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THESIS

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And My loving husband, Nirupam

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CONTRIBUTION OF AUTHORS

Chapter 1 explains a short introduction to QDs' syntheses, characterization, conventional QDs and pnictide quantum dots. Here, I am adapting a figure (Figure 4) from my first author review paper, ("Synthetic Developments of Nontoxic Quantum Dots", A. Das, P. T. Snee, ChemPhysChem, 2016, 17, 598-617) where I was the principle author and my adviser helped me to prepare manuscript. Chapter 2 describes one of my published manuscript ("Arsenic Silylamide: A Safe and Effective Precursor for Arsenide Semiconductor Nanocrystal Synthesis", A. Das, A. Shamirian, and P. T. Snee, Chemistry of Materials, 2016, 28(11), 4058-4064) where I was the principle author and major contributor of this project. My research adviser, Prof. Preston T. Snee assisted me for DFT calculation and manuscript preparation. Chapter 3 represents another published manuscript ("Synthesis of High-Quality AgSbSe2 and AgBiSe2 Nanocrystals with Antimony and Bismuth Silylamide Reagents", A. Das, B. Hsu, A. Shamirian, Z. Yang, P. T. Snee, Chemistry of Materials, 2017, just accepted), where I am the first author and major contributor of this project. My research adviser, Prof. Preston T. Snee assisted me to prepare this manuscript. Prof. Zheng Yang and Bo Hsu did the electrical measurement on pellets made of AgSbSe2 and AgBiSe₂ nanoparticles. In both chapters (chapter 2 and 3), Armen Shamirian was responsible for collecting TEM data. Chapter 4 represents a library of my unpublished work focused on water solubilization of quantum dots using hydrophilic phosphonic acids. Chapter 5 represents a brief conclusion of the previous chapters.

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LIST OF ABBREVIATIONS

DCC	N,N'-dicyclohexylcarbodiimide
DCM	Dichloromethane
EDC	1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide
EtOAc	Ethyl acetate
FWHM	Full width half maximum
LED	Light emitting diode
LHMDS	Lithium bis(trimethylsilyl)amide
mPEG	Methoxypolyethylene glycol
NC	Nanocrystal
NMR	Nuclear magnetic resonance
OA	Oleic acid
OLA	Oleylamine
ODE	1–Octadecene
PAA	Poly(acrylic acid)
PL	Photoluminescence
QD	Quantum dot
QY	Quantum yield
Sulfo-SMCC	Sulfosuccinimidyl-4-(N-maleimidomethyl)cyclohexane-1-carboxylate
TEM	Transmission electron microscopy
THF	Tetrahydrofuran
ТОР	Trioctylphosphine
ТОРО	Trioctylphosphine oxide
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray diffraction

SUMMARY

Pnictide semiconductor nanoparticles and quantum dots are an important class of materials due to their potential applications in solar cell, thermoelectricity, bioimaging and biosensors. However, scientific communities' attention on pnictide materials was negligible compared to conventional II-VI chalcogenide based QDs. This is primarily due to the challenging syntheses of group V semiconductor nanoparticles compared to II-VI families. This thesis focuses on the development of safe and effective methods for the synthesis of a wide variety of pnictide semiconductor nanoparticles, or quantum dots including materials within the III-V, II-V, I-V-VI2 and I₃-V-VI₄ families. In first chapter, I have reported a relatively air-safe and less hazardous arsenic precursor, bis-[N,N-bis-(trimethylsilyl)amido] chloroarsenic, [(Me₃Si)₂N]₂AsCl (arsenic silvlamide) that can be used to create a variety of crystalline, monodisperse II-V, III-V, and I₃-V-VI4 family semiconductor quantum dots. The mechanism of the formation of quantum dots was also elaborated with the help of DFT calculation and NMR experiments. Next, I have expanded silvlamide-associated the of these pnictide tris[N,Nscope precursors, bis(trimethylsilyl)amido]antimony, $[(Me_3Si)_2N]_3Sb$ and tris[N,Nbis(trimethylsilyl)amido]bismuth, [(Me₃Si)₂N]₃Bi towards the exploration of novel antimony and bismuth nanomaterials, AgSbSe₂ and AgBiSe₂. Furthermore, electrical measurements of these materials were performed to characterize the electrical properties of the nanoparticles. In addition to pnictide nanomaterials' syntheses, I have developed a series of hydrophilic phosphonic acids to solubilize QDs in aqueous solution using a variety of strategies. This project focuses to minimize the number of steps for water solubilization and enhance the efficacy of functionalization of QDs.

1 Introduction

1.1 INTRODUCTION

Nanotechnology is defined as "the design, characterization, production and application of structures, devices and systems by controlling shape and size at the nanometer scale."¹ The unique aspects of this subject are based on the study of nano-dimensional (10⁻⁹ m) materials and the strong correlation between the size of the materials and their properties. It was physicist Prof. Richard Feynman who first introduced the concepts of nanotechnology in his "There's plenty of room at the bottom" lecture series.² Soon after, it became one of the fastest growing field of study in science and engineering. In some sense, nanoscience is not a new paradigm, as nanoscale objects already exist in nature as catalysts, porous materials, certain minerals, soot particles etc. However, innovation and progress in the development of scientific tools have allowed this rapid expansion and development of human derived nanoscale technology.

1.2 QUANTUM DOTS AND THEIR APPLICATION

Quantum dots (QDs, also known as semiconductor nanocrystals) have become a major component of nanotechnology since their discovery in 1983.³⁻⁴ Over the past few years, semiconductor nanocrystals, have been studied as potential components of chemical⁵⁻⁸ and biological sensing^{9-¹³, photovoltaics¹⁴⁻¹⁷, lasers¹⁸⁻²¹ and light emitting devices²²⁻²⁵ due to their unique photophysical properties. These include broad absorption spectra, tunable and narrow emission profiles, and high resistance towards photobleaching compared to organic dyes (see fig. 1).²⁶⁻²⁷ Many of these properties are engendered through the quantum confinement of charge carriers, within the nanometer dimension of semiconductor crystals.^{3, 28-31}}



Figure 1. Quantum dots. (A) Photo of CdS/ZnS & CdSe/ZnS QDs. (B) Emission spectra of same QDs. (C) Corresponding absorption spectra.

1.3 QUANTUM CONFINEMENT

When a semiconductor nanocrystal absorbs a photon, an electron is excited to the conduction band from the valence band, leaving behind a hole in the valence bond. The coulomb attractive force between the hole and electron restricts their independent motion resulting in the formation of an electron-hole pair (e^- - h^+), or 'exciton'. The distance between the hole and electron is known as the Bohr-exciton radius. When the radius of the quantum dot is comparable to the excitonic Bohr radius, the excitons are strongly confined.³ The energy separation of the QD is expressed in the following equation:

$$\Delta E(r) = E_{gap} + \frac{h^2}{8r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

where, $m_{e,}^{*}m_{h}^{*}$ = effective masses of excited electron and hole, respectively, E_{gap} is the band gap of the bulk (unconfined) material, and r is the radius of QD.

There are two consequences that result from the strongly confined electronic structure. For one, the energy levels are quantized and discrete. As such, the electronic structure cannot be explained by a bulk band-like motif. The states are more like atomic energy levels, so quantum dots are sometimes referred as 'artificial atoms'.^{3, 32-33} Another consequence is the fact that the band gaps of quantum dots are inversely proportional to the size of the dots (see fig. 2). Therefore, the electronic properties of the materials can be tuned by altering the size of the dots.



CB: Conduction band; VB: Valence band; E_g : Band gap

Figure 2. Electronic properties of a bulk semiconductor and quantum dots. (A) Electronic structure of a bulk semiconductor (B) Electronic structure of QDs.



Figure 3. Energy diagram of type-I and type-II quantum dots

1.4 TYPES OF CORE-SHELL QUANTUM DOTS

Surface passivation of quantum dots plays an important role for tuning their optoelectronic properties. Growing an inorganic shell on top of the core is an interesting and widely used protocol to restrict surface oxidation and alter the dots' emissive properties. The choice of material for the shell is based on the band gap and crystal structure of the core quantum dots. The core-shell quantum dots are classified as either type-I or type-II heterostuctures (see fig. 3).

In the type-I core-shell heterostructure, the band gap of the core is smaller than the shell and the edges of valence and conduction bands of the core lies within the bandgap of the shell.³⁴ Thus, both the electron and the hole is strongly confined inside the core. This confinement in type-I core-shell heterostructure helps to reduce surface defects and enhance the optical properties of quantum dots.³⁵⁻³⁷ Examples include CdSe/ZnS³⁵, CdSe/CdS³⁷, InAs/CdSe³⁸, CdS/ZnS⁵ etc.

In the type-II configuration, the valence or conduction band edge of the shell lies within the band gap of core, but not both.³⁹ Due to this staggered alignment of band edges, the hole stays in the core while the electron is confined to the shell or vice versa. This spatial distribution of charge carriers leads to longer fluorescence lifetimes and lower quantum yield.⁴⁰⁻⁴¹ Examples include CdTe/CdSe,⁴⁰ CdSe/ZnTe,⁴⁰ CdTe/CdS,⁴² ZnTe/CdS,⁴³ ZnTe/CdSe,⁴³ ZnSe/CdS⁴¹ etc.

1.5 SYNTHESIS OF CORE-SHELL QUANTUM DOTS

After the discovery of quantum dots in 1981 by Russian physicist Ekimov and US chemists Brus and Steigerwald,⁴ there are numerous protocols developed to synthesize high quality crystalline quantum dots. These include hydrothermal,⁴⁴⁻⁴⁵ microwave assisted,^{44, 46} rapid injection,⁴⁷ decomposition of single source precursors,⁴⁸ chemical/thermal oxidation,⁴⁹⁻⁵¹ laser ablation⁵² and electrochemical etching.⁵³⁻⁵⁴ Usually, hydrothermal and microwave assisted synthesis leads to nanomaterials with low quantum yields, poor crystallinity and broad size distributions. However, the rapid injection protocol, first employed by Murray et al., is generally the best and most general method to synthesize different types of materials.⁴⁷ In this procedure, one or more precursor solutions are injected at an elevated temperature into a high boiling-point solvent. Initially, the concentration of precursor is higher than the nucleation threshold and



Figure 4. Common protocol (rapid injection method) to synthesize quantum dots. Adapted and reprinted with permission from Ref. 31, Copyright 2014 The Royal Society of Chemistry

nucleation of semiconductor nanocrystals proceeds at a rapid pace. As the concentration of precursors drops, the nucleation of new dots stops and particles start to grow. There may be an overlap period where nucleation and growth occur simultaneously. If nanocrystal are grown with a low precursor concentration 'Ostwald ripening' can occur, which leads to a broad size distribution of nanomaterials.⁵⁵ To control the growth and prevent Ostwald ripening, the solution can be cooled immediately after the injection of precursor at higher temperature at the subsequent nucleation stage. The rapid injection method accomplishes this by the sudden addition of a large quality of solvent when the precursors are added.

To improve the stability, quantum yield and to minimize toxicity, quantum dot cores can be over coated with shell of another inorganic material.^{35-36, 56} Generally the shell formation involves epitaxial growth via the slow injection of overcoating precursors. Otherwise, non-epitaxial shell growth can occur which causes strain and defect formation at the core/shell interface, leading to deep-trap states and poor optical characteristics.⁵⁷

Another important factor to synthesize high quality quantum dots is the purification of starting materials: oleic acid,⁵⁸ oleylamine, tetradecylphosphonic acid⁵⁹ and trioctylphosphonic acid.⁶⁰ Purified starting materials enhance the reproducibility of the protocol and result in better surface passivation that leads to greater stability, less toxicity, and higher quantum yield. Consequently, the properties of the QD products is improved, especially compared to organic dyes.

1.6 WATER SOLUBILIZATION AND FUNCTIONALIZATION OF QUANTUM DOTS

Quantum dots are highly robust 'fluorophores' that have potential applications in the biological arena as biosensors, biomarkers, and bioimaging tools.⁶¹⁻⁶³ However, the best quantum

dots are synthesized in hydrophobic solvents, which makes it very difficult to transfer dots from hydrophobic organic solvents into a hydrophilic aqueous one.⁶⁴ There are two primary protocols for water solubilization of quantum dots: 1) ligand exchange, and, 2) the encapsulation method.

The ligand exchange protocol involves replacement of the native hydrophobic ligands with hydrophilic ones to solubilize quantum dots in an aqueous solvent.^{62, 65-68} The most widely used ligand for this purpose is sulfur containing dihydrolipoic acid (DHLA).^{62, 69-71} Usually, ligand exchange with DHLA results in small hydrodynamic sized QDs that are suitable for biological applications. However, the quantum yield and the stability are significantly reduced.^{69, 72-73} Another modified ligand exchange approach involves silanization, where QDs are coated with a cross-linked, near-monolayer of silica.⁷⁴ Also, quantum yields are quite high and QDs are stable over months under ambient bench top condition.

The encapsulation protocol coats QDs with a layer of hydrophilic compounds, known as encapsulants, on top of their native ligands for aqueous solubilization.⁷⁵ Usually, the encapsulants are amphiphiles that have a hydrophobic part that interacts with the native ligands within the interior, whereas a hydrophilic portion stays outside and interacts with water. These ligands are typically block copolymers,⁷⁶ lipids,⁷⁷ phospholipids, or amphiphilic polymers.^{76, 78-80} While quantum yield of QDs remain same,⁵⁶ the hydrodynamic size becomes large, which is incompatible with biological studies.^{65, 81-82}

Functionalization of quantum dots is another important step to make it useful for biological applications.⁸³ Usually, hydrophilic functional groups such as primarily amines and carboxylic acids, exist on the surface of water-soluble QDs. The common coupling reagents to conjugate with biological moieties (proteins, peptides, DNA etc) have carbodiimide functionality. Examples

include 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC),^{69, 75, 84-85} and methylpolyethylene glycol carbodiimide (MPEG CD).⁸⁶ DMTMM.⁸⁵ is a similar reagent as EDC. To functionalize



Scheme 1. Different protocols for water-solubilization of QDs: Encapsulation and ligand exchange. Reprinted with permission from Ref. 87, Copyright 2014 The Royal Society of Chemistry

thiol groups on the QD surface, sulfosuccinimidyl-4-(N-maleimidomethyl) cyclohexane-1carboxylate (sulfo-SMCC) is an efficient coupling reagent.⁸⁶ Furthermore, there are examples of nonspecific,⁸⁸⁻⁹⁰ electrostatic ^{69, 76, 90-91} and adsorption^{56, 92} interactions that can be used for attaching biological moieties to QD surface devoid of any coupling reagents.

1.7 CONVENTIONAL QUANTUM DOTS AND HISTORICAL BACKGROUND

Over past two decades, several synthetic strategies have emerged to prepare II-VI (i.e. CdS, CdSe, CdTe),⁴⁷ IV-VI (PbS,PbSe),⁹³⁻⁹⁵ and III-V (InP, InAs)⁹⁶⁻¹⁰⁰ quantum dots, rods and other morphologies for applications in solar cells,^{16, 101} optoelectronic devices^{22, 102-103} and as fluorescent sensors.^{9-10, 104} Of these, research on II-VI (specifically cadmium chalcogenides) QDs are overwhelmingly reported in the literature due to the fact that their preparation is facile and precursors are mostly commercially available. If we look into the history, the scientific community's focus on cadmium chalcogenide began when Ekimov and Onushchenko first synthesized CdS dots in glass metals.⁴ At the same time Brus' group synthesized CdS QDs using cadmium and sulfur salts in water containing an amphiphilic polymer that served as the nanocrystals' nucleation centers.⁷⁶ The reaction was performed in air using commercially available precursors, which facilitated technological transferability to other research groups. In 1993, Murray et al. presented a procedure that produced high quality CdS, CdSe, and CdTe QDs by the rapid injection of precursors into a very hot amphiphilic coordinating solvent.⁴⁷ The elements became supersaturated and precipitated in the form of nuclei that grew into nanocrystals.¹⁰⁵ The great significance of this work is that semiconductor nanoscience became infinitely more accessible to the scientific community due to the improvement in the quantum dots' quality. This came at the expense of additional complexity as toxic and flammable dimethyl cadmium was used as a precursor, which necessitated air free conditions. This issue was resolved through the use of significantly safer cadmium salts¹⁰⁶ and phosphonates¹⁰⁷ as reagents.

Many applications for CdSe quantum dots became realizable by the inorganic passivation of the surface.³⁵⁻³⁶ Core-shell CdSe/ZnS quantum yields have been reported to be as high as 100%;⁵⁶ furthermore, they are more stable such that they may be dispersed into water for bioimaging

applications using the methods discussed in the previous section.⁶¹⁻⁶² CdSe/ZnS dots are also used in displays and are commercially available from LG, Samsung, and Sony.^{23, 108} To summarize, the scientific community has had significant incentive to invest in cadmium-based semiconductor quantum dot research, which has resulted in the development of robust synthetic procedures that produce highly stable, bright functional materials. However, one runs into several issues with quantum dot synthesis when investigating new materials outside of the cadmium chalcogenide semiconductor family.

1.8 PNICTIDE (GROUP V) QUANTUM DOTS

Pnictide semiconductor quantum dots are an important family of materials for their potential applications in solar cell,¹⁰⁹⁻¹¹¹ thermoelectricity,¹¹²⁻¹¹³ bioimaging,¹¹⁴⁻¹¹⁷ and lithium ion batteries¹¹⁸⁻¹¹⁹. They are mostly classified as III-V (e.g. InAs, InP, GaAs, GaSb), II-V (e.g. Cd₃As₂, Zn₃As₂), I-V-VI₂ (Cu/AgSbS₂, Cu/AgSbSe₂, Cu/AgBiS₂ and Cu/AgBiSe₂), and I₃-V-VI₄ (e.g. Cu₃AsS₄, Cu₃SbS₄, Cu₃SbSe₄, Ag₃AsSe₄) families of materials. However, scientific communities' attention was negligible towards examining pnictide materials compared to conventional cadmium chalcogenide QDs. The problem this thesis will address is the fact that, if the scientific community does not explore new materials, novel properties will not be realized. If we compare conventional quantum dots to pnictide ones, we find many interesting points to be considered. For example, InAs¹¹⁶ and InP¹¹⁷ have lower bandgaps for NIR fluorescence and less toxicity due to absence of Class-A elements. Thus, they are more efficient materials for bioimaging applications compared to CdSe QDs. GaAs is another interesting material for photovoltaics as it has better carrier dynamics compared to CdTe.¹⁰⁹ Also, I-V-VI₂ semiconductors, especially AgSbSe₂ and AgBiSe₂,

are efficient and inexpensive thermoelectric materials compared to well-known PbTe/AgSbTe₂.^{112,} ¹²⁰ All these facts prove that pnictide family semiconductors possess potential applications in different fields of science. Every new discovery also creates potential challenges and for pnictide semiconductor nanocrystals, it is always associated with synthetic problems.

The syntheses of group V QDs are extremely challenging and completely different compared to II-VI families. This is largely due to 1) the strong covalency of the crystal lattice, 2) the fact that pnictide ions require higher temperatures and longer annealing time to overcome higher reaction barriers.¹²¹

Primary Pnictide Semiconductor Families	Major Semiconductors
Group III-V	Binary: InP, GaP, InAs, GaAs, InSb, GaSb,
-	Tertiary: InGaP, InGaAs,InGaSb
Group II-V	Cd ₃ P ₂ , Zn ₃ P ₂ , AlP, Cd ₃ As ₂ , Zn ₃ As ₂ , AlAs,
	Zn ₃ Sb ₂ , ZnSb, Ni ₃ P, Co ₃ P, Cu ₃ P
Group I ₃ -V-VI ₄	Cu ₃ AsS ₄ , Cu ₃ SbS ₄ , Cu ₃ BiS ₄ , Cu ₃ AsSe ₄ ,
	Cu ₃ SbSe ₄ , Cu ₃ BiSe ₄ , Ag ₃ AsS ₄ , Ag ₃ SbS ₄
Group I-V-VI ₂	CuSbS ₂ , CuSbSe ₂ , CuBiS ₂ , CuBiSe ₂ ,
	AgSbS2, AgSbSe2, AgBiS2, AgBiSe2
Group I ₃ -V-VI ₃	Cu ₃ AsS ₃ , Cu ₃ SbS ₃ , Cu ₃ SbSe ₃ , Cu ₃ BiS ₃ ,
	CuBiSe3, Ag ₃ AsS ₃ , Ag ₃ SbS ₃ ,

Table 1. Pnictide semiconductor families and examples of semiconductors



Figure 5. Pnictide precursors: A) Established pnictide precursors. B) Reaction mechanism of tris(trimethylsilyl)pnictide with In (+3) salt.

The most well-known pnictide reagents follow the tris(trimethylsilyl)pnictide motif. Examples include (Me₃Si)₃P,¹²²⁻¹²⁶ (Me₃Si)₃As,^{98, 127} and (Me₃Si)₃Sb.^{125, 128-129} The chemistry of deadly gases like phosphine (PH₃),¹³⁰ arsine (AsH₃),^{125, 131-133} and stibine (SbH₃)¹³⁴ is similar to the above. Due to the presence of labile Me₃Si- ligands, pnictide ions can be easily generated under suitable conditions.¹¹⁵ All these pnictide reagents are highly air/ moisture sensitive, hazardous and expensive, and many are not commercially available.¹³⁵⁻¹³⁶ Furthermore, the synthetic procedures for their preparation are highly air-sensitive and require special instrumentation that is not viable in normal laboratory condition. Also, these reagents are not chemically stable and usage of these precursors sometimes creates products with poor crystallinity and introduces reproducibility problems.⁹⁷⁻⁹⁸ Unfortunately, all these complications have restricted the application of pnictide quantum dots for commercial and biological purposes.¹³⁷⁻¹³⁸

1.9 OVERVIEW OF THESIS

This thesis focuses on the development of safe and effective protocols for the synthesis of a wide variety of pnictide semiconductor nanoparticles, or quantum dots, including materials within the III-V, II-V, I-V-VI₂ and I₃-V-VI₄ families. I have reported a relatively air-safe and less toxic arsenic precursor that can be used to create a variety of crystalline, monodisperse II-V, III-V, and I₃-V-VI₄ family semiconductor quantum dots. Specifically, I have synthesized bis-[N,N-bis-(trimethylsilyl)amido] chloroarsenic, [(Me₃Si)₂N]₂AsCl (arsenic silylamide) and examined its use as an alternative pnictide precursor for quantum dots. The mechanism of the formation of quantum dots was also elaborated with the help of DFT calculation and NMR experiments. Next, I have expanded the scope of this research endeavor towards the exploration of novel silylamide-

associated antimony and bismuth precursors, tris[N,N-bis(trimethylsilyl)amido]antimony, [(Me₃Si)₂N]₃ and tris[N,N-bis(trimethylsilyl)amido]bismuth, [(Me₃Si)₂N]₃Bi. They have been successfully employed to synthesize two novel materials within the I-V-VI₂ family, AgSbSe₂ and AgBiSe₂. Furthermore, electrical measurements of these materials were performed to characterize the electrical properties of the nanoparticles. In addition to pnictide synthesis, I have demonstrated a series of hydrophilic phosphonic acids to solubilize QDs in aqueous solution using a variety of strategies. This project aims to minimize the number of steps for water solubilization and enhance the efficacy of functionalization of QDs.

2 Arsenic Silylamide: A Safe and Effective Precursor for Arsenide Semiconductor Nanocrystal Synthesis

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2.1 INTRODUCTION

Nanometer-scale colloidal semiconductor quantum dots, rods, and other morphologies are potential candidates for various applications in bioimaging,^{26, 140-142} photovoltaics,¹⁴³⁻¹⁴⁴ electronic devices¹⁴⁵⁻¹⁴⁶ and sensing^{10, 147} due to their unique optoelectronic properties. These include broad absorption spectra, narrow emission profiles, and high resistance towards photobleaching compared to organic dyes.^{3, 29} Furthermore, these properties may be tuned with size via the quantum confinement effect, where excitonic charge carriers gain kinetic energy due to localization within the ~nanometer dimensions of the semiconductor particles.³ The syntheses of II-VI (i.e. CdE, E=S, Se, Te) quantum dots have been extensively studied; however, the same is not as true for materials composed within the II-V and III-V semiconductor families (i.e. pnictides such as arsenides and antimonides).¹⁴⁸⁻¹⁴⁹ As discussed in the previous chapter, the colloidal synthesis of pnictide nanocrystals is challenging and different compared to the II-VI family due to the strong covalency of the crystal lattice and the fact that pnictide ions require high temperature, long annealing times, and precursors with labile ligands to overcome activation barriers. These impediments limit the scope of effective pnictide reagents, the use of which often result in the formation of polydisperse samples.¹²¹

Among pnictide semiconductors, metal arsenides are interesting as they are widely used in photovoltaics, electronic devices, and for biological imaging. Established strategies for their synthesis are based on the use of highly toxic arsine (AsH₃) gas, the desilylation reaction of

As(SiMe₃)₃, or the transmetallation of a semiconductor nanocrystal template.^{115, 131} Each method presents significant impediments for the practical and, most importantly, safe synthesis of materials. For example, arsine gas is easily generated from the acid digestion of metal arsenides. However, its use requires special types of glassware that needs to be properly sealed due to the fact that AsH₃ gas is extremely toxic and dangerous.¹³¹ While the reagent As(SiMe₃)₃ is a liquid and thus significantly safer to handle, it is not commercially available. Unfortunately, the synthesis of As(SiMe₃)₃ is a highly air and moisture sensitive multistep procedure and requires specialized glassware. The reaction yield is low,¹⁵⁰ and the reagent is pyrophoric. Transmetallation has been used to synthesize InAs and GaAs quantum dots.¹⁵¹ However, the template that was used in the synthesis (Cd₃As₂ nanoparticles) was created from As(SiMe₃)₃ via desilylation in the presence of metal salts.

The aim of this work is to explore the use of a non-volatile arsenide precursor that can be easily synthesized, is soluble in non-polar solvents, and has good stability under ambient condition, yet is sufficiently reactive in the presence of a reducing agent to produce semiconductor products in high yield. These properties were realized with bis[N,N-bis(trimethylsilyl)amido]chloroarsanic, [(Me₃Si)₂N]₂AsCl ("arsenic silylamide") as an alternative reagent compared to conventional arsenic precursors for quantum dot synthesis. I have studied this reagent due to its ease of synthesis, which involves the incorporation of the -N(Me₃Si)₂ ligand via one step metathesis reaction using commercially available AsCl₃ and lithium bis(trimethylsilyl)amide (LHMDS). The ligand imparts significant stability to the reagent most likely through the strong As-N bond. Furthermore, arsenic silylamide is a solid state chemical with minimal air sensitivity that enhances its ease of handling. I followed the general procedure by Hering et al.¹⁵² to synthesize arsenic silylamide as shown in Scheme 1, which was then used to synthesize quantum dots composed of II-V Cd₃As₂ and III-V InAs, while dots and other anisotropic shapes of I-V-VI Cu₃AsS₄ were realized. As it pertains to InAs synthesis, NMR investigations and quantum chemical modeling have shown that activation of the As-Cl bond using a reduced LiH·InCl₃ intermediate is the first step in the formation mechanism. A significant barrier is imposed by the coordination of "leftover" LiCl by the indium metal center, which is eventually shed with HCl to form a [N(SiMe₃)₂]₂As·InCl₂ intermediate. The metal center is likely reduced again to further activate free arsenic silylamide precursors in a cascade that eventually forms the InAs semiconductor nanocrystallite.



Scheme 1. Synthesis of bis[N,N-bis(trimethylsilyl)amido]chloroarsanic, [(Me₃Si)₂N]₂AsCl ("arsenic silylamide"), according to ref. 152. Reprinted with permission from Ref.139. Copyright 2016 The American Chemical Society.

2.2 EXPERIMENTAL

2.2.1 Materials

Arsenic chloride (AsCl₃, 99.5%), copper iodide (CuI, 99.995%), oleylamine (80-90%), and indium(III) chloride (InCl₃, 99.995%) were purchased from Acros Organics. 1-octadecene (ODE, 90%), lithium triethylborohydride (LiEt₃BH, 1.0 M solution in THF), hexane (anhydrous, 95%), and indium(III) acetate (In(OAc)₃, 99.99%) were bought from Alfa Aesar. Oleic acid (OA, 90%), lithium bis(trimethylsilyl)amide (Li[N(Si(Me)₃)₂], 97%), ethanol (>99.5%), cadmium acetate dihydrate (Cd(OAc)₂·2H₂O, 98%), sulfur (99.98%) were obtained from Sigma-Aldrich. Diethyl ether (purchased from VWR) was sparged with argon and dried using a Glass Contour Solvent System built by Pure Process Technology, LLC. Trioctylphosphine (TOP, 97%), was bought from Strem Chemicals Inc. Arsenic chloride, lithium triethylborohydride, and trioctylphosphine were stored and handled in an inert atmosphere glove box. Oleic acid was recrystallized according to the procedures in ref. ¹⁵³, while other chemicals were used without further purification.

2.2.2 Synthesis of bis[N,N-bis(trimethylsilyl)amido]chloroarsanic, [(N(SiMe3)2]2AsCl

The procedure developed by Hering et al.¹⁵² was used to synthesize bis[N,Nbis(trimethylsilyl)amido]chloroarsanic with minor modification to increase the reaction yield. The preparation is based on the metathesis reaction between arsenic chloride and lithium bis(trimethylsilyl)amide ("LHMDS"). First, 1.62 g LHMDS (9.7 mmol) was dissolved in dry hexane (10 mL) and was slowly added dropwise to a stirred solution of 800 mg AsCl₃ (4.41 mmol) in hexane (10 mL) at -60 °C under an inert N₂ atmosphere. The solution became white in color and turbid during the addition, and was kept stirring at -60 °C for 6 hours. The resulting white solution was warmed to and maintained at 0 °C for an additional 12 hours. Afterwards, the solution was filtered using a glass fritted funnel and the solvents were removed under reduced pressure, resulting a colorless, viscous liquid composed of [(Me₃Si)₂N]₂AsCl and the byproduct [(Me₃Si)₂N]AsCl₂. The byproduct was removed from the crude solution by reduced pressure distillation at 70 °C. After removal of the byproduct, the product was further recrystallized from a saturated hexane solution at -80 °C, resulting in the white solid product [(Me₃Si)₂N]₂AsCl, yield ~ 70%. The purity of the product was determined via ¹H and ¹³C NMR; ¹H NMR (25 °C, CDCl₃, 400 MHz) 0.33 (s) and ¹³C NMR (25 °C, CDCl₃, 400 MHz) 5.27(s); The reagent was stored in a -80 °C freezer in a sealed vial.



Figure 1. ¹H NMR and ¹³C NMR of [(Me₃Si)₂N]₂AsCl. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.
2.2.3 Synthesis of In[N(SiMe3)2]3

Indium tris[bis(trimethylsilyl)amide] was synthesized following the method of Bürger et al.,¹⁵⁴ and is reproduced here for completeness. First, 341 mg InCl₃ (1.54 mmol) was added into a two neck round bottom flask attached with reflux condenser under a dry nitrogen atmosphere. Next, 20 mL of dry ether was added to the flask and was heated to reflux. Next, 750 mg LHMDS (4.48 mmol) dissolved in 15 mL of dry ether was added dropwise into the refluxing InCl₃ / ether solution. The resulting mixture became turbid and was kept refluxing overnight. Afterwards, the solution was filtered through a glass fritted funnel under an inert N₂ atmosphere and the solvents were evaporated under reduced pressure. The product In[N(SiMe₃)₂]₃ formed as a pale yellow solid. yield:85%.

2.2.4 Synthesis of indium arsenide (InAs) nanoparticles

10 mL of 1-octadecene and 7 mL of oleylamine were added into a three neck round bottom flask and degassed at 110 °C for 2 hours. Afterward, the solution was cooled to 30°C. Next, 269 mg of [(Me₃Si)₂N]₂AsCl (0.625 mmol) dissolved in 1 mL ODE was added into the flask followed by an addition of 1.5 mL of 1.0 M LiEt₃BH / THF solution. This resulted in the formation of a brown discoloration. Finally, 0.25 mmol of an indium metal precursor (55 mg of InCl₃, 73 mg of In(OAc)₃, or 149 mg of In[N(SiMe₃)₂]₃) in 2 mL of TOP was injected into the flask, causing the solution to become black in color. The solution was heated slowly to and maintained at 250 °C for 30-35 min. Afterwards, the heating mantle was removed and the solution was allowed to cool to room temperature. The sample was stored under an inert atmosphere in a glovebox.

2.2.5 Synthesis of cadmium oleate (Cd(oleate)2)

In a three neck round bottom flask attached with thermocouple and reflux condenser, 10 mL of 1octadecene, 33 mg of cadmium acetate dehydrate (0.125 mmol), and 106 mg of oleic acid (0.375 mmol) were added and degassed for 1 hour at 120 °C. The temperature of the solution was increased to and maintained at 250 °C for 30 minutes to complete the reaction; afterward the solution was allowed to cool to room temperature. This solution was used without modification for the synthesis of Cd₃As₂ dots as discussed below.

2.2.6 Synthesis of cadmium arsenide (Cd3As2) nanoparticles

The synthesis follows the same general procedure employed for InAs nanoparticles. 10 mL of 1octadecene and 7 mL of oleylamine were added into a three neck round bottom flask and degassed at 110°C for 2 hours. Afterward, the solution was cooled to 30 °C. Next, 96 mg of [(Me₃Si)₂N]₂AsCl (0.224 mmol) dissolved in ODE was added into the flask, followed by 0.6 mL of 1.0 M LiEt₃BH / THF solution, resulting in a brown discoloration. Finally, 10 mL of the Cd(oleate)₂ solution discussed above was injected into the flask, which blackened the solution as observed in the synthesis of InAs dots. The solution was heated slowly to and maintained at 230 °C for 15-20 min. Afterwards, the heating mantle was removed and the solution was allowed to cool to room temperature. The sample was stored under an inert atmosphere in a glovebox. Generally, the Cd₃As₂ quantum dots are stable for 3-4 months inside glovebox under nitrogen atmosphere.

2.2.7 Synthesis of enargite (Cu₃AsS₄) nanoparticles

This synthesis is a derivative of the procedures described above. 10 mL of 1-octadecene and 7 mL of oleylamine were added into a three neck round bottom flask and degassed at 110 °C for 2 hours. Afterward, the solution was cooled to 30 °C. Meanwhile, 35 mg of CuI (0.186 mmol) was added to 6 mL of oleylamine in a vial with a septa cap under a nitrogen atmosphere. It was degassed at 60 °C for 30 minutes, heated to 80°C for one hour, and then allowed to cool to room temperature. In another septum covered vial, 30 mg of sulfur (0.93 mmol) was added to 5 mL of oleylamine. The solution was heated to 60 °C for 30 min to completely dissolve the sulfur. Next, 160 mg of [(Me₃Si)₂N]₂AsCl (0.371 mmol) dissolved in ODE was first added into the three neck round bottom flask followed by 0.9 mL of 1.0 M LiEt₃BH / THF solution, resulting in a brown discoloration. Finally, the CuI and S solutions were injected into the flask in that order. The solution turned black following the addition of CuI; however, subsequent addition of sulfur transformed the solution into a clear brown color. The solution was then heated to and maintained at 240-245 °C for 15 min. Afterwards, the solution was allowed to cool to room temperature, and the sample was stored under an inert atmosphere in a glovebox.

2.2.8 Mechanistic investigations via NMR

In this study, 1 equivalent of the reducing agent LiEt₃BH in toluene-d₈ was added to bis[N,Nbis(trimethylsilyl)amido]chloroarsenic (also dissolved in toluene-d₈) at -30°C under a nitrogen atmosphere in a glove box. Time-resolved ¹H NMR spectra were recorded immediate after until the sample warmed to room temperature. The THF peak at 1.47 ppm was used as an internal standard by setting the integration to 1.0.

2.2.9 Characterization

For characterization, a small quantity of each sample was precipitated with ethanol and centrifuged to remove impurities. The precipitate was then redispersed in dry hexane and characterized optically and by X-ray photoelectron (XPS) and X-ray diffraction (XRD) spectroscopy. Absorption and emission measurements were performed with a Varian Cary 300 Bio UV/Vis and a customized Fluorolog (HORIBA Jobin Yvon) modular spectrofluorometer, respectively. XPS analyses were performed on a Kratos Axis 165 using a monochromatic Al K α source operating at 12 kV and 10 mA to produce an X-ray power of 120 W. Spectra were collected with a photoelectron takeoff angle of 90° from the sample surface plane, in energy steps of 0.1 eV, and a pass energy of 20 eV for all elements. All spectra were referenced to the C_{1s} binding energy (284.8 eV). X-ray diffraction studies were performed on a D8 Advance ECO Bruker XRD diffractometer using monochromatized Cu K α (λ = 1.54056 Å) radiation. Transmission electron microscopy (TEM) measurements were performed using a JEOL JEM-3010 operating at 300 keV. A 300 mesh copper grid was used for InAs and 300 mesh gold grid were used for Cd₃As₂ and Cu₃AsS₄ nanoparticle imaging. ¹H NMR and ¹³C NMR spectra were recorded at various temperatures using Bruker Avance DRX 400 NMR spectrometer.

2.2.10 Quantum Chemical Modeling

All species were modeled using Density Functional Theory (B3LYP)¹⁵⁵⁻¹⁵⁶ using the Gaussian '09 package.¹⁵⁷ H, Li, C, N, O, and Cl atoms were described with a 6-311+g(d,p)¹⁵⁸⁻¹⁵⁹ basis set, while In atoms used the LANL2DZ basis set and effective core potential.¹⁶⁰ The arsenic substrate [(Me₃Si)₂N]₂AsCl was modeled using [N(SiH₃)₂]₂AsCl, while superhydride was modeled with LiMe₃BH. All geometry optimizations, including saddle points, were characterized with frequency analyses. Saddle

points were also examined using intrinsic reaction coordinate analysis. Zero point vibrational corrections were added to the energies. GaussView was used to visualize the results.¹⁶¹

2.3 <u>RESULTS AND DISCUSSION</u>

Nanocrystalline quantum dots and rods of InAs, Cd₃As₂, and Cu₃AsS₄ have been synthesized with [(Me₃Si)₂N]₂AsCl using LiEt₃BH ("superhydride") to activate the arsenic precursor. I have already discussed the motivations for synthesizing the reagent arsenic silylamide, which is a solid at room temperature with minimal air sensitivity. Although the chemical was handled inside a glove box before use, it can be stored safely in a sealed vial in a -80 °C freezer. However, this enhanced stability necessitates the use of superhydride during the synthesis of semicondutor nanomaterials as was also observed in a previous study on antimonide quantum dots using a similar precursor.¹⁶²

The reaction protocols to synthesize InAs, Cd₃As₂, and Cu₃AsS₄ nanoparticles all follow a general procedure where metal salts (In⁺³, Cd⁺², and Cu⁺¹), [(Me₃Si)₂N]₂AsCl, and superhydride are mixed in a coordinating solvent and are subsequently annealed briefly at a high temperature. Unfortunately, the resulting InAs and Cd₃As₂ particles were observed to have somewhat poor colloidal stability. The presence of the reducing agent was found to be crucial as, without it, products are formed only at very high temperature (~420°C) after prolonged annealing times (~2-3 hours). Usually, injection of LiEt₃BH and the arsenic precursor at lower temperature yields better results irrespective of the nature of the quantum dots. Injection at higher temperatures leads to the formation of a brown mass, most likely a decomposition product of the arsenic precursor. Discussed below are the results from each individual system, followed by the experimental and theoretical examination of the reaction mechanism.

2.3.1 Indium arsenide (InAs)

Indium arsenide is a direct low band gap (0.4eV) material that has potential applications for infrared detectors,¹⁶³ for telecommunication and photovoltaic systems, and *in vivo* bioimaging.¹¹⁴⁻¹¹⁵ Wells et al. first developed a strategy to react In³⁺ salts with As(SiMe₃)₃ at a high temperature (~400°C) to synthesize crystalline InAs quantum dots.¹²⁷ Zhang et al. produced InAs nanocrystals using in-situ generated arsine gas(AsH₃).¹³¹ Later modifications to this procedure were reported where the reaction temperatures, solvents, and the identity of the surface coordinating ligands (TOP, oleylamine, oleic acid, myristic acid, etc.) were altered.^{38, 132-133, 164} Further developments included the creation of core-shell quantum dots with narrow size distribution and 90% emission efficiency⁹⁸ that could be water solubilized.¹¹⁵ However, all these reported methods used highly toxic and volatile As(SiMe₃)₃ or AsH₃ gas to synthesize InAs nanocrystals.

In this study, InAs nanoparticles were synthesized using various In⁺³ salts with [(Me₃Si)₂N]₂AsCl in presence of LiEt₃BH. As stated previously, the particles were flocculated after synthesis and required pyridine to disperse the materials in hexane for analysis. Fig. 2 and 5 show TEM micrographs of crystalline 4-5 nm diameter InAs quantum dots that are well within the range of quantum confinement (<35 nm).¹⁰⁰ The crystal phase of the nanoparticles was confirmed by powder XRD. It is consistent with the characteristic pattern of the cubic phase of InAs with corresponding peaks of [111], [200], [220] and [311]. However, narrow XRD peak pattern for InAs shows the yield of InAs QDs formation may be low. Along with nanoparticles, microparticles also forms here. XPS result shown in Fig. 3A reveal a 1:1.3 In:As composition, where the excess arsenic is likely due to unreacted precursors that were used in excess as seen in similar studies.⁹⁵ The absorption spectrum is rather featureless (Fig. 3), which unfortunately is an indicator of polydispersity. Furthermore, no emission was observed from these samples.

Three metal precursors were used in this study, specifically InCl₃, In(OAc)₃, and In[N(SiMe₃)₂]₃. The most significant difference in their usage concerns the amount of indium metal particle byproducts that were formed which we believe is due to direct reduction of the precursor. The use of In[N(SiMe₃)₂]₃ resulted in the most metal byproducts followed by In(OAc)₃, while no byproducts were observed in the InCl₃ studies. The above reactivity trend of In⁺³ may be the result of the interaction of the arsenic reagent with the reduced metal species, as the DFT binding energy is strongest for LiHInCl₃ and weakest for LiHIn[N(SiMe₃)₂]₃ as shown in Fig. 24.



Figure 2. General characterization of Indium arsenide (InAs) NCs. (a) TEM image of InAs quantum dots. (b) X-ray diffraction pattern of the same. (c) XRD plot of same InAs in terms of $log_e(I)$ vs. 2 θ , where I= intensity. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 3. X-ray photoelectron and UV/Vis spectra of InAs NCs. a) XPS survey spectra of InAs quantum dots. b) UV/Vis spectra of InAs quantum dots. No emission was observed from this sample. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 4. X-ray diffraction patterns of nanoparticles synthesized as a function of reducing agents, [LiEt₃BH, LiBH₄, LiAlH₄, or NaBH₄, in the presence of InCl₃] and indium precursors [In[N(SiMe₃)₂]₃ or In(OAc)₃]. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 5. TEM micrographs of InAs nanocrystals in presence of LiEt₃BH. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.

As a result, LiHInCl₃ is best capable of "capturing" the arsenic reagent to reduce it. It was also found that the lithium ion is more labile in the LiHInCl₃ complex, which would favor reduced arsenic and LiCl products as part of the reaction mechanism discussed in the following section. I also examined a variety of reducing agents and found that LiEt₃BH, LiBH₄, and LiAlH₄ are all effective for the production of InAs nanomaterials as shown in Fig. 4. The use of sodium borohydride failed to result in the formation of InAs nanocrystals.

2.3.2 <u>Cadmium arsenide (Cd₃As₂)</u>

Cadmium arsenide is a narrow band gap (~0.15 eV)¹⁶⁵ semiconductor with a large excitonic bohr radius (~47 nm),¹⁶⁶⁻¹⁶⁷ high dielectric constant,¹⁶⁸ and high electron mobility.¹⁶⁹ All these features suggest that it has significant potential for use in photovoltaic and telecommunication devices. However, there are few examples of the synthesis of cadmium arsenide quantum dots. Henglein and co-workers first synthesized Cd₃As₂ nanocrystals from Cd²⁺ salts and arsine gas in aqueous solution.¹⁷⁰ Later, Harris et al. synthesized NIR emissive Cd₃As₂ nanocrystals using (TMS)₃As and Cd-myristate via a double injection method.¹⁶⁶ Recently, Yang et al.¹⁷¹ and Miao et al¹⁷² used toxic arsine gas to synthesize monodisperse Cd₃As₂ nanocrystals. As in other examples, these procedures are based on highly toxic, flammable, volatile arsenic precursors.

In this report, Cd₃As₂ nanoparticles were synthesized using Cd-oleate with [(Me₃Si)₂N]₂AsCl in the presence of LiEt₃BH. XPS result confirms the composition of Cd₃As₂ nanoparticles with slight excess of arsenic (1:1.3) (see Fig. 6). The crystal phase of the nanoparticles was confirmed by powder XRD and is consistent with characteristic pattern of the tetragonal phase of Cd₃As₂ with corresponding peaks at [224], [325], [220] and [408]. However, narrow XRD peak pattern for Cd₃As₂ shows the yield of Cd₃As₂ QDs formation is quite low. Along with nanoparticles, microparticles also forms here. Fig. 7 & 8 shows an X-

ray diffraction pattern and TEM micrographs of relatively small (3.7 ± 0.6 nm diameter) and crystalline Cd₃As₂ nanoparticles.

Three Cd⁺² salts were used in this study, specifically anhydrous CdCl₂, Cd(OAc)₂, and Cd(II)-oleate. However, crystalline Cd₃As₂ were formed with Cd(II)-oleate under the conditions employed whereas only cadmium metal nanoparticles originated from use of the other precursors. As in the InAs study, this is attributed to the increased self-reactivity of the reduced metal compared to arsenic silylamide. As observed in the InAs study, the absorption spectra of the samples were featureless, and no emission was observed; see Fig. 6.



Figure 6. XPS survey and UV/Vis spectra of Cd_3As_2 NCs. a) XPS survey spectra of Cd_3As_2 quantum dots. b) UV/Vis spectra of Cd_3As_2 quantum dots. No emission was observed from this sample. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 7. General Characterization of cadmium arsenide (Cd_3As_2) NCs. (a) TEM image of Cd_3As_2 nanoparticles. (b) X-ray diffraction pattern of the same. (c) High resolution TEM image of crystalline Cd_3As_2 showing lattice fringes. (d) Size distribution of Cd_3As_2 dots; red line is a Gaussian fit to the data. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 8. TEM micrographs of Cd₃As₂ nanocrystals in presence of LiEt₃BH. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.

2.3.3 Enargite (Cu₃AsS₄)

Orthorhombic copper arsenic sulfide (Cu₃AsS₄), known as enargite, is a member of I₃-V-II₄ family of semiconductors.¹⁷³⁻¹⁷⁴ It has a 1.32 eV direct bandgap with intrinsic p-type conductivity. The low bandgap and other electrical properties make it highly suitable for photovoltaic applications.¹⁷⁵⁻¹⁷⁷ However, Cu₃AsS₄ has attracted little attention from scientific community, which may be due to the difficulty with its synthesis. To our knowledge, there is only one report on the synthesis of tetragonal Cu₃AsS₄ (luzonite) and cubic Cu₁₂As₄S₁₃ (tennanite) nanocrystals,¹⁷⁸ but no reports for enargite QDs exists.

Ternary Cu₃AsS₄ dots, rods, and multipods were synthesized using CuI and sulfur with $[(Me_3Si)_2N]_2AsCl$ in presence of LiEt₃BH. Fig. 9 shows a TEM micrograph and X-ray diffraction spectrum of Cu₃AsS₄ nanoparticles which displays the characteristic complex pattern of the orthorhombic phase of Cu₃AsS₄. XPS results (Fig. 10) confirms the presence of copper, arsenic and sulfur; however, the atomic concentration of sulfur and arsenic are higher than expected (Cu:As:S = 0.36:1.08:2.71), most likely due to the fact that they were used in excess. A very interesting feature of this study is the anisotropic nature of the materials formed as seen in Fig. 9 and 12. Examination of several images suggests that the elongated structures are composed of smaller subunits, which suggests an "oriented attachment" mechanism for anisotropic growth.¹⁷⁹⁻¹⁸¹ This mechanism is commonly observed in the synthesis of semiconductor nanorods and wires. To provide a more analytical characterization, histograms the widths and lengths of ~100 anisotropic enargite nanorods are shown in Fig. 9c. A Gaussian fit to the width (5.5 \pm 0.9 nm) was used to re-create the length distribution by summing 2–4 random numbers that conform to the width statistics as shown in the red line fit in Fig. 9c. Overall the fit is not ideal (r²=0.60); however,

with the TEM data, we believe that smaller monomers of Cu_3AsS_4 quantum dots fuse together to form the rods and multipods of enargite nanocrystals.



Figure 9. General characterization of enargite (Cu₃AsS₄) NCs. (a) TEM images of crystalline Cu₃AsS₄ quantum dots and rods. (b) X-ray diffraction pattern of Cu₃AsS₄ nanocrystals. The low angle shoulder is likely due to organic byproducts (see ref. 182). (c) Histogram of the width and length of various Cu₃AsS₄ rods (circles) with fits to the data (solid lines). Inset: TEM image reveals how Cu₃AsS₄ rods are likely composed of fused monomers. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 10. XPS survey and UV/Vis spectra of Cu₃AsS₄ NCs. a) XPS survey spectra of Cu₃AsS₄ quantum dots. b) UV/Vis spectra of Cu₃AsS₄ quantum dots. No emission was observed from this sample. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 11. X-ray diffraction patterns of Cu₃AsS₄ quantum rods compared to enargite (PDF#: 00-035-0775), luzonite (PDF#: 00-010-0450), and tennanite (PDF#: 01-076-0101). The particles are clearly a match to the orthorhombic enargite structure. The standard sample data were calculated by convolving the known d-spacing with Lorentzian lineshapes as defined by the Debye-Scherrer equation. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 12. TEM micrographs of Cu₃AsS₄ quantum dots, rods, and multipods. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.

2.3.4 <u>Reaction mechanism for indium arsenide (InAs)</u>

Temperature dependent NMR and theoretical modeling have been used to investigate the reaction mechanism by which aresenide semiconductor nanoparticles are synthesized using arsenic silylamide, InCl₃, and reducing agent. The first, rather obvious step is that superhydride transforms arsenic silylamide into the reduced form via: $[(Me_3Si)_2N]_2AsC1 \rightarrow [N(SiMe_3)_2]_2AsH$. This is confirmed by ¹H NMR as shown in Fig. 13, and characterized theoretically as seen in Fig. 17. However, minimal activation of the As-Cl bond was observed when the same reaction was performed in the presence of InCl₃ as shown in Fig. 14. In this system, InCl₃ is likely reduced to LiHInCl₃ by superhydride, which is ~50 kcal/mol energetically downhill barrierless reaction as shown in Fig. 15. This is also consistent with the many reports on the use of InCl₃ in organic reduction reactions.¹⁸³ Warming the solution resulted in arsenic silylamide reduction (Figs. 14, 15, and 16), the overall integration of which becomes smaller over time as a black precipitate (most likely InAs quantum dots) formed. This must be due to the action of LiHInCl₃ as a reducing agent, which forms [N(SiMe₃)_2]_2AsH with a 28 kcal/mol barrier (Fig. 16).

The next steps were explored entirely computationally, where the end goal was to remove ligands from the metal center. It was found that InCl₃ can coordinate without a barrier to the reduced arsenic center to from a complex that can subsequently shed HCl over a 30 kcal/mol barrier (Fig. 18). Subsequent interaction with a second equivalent of reducing agent results in LiH transfer to the indium metal center, which we believe leads to a chain reaction of arsenic activation and indium coordination until the InAs quantum dot is formed. These results are summarized in Scheme 2. One issue concerns LiCl coordination to InCl₃, which occurs after activation of the As-Cl bond. The LiInCl₄ intermediate is very stable as loss of LiCl is highly energetically unfavorable (+42 kcal/mol, Fig. S15). Coordination of LiInCl₄ to the reduced arsenic substrate reduces the energetic cost of LiCl loss to +31 kcal/mol (Fig. 19); alternatively, HCl loss may occur with a similar +30 kcal/mol barrier (Fig. 20). However, the interaction energy of LiInCl₄ with [(H₃Si)₂N]₂AsH is (the model substrate) very low, so neither of the above likely occurs in a high temperature solution. Thus, it could be true that the most significant bottleneck of this reaction is the loss of LiCl by LiInCl₄ that forms after arsenic reduction.

2.3.4.1 Mechanistic investigations via NMR

Experimental procedure has been explained in section 2.2.8. Temperature dependent NMR spectra are given below to explain the reaction between [(Me₃Si)₂N]₂AsCl with InCl₃ in presence of LiEt₃BH.



Figure 13. Room temperature ¹H NMR spectrum of bis[N,N-bis(trimethylsilyl)amido]chloroarsenic in presence of LiEt₃BH reveals the formation of [(Me₃Si)₂N]₂AsH. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.

We have observed that [(Me₃Si)₂N]₂AsCl was reduced to [(Me₃Si)₂N]₂AsH in presence of LiEt₃BH (Fig. 13). However, when the same experiment was performed with an addition of 1 equivalence of InCl₃, the formation of reduced species was suppressed (Fig. 14). Increasing the temperature of the solution resulted in the reduction of bis[N,N-bis(trimethylsilyl)amido]chloroarsenic (Figs. 15, 16), the integration of which slowly decreased most likely due to InAs QD formation.



Figure 14. Room temperature ¹H NMR spectrum of bis[N,N-bis(trimethylsilyl)amido]chloroarsenic in presence of LiEt₃BH (1 equivalent) and InCl₃(1 equivalent). It shows that the formation of the reduced [(Me₃Si)₂N]₂AsH species (0.29 ppm) is suppressed. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 15. ¹H NMR spectrum of bis[N,N-bis(trimethylsilyl)amido]chloroarsenic in presence of 1 equivalent of both LiEt₃BH and InCl₃. It shows that the formation of the reduced $[(Me_3Si)_2N]_2AsH$ species (0.29 ppm) occurs after the solution is warmed to 60 °C. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 16. ¹H NMR spectrum of [(Me₃Si)₂N]₂AsCl, InCl₃ and LiEt₃BH at 70°C. More of the reduced [(Me₃Si)₂N]₂AsH species is observed after warming the solution to 70 °C. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.

2.3.4.2 Mechanistic investigations via quantum chemical modeling with DFT

The binding energies between two associating species shown in parenthesis are calculated using the counterpoise method to account for basis set superposition error. A "+" sign between to molecules signifies that the structures' coordinates, total binding energy and vibrational zero-point energy were calculated separately. Note that some structures seem to appear twice (ex: 5 & 15, 18 & 23), whereas in reality one of the geometries is optimized in the presence of another coordinating species. All theoretical calculations were performed in vacuum.



Figure 17. Reduction of [(SiH₃)₂N]₂AsCl by LiMe₃BH. It is energetically downhill with a moderate barrier. However, this reaction is suppressed in the presence of indium trichloride, which is the preferred substrate for reduction. Note that structure (5) has been cropped for clarity. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 18. Reduction of InCl₃ by LiMe₃BH. Complexation and subsequent reduction of InCl₃ by LiMe₃BH is significantly downhill energetically with no reaction barrier. The resulting complex is moderately bound and likely dissociated before LiH·InCl₃ reduces the [(SiH₃)₂N]₂AsCl substrate as shown in Fig. 19. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 19. Reduction of [N(SiH₃)₂]₂AsCl by LiH·InCl₃. It results in the formation of LiInCl₄. Given the low interaction energy of the reduced arsenic species with indium, the pair likely separates and further reactivity is dependent on the coordination of free InCl₃, which likely originates from the removal of LiCl from LiInCl₄. The complexation energy of LiInCl₄ with [(SiH₃)₂N]₂AsH was determined to be positive (+0.11 kcal/mol) due to the zero-point energy correction. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 20. Loss of LiCl from LiInCl₄. The removal of LiCl from LiInCl₄ occurs with no apparent reaction barrier and is highly endothermic. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 21. Loss of HCl by $InCl_3$ · $[N(SiH_3)_2]_2AsH$. The complexation of $InCl_3$ and hydrogen arsenic silylamide likely results in shedding of HCl, which is overall endothermic. Subsequent interaction with a borohydride reducing agent likely results in reduction of the indium moiety, which reacts with another chloroarsenic substrate. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 22. Loss of LiCl from LiInCl₄· $[N(SiH_3)_2]_2AsH$. The barrierless loss of LiCl from LiInCl₄ when complexed to reduced hydrogen arsenic silylamide is less endothermic by ~10 kcal/mol compared to LiInCl₄ alone, which is likely due to the energetic stabilization of the InCl₃ and $[(SiH_3)_2N]_2AsH$. We propose that structure (16) sheds HCl as shown in Fig. 20 as part of the reaction mechanism to form InAs nanoparticles. Overall, the lack of interaction of LiInCl₄ and $[(SiH_3)_2N]_2AsH$ likely means that this mechanism does not occur. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 23. Loss of HCl and LiCl from LiInCl₄·[N(SiH₃)₂]₂AsH. As an alternative reaction pathway to that shown in Fig. 18, the loss of HCl originating from the LiInCl₄ - reduced hydrogen arsenic silylamide complex was investigated. The reaction barrier is nearly identical to the energetic cost of shedding LiCl from the same. Subsequent loss of LiCl is barrierless and endothermic. Regardless, the lack of interaction of LiInCl₄ and [(SiH₃)₂N]₂AsH likely means that this mechanism does not occur. The complexation of HCl with LiInCl₃·As[N(SiH₃)₂]₂ was calculated via E(AB) – E(A) – E(B) to be -5.19 kcal/mol as well as using the counterpoise method (-6.13 kcal/mol). Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Scheme 2. First steps in the reaction mechanism of $InCl_3$ and superhydride to form InAs quantum dots based on NMR and theoretical modeling results. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 24. Explaining the trend in indium precursor reactivity via binding energies. The reactivity of indium precursors followed the trend $In[N(SiMe_3)_2]_3 < In(OAc)_3 < InCl_3$. The reduced metal species interacting with the arsenic substrate were all modeled at the B3LYP/LANL2DZ level of theory to describe this behavior. BE refers to the BSSE corrected binding energy of the arsenic substrate with the reduced metal complex. It was universally found that there are two minima where the Li⁺ and H⁻ atoms are in a cis or trans position with respect to the metal center. Regardless of the structure, LiHInCl₃ has the overall strongest interactions with the arsenic substrate which may explain the lack of metal nanoparticles due to self-reactivity when using InCl₃ as a reagent. Note that (28) & (29) are not identical to (10) due to the nature of the local minima of (28) and the different level of theory employed in (29). Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.

2.3.5 Reaction mechanism for cadmium arsenide (Cd3As2) and enargite (Cu3AsS4)

The reaction mechanism of formation of II-V and I-V-VI materials is very different than that observed for InAs. By examining the materials synthesized during the process of QD formation with XRD analysis, it was found that one type of nanomaterial initially forms which later converts into the product. In the case of Cd₃As₂, a portion of the solution was collected before heating to the final temperature, and was found to contain cadmium metal nanoparticles as evident from the XRD data shown in Fig. 25. In the case of enargite Cu₃AsS₄, it was found that CuI, arsenic silylamide, and the reducing agent form a mixture of copper and copper arsenide nanoparticles before injection of the sulfur precursor; see Fig. 26. Consequently, the synthesis likely proceeds either by a) diffusion of sulfur into Cu₃As or b) diffusion of As into Cu-S framework, which is commonly observed in ternary or quaternary nanoparticle synthesis.¹⁸⁴⁻¹⁸⁵ Overall these results demonstrate that the reaction schemes reported here using [(Me₃Si)₂N]₂AsCl and a reducing agent are versatile and can be used to form nanoparticles via a variety of reaction pathways.



Figure 25. XRD pattern of metallic Cd nanoparticles. X-ray diffraction patterns of materials synthesized from cadmium oleate and [(Me₃Si)₂N]₂AsCl precursor in presence of LiEt₃BH at 160 °C. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.



Figure 26. XRD pattern of Cu and Cu₃As nanoparticles. X-ray diffraction patterns of materials synthesized from CuI and [(Me₃Si)₂N]₂AsCl precursor in presence of LiEt₃BH at 260 °C reveals the formation of a mixture of copper metal and copper arsenide nanoparticles. Injection of the sulfur precursor results in the formation of Cu₃AsS₄ quantum dots as shown in Figs. 9 and 12. Reprinted with permission from Ref. 139. Copyright 2016 The American Chemical Society.

2.4 <u>CONCLUSION</u>

In this chapter, we have explored the use of bis[N,N-bis(trimethylsilyl)amido]chloroarsanic, [(Me₃Si)₂N]₂AsCl as an arsenic precursor to synthesize a variety of metal arsenide semiconductor nanomaterials within the III-V, II-V, I₃-V-VI₄ families. This precursor has minimal air sensitivity, low vapor pressure, and is significantly safer to handle. These advantageous features make arsenic silylamide a useful precursor compared to other commonly used reagents such as gaseous hydrides or pyrophoric tris(trimethylsilyl)arsenide. I applied this precursor to synthesize crystalline InAs, Cd₃As₂, and Cu₃AsS₄ nanomaterials. Furthermore, the syntheses of enargite Cu₃AsS₄ quantum dots, rods, and multipods are reported for the first time. In case of InAs, we also investigated the mechanism of synthesis using variable temperature NMR and DFT quantum chemical modeling. According to these studies, the activation of the As-Cl bond of arsenic silylamide occurs via hydride transfer from LiH·InCl₃, an intermediate that forms from the reduction of InCl₃ by a reducing agent. The step is followed by LiCl loss to form $InCl_2-AsH[(Me_3Si)_2N]_2$, which is reduced further in a cascade that ultimately creates InAs nanocrystals. However, we believe that the formation of Cd_3As_2 and Cu_3AsS_4 nanomaterials followed diffusion mechanisms.



Figure 27. XRD pattern of gallium arsenide nanoparticles.

Issues that need to be addressed concern the lack of colloidal stability of InAs and Cd₃As₂ particles prepared via the methods outlined here, which we believe is due to the low temperature employed in the early stages of the reaction. We attempted to broaden the scope of this precursor towards the synthesis of other arsenide nanomaterials, especially GaAs. We synthesized GaAs nanomaterials following similar protocol, but the results were not reproducible which restricted further investigation. To summarize, the use of arsenic silylamide addresses the difficulty with solution-based synthesis of these nanomaterials which could extend the scope of possible applications.

3 Synthesis of High-Quality AgSbSe2 and AgBiSe2 Nanocrystals with Antimony and Bismuth Silylamide Reagents

The content of this chapter has been published as "Synthesis of High-Quality AgSbSe₂ and AgBiSe₂ Nanocrystals with Antimony and Bismuth Silylamide Reagents", Adita Das[†], Bo Hsu[‡], Armen Shamirian[†], Zheng Yang[‡], Preston T. Snee^{†*} *Chemistry of Materials*, **2017**, DOI: 10.1021/acs.chemmater.7b01593 (just accepted). Adapted with permission from Ref.213. Copyright 2017 The American Chemical Society.

3.1 INTRODUCTION

This chapter discusses the development of pnictide reagents to synthesize low bandgap semiconductor quantum dots (QDs). This is important as the use of advanced semiconductor materials may help to address the problems associated with the non-sustainable consumption of environmental resources due to world-wide overpopulation. In this regard, semiconductors can be used to create solar panels and catalysts for alternative energy generation, as well as efficient lighting systems and "smart windows" for energy conservation.¹⁸⁶⁻¹⁸⁷ Furthermore, semiconductor thermoelectric materials can generate power from the excess heat that is the byproduct of processes such as fossil fuel combustion.¹⁸⁸ Many of these examples were not realized with bulk materials that have well-defined physical properties. Such limitations engender only a certain level of efficacy for use in applications. It is necessary to build advanced materials on the nanoscale to overcome this deficit, due to the ability to tune electronic properties with size.³ Bottom-up chemical syntheses have been used to create colloidal semiconductor nanocrystals that have size dependent properties engendered through quantum confinement.^{3, 189} This thesis covers my research on pnictides that have not been extremely explored, such as II-V, I-V-VI₂, I₃-V-VI₄ families. This is due to the fact that the syntheses of these systems require pnictide nanomaterials are intricate and dangerous and there are few low-cost commercially available non-pyrophoric precursors.^{121, 133, 139, 162}

Among pnictides, environmentally benign I-V-VI₂ semiconductor nanocrystals are an emerging class of materials due to their NIR band gaps, large absorption coefficients, and excellent electronic properties.¹⁹⁰⁻¹⁹¹ Dimetal chalcogenides have utility for photovoltaic and thermoelectric applications, making them promising alternatives for thermoelectric PbTe.^{120, 192} There are several examples of the synthesis of copper-based I-V-VI₂ quantum dots, whereas silver-based nanomaterials such as AgBiS₂, AgSbS₂, AgSbSe₂ and AgBiSe₂ are less common.^{112, 193-194} The majority of reports on their syntheses used high temperature (~1000 K) solid state reactions that required long annealing times. Furthermore, the products were reported to have poor crystallinity and significant poly-dispersity. Colloidal preparation of AgSbSe₂ has been reported to yield significantly more monodisperse materials.¹⁹⁵

Chapter 2 of this thesis discussed the use of an efficient, versatile, and most importantly nonpyrophoric arsenic pre-cursor, [(N(SiMe₃)₂]₂AsCl, to synthesize a variety of semiconductor quantum dots and rods.9 Herein we report the utility of additional silylamide-ligated pnictides, tris[N,N-bis(trimethylsilyl)amido]antimony (Sb[(N(SiMe_3)_2]_3) specifically and tris[N,Nbis(trimethylsilyl)amido]bismuth (Bi[(N(SiMe_3)_2]_3),^{162, 196} to synthesize silver dimetal chalcogenide quantum-confined nanocrystals. These reagents were prepared via a simple one step metathesis reaction between the pnictide halide (SbCl₃/BiCl₃) and Li[N(SiMe₂)₂]₃ as summarized in Scheme 1. Both compounds are stable and relatively easy to handle due to the fact that they are solid-state reagents. Furthermore, they are soluble in a variety of organic solvents. As a result, they have been successfully applied to the syntheses of monodisperse, crystalline AgSbSe₂ and AgBiSe₂ nanoparticles using high-temperature colloidal methods. Specifically, AgSbSe₂ nanoparticles were generated via hot injection method, while the optimal strategy for synthesizing AgBiSe₂ NCs used a 'heat-up' procedure. These processes are represented in Scheme 2.



Scheme 1. Synthesis of tris[N,N-bis(trimethylsilyl)amido]antimony, $Sb[(N(SiMe_3)_2]_3$ and tris[N,N-bis(trimethylsilyl)amido]bismuth, $Bi[(N(SiMe_3)_2]_3$. Reprinted with permission from Ref. 213. Copyright 2017 The American Chemical Society.



Scheme 2. (a) Synthesis of AgSbSe₂ NCs begins with solvent degassing. (b) Ag and Sb reagents are prepared separately. (c) Rapid injection of Sb and Ag precursors. (d) AgBiSe₂ NCs are prepared by heating up the solvent and precursors in a single reaction vessel. Reprinted with permission from Ref. 213. Copyright 2017 The American Chemical Society.

3.2 EXPERIMENTAL

3.2.1 Materials

Bismuth chloride (BiCl₃, 99.9%) and selenium shot (99.5%) were purchased from Strem Chemicals. Hexane (anhydrous, 95%) and antimony chloride (SbCl₃, 99%) were purchased from Alfa Aesar. Oleic acid (OA, 90%), oleylamine (OLA, 98%), lithium bis(trimethylsilyl)amide (Li[N(Si(Me)₃)₂], 97%), 1-dodecanethiol (DDT, 98%), ethanol (>99.5%), silver(I) chloride (AgCl, 99.995%) and sodamide (NaNH₂, 95%) were obtained from Sigma-Aldrich. Diethyl ether (purchased from VWR) was sparged with argon and dried using a Glass Contour Solvent System from Pure Process Technology, LLC. Antimony chloride, bismuth chloride, lithium bis(trimethylsilyl)amide (LHMDS) were stored and handled in an inert atmosphere glove box. Oleic acid was recrystallized according to the procedures in ref. ⁵⁸, while other chemicals were used without further purification.

3.2.2 Synthesis of tris[N,N-bis(trimethylsilyl)amido]antimony, Sb[(N(SiMe3)2]3

The procedure developed by Liu et al.¹⁶² was used to synthesize tris[N,Nbis(trimethylsilyl)amido]antimony. The preparation is based on a metathesis reaction between antimony chloride and lithium bis(trimethylsilyl)amide. First, 760 mg SbCl₃ (3.33 mmol) was dissolved in a mixture of dry ether (15 mL) and THF (3 mL) and was slowly added dropwise to a stirring solution of 1.7 g lithium bis(trimethylsilyl)amide (10 mmol) in ether (10 mL) at 0 °C under an inert N₂ atmosphere. The solution became white in color and turbid during the addition, and was kept stirring at 0 °C for an additional hour. The resulting white solution was warmed to room temperature and kept overnight. Afterwards, the solution was filtered using a glass fritted funnel and the solvents were removed under reduced pressure, resulting in a pale yellow colored $Sb[(N(SiMe_3)_2]_3 \text{ product}$. The product was recrystallized from a saturated hexane solution, resulting in the white solid product $Sb[(N(SiMe_3)_2]_3, \text{ yield} \sim 80\%$. The purity of the product was determined via NMR; ¹H NMR (25 °C, CDCl₃, 400MHz) 0.29 (s); see the spectrum in Fig. 1. The reagent was stored in a -80 °C freezer in a sealed vial.

3.2.3 Synthesis of tris[N,N-bis(trimethylsilyl)amido]bismuth, Bi[(N(SiMe3)2]3

Carmalt et al.¹⁹⁶ The procedure developed by was synthesize used to tris[bis(trimethylsilyl)amide]bismuth. The preparation is based on a metathesis reaction between bismuth chloride and lithium bis(trimethylsilyl)amide. First, 1.0 g BiCl₃ (3.17 mmol) was added into a round bottom flask under a dry nitrogen atmosphere. Next, 20 mL of dry ether and 5 mL THF were added to the flask, which was maintained the temperature at 0°C. Next, 1.6 g lithium bis(trimethylsilyl)amide (9.51 mmol) dissolved in 15 mL of dry ether was added dropwise into the BiCl₃ solution. The resulting mixture became yellow in color and turbid. It was kept stirring at 0 °C for another hour and then slowly warmed to room temperature. Afterwards, the solution was filtered through a glass fritted funnel under an inert N2 atmosphere and the solvents were removed under reduced pressure. Finally, the product was recrystallized from a saturated toluene solution, resulting in a yellow solid Bi[N(SiMe₃)₂]₃ product, yield ~ 90%. The purity of the product was determined via NMR; ¹H NMR (25 °C, toluene-d₈, 400MHz) 0.36 (s); see the spectrum in Fig. 1. The reagent was stored in glove box under inert atmosphere covered with aluminum foil.


Figure 1: ¹H NMR spectra of Sb[(N(SiMe₃)₂]₃ and Bi[N(SiMe₃)₂]₃. Reprinted with permission from Ref. 213. Copyright 2017 The American Chemical Society.

3.2.4 Synthesis of AgSbSe2 nanoparticles

First, 10 mL of oleylamine was added into a three neck round-bottom flask and degassed under vacuum at 110 °C for 2 hours. In a 7 mL septa-covered vial labeled "A", 5 mL of oleylamine and 1 mL of oleic acid were added and were subsequently degassed under vacuum. Next, 85 mg (0.5 mmol) of AgNO₃ was added to this vial, which was kept stirring at 80 °C under an N₂ atmosphere until the solid dissolved completely. Next, the vial was cooled to 40 °C, and 300 mg (0.5 mmol) of Sb[(N(SiMe₃)₂]₃ dissolved in 0.5 mL toluene was added while maintaining the nitrogen atmosphere. In a separate vial labeled "B", 98 mg of selenium (1.25 mmol) was dissolved in a mixture of 0.5 mL oleylamine and 0.5 mL dodecanethiol. Afterward, the oleylamine in the three neck round bottomed flask was heated to 180°C. The solution in vial "A" was injected into the flask at 180 °C followed by an injection of the solution in vial "B". This resulted in the formation of a dark brown coloration. The solution was maintained at 180 °C for 2-3 mins. Afterwards, the heating mantle was removed and the solution was allowed to cool to room temperature. The sample was stored under an inert N₂ atmosphere in a glovebox.

3.2.5 Synthesis of AgSbSe2 nanoparticles in presence of a reducing agent

First, 10 mL of oleylamine and 85 mg (0.5 mmol) of AgNO₃ were added into a three-neck round bottom flask and degassed at 110 °C for 2 hours. At the same time, 300 mg (0.5 mmol) of Sb[(N(SiMe₃)₂]₃ was dissolved in 0.5 mL toluene and 98 mg of selenium (1.25 mmol) was dissolved in a mixture of 0.5 mL oleylamine and 0.5 mL dodecanethiol. The oleylamine in threeneck round bottom flask was cooled to 30°C and 0.9 mL of 1(M) lithium triethylborohydride (0.9 mmol) and Sb[(N(SiMe₃)₂]₃ solution in toluene was injected into the flask at 30 °C followed by an addition of the solution of selenium precursor. This resulted in the formation of a black colored suspension, which was then slowly heated to 180°C and maintained at 180 °C for another 10 mins. Afterwards, the heating mantle was removed and the solution was quickly allowed to cool to room temperature. The sample was stored under an inert atmosphere in a glovebox. A similar procedure was employed to synthesize AgBiSe₂ NCs, however the poor size distribution of AgSbSe₂ nanoparticles obtained using this procedure caused us to abandon the use of reducing agents.

3.2.6 Synthesis of AgBiSe2 nanoparticles

First, 10 mL of oleylamine and 85 mg (0.5 mmol) of AgNO₃ were added into a three-neck round bottom flask and degassed at 110 °C for 2 hours. At the same time, 345 mg (0.5 mmol) of Bi[(N(SiMe₃)₂]₃ was dissolved in 0.5 mL toluene and 98 mg of selenium (1.25 mmol) was dissolved in a mixture of 0.5 mL oleylamine and 0.5 mL dodecanethiol. Afterward, the oleylamine in three-neck round bottomed flask was cooled to 30°C and the Bi[(N(SiMe₃)₂]₃ solution was injected into the flask at 30 °C followed by the selenium precursor solution. This resulted in the formation of a black colored suspension. The solution was slowly heated to 200°C and maintained

at 200 °C for an additional 10 mins. Afterwards, the heating mantle was removed and the solution was allowed to cool to room temperature. The sample was stored under an inert N_2 atmosphere in a glovebox.

3.2.7 Surface ligand treatment and pellet formation

The following procedure was applied to both AgSbSe₂ and AgBiSe₂ samples in an identical manner. First, 800 mg of a sample was precipitated with an ethanol / isopropanol mixture and centrifuged. Next, the material was dispersed into 10 mL chloroform to which 10 mL of 0.01 M sodamide (NaNH₂) solution in ethanol was subsequently added. Afterwards, the sample was repeatedly washed with isopropanol and chloroform. Finally, a fine powder of nanocrystals was obtained after drying under vacuum. After ligand treatment, 500 mg of each fine powder were pressed into form a pellet under an applied pressure of 7.4 metric tons (~ 16000 lbs.).



AgSbSe₂ stock solution

AgSbSe₂ fine black powder

AgSbSe₂ pellet

Figure 2: Step by step processing of QDs solution into nanopellets. Reprinted with permission from Ref. 213. Copyright 2017 The American Chemical Society.

3.2.8 Characterization

For characterization, a small quantity of each sample was precipitated with ethanol and centrifuged to remove impurities. The precipitate was then redispersed in dry hexane and characterized by optical, X-ray photoelectron (XPS), and X-ray diffraction (XRD) spectroscopies. Absorption measurements were performed with a Perkin Elmer LAMBDA 1050 UV/Vis-NIR spectrophotometer. XPS analyses were performed on a Kratos Axis 165 using a monochromatic Al K α source operating at 12 kV and 10 mA to produce an X-ray power of 120 W. Spectra were collected with a photoelectron takeoff angle of 90° from the sample surface plane, in energy steps of 0.1 eV, and a pass energy of 20 eV for all elements. All spectra were referenced to the C1s binding energy (284.8 eV). X-ray diffraction studies were performed on a D8 Advance ECO Bruker XRD diffractometer using monochromatized Cu K α (λ = 1.54056 Å) radiation. Transmission electron microscopy (TEM) measurements were performed using a JEOL JEM-3010 operating at 300 keV. A 300 mesh gold grid was used for TEM analysis. ¹H NMR spectra were recorded using Bruker Avance DRX 400 NMR spectrometer.

3.2.9 Electrical measurement

Electrical measurement [current-voltage (I-V) characteristics] of the AgSbSe₂ and AgBiSe₂ quantum dot pellets were measured using a Keithley 2400 source meter at room temperature. Copper wires were soldered using indium on various locations of AgSbSe₂ and AgBiSe₂ quantum dot pellets as electrode contacts for I-V measurements. Fig. 12 shows the two-terminal I-V characteristics of the AgSbSe₂ and AgBiSe₂ pellets. All the I-V measurements show linear behavior, from which the resistance values are extracted from a linear fit. The resistance values of the AgSbSe₂ sample shown in Fig. 12 are 74 Ω (red), 96 Ω (blue), 123 Ω (green) between contacts 1 and 2, contacts 2 and 3, and contacts 1 and 3, respectively. The resistance values of the AgBiSe₂ sample shown in Fig. 12 are 23 k Ω (blue), 28 k Ω (red), 25 k Ω (green) between contacts 1 and 2, contacts 2 and 3, and contacts 1 and 3, respectively. The I-V curves of AgBiSe₂ are slightly removed from the origin; however, this is within the precision of the source meter over the scan range employed for this sample.

3.3 <u>RESULTS AND DISCUSSION</u>

As part of my research into the development of pnictide quantum dot chemistry, I have developed two pnictide precursors, tris[N,N-bis(trimethylsilyl)amido]antimony, [(Me₃Si)₂N]₃Sb and tris[N,N-bis(trimethylsilyl)amido]bismuth, [(Me₃Si)₂N]₃Bi to synthesize crystalline AgSbSe₂ and AgBiSe₂ nanoparticles. Discussed below are the results from each individual system, followed by electrical measurement data on monolithic pellets of the materials.

3.3.1 Silver antimony selenide (AgSbSe2)

AgSbSe₂ is a narrow indirect bandgap (0.58 eV) semiconductor with intrinsic p-type conductivity. It is a promising candidate for thermoelectric applications due to its high Seebeck coefficient, low thermal conductivity and good stability.¹⁹⁷⁻²⁰⁰ Furthermore, it is considered to be an excellent photovoltaic material due to its strong absorption.¹⁹⁹⁻²⁰¹

The synthesis of AgSbSe₂ NCs was studied via the hot injection method. To this end, two separate solutions of precursors were co-injected into oleylamine at 180°C. One contained the

antimony and AgNO₃ reagents dissolved in an oleylamine and oleic acid mixture. This was done to enhance the crystallinity of the AgSbSe₂ nanoparticle products under the rational that oleic acid stabilizes the hard Sb (+3) ions while oleylamine stabilizes the soft Ag (+1) ions. The sequence of addition of precursors during the preparation of the antimony and silver injection solution as detailed in the experimental section is important as the product does not have a pure crystallinity if the protocol is not followed exactly. The second solution that was co-injected contained selenium dissolved in oleylamine and dodecanethiol.

$AgNO_3 + Sb[N(SiMe_3)_2]_3 + Se (oleylamine / 1-dodecanethiol) \rightarrow AgSbSe_2$

A variety of characterization results are shown in Fig. 3, all of which demonstrate the synthesis of ~9 nm crystalline nanoparticles of AgSbSe₂. XPS results shown in Fig. 4 confirm the stoichiometry of the products. The crystal phase of the nanoparticles is consistent with characteristic pattern of the cubic phase of AgSbSe₂. The absorption spectrum in Fig. 4 is featureless; however, the absorption onset (~1300 nm) is greater than the bulk bandgap. This is potentially due to quantum confinement, which affords the possibility for manipulation of the properties of artificial solids that incorporate these materials. The most interesting discovery concerns the fact that no reducing agents were required to activate either Sb[(N(SiMe₃)₂]₃ nor Bi[(N(SiMe₃)₂]₃ as was necessary for the synthesis of arsenic nanomaterials in our earlier study. In fact, inclusion of a reducing agent resulted in a bivariate distribution of nanoparticle sizes as discussed later, see Fig. 5.

There are important differences to note between the results of this study and previous demonstrations of AgSbSe₂ materials synthesis. For example, the preparation of nanocrystalline silver antimony dichalcogenide using solid state conditions results in polydisperse samples.²⁰¹ As such, colloidal methods are preferred, and indeed Lin et al. first demonstrated homogeneous 7-17

nm AgSbSe₂ NCs via the rapid injection procedure using SbCl₃ as the pnictide source.¹⁹⁵ The use of Sb[(N(SiMe₃)₂]₃ as presented in this report created a similar small size of NCs; however, our protocol requires $\sim 1/10^{th}$ the quantity of precursors. Furthermore, the use of SbCl₃ results in an initial bimodal size distribution that grew into a monodisperse population over 30 min. In contrast, we observed a reasonably monodisperse AgSbSe₂ NC population within 3 minutes of injection, which indicates homogeneous nucleation and growth. Consequently, there is considerable value in the use of Sb[N(SiMe₃)₂]₃ vs the dichloride as a precursor for nanomaterials.



Figure 3. (a) TEM image of AgSbSe₂ nanoparticles. (b) X-ray diffraction pattern of AgSbSe₂ NCs confirm their structure and crystallinity. (c) High resolution TEM image of crystalline AgSbSe₂ showing lattice fringes. (d) Size distribution of AgSbSe₂ dots. Reprinted with permission from Ref. 213. Copyright 2017 The American Chemical Society.



Figure 4. UV/Vis and X-ray photoelectron spectra of AgSbSe₂ NCs. a) XPS survey spectra of AgSbSe₂ quantum dots. b) UV/Vis spectra of AgSbSe₂ quantum dots. Reprinted with permission from Ref. 213. Copyright 2017 The American Chemical Society.



Figure 5. TEM micrographs of polydisperse AgSbSe₂ nanocrystals prepared with the use of a reducing agent. Reprinted with permission from Ref. 213. Copyright 2017 The American Chemical Society.



Figure 6. TEM micrographs of AgSbSe₂ nanocrystals. Reprinted with permission from Ref. 213. Copyright 2017 The American Chemical Society.

3.3.2 Silver bismuth selenide (AgBiSe₂)

AgBiSe₂ is another interesting member of the I-V-VI₂ semiconductor family that has excellent thermoelectric properties.²⁰² At room temperature, it is p-type with a hexagonal phase, and can undergo a structural transition to cubic via a rhombohedral intermediate phase.²⁰³ Both the hexagonal and rhombohedral materials are narrow band gap ($\sim 0.6 \text{ eV}$) semiconductors, while the high temperature cubic phase behaves like a metal with a high electrical conductivity yet a low thermal conductivity.^{112, 203} At present, there is only one other example of the colloidal synthesis of silver bismuth selenide.²⁰² This rapid injection process required long annealing times that yielded anisotropic nanoparticles, while our heat-up protocol using Bi[(N(SiMe₃)₂]₃ generated more homogeneous and spherical nanocrystals within ~10 min.

$$AgNO_3 + Bi[N(SiMe_3)_2]_3 + Se (oleylamine / 1-dodecanethiol) \rightarrow AgBiSe_2$$

We have synthesized AgBiSe₂ NCs at 200°C using Bi[(N(SiMe₃)₂]₃, AgNO₃, and selenium in an oleylamine solution. In contrast to the antimonide system, the rapid injection of precursors resulted in materials with broad and unidentifiable XRD patterns. This prompted the use of a heatup procedure, which produces significantly cleaner results as shown in Fig. 7. The results are consistent with the synthesis of small, ~6 nm diameter crystalline dots, albeit the materials are less monodisperse compared to AgSbSe₂ NCs; Fig. 7a, 7c, 9. The crystal phase of the nanoparticles was confirmed by powder XRD and is consistent with characteristic pattern of the complex hexagonal phase of AgBiSe₂. XPS result also confirms the composition of AgBiSe₂ nanoparticles although there exists a slight excess of selenium; see Fig. 8. As was observed in the antimonide materials, the absorption spectrum shown in Fig. 8 is featureless and has a higher energy onset (~ 1200 nm) compared to the bandgap, which is indicative of quantum confinement effects.



Figure 7. (a) TEM image of AgBiSe₂ nanoparticles. (b) X-ray diffraction pattern of AgBiSe₂ nanoparticles. (c) High resolution TEM image of crystalline AgBiSe₂ showing lattice fringes. (d) Size distribution of AgBiSe₂ dots. Reprinted with permission from Ref. 213. Copyright 2017 The American Chemical Society.



Figure 8. UV/Vis and X-ray photoelectron spectra of AgBiSe₂ NCs. a) XPS survey spectra of AgBiSe₂ quantum dots. b) UV/Vis spectrum of AgBiSe₂ quantum dots. Reprinted with permission from Ref. 213. Copyright 2017 The American Chemical Society.



Figure 9. TEM micrographs of various AgBiSe₂ nanocrystals. Reprinted with permission from Ref. 213. Copyright 2017 The American Chemical Society.

3.3.3 Electrical measurements

Room temperature current-voltage (I-V) behavior was measured to characterize the electrical conductivity of silver dimetal chalcogenide artificial solids. The materials were precipitated and processed by washing with a sodamide solution. FTIR spectroscopy confirm the removal of the original ligands as shown in Fig. 10. The resulting AgSbSe₂ and AgSbSe₂ nanoparticle powders were transformed into 13 mm \times 0.9 mm thick pellets in a press. Copper wires were soldered to the surface using indium as electrode contacts as seen in Fig. 11 inset. Also shown are the room temperature two-terminal I-V plots of the AgSbSe₂ and AgBiSe₂ quantum dot monoliths.

All the I-V measurements demonstrate linear resistive behavior, indicating Ohmic contact nature of the soldered electrodes. Three contact points were used to verify the proper resistance vs. electrode distance behavior as well as confirm good uniformity of the nanomaterials throughout the pellet, see Fig. 12. Overall, the conductivity is significantly smaller than bulk materials; furthermore, the bismuth NCs are much lower than the antimony materials despite their similar bulk transport properties.¹¹² This is likely due to both the smaller size and higher polydispersity of the AgBiSe₂ sample, as these factors increase the resistance in solid monoliths of semiconductor nanocrystals.²⁰⁴ The conductivity of the AgSbSe₂ NCs using the method of Lin et al. was reported to be significantly higher than observed here,¹⁹⁵ which may be due to the fact that we did not attempt to thermally anneal the NC pellets. As a result, a massive number of grain boundaries may have developed inside the pellet that ultimately increased the resistance of these pellets.



Figure 10. FT-IR spectra of oleic acid, oleylamine, 1-dodecanethiol, AgSbSe₂, and AgBiSe₂ nanocrystals after surface treatment of the particles. Reprinted with permission from Ref. 213. Copyright 2017 The American Chemical Society.



Figure 11. I-V measurement of AgBiSe₂ and AgSbSe₂ monolithic NC pellets (inset). Reprinted with permission from Ref. 213. Copyright 2017 The American Chemical Society.



Figure 12. Electrical (I-V) measurement of AgSbSe₂ and AgBiSe₂ NC monoliths. Reprinted with permission from Ref. 213. Copyright 2017 The American Chemical Society.

3.4 CONCLUSION

Silver dimetal chalcogenides (Ag-V-VI₂) are ternary semiconductors that have potential alternative energy applications due to their optimal band gaps and large extinction coefficients. The syntheses of these materials are challenging due to the lack of effective pnictide precursors. In this chapter, tris[N,N-bis(trimethylsilyl)amido]antimony, [(Me₃Si)₂N]₃Sb and tris[N,N-bis(trimethylsilyl)amido]bismuth, [(Me₃Si)₂N]₃Bi have been successfully applied to synthesize monodisperse, crystalline AgSbSe₂ and AgBiSe₂ nanoparticles. The rapid injection procedure was employed for AgSbSe₂ nanoparticles, whereas heat-up process was followed to produce AgBiSe₂ nanocrystals. The most interesting discovery involves the fact that no reducing agents were required to activate either Sb[(N(SiMe₃)₂]₃ nor Bi[(N(SiMe₃)₂]₃. The primary goal of using reducing agent is to activate pnictide-N bond which was necessary for the synthesis of arsenic nanomaterials as discussed in chapter 2. For bismuth and antimony, inclusion of a reducing agent

However, the presence of Ag metal helps to activate pnictide-N bond here and it results in the synthesis of better materials with enhanced monodispersity and crystallinity.

Furthermore, electrical measurements on monolithic pellets of processed AgSbSe₂ and AgBiSe₂ nanomaterials demonstrate linear current-voltage behavior at room temperature, indicating Ohmic contact formation which enhances utility for electronic device applications. These results reveal several paradigms concerning pnictide chemistry as it applies to the synthesis of nanomaterials.

4 Hydrophilic Phosphonic Acid Ligands to Water Solubilize Quantum Dots

4.1 INTRODUCTION

As discussed in chapter 1, colloidal semiconductor quantum dots are excellent candidates for numerous applications, primarily for fluorescence-based biological sensing and imaging due to their unique photophysical properties.^{9-10, 87, 104} Quantum dots are significantly resistant towards photobleaching compared to organic dyes, have tunable and narrow emission profiles, and are strongly absorptive at energies higher than their characteristic bandgaps.^{26-27, 74} However, the best method to synthesize bright quantum dots involve hydrophobic ligands that enables colloidal dissolution of QDs in nonpolar solvent.⁴⁷ However, water solubility is a necessary property for biological experiments.⁶¹⁻⁶² Thus, quantum dots must be processed to render them from organic phase to the aqueous phase, which remains a challenging chemical modification still today. So far, researchers have employed two primary protocols for water solubilization of QDs: 1) encapsulation, and 2) ligand exchange. To our knowledge, amphiphilic carboxylic acid polymers are commonly used ligands in the encapsulation method.^{75, 78-80} This protocol creates stable QDs aqueous dispersions with minimal loss in quantum yield; however, the hydrodynamic diameter of encapsulated quantum dots is very large which makes them incompatible for biological applications. Researchers have observed the difficulty with cytocellular staining of living cells and nonspecific adsorption onto the cell walls of QDs.⁸² Also, there are no instances of renal excretion of such large quantum dots in animal studies.⁶⁵ To avoid these problems, researchers developed the ligand exchange protocol, which functions via the removal of native hydrophobic ligands with hydrophilic ones for water solubilization of quantum dots. Thiol functionalized cysteine, dihydrolipoic acid (DHLA) or poly(ethylene glycol)-modified DHLA are ubiquitous in the ligand

exchange method.^{6, 65, 69} The ligand exchange protocol resolves many problems associated with encapsulation. For example, after processing, ligand-exchanged quantum dots are smaller and thus more biologically compatible. However, the ligand exchange process results in significant loss of quantum yield and reduced stability due to thiol oxidation which restricts its application in biological sensing.⁷³

Recently our group has demonstrated a method of ligand exchange by replacing the hydrophobic phosphonic acids on CdSe/ZnS QDs with thiol-functional ligands bound to Zn metal center.²⁰⁵ It imparts greater stability and minimal loss of quantum yield. Further research on this topic led our group to discover another simple way to water-solubilize QDs with a near monolayer of silane.⁷⁴ The procedure is less time consuming compared to SiO₂-encapsulating methods and yields highly stable, brighter water soluble quantum dots. However, there is so far no examples in literature where hydrophilic quantum dots are synthesized in one step that imparts comparable brightness and stability with QDs synthesized via high temperature rapid injection method. This is because long chain alkyl phosphonic acids are the best known ligands to synthesize high quality CdSe QDs in hydrophobic solvents due to favorable interaction of phosphonic acids with Cd (+2) on the surface. This interaction improves the monodispersity and passivates the surface defects of cadmium selenide quantum dots, which results in higher quality materials. Based on this paradigm, we designed a series of hydrophilic ligands with a phosphonic acid group at one end. A library of ligands is shown in scheme 1 that we have employed a variety of strategies to incorporate these ligands on top of CdSe quantum dots, including: 1) synthesis of QDs in polar solvents (DMF and water), 2) synthesis of QDs in hydrophobic solvents, and 3) ligand exchange via hydrophilic phosphonic acid ligands. However, none of these methods resulted in stable colloidal dispersions of QDs as discussed in the following sections.



Scheme 1. (a) Schematic diagram of hydrophilic phosphonic acid ligands. (b) A series of phosphonic acid ligands employed to water solubilize QDs.

4.2 EXPERIMENTAL

4.2.1 Materials

All chemicals were used as received unless noted. Phosphorous tribromide (99%) was purchased from Alfa Aesar. Methoxy poly(ethylene glycol, $M_n \sim 350$), methoxy poly(ethylene glycol, $M_n \sim 750$) were bought from Fluka. N-(3-bromopropyl)phthalimide (98%) and N-(8bromooctyl)phthalimide (98%) were bought from Oakwood Chemicals. Technical grade 1octadecene (90%), bis-trimethylsilyl sulfide (purum, >98%), cadmium acetate dihydrate (98%), sodium borohydrate (99%), cadmium oxide (99.99%), pyridine (anhydrous, 99.8%), carbon tetrachloride (99%), triethylphosphite (98%), oleic acid (OA, 90%), bromotrimethylsilane (98%), hydrazine monohydrate (98%), phthalimide potassium salt (98%), cadmium chloride (99%), sodium hydroxide (97%), and 3-phosphonopropionic acid (98%), propylene oxide (99%), 1,8dibromooctane (98%) were purchased from Sigma-Aldrich. Diethylzinc (95%) and trioctyl phosphine (99%) was purchased from Strem. Diethyl ether (purchased from VWR) was sparged with argon and dried using a Glass Contour Solvent System from Pure Process Technology, LLC. Phosphorous tribromide, bromotrimethylsilane, triethyl phosphite, diethylzinc, trioctyl phosphine, bis(trimethylsilyl) sulfide were stored and handled in an inert atmosphere glove box. Oleic acid was recrystallized according to the procedures in ref.⁵⁸, while other chemicals were used without further purification.

4.2.2 Synthesis of methoxy poly(ethylene glycol, Mn~350)-bromide, mPEG350-Br



Scheme 2. Schematic diagram of the synthesis of mPEG350-bromide from mPEG350

First, 0.4 mL of pyridine was slowly added to 2.00 g (5.7 mmol) of mPEG350 (1) in a round bottom flask at 0°C under a nitrogen atmosphere. Afterwards, 1.00 g of PBr₃ (3.8 mmol) was added dropwise to this mixture which was stirred at room temperature for 16 hours. Next, 10 mL of distilled water was added and the mixture was extracted 3x with CCl₄. The combined organic extracts were washed thoroughly with 10 mL of 10% NaCO₃, 5% H₂SO₄, distilled water and was further dried over anhydrous Na₂SO₄. The solvent was removed via rotary evaporation. The crude product was chromatographed on silica gel with CHCl₃: MeOH (10:1) as the mobile phase. A colorless viscous oil (2) was obtained. Yield: 50%; ¹H NMR (25°C, CDCl₃, 400MHz): 3.36 (s, - O-CH₃), 3.62 (m, -(CH₂CH₂O))_n-), 3.79 (t, CH₃O-CH₂CH₂-).



Figure 1. ¹H NMR of methoxy poly(ethylene glycol, $M_n \sim 350$)-bromide, mPEG350-Br.

4.2.3 Synthesis of methoxy poly(ethylene glycol, Mn~750)-bromide, mPEG750-Br



Scheme 3. Schematic diagram of the synthesis of mPEG750-bromide from mPEG750.

mPEG750-bromide (5) was synthesized in a similar way as mPEG350-bromide. First, 0.4 mL of pyridine was slowly added to 4.00 g (5.3 mmol) of mPEG750 (5) in a round bottom flask

at 0°C under a nitrogen atmosphere. Afterwards, 1.00 g of PBr₃ (3.8 mmol) was added dropwise to this mixture and the resulting mixture were stirred at room temperature for next 16 hours. Next, 20 mL of distilled water was added and the mixture was extracted 3x with CCl₄. The combined organic extracts were rinsed successively with 20 mL of 10% NaCO₃, 5% H₂SO₄ and distilled water. It was further dried over anhydrous Na₂SO₄ and the solvent was removed via rotary evaporation. The crude product was chromatographed on silica gel with a CHCl₃: MeOH (15:1) mobile phase, resulting in a colorless, viscous oil. Yield: 40%; ¹H NMR (25°C, CDCl₃, 400MHz): 3.28 (s, -O-CH₃), 3.55 (m, -(CH₂CH₂O))_m-).



Figure 2. ¹H NMR of methoxy poly(ethylene glycol, $M_n \sim 750$)-bromide, mPEG750-Br.

4.2.4 Synthesis of methoxy poly(ethylene glycol, M_n~350,750)-diethylphosphonate;

<u>mPEG(M_n~350,750)-PO(OEt)2</u>



Scheme 4. Schematic diagram of the synthesis of mPEG350,750-diethylphosphonate from mPEG350-bromide and mPEG750-bromide respectively

Excess triethyl phosphite (1.7 mL, 9.3 mmol) was added to 1.00 g (2.32 mmol) of mPEG350bromide (**2**) in a round bottom flask. The mixture was refluxed at 156°C for 24 hours. Afterwards, the excess triethyl phosphite was removed via reduced pressure distillation and a viscous, colorless liquid remained. Yield: 80%; ³¹P: 26.97(s); ¹H NMR (25°C, CDCl₃, 400MHz):1.21(t, -P(O)(OCH₂CH₃)), 3.26 (s, -O-CH₃), 3.62 (m, -(CH₂CH₂O))_n-), 3.99 (q, -P(O)(OCH₂CH₃)).

Similar procedure was followed to synthesize mPEG750-diethylphosphonate. Yield: 70% and Fig. 4 refers to ¹H NMR (400MHz) of mPEG750-diethylphosphonate. ¹H NMR (25°C, CDCl₃, 400MHz):1.18 (t, -P(O)(OCH₂CH₃)), 3.23 (s, -O-CH₃), 3.50 (m, -(CH₂CH₂O))_m-), 3.96 (q, -P(O)(OCH₂CH₃)); ³¹P: 26.91(s);



Figure 3. ¹H and ³¹P NMR of methoxy poly(ethylene glycol, $M_n \sim 350$)-diethylphosphonate, mPEG350-PO(OEt)₂



Figure 4. ¹H and ³¹P (box) of NMR of mPEG750-diethylphosphonate.

4.2.5 <u>Synthesis of methoxy poly(ethylene glycol, M_n~350)-phosphonic acid, mPEG350-</u>



Scheme 5. Schematic diagram of the synthesis of mPEG350-phosphonic acid from mPEG350-diethylphosphonate.

First, 500 mg (1.0 mmol) of mPEG-350 diethyl phosphonate (**3**) was dissolved in 20 mL of dry dichloromethane and 628 mg (4.0 mmol) of trimethylsilyl bromide was slowly added to it under an inert atmosphere. The solution was kept stirring for another 2 hours at room temperature. Next, the solvent was removed under vacuum resulting in a brown oil. This oil was dissolved in 20 mL of acetone and 0.5 mL of water and was kept stirring for half an hour to dissociate excess trimethylsilyl bromide. The solvent was removed under reduced pressure to leave a light yellow-colored oil. The oil was characterized via ¹H and ³¹P NMR. However, more than one product results from this protocol which leads me to conclude that this procedure is unsuccessful concerning the synthesis of mPEG350-phosphonic acid. ³¹P NMR (CDCl₃, 400MHz): multiple peaks between -28.98 and -27.94.



Figure 5. ³¹P NMR of the product (s) of the reaction between mPEG350-PO(OEt)₂ and bromotrimethylsilane.

4.2.6 Synthesis of 3-aminopropylphosphonic acid, H₂N-(CH₂)₃-PO(OH)₂



Scheme 6. Schematic diagram of the synthesis of 3-aminopropylphosphonic acid from N-(3-bromopropyl)phthalimide.

First, 3-aminopropylphosphonic acid was synthesized in three step reaction following the method of Schmidt et. al..²⁰⁶ An excess of triethyl phosphite (13 mL, 74 mmol) was added to 5.00 g (19 mmol) of N-(3-bromopropyl)-phthalimide (8) in a round bottom flask and the mixture was refluxed at 156°C for 24 hours. Afterwards, excess triethyl phosphite was removed via reduced pressure distillation and 3-[(phthalimido)propyl]-diethylphosphonate ester (9) was obtained; (yield: 75%). Next, 3.5 g (11.9 mmol) of 3-[(phthalimido)propyl]-diethylphosphonate ester was dissolved in 50 mL of ethanol and 3 mL of 80% hydrazine hydrate aqueous solution was added dropwise. The reaction mixture was stirred for 72 hours. Afterwards, the solution was diluted with another 20 mL of ethanol and phthalhydrazide was removed via filtration. Finally, the solvent was removed under reduced pressure to yield a pale yellow colored viscous liquid of 3-aminopropyldiethylphosphonate (10); yield: 60%. In the last step, 1.00 g (5.12 mmol) of 3-aminopropyldiethylphosphonate was dissolved into 50 mL 6M HCl in a round bottom flask and was refluxed for 2 days. Afterwards, the solvent was removed using a rotary evaporator and the residue was washed 3x with ethanol: water (1:1) solution. The hydrochloride salt of 3-aminopropylphosphonic acid was dissolved in ethanol, and a white precipitation of 3-aminopropylphosphonic acid (11) was observed after the addition of 1.5 mL of propylene oxide. The precipitate was filtered and was washed with a water /ethanol solution; yield: 50%. The purity of the product was confirmed by ¹H and ³¹P NMR. ¹H NMR (25°C, D₂O, 400MHz): 2.95(t, 2H), 1.77 (m, 2H), 1.54 (m, 2H); ³¹P: 22.31(s).



Figure 6. ¹H and ³¹P (box) of NMR of 3-aminopropylphosphonic acid.

4.2.7 Synthesis of 8-aminooctylphosphonic acid, H2N-(CH2)8-Br



Scheme 7. Schematic diagram of the synthesis of 3-aminooctylphosphonic acid

The QD ligand 8-aminopropylphosphonic acid (16) was synthesized following the same procedure as 3-aminopropylphosphonic acid (11). The purity of the product was confirmed via ¹H and ³¹P NMR. ¹H NMR (25°C, D₂O, 400MHz): 1.06 (m, 2H), 1.22 (m, 8H), 1.38 (m, 2H), 1.74 (m, 4H), 2.60 (t, 2H); ³¹P: 30.92(s).



Figure 7. ¹H and ³¹P (box) of NMR of 8-aminooctylphosphonic acid.

4.2.8 Strategy 1: Direct synthesis of CdSe quantum dots in polar solvents

we have used two different solvents, water and dimethylformamide (DMF) to synthesize CdSe QDs in the presence of hydrophilic phosphonic acid as QD ligands.

4.2.8.1 Direct synthesis of CdSe QDs in water

First, 4.5 mg (0.12 mmol) of NaBH₄ and 8 mg (0.1 mmol) of selenium were taken into a three neck round bottom flask attached with an addition funnel. The whole system was kept under an inert atmosphere at 0°C. Next, 5 mL of ethanol was added to this cold mixture. Initially, a vigorous foaming was observed in the first 5 mins which later subsided forming a clear solution of NaHSe. The whole apparatus was kept properly sealed and under nitrogen atmosphere, otherwise red coloration was observed due to the oxidation of NaHSe.

In another 2 neck round bottom flask, 154 mg (1 mmol) of 3-phosphonopropionic acid was dissolved into 40 mL of slightly basic (pH~8) water. Then, 73 mg (0.4 mmol) of CdCl₂ suspension in 2 mL of water was added to it dropwise with vigorous stirring. The total volume of the solution was 50 mL. This round bottom flask was connected with the flask containing NaHSe solution via rubber tubing (see scheme 8). Initially, the reaction flask was kept at 60°C for CdSe core synthesis.

Under stirring, H₂Se gas was generated by the reaction of the ethanolic solution of NaHSe upon the addition of 2 mL of 50 mM of H₂SO₄ acid. Afterwards, the gas was passed under the flow of nitrogen to reaction vessel containing Cd (+2) salt and ligand via the connected tubes. The temperature of the reaction vessel was increased slowly from 60 °C to 80 °C. However, a dark maroon colored solution formed and it was precipitated within 10 mins which indicates the formation of Se nanoparticles and no emission was observed.



Scheme 8. Schematic diagram of the direct synthesis of CdSe quantum dots in presence of phosphonic acid ligands in a polar medium.

4.2.8.2 Direct synthesis of CdSe QDs in dimethylformamide

I have used the same protocol to synthesize CdSe quantum dots in dimethylfomamide as solvent instead of water. In DMF, a pure solution of orange colored CdSe quantum dots formed that displayed a faint green emission. The experiment was repeated with 8-aminoctylphosphonic acid and 3-aminopropylphosphonic acid and the same result was observed.

4.2.9 Strategy 2: Synthesis of CdSe quantum dots in hydrophobic solvent

Here, 128 mg (1 mmol) of cadmium oxide, 836 mg (4 mmol) of 8-aminoctylphosphonic acid, and 5.00 g of trioctylphosphine oxide were taken in a three neck round bottom flask attached with a thermocouple and a reflux condenser. The solution was degassed at 120°C for 2 hours and then it was heated to 300°C for 15 mins. Usually, at this temperature, the brown color of cadmium oxide vanishes, indicating the formation of cadmium phosphonate. Once the solution became clear, 1 mL of TOPSe was injected immediately and it was kept at 300 °C for 15 minutes. Afterwards, it was cooled to room temperature. No indication of quantum dot formation was evident. Only a weak blue emission was observed. The similar procedure was followed for 3-aminpropylphosphonic acid as ligand and same result was observed.



Scheme 9. High temperature rapid injection synthesis of CdSe quantum dots in presence of phosphonic acid ligands.

I used a similar procedure with 1-octadecene as solvent in the presence of mPEG phosphonate ligands. The dark brown color of the solution became clear at 180°C and TOPSe was injected at 220°C. As in the previous example, no QDs were formed using this procdure.

4.2.10 <u>Strategy 3: Ligand exchange from hydrophobic to hydrophilic phosphonic acid</u> <u>ligands</u>

In this protocol, we have synthesized oleic acid coated CdSe/ZnS quantum dots and followed a ligand exchange protocol to replace oleic acid with different types of phosphonic acid ligands.

4.2.10.1 Direct synthesis of cadmium oleate, Cd(Oleate)2

First, 2.3 gm (8.25 mmol) of purified oleic acid, 500 mg (3 mmol) of cadmium oxide, and 10 mL of 1-octadecene were loaded into a round bottom flask attached with a thermocouple and reflux condenser. The mixture was degassed at 100 °C for 1 hour and then it was heated to 180 °C for another 1.5-2 hours until the solution became clear. Afterwards, this solution was cooled to room temperature and saved as Cd(oleate)₂ stock solution for further synthesis.

4.2.10.2 Synthesis of oleic acid-coated CdSe/ZnS quantum dots

First, 7 mL of Cd(oleate)₂ stock solution, 1.5 g of oleic acid and 20 g of ODE were loaded into a three neck round bottom flask. The solution was degassed for 2 hours at 110 °C and then the solution was heated to 240 °C. At this elevated temperature, 0.7 mL of TOPSe was quickly injected

into the solution. The solution became orange almost immediately, indicating the formation of CdSe cores. The solution was cooled to room temperature.

For shell formation, 15 mL ODE and 1.5 g of oleic acid were loaded into a 4-neck round bottom flask and was degassed at room temperature for 1 hour. In the meantime, 4 g of the CdSe quantum dot core solution was mixed with methanol, isopropanol, and hexane to initiate the precipitation of the dots. Then it was dissolved in 3 mL hexane and the QD solution was injected into 4-neck round bottom flask. Hexane was removed by degassing for 2 hours. After degassing, the temperature of the solution was increased to 160 °C and 45 mg of diethyl zinc and 120 mg of bis(trimethylsilyl)sulfide in 1 mL of ODE was added dropwise over 2 hours. It was kept at 160 °C for another half an hour. It was then cooled to room temperature. A red emission was observed, indicating the formation of core/shell CdSe/ZnS QDs.

4.2.10.3 Ligand replacement from oleic acid to phosphonic acid in biphasic medium

First, 0.3 g of CdSe/ZnS core-shell quantum dots were precipitated using ethanol/isopropanol/hexane solution. It was centrifuged and redispersed into 2 mL hexane. Next, 300 mg of 3-phosphonopropionic acid was dissolved into methanol, which was added dropwise to the QD solution and was kept for stirring overnight. The quantum dots went into the polar layer immediately, but kept precipitating from the polar layer. The same result observed with both 8-aminoctylphosphonic acid and 3-aminopropylphosphonic acid ligands and water in place of alcohol.



Scheme 10. Schematic diagram of ligand exchange protocol in biphasic medium.

4.2.11 Characterization

Absorption and emission measurements were performed with a Varian Cary 300 Bio UV/Vis and a customized Fluorolog (HORIBA Jobin Yvon) modular spectrofluo-rometer, respectively. ¹H NMR and ¹³C NMR spectra were recorded at various temperatures using Bruker Avance DRX 400 NMR spectrometer.

4.3 **RESULTS AND DISCUSSION**

As stated previously, water solubilization of QDs is a challenging issue as the majority of methods result in instable and quenched quantum dots. Our primary goal in this project is to synthesize a series of hydrophilic phosphonic acid ligands and apply them to solubilize CdSe QDs in water. According to the framework (scheme 1), we have selected following five compounds:

mPEG350-phosphonic acid, mPEG750-phosphonic acid, 3-aminopropylphosphonic acid, 8-amino propylphosphonic acid, and commercially available 3-phosphonopropionic acid. In case of mPEGphosphonic acids, the last step i.e. the synthesis of mPEG-phosphonic acid from mPEGphosphonate, was challenging. In presence of Me₃SiBr, a mixture of phosphonic acids were obtained due to partial hydrolysis of the mPEG moiety. However, I could not find a suitable procedure to hydrolyze the phosphonate ester without mPEG- hydrolysis.

After the synthesis of these ligands, the next step was to apply a procedure to water solubilize CdSe QDs. Here, we have followed three different strategies to incorporate phosphonic acid ligands on the surface of these quantum dots.

4.3.1 Strategy 1: Direct synthesis

In this strategy, we used $H_2Se(g)$ as a source of Se and CdCl₂ as a Cd (+2) source. However, in presence of phosphonic acid ligands in water, we have observed a white precipitation of Cd(phosphonate)₂ that did not dissolve in water even at an elevated temperature. After H₂Se gas was passed through the solution, a wine red-colored precipitation of selenium nanoparticles was observed. To decrease the interaction between Cd (+2) and phosphonic acid, a less polar solvent, dimethylformamide was used instead of water. In DMF, orange colored CdSe quantum dots were formed and characterized using UV-Vis spectrophotometer. A small amount of this sample was precipitated to remove other byproducts and dissolved into aqueous medium. Within few minutes, precipitation of quantum dots was observed. Most likely the ligands are weakly bound on the surface of QDs or dimethylformamide itself is acting as ligand to stabilize CdSe QDs. Due to weak
interaction between DMF and QD surface, it becomes highly unstable once it went into water medium.



Figure 8. UV/Vis spectra of CdSe quantum dots in DMF.

4.3.2 Strategy 2: Synthesis in high boiling point solvent

In this strategy, we attempted to apply mPEG350-diethylphosphonate and mPEG750diethylphosphonate ligands at higher temperature by synthesizing Cd(mPEG-phosphonate)₂ via hydrolysis of the ester bond catalyzed by Cd (+2) at a high temperature. A change in color of the solution from dark brown to colorless at a high temperature demonstrated the formation Cd(mPEG-phosphonate)₂. The same result was observed irrespective of the nature of ligands. In next step, we have used TOPSe as a source of selenium to generate CdSe quantum dot cores. However, no emission and change in color of solution was observed. To increase the reactivity of selenium precursor, we substituted TOPSe with Ph₂PSe; still same observation was noted. It is difficult to ascertain the reason behind these observations, yet we believe that, in presence of hydrophilic phosphonic acids, a stable polymerized cluster of Cd-phosphonate forms that is highly inert towards successive transformation into quantum dots.

4.3.3 Strategy 3: Ligand exchange

Here, we have used a biphasic approach to replace the native oleic acid ligands with polar phosphonic acid ones. In this protocol, we added a methanolic solution of phosphonic acid to a hexane solution of oleic acid-coated CdSe/ZnS QDs. Immediately after the addition of phosphonic acids, QDs transferred from nonpolar phase to polar phase. However, the dots started to precipitate from methanolic medium immediately after the phase transfer. Initially, as the QDs transferred from nonpolar phase to polar phase, we believe that the native ligands were displaced from the surface. However, after phase transfer, the ligands from the QDs fall off and it leads to permanent precipitation of QDs. This observation can be explained via thermodynamics. In a polar medium, phosphonic acids are solvated in a lower free energy state compared to solvated while conjugated to the QD surface, see scheme 11. Also, the transformation to freely solvated phosphonic acids to solvated phosphonic acid coated quantum dots is entropically favorable. Overall, basic thermodynamics restrict the solubilization of quantum dots into polar medium.

4.4 <u>CONCLUSION</u>

Water solubilization of quantum dots is a critical technique for many applications. This research represents an attempt to keep the stability and quality of QDs in an aqueous medium the same as that observed in a nonpolar medium. In this project, the idea was to mimic the interaction



Scheme 11. Solvation energy of polar phosphonic acid vs. phosphonic acid-coated QD

between alkyl phosphonic acids with CdSe QDs in water via modification of hydrophobic alkyl phosphonic acids into polar species. However, the outcome was always unfavorable as QDs always precipitated from the polar medium. It is difficult to ascertain the reason behind these observations. However, this could be a result of either self-polymerization of polar phosphonic acids under appropriate condition, weak interaction between QD and ligands, or the fact that ΔG of the free solvated state is lower.

5 Conclusion

Colloidal semiconductor nanocrystals, or quantum dots, are excellent tools for numerous applications such as alternative energy generation and biological sensing. Our group is well known for the synthesis of high quality quantum dots and demonstrating applications for bioimaging and bio-sensing. My research explored Group-V (P, As, Sb, Bi) semiconductor chemistry. The synthesis of pnictide semiconductor nanostructures is challenging as well as dangerous. At present, there are few options for pnictide precursors and considering their physical characteristics, it is difficult to use them under simple laboratory conditions. The majority of my research was focused on developing safe and effective group-V precursors for the syntheses of a wide range of pnictide semiconductor nanoparticles. For one project, I successfully synthesized an effective arsenic precursor, bis-[N,N-trimethylsilyl)amido chloroarsenic, which has minimal air sensititvity and low vapor pressure, and is significantly safer to handle than gaseous hydrides or pyrophoric tris(trimethylsilyl)arsine. A variety of arsenide nanomaterials with different compositions and shapes have been synthesized with this precursor. The discovery of enargite (Cu₃AsS₄) nanorods was the most interesting. The mechanisms that result in the formation of the products were explored with DFT and NMR analyses. The understanding behind mechanistic studies help us to expand the horizons for use of this precursor to other systems.

Considering the results with this arsenic precursor, we realized that other pnictide reagents incorporating the -N(TMS)₂ ligand are highly stable, solid, easy to synthesize, and safe to handle. I followed up on these arsenic studies via exploring two other pnictide precursors, Sb[N(SiMe₃)₂]₃ and Bi[N(SiMe₃)₂]₃, and their application to synthesize two silver based dichalcogenide nanomaterials, AgBiSe₂ and AgSbSe₂.

Future research on Group-V nanomaterial chemistry will likely explore phosphorous. Semiconductor phosphide nanomaterials are important class of materials due to their potential application in photovoltaics and bioimaging. However, the synthesis of safe and efficient phosphide precursors is as challenging as with other pnictides. The ubiquitous reagent, tris(trimethylsilyl)phosphine, [(Me₃Si)₃P] is highly flammable and extremely costly. During my research in Prof. Snee's group, I have also worked on the syntheses of different types of efficient phosphorous precursors (Fig. 1), mostly tris(triphenyltin)phosphide. Compound (1) and (2) were synthesized from white P₄ directly to avoid the use of PCl₃. As, the byproducts involved with PCl₃ production are acutely toxic, we followed Prof. Cummin's work to develop "Green P Precursors".²⁰⁷⁻²¹¹ Unfortunately, all of them were found unproductive towards the production of III-V nanomaterials. However, recent discoveries on the use of phosphorous alkyl amides reveals a new chapter to develop safer phosphide precursors for semiconductor nanomaterial synthesis.²¹²



Figure 1: Different types of phosphorous precursors

Apart from Pnictide precursor syntheses, I was involved in developing a library of hydrophilic phosphonic acid ligands to solubilize CdSe quantum dots in water. I prepared a series of modified hydrophilic phosphonic acids with a polar tail and followed a variety of strategies to apply these ligands for water solubilizing quantum dots. However, their use was unproductive. It

is difficult to ascertain the reason behind this behavior, although I conjecture that the interaction between QDs and phosphonic acids is weak, the ligands underwent self-polymerization, or that unfavorable thermodynamics resulted in the precipitation of quantum dots from the polar media. However, all these reasons restrict the use of these ligands for water solubilization.

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Chemistry, University of Calcutta, India	2008
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PROFESSIONAL EXPERIENCE

Graduate Research Assistant, with Prof. Preston T. Snee 2011-present University of Illinois at Chicago, Department of Chemistry, IL, USA Synthesized pnictide precursors for quantum dot synthesis, synthesized polar modified phosphonic acids for water solubilization of quantum dots.

Research Assistant, with Prof. Dilip K. Maiti2008-2010University of Calcutta, Department of Chemistry, IndiaSynthesized Cu (0) nanoparticles in an aqueous medium, applying in a reductive cleavage of
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PUBLICATIONS

- 1. Adita Das, Armen Shamirian and Preston T. Snee, "Arsenic Silylamide: An Effective Precursor for Arsenide Semiconductor Nanocrystal Synthesis" Chem. Mater. 2016; 28, 4058-4064; DOI: 10.1021/acs.chemmater.6b01577
- 2. Adita Das, Bo Hsu, Armen Shamirian, Zheng Yang and Preston T. Snee, "Synthesis of High Quality AgSbSe₂ and AgBiSe₂ Nanocrystals with Antimony and Bismuth Silylamide Reagents" *Chem. Mater.* 2017; (just accepted); DOI: 10.1021/acs.chemmater.7b01593
- 3. Adita Das and Preston T. Snee; "Synthetic Developments of Nontoxic Quantum Dots" Chem. Phys. Chem. 2016, 17, 598 –617; DOI: 10.1002/cphc.201500837
- Christina M. Tyrakowski, Armen Shamirian, Clare E. Rowland, Hongyan Shen, Adita Das, Richard D. Schaller, and Preston T. Snee, "Bright Type II Quantum Dots" Chem. Mater. 2015, 27, 7276–7281; DOI: 10.1021/acs.chemmater.5b02040
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- Krishnanka S. Gayen, Tista Sengupta, Yasmin Saima, Adita Das, Dilip K. Maiti and Atanu Mitra, "Cu(0) nanoparticle catalyzed efficient reductive cleavage of isoxazoline, carbonyl azide and domino cyclization in water medium" Green Chem. 2012, 14, 1589–1592; DOI: 10.1039/C2GC35252D

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