Synthesis and Characterization of Infrared Quantum Dots

by

Daniel Kelly Harris

Submitted to the Department of Materials Science and Engineering on May 23, 2014, in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Abstract

This thesis focuses on the development of synthetic methods to create application-ready quantum dots (QDs) in the infrared for biological imaging and optoelectronic devices. I concentrated primarily on controlling the size and size distribution of indium arsenide and cadmium arsenide QDs.

In the nanocrystal community, classical nucleation and growth is often invoked to explain size focusing. However, this model lacks predictive power and contradicts what is known about the chemistry of QD growth. I try to relate my experimental approach and my conclusions to our understanding of the mechanism of particle growth. This approach led me to explore the role of precursor conversion rate in the growth of III-V QDs and to develop a continuous injection synthesis method that I used to make both III-V and cadmium arsenide QDs.

Cadmium arsenide (Cd₃As₂) is a narrow gap semiconductor that can form QDs with tunable emission between 530nm and 2000nm. I developed a synthetic strategy to precisely control the size of Cd₃As₂ QDs while maintaining a narrow size distribution. Continuous precursor injection was used to drive growth and suppress size broadening. The quantum yields of Cd₃As₂ QDs produced using this method ranged as high as 80%, and their emission is tunable over a broad range with narrow linewidths. However, they were found to be unstable in ambient conditions. Nevertheless, by processing in inert conditions we were able to make a crude photodetector that demonstrates that Cd₃As₂ QDs are sufficiently stable for use in optoelectronic devices. Although growth of a Cd₃P₂ shell provided enough added stability to observe emission after ligand exchange into water, these core-shell structures do not seem to be robust enough for biological applications.

Indium arsenide (InAs) QDs are more easily stabilized with a core-shell structure. However, the spectral linewidths are broad and existing synthetic techniques produce only small particles with limited spectral tunability. Models predicted that decreasing precursor reactivity would produce larger, more monodisperse particles. Therefore, I chemically modified the group-V precursor to reduce reactivity. I made a library of group-V precursors, and I developed a framework for comparing the QDs that they produced and measuring the kinetics of precursor conversion and particle growth.
Although we successfully reduced precursor reactivity, we found that the effect on particle size was minimal and that the least reactive precursors produced particles with inferior size distributions.

To find another way to try to improve III-V synthesis, I adapted the continuous injection method developed for making Cd$_3$As$_2$. Using this strategy, I was able to produce InAs QDs with broadly tunable size and narrow spectral features. However, continuous injection ceases to drive particle growth beyond about 5nm in diameter. We examined why particle growth stops, and proposed a strategy to prolong growth and size focusing.

Ultimately, the continuous injection technique allowed us to produce InAs QDs with infrared emission and narrow spectral features that were ideally suited for producing QDs optimized for deep tissue imaging in mice. By adding a shell of CdSe, CdS, or ZnSe, the quantum yield and stability were enhanced. These emitters allowed us to see biodistribution and biological processes occurring inside live mice.

Although we found that precursor chemistry did not affect particle growth to the degree we hoped, we were able to produce application ready QDs via a continuous injection procedure. Continuous injection synthesis of QDs is a precise way to tune QD size while maintaining narrow size distributions. We have used this technique to produce QDs with the specifications required for high impact applications.

Thesis Supervisor: Mounqi G. Bawendi
Title: Lester Wolfe Professor of Chemistry
To my Mother and Father
Acknowledgments

My parents have encouraged and supported me at every turn. They have always challenged me to work hard and excel at the things that I enjoy. My sister Amanda has been a great friend and advisor on pretty much everything that isn’t related to science. In high school, two teachers had special roles in my development as a scientist. Temba Maqubela and Clyfe Beckwith taught me to understand and enjoy chemistry and physics. At USC, Professor Anupam Madhukar taught me how to think deeply and critically about both simple and complicated things. Siyuan Lu and Zach Lingley awed me with their intelligence and enthusiasm for their research.

Moungi Bawendi is brilliant and inspirational. His advice, guidance, and standards for intellectual and logical rigor define how I read and write about science. Incredibly, Moungi manages to create a lab environment with low pressure and high expectations.

Peter Allen was my mentor when I joined the Bawendi group and he taught me both healthy skepticism and the ability to recognize a good idea when you are lucky enough to have one. Brian Walker was heroically generous with his time and perspective. August Dorn and David Strasfeld taught me about QD devices. I never fail to seek the advice of Ou Chen when it comes QD growth or anything related. I am sure he knows more about nanoparticle growth than anyone on earth. Hee Sun Han, Russ Jensen, JM Lee, Gyuweon Hwang, Raoul Correa, Jian Cui, Cliff Wong, Darcy Wanger, Jenn Scherrer, He Wei, Dorthe Eisele, Ou Chen, and Jose Cordero are great friends.

My classmates in DMSE were an important part of my formative months at MIT. Without Nick Thompson, Reid Van Lehn, Adam Jandl, Neil Patel, Brian Spatocco, Jocelyn Newhouse, and Max Solar I wouldn’t have survived my first year.

Peter, Brian, Hee Sun, JM, and Dave all contributed to the work on Cd3As2. Brian Walker helped a great deal in shaping the initial trajectory of the experiments related to precursor reactivity. Daniel Franke has been a great addition to the Bawendi group. His help and insights helped shape the second chapter of precursor work. Jinyoung Baek and Lisi Xie from the Jensen group are responsible for the microfluidic work in
the fifth chapter and for helping shape my perspective through many useful discussions of nanocrystal growth. Flurin Hanseler also influenced my thinking on particle growth mechanisms.

Ou and I discussed shell growth and the continuous injection synthesis of InAs regularly. His insights have been invaluable.

I worked with Oliver Bruns and Thomas Bischof to design particles optimized for second window biological imaging.

The staff at MIT do an outstanding job of educating students. Scott Speakman stands out for his work running the X-Ray facility in CMSE. His dedication to student safety and education is remarkable. Jeff Simpson in the DCIF went to great lengths to educate me about NMR and to help me design and execute successful experiments.

Working with and befriending so many talented and driven colleagues at MIT has made graduate school a true pleasure.
Contents

1 Introduction
  1.1 Quantum Confinement ........................................... 19
    1.1.1 Making Quantum Confined Structures ................. 20
    1.1.2 Structure and Properties of Colloidal Quantum Dots ... 21
  1.2 Optical Properties of Quantum Dots ......................... 23
  1.3 Applications of Colloidal QDs ............................... 24
    1.3.1 Biology ................................................ 24
    1.3.2 Photodetectors and Photovoltaics .................... 24
    1.3.3 Downconversion ....................................... 25
  1.4 Thesis Overview ............................................... 25

2 Particle Size Focusing ........................................... 29
  2.1 A General Treatment ....................................... 29
  2.2 Nucleation .................................................. 32
    2.2.1 Volmer-Weber Theory of Nucleation Rate ............ 34
  2.3 LaMer and Dinegar ......................................... 34
  2.4 Lifshitz, Slyozov, and Wagner Theory for Particle Coarsening (Ostwald Ripening) ........................................ 36
  2.5 Quantum Dot Growth in Theory and Practice ................ 36
  2.6 Conclusion .................................................. 39

3 Synthesis of Cadmium Arsenide Quantum Dots ....................... 41
  3.1 Introduction and Background .................................. 41
3.2 Synthesis and Characterization of Cadmium Arsenide QDs .......... 42
3.3 Synthesis of Cd$_3$As$_2$ QDs by Rapid Precursor Injection .......... 43
  3.3.1 Effect of Temperature ..................................... 44
  3.3.2 Surfactant Mixtures .......................................... 44
  3.3.3 “Magic Sized” Cd$_3$As$_2$ Clusters .......................... 45
3.4 Synthesis of Cd$_3$As$_2$ QDs by Continuous Precursor Addition ...... 48
3.5 Structural and Chemical Characterization of Cd$_3$As$_2$ QDs .......... 50
3.6 Overcoating of Cd$_3$As$_2$ QDs .................................. 52
3.7 Photodetectors from Cd$_3$As$_2$ QDs .............................. 56
3.8 Conclusion ......................................................... 57

4 Group-V Precursors for InP and InAs QD Synthesis ................. 59
  4.1 Introduction .................................................... 59
  4.2 Precursor Synthesis ............................................. 60
  4.3 QD Synthesis and Characterization ............................. 61
    4.3.1 QD Synthesis .............................................. 61
  4.4 Measurement of Precursor Reaction Kinetics ..................... 65
    4.4.1 in situ UV-Visible Absorbance Spectroscopy for Measurement of Particle Formation .......................... 65
    4.4.2 $^1$H NMR Spectroscopy for Measurement of Precursor Reaction Kinetics ............................ 67
  4.5 Hydrolysis Products ............................................. 71
  4.6 Conclusion ..................................................... 72

5 Systematic Study of Precursor Reactivity and Particle Formation .... 75
  5.1 Motivation and Precursor Selection ............................. 75
  5.2 Precursor Synthesis ............................................. 76
  5.3 QD Synthesis .................................................. 77
    5.3.1 Batch Mode ............................................... 77
    5.3.2 Microfluidic Synthesis ................................... 79
  5.4 Characterization of Reactivity ................................ 83
A.1.6 Transmission Electron Microscopy (TEM) 131
A.1.7 Wide Angle X-Ray Scattering (WAXS) 131
A.1.8 Energy Dispersive Spectroscopy (EDS) 131
A.1.9 Nuclear Magnetic Resonance (NMR) 131
A.1.10 Quantum Efficiency Measurements 132
A.2 Additional Figures and Tables 132

B Group-V Precursors for InP and InAs QD Synthesis 135

C Systematic Study of Precursor Reactivity and Particle Formation 139
C.1 UV-Vis 141
### List of Figures

1-1  Quantum Confinement ......................................................... 20
1-2  Core Shell QD ................................................................. 22
1-3  Size Series of CdSe QDs ..................................................... 22
1-4  Spectral inhomogeneity among QD materials ........................... 27
2-1  Kinetics of Particle Fusion .................................................. 31
2-2  $\Delta G_r$ ................................................................. 33
2-3  LaMer model for Nucleation and Growth .................................. 35
2-4  Modeled Particle Size Distributions ....................................... 38
3-1  Absorbance and emission of 3nm Cd$_3$As$_2$ QDs ....................... 43
3-2  TEM of Cd$_3$As$_2$ particles with unknown phase ....................... 45
3-3  XRD of large nanocrystals with unknown phase ......................... 46
3-4  Absorbance and emission spectra taken from a solution of Cd$_3$As$_2$ clusters one minute after injection at 130°C .......................... 47
3-5  Absorbance and photoluminescence of Cd$_3$As$_2$ QDs .................. 48
3-6  Evolution of optical linewidths during CI .................................. 49
3-7  TEM of Cd$_3$As$_2$ QDs ................................................... 51
3-8  Wide angle x-ray scattering of Cd$_3$As$_2$ QDs ......................... 51
3-9  Cd$_3$As$_2$(Cd$_3$P$_2$) Core Shell QDs .................................... 54
3-10 Cd$_3$As$_2$(Cd$_3$P$_2$) QDs before and after water solubilization .... 55
3-11 Cd$_3$As$_2$(CdS) Core Shell QDs ....................................... 55
3-12 Cd$_3$As$_2$ photodetector ............................................... 57
4-1 Indium arsenide absorbance and PL spectra for TMGe$_3$As and TMSi$_3$As
4-2 Indium phosphide absorbance and PL spectra for TMGe$_3$P and TMSi$_3$P
4-3 TEM of InAs and InP from TMGe$_3$V and TMSi$_3$V
4-4 XRD
4-5 \textit{in situ} absorbance measurements
4-6 TME$_3$P reaction with InMy$_3$ observed by $^1$H NMR
4-7 TMGe$_3$P intermediates
4-8 Order plot for the reaction of TMGe$_3$As with InMy$_3$ (NMR)
4-9 Order plot for the reaction of TMGe$_3$As with InMy$_3$ (UV-Vis)
4-10 Precursor conversion in the presence of myristic acid and water
5-1 Precursors for synthesis of InAs and InP
5-2 Absorbance spectra of InAs QDs growing from different arsine precursors
5-3 Absorbance spectra of InP QDs growing from different phosphine precursors
5-4 Absorption spectra of InAs QDs grown from TMGe$_3$As and TMSi$_3$As
5-5 Mixing and aging temperature comparison for phosphine precursors
5-6 Two Stage Microfluidic Reactor
5-7 $^1$H NMR spectra of TMGe$_3$As and iPrDMSi$_3$As reacting with InMy$_3$
5-8 Relative concentration of TMGe$_3$As and iPrDMSi$_3$As during reaction with InMy$_3$
5-9 $^1$H NMR spectra of TMGe$_3$P and iPrDMSi$_3$P reacting with InMy$_3$
5-10 Relative concentration of TMGe$_3$P and iPrDMSi$_3$P during reaction with InMy$_3$
5-11 Precursor concentrations during reaction of TMGe$_3$P and iPrDMSi$_3$P with 3mM InMy$_3$
5-12 UV - Vis Kinetics for arsenic precursors
5-13 UV - Vis Kinetics for phosphorous precursors
6-1 InAs CI Absorbance Spectra
6-2 Absorbance peak and PL FWHM evolution during continuous injection
<table>
<thead>
<tr>
<th>Page</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-3</td>
<td>PL of InAs during CI growth</td>
</tr>
<tr>
<td>6-4</td>
<td>Particle size during CI</td>
</tr>
<tr>
<td>6-5</td>
<td>TEM of InAs QDs during CI growth</td>
</tr>
<tr>
<td>6-6</td>
<td>InAs Absorption spectra during continuous injection</td>
</tr>
<tr>
<td>6-7</td>
<td>Evolution of absorbance peak and PL FWHM during continuous injection</td>
</tr>
<tr>
<td>6-8</td>
<td>Change in particle volume and injected equivalents during continuous injection</td>
</tr>
<tr>
<td>6-9</td>
<td>Comparison of InAs QDs grown by CI with and without amines</td>
</tr>
<tr>
<td>6-10</td>
<td>Histogram of InAs QD diameters grown with oleylamine</td>
</tr>
<tr>
<td>6-11</td>
<td>Volume weighted histogram of InAs QD diameters grown with oleylamine</td>
</tr>
<tr>
<td>6-12</td>
<td>Absorption spectra of InP grown by continuous injection</td>
</tr>
<tr>
<td>6-13</td>
<td>Spectral evolution during InP QD growth by CI</td>
</tr>
<tr>
<td>6-14</td>
<td>TEM of InP grown by CI</td>
</tr>
<tr>
<td>6-15</td>
<td>Absorbance and PL of InAs grown by CI</td>
</tr>
<tr>
<td>7-1</td>
<td>Tissue transmission in the NIR and SWIR</td>
</tr>
<tr>
<td>7-2</td>
<td>InAs core shell absorption spectra</td>
</tr>
<tr>
<td>7-3</td>
<td>InAs core shell QD emission spectra</td>
</tr>
<tr>
<td>7-4</td>
<td>SWIR QDs: Multiplexing, size series colored vials</td>
</tr>
<tr>
<td>7-5</td>
<td>Color QD-SWIR imaging for multiplexing and functional imaging</td>
</tr>
<tr>
<td>7-6</td>
<td>QD-SWIR imaging of heartbeat and breathing in a mouse</td>
</tr>
<tr>
<td>A-1</td>
<td>QY of Cd₃As₂ QDs decreases with increasing emission wavelength</td>
</tr>
<tr>
<td>A-2</td>
<td>NMR showing quantitative reaction yield of TMSi₃As with cadmium(II) myristate</td>
</tr>
<tr>
<td>B-1</td>
<td>InAs and InP Absorbance Spectra for Si and Ge precursors</td>
</tr>
<tr>
<td>B-2</td>
<td>Protonolysis of TMGe₂Pb by methanol</td>
</tr>
<tr>
<td>B-3</td>
<td>³¹P and ¹H NMR of TMGe₂P reaction with InMy₃ and octylamine</td>
</tr>
<tr>
<td>C-1</td>
<td>InAs QDs made from various arsine precursors</td>
</tr>
<tr>
<td>C-2</td>
<td>Absorbance of InP by Precursor</td>
</tr>
</tbody>
</table>
C-3  Arsenic precursor absorbance rise fits . . . . . . . . . . . . . . . . . .  142
C-4  Phosphine precursor absorbance rises (4.3mM InMy₃) . . . . . . . .  143
C-5  Phosphine precursor absorbance fits (4.3mM InMy₃) . . . . . . . .  143
C-6  Instrument instability during phosphine absorbance traces. . . . .  144
C-7  Phosphine precursor absorbance rise fits . . . . . . . . . . . . . . . . .  145
List of Tables

5.1 Comparison of experimental conditions in batch mode and microfluidic reactors ........................................ 79
5.2 Comparison of precursor conversion rates (NMR) ......................................................... 83
5.3 Arsenic and phosphorous precursor reaction time constants from UV Vis 87

6.1 Range of particle absorbance peaks produced by different synthetic methods ........................................ 93

7.1 Summary of InAs overcoating results ........................................................................... 114

A.1 EDS measurements of atomic composition of a sample of Cd$_3$As$_2$ QDs 133
Chapter 1

Introduction

1.1 Quantum Confinement

When the smallest dimension of a semiconductor approaches the size of the Bohr radius of the exciton, the boundary conditions imposed by the crystallite surface begin to significantly affect the electronic states of the system. Requiring the electron and hole wavefunctions of the exciton to terminate at the interface is a more restrictive boundary condition than those used to derive the bandstructure of an infinite crystal. Therefore, quantum confinement results in a blueshift of the transition between the ground state of a semiconductor nanostructure and its first excited state. The exciton Bohr radii of typical semiconductors range from 3nm for CdS [1] to >50nm for InSb [2]. Therefore, semiconductor nanostructures have size-dependent electronic and optical properties. Systems confined in one dimension are known as quantum wells. Those confined in two dimensions are quantum wires, while materials that experience three dimensional confinement are known as quantum dots (QDs). The effective band edge of a three dimensionally confined quantum dot is given (according to the particle in a sphere model using the effective mass approximation) by equation 1.1 [3].

\[ E_{\text{eff}} \cong E_g + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\varepsilon R} \]  

(1.1)
1.1.1 Making Quantum Confined Structures

Quantum wells are typically made using chemical vapor deposition (CVD) or molecular beam epitaxy (MBE). Quantum dots are made using two starkly contrasting methods: MBE, and solution phase growth. In MBE growth, UHV systems (background pressure $<10^{-11}$Torr) are used to deposit material atom by atom. Substrate orientation, composition, temperature, and atomic flux are all precisely controlled to minimize defect formation. Under certain conditions, nanoscale islands form to minimize strain due to lattice mismatch[5, 6]. The apparatus used for MBE growth is well suited to *in situ* characterization techniques such as x-ray and electron scattering to study the surface as it evolves[7]. Solution phase chemical methods are also used to make three dimensionally confined nanostructured materials. These techniques, which have been successfully implemented since the late 1980s, are comparatively dirty and difficult to characterize *in situ*. Nevertheless, chemists have had remarkable success making high quality nanocrystals in solution[8, 1].

Solution methods for the synthesis of inorganic quantum dots[8, 1, 9] typically involve the combination of precursor reagents in a high boiling point solvent at temperatures between 100°C and 350°C. The solution usually also contains surfactants or ligands that bind to the surface of the particle as it grows and provide an oleophilic layer for solubility. Typical surfactants include fatty acids (carboxylic and phosphonic acids are most common), fatty amines, phosphines, and phosphine oxides. Many
.syntheses use the fatty acid salts as a precursor for the cation, blurring the distinction between precursor and ligand. Control of solution temperature and surfactant chemistry are the main handles for modulation of QD size. Ligands will have different binding strengths to different crystallographic facets. This means that growth rates in different directions can be controlled using ligand chemistry and used to create nanostructures with different shapes[10]. In general, fairly uniform ensembles of nanoparticles can be produced through these techniques, and post synthetic size selective purification is not necessary for well developed materials.

1.1.2 Structure and Properties of Colloidal Quantum Dots

Most colloidal QDs are made from binary compound semiconductors. Popular, established systems include III-V materials such as indium arsenide (InAs) and indium phosphide (InP); II-VI materials such as cadmium sulfide (CdS), cadmium selenide (CdSe), and cadmium telluride (CdTe); and IV-VI semiconductors such as lead sulfide (PbS), lead selenide (PbSe), and lead telluride (PbTe). Quantum dots can also be made from from mercury chalcogenides, ternary I-III-VI semiconductors such as CuInSe, and II-V materials such as Cd₃As₂ and Cd₃P₂[1, 11, 12, 13, 14].

As synthesized, QDs typically range from 2-10nm in diameter, with a coating of organic surfactants on the surface. However, due to the nature of quantum confinement, the exciton wavefunction has significant overlap with the nanoparticle surface. Interface states such as dangling bonds can provide a pathway for non-radiative decay of the QD excited state. Therefore, when high photoluminescence quantum yield (QY) is desired, it is common to surround the nanocrystal (core) with a higher bandgap material (shell) in order to reduce the interaction strength between the exciton and the nanoparticle surface and thereby increase QY (figure 1-2). Typical shell materials are the II-VI materials, which have been found to be most stable in ambient conditions. Band alignment between core and shell is important, and can be used either to confine the exciton to the core (type I alignment) or to spatially separate electron and hole to allow emission at a wavelength redder than what would be indicated by core or shell bandgap alone (type II alignment)[9].
Figure 1-2: The structure of a core-shell QD. Adapted from [4]

Figure 1-3: The left panel shows absorption spectra for CdSe QDs of different sizes[15], while the right panel shows a typical experimental setup for the synthesis of colloidal quantum dots.
1.2 Optical Properties of Quantum Dots

The defining property of quantum dots is their size dependent absorbance and photoluminescence (figure 1-3). Quantum confinement allows the absorption edge and photoluminescence peak to be size tuned to energies above the bulk bandgap. Furthermore, shell growth offers an additional means to control the band edge energy features by changing the confinement landscape. Narrow linewidths are desirable for both applications and fundamental study. Of course, due to the size-dependence of the optical spectra, size inhomogeneity leads to broadening of the spectral linewidths.

For CdSe, the best studied and most successful quantum dot material, homogeneous photoluminescence linewidths (those representing the PL from a single quantum dot) range from 50-60 meV[16]. In the best samples of core-shell CdSe(CdS) QDs[17], the ensemble linewidth and the homogeneous linewidth are nearly identical. However, for other materials such as InP and InAs, sample inhomogeneity dominates the spectral linewidth (figure 1-4)[16, 17].

High quantum yield is also critical for performance in many applications. Quenching of fluorescence QY is believed to be related to the presence of defects at the interface between core and shell and at the particle surface. Again, CdSe QDs have the highest reported QYs of any other material, with many reports of QYs approaching unity[17]. However, at the time of writing of this thesis, QDs from other materials fail to reach this level of performance. InP(ZnS) QDs have been reported with QYs as high as 70%[18]. Infrared materials such as PbS and PbSe have QYs ranging as high as 60%[19]. InAs(CdSe) can be synthesized with QYs as high as 30% (values as high as 90% have been reported by some authors[20]).*

There are several other interesting phenomena associated with the emission of quantum dots. These include “blinking” of the emission of a single QD, as well as the diffusion of the spectrum of a single QD[22]. Although these issues become important for certain applications (high flux environments and single particle tracking), I will

---

*The measurement of absolute QYs is challenging. Infrared dye standards are unreliable, and reported QYs have been found to vary by as much as a factor of 10 from true QYs[21]. Reported QYs should be treated with caution.
not address them in this thesis.

1.3 Applications of Colloidal QDs

Although QDs are an attractive model system for fundamental study, interest in their development is driven primarily by a belief that their properties make them valuable for applications. QDs compete with organic molecules for applications in biological labeling, solid state lighting, and solution processable optoelectronic devices.

1.3.1 Biology

QDs are useful fluorophores for biology because they have broad, strong absorption as well as narrow, photostable and tunable emission. Furthermore, their optical properties and surface chemistry can be decoupled using ligand chemistry, making them a modular probe for functionalization and targeting.

A second advantage of quantum dots for biology is that (unlike organic dyes) they can be made bright and robust emitters in the short wavelength infrared (SWIR)\(^\dagger\). This is attractive because there is a transparent window in biological tissue ("second window") that enables deep tissue imaging\cite{23, 24}. Therefore, SWIR imaging with QDs could be an inexpensive way to study dynamic biological processes within the body without resorting to expensive and relatively slow processes such as MRI, CT, or PET. The toxicity of the materials used to make SWIR QDs is a concern for \textit{in vivo} imaging in humans. However, it may prove ideal for animal models (where most organs lie within the imaging depth).

1.3.2 Photodetectors and Photovoltaics

A revival of interest in renewable energy has driven research into quantum dot photovoltaics (PV). The QDs usually represent the absorbing medium. Asymmetry in the contacts drives charge separation to produce power. Although QDs are poor

\(^\dagger\)We will use the term SWIR to refer to the wavelength range where InGaAs detectors are sensitive, approximately 900nm-1700nm
conductors relative to bulk semiconductors, they can be processed in solution. Solution processability means that QD PV devices can be mass produced using highly cost-efficient production techniques such as roll-to-roll printing.

The second reason that QD solar cells have attracted interest and funding is the possibility of efficient multiexciton generation (MEG). MEG occurs when a high energy photon (with energy >2\(\times\) the bandgap) is absorbed and generates two excitons. MEG reduces thermalization losses that reduce the efficiency of conversion of radiative energy to electrical energy\[25\]. The degree to which MEG is enhanced in quantum dots is controversial, and was recently found to be lower than previous reports\[26\].

Most research in QD PV and QD photodetectors has focused on improving the conductive properties of the QD films. This involves primarily studying and modifying the surface passivation to eliminate or reduce non-radiative recombination sites and charge trap states, increasing the coupling between QDs, and controlling the carrier density and type\[27\].

1.3.3 Downconversion

The most successful commercial applications of these materials have taken advantage of their narrow and tunable photoluminescence and broad absorbance. These properties make them well suited to light shaping applications such as phosphors for white-light LEDs, solar concentration, and dual-band photodectors\[28, 29, 30\]. Dual-band photodetectors downconvert UV light for efficient detection by an IR camera\[30\]. Downconversion in lighting and display applications use the same principle to convert high energy photons (principally from blue GaN LEDs) to green and red light that is optimized for a high color gamut or color temperature.

1.4 Thesis Overview

The primary goals for the synthesis of colloidal quantum dots for photoluminescence applications are:
• Elimination of inhomogeneous spectral broadening

• Development of synthetic methods to tune nanocrystal size while maintaining narrow size distributions

• Design of structures with high fluorescence QY

Although these challenges have been conquered for cadmium based visible QDs\cite{17}, significant hurdles remain for cadmium free visible QDs as well as for infrared QDs. Indium phosphide is the most promising material for a cadmium free visible emitter. However, PL linewidths for InP core shell QDs are about 180 meV, in contrast to linewidths of CdSe core shell QDs which can be as low as 75 meV. Furthermore, QYs for InP are lower and less stable than they are for CdSe based QDs. In the infrared, there is no material that meets these requirements. The most studied materials, PbS and PbSe, have rock salt crystal structures that are incompatible with defect free epitaxial growth of the wide bandgap, air stable shell materials used to stabilize II-VI and III-V QDs. Although the lead chalcogenides have good size distributions and fairly high QYs, they are unstable with respect to oxygen, water, and high temperature. Indium arsenide QDs offer the potential for epitaxial shell growth and therefore higher quantum yield and stability, yet currently the spectral linewidths and tunability of InAs QDs are inferior to those of PbS or PbSe.

This thesis focuses primarily on developing synthetic techniques to make infrared emitting quantum dots with a broad range of sizes, narrow size distribution, and high QY. Most of our efforts have been devoted to first two goals (size distribution and size tunability). To provide context for this work, the second chapter will discuss current and historical thinking about the physical processes that drive size focusing during particle growth.

The third chapter will present a discussion of size focusing in infrared Cd$_3$As$_2$ QDs. We developed a synthetic strategy that allows us to produce high quality Cd$_3$As$_2$ samples with emission ranging from green to infrared (530 nm-2000 nm). Different methods of producing Cd$_3$As$_2$ QDs are discussed, and their relative merits are compared. We found that a continuous precursor injection method offered superior
Figure 1-4: Solution PCFS experiments reveal that inhomogeneous broadening dominates for InP QDs, while for CdSe inhomogeneous broadening does not contribute significantly to ensemble linewidth[31].

control over particle size and size distribution.

The fourth chapter approaches the issue of size focusing in QDs from a different perspective. As will be discussed in detail in the second chapter, precursor conversion rate is widely believed to be a critical parameter that determines QD final size and size distribution. A highly reactive precursor would be expected to result in the formation of many small particles, leaving little precursor material for growth and size focusing and resulting in samples with small average sizes and poor size distributions. As a result, I began to establish a framework to investigate the synthesis of III-V QDs from less reactive precursors. The fourth chapter deals with a discussion of the development of novel precursors for the synthesis of group V containing QDs. The QDs made from these precursors (with otherwise identical conditions) are compared. The precursor reactivity is characterized using complementary techniques to study molecular pathways as well as particle formation. Molecular information is obtained at rarefied conditions with NMR spectroscopy, which is used to measure the disappearance of reactants and the appearance of products simultaneously. Then, UV-Vis spectroscopy is used in situ to study absorbance rise associated with nanocrystal
formation at more realistic nanocrystal growth conditions. Together these measurements form complementary pictures that trace nanocrystal growth from its origins as a molecular process to the ultimate emergence of larger structures.

The fifth chapter builds on this work with the synthesis of a larger library of precursors with significantly slower reaction kinetics. The conclusions of the previous chapter are tested with a larger range of precursor reactivities. We find that although we are able to slow precursor reactivity substantially, the effect on particle growth is weaker than models predict.

The sixth chapter describes the continuous injection synthesis of InAs and InP QDs. We find this method to be far more effective at controlling particle size and size distribution than precursor chemistry. Although we are able to use this technique to make particles over a much wider range of sizes than we were using temperature or precursor chemistry, there is still room for improvement. We speculate on why growth appears to slow as particle size reaches 5nm, and discuss strategies to prolong the period of growth and size focusing.

In the seventh chapter, I show that the CI technique can be used to make application ready QDs for deep tissue imaging in vivo in the SWIR. I discuss the motivations driving work in QD fluorophores for this space, the challenges associated with making IR QDs that meet these requirements, and the use of InAs-based QDs in biological imaging experiments. The infrared is an attractive space for optical imaging because of low scattering, low autofluorescence and the relative transparency of tissue in the NIR and SWIR regions.
Chapter 2

Particle Size Focusing

The size distribution of a sample of QDs limits spectral linewidth in most cases. Much of the research in this thesis was conducted with the goal of improving the size distribution and achieving greater control over particle size.

In order to move away from the empirical approach that has dominated developments in QD synthesis over the last 25 years, I summarize current understanding of the processes that drive size focusing in colloidal QDs.

Remarkable control of particle size and size distribution is possible for a few systems. However, for other materials, this level of control has not been achieved despite considerable experimental effort. This discussion provides context so that we can understand what processes control nanoparticle growth and size distribution. We hope to learn why some materials can be synthesized with much more control of size and size distribution than others and to develop synthetic techniques to produce application ready infrared materials.

2.1 A General Treatment

To begin, I will outline a (relatively) general set of rate laws that govern particle growth from which common models are derived via simplifying assumptions. If we define a particle as a structure consisting of an integer number of indivisible subunits (atoms, or more generally, “monomers”), then if we consider a dynamic ensemble of
particles we can describe the system by a set of rate laws. In general, particles can change their size either by addition or removal of material from the particle. We will simplify this by considering only two-body particle fusion (coalescence) and fission. Fission events other than the desorption of a single monomer will be ignored. The concentration of particles with \( n \) subunits, \( C_n \), can be described by the following differential equation.

\[
\frac{dC_n}{dt} = \left( \sum_{l+p=n} k_{l+p}^{fus} C_l C_p + k_{n+1}^{fis} C_{n+1} \right) - \left( \sum_{m} k_{m,n}^{fus} C_m C_n + k_n^{fis} C_n \right) \tag{2.1}
\]

Of course, this treats only the particle number, and does not address the issue of shape, crystallinity, or defect formation. For now, we will assume that the particles are sufficiently small that any defects or shape inhomogeneity is rapidly eliminated through thermal annealing.

In principle, with knowledge of the values of \( k_{l+p}^{fus} \) and \( k_n^{fis} \), the system of equations 2.1 for all values of \( n \) and \( m \) perfectly describes the evolution of the system. A cartoon of some example fusion processes is shown in figure 2-1. All models of particle growth make assumptions about the values of these rate constants.
Figure 2-1: This cartoon shows several possible fusion events and rates for a particle with $n = 5$. 
2.2 Nucleation

The theory of nucleation deals specifically with the rates of fusion and fission at very small particle sizes. For clarity of language, I will consider a phase change from solute to solid. Although nucleation is an inherently kinetic process, it is most clearly introduced in a thermodynamic description. In this description, the free energy change $\Delta G_r$ for the formation of a solid particle of radius $r$ from solution is considered in terms of the driving force for phase change, the bulk free energy change $\Delta G_V$ and the isotropic interfacial surface energy $\gamma_{SL}$. Geometry gives the following expression for the free energy change upon solidification to a particle of radius $r$:

$$\Delta G_r = \frac{4}{3} \pi r^3 \Delta G_V + 4 \pi r^2 \gamma_{SL}$$

(2.2)

The surface energy gives rise to a $\Delta G_r > 0$ at sufficiently small sizes, even when the bulk driving force $\Delta G_V < 0$ (figure 2-2). This barrier explains the phenomena of supersaturation, when a phase change does not occur even when it is thermodynamically favorable. Thermodynamically, clusters with radii smaller than $r^*$, the critical radius, will be thermodynamically unstable. The nucleation rate is the inverse of the frequency at which statistical fluctuations result in the formation of stable particles with $r > r^*$. The activation barrier $\Delta G^*$ for particle growth is given by equation 2.3, while the critical radius, $r^*$ is given by equation 2.4.

$$\Delta G^* = \frac{4 \pi \gamma_{SL} r^*}{3} = \frac{16 \pi \gamma_{SL}^3}{3 \Delta G_V}$$

(2.3)

$$r^* = \frac{2 \gamma_{SL}}{\Delta G_V}$$

(2.4)

Clearly, the activation barrier and critical radius both increase as the magnitude of $\Delta G_V$ shrinks. The magnitude of $\Delta G_V$ decreases as supersaturation decreases. The dependence of $\Delta G_V$ on monomer concentration is given by equation 2.5. This therefore implies that nucleation will be a self regulating process. As the phase change begins to occur through the formation of nuclei, the supersaturation must decrease.
Figure 2-2: Free energy of particle formation as a function of particle radius, \( r \). Also included are contributions from the free energy of phase change (tan curve) and the surface energy (green curve) as solute is consumed. This will reduce \( \Delta G_v \) and reduce the rate of nucleation until it becomes negligible.

\[
\Delta G_v = -NkT \ln \left( \frac{C_1}{C_{\text{sat}}} \right)
\]

The kinetic description of this picture modifies the activation energy for adsorption or desorption by the marginal surface energy penalty. Therefore a particle with \( r < r^* \) shrinks since the rate of addition of material is out-competed by dissolution, while the opposite is true above the critical radius.

Most treatments model particle growth by simplifying equation 2.1 by assuming that the addition and dissolution of a single monomer unit are the only relevant
processes (equations 2.6-2.7).

$$\sum_{i+p=n} k_{i,p}^{fus} C_i C_p = k_{n-1,1}^{fus} C_{n-1} C_1$$  \hspace{1cm} (2.6)

$$\sum_{m} k_{m,n}^{fus} C_m C_n = k_{n,1}^{fus} C_n C_1$$ \hspace{1cm} (2.7)

The rate equation for $C_n$ becomes:

$$\frac{dC_n}{dt} = \left( k_{n-1,1}^{fus} C_{n-1} C_1 + k_{n+1}^{lis} C_{n+1} \right) - \left( k_{n,1}^{fus} C_n C_1 + k_{n}^{lis} C_n \right)$$ \hspace{1cm} (2.8)

### 2.2.1 Volmer-Weber Theory of Nucleation Rate

Nucleation rates can be modeled most simply as heterophase fluctuations[32]. By assuming that the distribution of clusters with size $r < r^*$ is the same as the equilibrium distribution if the phase change was unfavorable (that is, that $\Delta G(r) = \infty$ for all $r > r^*$), the pseudo-equilibrium concentration of subcritical clusters can be approximated (equation 2.9-2.10).

$$r < r^* \quad C_n = C_0 e^{-\frac{\Delta G_V}{kT}}$$ \hspace{1cm} (2.9)

$$r > r^* \quad C_n = 0$$ \hspace{1cm} (2.10)

Once the concentration is obtained, the nucleation rate is then given by the rate at which atoms are added to a cluster of radius $r^*$.

### 2.3 LaMer and Dinegar

The work of LaMer and Dinegar on the growth of monodisperse hydrosols of sulfur is the canonical example of the colloidal synthesis of highly monodisperse particles. In this report, the authors describe how careful control of supersaturation can be used to synthesize an ensemble of highly monodisperse sulfur colloids. The concentration of solute is increased above the nucleation threshold to induce a temporally discrete
burst of nucleation (figure 2-3, II). The burst is confined to a relatively narrow period of time because the conversion of monomers to stable nuclei relieves the degree of supersaturation such that the driving force for crystallization, $\Delta G_V$, diminishes and the activation barrier for nucleation, $\Delta G^*$, rises. As a result, the rate of nucleation after phase II falls to practically zero. In addition, the authors show that following nucleation, the supersaturation is completely relieved by the addition of monomers to existing nuclei by diffusion limited growth. Diffusion limited growth leads to size focusing because the flux of monomers to the particle surface is independent of radius. Therefore, the diameters of the smallest particles increase faster than the diameters of the largest particles. By comparing the diffusivity of monomer in solution with their observed growth rates and particle concentrations, LaMer and Dinegar are able to explain their observations quantitatively[33].

Figure 2-3: Plot of monomer concentration nucleation and growth showing periods of: (I) Monomer concentration increase, (II) Rapid nucleation to partially relieve supersaturation, and (III) diffusion limited growth to completely relieve supersaturation. Adapted from [33]
2.4 Lifshitz, Slyozov, and Wagner Theory for Particle Coarsening (Ostwald Ripening)

At low supersaturations, the process known as Ostwald ripening describes the evolution of a population of particles due to differential solubilities as a consequence of the Gibbs-Thompson effect. The increased chemical potential of atoms in smaller particles is due to the increase in curvature (equation 2.11).

\[ C(r) = C_0 \exp\left(\frac{2\gamma V_{Molar}}{rRT}\right) \]  

(2.11)

This size dependent chemical potential leads to the growth of the largest particles at the expense of the smallest. The effect on an ensemble of particles is that the volume of the average sized particle grows linearly in time[34]. In the context of particle synthesis the Ostwald ripening process is characterized by three things:

1. Decrease in the number (concentration) of particles present in solution

2. Increase in average size \((Diameter \propto t^{1/3})\)

3. Increase in polydispersity

2.5 Quantum Dot Growth in Theory and Practice

The work of Lamer and Dinegar is commonly used to explain the narrow size distributions achieved during the synthesis of colloidal QDs and infer diffusion limited growth[35, 36, 37, 38, 39, 40]. However, the classical model was developed to describe a phase change and not a chemical reaction. Although many colloidal QD syntheses result in narrow size distributions that undergo periods of size focusing and defocusing, there is little justification for the assumptions of a critical cluster size, a size dependent specific energy of formation, or the absence of coalescence processes.

Indeed, computational methods have been used to estimate the cluster formation energies for small CdSe clusters \(((\text{CdSe})_8\) and smaller) and they have found the forma-
tion energy to be linear with the number of CdSe units[41]. Furthermore, estimates of diffusion controlled growth rates differ by orders of magnitude from experimental observations[39]. Rempel et al. demonstrate theoretically that size focusing and defocusing can be achieved by a growth rate controlled entirely by precursor reaction control with size-independent monomer adsorption and desorption rate constants[39]. In this model, precursors convert to monomers which then crystallize. This model successfully demonstrates that size focusing can be achieved entirely through the kinetics of precursor conversion. However, the size distributions described by this model show the persistence of particles with small sizes in disagreement with experimental evidence (figure 2-4). Another key finding of this model is that the size-focusing regime continues only so long as precursors continue to feed the QD growth.

The important role of precursor conversion kinetics in particle growth is also predicted using the traditional CNT-LSW approach. Clark et al. derive the effect of monomer production rate on the evolution of the particle size distribution (PSD)[42]. By beginning with the assumption of a Gaussian size distribution, they show that if the focusing effect of particle growth from reaction-controlled monomer supply is larger than the defocusing effect from coarsening, the size distribution improves. They propose that control of monomer supply might be a superior method of controllably synthesizing high quality particles.

Both models predict that QDs formed from precursors that react more slowly appear to show size focusing regimes that persist through the formation of larger particles in agreement with experimental evidence[43, 44]. However, a complete qualitative description of nanoparticle growth is not obtained by either. Clark’s model does not treat the initial stages of nanoparticle formation, and Rempel’s predicts a size distribution that contains small particles not seen experimentally.

Several authors propose plausible mechanisms that include coalescence of clusters or small particles to explain QD growth[44, 45, 46, 47, 48]. Coalescence is also invoked to explain the discrepancy of measured size by small angle x-ray scattering (SAXS) and the crystallite domain size measured by wide angle x-ray scattering (WAXS) [49, 50]. Coalescence was directly observed alongside growth from
“monomers” (species too small to image by TEM) during the growth of Pt nanoparticles in an electron transparent flow cell in TEM[51]. Allen et al. studied the precursor conversion kinetics for the synthesis of indium phosphide QDs and concluded that the precursor conversion occurred much faster than the particle growth. They postulated that the particle growth occurred by the ripening of “non-molecular precursors” (clusters or small particles) to explain the temporal separation between particle growth and the depletion of the molecular precursors[44]. Similarly, Cossairt et al. observed that the evolution of a sample’s absorption spectrum continues well after the consumption of the cadmium and selenium precursors. They also characterized the formation of so-called “magic sized” clusters* (MSCs) of cadmium selenide and suggest that MSCs are building blocks for the formation of larger particles [45, 48]. A coalescence-type mechanism is also proposed by Lu et al. who show with high resolution transmission electron microscopy (HRTEM) that ≈ 20nm nanocrystals appear to have been formed by the coalescence of smaller (≈ 5nm) nanoparticles[46]. When the model of Rempel et al. was adapted to include a size-dependent coalescence process, the model produced a more realistic size distribution (figure 2-4 )[52].

*“Magic sized” clusters is a term used to refer to particles that are molecularly-defined and that persist due to a special thermodynamic stability associated with a particular cluster size.
2.6 Conclusion

The classical theory of nucleation relies on assumptions about the thermodynamics of small particle formation that do not account for the chemical side products formed during QD growth. After considering the chemical reactions known to occur during QD growth, computational results do not support the idea that the formation of small clusters is an activated process\[53\]. In addition, size focusing in the LaMer model is understood to occur due to diffusion limited growth. However, in the nanocrystal literature, authors do not dare speculate even on the identity of a "monomer" species, much less put forward experimental evidence of its existence or speculate on solubility\[43\]. It is therefore entirely inappropriate to use this model as a framework to guide experimental efforts to improve the quality of materials where existing synthetic techniques are inadequate.

Although the classical picture of nucleation and growth is founded on assumptions about the mechanism and thermodynamics of nanoparticle growth that we know or suspect to be false, this framework remains pervasive in the language of the nanocrystal synthesis community\[40, 43\]. As a result, the improvement of nanoparticle synthetic techniques is driven at best by a trial and error approach entirely without theoretical guidance, or at worst, by an inappropriate model. In this thesis, I attempt to develop improved methods for the synthesis of semiconductor nanoparticles, primarily those that are fluorescent in the infrared, by controlling the precursor reaction rate and concentration. These parameters are predicted to be important to nanocrystal formation by both the nucleation and growth and the coalescence models\[52\]. The results of these experiments provide insight into which processes are important for controlling nanocrystal growth.
Chapter 3

Synthesis of Cadmium Arsenide Quantum Dots

Reproduced in part with permission from [11]. Copyright 2011 American Chemical Society

3.1 Introduction and Background

QDs emitting in the infrared are challenging to synthesize, in part due to the lack of understanding regarding the mechanism of growth of III-V QDs. The lack of available IR emitters inspired me to pursue the synthesis of cadmium arsenide (Cd₃As₂) QDs which emit in the 1-2μm range.

Bulk Cd₃As₂ is a II-V semiconductor with exotic electronic properties. Although there is some debate in the literature regarding the band structure of this material, most experimental results and theoretical predictions suggest an inverted band structure with a band gap of -0.19 eV [54, 55, 56]. Bulk Cd₃As₂ has high carrier concentrations (2 × 10¹⁸ cm⁻³) and electron mobilities (10,000 cm²/V·s) [55]. In addition, the electron and hole effective masses are mₐ* = 0.016 m₀ and mₜ* = 0.12 m₀, giving an estimated exciton Bohr radius of 47 nm. Thus, this material is expected to show extreme quantum confinement similar to that observed in PbSe (exciton Bohr radius of 45 nm) [2]. The narrow band gap combined with the large exciton Bohr radius en-
ables the synthesis of QDs that show band edge emission over a wide spectral range from 0.6 eV to 2.3 eV (530-2000 nm). QDs made from materials with inverted bulk band structure present theoretical challenges because the bands are strongly mixed away from the zone center. The use of a tight binding model to describe the evolution of states in quantum confined negative gap semiconductors has predicted novel properties such as intrinsic surface gap states and an excitonic insulator phase[57]. Thus the synthesis of high quality cadmium arsenide QDs could enable the experimental study of the optical properties of QDs made from a material with an inverted band structure. Much like bulk III-V and II-VI semiconductors, II-V semiconductors are isomorphic and readily form solid solutions[58], which may enable the development of II-V QD heterostructures and alloys.

Reports of the synthesis of II-V semiconductor nanocrystals have appeared previously [59, 60, 61, 12, 62, 63], but to our knowledge, the only report of the preparation of Cd$_3$As$_2$ QDs used an aqueous method involving arsine gas that produced a solution with absorbance and emission features in the visible and fluorescence QYs of 10% [62].

### 3.2 Synthesis and Characterization of Cadmium Arsenide QDs

My initial synthetic approach was inspired by previous reports of the synthesis of Cd$_3$P$_2$ QDs from cadmium(II) oleate and tris(trimethylsilyl)phosphine (TMS$_3$P). These procedures used a single rapid injection of the phosphorus precursor into a hot solution containing cadmium(II) oleate to form Cd$_3$P$_2$ QDs. These reports vary injection temperature[63], growth time[63], and surfactant concentration[12] to control Cd$_3$P$_2$ QD size. However, these experimental handles provide only limited size tunability for Cd$_3$As$_2$ QDs. Despite the ability to produce Cd$_3$As$_2$ QDs with narrow size distributions that resulted in absorbance spectra with multible visible absorbance peaks, a single injection synthesis was unable to produce particles that grew larger
than ~3nm. To reliably produce large Cd₃As₂ QDs with narrow spectral features (figure 3-1), I developed a two-step procedure that uses an initial fast injection of tris(trimethylsilyl)arsine (TMSi₃As) into a solution containing cadmium(II) myristate at 175°C to form small nuclei followed by the slow, continuous addition of additional TMSi₃As to promote growth[11]. This strategy is inspired by the methods commonly used to synthesize core-shell particles[64, 65, 66, 67, 20, 9].

### 3.3 Synthesis of Cd₃As₂ QDs by Rapid Precursor Injection

I initially explored the synthesis of Cd₃As₂ QDs by a single rapid precursor injection at high temperatures. I varied surfactant chemistry by adding various concentrations of carboxylic acids and/or primary amines to the growth solution. I was able to
produce particles with emission peaks <1500nm with narrow size distributions using a single injection at various temperatures and surfactant mixtures.

3.3.1 Effect of Temperature

Temperature is a common handle that is used to control nanoparticle growth. For many systems (CdSe, PbS, PbSe, InAs, InP), larger nanoparticles can be grown by increasing growth temperatures [1]. The appropriate temperature range for growth of high quality nanocrystals varies depending on precursor reactivity and ligand binding strength. Chen, et al. argue that [17] high growth temperatures (>300°C for growth of CdSe QDs) are required for high quality (defect free) nanocrystals, but that slow precursor conversion at elevated temperature is essential for controlled growth at high temperatures. However, PbS and PbSe QDs are unstable in solution at temperatures >150°C. Nevertheless, large, high quality particles are easily produced.

Other materials employing highly reactive precursors such as the III-V QDs, are produced by mixing molecular precursors at modest temperatures, and heating to promote particle growth.* My starting point for injection temperature was guided by the highly reactive arsenic precursor used for Cd₃As₂ QD synthesis. I began with an injection temperature of 150°C. I explored growth temperatures ranging from 130°C to 250°C, but was unable to produce high quality particles with emission redder than 1500nm.

3.3.2 Surfactant Mixtures

Surfactants are also able to control NC growth via their simultaneous effect on the nanoparticle surface activity and the reaction rate of precursors [68, 69]. The presence of amines did little to promote growth, but the combination of elevated temperature and the presence of free carboxylic acid in solution allowed the production of particles with narrow emission ranging from 800-1500nm. However, my attempts to increase particle size further were frustrated by the unexpected formation of 10-20nm diameter,

*note that the success of this strategy cannot be explained by CNT/LSW theory.
spherical nanoparticles with a crystal structure that did not match that of Cd$_3$As$_2$ (or any phase listed in the ICSD). These particles showed featureless absorbance spectra and no observable photoluminescence at wavelengths between 400nm-3000nm.

3.3.3 “Magic Sized” Cd$_3$As$_2$ Clusters

Initial injections at lower temperatures (130°C) resulted in smaller particles showing well-defined absorbance features and narrow emission at wavelengths as blue as 530nm (figure 3-4). These features closely resemble those attributed to Cd$_3$P$_2$ magic sized clusters[70]. With continued heating, the features became less well-defined and shifted to the red, ultimately resembling the spectra of QDs synthesized at 175°C.
Figure 3-3: XRD of large nanocrystals shown in figure 3-2. Calculated intensities for representative known phases of Cd-As are shown here.
Figure 3-4: Absorbance and emission spectra taken from a solution of Cd$_3$As$_2$ clusters one minute after injection at 130°C
3.4 Synthesis of Cd$_3$As$_2$ QDs by Continuous Precursor Addition

Ultimately, we settled on a two injection scheme. We injected TMSi$_3$As dissolved in tri-n-octylphosphine (TOP) into a solution containing 1-octadecene (ODE) and a twenty-fold excess of cadmium(II) myristate at 175°C. The solution temperature was maintained at 175°C for 20 minutes to produce cadmium arsenide QDs emitting at 850nm. After 20 minutes, a solution of TMSi$_3$As in TOP was added via syringe pump over several hours. Aliquots were taken periodically to monitor absorbance and emission properties. When the emission of the QDs reached the desired wavelength, the addition of TMSi$_3$As was halted and the solution cooled to room temperature. Absorbance and emission spectra were taken without purification. When necessary, appropriate blanks were used to collect absorbance spectra.

![Absorbance and Photoluminescence spectra](image)

Figure 3-5: Absorbance (a) and Photoluminescence (b) spectra of Cadmium Arsenide QDs during a single synthesis. Gold spectra were taken after the initial fast injection of TMSi$_3$As but before the beginning of additional precursor injection by syringe pump, while Cardinal spectra were taken during the continuous addition of additional precursor by syringe pump.

I arrived at the seeded growth strategy after being unable to synthesize monodisperse samples of Cd$_3$As$_2$ QDs emitting beyond 1.5μm using the more common single injection approach. I observed sharpening of the spectral features upon beginning the syringe pump injection (figure 3-5). Measurements of particle size before and after
beginning the syringe pump injection show that the particle size increases commensurate with the additional precursor added through the syringe pump. Between the beginning and the end of the continuous addition of arsenic precursor, the particle volume increased by a factor of \(\sim 10\). The amount of TMSi\(_3\)As added during the continuous injection step was 10 times the amount added during the initial injection. Therefore, particle growth is primarily due to the addition of new material to existing nuclei and not an Ostwald ripening mechanism that would result in a loss of nuclei and a log-normal size distribution\[71\]. \(^1\)H NMR confirms that TMSi\(_3\)As is completely depleted after exposure to cadmium(II) myristate (figure A-2), eliminating the possibility that the increase in QD size is due to incomplete reaction and particle ripening. This implies that the precursor addition rate that I selected is slow enough to inhibit the formation of new particles. In addition, analysis of the full-width at half max (FWHM) of the emission peak shows that addition of precursor results in a narrowing of emission peak width by \(\approx 35\%\) (figure 3-6).

Figure 3-6: Emission peak location and full-width at half-maximum (FWHM) showing decrease in FWHM and accelerated growth rate after beginning the syringe pump injection.

QYs measured immediately after removal from the growth solution using an integrating sphere ranged as high as 85% for some samples with emission peaks of
\~900nm. More typical values ranged from 20\% to 60\%. The measured QYs decreased substantially for larger particles (figure A-1). This decrease could result from increased rates of multiphonon relaxation for dots with narrower band edges in accordance with the energy gap law[19]. Like most other IR-emitting materials, Cd$_3$As$_2$ QDs were found to be air sensitive with QYs declining to <1\% after a few days in ambient conditions (figure 3-9).

### 3.5 Structural and Chemical Characterization of Cd$_3$As$_2$ QDs

Following growth, the solution was transferred to a glovebox with a nitrogen atmosphere to prepare samples for structural characterization. The growth solution was purified by adding a small amount of acetone to induce flocculation and then centrifuging. The supernatant was discarded and the resulting precipitate was re-dispersed in hexane or chloroform. This process was repeated three times before drop-casting onto a TEM grid or silicon zero-background holder for wide angle x-ray scattering (WAXS). WAXS measurements were performed in a helium flow cell because the Cd$_3$As$_2$ QDs were found to be unstable in air. Although all practical steps to eliminate air exposure were taken, both TEM and XRD measurements exposed the samples to air for \~5s.

The WAXS pattern is consistent with that expected for \(\alpha\)-Cd$_3$As$_2$, the stable room temperature phase of Cd$_3$As$_2$ (figure 3-8). However, due to the broadening associated with small crystallite size, the \(\alpha'\) and \(\beta\) phases cannot be excluded. Application of the Scherrer formula implies an average crystallite size of 2.5nm. This is consistent with the size observed by TEM. It should be noted that due to the large unit cell of \(\alpha\)-Cd$_3$As$_2$ (\(a=12.65\AA, c=25.44\AA\))[72], a 2nm diameter QD has a volume equivalent to roughly one unit cell. Elemental analysis was performed using energy dispersive x-ray spectroscopy (EDS) within the TEM. The average ratio of cadmium to arsenic was measured to be 3:2 to within experimental error (table A.2).
Figure 3-7: (a) TEM of 2.2nm Cd$_3$As$_2$ QDs with emission peak at 1.33eV, (b) 4.5nm Cd$_3$As$_2$ QDs with emission peak at 0.76eV. Scalebar is 20nm for both (a) and (b).

Figure 3-8: WAXS of Cd$_3$As$_2$ QDs with an emission peak at 1000nm. The pattern was collected with Cu Kα radiation using a helium flow cell. The blue lines represent expected peak values for α-Cd$_3$As$_2$ (PDF 00-056-0233).
3.6 Overcoating of Cd$_3$As$_2$ QDs

A high bandgap shell has proven essential for maintaining stability and maximizing quantum yield for II-VI and III-V semiconductor QDs[9]. Cadmium phosphide (Cd$_3$P$_2$) was identified as a potential shell material due to its similar crystal structure and larger bandgap ($E_g \sim 0.5eV$)[58, 73]. An amount of TMSi$_3$P equivalent to 1-2 monolayers was dissolved in TOP and added dropwise to a solution of $\sim$2.5nm diameter Cd$_3$As$_2$ QDs at 175°C. Addition of TMSi$_3$P resulted in continuous redshifting of ensemble emission (figure 3-9), which suggests weaker confinement of the exciton as QD size increases as TMSi$_3$P reacts to form Cd$_3$P$_2$ on the dot surface. Elemental analysis of Cd$_3$As$_2$(Cd$_3$P$_2$) QDs by EDS confirmed that the dots had an atomic composition of 62.7% Cadmium, 10.5% Arsenic, and 26% Phosphorous. The ratio of phosphorous to arsenic measured by EDS is consistent with the ratio added to the reaction (3:1 P:As). The shell growth was found to significantly extend the shelf-life of Cd$_3$As$_2$ QDs stored in ambient conditions (figure 3-9). The shell provided sufficient stability to observe emission after surfactant exchange and dissolution in water, although the QY was <1% after exchange (figure 3-10). During exposure to air or water, the emission peak of the core-shell structure blueshifts. The blueshifted spectrum of a core-shell solution resembles the emission spectrum of the Cd$_3$As$_2$ cores (figure 3-9), suggesting that the shell is dissolving or deteriorating. The decrease in QY is consistent with shell deterioration.

A similar attempt to grow Cd$_3$As$_2$(CdS) core shell QDs was made, despite the fact that the crystal structure(s) of CdS are incompatible with defect free epitaxial growth on Cd$_3$As$_2$ particles. Cd$_3$As$_2$ particles were synthesized by adding 0.05 mmoles of TMSi$_3$As in 0.8mL of TOP to a solution containing 0.3 mmoles of cadmium(II) myristate at 150°C. After 15 minutes, when the Cd$_3$As$_2$ particles had an absorbance peak of $\sim$760nm, I began dropwise addition of 0.15 mmoles of bis(trimethylsilyl)sulfide in 3mL of TOP at a rate of 1.5mL/hr. As the sulfur was added to the solution, the absorbance and emission peaks redshifted and broadened (figure 3-11). The QY of the Cd$_3$As$_2$ cores just before the addition of sulfur was measured to be 45%. No
decrease in QY was observed after the addition of the first 1.5mL of sulfur solution, however, the QY of the final core-shell material fell to 22% after the addition of the complete 3mL of sulfur solution. The QY fell to 4% after purification and to <1% after two days in ambient conditions. Although the redshift in optical spectrum during overcoating suggests shell growth, it does not appear that the growth of a CdS shell provided significant additional stability toward deterioration in ambient conditions.
Figure 3-9: (a) QY measurements showing enhanced stability of Cd$_3$As$_2$(Cd$_3$P$_2$) core-shell QDs relative to cores. Emission spectra showing (b) redshift upon addition of TMSi$_3$P and (c) blueshift upon aging in air. QD samples were stored in NMR tubes under identical ambient conditions during this experiment.
Figure 3-10: $\text{Cd}_3\text{As}_2(\text{Cd}_3\text{P}_2)$ QDs before and after water solubilization with PEG-PIL.

Figure 3-11: $\text{Cd}_3\text{As}_2(\text{CdS})$ core-shell QDs.
3.7 Photodetectors from Cd$_3$As$_2$ QDs

The development of solution processable infrared optoelectronic devices is one of the main motivations for the synthesis of infrared emitting QDs. Therefore, we set out to determine whether cadmium arsenide QDs could be used as the active absorbing medium for a simple photoconductor using similar techniques to those applied to other colloidal QDs.

As synthesized, QDs are surrounded by hydrophobic surfactant molecules—typically the conjugate bases of fatty acids. These ligands bind to the surface of the QD, providing solubility and mediating particle growth in organic solvents. They also passivate surface states and help balance charge, providing chemical stability and improving optical properties. However, the long hydrocarbon chains that provide stability in hydrophobic solvents represent an insulating barrier that limits the interdot movement of charge carriers. In order to reduce this barrier and improve the conductivity of QD films, the ligands with long alkyl chains are exchanged for ligands with much shorter chains, often with linker molecules believed to bring adjacent QDs into intimate contact. The investigation of surface modifications of QDs for thin film devices has been driven by a great interest in solution processable solar cells—particularly PbS QD solar cells.

We developed a simple proof of principle photoconductor made of Cd$_3$As$_2$ QDs that shows that established techniques for the manipulation of QD thin films can be applied to this unusual material.

A purified sample of Cd$_3$As$_2$ QDs with an absorbance peak at 1150nm was redissolved in octane and spin-coated onto a silica substrate with interdigitated gold electrodes with 10$\mu$m spacing. After overcoating, ligand exchange was performed in the film by soaking in a solution of 1,3 benzenedithiol in acetonitrile and washing with acetonitrile. EQE was measured as a function of wavelength (figure 3-12), by using a spot size limited excitation and comparing the photocurrent to the response of a calibrated germanium detector.
Figure 3-12: EQE measurement of a photoconductor made from a film of Cd$_3$As$_2$ QDs. The absorbance spectrum of the QDs in hexane is overlayed. It is apparent that quantum confinement is maintained. The device was operated at 50V of bias.

### 3.8 Conclusion

Cd$_3$As$_2$ QDs were synthesized with narrow size distributions and a broad range of size tunability that enabled them to emit between 530nm and 2000nm. Although we were unable to successfully stabilize the particles in ambient conditions, their properties were found to be quite stable under inert conditions. The high quantum yields in the NIR make them promising candidates for emissive applications in that spectral range where they can be protected from oxygen and water, such as device applications including LEDs or downconversion.

Additional experimental details and figures are available in appendix A.
Chapter 4

Group-V Precursors for InP and InAs QD Synthesis

Reproduced in part with permission from [74]. Copyright 2012 American Chemical Society.

4.1 Introduction

Indium phosphide (InP) and indium arsenide (InAs) QDs have proven difficult to synthesize with the narrow size distributions characteristic of cadmium selenide (CdSe) and lead selenide (PbSe) QDs[44]. InP QDs are of interest for applications that require cadmium-free, visible-emitting QDs, while InAs is of interest for applications involving near-infrared emission. Rapid precursor conversion rates for the group-V precursors used in InP and InAs QD synthesis are believed to prevent the formation of QD ensembles with narrow particle size distributions[44]. In this chapter, I identify less reactive precursors for phosphorous and arsenic containing QDs and show that they can enable the synthesis of QDs with narrower size distributions than existing precursors.

Walker and Allen’s study[44] of the InP QD growth mechanism revealed that the role of precursor conversion in the growth of InP QDs is fundamentally different than the role of precursor conversion in the growth of CdSe[75] and PbSe[76]
QDs. In particular, it was found that the selenium precursor conversion rate limits the formation and growth of CdSe and PbSe QDs, while the phosphorous precursor conversion precedes InP particle growth. Following precursor conversion, InP QD growth proceeds via a ripening process associated with a broadening of the particle size distribution[44, 75, 43, 77, 76, 42].

Despite the perceived importance of precursor reactivity for the synthesis of high quality QDs, little progress has been made toward the development of less reactive group-V precursors. To date, most reports of high quality III-V QDs have used tris(trimethylsilyl)arsine (TMSi$_3$As) or tris(trimethylsilyl)phosphine (TMSi$_3$P) as a group-V source. Joung et al. reported that by using tris(tert-butyldimethylsilyl)phosphine, they were able to make larger InP QDs than by using TMSi$_3$P[78]. However, they did not attempt to characterize the precursor reactivity, nor did they show an improvement in size distribution.

We wanted to see if we could reduce precursor reactivity by using a group-V source that did not contain a labile Si-P or Si-As bond. A previous study of tris(trimethyl-group-IV)stibines mentioned that the thermal and air stability of the stibines increased as the group-IV element changed from silicon to germanium to tin[79]. We speculated that tris(trimethylgermyl)arsine and tris(trimethylstannyl)arsine and their phosphorous analogues might be less reactive precursors for the synthesis of III-V QDs. We have synthesized these molecules and used them to make InAs and InP QDs. We have also measured their reaction kinetics using UV-Vis and NMR spectroscopy and shown them to be less reactive than TMSi$_3$As and TMSi$_3$P.

### 4.2 Precursor Synthesis

Tris(trimethylsilyl)arsine (TMSi$_3$As) and the similar molecules TME$_3$V (E=Si, Ge; V=P, As) were synthesized for evaluation as QD precursors. Previous syntheses of TMGe$_3$V have relied on the direct reaction of chlorotrimethylgermane (TMGeCl) with (NaK)$_3$(P,As)[79]. Instead, we synthesized TME$_3$V from TMSi$_3$V using an adaptation of a technique previously used to synthesize TMGe$_3$Sb and TMSn$_3$Sb.
from TMSi₃Sb[80]. TMGe₃As was synthesized by mixing TMSi₃As with an excess of TMGGeCl and heated. Because the boiling point of chlorotrimethylsilane (TMSiCl) is lower than that of TMGGeCl, the exchange is driven to completion as the TMSiCl is distilled off of the reaction mixture to leave the desired product. This procedure was also adapted to make TMSn₃As and TMSn₃P.

### 4.3 QD Synthesis and Characterization

#### 4.3.1 QD Synthesis

In order to determine if these molecules would be useful for synthesizing high quality colloidal QDs, QDs were prepared by reaction with indium(III) myristate (InMy₃) using the different group-V sources under otherwise identical conditions[68]. Aliquots were removed from the growth solution and characterized by measuring absorbance spectra (figures 4-1 - 4-2). In order to ensure that the results were as comparable as possible, all experimental parameters were kept the same (stirring rate, flask size, etc). The absorbance spectra for the aliquots from the indium phosphide solutions prepared using TMGe₃P and TMSi₃P were similar (the absorbance peak from the TMGe₃P sample was slightly better defined), but the absorbance spectra from the aliquots from the indium arsenide solutions prepared from TMGe₃As showed significantly better defined features than those prepared from TMSi₃As (the HWHM of QDs prepared from TMGe₃As is 37nm (101meV) vs. 45nm (120meV) for TMSi₃As, a 21% difference). The sharp features in the absorbance spectrum are an indication of a narrow particle size distribution, suggesting that the indium arsenide particles prepared from TMGe₃As have superior size distributions than those prepared from TMSi₃As. Particles synthesized in this way were further characterized by photoluminescence spectroscopy, transmission electron microscopy (TEM), and X-ray diffraction (XRD) (figures 4-1 - 4-4). Attempting the same synthesis using TMSn₃P and TMSn₃As did not produce QD samples with sharp absorbance features.

The optical data show that InAs QDs have better defined absorbance features
Figure 4-1: Absorbance and PL spectra for the synthesis of InAs QDs made from TMSi$_3$As and TMGe$_3$As. PL spectra were collected with 500nm excitation.

when synthesized from TMGe$_3$As, however, the absorbance peaks occur at similar locations for TMGe$_3$As and TMSi$_3$As. Conversely, InP made from TMGe$_3$P and TMSi$_3$P show similar peak shapes, but the TMGe$_3$P produces slightly larger QDs (though this difference in absorbance peak fades as the particles grow). Structural characterization by TEM (figure 4-3) and XRD (figure 4-4) do not reveal any qualitative differences.
Figure 4-2: Absorbance and PL spectra for the synthesis of InP QDs made from TMGe$_3$P and TMSi$_3$P. PL spectra were collected with 400nm excitation.
Figure 4-3: TEM images of InAs made from TMSi$_3$As (A), TMGe$_3$As (B), and InP made from TMSi$_3$P (C), and TMGe$_3$P (D).

Figure 4-4: XRD of InAs and InP QDs synthesized with the different precursors.
4.4 Measurement of Precursor Reaction Kinetics

During QD synthesis, it was observed that the color change that occurred upon injection of group-V precursor seemed to occur smoothly over several seconds for the TMGe₃V precursors, while nearly instantaneously for the TMSi₃V precursors. In order to quantify this observation, an absorbance dip probe was used to measure the rise in absorbance after precursor injection at 130°C, the injection temperature used for QD growth.

4.4.1 *in situ* UV-Visible Absorbance Spectroscopy for Measurement of Particle Formation

Previous experiments have indicated that the extinction coefficient of QDs in the UV region scales with particle volume[43, 81]. Thus we used the absorbance at 310nm to monitor the formation of InAs and InP clusters (figure 4-5a-b). Although the absorbance in the UV rose quickly, the particles did not show absorbance features without heating at elevated temperature. In order to directly compare the rate of absorbance rise upon injection of the two different precursors, a large excess of indium(III) myristate was used and the TMGe₃As and TMSi₃As solutions were injected alternately. This eliminated any source of error from variations in concentration. The absorbance rise appeared to be insensitive to when in the injection sequence they occurred. When the absorbance traces were normalized by the intensity change and overlaid for comparison, the two traces for each precursor were nearly identical (figure 4-5c-d). These results clearly show that the particle formation occurs more slowly for the TMGe₃V precursors than for the TMSi₃V precursors, suggesting that the precursor conversion is the rate limiting step in small particle or cluster formation— at least for particles synthesized using the TMGe₃V precursors. In fact, the absorbance rise for the TMSi₃V based precursor occurs on a timescale that is competitive with the time required for mixing. Although these data clearly show that the absorbance rise is much slower for the TMGe₃V precursors than for the TMSi₃V precursors, the data are difficult to directly attribute to molecular precursor conversion.
Figure 4-5: Absorbance traces during precursor injection at 130°C for InP (a) and InAs (b). The injection of silyl-V and germyl-V precursor was alternated so that the absorbance rise could be directly compared. The absorbance rise at 310 nm (from a,b) is normalized truncated, and adjusted so that each injection is plotted with t=0 (c, d). The TMSi₃V precursor injections in (c) and (d) are offset for clarity.
4.4.2 \(^1\)H NMR Spectroscopy for Measurement of Precursor Reaction Kinetics

In order to compare the rates of molecular precursor conversion, NMR spectroscopy was used to monitor the evolution of precursor concentration in time.

An NMR tube was loaded with InMy\(_3\) (1-5mM) and tri-n-octylphosphine (TOP) (30mM) in 680\(\mu\)L of d8-toluene. Just before the NMR tube was inserted into the instrument, a solution containing both group-V precursors was injected (20 \(\mu\)L, [TMGe\(_3\)P]=[TMSi\(_3\)P]=4mM). A time series of NMR spectra (figure 4-6a) shows that the TMSi\(_3\)P peak disappears much faster than the TMGe\(_3\)P peak. The reaction was performed under pseudo-first order conditions, where the concentration of indium was >10x that of the phosphorous or arsenic. Exponential fits to the data indicate that under these conditions the reaction rate of TMSi\(_3\)P is more than 4x faster than the reaction rate of TMGe\(_3\)P. The concentration of TME\(_3\)P over time was consistent with a reaction with first order dependence on phosphorous precursor (figure 4-6b). An intermediate was observed (figure 4-6a) that was believed to be similar to that reported for the reaction of InMy\(_3\) with TMSi\(_3\)P in the presence of amines[68]. This intermediate peak is observed to be present when the TMGe\(_3\)P precursor is allowed to react without the presence of the TMSi\(_3\)P precursor, and a second intermediate is also observed (figure 4-7). The second intermediate occurs at 0.28ppm and is obscured by the presence of TMSi-Myristate in figure 4-6.

A similar experiment was performed with the two arsenic precursors. However, the reaction rate of TMSi\(_3\)As was too fast to observe, as no TMSi\(_3\)As remained after the NMR tube containing the reaction mixture had been inserted into the NMR spectrometer and the instrument prepared for acquisition. However, the reaction of TMGe\(_3\)As was readily observed to proceed from TMGe\(_3\)As to TMGe-myristate. By assuming that the height of any remaining TMSi\(_3\)As peak in the NMR spectrum was less than the level of the noise, and because the time between precursor mixing and the acquisition of the first spectrum was <1.5 minutes, we can infer that the rate constant for the reaction of TMSi\(_3\)As was at least 30x faster than the reaction
Figure 4-6: A time series of NMR spectra showing simultaneous reaction of TMSi$_3$P and TMGe$_3$P with 2.5mM InMy$_3$ (a), integrated peak area for TMSi$_3$P and TMGe$_3$P normalized and plotted on a semilog plot (b), and integrated peak areas normalized by total proton concentration associated with the corresponding TME-peaks (c).
Figure 4-7: $^1$H NMR spectra showing the evolution of the precursor concentration as well as two intermediates for the reaction of TMGe$_3$P with InMy$_3$. The reaction solution was 3mM InMy$_3$. 
Figure 4-8: Order plot for the reaction of TMGe₃As with InMy₃ obtained from rate constants fit from ¹H NMR data.

rate of TMGe₃As under the same conditions. We also found that we could slow the reaction rate by increasing the concentration of TOP, an effect similar to that observed previously with indium phosphide and octylamine\[44\].

In order to further characterize the reaction between InMy₃ and TMGe₃As, the concentration of InMy₃ was varied and the reaction was determined to be second order in indium (figure 4-8). This result differed from the reaction order determined by observing the absorbance rise times with varying concentrations of indium at 130°C (figure 4-9). The apparent discrepancy between the reaction order observed using these two sets of conditions and measurement techniques suggests a chemical mechanism that is sensitive to changes in temperature, TOP concentration, or both.
4.5 Hydrolysis Products

After the publication of our report of precursor chemistry for III-V QD synthesis, Gary et al. reported on the reactions of acidic protons with TMSi₃P to form secondary and primary phosphines[74, 82]. They predicted that the formation of these species would be catalytic—that they would provide a faster chemical mechanism for the formation of InP. We hypothesized that the “intermediates” that we observed in figure 4-7 may have been hydrolysis products described by Gary et al. This was confirmed by synthesizing the primary and secondary phosphine analogs by adding methanol to the original precursor and characterizing using ³¹P and ¹H NMR spectroscopy. Assignment of structure to bis(trimethylgermyl)phosphine and trimethylgermylphosphine was done using the peak splitting due to ¹Jₑ₃⁻₇ coupling of the ³¹P NMR peaks in a manner characteristic of R₂PH or RPH₂ (figures B-2 - B-3). By comparison to the results of Gary et al., we see that the intermediate observed by Allen and Walker has a ³¹P chemical shift consistent with that of (TMSi)₂PH[82, 68].

Acidic protons are required in order for these species to form. Although we made every effort to exclude myristic acid and water, it is apparent that the reaction of the precursor with either trace quantities of acid or water are significant. In order to explore how these impurities might affect the precursor conversion, I added water.
or acid to a nominal concentration of approximately 3mM and compared the rate of disappearance of TMGe$_3$P. I found that the reaction actually slowed when these impurities were added (figure 4-10).

Therefore, the presence of acid and water actually slow the depletion of TMGe$_3$P rather than provide a catalytic pathway (figure 4-10). Furthermore, because the NMR signal from the hydrolysis products of TMGe$_3$P is much higher than it is for the hydrolysis products of TMSi$_3$P, we can conclude that the hydrolysis of TMGe$_3$P occurs much more readily than for TMSi$_3$P. The two precursors seemed to behave differently in the presence of acidic protons, with TMGe$_3$P reacting much more readily to form higher concentrations of primary and secondary phosphines.

### 4.6 Conclusion

We identified two precursors for III-V QD growth that are less reactive and produce particles with similar or superior properties. We have shown that TMGe$_3$As can be used to significantly improve the size distributions of InAs QDs and have shown that the rates of precursor conversion are slower for the TMGe$_3$V precursors than for their TMSi$_3$V analogues (TMGe$_3$P reacted 4x more slowly than TMSi$_3$P, while TMGe$_3$As reacted at least 30x more slowly than TMSi$_3$As). Although even the less reactive germanium based precursors react completely before the particles reach their
final size, the use of TMGe$_3$As still results in significant improvements in InAs QD size distribution. This may be because the precursor conversion has been slowed sufficiently that precursor conversion occurs on a timescale slower than mixing. As a result, the size distributions of clusters may be more uniform and therefore result in a more uniform size distribution of QDs following the ripening step.

We also determined that the different chemistry of the phosphorous precursors resulted in mechanistic differences that were not expected. Despite the apparent difference in the hydrolysis behavior observed by NMR, the nanocrystals formed by the two InP precursors were remarkably similar. However, the comparison of only two precursors does not provide enough information to draw general conclusions about nanocrystal growth.

Additional experimental details and figures are available in appendix B and the supporting information of [74].
Chapter 5

Systematic Study of Precursor Reactivity and Particle Formation

Daniel Franke and I worked together on the work described in this chapter. Some of these experiments are described in his Master’s thesis[83].

5.1 Motivation and Precursor Selection

In order to more fully study the effect of precursor conversion, we set out to synthesize and characterize additional precursors for the synthesis of InAs and InP QDs. Although this chapter describes experiments that are similar to those in chapter 4, it focuses more on interpreting the results from a systematic study of precursor reactivity and QD growth using the characterization techniques and conditions developed in the previous chapter.

Our experience revealed that molecules with Ge-P[As] and Si-P[As] bonds produced QDs cleanly without insoluble byproducts. Therefore, we proposed the molecules for phosphine and arsine precursors seen in figure 5-1. Bulkier alkyl groups were selected with the expectation that they would slow the reaction through steric hindrance.
5.2 Precursor Synthesis

The reactive distillation scheme described in the previous chapter is attractive because it allows the rapid, one step synthesis of small quantities of precursors. Therefore, we initially pursued the synthesis of all of the molecules in figure 5-1. However, we found that this technique was unsuccessful for the synthesis of tris(isopropylidimethylsilyl)phosphine[arsine]. It was, however, successful for the synthesis of tris(triethylgermyl)phosphine[arsine].

Tris(triethylgermyl)phosphine[arsine] were synthesized by mixing tris(trimethylsilyl)phosphine[arsine] (4 mmoles) with excess triethylgermanium chloride (16 mmoles) under inert conditions. The mixture was placed in a distillation setup, and the reaction was heated to 140°C under argon. The boiling point of trimethylsilyl chloride is 57°C, so any trimethylsilyl chloride produced during the reaction would condense in the receiving flask. The boiling point of triethylgermanium chloride is 176°C[84]. After the reaction was complete, the remaining excess triethylgermanium chloride was removed by vacuum distillation. After evolution of the triethylgermanium chloride, the remaining product was purified by vacuum distillation.
5.3 QD Synthesis

5.3.1 Batch Mode

Synthesis of QDs in batch mode was performed in a manner similar to that in the previous chapter. A stock solution of InMy₃ (75mM) in octadecene was prepared and split into flasks (4mL each) for the synthesis of QDs from each precursor. After degassing on a schlenk line at 100°C for 30 minutes to a pressure of <10 mtorr, the solution was placed under argon and heated to 130°C. With vigorous stirring, 0.1 mmoles of arsenic or phosphorous precursor were rapidly injected through a septum. After 4 minutes, the temperature controller was set to 220°C. After 20 minutes, the heating mantle was removed and the solution was allowed to cool. Aliquots were taken periodically at the same times for each precursor. Figures 5-2 - 5-3 show the evolution of QD absorbance spectra during particle growth from different precursors.

As is clear in figures 5-2 and 5-3, the QDs synthesized from the various precursors have different sizes and size distributions. All absorbance spectra are unscaled, and UV absorbance can therefore be qualitatively interpreted as related to total concentration of InP or InAs. For InAs, it is clear that the precursors have reacted completely by the time of the first aliquot (figure 5-2), whereas for InP, it appears that iPrDMSi₃P has yet to react completely by the first aliquot. It does, however, seem to be completely reacted (absorbance is saturated) by the second aliquot at 7 minutes. For InAs (figure 5-2) the QDs made from TMGe₃As and TMSi₃As seem to have the sharpest, bluest absorbance peaks, while TEG₃As and iPrDMSi₃As have less well defined, redder absorbance peaks. This could be caused by less reactive precursors. The situation for InP is qualitatively similar, with the exception of QDs grown from iPrDMSi₃P. This sample shows less intense absorbance at all wavelengths, and no absorbance peak. This could be due to a precursor reactivity that is too low to produce QDs at the temperatures used in this experiment.
Figure 5-2: Absorbance spectra of different aliquots of InAs QDs showing how samples from different precursors lead to different peak shapes and locations

Figure 5-3: Absorbance spectra of different aliquots of InP QDs showing how samples from different precursors lead to different peak shapes and location
5.3.2 Microfluidic Synthesis

During a QD growth by hot injection, experimental parameters (e.g., temperature) are constantly changing during the reaction. The time dependence of temperature, the injection speed, stirring rate, etc. are all difficult to reliably reproduce and characterize. Growing QDs in a continuous flow reactor makes it possible to produce QDs from a system at steady state. This makes it easier to minimize variations in experimental conditions, and is a technique that is well suited to comparing QDs grown from different precursors at otherwise identical conditions.

This work uses a two-stage silicon microfluidic reactor[85] for QD growth. In the first stage, precursors are mixed and maintained at a (relatively low) “mixing temperature.” In the second stage, the temperature is increased for QD growth. A schematic of the reactor is shown in figure 5-6. The two-stage microfluidic reactor mimics growth in batch mode by combining the reagents at low temperature, then heating to drive QD growth.

Microfluidic synthesis was used to isolate the effect of precursor chemistry on QD growth and to observe this as a function of mixing and aging temperatures. Although the precursors are the same as those used in batch synthesis, there are several modifications to the reaction solution that must be made in order to accommodate the microfluidic synthesis. These differences are summarized in table 5.1.

<table>
<thead>
<tr>
<th></th>
<th>Batch Mode</th>
<th>Microfluidic Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>[InMy₃]</td>
<td>60 mM</td>
<td>30 mM</td>
</tr>
<tr>
<td>[R₃(IV)₃V]</td>
<td>30 mM</td>
<td>10 mM</td>
</tr>
<tr>
<td>Mixing Time</td>
<td>4 minutes (before temp increased)</td>
<td>2 minutes</td>
</tr>
<tr>
<td>Aging time</td>
<td>20 minutes</td>
<td>4 minutes</td>
</tr>
<tr>
<td>Solvent</td>
<td>ODE</td>
<td>supercritical octane</td>
</tr>
<tr>
<td>Temperature Gradient</td>
<td>gradual heating over 5 minutes</td>
<td>sharp</td>
</tr>
</tbody>
</table>

Table 5.1: Comparison of experimental conditions in batch mode and microfluidic reactors

Because of the differences in temperature gradients, residence time, and solvent viscosity, the results from a microreactor growth with mixing temperature of 130°C and growth temperature of 220°C cannot be directly compared to a batch mode
Figure 5-4: Absorption spectra of InAs QDs grown from TMGe₃As and TMSi₃As. The mixing temperature was 130°C for all samples. The aging temperature is as indicated. (Data collected by Jinyoung Baek)

The results of figure 5-4 are striking. They suggest that precursor chemistry is important only at modest QD growth temperatures. At high temperature, the absorbance spectra are indistinguishable and the growth behavior is dominated by thermal processes independent of the precursor chemistry. The results with the phosphine precursors in figure 5-5 reveal that differences in growth behavior persist at higher temperatures for the phosphine precursors. The QDs grown from TMSi₃P at growth temperatures above 220°C all show well defined absorbance peaks, while for QDs grown from TEG₃P and iPrDMSi₃P, well defined spectral features do not appear until 320°C. TMSi₃P has the sharpest peak definition of the three, with iPrDMSi₃P having the poorest. These results suggest that the InP QDs are affected by precursor kinetics at growth temperatures much higher than InAs QDs grown under similar conditions.
Figure 5-5: In the top row, growth temperature is fixed at 320°C and mixing temperature is varied as indicated. In the bottom row, mixing temperature is fixed at 130°C and growth temperature is varied. (Data collected by Lisi Xie)
Figure 5-6: A diagram of a two stage microfluidic reactor for the synthesis of colloidal QDs in supercritical octane. The first stage is for precursor mixing and initial reaction (a); the second stage is for heating and QD growth. The temperatures of the two stages are controlled independently. Reproduced from [85]
5.4 Characterization of Reactivity

5.4.1 NMR

Unfortunately, $^1$H NMR did not prove to be as useful a technique for the characterization of the reactivity of iPrDMSi$_3$As, TEG$_3$As, iPrDMSi$_3$P and TEG$_3$P. The triethylgermanium species do not have a $^1$H spectrum well suited for this type of experiment because the peaks of the protons are split to a triplet and a quartet. However, iPrDMSi$_3$As and iPrDMSi$_3$P both have singlet peaks in their $^1$H spectra from the two methyl groups. We attempted to apply the same experimental setup developed in the previous chapter to iPrDMSi$_3$As and iPrDMSi$_3$P, but we found that the precursors did not react at these conditions at a rate that was practically observable (figures 5-7 - 5-11). The experiment duration and the signal to noise ratio allow us to put a lower bound on the rate constant by assuming a pseudo first order rate law. The time constants obtained for these reactions are summarized in table 5.4.1.

\[ N > S(1 - e^{-t/\tau}) \]  \hspace{2cm} (5.1)

\[ \tau > \left( \frac{t}{\ln \left( 1 - \frac{1}{S/N} \right)} \right) \]  \hspace{2cm} (5.2)

We also considered using $^{31}$P NMR to study the phosphorous precursors. Unfortunately, this did not prove to be practical due to the decreased sensitivity of the $^{31}$P

<table>
<thead>
<tr>
<th>Precursor</th>
<th>TMSi$_3$P</th>
<th>TMGe$_3$P</th>
<th>iPrDMSi$_3$P</th>
</tr>
</thead>
<tbody>
<tr>
<td>[InMy$_3$]=$2.5$mM</td>
<td>[InMy$_3$]=$3$mM</td>
<td>[InMy$_3$]=$3$mM</td>
<td>(&gt;150,000)</td>
</tr>
<tr>
<td>(\tau) (s)</td>
<td>307</td>
<td>1316</td>
<td>(&gt;150,000)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Precursor</th>
<th>TMSi$_3$As</th>
<th>TMGe$_3$As</th>
<th>iPrDMSi$_3$As</th>
</tr>
</thead>
<tbody>
<tr>
<td>[InMy$_3$]=$5$mM</td>
<td>[InMy$_3$]=$5$mM</td>
<td>[InMy$_3$]=$5$mM</td>
<td>(&gt;25,000)</td>
</tr>
<tr>
<td>(\tau) (s)</td>
<td>(&lt;45)</td>
<td>77</td>
<td>(&gt;25,000)</td>
</tr>
</tbody>
</table>

Table 5.2: Reaction time constants obtained by $^1$H NMR for phosphine and arsine precursors. Indium myristate concentrations are as indicated. The solvent was conducted in 30mM TOP in d$_8$ toluene at 22°C[83].

83
Figure 5-7: \(^1\text{H} \) NMR spectra of TMGe\(_3\text{As}\) and iPrDMSi\(_3\text{As}\) reacting with 5mM InMy\(_3\), 30mM TOP in d8 toluene at 22°C[83].

Figure 5-8: Relative concentrations of TMGe\(_3\text{As}\) and iPrDMSi\(_3\text{As}\) during reaction with 5mM InMy\(_3\), 30mM TOP in d8 toluene at 22°C[83].
Figure 5-9: $^1$H NMR spectra of TMGe$_3$P and iPrDMSi$_3$P reacting with 5mM InMy$_3$, 30mM TOP in d8 toluene at 22°C[83].

Figure 5-10: Relative concentrations of TMGe$_3$P and iPrDMSi$_3$P during reaction with 5mM InMy$_3$, 30mM TOP in d8 toluene at 22°C[83].
5.4.2 UV-VIS

Although we were unable to observe the reaction of these precursors by NMR spectroscopy, their reduced reactivity should make them well-suited to the in situ absorbance measurements performed in the previous chapter. This data is perhaps more useful than the NMR experiments since the conditions much more closely approximate those actually used for the synthesis of QDs. Figures 5-12 and 5-13 show the absorbance rises following precursor injection.

For indium arsenide, the data show a striking decrease in the rate of absorbance rise following injection of TEG$_3$As and iPrDMSi$_3$As compared to TMGe$_3$As and TMSi$_3$As. Absorbance rise traces were collected following the injection of arsenic precursors. 100µL of 25mM solution of arsenic precursor was injected into 20mL of 4.3mM InMy$_3$, 0.6M TOP in octadecene at 130°C. Although quantitative measurement of the absorbance rise is challenging since for iPrDMSi$_3$As and TEG$_3$As, the rise does not fit a single exponential, the rate of absorbance rise can be compared semiquantitatively by fitting to an exponential function with a linear term to account for the slower component of the absorbance rise. The observed time constants are
Table 5.3: Time constants derived from fitting the absorbance rise following the injection of arsenic and phosphorous precursors. *For the TEG₃As and iPrDMSi₃As time constants, a linear term was included in the fit to account for the slow component of the absorbance rise. **For the TEG₃P and TMGe₃P time constants, a biexponential fit was used and the fast time component is presented here.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>τ (s) [lnMy₃]=4.3mM</th>
<th>Precursor</th>
<th>τ (s) [lnMy₃]=50mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMSi₃As</td>
<td>0.44 ± 0.03</td>
<td>TMSi₃P</td>
<td>2.41 ± 0.11</td>
</tr>
<tr>
<td>TMGe₃As</td>
<td>3.31 ± 0.05</td>
<td>TMGe₃P</td>
<td>0.768** ± 0.09</td>
</tr>
<tr>
<td>iPrDMSi₃As</td>
<td>120.4* ± 0.15</td>
<td>TEG₃P</td>
<td>1.63** ± 0.15</td>
</tr>
<tr>
<td>TEG₃As</td>
<td>295.7* ± 0.5</td>
<td>iPrDMSi₃P</td>
<td>68.06 ± 0.20</td>
</tr>
</tbody>
</table>

In situ absorbance measurements were also performed for the injection of the phosphines during formation of InP QDs (figure 5-13). Absorbance traces at 280nm were collected for the injection of 50µL of 60mM solutions of iPrDMSi₃P, TMGe₃P, TEG₃P, and TMSi₃P into a solution that was 50mM InMy₃ with 0.5M TOP in octadecene at 130°C. A summary of time constants obtained from fitting is included in table 5.3. The InP experiment was conducted with a concentration of InMy₃ that was approximately 10x higher than it was for the InAs experiment. I used a higher concentration because at the conditions used for figure 5-12 (4.33mM InMy₃ 0.6M TOP), the absorbance rise of TEG₃P and iPrDMSi₃P occurred over 4 hours or more. This was so slow that the instrument was not stable over the course of the measurement and reliable data could not be obtained. Qualitatively it is clear that the reactivities of TEG₃P and iPrDMSi₃P are greatly reduced compared to TMGe₃P and TMSi₃P at the same conditions. These results are presented in appendix C.
Figure 5-12: Absorbance rise traces following the injection of arsenic precursors. 100μL of 25mM solution of arsenic precursor was injected into 20mL of 4.3mM InMy₃, 0.6M TOP in octadecene at 130°C.

Figure 5-13: Absorbance at 280nm monitored during the injection of 50μL of 60mM solutions of iPrDMSi₃P, TMGe₃P, TEG₃P, and TMSi₃P into a solution that was 50mM InMy₃ with 0.5M TOP in octadecene at 130°C.
5.5 Conclusion

Although we have demonstrated that we can slow precursor reactivity by more than two orders of magnitude via structural modifications to the group-V precursors, our results suggest that reducing precursor conversion rate by itself may not be sufficient to produce III-V QDs with the narrow size distributions and wide range of size tunability that is possible for other QD materials such as CdSe and PbSe. We see that replacing methyl groups with bulkier substituents such as isopropyl or ethyl groups results in much slower reaction kinetics. In addition, iPrDMSi$_3$As, TEG$_3$As, and TEG$_3$P seem to produce slightly larger particles in batch mode synthesis than their more reactive cousins. This trend is qualitatively consistent with theoretical predictions based on various models of nanoparticle growth, but the strength of the effect is much weaker than predicted [39, 52, 42, 33, 86]. However, the observed size distributions are much broader for the QDs made from the less reactive triethylgermyl and isopropyldimethyl precursors. The models suggest that a less reactive precursor should produce fewer “nuclei” initially, and that the growth of these nuclei would be fed by the additional material produced via precursor conversion—resulting in an extended period of size focusing alongside growth.

In order to better understand how precursor conversion rates might affect growth, we turned to microfluidic synthesis of QDs to observe the effect of precursor chemistry at a variety of different mixing and aging temperatures. In figure 5-4, we see that differences in absorption peak location and definition fade as the growth temperature increases to 250°C. At 300°C, the spectra of the QDs grown from the two different precursors are indistinguishable. This suggests that for InAs QDs, the kinetics of precursor conversion during the mixing stage do not impact the final size or size distribution of the particles when grown at sufficiently high temperature.

The behavior of InP QDs grown from different phosphine precursors is somewhat different from that of InAs (figure 5-5). These data show that the particle size and size distribution do depend weakly on the precursor chemistry. It is clear that the particle size distribution for particles grown from less reactive precursors is inferior.
Our results are in agreement with other recent reports of alternative phosphine pre-
cursors [78, 87]. These results indicate that precursor reactivity is not a powerful
tool for the control of QD size and size distribution. Precursor conversion rate has a
much weaker effect on nanocrystal size than theories predict [52, 40], and the small
increase in size comes at the cost of a significantly broader size distribution.

Additional figures of absorption spectra and details of fitting of the absorbance rise data
are available in appendix C.
Chapter 6

Continuous Injection Synthesis of InAs and InP

6.1 Motivation

After pursuing precursor chemistry as a means to try to modulate the kinetics of growth to yield larger particles with narrower size distributions, we found that despite slowing precursor conversion rates by two or three orders of magnitude, the particle size distributions did not improve. Although the mean size of the particles produced was slightly larger, the effect was weak and the larger particles had inferior size distributions. The master equation for the kinetics of particle growth is not sensitive enough to precursor conversion rate to make group V precursor chemistry alone a satisfactory method for controlling particle size and minimizing size distribution.

In the more general approach where coalescence events are considered, the trajectory of an atom of arsenic injected into a reaction solution may involve the formations of smaller clusters that have little memory of the initial precursor conversion rate. That is, that the precursor conversion rate may change only distribution of clusters formed initially. If the coalescence of those clusters is, in fact, the rate limiting step, then precursor conversion rate would be expected to have only a modest effect.

If coalescence becomes slower as particle size increases, then decreasing precursor conversion to a rate such that it is relatively slow compared to particle growth is
expected to produce larger particles with inferior size distributions [52]. This is precisely what was observed by Gary et al.[87] and Joung et al.[78].

Therefore, instead of seeking to control the particle growth by changing only the initial precursor conversion rate constant, we used a continuous injection to modulate the rate itself by limiting concentration. By controlling both precursor chemistry and the rate of precursor addition, we were able to achieve much better control of particle growth than we saw using precursor chemistry alone.

6.2 Historical Perspectives on III-V Synthesis

In the early 1990s, the techniques used to produce high quality CdSe nanocrystals were applied to the synthesis of III-V materials. The earliest such synthesis was reported by the Alivsatos group in 1990 describing the synthesis of GaAs from GaCl$_3$ and TMSi$_3$As[88]. Subsequent reports describe InP[89, 90, 91] and InAs[90, 92]. Most of these reports used InCl$_3$ dissolved in tri-n-octylphosphine (TOP) or tri-n-octylphosphine oxide (TOPO) and required days of reflux to produce nanocrystalline material. None of these methods were able to produce InAs with excitonic absorbance peaks without a size selective precipitation step. This InCl$_3$ synthesis has been used to make InAs cores that are the basis of core-shell structures[93, 66], and as of this writing is still used by some authors when larger QDs are desired[94]. Multiple fast injections of arsenic precursor are used to produce larger particles, though these require size selective precipitation in order to produce narrow size distributions[93].

Although our group has found that this synthesis can produce particles with reasonable size distributions, the synthesis is extremely sensitive to the batch of TOP that is used as a coordinating solvent. TOP and TOPO are well known to contain impurities that have strong effects on QD growth[95, 96]. The nature of the impurities and a detailed characterization of their effect on III-V QD growth has not been undertaken at this time and I have avoided the use of this synthesis for this reason.

In 2002, Battaglia et al. reported the use of indium(III) myristate (and other indium carboxylates) for the synthesis of InAs and InP in a non-coordinating solvent[97].
The authors note that the size distributions obtained by this method are superior to the InCl$_3$ syntheses used previously. Furthermore, this scheme uses less expensive reagents and is less susceptible to impurities that limit reproducibility. However, this procedure is only able to produce relatively small nanocrystals.

<table>
<thead>
<tr>
<th></th>
<th>InP</th>
<th>InAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>InCl$_3$</td>
<td>520-731nm</td>
<td>920-1180nm</td>
</tr>
<tr>
<td>InMy$_3$[97]</td>
<td>500-600nm</td>
<td>600-850nm</td>
</tr>
</tbody>
</table>

Table 6.1: Range of particle absorbance peaks produced by different synthetic methods

For indium arsenide in particular, the limited range of sizes that can be made from InMy$_3$ using this method is problematic because many of the applications require larger dots emitting in the InGaAs range of 900nm-1700nm. Therefore, synthesis of InAs QDs with narrow size distributions that emit in the infrared has been a key goal of this thesis.

### 6.3 Continuous Injection Synthesis of InAs QDs

#### 6.3.1 Standard CI Synthesis of InAs

In order to synthesize InAs QDs with a broader range of sizes and narrower size distributions, we sought to apply the same continuous injection strategy that we used to make Cd$_3$As$_2$ QDs. We chose to use the TMGe$_3$As precursor for the continuous injection synthesis because we observed it to be more thermally stable and more resistant to oxidation in the syringe pump during continuous injection.

A typical CI growth procedure begins with the injection of 0.05 mmol TMGe$_3$As dissolved in 1mL of TOP into a flask containing 1 mmole of indium(III) myristate or indium(III) oleate in 5 mL of ODE at 295°C. After 10 minutes, an aliquot was removed, and a syringe pump injection of 0.17 M TMGe$_3$As in ODE was started at a rate of 1mL/hr. Aliquots were removed periodically and characterized by absorbance (figure 6-1) and photoluminescence (figure 6-3) spectroscopies to monitor the evolution of QD size and size distribution.
We found this procedure to dramatically increase the growth rate of the InAs QDs, and saw that it resulted in significant narrowing of the photoluminescence linewidths. Absorbance spectra (figure 6-1) show that the peak location redshifts dramatically shortly after injection, and the peak definition is significantly narrower (figure 6-3). Photoluminescence linewidths typically shrank to a minimum of around 100-125meV from a starting value of over 200meV for the samples removed from the growth solution at 10 minutes, prior to starting the continuous injection.

The simultaneous redshifting and narrowing of the photoluminescence spectrum is initially very promising. However, the behavior of the system changed after the particles reached sizes of about 4.5-5nm. After the absorbance peak reached a wavelength of approximately 1000-1100nm, the peak definition faded and the growth slowed (figures 6-1, 6-3, and 6-2). To better understand why size focusing occurred at the beginning of the continuous injection and, more importantly, why the size distribution broadened as the absorption peak shifted beyond 1000nm, we compared the particle growth rate with the rate of material added to the reaction solution. We expected that if we could avoid the formation of new particles during growth, then the size distribution would improve. For this to occur, particle volume must increase in lock step with the amount of precursor added to the growth solution. As mentioned in chapter 4, UV absorbance is believed to scale with the quantity of InAs material in solution (independent of particle size). Particle size was calculated using an empirical relationship between diameter and absorption peak developed by Yu et al.[93].

Particle size and total InAs concentration are normalized to the aliquot taken immediately before the beginning of the continuous injection and plotted in figure 6-4. These data clearly show that particle growth is commensurate with precursor addition initially. During this time, the PL linewidth drops rapidly before becoming very broad after about 65 minutes. The minimum FWHM achieved during this synthesis occurs at about 45 minutes, and corresponds to the point on figure 6-4 where the material added and the QD volume diverge. It must result in the formation of InAs that does not relieve the quantum confinement of existing particles. The most obvious interpretation of this result is that material added after 45 minutes results in the
formation of new particles.

To investigate the nature of the broadening of the linewidth during growth, TEM was used to characterize the aliquots taken at 10 minutes, 45 minutes, and 140 minutes. Figure 6-5 shows that the initial 10 minute aliquot and the 45 minute aliquot have approximately spherical shapes with a mean size measured to be 4.5nm by hand from TEM images (N=106). However, the particles in the 140 minute aliquot have asymmetric shapes. These shapes seem to have lobes that do not share the symmetry of the zincblende crystal structure. The average lobe diameter was measured to be approximately 3.5nm (N=35). This is consistent with a growth trajectory in which the particles of 4.5nm diameter coalesce with smaller particles that are not fully absorbed into the parent to form a spherical shape.

Therefore, it appears that the broadening in the optical spectra is driven in part by shape inhomogeneity. In the general model of particle growth, it was assumed that the particle rapidly reorganized to minimize surface energy. Presumably this would be driven by surface diffusion. It appears that as the particles grow larger than \( \approx 4.7 \) nm, where the ensemble absorbance peak reaches about 1\( \mu \)m, this assumption is no longer valid, and the reorganization is slow relative to the frequency of coalescence. For size focusing to continue at sizes greater than 5nm, the new conditions must be modified to minimize shape inhomogeneity. In principle, this could be done either by increasing the rate of surface diffusion to promote reorganization or by decreasing the rate of growth. We believe that increasing the rate of reorganization is a preferable solution, since other processes detrimental to particle growth will have relatively fixed rates (diffusion of oxygen through septa, thermolysis of organic reagents, precursor stability in the syringe, etc.).

6.3.2 CI Synthesis with Changes to Surfactant Mixture

The surface of the nanocrystals is partially passivated by organic surfactants, therefore changing the surfactant composition may be an effective way to increase the rate of surface diffusion. This should suppress the development of shape inhomogeneity.

*This size is slightly smaller than the diameter predicted by the sizing curve (4.7nm) [93].
Figure 6-1: Absorbance spectra of aliquots taken at various times during the continuous injection described in section 6.3.1.
Figure 6-2: Absorbance peak and PL FWHM evolution during continuous injection (section 6.3.1)
Figure 6-3: InAs photoluminescence spectra during continuous injection. (section 6.3.1)
Figure 6-4: The OD at 300nm is proportional to the total concentration of InAs in the growth solution. The QD size is calculated based on the absorbance peak using a sizing curve. The curves initially overlap quite well, suggesting that material added to the growth solution is added to existing particles at first. After about 45 minutes, the particle growth rate appears to slow. (section 6.3.1)
We felt that this was preferable to increasing the temperature above 295°C because the solvent and reagents become unstable at very high temperatures. We have investigated a few possible changes to the surfactant composition in the hopes of enhancing the rate of surface diffusion without disrupting other aspects of the growth. Primarily, we investigated increasing acid concentration and adding amines to the reaction solution. Unfortunately, most of these efforts resulted in either no observable change in growth behavior, or a change so dramatic that particle growth was unacceptably disrupted (for example, by the formation of other inorganic products or turbidity).

However, we did have some modest success by modifying the procedure described in section 6.3.1 to include the injection of 0.17M InMy₃ in oleylamine alongside the arsenic precursor. This produced particles with striking absorbance features (figure 6-6) and emission spectra with linewidths as low as 95 meV (figure 6-7). We see that QD growth continues in line with precursor addition until growth was halted at 145 minutes (figure 6-8). Growth had to be halted for two reasons. The InMy₃ was not well dissolved by oleylamine, so the syringe pump clogged repeatedly. Secondly, the
growth solution became extremely gelatinous, and would bump uncontrollably. This is likely due to the formation of amides via a reaction that evolves water. TEM images reveal that the particle shape is indeed much more spherical than was the case in the previous experiment without amines. However, there is a clear population of small particles visible in the TEM images (figure 6-9). A histogram of particle sizes (figure 6-10) reveals that, in fact, most particles have diameters < 3nm. However, ensemble properties such as absorbance spectra are determined by the volume weighted size distribution (figure 6-11), which peaks near 5nm as expected by the absorbance and PL spectra.

Surfactant chemistry is a promising means to enhance the effectiveness of growth by continuous injection, however care must be taken to ensure that the change of surfactant chemistry does not cause more problems than it solves.
Figure 6-7: Evolution of absorbance peak and PL FWHM during continuous injection (section 6.3.2)

Figure 6-8: Change in particle volume and injected equivalents during continuous injection (section 6.3.2)
Figure 6-9: TEM images of InAs QDs grown by CI without amines (a) and with amines (b)

Figure 6-10: Histogram of InAs QD diameters when grown with oleylamine measured by TEM (section 6.3.2)
Figure 6-11: Volume weighted histogram of InAs QD diameters when grown with oleylamine measured by TEM (section 6.3.2)

6.4 Continuous Injection Synthesis of InP QDs

Although the focus of our work so far has been on InAs, we have also attempted to make InP QDs using a continuous injection strategy. However, due to the chemistry of InP synthesis, we had to adjust our strategy slightly. InP QD growth is known to be negatively effected by the presence of excess carboxylic acid[85], but we believe that the presence of some acid is beneficial to the continuous injection process as it may preferentially digest smaller particles. Therefore, we used a two-pot approach, where we synthesized and purified InP QDs with an absorbance peak at 525 nm for use as seeds. We then redissolved these seeds in an indium myristate solution for continued growth.

For seed growth, 1 mmole of indium(III) acetate was mixed with 3 mmoles of myristic acid and 5 mL of ODE. This solution was heated under vacuum at 115°C for 60 minutes to remove acetic acid displaced during the formation of InMy₃. The resulting clear solution was heated to 150°C under argon, and 0.5 mmoles of TMSi₃P dissolved in 1mL of TOP was injected. The temperature controller was immediately
switched to 275°C for growth. The solution was cooled 7 minutes after injection.

0.5 mL of the growth solution was removed to atmosphere, and the particles were purified by adding acetone and centrifuging the turbid solution. Hexane was used to redissolve the pellet of InP QDs at the bottom of the centrifuge tube. This was repeated once more, and the resulting stock solution was diluted for measurement of its absorbance spectrum and found to have an OD of 100 at 300 nm.

A solution of 1 mmole of InMy3 in ODE was prepared by again adding 1 mmole of indium(III) acetate, this time with 3.1 mmoles of myristic acid. Acetic acid was removed by evacuating at 115°C. The reaction vessel was allowed to cool and 630 mg of the solution of InP cores was added to the reaction vessel and vacuum was applied briefly to remove the hexane as the reaction solution was heated to 250°C. The reaction timer was started as the solution reached 150°C. Aliquots were removed at $t = 0\min$, $t = 10\min$, and $t = 18\min$ prior to starting the continuous injection at $t = 18\min$. Absorption spectra were taken of these aliquots, and they reveal that the InP cores were somewhat unstable in the reaction solution (figure 6-12). The absorption peak blueshifted from 525 nm to 510 nm at $t = 18\min$ and the half width at half max (HWHM) of the absorption peak increased from 111 meV for the initial seeds to 132 meV for the aliquot removed at $t = 18\min$.

However, it is apparent that as the reaction proceeds, the particle growth slows and the features become less defined as it did with InAs grown without oleylamine. TEM images suggest that both shape inhomogeneity as well as size inhomogeneity contribute to the spectral broadening observed.
Figure 6-12: Absorption spectra of aliquots removed from the growth solution as InP QDs were grown by continuous injection.

Figure 6-13: Absorption peak and HWHM for InP QDs grown by CI. The HWHM drops sharply after the CI starts and the peak position begins to redshift.
6.5 Conclusion

Continuous injection is capable of producing samples with sizes over a broader range and with narrower spectral linewidths than previous methods. The example spectra shown in figure 6-15 show outstanding peak definition at a wavelength redder than was previously possible. However, this technique has limitations. Despite exploration of growth conditions including temperature, surfactant chemistry, surfactant concentration, and precursor addition rate, I was unable to grow InAs to sizes larger than about 5nm. Continued precursor injection resulted in shape inhomogeneity and spectral broadening without continued redshifting of spectral features.

Surfactant chemistry is important for the control of particle growth. Phosphonic acids are known to dissolve nanoparticles into the cation salt and anion hydride gas at high temperatures[43]. Small concentrations of excess acid may digest clusters without affecting larger particles and may help guide the growth trajectory toward a size focusing regime. However, there appear to be constraints on the composition of the growth solution. When experimenting with different acid and amine mixtures, we observed the formation of inorganic structures other than InAs (In$_2$O$_3$ or As). In addition, acids and amines underwent undesirable side reactions when they were present together. However, the presence of amines seemed to prolong the size focusing regime, permitting the growth of slightly larger particles. In addition, TEM reveals
that the QDs grown in the presence of amines had more spherical shapes, suggesting that amines may enhance the rate at which diffusion and/or grain boundary migration occur, thereby eliminating shape inhomogeneities. It is likely that additional optimization of surfactant mixtures, precursor and surfactant addition schemes, growth rates, QD concentration, etc. could further improve the quality of materials produced by the CI technique.

The continuous injection method can be used to precisely and reproducibly produce InAs particles with a broader range of sizes and narrower spectral features than was possible previously. Particles can be synthesized with average sizes between 2.5-5nm, with absorbance peaks ranging between 600-1120nm and narrow spectral features, without the use of any size selective post-processing. Preliminary attempts to adapt this method to the synthesis of InP show that continuous precursor injection promotes particle growth and size focusing. Therefore, we believe that this method will prove to be a general approach capable of producing high quality samples of III-V QD cores.

Figure 6-15: Absorbance and PL of high quality InAs sample grown by CI with amines.
Chapter 7

Synthesis of InAs QDs for Biological Imaging

The experiments in this chapter were performed with Daniel Franke, Oliver Bruns, and Thomas Bischoff.

7.1 QDs in Biology

QDs are an attractive material for fluorescent biological probes because many of their optical properties compare favorably to those of organic fluorophores: QDs have strong, broad absorbance; narrow, symmetric emission with high QY; and high photostability. However, QDs are synthesized with oleophilic ligands on their surface. As a result, much of the research into development of QD based tools for biological imaging has focused on the design of a ligand system that stabilizes the particle, minimizes any drop in PLQY, and provides modular biological functionality[98, 68, 99, 67, 100, 101, 102].
7.2 NIR/SWIR Imaging in Biology

7.2.1 Motivation

The near infrared (NIR) spectral region offers two main advantages for biological imaging: decreased autofluorescence of biological media compared to the visible and increased transmission through tissue at these wavelengths (figure 7-1). A water absorbance band around 1050nm divides the useful imaging regions to the “first window” from 700-900nm, and the “second window” from 1100-1400nm. Models of absorption and scattering suggest that some regions of the second window may be as much as six orders of magnitude more transmissive than the first window [103].

Conventional organic fluorophores struggle in the NIR. However, QDs are well suited to operating in this wavelength range [67, 68, 104]. Until recently, imaging technology constrained the wavelength range that was useful for biological imaging experiments to the sensitivity of silicon-based camera technologies (the “first window”). However, calculations predicted that the decrease in wavelength dependent scattering further into the infrared could substantially increase the imaging depth in the second window by as much as six orders of magnitude [103]. Recently, infrared camera technology has become more available in the US, and as a result, there is strong interest in the development of biocompatible infrared probes.
In principle, colloidal QDs have much higher QYs, small hydrodynamic diameter, and can be functionalized for various biological applications (though, significantly, they contain toxic heavy metals) [4]. They can be made to emit in the second infrared imaging window with QYs >20%, and their emission can be tuned by changing their size and composition. Functionalization for biological imaging can be achieved using established ligand chemistries developed for visible QDs[68]. Possible QD materials
for biological imaging include the lead chalcogenides (PbS and PbSe), InAs, and the silver chalcogenides (Ag₂Se and Ag₂S). Ag₂Se has been made to emit with wavelengths between 700nm and 1300nm and has been reported to have QYs ranging as high as 30%* at 1300nm in one report[108], although other authors report values between 1-3%[109, 110]. The lead chalcogenides are promising candidates, with high QY values (>50 %) in organics. However, these materials are air sensitive and have the rock salt crystal structure, which eliminates the possibility of growing a defect-free epitaxial shell to protect the surface. Nevertheless, PbS(CdS) and PbSe(CdSe) core shell QDs have been prepared with good QYs despite the differences in crystal structure, but their stability upon ligand exchange is not well studied, and the suspicion is that defects necessarily associated with shell growth will be an Achilles heel that limits their performance. In addition to the incompatibility of the rocksalt crystal structure with the typical shell materials, the lead chalcogenides have long lifetimes >1μs that will limit the photoluminescence signal in high flux applications such as confocal imaging. Indium arsenide is the most promising material in principal. The crystal structure is compatible with the growth of thick, higher bandgap shells such as CdSe, CdS, or ZnS to create stable emitters in the NIR with high QYs reportedly reaching as high as 90%[111].

7.4 Synthesis of InAs core shell QDs for Biological Imaging

Our goal was to create a size series of QDs with bright, narrow emission spanning the sensitivity of an InGaAs camera (900-1700nm) for multiplexed biological experiments. Because InAs QDs coated only by their native ligands have a QY of < 1 %, we used InAs based core-shell QDs of varying thicknesses and compositions to meet these

---

*This value was obtained by reference to an old sample. The QYs of the samples in the reference that the author cited were referenced to IR-26 dye, with the assumption that the QY was 0.5%. Semonin et al. determined the QY of IR-26 to be 0.05%[19]. This is the least reliable measurement of QY that I have seen published. If one is to assume that the true QY was ≈ 3%, that puts the behavior of this material in line with what other authors have reported.
requirements.

A large batch of InAs cores was synthesized using the method described in chapter 6. A crude purification was performed by adding acetone to the growth solution, and redissolving in hexane once in ambient conditions. The InAs cores were stored under ambient conditions for a few days or weeks before overcoating.

The size and concentration of InAs cores were determined by using the absorbance peak wavelength and the optical density of the stock solution at 450nm according to the empirical relationship obtained by Yu et al.[93]. The amount of overcoating material required for the desired shell thickness was estimated using the density of the overcoating material and the size and concentration of the cores.

Overcoating of InAs with CdSe was adapted from Xie et al.[20]. 30 nmoles of 4.95nm diameter InAs cores in 1mL of hexane was dissolved in 3mL of ODE and 2mL of oleylamine. Vacuum was applied at room temperature to remove the hexane, and then the solution was briefly turned to argon in order to add 0.8mL of 0.05M TOPSe (about 1 monolayer (ML) worth of Se) in ODE to the reaction. The solution was heated to 100°C for 1 hr under vacuum, before turning to argon and heating to 220°C. Syringes of 0.045M of cadmium(II) myristate in TOP (prepared as described in chapter 3, [112]) and 0.05M TOPSe in ODE were prepared in air, and after the solution reached 220°C, the cadmium(II) myristate and TOPSe solutions were added to the solution via syringe pump at a rate of 2mL/hr. During the overcoating, the PL peak shifted from 1080nm to 1420nm. The large redshift observed here is due to the loss of confinement due to the low conduction band offset between CdSe and InAs resulting in pseudo-type II behavior. After purification by acetone precipitation, the PL peak was found to blueshift to 1380nm. The QY of the purified solution was measured to be 7 % with a FWHM of 250nm. This reaction was designed to add about 6ML to the InAs cores. Similar procedures were performed to produce particles with bluer wavelengths by using 1.5ML and 3ML. A summary of the products is given in table 7.4.

InAs(CdSe)(ZnSe) was prepared as follows by adaptation from Aharoni et al.[113]. 45 nmoles of 4.8nm diameter InAs in 2mL hexane were added to 4mL of ODE and
3mL of oleylamine. As before, hexane was removed under vacuum and 0.025 mmoles of TOPSe was added before heating to 230°C. 0.5mL each of syringes containing 0.05M cadmium(II) oleate with 4 equivalents excess acid and 0.05M TOPSe in ODE were added at 1mL/hr. To grow the ZnSe shell, 0.6mL of 0.05M diethyl zinc was added over about 1s and the temperature was increased to 250°C. 15 minutes later, 0.6mL of 0.05M TOPSe was added. Alternating injections of 0.05M diethylzinc and 0.04M ODE-Se were repeated. At 60 minutes, 0.75mL of diethylzinc solution was added. At 73 minutes, 0.95mL of ODE-Se solution was added to complete the third monolayer of shell material. At 87 minutes, 1mL of oleic acid was added to the solution. At 100 minutes, 0.95mL of the diethylzinc solution was added, followed by 1.2mL of ODE-Se at 113 minutes. At 120 minutes, the temperature was increased to 290°C for 40 minutes to anneal the solution. After purification, the final solution had a PL peak at 1075nm with a QY of 31% with a FWHM of 144nm.

InAs(CdS) particles were grown by taking 90 nmoles of 4.9nm InAs cores in 5mL of hexane and diluting in 10mL of ODE and 7.5mL of oleylamine. After degassing and adding 1 monolayer worth of cadmium(II) oleate, the solution was heated to 100°C under vacuum for 1 hour. The solution was turned to argon and heated to 240°C for growth. 8mL of 0.05M Cd(Oleate)\(_2\) and 0.045M ODE-S were added by syringe pump at a rate of 5mL/hr. After shell growth, the emission redshifted from 1073nm to 1150nm.

Absorption and emission spectra are shown in figures 7-2-7-3.

<table>
<thead>
<tr>
<th>Monolayers</th>
<th>PL Peak (nm)</th>
<th>PL FWHM (nm)</th>
<th>QY (organics) %</th>
<th>QY (water) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CdSe)(_{1,5})</td>
<td>1125</td>
<td>120</td>
<td>9.7</td>
<td>8</td>
</tr>
<tr>
<td>(CdSe)(_3)</td>
<td>1190</td>
<td>191</td>
<td>13.3</td>
<td>6.7</td>
</tr>
<tr>
<td>(CdSe)(_6)</td>
<td>1360</td>
<td>250</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>(CdSe)(_1)(ZnSe)(_3)</td>
<td>1074</td>
<td>144</td>
<td>31</td>
<td>31</td>
</tr>
<tr>
<td>(CdS)(_5)</td>
<td>1175</td>
<td>206</td>
<td>35</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 7.1: Summary of InAs overcoating results

Water solubilization was performed by taking a solution of QDs in hexane or chloroform and mixing with 50 weight equivalents of 1,2-dioleoyl-sn-glycero-3-phosphoethanolamine-N-[methoxy(polyethylene glycol)-2000] ammonium salt (PEG-Lipids)
Figure 7-2: InAs core shell absorbance spectra taken in organics before ligand exchange.
Figure 7-3: InAs core shell QD emission spectra taken in hexane before ligand exchange.
(25mg/mL in chloroform from Avanti Polar Lipids). The mixture was allowed to evaporate under a gentle stream of air and then dried on the vacuum line. Water was added to the desired concentration to form a homogeneous solution. This procedure is adapted from [114] and is not believed to disrupt the native ligands on the QD surface.

Another water solubilization was performed using poly(maleic acid-alt-1-octadecene) (PMAOD) obtained from Sigma Aldrich based on a procedure adapted from [115]. This procedure is known to leave the nanoparticles with negative charge[115].

A third procedure was used to make the QD solution biocompatible by forming a lipid emulsion. 20mg of lipids extracted from human triglyceride rich lipoproteins were mixed with 1 mg (dry weight) of QDs in CHCl₃. The chloroform was removed under a gentle air stream to form a QD-lipid film. 2mL of 0.9% NaCl saline solution was added. A probe sonicator was used to create a milky solution of nanosomes with QDs inside.

**7.5 Deep Tissue Imaging in Live Mice**

Water soluble InAs QDs were used for a variety of biological imaging experiments to demonstrate penetration depth, time resolution, and the capability for multiplexed imaging. In figure 7-4a, several vials of QDs with different emission wavelengths were imaged using a tunable liquid crystal filter (TLCF) with a 20nm bandwidth. The center wavelength of the filter was tuned in 25nm steps from 850nm to 1700nm. Images were acquired with a miniSWIR imager from Raytheon. This image series was deconvolved into 5 different color channels by linear unmixing and mapped to the false color image that is shown. This photograph proves that multiplexed SWIR imaging is possible using the size tunable emission of QDs.

Two color imaging in a nude anesthetized mouse is demonstrated by injection of one sample of QDs encapsulated by PEG-Lipids through the tail vein, and injecting another color intraperitoneally. These two injections demonstrate that different biodistribution patterns can be resolved in vivo, and that the QDs produced here
are sufficiently bright for imaging in vivo. An 808nm laser was used as an excitation source and the miniSWIR imager from Raytheon was used with the TLCF to collect the images. The same deconvolution procedure that was used to create the image of the vials was used to separate the colors in figure 7-4.

Multiplexed imaging of different biodistribution patterns in a mouse was also performed by using different surface functionalizations and injection times (figure 7-5). InAs(CdSe)\(_1\)(ZnSe)\(_3\) (QD 1080) in a lipid emulsion was injected via the tail vein. Ten minutes later, a sample of InAs QDs obtained from QD Vision and emitting at 1280nm solubilized using PMAOD was injected via the tail vein. 40 minutes after the injection of QD 1280, the animal was opened to expose its organs.

The false color image in figure 7-5 was created by combining an image collected using a 1250nm long pass filter with another image collected using a 850nm-1100nm bandpass filter. The different biodistribution in this case is due to the different surface functionalization as well as different injection times. The green channel (representing signal from QD 1080) appears primarily in the liver because the large size of the nanosomes results in rapid clearance. The QD 1280 sample was injected later and partially cleared by the liver. The signal from the red (QD 1280) channel appears both in the liver as well as the blood. This signal is visible at the edge of the opening of the body cavity because the QD 1280 is still circulating in the blood. The images reveal that two colors can be clearly resolved and imaged in vivo.

The images in figure 7-5 show that our setup is capable of creating multiplexed SWIR images. Time resolution for this image is somewhat limited because the image must be created by combining still images collected using different sets of external filters. Much faster time resolution can be obtained easily using a single color channel. In fact, video rate imaging was performed in order to observe high speed dynamic biological processes in a live mouse. A single tail vein injection of QDs in PEG lipids was performed on an anesthetized mouse. Wide field imaging is performed with sufficient time resolution to observe the animal’s breathing and heartbeat. The accumulation of QDs in the liver results in the region of interest (ROI) highlighted in blue in figure 7-6a, while blood in the heart is visible in the ROI highlighted in
Figure 7-4: (a) A hyperspectral image of vials containing different samples of InAs QDs with emission ranging from 1000nm to 1500nm. (b) A hyperspectral photograph of a mouse with intravenously injected QDs (red) and intraperitoneally injected QDs (green)
Cumulative intensity traces for these two ROIs are shown in figure 7-6b. As the heart expands and contracts, the blood volume fluctuates, resulting in a fluctuation in signal detected from this ROI. Similarly, as the animal breathes, the position of the liver changes slightly, perturbing the detected signal. FFT power spectrum analyses of these signals are presented in figure 7-6 c-d and they reveal that the animal is breathing at an approximate rate of 112 breaths per minute and has a heartbeat of approximately 320 beats per minute.
Figure 7-5: (a) Two different SWIR QDs, color coded green and red are functionalized differently for multiplexing. SWIR-QDs in a lipid emulsion (QD 1080) and PEGylated SWIR-QDs (QD 1280) are injected subsequently into a mouse. The mouse was sacrificed and opened to perform color SWIR imaging. The PEGylated SWIR-QDs (QD 1280) are detected selectively with 1250nm longpass filter (b) and the SWIR-QDs in a lipid emulsion (QD 1080) is imaged with combination of a 850 nm longpass and a 1100 nm shortpass filter (c). The overlay of both is shown in (d) and an overlay with an additional reflected light picture in grayscale is shown in (e).
Figure 7-6: High-speed QD-SWIR imaging for contact free monitoring of heart and breathing rate in awake mice. (a) QD-SWIR imaging at video-rate (30 frames/s with QDs emitting at 1300 nm) allows imaging of vital signs like heartbeat (detected in red ROI) and breathing rate (detected in blue ROI). The breathing rate of this anesthetized mouse is 112 breath/min and the heart rate is 320 beats per minute.
7.6 Conclusion

The second imaging window is attractive because low absorbance and scattering make it possible to image through tissue with infrared light. The continuous injection method for QD synthesis described in chapter 6 allowed us to produce highly uniform InAs QD cores with absorbance peaks around 1050nm. These could then be overcoated with different shell compositions to emit at wavelengths spanning the sensitivity of our detector. Our InAs core shell QDs were synthesized with sufficient QY, stability, and wavelength tunability to take advantage of the second imaging window and image biological function at video rates and multiplex to create false color still images of biodistribution in a living mouse.
Chapter 8

Conclusion

The size tunability, photostability, and modular surface chemistry of QDs makes them potentially useful for applications in optoelectronic devices and biology. QDs emitting in the infrared have superior performance over other fluorophores in the IR, and their development has been driven by interest in QD photovoltaics as well as biological imaging. However, existing synthetic techniques produce samples with significant size inhomogeneity, poor QYs, poor stability, or limited size tunability. The research described in this thesis attempted to develop methods to produce infrared emitting materials that addressed these limitations.

QDs made from the lead chalcogenides are the best studied infrared material due to their suitability for solar applications. Their size is readily tuned with narrow size distributions, but they are undesirable for some applications due to some of their properties. For example, the long lifetimes of these materials will limit their performance in high flux applications such as confocal imaging and their rock salt crystal structure is expected to limit the ability to stabilize them with high bandgap II-VI shells.

QDs made from indium arsenide also show promise for applications in the infrared, but they are difficult to synthesize with the same range of spectral tunability and narrow spectral features that can be achieved for the lead chalcogenides. The challenges associated with the synthesis of InAs and InP QDs were believed to be related to the highly reactive group-V precursors used for their synthesis. It was thought that
the high reactivity of the phosphine or arsine precursors led to the formation of small QDs with broad size distributions. Efforts to make the particles larger succeeded only at the expense of the particle size distribution and the spectral linewidth.

I began by looking to develop a synthesis for Cd₃As₂, a material that had been largely overlooked by the nanocrystal community. The narrow bulk band gap of this material implied that its spectral features could be tuned well into the infrared. After unsuccessfully trying to control particle size while maintaining narrow spectral features using a conventional single injection approach, I used a continuous injection growth method to successfully tune the emission peak of Cd₃As₂ QDs from 530nm to 2000nm. These particles had sharp spectral features and high QYs. Unfortunately, the particles proved extremely sensitive to ambient conditions. Attempts to stabilize them with higher bandgap shells of Cd₃P₂ or CdS had modest success, but it appears that Cd₃As₂ QDs will likely be limited to applications (such as devices) where they are not exposed to oxygen or water.

In order to produce stable IR emitting nanoparticles, I looked to improve the size distribution and range of size tunability of InAs QDs. These materials have been studied previously, but existing synthetic techniques produce either very small or very polydisperse samples of InAs QDs. Based on previous research conducted in our group, we believed that these synthetic limitations were associated with the highly reactive group-V precursors used for the synthesis of InAs and InP QDs. In order to improve the quality of III-V QDs, we therefore looked to make less reactive group-V precursors. By making subtle modifications to the structure of the group-V precursor molecules, we were able to slow the reaction rate by approximately three orders of magnitude. However, the QDs made from these less reactive precursors did not improve as theory had suggested that they might. Although we observed improvements in size distribution in one case, the less reactive precursors generally produced only slightly larger QDs with inferior size distributions.

After discovering that precursor chemistry seemed to have only limited effect on particle size and size distribution, we adapted the two step seeded growth synthesis used to control the growth of Cd₃As₂ for the synthesis of InAs. We found that
this technique was far more effective at achieving size control without sacrificing the particle size distribution. We were able to use this technique to make InAs with absorption peaks between 700nm and 1100nm with spectral linewidths as low as 95 meV. Despite the success of this technique in this size range, we found that the spectral features broadened after the absorbance peak reached about 1050nm. TEM images revealed that shape inhomogeneity likely contributed significantly to the spectral broadening that we saw. Changes in surfactant composition showed some promise for minimizing shape inhomogeneity and prolonging growth. Although it may be possible to prolong growth even further, the continuous injection method already enables the synthesis of application-ready InAs cores ideally suited for SWIR imaging in live mice.

8.1 Future Directions in III-V QD Synthesis

Currently, the continuous injection method shows significant promise for the synthesis of III-V QD cores. Although the synthesis of InAs QDs is already much improved over existing techniques, there is need for further development. Furthermore, the synthesis of InP by continuous injection is not well developed and should be explored further. Given the large number of strongly interacting experimental conditions (temperature, reagent concentrations, surfactant concentrations, injection rate), parameter space is enormous. I suspect that reagent/particle concentration, injection rate, and surfactant chemistry will likely be the most effective means to improve the CI technique further. Purifying the QDs during growth and restarting using larger seeds has also been suggested with the rationale that impurities or side products might accumulate and be detrimental to the particle growth.

The black box between molecular reagents and ensembles of nanoparticles is still quite dark. Although precursor conversion rate alone does not seem to be a promising route to improve III-V nanoparticle synthesis, it could be used to further study and understand the early stages of nanoparticle growth by studying how different chemical precursors change the system’s behavior during a continuous injection synthesis. By
controlling precursor conversion rate and injection rate independently, it should be possible to decouple the initial precursor conversion rate from the concentrations of small clusters that we believe are likely to form during the initial stages of particle growth. This type of study would be a powerful way of testing and refining the type of population balance models developed by Rempel et al. and Hanseler et al. [39, 52].

A detailed understanding of the impurities present in the reaction solution will likely be essential to fully understanding and controlling III-V nanoparticle growth. The indium precursors are particularly difficult to characterize, and it is possible that oxide or hydroxide impurities (In(My)$_{3-2x-y}$O$_x$(OH)$_y$) are important for particle growth. In addition, the molecular structure of the indium precursor is not well understood. Cadmium precursors are believed to be coordination polymers even at growth temperatures [43]. The three fold coordination of the indium carboxylates could lead to complex oligomeric structures that may be strongly influenced by temperature, surfactants, or impurities. The results of chapter 4.5 show that water or acid impurities are important to the molecular mechanism of precursor conversion. These species are present despite taking care to purify and characterize the reagents well beyond what is usually done to prepare reagents for QD synthesis.
Appendix A

Cadmium Arsenide Quantum Dots

A.1 Experimental Details

A.1.1 Materials

Cadmium (II) myristate was prepared as described by Chen et al[112]. 60 mmoles of NaOH (99%, Mallinckrodt) and 60 mmoles myristic acid (99%, Sigma Aldrich) were dissolved in 1L of methanol. 20 mmoles of Cd(NO₃)₄·H₂O (99.9%, Alfa Aesar) were dissolved in 100mL of methanol (99%, Sigma Aldrich), and added dropwise to the sodium myristate solution. The resulting precipitate was washed three times with methanol and recrystallized once from 1-butanol (99%, JT Baker). Cd₃As₂ QDs: In a typical core synthesis, 1 mmole of cadmium (II) myristate was dissolved in 5mL of 1-octadecene (90%, Sigma Aldrich) (ODE), to form a clear solution at 100°C. This solution was degassed under vacuum until the pressure stabilized, typically below 100mtorr. The injection solution was prepared in an inert glovebox by dissolving 0.05mmole of tris(trimethylsilyl)arsine (99%, Nanomeps) (TMSi₃As) in 0.8mL of tri-n-octylphosphine (97%, Strem) (TOP) under minimal lighting. The injection solution was swiftly injected into the cadmium (II) myristate solution at 175°C under vigorous stirring. After maintaining the solution at 175°C for 20 minutes, a solution containing 0.5 mmoles of TMSi₃As in 10mL of TOP was injected via syringe pump at a rate of 1.5 mL/hr.
A.1.2 Cd$_3$As$_2$(Cd$_3$P$_2$) core shell QDs

Core-shell QDs were prepared by injection of 0.05 mmoles TMSi$_3$As into 5mL of ODE containing 0.5 mmoles of cadmium myristate at 130°C. The solution was heated to 175°C before beginning addition of a solution containing 0.15 mmoles tris(trimethylsilyl)phosphine dissolved in 3mL of TOP at a rate of 1.5mL/hr.

A.1.3 Preparation of water soluble QDs via ligand exchange

Poly imidazole ligands (PIL) were synthesized and used for ligand exchange to displace the native ligands of QDs as described in the literature[116]. To summarize, QDs (1 n mole) were precipitated using hexanes (30 uL), CHCl$_3$ (30uL) and EtOH(200uL) and brought into 50uL of CHCl$_3$. The QD stock solution was mixed with solution a of PIL (4mg) in CHCl$_3$ (30uL), and stirred for 30 min at RT, after which 30uL of MeOH was added followed by stirring for an additional 20 min. QD samples were precipitated by the addition of EtOH (30uL), CHCl$_3$ (30uL), and excess hexanes. The sample was centrifuged at 4000g for 2 minutes. The clear supernatant was discarded, and the pellet dried in vacuo, followed by the addition of PBS (500uL, pH 7.4). The aqueous sample was then filtered through a 0.2 um syringe filter before measuring the emission spectrum.

A.1.4 Absorption Spectroscopy

Absorption spectra were collected on an HP 8453 spectrometer for samples with first absorption peaks of 800nm and below. For samples with an absorption peak wavelength longer than 800nm a Cary 5000 UV-VIS-NIR spectrometer was used in double beam mode.

A.1.5 Photoluminescence Spectroscopy

Emission spectra with peak emission wavelength less than 900nm were collected with an ocean optics fiber optic spectrometer with excitation by a 594nm HeNe laser. For
samples with emission peaks between 900nm and 1300nm a SpectraPro 300i spectrometer was used in conjunction with a liquid nitrogen cooled InGaAs camera with 512 pixels. For Emission peaks longer than 1300nm a SpectraPro 300i spectrometer was used in conjunction with a liquid nitrogen cooled indium arsenide photodiode from Hammamatsu.

A.1.6 Transmission Electron Microscopy (TEM)

TEM samples were prepared by drop casting a purified solution of QDs from hexane onto a 400 mesh copper grid with a carbon film (Ted Pella). TEM images were collected on JEOL 200CX and JEOL 2010 microscopes. Sizes were determined by taking the average diameter of 100 QDs measured using Adobe Photoshop.

A.1.7 Wide Angle X-Ray Scattering (WAXS)

The WAXS measurement was carried out on Rigaku High-Power Rotating Anode X-Ray Powder Diffractometer with a 185mm radius goniometer using an accelerating voltage of 50kV and a current of 250mA. Copper Ka radiation was used (1.5406 Å). A home-built helium flow cell was used to minimize exposure to air.

A.1.8 Energy Dispersive Spectroscopy (EDS)

EDS measurements were performed using a JEOL 2010 TEM operated at 200kV. Measurements were taken from 8-10 spots, each near the center of a window to avoid saturating the detector with signal from the copper grid. Data analysis was performed using the INCA software, and the relative compositions of the expected elements were calculated.

A.1.9 Nuclear Magnetic Resonance (NMR)

In a glovebox with an inert atmosphere, TMSi₃As was diluted in toluene (d8) (99%, Cambridge Isotopes, dried over 3A molecular sieves), with a diphenylmethane internal
standard (3.771 ppm). An analogous cadmium (II) myristate solution was prepared with toluene (d8)/diphenylmethane, which was then heated to 100°C to ensure complete dissolution. The TMSi₃As solution was added to an excess of the hot cadmium (II) myristate solution, and the solution immediately turned deep brown. 1H NMR spectra were taken after 1 minute and 5 minutes. 1H NMR spectra were also taken of the TMSi₃As solution at 20°C and the cadmium (II) myristate solution at 80°C.

All 1H NMR spectra were taken on a Varian INOVA 500 MHz Nuclear Magnetic Resonance spectrometer fitted with a broadband tunable probe.

A.1.10 Quantum Efficiency Measurements

Quantum efficiencies were measured using a teflon integrating sphere from Si-Photonics. A 785nm diode laser was used as the excitation source. A NIST traceable calibrated germanium photodiode from Newport (818-IR) was used as the detector. An 800nm colored glass longpass filter was used to block the excitation beam. Quartz NMR tubes were used to insert the sample into the integrating sphere, and a solvent blank was used to ensure as uniform of an environment inside the integrating sphere as possible. Photocurrent was adjusted by the external quantum efficiency of the detector in order to calculate the quantum yield.

A.2 Additional Figures and Tables
Figure A-1: QY decreases with increasing emission wavelength.

<table>
<thead>
<tr>
<th>Measurement Num.</th>
<th>At. % Cd</th>
<th>At. % As</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60.27</td>
<td>39.73</td>
</tr>
<tr>
<td>2</td>
<td>57.33</td>
<td>42.67</td>
</tr>
<tr>
<td>3</td>
<td>58.08</td>
<td>41.92</td>
</tr>
<tr>
<td>4</td>
<td>60.69</td>
<td>39.31</td>
</tr>
<tr>
<td>5</td>
<td>59.38</td>
<td>40.62</td>
</tr>
<tr>
<td>6</td>
<td>59.30</td>
<td>40.70</td>
</tr>
<tr>
<td>7</td>
<td>61.39</td>
<td>38.61</td>
</tr>
<tr>
<td>8</td>
<td>58.95</td>
<td>41.05</td>
</tr>
</tbody>
</table>

Average (%): 59.42, 40.57
Std. Dev. (%): 1.34, 1.34

Table A.1: EDS measurements of atomic composition of a sample of Cd₃As₂ QDs
Figure A-2: a) TMS$_3$As in toluene-d$_8$ at 20°C. b) The reaction mixture of TMS$_3$As with excess Cd(MA)$_2$ in toluene-d$_8$, mixed at 100°C and cooled immediately. c) The reaction mixture of TMS$_3$As with excess Cd(MA)$_2$ mixed at 100°C and heated for 5 minutes before cooling.
Appendix B

Group-V Precursors for InP and InAs QD Synthesis
Figure B-1: Absorption spectra of aliquots taken during growth of InAs (a, b) and InP (c, d) using the silyl-V precursor (a,c) and the germyl-V precursor (b, d)
Figure B-2: Protonolysis of TMGe₃P by methanol. ³¹P and ¹H NMR spectra show the formation of species with chemical shifts that match those observed in figure 4-7. The spectra labeled "³¹P TMGe₃P + MeOH" shows that the ³¹P peak at -227.95ppm is split by a spin 1/2 nucleus with coupling constant of 175Hz. This is similar to the ¹J₃¹P-¹H coupling constants observed for PH₃ (183Hz), TMSiPH₂ (179Hz), and TMSi₂PH (186Hz) [82]. We assign the ³¹P¹H peak at -227.95ppm to TMGe₂PH and the corresponding ¹H peak at 0.36ppm to the protons on the TMGe groups in TMGe₂PH.
Figure B-3: $^{31}$P and $^1$H NMR of TMGe$_3$P reaction with InMy$_3$ and octylamine. The spectra were collected immediately after mixing, and again after 18 hours. We assign the $^{31}$P peak at -234.1ppm to TMGePH$_2$, and the $^1$H doublet at 0.27ppm to the TMGe protons in this species.
Appendix C

Systematic Study of Precursor Reactivity and Particle Formation
Figure C-1: InAs QDs made from various arsine precursors.

Figure C-2: InP QDs growing under otherwise identical conditions, compared by precursor.
C.1 UV-Vis
Figure C-3: As precursor absorbance rise fits
Figure C-4: Phosphine precursor absorbance rises (4.3mM InM$_3$). The data is corrected for the discontinuous changes like those seen in figure C-6.

Figure C-5: P precursor absorbance fits (4.3mM InM$_3$). Data was corrected for the jumps seen in figure C-6.
Figure C-6: The uncorrected absorbance during the TEG$_3$P/TMSi$_3$P trace in figure C-4.
Figure C-7: P precursor absorbance rise fits. The [InMy3] is 50mM, approximately 10x greater than it was for the acquisition of the data presented in figure 4-5 and C-4.
Bibliography


152


154


[80] M. Atesa, H. Breuniga, and M. Denkera, “Formation of (Me3M)3Sb (M = Ge, Sn, Pb) and (Me3M)4Sb2 (M=Pb) by Reaction of (Me3Si)3Sb with Me3MCl,” Phosphorus, Sulfur Silicon Relat. Elem., vol. 102, pp. 287–289, 1995.


157


