthesis and Optimization of gQDs………………………………………………………………91

Figure 4.3: Absorption, emission and TEM of Core CdSe particles used………93

Figure 4.4: Absorption, emission and TEM of CdSe/CdS 9ML gQDs…………95

Figure 4.5: Blinking statistics and bleaching trace for gQDs in Figure 4.4………96

Figure 4.6: TEMs of gQD samples grown using different precursor addition rates in FABRS…………………………………………………………………………………96

Figure 4.7: Blinking and bleaching data obtained from samples in Figure 4.7 grown using different precursor addition rates………………………………………97
LIST OF SCHEMES AND TABLES

**Table 1.1:** Common QDs of various materials are tuned to produce emission wavelengths across the visible and infrared. .......................................................... 3

**Scheme 1.1:** Standard set up for QD synthesis ........................................... 6

**Scheme 1.2:** Pathways for exciton recombination: emission, trap states, Auger Recombination ........................................................................................................ 9

**Scheme 4.1:** FABRS diagram with customized flask and in-situ monitoring........ 86

**Scheme 4.2:** High-Throughput Processing for gQDs on FABRS ................. 87
### LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>APD</td>
<td>Avalanche Photodiode</td>
</tr>
<tr>
<td>C</td>
<td>Celsius</td>
</tr>
<tr>
<td>CdS</td>
<td>Cadmium Sulfide</td>
</tr>
<tr>
<td>CdSe</td>
<td>Cadmium Selenide</td>
</tr>
<tr>
<td>CINT</td>
<td>Center for Integrated Nanotechnologies</td>
</tr>
<tr>
<td>CRI</td>
<td>Color Rendering Index</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous Wave</td>
</tr>
<tr>
<td>DOE</td>
<td>Department of Energy (US)</td>
</tr>
<tr>
<td>EL</td>
<td>Electroluminescent</td>
</tr>
<tr>
<td>EMCCD</td>
<td>Electron Multiplying Charge Coupled Device</td>
</tr>
<tr>
<td>eV</td>
<td>Electronvolts</td>
</tr>
<tr>
<td>FABRS</td>
<td>Fully Automated Batch Reactor System</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Max</td>
</tr>
<tr>
<td>gQD</td>
<td>Giant Quantum Dot</td>
</tr>
<tr>
<td>InGaAs</td>
<td>Indium Gallium Arsenide Detectors</td>
</tr>
<tr>
<td>InP</td>
<td>Indium Phosphide</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
</tr>
<tr>
<td>mA</td>
<td>milliAmpere</td>
</tr>
<tr>
<td>ML</td>
<td>monolayer of shells</td>
</tr>
<tr>
<td>ml</td>
<td>millileter</td>
</tr>
<tr>
<td>mm</td>
<td>Millimeter</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>ns</td>
<td>Nanosecond</td>
</tr>
<tr>
<td>ODE</td>
<td>1-Octadecene</td>
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</table>

xv
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>PbSe</td>
<td>Lead Selenide</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PLMA</td>
<td>Polylaurylmethacrylate</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier Tube</td>
</tr>
<tr>
<td>ps</td>
<td>Picosecond</td>
</tr>
<tr>
<td>QD</td>
<td>Quantum Dot</td>
</tr>
<tr>
<td>QY</td>
<td>Quantum Yield</td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>SILAR</td>
<td>Successive Ionic Layer Adsorption&amp;Reaction</td>
</tr>
<tr>
<td>SNSPD</td>
<td>Superconducting Nanowire Single Photon Detector</td>
</tr>
<tr>
<td>SSL</td>
<td>Solid State Lighting</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TOP</td>
<td>Triocetylphosphine</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>W</td>
<td>Watt</td>
</tr>
<tr>
<td>ZnS</td>
<td>Zinc Sulfide</td>
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Chapter 1: Introduction

1.1 Quantum Confinement

As we look towards a more sustainable world, semiconductors are arguably one of the most researched materials as potential solutions for energy transport, collection, and conversion. Semiconductors (including silicon) are used in a variety of applications, most notably computer chips and components, solar cells, and light emitting diodes (LEDs) which are all currently available to consumers around the world. A semiconductor material has an electrical conductivity between that of an insulator (glass) and metal conductors (gold or silver). As shown in Figure 1.1, the energy gap, (bandgap energy) between the valence band (ground state) and the conduction band (excited state) contains the Fermi level, much like the bandgap of an insulating material, but is smaller than that of an insulator, allowing for movement of electrons from the populated ground state at room temperature (RT) to the excited state across the band gap. When an electron populates the conduction band, a hole is left in the valence band, and this electron-hole pair makes up an exciton. Bulk semiconductors have composition defined bandgap energy \( E_g \) which can be slightly tuned by the addition of dopants, small amounts of material that will either expand or reduce the bandgap.
The size of an exciton in semiconductors is determined by the Bohr radius, $a_{\text{Bohr, exciton}}$, or the most probable distance between the electron and hole in an exciton, which depends on the effective masses of each particle and the dielectric constant of the material.\(^9\) As a result, the Bohr radius varies depending on the material (for bulk cadmium selenide (CdSe) for example, the Bohr radius is 5.4 nm).\(^10\) The exciton will experience quantum confinement when the size of a material is physically smaller than $a_{\text{Bohr, exciton}}$, resulting in extremely useful electronic and spectroscopic properties of the materials, most notably that the bandgap is now size dependent; the smaller the particle the larger the bandgap, and the higher the emission energy.\(^11\) This can be explained using a particle in a box model, as the box is made smaller, the energy between the states must increase as shown in Figure 1.2. When the particles are spherical (zero dimensional) quantum confined materials are known generally as

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**Figure 1.1:** Diagram showing the difference in valence band and conduction band energies for a metal, semiconductor and insulator. The Fermi Level is the highest energy state occupied by electrons at absolute zero. In metals, the valence and conduction bands overlap, and the Fermi Level is found within the band overlap allowing electrons to flow freely, making metals good conductors of current. Insulators on the other end of the spectrum have a very large bandgap, across which electrons cannot move from the valence band to the conduction band, and so they are terrible conductors of current. Semiconductors like insulators have the Fermi level between the valence and conduction bands, but a much smaller bandgap, allowing for electrons to jump the gap and allowing current to flow at room temperature.

The size of an exciton in semiconductors is determined by the Bohr radius, $a_{\text{Bohr, exciton}}$, or the most probable distance between the electron and hole in an exciton, which depends on the effective masses of each particle and the dielectric constant of the material.\(^9\) As a result, the Bohr radius varies depending on the material (for bulk cadmium selenide (CdSe) for example, the Bohr radius is 5.4 nm).\(^10\) The exciton will experience quantum confinement when the size of a material is physically smaller than $a_{\text{Bohr, exciton}}$, resulting in extremely useful electronic and spectroscopic properties of the materials, most notably that the bandgap is now size dependent; the smaller the particle the larger the bandgap, and the higher the emission energy.\(^11\) This can be explained using a particle in a box model, as the box is made smaller, the energy between the states must increase as shown in Figure 1.2. When the particles are spherical (zero dimensional) quantum confined materials are known generally as
quantum dots (QDs), and when CdSe is used, smaller dots are blue emitters, larger sized QDs red (Figure 1.2). The choice of materials for QDs is chosen based on the desired application and optical properties, with some examples given in Table 1.1.

As shown in Figure 1.3 the emission of QDs is generally very narrow and the absorption is broadband over a large range of wavelengths. These qualities make QD materials useful for a wide range of applications, from specific applications that require a high color purity (narrow linewidth) (displays, for example), or broadband absorption (solar cells), to

<table>
<thead>
<tr>
<th>Material</th>
<th>Tunable Emission Range</th>
<th>Material</th>
<th>Tunable Emission Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium Sulfide (CdS)</td>
<td>400-470 nm</td>
<td>Indium Phosphide (InP)</td>
<td>450-950 nm</td>
</tr>
<tr>
<td>Cadmium Selenide (CdSe)</td>
<td>470-650 nm</td>
<td>Indium Arsenide (InAs)</td>
<td>700-3500 nm</td>
</tr>
<tr>
<td>Cadmium Telluride (CdTe)</td>
<td>540-750 nm</td>
<td>Lead Selenide (PbSe)</td>
<td>750-5000 nm</td>
</tr>
<tr>
<td>Zinc Selenide (ZnSe)</td>
<td>375-550 nm</td>
<td>Lead Sulfide (PbS)</td>
<td>700-3500 nm</td>
</tr>
</tbody>
</table>

Table 1.1: Materials used to generate QDs across the visible and infrared. The range of emission wavelengths that can be achieved using size tuning for each material are listed. This work specifically uses CdSe and PbSe extensively for QDs that emit in the visible and infrared respectively.
more general applications that need bright emitters in a wide range of colors (lighting,20–22 biological tracking,23–25) and photodetection26,27. Infrared emitting QDs could be used for telecommunication applications,28 biological tracking,29 and defense applications.30 A large variety of device structures and integrations can be realized using QDs as an exciton can be generated with a photon or electrically and the materials are solution processable, eliminating many of the expensive techniques needed for similar organic based materials.17,31 For example, one could use QD materials as an emissive or absorptive material on a flexible substrate, like a roll up solar cell or light emitting diode that could be easily packed and carried into the wilderness. As a result, ever since the discovery and successful synthesis of QD materials, there has been significant interest in their optimization for potential application integration.

1.2 Quantum Dot Synthesis

1.2.1 Nanoparticle Growth Mechanisms

In 1950, LaMer and Dinegar published a seminal paper for the nanoscience and materials community describing the growth mechanisms for colloidal dispersions in saturated solutions.32 The authors put forth a theory of nucleation that has been at the center of the design of nanoparticle synthetic methods since. The proposed method is shown in Figure 1.4, and consists of three regimes. In the first, precursors are suspended in solvent
and form monomers rapidly until the solution almost reaches supersaturation (I). When the solution reaches supersaturation, the monomers will very quickly begin to self-nucleate and form small clusters in burst nucleation (II). This burst event very rapidly decreases the concentration of the remaining free monomers in solution, so growth now proceeds by diffusion of the nuclei formed (III). This growth, if allowed to proceed for very long periods of time, will produce extremely size disperse samples, as the combining of nuclei cannot be controlled. However, if the temperature and time of growth are precisely controlled however, uniform size and shape particles can be synthesized.

1.2.2 Quantum Dot Synthesis Using Hot-Injection Methods

In 1993, Murray, Norris and Bawendi published a synthetic procedure for high quality monodisperse CdSe QDs, using a hot injection method. Generally, one of the organometallic precursors for the QDs (in the CdSe specific case, the cadmium) is heated with coordinating solvents under inert atmosphere in a flask to high temperature (300
(Scheme 1.1). At the same time, the anionic precursor with coordinating ligands is loaded at room temperature into a syringe, and then swiftly injected into the hot cationic solution. The rapid injection of precursor creates a burst of nucleation and temperature drop, allowing for an immediate reduction in rate of nanoparticle growth. Slow reheating of the reaction allows for uniform annealing and crystallite growth by Ostwald ripening (high surface energy small particles are less stable, and are therefore likely to return to solution, and the material can be added to larger particles).

In this way, the size of the particles can be tuned, the tighter the size distribution, the higher the reaction temperature needed to maintain a steady growth, and, conversely the more broad the distribution, the lower the growth temperature needed. In addition to low temperature, the coordinating ligands chosen can reduce reaction rates by serving as a steric barrier to the addition of further materials to the surface of the QD.\textsuperscript{33}

The optical properties of a CdSe QD provide insight into the quality and size dispersity of the synthesized particles. The room temperature absorption spectra for CdSe (Figure 1.3) shows several clearly resolved transitions, the lowest energy 1s transition can be
used to determine the size of particles synthesized. A sizing method described by Jasieniak et. al. is used for CdSe core sizing, the diameter of the particles can be determined by

\[ D(\text{nm}) = 59.60816 - 0.54736\lambda + (1.8873 \times 10^{-3}\lambda^2) - (2.85743 \times 10^{-6}\lambda^3) + (1.62974 \times 10^{-9}\lambda^4) \]  

(eq. 1.1)

where \( \lambda \) is the wavelength in nanometers (nm) of the 1s absorption peak. In addition to the size of the dots, the molar extinction coefficient of the sample can be determined from the following equation:

\[ \varepsilon_{1s} \left(10^5 M^{-1} \text{cm}^{-1}\right) = 155,507 + 6.67054 \times 10^{13} \exp\left(-\frac{E_{1s}}{0.10551}\right) \]  

(eq 1.2)

where \( E_{1s} \) is the energy (in eV) of the 1s absorption peak. The concentration of the stock solution of these products can then be determined using the Beer-Lambert law.

Additionally, the high temperatures used by Murray et. al. for CdSe core synthesis allowed for significant annealing of the QD samples. This produced crystalline QD materials that had less defects and better surface passivation due to the chosen ligands than previously described synthetic procedures. As a result, these samples had better quantum yields (QYs) than QDs produced using other synthetic methods (5-15%). It has been estimated that only \(~1/2\) of the surface sites of CdSe cores are passivated by the organic ligands used during the growth process, and this incomplete passivation of surface sites leads to the low QY and stability of these materials in ambient conditions. Therefore, it was determined that further passivation of the surface was necessary not only for material stability, but for further optimization of optical properties.
1.3 Surface Passivation and Shell Growth

1.3.1 Surface Passivation of QDs

Bare CdSe cores are passivated by organic ligands, however, QYs were still fairly low and there was minimal stability of the dots under ambient storage conditions. The lack of stability of these materials was analyzed further in 1996, when the first measurements on single QDs were conducted by Nirmal et. al. using continuous laser excitation.\textsuperscript{36} Until this important addition to the literature, measurements on QDs had been done at the ensemble level; many dots in a solution were scanned for optical properties and structural information. This paper provided the first glimpse at the qualities of single nanocrystals within the larger ensemble and is the first reported observed fluorescence intermittency or “blinking” of QDs. When a single dot was observed under continuous excitation the fluorescence would turn on and off randomly, which is especially evident in CdSe QD core particles.\textsuperscript{36} The cause of dot blinking was determined to be a result of both Auger recombination, a process that occurs when the QDs are populated with more than one exciton (electron-hole pair), and hot carrier trap states in the QD that cause non-radiative decay processes.\textsuperscript{36–38} As shown in Scheme 1.2, when a nanocrystal is populated with a single electron-hole pair and the electron is in the valence band, the electron can either relax back down to the conduction band to recombine with the hole (radiative decay or emission) or relax through a non-radiative pathway (heat, for example) as a result of trapping. When a QD is populated with multiple exciton pairs however, a different process, Auger recombination, can occur. When excitons are generated, the energy obtained from the recombination of a single electron hole pair, instead of emitting a photon, can be transferred to another carrier (hole or electron) and eject it from the particle. The resulting ionized nanoparticle causes subsequently generated electron-hole pairs to transfer energy to the charged carrier in the QD (this is a trion)
and decay non-radiatively very fast, leading to the dot being “off” during this process.\textsuperscript{37,39}

Once the trapped particle is released from the surface, newly generated electron-hole pairs can radiatively recombine, resulting in the dot being “on”. For core only particles, the ratio of surface to interior atoms is large, leading to a number of sites on the surface that need to be passivated in an effort to prevent trap sites where carriers can be held for long periods of time.\textsuperscript{40} It has been determined that for CdSe particles specifically, dangling bonds on Cd provide trap sites for electrons, while dangling bonds on the Se provide sites for holes.\textsuperscript{35,41} Consistent and complete passivation of these sites is necessary for high performing nanoparticles, and organic ligands alone would not provide the solution.\textsuperscript{35}

Although the QDs have some amount of passivation from the organic ligands, these ligands can be labile and come off and on the surface of the QD in solution and be damaged as a result of continuous laser excitation.\textsuperscript{42} This prompted the field to look towards surface passivation that would be more permanent, and could perhaps be grown directly on the surface of the core QDs. In 1996, Hines and Guyot-Sionnest published the first example of

\begin{itemize}
\item a) standard exciton recombination between electron and hole, resulting in emission from particle at the energy of the bandgap.
\item b) electron is trapped in states lying below the conduction band and does not recombine with hole to produce emission.
\item c) Auger process in multie excitonic system. Energy released when electron and hole recombine is given to other electrons in conduction band, kicking out electron in QD d). Upon subsequent excitation, Auger process very fast, and usually inefficient non-radiative decay is observed.
\end{itemize}
inorganic passivation of the surface of CdSe QDs using zinc sulfide (ZnS).\textsuperscript{42} ZnS has a larger bandgap than CdSe, and so shelling of the core materials produces a “Type 1” band alignment, which is shown in Figure 1.5. The capping of the cores with the larger bandgap material confines the carriers to the core structure (so the emission wavelength of the material is still predominately determined by the size of the core), but the inorganic shell passivates the core surface sites.\textsuperscript{42,43} Although it is noted that the lattice mismatch of CdSe and ZnS is rather large (12%) the ZnS shell could still be grown at low temperature on the core, resulting in an interface that is minimally alloyed. This was confirmed by the emission measurements after shelling, the peak position had a minimal shift and minimal broadening. The addition of the shell improved emission drastically from the core only particles, the QY of the core shell particles was nearly 50\%, and the particles were stable for long periods of time when stored in air. Furthermore, when blinking measurements by Nirmal \textit{et. al.} were made on CdSe particles with a ZnS shell, the dots were “on” significantly more than they were “off” leading one to the conclusion that Auger ionization and charging and other non-radiative pathways are now greatly suppressed compared to the core only nanoparticles.\textsuperscript{36} In fact, the “on/off” times directly correlated with the number of shells that had been grown on the core particles, the fewer the shells, the longer the time the dots were observed to be “off”. Particles with a thin layer of ZnS shell were studied in this experiment, and the samples showed some reduced blinking. However the effect of shell thickness was not thoroughly demonstrated.\textsuperscript{36} 

1.3.2 Band Alignment and Emission Tuning

A short discussion regarding band alignment and emission tuning is appropriate here, as the implications later in this work will benefit from a basic understanding. The
CdSe/ZnS particles described in 1.3.1 were described as being a Type I band structure particle, the structure of which is shown in the band diagram in Figure 1.5. A type I structure consists of a core material surrounded by a shell material with a larger bandgap, and the electron and hole are confined to the core, and the emission energy of the particle is determined by the core bandgap only. This type of structure has advantages in that the emission wavelength will not change much from the addition of the shell on the core, and the shell provides a barrier to environmental quenching. However, the significant overlap of the electron-hole wavefunction does not diminish Auger recombination efficiency.43

On the other end of the spectrum, type II structures allow for full delocalization of either the hole or electron into the shell, and the isolation of the corresponding particle to the core. In this case, the emission is determined by the energy gap between (in the example
shown in Figure 1.5) the hole in the core valence band, and the electron in the shell conduction band. In this case, the reduced overlap between the electron-hole wavefunction is desirable for applications that require significant carrier separation (such as a solar cell that needs the isolation of hole and electron for collection and storage) or applications that do not require extremely efficient emissive pathways.43

In the middle, and the focus of many of the QDs mentioned in this dissertation, is a quasi-type II band structure, which produces only partial delocalization of one of the carriers into the shell. In the case shown, the hole is confined to the core while the electron is allowed to partially delocalize into the shell. This structure results in emission from the core that is slightly shifted to lower energies when the shell material is grown. Partial delocalization of one carrier results in reduced electron-hole wavefunction overlap, and thus a reduction in the Auger recombination. In this way, these particles can still produce emission determined by the band structure of the core, can emit from charge multiexciton states.43

1.3.3 Traditional Shell Growth

The first example of CdSe/ZnS core/shell QDs were grown using a process that grew both the cores, and then the shell in the same flask, only isolating the materials after the shell growth was complete.42 The cores were grown using selenium trioctylphosphine (SeTOP) and dimethyl cadmium (Me2Cd) that were injected into trioctylphosphine oxide (TOPO) at a very high temperature (350 °C) and quickly removed from heat for growth of the materials at 300 °C. At this temperature the shell precursors, bis(trimethylsilyl) sulfide (TMS2S) in TOP and dimethyl zinc (Me2Zn) in TOP were injected in 5 aliquots in short intervals (<30 seconds) into the solution. It was determined that for this specific experiment,
the total mole ratio of injections for core:shell was \(~1:4\), and the final thickness in diameter of ZnS shell added was determined to be \(~12\ \text{Å}\).\(^{42}\) If we consider that the lattice parameter for zincblende ZnS is 5.4 \(\text{Å}\),\(^{44}\) we can calculate that \(~2\) monolayers of shell (1/2 lattice parameter and ½ the thickness of increase in diameter) was added to the surface of the CdSe QD. This, on one hand, is a remarkable result; only a couple monolayers of shell is enough to significantly passivate the surface of the core QD, improving properties drastically. The larger bandgap material serves as a barrier to ionization and removes potential surface trap states.

In 2003, the Peng group published a new shell growth procedure that utilized a successive ionic layer adsorption and reaction (SILAR) growth process for CdS shells on CdSe QD cores.\(^{45}\) This growth process utilizes low reactivity stable precursors for shell growth that both cuts down on the amount of side products that would be produced when the shell precursors were introduced into solutions of cores, and helped to improve the uniformity of shell growth. Additionally, the layer by layer addition significantly reduces homogeneous nucleation of shell precursor nanoparticles, and therefore allows for shell growth at much higher temperatures than previously reported. The SILAR process grows each monolayer of shell in succession, so only the amount of cadmium and sulfur precursor for one shell is introduced into the flask. This specific reaction utilized octadecene (ODE) and octadecylamine as stabilizing ligands in solution, CdSe core particles and cadmium oleate and sulfur in ODE for shell precursors. The exact amount needed for each monolayer was calculated using the size of the particle and ½ the wurtzite c lattice parameter of the CdSe structure (since there is a small mismatch between CdSe and CdS bulk crystal structures). This gives a value of 0.7 nm diameter change for each monolayer of shell grown, which is taken into account for each calculation of precursor volume.\(^{45,46}\) The SILAR process was run
at 240 °C, argued by the authors to be the optimal temperature for consistent shell growth and prevention of Ostwald ripening. Although the authors don’t specifically state how long they wait after each precursor addition before the next is introduced, it is likely short as they only observe the affects over 5 minutes for initial experiments. Later, the authors describe a process in which they let the reaction anneal after the addition of all the stock solution for longer anneal times, but at a lower temperature than injection (190 °C), to increase the optical properties of the materials, which they note is ineffective. The majority of the materials in this study utilize 5 monolayers of shells grown on CdSe cores, after which the authors observe elongation of the particles and a loss in shape uniformity. These particles have a noticeable red shift in the emission as the shell is grown on the particles, and in general have a QY of ~40%.

### 1.3.4 Thick Shell Growth for Giant-Quantum Dot Synthesis

In 2008, Chen et al. described for the first time the synthesis of a “giant” quantum dot (gQD) that had a very thick (15-20 monolayer) shell around a CdSe core. This very thick
shell more effectively isolates the wavefunction of the QD core from the surface of the QD, reducing the effects of surface defects or ligand interactions. “Giant” QDs can be thought of as the giant shrimp of the otherwise standard size shrimp QD world; the reported gQD product diameter is between 15-20 nm, instead of closer to 5-10 nm, and the ratio of core to shell is nearly 1:100 (standard QDs are 1:<10). The particles grown, as shown in Figure 1.6 maintain size and shape dispersity, and experience a red shifting in the emission as the shell grows thicker, due to the extension of the electronic wavefunctions from the core into the shell, as the effective size of the core is increased. The emission of the particles was still predominantly from the core, however the absorption now was mostly in the much thicker and larger volume shell. This produces a large effective Stokes shift in the system.

GQDs showed improved stability of the material when compared to standard core-shell QD syntheses. The product could be washed multiple times, removing ligands from the surface of the dot each time the sample was crashed out and resuspended, with no loss in emission intensity or drop in QY. This was extremely different than the results that were obtained from thinner shell samples, for which multiple washes and removal of ligands saw an average drop in QY of around 30%, and for core only samples an average drop of 80% was observed. Additionally, if a ligand exchange was done, say to mercaptosuccinic acid for the suspension of gQDs in water, no drop in QY or intensity was observed.

Arguably the most important result, is that the gQD products exhibit suppressed blinking and did not photobleach, even under continuous excitation for several hours at the single dot level. This was a revolutionary result for the field, as it allowed for the first time the observation of a single dot for a long period of time which enabled long tracking of single gQDs for a variety of applications, including tagged biomolecules. In these initial
experiments, over 25% of the dots were on 100% of the time, and nearly 40% of the dots have an on time fraction of 0.8. When compared to standard QDs many of the standard samples are off a large percentage of the time, and this sample photobleaches over the observation time. No such photobleaching was seen in the gQDs. For the first time, it was shown that the growth of a very thick shell improved many of the properties that had limited the widespread use of QDs in various applications including single molecule tracking.

It is now known that the absence of blinking in gQDs can be attributed to two mechanisms, the suppression of the Auger processes that are responsible for the dark states in standard QDs and hot carrier trapping.\textsuperscript{39,51} CdSe/CdS gQDs are a quasi-type II particle, that is the hole is confined to the core while the electron is able to delocalize into the thick shell, as shown by the band alignment diagrams in Figure 1.5. Using a thinner shell QD as a reference, experiments using pulsed laser excitation at different powers (to generate single or multi excitons in the sample) were run to observe the differences between the samples that blink, and the gQD samples that do not. For the reference sample, at low pump powers where only one exciton is generated, a 24 ns decay is observed, and categorized as the radiative recombination lifetime for the exciton generated in the QD. However, when higher pump powers are used and multiexcitons are generated a much faster picosecond timescale component evolves in the decay dynamics, which is due to the Auger decay of multiexcitons. When this shorter component is extracted and measured to be ~200 ps, it matches previously measured biexciton Auger recombination values for CdSe QDs, indicating that these biexcitons will be non-emissive and decay as a result of Auger processes.\textsuperscript{39}

The same measurements on gQDs produced very different results, the single exciton lifetime measured 42 ns, but at higher excitation powers, the faster multiexcitonic
component persists for a much longer time than the reference QDs, the lifetime was measured to be ~10 ns, suggesting a significant suppression of the Auger dynamics in the gQD samples. Further experiments at low temperature 4 K, revealed that a biexciton emission peak can be observed in the gQD samples when continuous wave (CW) illumination at 535 nm is used, confirming that biexcitons are emissive in the gQDs, and Auger is significantly suppressed. No similar peak was observed in the standard QD sample. With continuous excitation at 405 nm, it was observed that both neutral and charged gQD species exist in the ensemble. Neutral gQD PL spectra are similar to that observed when samples were observed using 535 nm illumination. The charged gQDs however, show instead of the single and bi-exciton peaks, show spectral signals that are consistent with the existence of trions and charged biexcitons, both of which are highly emissive. The charged biexcitons are a result of the combination of carriers in the first excited state (either electron or hole). The emission observed for these species again confirms that the rate of Auger recombination is significantly reduced. This is an important discovery, as the efficient multiexcitonic emission in the gQDs makes them a potential material for lasing and light emitting applications.

1.3.5 gQD Initial Studies

In an effort to begin to understand important parameters and conditions that produce high quality gQD materials, experiments varying the annealing times for each precursor during the SILAR process, the identity of the amine ligand used during the synthesis and the non-coordinating solvent used, the CdSe starting core size, and the amounts of precursors used were conducted. The size and shape dispersity, blinking statistics, and QY were used as measures of product quality for these experiments. First,
anneal times after the addition of each precursor was studied, as the previously mentioned paper published by Peng et. al. used fairly short anneal times, but the first gQD paper published by the Hollingsworth lab used anneal times of 3 hours after cadmium addition and 1 hour after sulfur addition. If shorter anneal times produce the same quality of particle, it would drastically cut down on the time it takes to synthesize materials (especially if the thickest shells are desired for optimal properties). The long anneal times for gQDs are indeed important for sample quality, and furthermore after cation addition, a longer anneal time than after anion addition produces the best performing materials. Although short anneal times produces the right size of particles for the number of monolayers added, the particles optical properties in the ensemble especially at thinner shells was not as good as they were for longer anneal times and produced more irregular shells. For QY optimization specifically, long anneal times after the cation addition, and shorter anneal times after sulfur addition produced products with the highest values (>45% for this method compared to 35% for longer anneals after sulfur than cadmium).

An interesting observation during SILAR at thicker shell thicknesses (>7 monolayers) is solubility cycling after the additions of cation and anion. When the cadmium precursor is added to the solution a cloudy solution is observed, and when the subsequent sulfur injection is completed, the solution clears up again. The addition of sulfur actually has a titrating effect, the reaction was observed to clear up every time a drop was introduced into the reaction vessel. This observation could have significant batch to batch consequences, as the turbidity of a solution can affect how each of the sulfur and cadmium atoms interact with the surface of the quantum dot they are to attach to. Trying to understand this turbidity in more depth is extremely important for reaction reproducibility and scale up for future applications. Therefore, as a first step, the ligands in the reaction were modified to
understand their influence on the turbidity observed. First octadecene was replaced with octadecane, and the turbidity onset was pushed to later monolayers (11 monolayers for onset). Additionally, the amount of dilution in the solution with OD at later monolayers was explored, and the result from these changes was highly symmetric and spherical gQD particles with moderate QYs. The solubility cycling was determined to be a result of the dipole interactions between the particles as they grow larger. The solutions only have cadmium stabilizing ligands, so when cadmium is added to the solution of large faceted particles, the cadmium will occupy standard (typically wurtzitic lattice that has large dipole moments) sites, and is stabilized into those sites for the duration of the anneal time. When sulfur is added however, and has no stabilizing ligands in the solution, it leads to surface reconstruction that maximizes bonding and minimizes surface dangling bonds, relaxing the large dipole moments that existed after cadmium addition.  

For the SILAR reaction, a primary amine (oleylamine) and oleic acid are used as the ligands, the amine is added in its entirety at the beginning of the reaction and the oleate is added as each cadmium addition is made. The amine serves two purposes; it can deprotinate the oleic acid to oleate, that can then covalently bind to the bare cadmium surfaces of the dot, and itself can coordinate to the cadmium serving as a ligand. The extent to which the amine serves as a ligand therefore depends on the amount of oleate in the solution, for lower concentrations (in the case of a 1:4 cadmium:oleic acid addition) amines will dominate on the surface of the QD, when the concentration of oleate is high (1:10 cadmium/oleic acid) oleate dominates on the surface. The QY in each of these cases is fairly high, the oleate dominated particles appear to be more faceted than the amine dominated solutions. When experiments were done with a secondary amine instead of the primary amine, the particles were non-emissive. It was determined that the particles were exclusively oleate capped as the
secondary amine was too bulky to bind to the surface of the dots. When the primary amine was excluded entirely, the sample had the earliest onset of precipitation (at monolayer 3).48

In addition to ligand effects, the initial core size was explored, and had a drastic effect on the onset of non-blinking behaviors of the dots. Larger initial core sizes led to samples that were blinking suppressed at much thinner monolayer additions than smaller core sizes. Therefore, the total particle volume determines the extent to which a sample will be non-blinking. It was found that the minimum volume required to transition to nonblinking behavior is ~750 nm³ whether achieved through a small core and very thick shell or a larger core and thinner shell. As the volume continues to increase, the non-blinking behavior of the sample also increases, so the largest cores with the thickest shells will have the largest on-time fractions of dots. The volume thresholding behavior applies to the PL lifetime of gQDs as well, however unlike the blinking behavior of samples, the lifetime does not continue to increase with increasing volume, they plateau around 65 ns. This suggests that although the hole is confined to the core and the electron is allowed to delocalize as mentioned earlier for this quasi-type II particle, the extent of delocalization is limited by the Coulombic interactions between the carriers, likely explaining the lifetime plateau.48

1.4 Further Optimization and Materials Development

1.4.1 Optimization of CdSe/CdS system

Although possessing significantly enhanced stability compared to conventional core/shell QDs, gQDs remain insufficient for energy demanding technology such as solid state lighting (SSL). So far, research has been completed on the CdSe/CdS gQD system and some initial steps towards material optimization have been completed. However, for specific
applications requiring bright and stable gQD emitters, there are still many more parameters for optimization that can be explored. As a specific example, there is interest in utilizing gQD materials as downconverters for lighting applications.\textsuperscript{21,22,52} In order to be an effective downconverting material for blue light to white light, the samples must be stable at high photon flux and high temperature conditions, and must be able to be able to be loaded into the system at high concentrations without any loss in performance. Compared to QDs that suffer from self-reabsorption and energy transfer due to their small Stokes shift, gQDs are already potentially a better fit as they have a very large effective Stokes shift. How the materials react to high temperatures and high photon flux though must be explored, and is discussed further as a part of the work in this thesis. As we learn more about the performance of these materials in devices, synthetic optimization can be done to help improve the performance of these materials so they can be integrated into a wider range of applications. This optimization includes but is not limited to further investigation into the injection rates of precursors, temperature of the SILAR reaction, the percentage of a monolayer that is introduced into the reaction for each injection, the identity and structure of the cores used, and the identity of the amine used in the reaction. Especially as we look towards the commercial scale up of gQD materials, a thorough understanding of each variable influencing material quality is important. Some of the work following in this thesis aims to study several of these variables using an automated reactor system that for the first time allows for precise control of almost every aspect of the system. This automated system will not only allow us to work towards understanding what variables are especially important for the synthesis of high quality materials, but also offers us the ability to scale up materials for integration into devices and other applications.
1.4.2 Materials Development

We have described the red emitting CdSe/CdS gQD system in some depth already, however we seek to develop similar materials in all wavelengths across the visible and infrared. Although several other reports of blinking suppressed QDs have been published, they have all focused on systems that have red emission. Reports of other “giant” QDs in the green\textsuperscript{33} have been published, but none display the pronounced blinking suppressed behavior that is seen in our gQDs. In 2012, Dennis \textit{et. al.} published the first report of a near infrared InP/CdS gQD with suppressed blinking.\textsuperscript{54} Since then we have sought to develop nonblinking QD nanoparticles further into the infrared and at higher energies in the visible. This thesis details work specifically done on the lead chalcogenide QDs, affording significant blinking suppressed near infrared (NIR) PbSe QDs, that, for the first time can be observed using standard detection techniques at the single dot level.

1.5 Outline of Thesis and Specific Acknowledgements

We begin with a discussion in Chapter 2 with the implementation of the visible emission gQDs (CdSe/CdS) into a device where they are used as LED downconversion materials on top of a blue emitting LED. I designed the set-up of these experiments, suspended all dots in polymer, completed temperature and current experiments, and built the devices. Krishna Acharya and Matthew Buck synthesized the materials for these measurements, and Joseph Torres and Christopher Hamilton made the aerogel samples for the spacer experiments. Janardan Kundu completed the measurements on competing downconverting materials, and Xuedan Ma completed the lifetime measurement on the gQDs. I was responsible for producing the draft of the ACS Applied Materials and Interfaces paper that was published on this work, and Dr. Jennifer Hollingsworth and Dr.
Han Htoon made further edits and improvements to the paper. Chapter 3 focuses on one of the new materials we’ve developed; stable infrared emitting PbSe/CdSe/CdSe gQDs. I was responsible for the synthesis of the materials that are described, with the exception of the tetrapods, as well as steady state optical spectra and TEM sizing and work up. William DeBenedetti worked on initial experiments to develop these materials, and Nicolai Hartmann and Xuedan Ma were responsible for the stability spectroscopic measurements. Ajay Singh took high resolution TEM images of these materials, and completed the TEM crystal structure analysis. Darrick Williams took XRD. I was responsible for writing the initial draft of the Journal of American Chemical Society paper published about this research, and Dr. Jennifer Hollingsworth and Dr. Han Htoon made further edits and improvements to the paper. Chapter 4 discussed our newest work focused on the high-throughput synthesis for optimal material development and combinatorial chemistry design of gQD libraries using our Fully Automated Batch Reactor System (FABRS). I was responsible for all materials synthesis (QD cores, precursor synthesis, and automated reaction design) and all reactor upkeep. I was also responsible for optical data collection, and optical data workup. Radhika Iyer and Sophia Jeffrey, two very diligent high schoolers, were responsible for helping take some of the wide field blinking measurements and quantum yields. Joanna Casson and Chris Sheehan spent many hours taking TEM and STEM images of my materials for these experiments. I was responsible for producing the first draft of the manuscript associated with this work and Dr. Jennifer Hollingsworth made further edits and improvements to the paper.
1.6 References


Chapter 2: gQDs as Downconversion Materials for SSL Applications

This work has been published and can be found as Hanson, C.J., Buck, M.R., Acharya, K., Torres, J.A., Kundu, J., Ma, X., Bouquin, S., Hamilton, C.E., Htoon, H., Hollingsworth, J.A., ACS Appl. Mater. Interfaces 2015, 7, 13125-13130

2.1 Introduction

An area of significant interest and focus for the Department of Energy (DOE) is the adoption of solid state lighting (SSL) as the primary source for illumination in both residential and commercial applications to bring energy usage and consumer costs down. In 2010, the total amount of energy consumed in the US was 3,883 Terawatt hours, 20% (or 700 Terawatt hours) of which was used for conventional lighting.\textsuperscript{1,2} SSL solutions are the leading technology of interest as we look towards lower energy cost effective solutions, but adaptation in all sectors has stalled due to up-front costs of the bulbs and the blue hue spectral profiles considered unacceptable for many applications. SSL bulbs rely on semiconductor light emitting diodes (LEDs), which produce light as a function of hole and electron recombination at the p-n junction of a diode. For the most part, the bulbs on the market contain a high energy blue emitting diode partially downconverted using a broadband yellow phosphor, giving the appearance of white light.\textsuperscript{3} The most common phosphor used for these applications is cerium (III) doped yttrium aluminum garnet (YAG:Ce\textsuperscript{3+})\textsuperscript{4} because it has a high QY (photons out/photons in) and is extremely insensitive to flux-density saturation (linear increase in emission intensity with increasing excitation intensity).
However, YAG:Ce$^{3+}$ has a large spectral full width at half max (FWHM) and does not extend far enough into the red to produce “warm white” light, which is desirable for many applications. As an addition to the yellow phosphor, there is interest in the development of red emitters, which can provide a better “warm” temperature resulting in an ideal color rendering index (CRI) value.\(^5\) The full width half max (FWHM) of the red emitter is important for spectral efficiency of the LED (the more narrow the emitter, the more efficient) as photons in the far red are not detected by the human eye, and therefore contribute to energy consumption but not useful light.\(^6\) Red phosphors can be included in LEDs as either the primary phosphor for down conversion of blue light, or as an addition to a LED already containing a green or yellow phosphor.\(^7\) As many commercial LEDs currently available already contain YAG:Ce$^{3+}$ as a down converting phosphor, a narrow band red emitter could be included to fill the red spectral gap.\(^7,8\) Currently available red phosphors are rare earth ion emitters and have broadband emission.

Finding a stable, narrowband, efficient red phosphor is extremely difficult, as many existing materials do not fulfill all of these requirements. For example, europium (II) nitridosilicate ($\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$) has a high quantum yield and stability, but an extremely broad emission band (>100 nm) with most of the emission outside the region visible by eye in the near IR.\(^5,9\) This results in a poor luminous efficacy of radiation (the ratio of luminous flux to power, a measure of how well a light source produces visible light)\(^4\). Other rare earth emitters, particularly trivalent line emitters such as $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ provide the optimal narrow band emission that is desired for lighting applications, but lack broadband and efficient excitation pathways in the UV/blue wavelengths.\(^4,7\) In addition, the synthesis of these materials is costly, and usually requires extremely high temperatures and pressures (>1000 °C) and the long radiative lifetimes of these materials lead to rapid flux saturations and
reduced stability and efficiency.\textsuperscript{2,4} In addition to stability and spectra excitation concerns, many of the phosphors considered are synthesized using rare earth components that could experience short or long term supply disruptions depending on political climates. For these reasons an alternative is actively being sought.\textsuperscript{2}

QD’s offer a potential alternative down-conversion material for lighting applications, as they are bandgap emitters with narrowband emission (FWHM 25-35 nm) and broadband absorption that extends well into blue/UV wavelengths.\textsuperscript{8,10-12} Although previous experiments using Ce:YAG and red emitting QDs have produced high CRI values for a demonstration of a white LED, there are still several challenges specific to the inclusion of QDs that has prevented the widespread usage of these materials as downconverters.\textsuperscript{8} QDs can be synthesized in large batches reproducibly with high QYs, but the cores themselves are unstable so they must be protected from decomposition using a large organic ligand layer, or, more commonly, a larger bandgap semiconductor material shell.\textsuperscript{13} Thin shells are commonly used, and protect the dots from some decomposition and increase QY,\textsuperscript{14} but do not prevent fluorescence intermittency, photobleaching, solid state quenching and auger recombination processes.\textsuperscript{15} More importantly, close packed QDs experience quenching as a result of dot to dot energy transfer causing substantial self-reabsorption and emission which drastically decreases the down conversion efficiency and severely limits the incorporation into LED applications.\textsuperscript{16,17}

However, as described in Chapter 1, gQDs provide an interesting alternative to the standard QDs as phosphors for efficient lighting applications as dark processes are suppressed and gQDs do not photo bleach under prolonged excitation.\textsuperscript{15,18} Additionally, because the absorption of the gQDs is mostly in the shell, and the emission of the dots is
from the core there is little overlap, and the problem of self-reabsorption is solved as a result of this large effective Stokes shift.\textsuperscript{19} This means that the gQDs can be packed in a high density with little consequence on the emission intensity and down conversion efficiency.\textsuperscript{15,19}

### 2.2 Experimental Design

To first understand the differences between standard “thin-shell” QDs and the gQDs, highly concentrated samples of each were distributed into a polymer (poly(lauryl methacrylate) PLMA), cured, and tested for solid state downconversion efficiency using a Philips Lumiled high power “royal blue” Luxeon Rebel ES LED as the excitation source.\textsuperscript{20} The PLMA polymer was chosen as it is compatible and can easily permeate within the gQD/QD oleate and oleylamine surface ligands allowing for a uniform distribution of material throughout the polymer and affording films that do not suffer from particle scattering losses.\textsuperscript{21} The polymer also helps to stabilize the gQD/QD material, and prevents emission efficiency losses usually observed when transitioning from solution to solid state. A thin piece of this polymer-dot composite was attached to the LED using optically clear adhesive cured by UV. Several samples of gQDs were used with varying QYs, for comparison to the standard QDs with high QYs and the samples were made with

![Figure 2.1: Device schematics for testing of gQDs as a downconverting material. a) is the case in which there is no spacer between the gQD layer and the LED, for direct on chip measurements. b) is the case in which a small spacer of either PDMS or Aerogel is placed between the gQD and LED as described in the text](image)
identical masses of gQDs or QDs suspended in polymer (2 mg in 6 mL of polymer) affording an optical density of 2-2.5 at 450 nm. All measurements were made using an integrating sphere attached to a photomultiplier tube (PMT) detector on a Nanolog Fluorometer (Horiba) to record all light emitted from both the source (the blue LED) and the gQD downconverters. gQDs were synthesized using both the SILAR and continuous injection methods, and QDs with thinner shells were taken as aliquots during the shelling process for gQDs. For stability experiments, the same polymer samples were made with lower concentrations of either gQDs or QDs and were either glued directly on the LED chip, or on top of a small spacer of either polydimethylsiloxane (PDMS) or Aerogel (Figure 2.1) for measurements.

2.3 Results: Comparing QD to gQD Efficiency

Initially, to understand the impact the large effective Stokes shift of the gQDs has on the downconversion efficiency of blue light to red, several samples of gQDs and QDs were suspended in polymer and tested directly over the commercial LED. gQD samples with QYs in solution between 30-90% were studied compared to a sample of QDs with a QY in solution of 40% to observe solution state vs. close packed solid state QYs. The peaks of the blue LED electroluminescence (EL) and the down converted photons from the gQDs/QDs when the LED was driven at 200 mA are shown in Figure 2.2a. It was observed that the amount of light down converted by the gQDs is much greater than the amount converted for the QDs, even though the QDs may have had a higher initial solution QY than the gQDs. The standard QDs with a 40% QY in solution only successfully down convert 13% of the blue LED in the solid state (Figure 2.2b), which is attributed to the large amount of self-reabsorption experienced by QDs because of a characteristically small Stokes shift.
(absorption and emission overlap). In dilute solution this effect is not as pronounced as close packed solid state samples. In this instance, the distance between the QDs is drastically reduced, allowing for significant energy transfer between dots.

For gQDs however, the comparison of solution vs. solid state QY presents extremely different results, for gQDs with solution QYs of 30%, 30% of the LED light is down converted efficiently. Further testing utilizing gQDs with a range of QYs in solution (30-90%) showed near-unity down conversion efficiency with solution state QY for all gQD samples. Therefore, it can be assumed that if a 100% QY gQD was synthesized, the down conversion efficiency would be 100%. The stark difference between the efficiencies of standard QDs and gQDs can be attributed not only to the reduction of self-reabsorption, but also to the difference in the absorbance cross sections of the QDs vs the gQDs. Previously, it was shown that the absorbance of gQDs with 12 ML of shell was ~12x greater than that of a QD with 3 ML of shell, meaning that fewer blue photons are absorbed by the thin shell QD.22,23 This explains the large amount of blue EL left in Figure 2.2a from the QD/PLMA downconverting material (~12%) as opposed to the gQD/PLMA downconverting material (~1-2%). Therefore, nearly 6-12 less photons absorbed by the QD layer than the gQD layer.
which corresponds nicely to earlier comparisons of the absorbance cross section. If absorbance cross section alone was the primary source of loss for QD phosphor materials, a 40% QY sample for example would still only have a 30% downconversion efficiency. These results confirm our findings that the self-reabsorption is extremely detrimental to the overall downconversion efficiency of the phosphor, but the absorbance cross sections also contribute to the loss in efficiency. We could indeed increase the concentration of QDs and gQDS in the polymer in an attempt to absorb more of the blue EL, but the further increase of the QD sample concentration would also increase the amount of self-reabsorption, leading to consistently low downconversion efficiency for standard dots.

2.4 Results: Other Limitations on gQD Down Conversion

2.4.1 Thermal Effects on gQD Emission

Although we have shown that by using the gQD materials we have the possibility to approach 100% down conversion efficiency with a 100% QY gQD material placed “on chip”, there are two significant limitations that have yet to be discussed, “on chip” temperature and high driving current from the electroluminescent LED. The former, high on chip temperature can cause thermal quenching of QD PL which is a well-known and understood phenomenon.\textsuperscript{24,25} PL quenching observed in previous studies may or may not also include changes in PL lifetime, “dynamic” or “static” quenching respectively.\textsuperscript{24} Previously the Htoon lab showed that nonemissive (dark) processes from QD blinking (a well-known photophysical process in QD research) can either be dynamic or static. Respectively, A-type blinking results in overall intensity reductions accompanied by PL lifetime shortening whereas B-type photodarkening occurs as a results of “hot” electron
trapping to surface states or surface defects, and as a result exhibits no changes in lifetime.\textsuperscript{26}

We therefore sought to understand the thermal effects of placing the gQDs in polymer directly on chip as the temperature on the surface of the chip will go up as the chip is running, and can change the color of the phosphor.

We observed the amount of temperature quenching in blocks of gQD phosphor in polymer at the same concentrations used for the earlier downconversion studies. It was found that quenching is reversible from room temperature to $\sim$100 °C (Figure 2.3a) and is

![Figure 2.3: a) gQD in PLMA heated in a temperature controlled sample holder in a Horiba Nanolog Fluorometer integrated intensity. The broadening and decrease in emission is completely reversible over multiple cycles. b) shows the wavelength shift of the emission peak as the same sample is heated. c) shows PL lifetime measured on the gQD sample, while heated, and shows minimal decrease in the lifetime, the initial value of which is also recovered when the sample is cooled. d) Emission intensity of phosphors used for LEDs to applied current.](image)
accompanied by a less than 10 nm red-shifting of the emission of the gQDs, which is also reversible (Figure 2.3b). PL lifetime measurements were made on samples heated to 85 °C and shows that the quenching is relatively “static” which could imply a mechanism related to B-type blinking and the existence of surface traps that are apparent at higher temperatures (Figure 2.3c). This result is interesting, as it has been shown that B-type blinking is suppressed in gQDs, however there are two potential processes that could lead to this seemingly contradicting result. First, heating may activate a carrier that escapes to a pre-existing trap state, and at room temperature this carrier is confined to the nanoparticle and the B-type blinking is suppressed. The other possibility that may in addition/instead of contribute to the “static” PL quenching upon heating is thermally induced formation of a temporary trap-state which may allow the B-type quenching to be the predominate mechanism at higher temperatures.

2.4.2 Flux Saturation Measurements

In addition to thermal quenching, materials used as down converters for LEDs are subject to flux saturation, in which a material has a slower “photon cycling rate” and is therefore unable to down convert all available photons. For many of the rare earth phosphor emitters (most notably Eu$^{3+}$ which has been studied at length) that have very long fluorescence decay lifetimes (microsecond or longer) this is the case, and at very high powers a second excitation can be generated in an emitter already in an excited state. However, visible QDs and gQDs have much faster PL lifetimes (10-100 ns time scales) and so should be fairly resistant to flux saturation. As shown in Figure 2.3d the flux dependent PL intensities is compared for a slower response Eu$^{3+}$ nitrate sample in a binder (gamma-butyrolactone), a faster response rare-earth phosphor currently commonly used for LED
phosphors Ce\textsuperscript{3+}:YAG in the same binder, and a sample of CdSe/CdS gQDs. In this set up, the samples were placed 6 mm away from the LEDs (with an air “spacer”) and the PL was recorded on a spectroradiometer. As shown in Figure 2.3d the gQDs and the Ce\textsuperscript{3+}:YAG samples had a linear response to an increase in flux, suggesting that there is no flux saturation in these samples. However for the Eu\textsuperscript{3+} sample, the response shows flux saturation, and the response is non-linear.

However, we must address the limitations of samples at ultra-high flux (5-10 W/mm\textsuperscript{2}), the situation in which the number of electron-hole pairs exceeds one per gQD. In fact, we can calculate the maximum and minimum number of excitons using the absorption cross section of dots with 12-16 monolayers of shell (absorption cross section is 100-200 x 10\textsuperscript{-15} cm\textsuperscript{2})\textsuperscript{23}, at a specific excitation rate and energy as follows:

**Excitation Rate:** $R = 5-10 \text{ W/mm}^2 = 500-1000 \text{ W/cm}^2$

**Absorption Cross Section for dots with 12-16 monolayers of shell:** $X = 100 \times 10^{-15} - 300 \times 10^{-15} \text{ cm}^2$

**Photon Energy:** $E = 3.1 \text{ eV} = 4.96 \times 10^{19} \text{ J}$

**Exciton Generation Rate:** $E*R = (R * X)/E = 1.0 \times 10^8 - 6.0 \times 10^8 \text{ s}^{-1}$

**Lifetime:** Measured to be 30-100 ns

**Average Exciton Population per dot:** $n = E*R*\text{Lifetime} = 3-60 \text{ excitons per dot}$

With LED excitation we are clearly within the multiexciton regime at these very high power fluxes for samples of both gQDs and QDs. In the case of standard QDs, Auger recombination competes with radiative decay when in the multiexciton regime, leading to
shortened lifetimes as the number of excitons per dot increases.\textsuperscript{27} As a result, standard QDs are not ideal phosphors for high power applications, such as automotive lights or cell phone camera flashes, because at high photon flux, the dots will not emit efficiently.\textsuperscript{26,29} However, gQDs are a viable option as phosphors for high power applications as Auger processes in gQDs is greatly suppressed, and so at room temperature biexciton and multiexciton processes result in efficient emission.\textsuperscript{30}

2.4.3 High Power LED Measurements

For high power applications, not only is the phosphor exposed to both high photon flux, but high temperatures and the combined effect of both on the stability of the gQDs must be understood. Therefore, the phosphor QD emitters were tested in a device-like configuration, that is, the gQD or QD films were affixed either directly to the surface of the LED or onto a thin spacer layer placed between the LED chip and the film to minimize the conductive heating of the phosphor by the LED junction (Figure 2.1). The stability of the phosphor was tested as a function of LED driving current as it was increased from 50 mA to 500 mA. The samples were held at each current point for 3 minutes to ensure stabilization of the system, and the samples were measured in the integrating sphere for collection of all photons. The QD directly on chip sample succumbs to thermal quenching and/or flux quenching almost immediately, and is the lowest performing sample of any of the gQD samples tested.

Two different materials were used for spacers, either 2 mm of another polymer PDMS (polydimethylsiloxane) or 2 mm of a silica aerogel spacer. PDMS was chosen as it is optically clear, and compatible with the current polymer silicone chemistry used for lighting applications while silica aerogel was used as it has an extremely low thermal conductivity (~5
mW m⁻¹ K⁻¹, which should allow for exceptional protection of the gQD and QD films from conductive heating. As a first test, samples of a gQD film directly on chip, a QD film directly on chip, a gQD film on the aerogel spacer on chip, and a gQD film on the PDMS spacer on the chip were tested at the different currents with the results presented in Figure 2.4. It was found that the device with the highest output intensity (i.e. largest amount of down converted light) is the gQD film placed directly on the LED chip run at 200 mA. At currents lower than 200 mA, this device has the largest output intensity when compared to the devices with the spacer layers or the device with the QDs alone. However, above 200 mA we do not observe a further increase in output intensity of this device, which we attribute to the conductive heating of the gQD layer. To understand this effect better, we tested the spacer layer samples at the same range of currents. At all currents the output intensity is less than that of the gQD on chip sample, but this can be attributed to the imperfect transmittance of the blue EL through the spacer. We assume that for the PDMS, photons are lost due to waveguiding out the sides of the device, where as in the aerogel sample the blue LED light is scattered when it passes through the sample (Figure 2.5). From 0 mA to 200 mA the emission intensity trends of the gQD films directly on chip and gQD films on the spacers look very similar, however at 250 mA and above, the samples of the gQD film directly on chip and the gQD film on the PDMS spacer experience a decrease in the emission intensity from their max values at 200 mA. In contrast the gQD film on the aerogel spacer levels out and maintains the maximum emission intensity value out to 400 mA, where it only slightly decreases from 400-500 mA, which is assumed to be a direct result of the aerogel's unique protection of the gQDs from thermal quenching. Compared to the gQD film directly on chip, both samples with the gQD film on spacer outperform the directly on chip sample from 400-500 mA, suggesting that conductive heating causing
thermal quenching is an important parameter to assess when determining the performance of a given phosphor directly on LED chips.

Another metric of interest for phosphors utilized for white light generation for high powered blue LEDs is the stability of the phosphors over time when exposed to a high driving current. The stability of our gQD phosphor and standard QD phosphors at high currents was tested utilizing various device architectures with different thickness of PDMS spacers (ranging from 0.3-1.5 mm thicknesses) at a current of 500 mA for 30 minutes (Figure 2.4b). The devices were turned on, and an immediate “on” intensity measurement was attempted, however it was observed that with the thinner spacers for the gQDs and the devices using the QDs that there is rapid quenching, that could not be measured within the instrument limitations. Therefore the instant on time is only recorded for the gQDs on the thickest spacer. The intensity of the phosphor was then measured every 5 minutes for a total of 20 or 30 minutes, and in all cases steady state intensity was reached after an initial decrease in intensity after the LED is turned on. The QDs on the PDMS are quenched significantly, no matter how thick the PDMS spacer is. For the gQD samples however, the steady state intensity correlates well with the thickness of the spacer (the thicker the spacer, the brighter the dots will be at the steady state intensity).
as the thick spacers provide protection of the phosphor layer from the high flux operation. For the gQDs on the thickest spacer (1.5 mm) it is observed that ~55% of the original intensity of the gQDs is maintained for at least 30 minutes. Using our earlier results of the amount of PL quenching of the gQDs vs the temperature of the phosphor sample, if the assumption is made that all of the gQD PL quenching is a result of thermal quenching, the gQD layer on the 1.5 mm PDMS spacer is at a temperature of ~65 °C. However, when the peak positions of the samples are observed with various spacer thicknesses, the peak position changes by 25-30 nm, much larger than is seen in the gQD heating only experiments, even up to 100°C (only a ~10 nm shift is observed, as shown previously in Figure 2.3b) and so other mechanisms of quenching leading to PL instability when the phosphors are used on LEDs run at high currents. This large shift indicates that other processes besides heating contribute to PL quenching, when gQDs are placed on the LED. One possible explanation of this trend is energy transfer of excitons from smaller blue dots in the ensemble (higher energy emitters) to redder dots in the ensemble (larger lower energy emitters) by non-radiative dipole interactions. This could also be a result of self-reabsorption, in which bluer photons are absorbed by other gQDs in the ensemble. However, we do no expect that either of these mechanisms is the cause of the large observed red shift, as we have shown in the past that the thick shell on the gQDs
prevents both energy transfer and self reabsorption compared to the conventional QDs, and neither process would be expected to yield red-shifting dependent on driving current, which we observe. As peak position and PL intensity are important parameters that must be controlled for lighting applications, the observed nonthermally induced red shifting is being investigated further. We suspect that much of the red-shifting and PL quenching could be a result of a collection of charge in the local environment of the emitters, as the red shifting shows some flux-dependence. This collection of charge could lead to photocharging (either by carrier trapping or carrier injection) for both gQDs and QDs, and is therefore an important topic of further study.

2.5 Conclusions and Outlook

In conclusion we have explored the use of gQDs as a downconverting material for commercial blue LEDs. The comparison between thick-shelled gQDs and standard thinner shell QDs was done by suspending both materials in PLMA polymer blocks, and affixing these blocks to the top of blue LEDs. We show for the first time that the gQD nanocrystals have the same QY in solution and in solid state, and therefore have the potential to have downconversion efficiencies on blue LEDs that match the QY of the starting samples. This is in contrast to standard QDs, which are unable to maintain solution QY in solid state, due to significant energy transfer and self-reabsorption. However, direct on chip experiments show that at particularly high fluxes, both QDs and gQDs suffer from thermal quenching effects, and potential charging effects. In the case of gQDs, these can be reduced by the introduction of a small spacer layer, either another polymer, PDMS layer, or an aerogel layer that provides some protection for the downconverting material from the surface of the chip. This suggests that for the next generation LEDs, the placement of downconverting materials
must be carefully considered, as thermal effects on the phosphor should be minimized. We are hopeful however, that in future commercial products, gQDs will be integrated as the narrow red line emitters to produce warmer white light. There is certainly further work to be done to understand the stability of these materials over extended periods of use, specifically in high stress (current, high humidity, high temperature) environments. Results from these experiments will drive synthetic modification and optimization for commercial integration.

2.6 Materials and Methods

Materials: Selenium (Alfa Aesar, amorphous shot, 1-3 mm, 99.999%), sulfur powder (Acros Organics, 99.999%), trioctylphosphine oxide (TOPO, 99%, Acros), trioctylphosphine (TOP, 90%, Sigma Aldrich), octanethiol (98%, Alfa Aesar), octadecylphosphonic acid (ODPA, Alfa Aesar), oleyl amine (technical grade, 70%, Aldrich or Acros Organics), 1-octadecene (ODE, technical grade 90% Acros), n-octadecane (OD, 99%, Alfa Aesar), CdO powder (Alfa Aesar, 99.998%), oleic acid (OA, 90%, Alfa Aesar), hexane (anhydrous, 99.9%, Acros Organics), acetone (99.8%, Optima™ Fisher Scientific), ethanol (anhydrous, Fisher Scientific) were used as received without any further purification, and all syntheses were performed under Ar atmosphere using standard air free Schlenk technique.

Quantum Dot (QD) Syntheses:

Preparation of stock solutions: 0.5 M Cd-oleate solution was prepared by dissolving CdO powder in OA at 180 °C, followed by vacuum removal of water at 80°C. Similarly, 0.2 M Cdoleate solutions (10:1 molar ratio oleic acid:Cd) were prepared by heating CdO powder and oleic acid in either ODE or OD. Stock solutions of TOP-Se were prepared by stirring Se in TOP for several hours under air-free conditions. Sulfur-containing solutions were
typically 0.2 M and were prepared by dissolving sulfur powder in either ODE or OD at 180°C, or simply mixing octanethiol with ODE.

**CdSe QD core synthesis:** *Wurtzite CdSe QD cores* were synthesized according to modified (scaled up 3-fold) literature. Briefly, TOP-Se solution (1.0 M, 1.40 mL) was injected into a mixture of TOPO (23.27 mmol, 9 g), ODPA (2.43 mmol, 0.84 g) and CdO (1.40 mmol, 0.18 g) held at 380 °C under Ar. The reaction was temperature quenched by removing the heating mantle after the QDs had achieved the desired size as assessed by optical absorption spectroscopy (i.e., just before removing heating mantle, 1s absorbance peak was 565 nm; final 1s absorbance peak was 577 nm, equivalent to a CdSe QD diameter of 3.7 nm; emission FWHM: 27.8 nm). CdSe core QDs were flocculated using acetone and dispersed in hexane. *Mixed wurtzite/zinc-blende CdSe QD cores* were prepared according to previously published literature, with slight modifications. Briefly, a room-temperature solution containing 4 mL of 1 M TOP-Se, 3 mL oleylamine, and 1 mL ODE was rapidly injected into a 300 °C solution containing 0.750 mL of 0.5 M Cd-oleate, 1.2 g TOPO (Strem, 90%), and 9 mL of ODE. The temperature recovered and was maintained at 270 °C, and after 5 min, a solution containing 3 mL of 0.2 M Cd-oleate in ODE and 6 mL of 1 M TOP-Se was added dropwise over ~1h. The resulting nanocrystals exhibited a 1s absorbance peak at 605 nm, corresponding to an approximate size of 4.8 nm.

**CdSe/CdS QD synthesis:** *Continuous injection/high-temperature QD synthesis* – Standard CdSe/CdS QDs were synthesized according to a modified literature procedure. A mixture of ODE (5 mL) and oleyl amine (5 mL) was degassed at 80 °C for 1 h. Wurtzite CdSe cores (2×10⁻⁷ mol) in hexane were added, and vacuum was applied briefly to remove the volatile hexanes. The temperature was raised to 310 °C, at which point slow injection of a mixture of
CdSe/CdS giant quantum dot (gQD) syntheses: Continuous injection/high-temperature gQD synthesis – CdSe/CdS gQDs were synthesized according to a modified literature procedure.36 A mixture of ODE (5 mL) and oleyl amine (5 mL) was degassed at 80 °C for 1 h. Wurtzite CdSe cores (2×10^{-7} mol) in hexane were added, and vacuum was applied briefly to remove the volatile hexanes. The temperature was raised to 310 °C, at which point slow injection of a mixture of cadmium oleate (0.2 M in OD) and S/ODE (0.2 M in ODE) was initiated (injection rate: 3 mL/h). Sufficient precursor was added to achieve a CdS shell thickness of 12 or 16 CdS MLs. This preparation generally afforded higher QYs (assessed as above) compared to the below layer-by-layer/moderate-temperature approach; however, gQDs prepared by this route exhibited photobleaching: ~50% degradation of PL intensity over 1 h obtained from an ensemble of gQDs dispersed at the single-dot level (continuous laser excitation) compared to the absence of photobleaching observed previously for gQDs.22 Successive ionic layer adsorption and reaction (SILAR) moderate-temperature gQD synthesis – CdSe/CdS gQDs were synthesized according to previously published methods.15,18 Briefly, 2.0 x10^{-7} mol of purified, mixed-phase CdSe cores in hexanes was mixed with 5 mL oleylamine and 5 mL OD. Hexanes were removed in vacuo at 80 °C, and the temperature was raised to 240 °C for SILAR. Alternating injections of 0.2 M Cd-oleate and 0.2 M sulfur (both in OD) were performed in a dropwise fashion, allowing 3 h of solution-phase annealing after each Cd-oleate addition and 1 h after each S addition. The delivered precursor volumes were calculated to yield one ML of CdS shell per addition cycle.18
Spacer Layer Fabrication

Polydimethylsiloxane (PDMS) spacer layer preparation: PDMS was formed using a Dow Corning Sylgard 187 Silicone Elastomer kit with the elastomer and curing agent used in a 10:1 ratio. The PDMS was cured for 1 h at 100 °C in an oven, and then cut using a razor blade into 0.3-1.5 mm spacers.

Aerogel (AG) spacer layer preparation: Silica gels: Silica alcogels were prepared by base-catalyzed hydrolysis and condensation of tetramethoxysilane (TMOS). TMOS was diluted with methanol in a jar. After thorough mixing, 0.02 M aqueous ammonium hydroxide (NH$_4$OH) was added to the mixture. After further mixing, the sol was poured into a stainless steel mold and allowed to gel. For a silica aerogel of 100 mg/mL final density, the quantities were: 6.0 g TMOS, 15.3 g methanol, 5.2 g 0.02 M NH$_4$OH; gelation was complete in approximately 3 h. For other densities, the amount of TMOS precursor was adjusted accordingly (Figure 2.5). Supercritical drying of alcogel to form aerogel: Alcogels were loaded into an autoclave; methanol was introduced and the system was pressurized to 140 atm. The vessel was then heated over 4 h to 265 °C, maintaining constant pressure by slowly releasing methanol. The vessel was then held at constant temperature and pressure (140 atm, 265 °C) for 1 h. Pressure was then slowly released over 2 h while maintaining temperature. Finally, the reactor was evacuated and allowed to cool to room temperature overnight. Aerogels of different densities (mg of TMOC per S4 cc) were formed and sliced into 1-3 mm pieces to be used as spacers on light-emitting diodes (LEDs).

Composite Film Preparation and Device Assembly QD and gQD poly(lauryl methacrylate) (PLMA) composite blocks were prepared according to literature. Lauryl methacrylate (LMA), ethyleneglycol dimethacrylate (EDMA), and azobisisobutyronitrile
(AIBN) were purchased from Sigma Aldrich and used as received. The QDs and gQDs were processed in the same manner from growth solution. Namely, nanocrystals were initially precipitated out of growth solution by centrifugation, without addition of solvent or non-solvent. The precipitate was then re-suspended in hexanes, and a non-solvent – ethanol in this case – was added in excess to induce complete particle flocculation, or a “hard crash.” Upon centrifugation, all nanocrystals precipitated. This process of re-suspension/precipitation was repeated a second time, with the final precipitate brought back up into hexanes for storage prior to use. For preparation of the QD/gQD-PLMA composite films, after using dry air to evaporate (blow off) the volatile hexane solvent, 2 mg nanocrystals were re-suspended in 6 mL of prepared monomer mixture [lauryl methacrylate (LMA), ethyleneglycol dimethacrylate (EDMA) crosslinker and azobisisobutyronitrile (AIBN) thermally activated radical initiator in a 1:4:1 (w/w) ratio]. The nanocrystal/monomer mixture was placed into a cuvette (1 cm x 1 cm PMMA), then transferred to a vacuum oven that is cycled two times between full vacuum (~-25 inHg) and argon purge to remove any remaining volatiles (pump/purge cycle also appears to aid in limiting bubble formation in the resulting polymer). The oven is then brought to 80 °C and held under static vacuum (~-5 inHg) overnight. The resulting nanocrystal/polymer blocks were removed from the cuvette “mold” then sliced into thin slabs to be adhered to LEDs. An optically transparent UV-curing adhesive (Norland Optical Adhesive NOA68, Thorlabs) was used for this step. When employed, a spacer layer was similarly applied to the LED, with the QD layer then carefully adhered to it. The LEDs were purchased from LUXEON star LEDs, and were a Philips Royal Blue Rebel ES LED mounted on a 20 mm “cool base.”
Optical Characterization

Obtaining emission spectra from down-converted LEDs: Emission spectra were collected using an integrating sphere attached to a Horiba Scientific Nanolog spectrofluorometer. The fluorometer’s halogen source was turned off so that all light collected derived from either the blue LED electroluminescence (EL) or from the downconverted light generated by QD / gQD photoluminescence (PL). EL and PL spectra were detected using a visible photomultiplier tube (PMT) intensity-corrected to account for sensitivity differences across the spectral range detected. Use of an integrating sphere allows for quantitative collection of light output (the coating on the inside of the sphere reflects light from all angles, causing light in the sphere to be quantitatively transferred to the spectrometer for analysis). In all LED measurements, fluorometer settings were as follows: 2 nm emission slit, 1 nm step size, and 0.05 s integration time. An ND 4.0 filter was used in front of the emission slit to enhance reproducibility. Namely, it is known that using small slit sizes can introduce inconsistencies between scans as the likelihood of the slit opening to the same extent each time is reduced for small slit sizes. Therefore, to improve reliability but stay within the linear regime of the PMT detector, an ND filter was used to reduce the amount of light impinging on the detector. In this configuration, the resulting counts per second for the maximum of the blue LED EL peak in the absence of QD or gQD down-converter material was $1.7 \times 10^7$ for an LED driving current of 500 mA. In general, LEDs were powered by a Gwinstek GPR-11H300 Laboratory power supply that allows for controlling current and voltage.

Assessing thermal quenching and red-shifting: The temperature “calibration curve” was obtained by assessing the impact of controlled heating on gQD PL intensity. A Horiba
thermostated sample holder was used to simultaneously heat the gQDs and collect PL. The gQD/PLMA composite block was held at each set-point temperature for 5 min to ensure equilibration prior to further temperature ramping (or reductions in the case of cooling).

**Determining down-conversion efficiency:** Down-conversion efficiencies were calculated by comparing the integrated area of the LED EL peak (energy scale) in the absence of QDs / gQDs with the integrated area of the down-converted PL. Percent remnant EL was similarly obtained by comparing the LED EL before and after addition of the QD / gQD layer. In all cases, spectra were corrected for detector sensitivity to ensure accurate comparison across different spectral regions. **Assessing flux saturation behavior:** Eu(III) nitrate salt and Ce(III)-doped Y$_3$Al$_5$O$_{12}$ (YAG:Ce) were each blended with a gamma-butyrolactone binder as previously reported. These, along with a gQD/PLMA composite sample, were successively held 6 mm away from a blue LED source. The respective down-converted photons were collected using a Konica Minolta Spectroradiometer CS-2000 (with a 550 nm long pass filter placed between the detector and the samples to cut out residual 450 nm LED light).

**Temperature-dependent PL lifetime measurements:** PL decay curves were measured with a home-built micro-PL system integrated with a time-correlated single-photon counting system (B&H). The temperature of the QD samples in cuvettes (1 mm path-length) was controlled by a temperature controller. A 440 nm pulsed diode laser (PicoQuant) was used to excite the QDs at a repetition frequency of 250 KHz. Emission from the samples was directed to a single-photon avalanche diode (APD, ID Quantique). Each time after the temperature was changed, the sample was allowed to sit for ~10 minutes to reach thermal
equilibrium before a measurement was taken. The integration time for each decay curve was typically 5 to 6 minutes.

2.7 References


Chapter 3: Infrared PbSe/CdSe/CdSe gQDs

This work has been published and can be found as Hanson, C.J., Hartmann, N.F., Singh, A., Ma, X., DeBenedetti, W.J.I., Casson, J.L., Grey, J.K., Chabal, Y.J., Malko, A.V., Sykora, M., Piryatinski, A., Htoon, H., Hollingsworth, J.A., J. Am. Chem. Soc. 2017, 139, 11081-11088

3.1 Introduction

Infrared emitting QDs could potentially be used for a wide range of applications, including fiber optic communications (1300-1600 nm),\textsuperscript{1} biological tracking and diagnostics (1350nm and mid-infrared sources),\textsuperscript{2,3} defense (mid-infrared),\textsuperscript{4} environmental monitoring,\textsuperscript{5} photodetectors,\textsuperscript{6} lasing,\textsuperscript{7} gain media for amplified spontaneous emission,\textsuperscript{8} light emitting diodes,\textsuperscript{9} and photovoltaics (near-infrared).\textsuperscript{10} Of particular interest are Lead Selenide (PbSe) QDs that have PL wavelength tuning from near-infrared to the mid-infrared (900 nm~4000 nm) with particle size tuning.\textsuperscript{11,12} This extreme size dependent spectral tunability (when compared to CdSe for example) is the result of the large exciton Bohr radius for PbSe (46 nm,\textsuperscript{12} CdSe for comparison is 5.4 nm\textsuperscript{13}). However, despite the potential for the use of these QDs their integration into applications has been stalled by the lack of long term stability in air.\textsuperscript{14-16} PbSe QDs kept in air, in the presence of light and at room temperature are known to exhibit rapid photooxidation degradation shown by both a significant blue shift in emission and loss of PL intensity.

Efforts so far have been dedicated to stabilizing the surface of PbSe QDs to prevent the oxidation of the surface lead and selenium.\textsuperscript{12,17-19} This has included inorganic shelling and cation exchange (to produce PbSe/thin shell CdSe QDs)\textsuperscript{12} and inorganic/ organic surface
treatments such as halide passivation either during or post synthesis to generate PbX₂ (X = Cl, Br, I)\textsuperscript{17,18,20} or improved organic passivation using phosphonic acid ligands.\textsuperscript{19} The enhanced stability of PbSe QDs following these efforts have been monitored by following the PL and absorption trends as a function of time and storage, and the performance of these materials in devices over time.\textsuperscript{20} However, the tests for environmental stability of the PbSe QDs using these different methods have been done at an ensemble level.

Single dot emission measurements of these materials have been experimentally inaccessible to date due to their characteristically long PL lifetimes (≥ 1 µs) and rapid photobleaching.\textsuperscript{21,22} Although there have been some cases of relatively fast emitting lead sulfide (PbS) QDs (500-1000 ns solution phase lifetimes),\textsuperscript{23} the radiative recombination of excitons is sufficiently slow resulting in a low PL signal. This combined with low QD QYs, instability, and high detector background noise (when standard detection techniques such as Indium Gallium Arsenide (InGaAs) detectors or avalanche photodiodes (APDs) are used) has made the measurement and visualization of single infrared emitting QD emission on standard techniques impossible.\textsuperscript{24} With advanced detection techniques such as a superconducting nanowire single photon detector (SNSPD), single dot PbS/CdS QD emission has been measured.\textsuperscript{23}

The ability to measure and make use of single photons from infrared emitting QDs could be greatly enhanced if the rapid photobleaching of these materials could be significantly suppressed. We have observed that a low concentration of these materials spread onto glass substrates measured with laser excitation at low temperature photobleach within seconds, making our measurements impractical. However, we have also found for the visible CdSe QD system, the addition of a very thick shell on the core not only stabilizes the
dots and prevents photobleaching and fluorescence intermittency.\textsuperscript{25–29} We therefore sought to employ this strategy on the infrared QD emitters, and show for the first time that PbSe emitters can be rendered ultrastable with the addition of a thick CdSe shell for long periods of time under very high laser excitation powers (50-300 W/mm\textsuperscript{2}). In addition, we report that the crystal structure (which can be synthetically directed) of the PbSe/CdSe gQDs determines the PL efficiency, and therefore our ability to detect single-dot measurements.

### 3.2 Experimental Design

The full experimental and product characterization details can be found in 3.5, but briefly, PbSe QDs were synthesized using a previously published procedure then isolated and subjected to partial cation exchange of Pb for Cd on the surface.\textsuperscript{12} This effectively reduces the core size of the starting PbSe core, as the formation of the CdSe shell from cation exchange maintains the initial size of the particle as the sacrificial replacement of Cd for Pb proceeds. Therefore, thicker CdSe shells can be obtained if initially larger PbSe QDs are used, and the time for cation exchange is increased. The PbSe/CdSe dots are isolated after the cation exchange, and washed up to be used for larger shell growth. Subsequent shells are grown using a SILAR method, described in both 3.5 and in previous gQD synthesis for CdSe/CdS dots.\textsuperscript{27,29} Shell precursors are cadmium oleate as the cation, and either selenium 1-octadecene (Se-ODE) or selenium trioctylphosphine (Se-TOP) as the anion for shell growth on the cation exchanged PbSe/CdSe nanoparticles. SILAR proceeds to 10ML of shell with 10 minute anneal times.

The product is characterized for size and shape using standard and high resolution TEM and X-Ray diffraction. Steady state optical characterization was completed using a UV-Vis-NIR spectrophotometer for absorption, and a home built confocal laser microscope
setup with 830 nm excitation mode locked laser and a 2D InGaAs camera for emission. For PL stability measurements the QDs were continuously irradiated and the final PL value of the QDs after an hour was compared to the initial value. PL decay curves were obtained by exciting the sample with a 440 nm diode laser with a 100 kHz repetition rate. A SNSPD detector was used to detect the PL signal. Single QD measurements were obtained using a ProEM 512 EMCCD camera with a 900 nm longpass filter. The sample was excited using a 405 CW laser.

3.3 Results and Discussion

3.3.1 Synthesis Controls Crystal Structure

To understand the effect the selenium precursor has on the shell growth, two sets of reactions were done using the same initial materials. PbSe cores (5.6 ± 0.5 nm diameters with a 1561 nm 1s exciton absorption peak) were suspended in toluene and added to an excess of cadmium oleate and heated to 90 °C for 2.5 hours. This process resulted in a material with a partial cation exchange of Pb for Cd, and thus a shrinking of the PbSe core with the growth of the new CdSe shell as the total diameter of the particle remained constant throughout this process. The new core diameter was determined from the 1s peak in the new absorption spectra to be ~4.1 nm (post exchange PL emission peak maximum: 1410 nm) implying that the CdSe cation exchange thickness was ~1 nm.\textsuperscript{12} This partial cation exchange results in CdSe shells with a zinc-blende (\textit{\textit{z}b}) crystal structure and the selective formation of \{111\} rock salt \textit{rs}-PbSe/\textit{z}b-CdSe interfaces in the nanoparticle.\textsuperscript{12,30} These \textit{rs}-PbSe \textit{z}b-CdSe particles were then subjected to further CdSe shell growth using SILAR at 240 °C (up to 6.5 monolayers of CdSe added, over 10 monolayer additions) with cadmium oleate as the source for cadmium, and either Se-ODE or Se-TOP as the selenium source (Figure 3.1). When Se-
ODE is used as the selenium source, the PbSe/CdSe/CdSe gQDs are cubic in shape and possess a zinc blende structure \((r)-\text{PbSe}/(z\textbf{b})-\text{CdSe}/(z\textbf{b})-\text{CdSe}\) (Figure 3.2a,b). On the other hand, when Se-TOP is used as the selenium source, the resulting gQDs were hexagonal bipyramidal or quasi-spherical in shape with a predominately wurtzite crystal structure \((r)-\text{PbSe}/(z\textbf{b})-\text{CdSe}/(w)-\text{CdSe}\) (Figure 3.2 c-f).

Previous experiments in the visible CdSe/CdS core/thick shell system note that the crystal structure of the core dictates the crystal structure of the shell.\(^{29,31-33}\) In instances reporting wurtzite shell growth on a wurtzite core, the results are expected as the wurtzite is the thermodynamically favored phase for both CdSe and CdS.\(^{29,34}\) However, in the reported cases of zinc blende heteroepitaxial growth, there have been several explanations given to understand the influence of the core on the shell growth encompassing both thermodynamic\(^{33}\) and kinetic\(^{32}\) arguments. For the former, the growth is slow, as a result of the slow addition and low reactivity of the sulfur precursor, and so the original structure of the core is maintained. In the latter, low reaction temperatures and dynamic passivating ligands allows for the kinetic product.
In our experiment, we find that the shell can grow either epitaxially or into the bulk thermodynamic phase, the latter being the reaction utilizing TOP as the ligand for selenium. Our assertion is that the presence of this coordinating solvent (~1% of total volume after 1 shell addition, 30% of total volume after 10 shell addition cycles) has several important effects that lead to the growth of the hexagonal shell. First, the reaction rate may be slowed with the addition of TOP, as the ligand will stabilize the solvated version of selenium, and, once the selenium has attached to the nanocrystal surface, can passivate the selenium surface sites, reducing reactivity towards cadmium. Second, it has been shown that strongly coordinating solvents, including TOP, can render the metal-chalcogenide bond-making reversible, which favors the formation of the thermodynamically lowest energy surface. Lastly, the TOP may further lower the surface energy of the wurtzite facets, making it more thermodynamically favored than the zinc-blende facets. We have observed similar nonepitaxial growth in the $\gamma$-InP/$\omega$-CdS core/thick shell QD system. Although this system does not use TOP as a ligand, oleylamine comprised a significant percentage of the total solvent volume (50%). As a strongly coordinating amine, it is likely that it had similar effects as the TOP in the $\times$-PbSe/$\gamma$-CdSe/$\omega$-CdSe system and promoted the formation of the thermodynamic product.

Furthermore, for the case where Se-TOP is used, we have found the particle shape can also be influenced by the thickness of the initial cation exchanged $\gamma$-CdSe shell. When we start with larger PbSe cores (7.2 ± 0.2 nm diameter) and let the cation exchange process proceed for 12 hours instead of 2.5, we were able to grow a shell 1.7 nm thick. When Se-TOP was used for SILAR on this sample, we obtained the same $\times$-PbSe/$\gamma$-CdSe/$\omega$-CdSe structure, however instead of further CdSe shelling, the $\omega$-CdSe formed tetrapodal arms (Figure 3.2 e-f). We hypothesize that the growth of tetrapods is promoted in the thick shell
case because after the thick CdSe shell from cation exchange has well-defined zinc-blende facets, as opposed to the thin shell that possesses more of the rock-salt character of the core. The \{111\} facets of \( zb \)-CdSe create an interface with the \{0001\} facets of the \( w \)-CdSe. This mechanism of “seeding” wurtzite arms by zinc blende cores has been shown in several other nanocrystal systems, including \( zb \)-CdSe/\( w \)-CdS and \( zb \)-CdTe/\( w \)-CdSe tetrapods. In these two instances, it was assumed that the fast growth (aided by an high Cd precursor concentration) resulted in the anisotropic particle.

In another example, \( w \)-CdSe arms were grown at low temperature on PbSe/\( zb \)-CdSe QDs. The low temperatures were believed to delay the onset of growth, and the generation of a supersaturation of precursors, leading to faster growth. In contrast with our SILAR approach however, we do not expect to have any supersaturation conditions of either of the precursors, as the precise amount needed for...
1ML is added slowly to the reaction pot. Instead, we propose that the larger PbSe/CdSe QD with a much thicker zb-CdSe shell has a shape-directing effect, which is potentially aided by TOP, a coordinating ligand. The growth continues in the thermodynamically stable wurtzite phase, but is enhanced in the c-direction of the faceted core, and results in an elongated growth. This suggests that once seeded by the faceted core, the higher ligand affinity for the non-polar facets affords preferential growth on the (0001) surface, and therefore elongated growth (Figure 3.2g)\cite{40,41}.

From the results observed with the Se-TOP precursor, we assume that in the PbSe/CdSe/CdSe case, unlike the CdSe/CdS gQD case, the structure directing ability of the core is less favored than the lowest energy thermodynamic phase for the shell. Consequently, in the reaction that does not include TOP (Se-ODE precursor used) the reaction proceeds much faster and/or in a less reversible fashion towards the kinetically favored product, and allows for the shell structure to be dictated by the core, even at the high reaction temperatures. These nanoparticles exhibit a rs-PbSe/zb-CdSe/zb-CdSe structure and are cubic in shape. The high-resolution TEM and X-ray data confirm that these particles have a strong zinc blende character, dictated by the original crystal structure of the core (Figure 3.2g).

### 3.3.2 Ensemble Optical Properties of PbSe/CdSe/CdSe gQDs

PbSe cores display narrow infrared emission bands that can be tunable across a wide range depending on the size of the particle. Upon cation exchange with CdSe, the PbSe emission shows a characteristic blue shift and broadening of the emission band (Figure 3.3 I)\cite{12}. The cation exchange dots were washed in an air free environment twice with acetone/hexanes and resuspended in hexanes. Oleylamine, octadecene and a 1nM
concentration of dots were added to a flask and held under vacuum to remove the hexanes, then heated to 240 °C under argon. Upon heating to 240 °C, the emission of the \( \text{rs-PbSe/zb-CdSe} \) particles shifts further to higher energies (bluer wavelengths) and broadens (Figure 3.3 II).\(^{39}\) Then, as shells are added by SILAR to the QDs, the emission shifts slightly back to lower energies (redder wavelengths) (Figure 3.3 III-V). This red shifting is consistent with the description of the PbSe/CdSe valence and conduction band alignments as a “quasi-type II” such that the hole is localized to the PbSe core, and the electron is delocalized into the shell. It has been seen in other core/shell systems that the spatial separation of the carriers increases as the shell thickness increases, resulting in a red-
shift of the PL as the exciton size increases.\textsuperscript{26,29} In the case of CdSe/CdS core/thick shell QDs, the band alignment is quasi type II, such that the excited state hole is confined to the CdSe core, while the electron is partially delocalized into the shell. Thus, as the shell thickens, the separation increases, slowing down the electron-hole recombination. It has been suggested that PbSe/CdSe is also a quasi type II system.\textsuperscript{42} We can model the PbSe/CdSe electronic structure as a function of the core size and shell thickness using an effective mass two band model, the results of which are shown in Figure 3.4. For a specific set of PbSe core sizes and CdSe core thicknesses, a quasi type II localization regime is expected. We show two examples in Figure 3.4 that correspond to the results we observe.
with our system, the first (c) being the situation in which you have a large core with a thinner shell (the core particles after cation exchange) and the second (d) a smaller core with a thicker CdSe shell (the SILAR grown gQDs).

Some of the most interesting results obtained on the PbSe/CdSe/CdSe system relate the crystal structure to the PL stability and efficiency. We find that the rs-PbSe/zb-CdSe/zb-CdSe nanocrystals have a 3-10 fold higher QY when compared to the rs-PbSe/zb-CdSe/w-CdSe; the QY of the former was determined to be 18 ± 3.9%. The lower emission efficiency can likely be attributed to increased strain between facets that are not \{111\} and \{0001\} matched on the core. This mismatching between the rs-PbSe/zb-CdSe and nonequivalent planes on the w-CdSe causes strained interfaces on the surface as the shell grows conformally on the zinc-blende surface, and likely leads to the diminished optical properties of the rs-PbSe/zb-CdSe/w-CdSe.

![Figure 3.5](image-url)

**Figure 3.5:** a) from left to right, images of clusters of rsPbSe/zbCdSe/zbCdSe with increasing shell thickness (cation exchange only to thickest shells) intensity is measured at 0 min and 60 min. b) % intensity remaining after 60 minutes of observation time, measured from the images in a). Cation exchange thickness is ~2 ML of shell, and shows the greatest loss in intensity. The thickest shell samples have stable intensity throughout the 60 minute measurements. c) Lifetime measurements of each sample; the lengthening of the lifetime with thicker shell suggests the SILAR shell growth removes non-radiative pathways, further stabilizing the material.
material. Additionally, it is possible that the strained shell growth causes asymmetry in the shell coating, which results in a varied shell thickness across the nanostructure. In these regions the gQD would be more susceptible to photobleaching and darkening.\textsuperscript{43,44} The tetrapod $rs$-PbSe/$zb$-CdSe/$wb$-CdSe nanoparticles were completely non-emissive, likely due to the fact that the majority of excitons created would end up in the arms of the tetrapods, which dominate the total absorption cross section. This means any excitons created here must migrate to the core to be able to observe IR PL, an unlikely result when in completion with nonradiative processes in the tetrapod arms.\textsuperscript{45–47} As a result, these nanoparticles were either insufficiently stable or insufficiently emissive to conduct any further tests on them. We therefore acquire all further optical data at both ensemble and single dot from the $rs$-PbSe/$zb$-CdSe/$zb$-CdSe sample.

With the growth of a thick $zb$-CdSe shell on the $rs$-PbSe/$zb$-CdSe cation exchanged dots we observed a red PL shift as the thickness of the shell increased, but what effect does the thick shell have on the stability of the dots in ensemble measurements? Samples of $rs$-PbSe/$zb$-CdSe/$zb$-CdSe were drop-cast into films and observed using a home-built confocal laser microscope (excitation at 830 nm with 130 fs pulse duration, and 90 MHz repetition rate) with a 2D InGaAs camera. The clusters of dots were observed under continuous excitation for an hour by a laser beam $\sim50$ $\mu$m in diameter with a power of 50 W/mm$^2$. The PL stability was measured by comparing the final QD PL intensity after 60 minutes to the initial intensity for multiple positions in the QD films ($PL_{\text{final}}/PL_{\text{initial}}$). The results were remarkable (Figure 3.5), $PL_{\text{final}}/PL_{\text{initial}}$ was the lowest ($<30\%$) for the $rs$-PbSe/$zb$-CdSe cation exchanged particles with only $\sim2$ monolayers (ML) of shell. When this sample was heated to 240 $^\circ$C there was a small enhancement in stability ($\sim35\%$), and when even just 1ML of shell is added by SILAR, the stability is enhanced significantly ($\sim65\%$). For the thickest shell
QDs (6.6 and 8.6 ML) photobleaching over 1 hour was completely suppressed. In addition to suppressed photobleaching, we also observed a shell-thickness dependence for the average PL lifetime that roughly follows the trend observed for emission stability. These measurements were obtained using a four-channel SNSPD detector (Single Quantum Eos 210; 440 nm excitation at 100 kHz repetition rate), and the average lifetimes increased as a function of both initial QD heating and shell thickness, with the lifetimes of the two thickest shells being about the same. The correlation between the emission stability and lifetime increase suggests that as shells are added with SILAR, the contributions of rapid, nonradiative processes to overall exciton recombination are removed through passivation of surface traps. Initially with cation exchange we passivate the surface located traps on the PbSe nanocrystal, and, with further shell thickening, spatially separate carriers between the core and the shell in this quasi type II system and prevent the interaction of carriers located in the core with any remaining surface traps. We believe the latter effect to be the most important in preventing the processes that lead to photo-oxidation, as the thick shell will isolate the emissive core.

3.3.3 Single Dot Measurements with Standard Detection Techniques

Using the thickest shell (~8.6ML) \( r_\alpha \)-PbSe/\( z_\beta \)-CdSe/\( z_\beta \)-CdSe QDs, we sought to observe emission stability and stability at the single dot level using standard silicon detection techniques. Using a Princeton Instruments electron multiplying charge-coupled device (EMCCD) camera with a 900 nm long pass filter, 405 nm excitation at 330 W/mm\(^2\) continuous wave (CW) excitation we were able to observe single dots in a dilute sample dropcast onto a glass substrate. Several samples of thick shell dots were tested (3.0 ML and 8.6 ML of shells respectively) and showed significant single dot stability over an hour of
observation time at this very high excitation power (Figure 3.6). When cation exchanged only QD products were used ($rs$-PbSe/$zb$-CdSe), the dots photobleached rapidly under these extreme conditions, and no data could be collected.

Additionally, we could collect blinking data from the thick-shelled $rs$-PbSe/$zb$-CdSe/$zb$-CdSe dots using the EMCCD detector. Both the 3.0 ML and 8.6 ML samples showed suppressed blinking behavior, with nearly 10% of the population possessing an on-time fraction of $>50\%$ and $\sim 70\%$ of the population on $>20\%$ of the 1 hour observation time (Figure 3.6). To compare, 0% of a population of a reported high-quality CdSe/ZnS QD sample possessed an on-time percentage of $>20\%$ for similar conditions.\textsuperscript{25} A direct comparison with other single dot IR emitters is difficult, as the ability to obtain blinking studies for QDs emitting $>1\ \mu m$ have been hindered by material instabilities and observation techniques.\textsuperscript{21,25} To date, this is only the second example of suppressed blinking behavior for IR-active colloids to date, the first being InP/CdS core/thick-shell with type II character that showed single dot-level stability.\textsuperscript{28}
3.4 Conclusions

Growing shell materials on lead chalcogenide materials has been difficult in the past due to both a significant lattice mismatch with many higher bandgap materials and the low temperatures that must be used to prevent Ostwald ripening. However we have shown that after a thin shell of CdSe is synthesized at low temperature by cation exchange on the PbSe QDs, high temperatures and a SILAR process can be used to grow thick shells on these nanocrystals. The structure of these nanocrystals, and the resulting emissive properties, is determined by the Se precursor used during the SILAR process. Use of SeTOP results in the thermodynamically favored wurtzitic shell structure on the $rs$-PbSe/$zb$-CdSe/$w$-CdSe, and the dots are nearly non-emissive and not stable enough for single dot measurements. When $rs$-PbSe/$zb$-CdSe cation exchange particles with thicker CdSe shells are used, the subsequent growth by SILAR results in tetrapod nanocrystals with wurtzite crystal phase arms. These particles are non-emissive in the IR, as the carriers likely recombine in the arms instead of the core. However, if SeODE is used instead as the Se precursor for SILAR, $rs$-PbSe/$zb$-CdSe/$zb$-CdSe particles are formed, which emit strongly in the IR. These particles are quasi-type II in nature, and exhibit longer lifetimes and increasing PL stability with shell growth. These particles can be observed at a single dot level using standard detection techniques with very high excitation powers for over an hour of observation time with no photobleaching. The ability to make particles now in the near and mid-infrared that are stable emitters now allows for their integration in many new and exciting applications, including optical biological tags and IR detectors and sensors.
3.5 Experimental Details

**Materials:** 1-Octadecene (ODE, 90%), oleylamine (OAm, 70%), cadmium oxide (CdO, 99.99%), and trioctylphosphine (TOP, 90%) were purchased from Acros Organics. Lead(II) oxide (PbO, 99.9998%), selenium shot (Se, 99%), and oleic acid (OA, 90%) were purchased from Alfa Aesar. Tetrachloroethylene (TCE, 99+% spectroscopic grade), 1,2-dichlorethane (DCE, 99.8%, anhydrous), and diphenylphosphine (DPP, 98%) were purchased from Sigma-Aldrich. All chemicals were used without further purification.

**Synthesis:** PbSe QDs were synthesized and subjected to partial exchange of Pb for Cd using a previously described method. For example, 600 mg of PbO, 6 mL of OA, 8 mL of ODE, and 8 mL of TOP were degassed at 110 °C for 2 h. The resulting mixture was then heated under flowing argon to 205 °C to obtain an optically clear solution before cooling to 150 °C. Eight mL of a 1 M TOPSe solution and 50 µL of DPP were injected swiftly into the lead solution, causing an immediate drop in temperature to ~125 °C and affording nucleation and growth of PbSe nanocrystals. After 2 min, the reaction was terminated by removing the flask from heat and submerging the flask in an ice bath. The QDs were precipitated from the growth solution by adding acetone, and then subjected to two cycles of suspension and precipitation using toluene and acetone, respectively. The processed QDs were dispersed in a minimum amount of toluene and QD concentration determined by measuring the 1S absorbance peak, from which the molar absorptivity can be calculated. In this case, the solution concentration was $1.07 \times 10^{-5}$ M. A 10 mL portion of these QDs [5.6 ± 0.5 nm in diameter as determined by transmission electron microscopy (TEM) analysis] was injected into 16 mL of 0.2 M Cd-oleate in ODE (1:4 molar ratio Cd:oleic acid) and allowed to stir at 90 °C for 2.5 to 12 h, resulting in a CdSe shell ~0.75 to 0.90 nm thick by the sacrificial replacement of Pb for Cd. Growth of thicker shells by cation exchange could be realized.
using the same experimental parameters but starting with larger PbSe cores and exposing these to the Cd solution for longer times (≥12 h). The cation exchanged product was subjected to two cycles of precipitation and resuspension using hexanes and ethanol, respectfully. The PbSe/ CdSe QDs were suspended in hexanes, with concentration assessed as before by determining absorbance as the PbSe 1S peak.48,49

The PbSe/CdSe core/shell QDs synthesized using the cation exchange approach for shell growth were subjected to further shell growth using the method of successive ionic layer adsorption and reaction (SILAR) growth. Separately, stock solutions of 0.2 M Se in ODE and 0.2 M Cd-oleate in ODE (1:4 molar ratio Cd:oleic acid) were prepared and used as precursors for the SILAR monolayer-by-monolayer additions.27,29,50 Alternatively, for SILAR growth employing a Se-TOP precursor, a 0.2 M Se solution in TOP was prepared by dissolving Se shot (0.79 g) in TOP (50 mL) by first degassing the mixture under a dynamic vacuum at 90 °C for 1 h and then heating at 180 °C until a clear solution was obtained. ODE (5 mL) and OA (1 mL) were then degassed under a dynamic vacuum at 100 °C for 1 h. The temperature was lowered to 30 °C and the flask opened to flowing argon. PbSe/CdSe QDs (2.5 mL of a 3.91 × 10⁻⁶ M solution in hexanes) prepared by cation exchange were injected into the ODE/ OA mixture. Hexanes were removed under a dynamic vacuum, such that the QD concentration was 1 nM. Under flowing argon, the QD solution was slowly heated to 240 °C over ~10 min. The Cd precursor solution was added in an amount equivalent to 1 /2 monolayer of CdSe shell, followed by the equivalent amount of Se precursor, waiting 10 min in between each addition. Precursor addition quantities were calculated for each subsequent monolayer based on the known QD concentration and assuming that each addition of Cd and Se precursor afforded a full monolayer of shell growth and corresponding increase in QD size.27,29,50 PbSe/CdSe/CdSe QDs (or tetrapods)
were extracted at different points in the SILAR growth process and precipitated by adding ethanol. Cycles of suspension and precipitation using hexanes and ethanol, respectively, were applied to remove excess ligands. QDs were suspended in TCE for absorption and emission measurements and in hexanes for the preparation of samples for structural analysis by TEM.

**Structural Characterization:** Nanocrystal size and shape were assessed by transmission electron microscopy (TEM) using a JEOL 2010 instrument operating at 200 kV. High-resolution TEM and annular dark-field scanning TEM (ADF-STEM) images were acquired using an FEI-Titan 80-300 instrument operating at 200 kV. X-ray diffraction was collected on a Rigaku Ultima III diffractometer that uses a Cu Ka (1.5406 Å) X-ray source. The Jade 9.0 data analysis program was used for semiquantitative analysis of the relative contributions of wurtzite and zinc blende phases to the XRD powder pattern. Specifically, a whole pattern fitting and Rietveld refinement method was employed. R-fitted values of <10% were obtained in all cases, indicating adequate agreement between experiment and model results. QD films for both TEM and X-ray were drop-cast out of hexanes onto Cu grids and zero-background Si substrates, respectively.

**Optical Characterization:** Absorption spectra were collected using a Cary Varian 5000 UV–Vis-NIR spectrophotometer. Photoluminescence (PL) measurements were performed on a home-built confocal laser microscope. For PL spectroscopy and imaging measurements, output pulses with a wavelength of 830 nm from a mode-locked Ti:sapphire laser (130 fs pulse duration, 90 MHz repetition rate, Chameleon, Coherent) were used to excite the samples. An air objective (100×, NA = 0.80, Olympus) was used to focus the laser beam and collect the PL emission. The PL signal from the QDs was spatially imaged and spectrally resolved by a 2D InGaAs camera equipped on a 300 mm spectrograph. The
integration time for the PL spectra was 5 s. The samples were drop-cast on glass coverslips for measurement. For PL stability measurements, QDs were continuously irradiated by a semihomogeneous excitation laser beam (\( \sim 50 \mu \text{m} \) in diameter, 50 W/mm\(^2\)) for 1 h. The final PL value of the QDs (at \( t = 1 \) h) was compared to the initial value (at \( t = 0 \) s) (called PL\(_{\text{final}}$/PL\(_{\text{initial}}$), and for each sample, the average value from four to six different positions was used to quantify the PL stability. PL decay curves were obtained by exciting the samples with a 440 nm diode laser (PicoQuant) at a repetition frequency of 100 kHz. A four-channel superconducting nanowire single photon detector (Single Quantum Eos 210) was used to detect the PL signal. Each decay curve was fitted with a double exponential function. For each sample, five different positions were measured to obtain an average lifetime. Single-QD measurements were obtained using a ProEM 512 EMCCD (Princeton Instruments) camera with a long pass filter of 900 nm to ensure that only emission in the near-infrared contributed to the observed signal. The detected signal was split from the excitation with a 442 dichroic beam splitter (Semrock Di02-R442-25x36). Samples were excited using a 405 nm continuous wave (CW) laser (330 W/ mm\(^2\)). To ensure that single QDs were being observed, a QD stock solution was successively diluted, and emission from the resulting solutions spread onto glass substrates was observed until a series of dilutions was reached for which the number of emissive spots on the substrate scaled linearly with the dilution factor. The final ultradilution used for the widefield blinking/bleaching measurements shown here yielded 20 QDs/50 \( \mu \text{m}^2\) area. The ultradilute solutions are prepared just prior to deposition onto a glass substrate to avoid QD clustering resulting from ligand destabilization.
Effective mass calculations: An effective mass two-band model (disregarding the fine structure details) was adopted for the calculations. The model provides 1S electron and hole envelope wave functions and associated eigenenergies for the core shell heterostructures. This allows us to evaluate the electron and hole density distributions and the electron-hole overlap integral. Furthermore the exciton binding energy is calculated by accounting for the core and shell polarization corrections (i.e., dielectric confinement). This allows for the evaluation of the 1S exciton energy defined as the difference between the electron and hole state energies plus the exciton binding energy. We further converted this energy into the wavelength (nm) units. To identify electron (hole) localization within the PdSe core we required its energy to be less than the CdSe conduction (valence) band offset. The model was parameterized using experimentally validated values of the effective masses for PbSe to \( m^*_{e} = 0.047 \) and \( m^*_{h} = 0.040 \) and for CdSe to \( m^*_{e} = 0.12 \) and \( m^*_{h} = 0.8 \)

as well as the CdSe-PbSe conduction band offset to 0.6 eV.\(^\text{21}\) Bulk values of the band gap energy for PbSe (0.27 eV) and CdSe (1.74 eV) were used to for subsequent confinement potential reconstruction. The exciton binding energy calculations accounted for the high frequency dielectric constants of PbSe and CdSe set to 22.0 and 5.8, respectively.

3.6 References


77


Chapter 4: Automated High-Throughput Synthesis of gQD Materials

4.1 Introduction

Applications in energy and electronics (photovoltaics,\textsuperscript{1,2} LEDs,\textsuperscript{3–5}) , environment (breakdown of oil into biodegradable components, removing water pollutants\textsuperscript{6} ), medicine\textsuperscript{7} (diagnostics, drug carriers), manufacturing and materials (incorporation to change materials properties\textsuperscript{6} ), commercial goods\textsuperscript{8} (sunscreens, adhesives, and coatings), has driven significant interest in large scale manufacturing of high quality nanocrystals. However, there is still a sizeable gap between experiments conducted and products obtained in a laboratory, versus the amount of product that must be produced for a commercial application. This is attributed to the fact that when reactions of nanoparticles are scaled up, the control over reaction parameters and thus the uniformity and dispersity of the materials can be lost as the volume of the reaction increases.\textsuperscript{6} In addition, the ability to run high-throughput experiments is also of great interest to industry, as the ability to change parameters in a systematic way to obtain an ideal material specific to application could further the integration of these products across commercial sectors. If experiments are short, this could be done by hand efficiently, but, if reactions require significant time or many steps, the development of an automated system to run reactions in a controlled manner would significantly accelerate material development.\textsuperscript{9}

Although there are some commercially available products, most commonly of gold, silver, platinum, silica, magnetite (Fe\textsubscript{3}O\textsubscript{4}), and thin shell QD material, there are many materials that are not commercially produced due to the time required to make them, the cost of materials for scale up, or the limited size of batches that can be produced. Potential
methods for scale up that have been reported recently include batch droplet reactors,\textsuperscript{6,10–12} slow heat up methods,\textsuperscript{13} and microwave assisted flow or batch processing,\textsuperscript{14–16} but as of yet none address the challenges of synthesizing materials with many steps, (e.g. the number of precursor additions required for SILAR) such as gQDs, which are not available commercially at this time. Currently, to synthesize gQDs by hand, it takes 5-7 days, as the precursors must be annealed for 1-3 hours after addition.\textsuperscript{17–19} There is significant interest therefore, to automate these types of reactions, not only for scale up and industrial applications, but also for discovery of new materials, high-throughput synthesis to scan multiple parameters of interest quickly, in-situ diagnostics and precise and consistent reaction conditions.\textsuperscript{9}

Towards this goal, we have developed an automated reactor system with an industrial partner that allows for multistep reaction processes to be completed at small or large volumes, heated syringe pumps for maintaining the precursors in a liquid state, in situ turbidity and optical measurements, and autosampling for aliquot removal. These automated reactor systems also cut the amount of time required to complete a reaction drastically, from 5-7 days to only 2-3 days, as they can work through the night, unlike post-doctoral scholars and graduate students! Additionally, these automated reactor systems remove the human element from the SILAR process, as they dispense the precise amount of each precursor needed, at each specified time, for each monolayer. Nanoparticle synthesis is known to vary depending on researcher technique and coffee intake; this system removes these variables affording consistent result across all batches of nanoparticles synthesized. A figure showing the overall advantages of an automated synthetic route to gQDs is shown in Figure 4.1. With this system we can produce batches of high quality core/shell QDs reliably and quickly and can conduct high-throughput combinatorial chemistry experiments with ease.
4.2 High-Throughput Combinatorial Chemistry Design

One of the fastest growing areas of interest in nanoscience is combinatorial chemistry, or the ability to generate materials simultaneously in mass quickly to survey reaction parameter space for desirable properties.\textsuperscript{9,20} Combinatorial chemistry approaches have their conceptual roots in biological immune system responses.\textsuperscript{21,22} When a new species enters the immune system, large numbers of antibodies are screened to determine which one will bind the best, and the specific target will be reproduced in large quantities to affect an immune response.\textsuperscript{23,24} It is easy to predict, therefore, that combinatorial chemistry techniques were first widely used in both organic and pharmacological chemistry experiments, as a way to quickly screen new materials for biological applications. Usually, a two-step process is employed; first a library of compounds is identified and produced, then the large number of reactions is scanned for an optimal product (based on a set of predetermined factors), which can then be researched further or scaled up. With this technique, we can potentially very quickly reduce the size of the haystack we are trying to find the needle nanomaterial. In
pharmaceutical development, combinatorial chemistry has allowed for significant advances in a shorter period of time for drug design as many compounds can be screened for viability.\textsuperscript{25}

Nanoscience, much like organic chemistry and drug development, has an abundance of variables that can be tested and controlled, and can therefore benefit from combinatorial studies.\textsuperscript{9,20} However, not only can the types of materials used to generate various nanoparticles be screened, but also the synthesis itself has a large number of reaction parameters that can be controlled. For example, the temperature of the reaction can be modified to change nucleation and growth rates, which in turn affects the size, shape and dispersity of resulting particles.\textsuperscript{9,17} Additionally, as mentioned, synthesis of disperse particles is usually done by hot injection, so the rates of injection have large effects on the quality of particles obtained.\textsuperscript{26–28} The ability to precisely control these parameters is necessary to optimize materials for large-scale applications.

\subsection*{4.2.1 Combinatorial Chemistry}

As of now, we know of one other study utilizing automated synthesis at small scales for high throughput combinatorial chemistry. Emory Chan at Berkeley Labs and the Molecular Foundry utilizes a microplate reactor system “WANDA” to synthesize lanthanide doped upconverting nanomaterials.\textsuperscript{9} WANDA has the ability to change the temperature of the reactions, the precursor addition rates, and stir rates, and can do 96 reactions at the same time. However, the reaction size is limited to <20 ml, so each reaction will only be completed at small scale, and any scale up would face the same challenges previously mentioned. Using this system, Chan’s lab is able to narrow down from the thousands of possibilities for lanthanide doping to a few particles of interest, depending on the application
specific properties that need to be optimized. His method uses a four tier screening system, the first set of reactions (of which 100-1000 samples can be scanned per week) are tested for one or two of the most important properties. The second tier refines the best particles from the first test, and runs 10-100 of these per week to test for a couple of the next most important properties. The third tier tries to narrow the field down to 1-10 samples, and includes full characterization on these particles. From this third tier, the fourth tier is chosen, hopefully only a couple samples that are chosen for scale up. The WANDA system has an advantage in that the plate style reactor system can have analysis performed on all the samples simultaneously, saving lots of time if all 96 wells are full of samples. Because the particles of interest in this specific study are upconverters, initial properties of interest include emissive properties, QY, size and crystal structure (which can drastically alter the luminescence properties).

Chan describes some of the limitations that can exist in high throughput synthetic methods. First, the systems to be studied by combinatorial chemistry must be able to undergo high throughput processing, have a wide range of precursors that can be used, and quantifiable properties. Additionally, he suggests that the knowledge that is obtained from the combinatorial process may not be able to be efficiently transferred to larger scale synthesis. He suggests that while combinatorial chemistry processes rely on quick acquisition and analysis of materials that are generated, the researcher must remember that quality, not quantity of materials generated is of utmost importance. Combinatorial chemistry doesn’t help to advance a field by producing tons of bad materials; instead the researcher designing experiments should focus on the quality of analysis on the materials produced, and the path forward once suitable parameters have been determined. However, Chan suggests that the outlook for combinatorial studies is extremely positive, and necessary for advancement,
especially for the generation of materials requiring dopants for optimization of emissive properties. The number of combinations possible with dopants and materials enormous, and without combinatorial chemistry, he suggests, we will never be able to research them all. He suggests that in the future, to tackle this large library of compounds, design of experiments and theoretical studies must be completed, and advanced algorithms for analysis must be generated and utilized.  

4.3 Automated High-Throughput Synthesis with FABRS

4.3.1 FABRS System Design

With the help of an industrial partner, we have a custom one of a kind fully-automated batch reactor system (FABRS) to synthesize nanoparticles, specifically gQDs at small and large scale. The FABRS system has the ability to precisely control the stirring rates, precursor addition rates, precursor temperature, reaction temperature and can remove aliquots of samples for testing during the reaction all under inert atmospheric conditions. One of the novel aspects of our system is the addition of in-situ monitoring of the turbidity and the optical properties of the sample during the reaction. We can take instantaneous readings of the absorption and emission of the product in the flask, and have real-time feedback of the optical properties (and potentially the overall quality) of the nanoparticles being synthesized. Scheme 4.1 shows a simplified version of one of the reactor vessels. We show our custom glassware that allows for reactions to be run at smaller (~ 20 ml) and larger (~ 1 L) volumes which gives us the opportunity to scale reactions up under controlled and repeatable conditions. We have 8 total units, which allows us to do High –Throughput Combinatorial Chemical reactions to develop and optimize nanoparticle materials before scaling up to industrial levels. Scheme 4.2 outlines our process, integrating theoretical
measurements and modeling for identification of parameters of interest, synthesis using the reactor systems, and product analysis.

**4.3.2 Optimal Coverage Algorithm for gQDs**

As a first set of reactions on FABRS, we chose to focus on further optimization of CdSe/CdS gQDs. Previous work by Ghosh *et. al.* in our laboratory presented the first comprehensive study of parameters affecting emissive and structural properties of gQDs.\(^{17}\) This work looked specifically at the affect annealing times, ligand coordination and identity, starting core size, and reaction stoichiometry have on the size, shape, crystal structure and optical properties (blinking, QY, bleaching, PL). It was deduced from these experiments that longer anneal times were preferred for high quality particles at large monolayer thicknesses.

\[\text{Scheme 4.1: Left, custom flask used for reactions in reactor system. Flask has positions for probes and can be completely sealed to be put under vacuum or argon. The flask has a small bulb region at the bottom for small volume reactions, and is large enough for scale up to larger reaction volumes. Right is a simplified schematic of the automated reactor system highlighting our custom parts that allow for complicated reaction processes to be conducted.}\]
(16-20 ML of shell), and, specifically, the annealing time after cadmium addition should be longer than that of the sulfur addition. Another interesting observation is the onset of turbidity as thicker shells are added. After about 7 monolayers of shell, when cadmium was added the solution became cloudy and turbid, and stayed cloudy until the sulfur precursor was added to the reaction. The addition of sulfur drop by drop would quickly clear up the solution, which would cycle back to cloudy and turbid when cadmium was added again. This continues until about ML 11, when the turbidity observed with the addition of cadmium never fully went away with the addition of sulfur for the rest of the ML grown. This solubility cycling was attributed to the large dipole moments of the gQD, causing them to want to align into oriented attachment. As a reminder, only ligands that bond to the Cd faces are used in the SILAR growth, so when Cd is added to the surface, it can be easily passivated with a ligand. However, when sulfur is added to the gQD, it must cause some surface reconstruction to minimize dangling bonds, as it does not have solution ligands to help passivate the surface. In this way, one could view the destabilization/destabilization cycles as a direct result of the change in the dipole moment of
the particles as the cadmium bonds to mostly wurtzitic faces, causing a larger dipole moment and the sulfur then promotes surface reconstruction (and a smaller dipole moment).\textsuperscript{17} One of the advantages of FABRS is the direct measurement of the turbidity in the reaction, allowing us to, for the first time, obtain relative measurements on the extent of turbidity during the reaction as monolayers are grown on the QD.

The ligands chosen for the reaction also influenced the quality of particles obtained at the end of shell growth with SILAR. The first report of gQD synthesis used the primary amine octylamine (added immediately at the start of the reaction) with oleic acid (added with the cadmium precursor as cadmium oleate) as ligands for shell growth. The amine was found to potentially serve two purposes, as a coordination ligand to the cadmium and as a way to deprotonate oleic acid so it can covalently attach to cadmium. In the initial experiments, the amount of oleic acid changed during the course of the reaction, for thinner shells, a 1:4 Cd:Oleic Acid precursor was used, and amine was more prevalent as the coordinating ligand. For thicker shells, a 1:10 Cd:Oleic Acid precursor was used, and the dominating ligand binding to the surface of the quantum dot was oleate. When instead, a secondary amine was used, the dissolution and turbidity observed in the reaction at thicker shells completely disappeared, and the sample remained homogeneous throughout shell growth. However, the optical properties did not improve, as these particles were nonemissive. The complete elimination of the amine was found to produce inhomogenous solutions at much lower monolayers (3ML instead of 7ML) and produced faceted hexagonal particles with good QY.\textsuperscript{17} Further studies on the importance of the amine precursor by Tan \textit{et. al}, who show with shorter anneal times and a very reactive sulfur precursor that the use of tertiary amines suppresses side nucleation (and therefore CdS particles in addition to the core/shell materials) and drives the reaction towards shell development.\textsuperscript{29}
Additionally, Ghosh et.al. stress the importance of core size for desirable gQD properties. As discussed previously, as the size of the starting core increases, less monolayers of shell need to be added to achieve blinking suppression. Therefore, blinking suppression is a direct result of total QD particle volume, the particle must be >750 nm$^3$, and above that threshold, the non-blinking fraction increases linearly with volume. PL lifetime of the particles shows a similar threshold dependent on volume of nanoparticle, but does not experience the same linear relationship that blinking does with particle size, plateauing out at $\sim$65ns.$^{17}$ The quasi-type II band alignment of gQD particles can explain this trend in PL lifetime, as the hole is confined to the CdSe core, and the electron wavefunction is allowed to extend into the shell material resulting in electron delocalization across the particle causing spatial separation between the exitonic components. This increases the PL lifetimes, and, as the shell gets thicker, this separation extends, lengthening the lifetime as far as the Columbic attraction between the electron and hole allow. As a result, the number of shells that must be added to a QD to achieve non-blinking properties depends on the original core size, and if a large core is used for shell growth, one can get away with adding fewer shells, and therefore hopefully maintain high quantum yields with suppressive properties.

With the results from these initial experiments into the dependence of particle quality on reaction conditions, we set out to understand how other parameters affect shell growth, optical properties, and structure and dispersity of the CdSe/CdS gQDs. Several interesting reports have been published on similar materials since the paper by Ghosh et. al. most notably research by Chen et.al. with a low reactivity sulfur precursor and a continuous injection method at high temperatures to obtain high quality gQD particles,$^{30}$ and a report by Tan et. al. observing the quality of gQD particles using a reactive sulfur precursor (bis(trimethylsilyl)sulfide ((TMS$_2$)S)) with additions of both precursors at the amounts
needed for a ML and 0.5ML and changing the orders of additions. In the former, Chen et al. report the synthesis of a high quality CdSe-CdS particle with 7ML of shell that displays non-blinking characteristics (94% on time), a very high QY (97%), a narrow PL peak, and high uniformity. The reaction is done using a continuous injection method instead of SILAR, at a high temperature (310°C) owing to the low reactivity of the sulfur precursor (the cadmium precursor is Cadmium oleate, the same as in the reactions in the Hollingsworth laboratory), and uses starting cores produced using two different synthetic methods, resulting in either fully Wurtizitic or fully Zinc Blende core structures, instead of the mixed phase structure seen in the cores used for the Ghosh et al. study. It was found that with the reaction conditions chosen by Chen et al. the shell structure depended solely on the starting core structure, when the hexagonal core was used, the shell was hexagonal, when cubic, the shell was cubic. This epitaxial shell growth is attributed to the fact that the slow reaction rate of the precursor, which allows for the original structure of the core to be maintained as the shell of the particle grows continuously. Due to the results obtained by Chen et al. under these high temperature conditions, we thought it was only prudent to test our SILAR reaction on FABRS using a series of higher temperatures than traditionally used for this synthesis in the Hollingsworth lab. We chose to run a series of reactions between 240°C and 300 °C to see if the higher temperatures would potentially improve optical properties (particularly QY) for our gQD samples.

Tan et al. produced some interesting results with the much more reactive (TMS)$_2$S precursor. Due to the much more reactive precursor, the SILAR process could be run at a lower temperature, 200 °C when compared to SILAR experiments in our laboratory. A concern of the more reactive precursor is the formation of small CdS particles in the solution in addition to the shell growth, indeed, Tan et al. suggests that when single ML...
amounts of each precursor are added, cadmium is left in the solution that has not attached to the surface of the dot as part of the shell, and reacts with the sulfur when introduced into the reaction. Therefore, experiments were done in which a sub-monolayer amount of precursors was added to see if improvements to the product were observed. It was seen that for the sub-monolayer experiments, the red shift of the product was larger than that of the exactly one-monolayer experiments, suggesting that the shell growth was more extensive and complete in the sub-monolayer experiments. Additionally, the size and shape variation of these particles exhibited a distribution that was more narrow than the one-monolayer samples.\textsuperscript{31}

Therefore, with these previous experiments in mind we set out to build an optimal coverage algorithm for a specific set of experiments on FABRS to test parameters that have been shown in the past to make a difference in the quality of particles obtained. In addition to temperature and precursor addition amount, a parameter that has been largely uncontrolled until now, precursor addition rate, will also be studied. We present in Figure 4.2 our specific optimal coverage algorithm for FABRS first high-throughput reactor experiments. A reaction will be run at each point, tested for quality in size and shape

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.2.png}
\caption{Optimal Coverage Algorithm experimental design for reactions to be conducted in FABRS. Each red spot is a set of reaction conditions to be explored in this initial study. The rate of precursor addition, for example, has never been studied in a thorough way until now. The best particles as identified optical and structural properties will define the maxima in this system, where further optimization can be done.}
\end{figure}
dispersity, optical properties including PL peak width, QY, blinking statistics, and PL lifetime and bleaching. As reactions are completed, and the best performers identified, we can narrow down our area of interest to optimize across these variables, to move on towards the study of other variables of interest.

4.3.3 CdSe Core Synthesis for Reactions

Before any experiments can be run on the automated reactors, CdSe cores had to be synthesized. The procedure for core synthesis is as follows, and, although multiple batches of cores had to be made to complete all reactions in Figure 4.2 special care was taken to obtain cores that were about the same size with the same FWHM for all reactions in the series. 1.5 ml of a 0.5 M solution of Cadmium Oleate was added to 2.4 g trioctylphosphineoxide (TOPO, 99% Sigma Aldrich) and 18 ml of 1-Octadecene (ODE, 90% Sigma Aldrich) and degassed under vacuum for 2 hours at 100 °C, after which the solution was placed under Argon and heated to 300 °C. Meanwhile 4 ml 2 M TOPSe (90% Trioctylphosphine (Sigma Aldrich) and 99.99% Selenium Shot (Strem)), 6 ml Oleylamine (OAm 70% Sigma Aldrich), and 2 ml ODE were mixed in a glovebox, and brought out in a syringe with a large gauge needle (16 gauge). When the cadmium solution reached 300 °C the selenium solution was swiftly injected into the reaction, which lowered the temperature to ~230 °C. Growth of the cores was monitored for 7 minutes at 270 °C, at which point the reaction was removed from heat and allowed to cool. The resulting QDs were tested for quality (PL FWHM ~25 nm, 1s peak 575 nm) and transferred to a vial under argon for transfer to a glove box. The CdSe QDs were washed in the glovebox with a single precipitation out of growth using Ethanol and resuspended in Hexanes then stored in the
glove box freezer to maintain quality and QD concentration. Figure 4.3 is steady state optical spectra and TEM from a core sample used in this study.

### 4.3.4 General Procedure for SILAR in FABRS

The size and concentration of the cores in Hexanes was determined using the absorbance at the 1s peak. Sizing and sample concentration was determined using the method described by Jasieniak *et. al.* on known dilutions of samples from the freezer, in general it was found that 1ml of CdSe QD cores were needed for SILAR reactions using a 2.0E-7 M concentration of cores. The precursor addition amounts needed per ML of shell grown were calculated using the method described by Tan *et. al.* with precursor concentrations set to 0.2 M.\(^{31}\) For this set of experiments specifically, shells were grown to 9 ML only, with a large aliquot (8 ml) of sample removed from the automated reactor flask after 6 ML of growth. The amount removed for this aliquot was taken into account for further precursor additions by determining the percentage of solution remaining after the aliquot was removed compared to the volume of the solution if no aliquot had been removed, then multiplying each subsequent precursor amount by that percentage for each following monolayer.

The SILAR reactions in the FABRS followed the same steps for set up, the differences only being in parameters that can be set in the software for the system. 5 ml of
ODE and 5 ml of OA was added to the custom flasks for the system, and degassed at 80 °C under vacuum for 2 hours at a 600 RPM stirring rate. The system was then placed under argon, and the reaction vessel was cooled to 50 °C, at which point point 2.0E-7 M CdSe cores in hexanes was injected. The solution was placed back under vacuum to remove the hexanes at 70 °C and 600 RPM for 1 hour. During this time, the precursors, 0.2 M Cadmium Oleate (1:10 Cadmium : Oleic Acid) and 0.2 Sulfur ODE were loaded into the special heating shrouds for each syringe, and held at a temperature of 65 °C for the entirety of the procedure. At this point, the reaction was placed back under Argon, the stirring rate set for 600 RPM for all reactions, and the specified procedure for each experiment the user defined was started. The reactions featured a 1.5 hour “ramp up” period for the temperature in the flask to reach the set temperature for the reaction, and 2 hour anneals after cadmium addition and 1 hour anneals after sulfur addition. In the case where an aliquot was removed, care was taken to keep the anneal times consistent, so sometimes an aliquot was removed slightly before the end of the 1 hour sulfur anneal. After the reaction completed, it could be held under argon at 60 °C until the user returned to remove the flask. At this point the system is immediately cleaned with hot ODE solution (80 °C) to remove any precursors or reaction solution left in the precursor delivery lines or autosampler respectively.

4.4 CdSe/CdS 9ML Shell Results from FABRS

4.4.1 Optimal Coverage Results
Initial experiments with FABRS underscored the importance of finding the right stirbars for our specially designed flasks; as the volume of the reaction increases, the reaction must be stirred reliably, which proved to be a challenge as the larger section of the flask (shown in Scheme 4.1) was filled. After many attempts, we chose to go with multiple wing shaped stirbars from V&P scientific that would allow for consistent stirring in all regions of the flask. The first “baseline” experiment run was at 240 °C with exactly 1 ML amount of precursor added at an addition rate of 0.1ml/min. Previous testing showed that this addition rate produces very uniform particles and is a good mid-point in our precursor addition rate range. An example of the TEM and optical properties of these particles is shown in Figure 4.4. We expect that these particles will not be fully blinking suppressed, as we are only growing 9 ML of shell. However, we do see that out of 100 particles analyzed nearly 45% of the dots are blinking suppressed, and experience minimal photobleaching (Figure 4.5).

Comparisons were first done at different temperatures and different precursor addition rates. Therefore, for samples run at 0.1 ml/min and exactly 1 ML of precursors added, SILAR was performed at 210 °C, 240 °C, and 270 °C. The blinking and bleaching results are presented in Figure 4.6, and it is immediately clear that the sample run at 240 °C
has the best blinking statistics of the three samples presented. However, the photobleaching results of the higher temperature sample (270 °C) appear to have less intensity decrease than the sample run at 240 °C. The sample run at 210 °C had less than ideal blinking statistics and comparable bleaching results to that of the sample run at 240 °C, and so it was determined that at least, under these conditions, the samples run at 210 °C performed worse than the samples synthesized at 240 °C. Further analysis of QY and PL lifetime are currently ongoing.

Additionally, experiments to understand the effect of a slow addition rate (0.05 mL/min), a medium addition rate (0.1 mL/min) and a fast addition rate (1 mL/min) was conducted for reactions run at 240 °C with addition amounts of 1 ML of precursor. The
results were interesting; the shape and size distribution of the particles looked fairly consistent, as shown in Figure 4.7. The blinking and bleaching data in Figure 4.8 shows similar results for all the samples, with perhaps slightly better bleaching data for the sample run with the slowest addition rates. This suggests that potentially some research into slower addition rates could be useful to prevent dot bleaching, however this may be elucidated by the experiment run at slow addition rates at a higher temperature, as the previous experiment showed improved results with respect to bleaching. These experiments are ongoing, and we expect to be able to produce a full workup of the optimal coverage algorithm within a couple months.

4.5 Conclusions

The FABRS system allows us to explore the influence of many properties on the gQDs simultaneously and in an extremely controlled setting. The system not only removes the human error element of nanoparticle synthesis, but allows for a level of control over
parameters that have not been easy to monitor in previous experiments. We have also obtained results on the turbidity of the solution during a synthesis, and although not presented here, has given us great insight into reaction properties during the addition of each precursor. We expect to be able to generate new materials, optimize these and current materials, and explore the conditions necessary for scale up at a rate that will allow for significant progress in this field. We have already identified several new parameters of interest for study on the gQD system alone, and expect to be able to lead the field of automated nanoparticle synthesis with FABRS.

4.6 References


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