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Synthesis and Characterization of PbS Quantum Sheets Through Lamellar Assembly, and Updates to the CdSe Quantum Wire Synthesis

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Synthesis and Characterization of PbS Quantum Sheets Through Lamellar Assembly, and Updates to the CdSe Quantum Wire Synthesis

by

Paul J. Morrison

A dissertation presented to the Graduate School of Arts and Sciences of Washington University in partial fulfillments of the requirements for the degree of Doctor of Philosophy

December 2014

Saint Louis, Missouri
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Acknowledgements

I would like to thank first and foremost my family for putting up, and helping me out with, the entirety of my academic career thus far. My parents have been very supportive of my efforts to pursue (most) of my ideas stemming from in- and outside the classroom. My girlfriend, Calynn, has also been a source of nonstop support in my life and during the absolutely exhausting process of writing this rag. Without her assistance (or her office space), my entire thesis and defense would have become even further drawn out.

I would also like to thank my friend Erika Sesti. We started the program in the same year, and she has become my best friend in Saint Louis. We go see movies together, we play games together, and now we rock climb together! She has been an exceptionally cheerful friend over these years and has made the stay in graduate school far more bearable for it. Jeremey Buckingham has also helped me a great deal over these many years. When I lost my first residence almost a year into my first year, he and his dog (Cricket Thunder Buckingham) gave me a place to stay before finding a new apartment. He has also taught me how to brew my own wine and cider, which has become a very fulfilling hobby since we started in 2009.

My advisor, Bill Buhro, was instrumental to my current understandings of nanomaterials and how to synthesize them properly. Without his patience, there is a more than slight chance that I would not have finished. Rich Loomis, essentially my co-advisor, deserves a fair amount of recognition on this front as well. His mentorship and...blunt discussions were very helpful in keeping my head in the game so to speak, and to keep everything in perspective.

My labmates were all my best sources of help for the work directly. Fudong Wang, maybe one of the most talented scientists I have ever known, runs the lab supremely and was
always around to help everybody with the real intellectual challenges that a research laboratory is built upon. Other comrades from the laboratory I would like to thank are: Vernal Richards, Yuanyuan Wang, Yi-Hsin Liu, Waynie Schuette, Yang Zhou, and Linjia Mu were all key members of the lab. Learning and teaching all of the knowledge, techniques and ideas crucial to each of our projects made the laboratory experience amazingly rewarding (even when we were all wrong!).
Abstract of the Dissertation

Synthesis and Characterization of PbS Quantum Sheets Through Lamellar Assembly, and
Updates to the CdSe Quantum Wire Synthesis

by

Paul J. Morrison

Doctor of Philosophy in Chemistry

Washington University in St. Louis, 2014

Professor Bill Buhro, Chair

This dissertation reports the novel synthesis of PbS quantum plates (QPs) via a reaction executed at low temperatures. The PbS QPs are grown in a template-assisted mechanism, with the first excitonic peak observed in the visible region of light at ~620 nm (2.0 eV), at an energy radically different than the band gap of bulk PbS (~3000 nm, 0.42eV). The large energy shift is due to the extremely thin dimension of these nanoplates, which is determined to be ~1 nm in thickness. Thickness measurements are made in a powder X-ray diffractometer (XRD) at low angles (between 2-15º 2θ). These measurements show a series of reflections in highly lamellar structures and give a spacing easily calculated using a modified version of the Bragg diffraction equation and applied to a straight line. During experimentation, a discrepancy was noticed while observing the lamellar template under various conditions. The TEM consistently showed an expanded d spacing of lamellar templates that does not fit with data from the XRD. The high vacuum atmosphere of the electron microscope induces a consistent expansion of template systems, as shown here for the first time, and proven from multiple previously published results.

An improvement on CdSe quantum wire (QW) growth using alternate synthetic procedures and shell growth avenues is also reported. Also presented here are the underlying fundamentals for a new shell growth opportunity with a previously overlooked material: MgSe. Quantum
wires made from CdSe are uniquely accommodating to MgSe as a shell material due to its intrinsic properties: much closer lattice parameters versus CdSe’s current widely used shell (CdS), a highly insulating band gap (4.0 eV), and the ability to be grown in many of the common semiconductor crystal structures (rock salt, zinc blende, and wurtzite).
Chapter 1:

INTRODUCTION
Quantum nanostructures are being considered for a variety of optoelectronic applications, most notably, solar cells, also referred to as photovoltaic (PV) cells. Quantum confinement effects, observed in quantum nanostructures, broaden the range of suitable photovoltaic materials, and solution-phase processing offers the allure of economical production costs. Despite promise, the use of quantum nanostructures in photovoltaic devices is not without challenges. Charge carrier mobility in these devices is perhaps the most formidable, as it is two-fold. In semiconductor nanomaterials, charge carriers exist as bound electron-hole pairs (in this case, referred to as an exciton), which must separate if a current is to be produced. Once generated, a charge will navigate to its respective cathode or anode, and in between multiple nanostructures. If these charged particles recombine or relax before reaching their destinations, a large portion of the energy captured will be lost as through radiative or, more commonly, non-radiative emissions, and therefore cannot enter the functional circuit.

The efficiency of intraparticle charge transport is mediated by the presence or absence of potential energy minima (also known as traps), usually on the imperfect surface of the crystal. Controlling the chemistry at the surface of the particle is crucial to overall efficiency. Interparticle charge transfer is equally as important. Charges must be able to “hop” from one particle to another, or travel large distances within a single particle. Optimizing the morphology of the nanostructure provides a simple method to improving the efficiency of the interparticle charge transfer step.

Surface passivation refers to deliberately modifying the surface to mitigate the number of trap sites, thereby maximizing the efficiency of intraparticle charge transport. This will allow the excitons to travel freely in the nanomaterial without becoming “stuck” in a potential energy minima. The photoluminescence quantum yield (PLQY) provides a convenient method of
quantizing the degree and effectiveness of surface passivation. PLQY is defined in equation 1-1, where $\Phi$ is quantum yield, $B$ denotes the respective values used in a blank sample, $A$ is absorbance, $n$ is the refractive index, and $Int$ is the integration of area under the luminescence peak in question. The radiative recombination of the electron-hole pairs is not desirable in an actual PV device, however, higher quantum yield values indicate better intraparticle charge transport, and are therefore an important consideration along the way to device manufacture.

$$\frac{\Phi}{\Phi_B} = \left( \frac{Int}{Int_B} \right) \left( \frac{1 - 10^{-A_B}}{1 - 10^{-A}} \right) \left( \frac{n^2}{n_B^2} \right)$$  \hspace{1cm} (1-1)$$

The highest PLQY materials to date\textsuperscript{5,6} (quantum dots, QDs, and quantum rods QRs) are also the least desirable materials to be used in a PV cell, as the small morphologies cannot transfer charge across long distances efficiently.\textsuperscript{7} Every instance a charge is required to cross an interface (in this case, jumping from dot-to-dot, or rod-to-rod) a loss in efficiency will take place, as shown in Figure 1.1. QD/QR based solar cells are problematic because a considerable amount of energy collected from sunlight is then simply re-emit through radiative or thermal recombination before it can be utilized.

![Figure 1.1](image-url)  \hspace{1cm} \textbf{Figure 1.1.} Diagram demonstrating losses incurred during transport during PV cell charge separation. (a) The projected pathways of charge separation pathways in a QR-based PV cell. (b) The charge separation pathways for a QW-based PV cell. Note that each barrier that a charge must cross will be a loss in captured charge. Therefore, a QW-based solar cell will be preferable to a QR or QD (not shown).
Different nanomaterial morphologies are currently being studied in order to overcome the efficiency losses that result from interface crossings by charge carriers. In expanding from a 0D (dot) structure to 1D (wire) and 2D (well, plate) structures, the number of interparticle transfers required for a charge carrier to reach its destination is dramatically reduced. As stated in Figure 1.1, a quantum wire would therefore be preferable to a dot or rod morphology. Rational morphological design will allow for these materials to be used more effectively, both as antennae and as conduits for charges to enter the functional circuit.

This dissertation reports the novel synthesis of PbS (Chapter 2) quantum plates (QPs) \textit{via} a reaction executed at low temperatures. The PbS QPs are grown in a template-assisted mechanism, which has recently been confirmed in other 2D nanomaterial syntheses\textsuperscript{8,9}, with the first excitonic peak observed in the visible region of light at ~620 nm (2.0 eV), at an energy radically different than the band gap of bulk PbS\textsuperscript{10} (~3000 nm, 0.42 eV). The large energy shift is due to the extremely thin dimension of these nanoplates, which is determined to be ~1 nm in thickness. Thickness measurements are made in a powder X-ray diffractometer (XRD) at low angles (between 2-15° 2θ). These measurements show a series of reflections in highly lamellar structures and give a spacing easily calculated using a modified version of the Bragg diffraction equation and applied to a straight line. During experimentation, a discrepancy was observed in the spacing of the lamellar template under various conditions. The TEM consistently shows an expanded \( d \) spacing of lamellar templates that does not fit with data from the XRD. The high vacuum atmosphere of the electron microscope induces a consistent expansion of template systems, as shown here for the first time, and proven from multiple previously published results.
An improvement on CdSe quantum wire (QW) growth (Chapter 3) using alternate synthetic procedures and shell growth avenues is also reported. Re-tooling the synthesis based on a report regarding the nature of a widely used nanomaterials synthetic solvent, TOPO\textsuperscript{11}, allowed us to hone the parameters of the wire growth and increase the PLQY. Also presented are the underlying fundamentals for a new shell growth opportunity with a previously overlooked material: MgSe. Quantum wires made from CdSe are uniquely accommodating to MgSe as a shell material due to its intrinsic properties: much closer lattice parameters versus CdSe’s current widely used shell (CdS), a highly insulating band gap (4.0 eV),\textsuperscript{10} and the ability to be grown in many of the common semiconductor crystal structures (rocksalt, zinc blende, and wurtzite).

**Lamellar Assembly**

A recent revelation in nanomaterial synthesis involves the purification of metastable precursor clusters of CdSe.\textsuperscript{8} These clusters are grown at low temperature (room temperature) and induced to aggregate and grow into highly efficient (with respect to PLQY) nanomaterials. This has prompted further work to be done to explore whether or not CdSe is unique to growing these clusters. Thus began the probe to explore IV-VI semiconductors (PbSe and PbS) as possible additions to the molecular cluster precursor family.

One of the most notable facets of the (CdSe)$_{13}$ and (CdSe)$_{34}$ syntheses is the template in which the clusters grow. Aliphatic primary amines, when used as a solvent, organize themselves in a layered fashion similar to a detergent micelle.\textsuperscript{12} These layers are formed with a hydrophilic layer, which contain the M$^{n+}$ ions, as well as other charged species in solution, such as counterions and the charged heads of the amines used in the construction of the layered template. The
The hydrophobic layer will therefore be composed of the (usually) straight-chain hydrocarbon tails of the amine in use, as shown in Figure 1.2.

**Figure 1.2.** Template assembly before reaction. The hydrophilic layer contains galleries of charged species, including the \( \text{M}^{n+} \) (Pb\(^{2+}\) and Cd\(^{2+}\) in the case of our laboratory) precursors of our syntheses. The hydrophobic layer is (according to low angle XRD) almost completely comprised of primary aliphatic amines.

There will be little to no room for other non-polar species to be present in the hydrophobic area of the template, as this will disrupt the stability of the bilayer. Even secondary amines of the same size as the template amines are disallowed in this layer due to their extra steric bulk.\(^8\) This presents an interesting synthetic route: the thickness of the hydrophilic layer will, in some part, influence the thickness of the nanomaterial made inside it; thinner hydrophilic galleries will produce thinner sheets, and thicker galleries will be responsible for thicker sheets. There are to date two strategies for influencing this dimension: reaction temperature and chlorocarbon additives.\(^13\) Temperature plays a role such that higher temperatures have been observed to make thicker structures; a finding that mirrors the same observations made when making QDs\(^14\) as well. Dilution of the hydrophilic layer can be achieved with other polar chemicals/solvents, with most of what is currently being used being small molecule chlorocarbons.\(^9\) It is currently unknown what role these chlorocarbons play. Whether they are directly dispersed in the hydrophilic layer or if they merely reside in the barrier between the hydrophobic/hydrophilic layer in order to influence the reaction is a matter of debate.
PbS Sheets

The initial PbSe work done showed us a great deal about the IV-VI reactions, but was not without issues; the reaction proceeds far too quickly at room temperature, and gives highly inconsistent results. While there is evidence of lamellar assembly and 2-D growth, much of the sample can be filled with superfluous and inconsistently shaped “nanojunk.” Therefore, further experimentation was carried out in lower temperatures (-42 °C) in order to control the reaction. This change made the reaction far more manageable, but still present was the problem of stability once the PbSe product was brought back up to room temperature for instrumental characterization. Below, in Figure 1.3 are some representative images from PbSe experimentation. Here, various 2-D structures are evident, indicating PbSe most likely grows in a template fashion

![Figure 1.3: TEM samples of PbSe. These bundled clusters of quantum belts (QBs) were stable for examination under the TEM electron beam, but degrade to PbO very quickly under ambient conditions.](image)

Ultimately, the PbSe project was shelved due to its difficult nature in favor of PbS. A simple change of injection reactants and temperature were all that was needed to change the synthesis from PbSe to PbS. Instead of being an instantaneous reaction, the sulfur precursor (thiourea) reacts slowly and is easier to control than the selenium precursor (selenourea). Due to the slower...
reaction kinetics, there is far less amorphous “nanojunk” found when examining these samples under the TEM. Some initial samples even share many similarities to the PbSe experiments: long, thin belt-like structures, usually seen in clusters or self-stacking bundles. A similar problem still exists, as PbS is not completely stable in air. Instead of degrading in a number of hours, PbS degrades to PbO over the course of a number of days, which can be observed by a change in color from rust-red to black as well as a precipitation of the black powder. This process is hastened when under a high intensity beam during certain experimentation.

Fine tuning of synthetic procedure yielded the most interesting morphology for these crystals: hexagonal plates. This is unusual if you look at other crystals of the same type; the bulk structure for all IV-VI structures is rock salt (or at least a distorted form of rock salt, known as the GeS structure),\(^{10}\) seen in Figure 1.4.

![Figure 1.4](image)

**Figure 1.4.** Representative image of the IV-VI rock salt structure. Each of the IV-VI semiconductors is (sometimes loosely) based on an MX structure in which each ion has a coordination number of 6.

The cubic morphology is what is most often observed in rock salt crystals (crystal vectors [100] and [010] are often found perpendicular to the viewing axis during HRTEM experiments) so a hexagonal shape is puzzling, however not unreasonable. When looking down the body
diagonal of the rock salt unit cell, the [111] direction, you can clearly see the hexagonal features of its close-packed structure. These plates do not share a crystal structure with the bulk PbS, which will be explained in further detail in Chapter 2.

**CdSe Wires**

Quantum wires have long been grown with a variety of synthetic methods, including chemical-vapor-deposition (CVD),\textsuperscript{15} vapor-liquid-solid (VLS),\textsuperscript{16} and our own in-house specialty: solution-liquid-solid (SLS).\textsuperscript{4,11} As their names suggest, both VLS and SLS share similar mechanisms, such as a metallic liquid catalyst particle through which the reagents are dissolved and from which the wire is grown. SLS, being a much more accessible method, is done in a standard solution phase, available in most laboratories. The reaction is set up in a similar method to that of QD syntheses, except for the addition of metal catalyst nanoparticles (NPs), as shown in Figure 1.4. These catalyst NPs are made of a solid metal at room temperature and reach their melting point below the reaction temperature. Thus, the choice of metal used for a catalyst NP will be based on the melting point needed for the reaction. Based on this criteria, our choice of catalyst NP has primarily been bismuth particles in the range of 5-20 nm.
New work on the CdSe wire project explores a number of different variables in the current synthesis and their effects (or non-effects) on PLQY. Overall, it appears that minor variations in the concentrations of Cd$^{2+}$ and acids (the type of variations that will occur over a large number of synthetic procedures) has little effect, in the immediate term, on wire growth and PLQY. The largest contributing factor that were found to reproducibly influence PLQY was the reaction temperature. By modifying the reaction temperature to just above the melting point of the selected Bi NP catalysts, it will enhance the photoluminescence by noticeable margins. This improves the current standard PLQY from the range of 0.1-0.4% up to 1%. A standard wire extinction and photoluminescence spectra are shown below in Figure 1.6. Clearly defined features of the first excitonic peak ($n = 1$) at 671 nm (1.85 eV) as well as the emission at 679 nm (1.82 eV) are evident. This loss in energy between absorption and emission is a classic Stokes shift, which occurs due to a relaxation of the excited electron-hole pair after absorption, but before emission.
Figure 1.6: CdSe wire extinction and PL. The rising absorbance during the first peak’s rise and thereafter is due to particle scattering from the nanomaterials in suspension. While both axes are in arbitrary units, the instrument values are kept for reference purposes; the y-axis is arbitrarily scaled in order to observe the relative position to the first excitonic peak.

Core-Shell Nanomaterials

In addition to synthesizing CdSe nanowires with a higher than before PLQY, there exists a strategy for insulating any surface defects (known as “trap” sites) that involves growing another semiconductor shell on the outside of the wire itself. This shell material is usually chosen based on the desired properties for the material in question. There are a number of “types” for these properties, as shown in Figure 1.7. All of these types can be useful in different scenarios, but for the time being, my work is focused on the Type I core shell system in which the core is (ideally) completely insulated by the shell material. This is the most straightforward approach for our purposes because it allows our laboratory to use many of the same instrumentation in order to study the core-shell material. When studying the Type II core-shell nanomaterials,
photoluminescence will not be as useful because of the charge separation of the exciton and the apparent PLQY will plummet.

**Figure 1.7.** Different types of Core-shell growths. Dark blue boxes in the center represent the band gaps of a core material. The light blue bars sandwiching the core represent the band gaps of a shell material. Type I is a complete electronic insulation by the shell material in which the exciton will be contained entirely in the shell. Type II is shown twice to illustrate that there are two different scenarios in which a Type II junction can be used. Type IIa will have the exciton hole settle in the shell material, while the electron will remain in the core. For Type IIb, the reverse is true; the hole will remain in the core, while the electron exits to the shell material.

Therefore, shell material selection is a crucial factor in designing a core shell material. Many materials will have a useful band gap, but fail to have lattice parameters closely matching those of the core material. For this reason it is difficult to find a useful shell materials outside of the quantum dot regime. In quantum dots, due to the small surface size, a lattice mismatch of ~10% is not impossible for epitaxial (uniform crystalline) growth.\(^\text{19}\) When sizing up to a wire however, this 10% becomes too much for the shell (or core) to bear and will often times lead to non-uniform growth.\(^\text{20}\) These shells will not be useful in insulating the core and cannot be counted as a true core-shell nanowire.
MgSe as a Shell Material

This dilemma of the core-shell nanowire leads to a problematic conclusion: there appears to be no acceptable shell material if the lattice parameters of CdS are too small for a CdSe QW. If we are only looking at the standard II-VI or III-V semiconductors and their relative differences in lattice parameters (see Chapter 3), then there are a number of matches with very small mismatch, in the range of 0.2-0.5%\(^\text{19}\). InAs, GaSb, and ZnTe are immediate choices for these purposes. The problem then arises when looking at the respective band gaps of these materials. Both ZnTe and GaSb are type II systems and InAs is a “reverse” type I, where the shell material will localize the electron and hole apart from the core. While these are not uninteresting materials, they don’t suit our purpose of realizing an efficient CdSe QW. If we expand our search to include uncommon II-VI materials (alkaline earth chalcogenides), then we find MgSe. It has a lattice mismatch (vs. CdSe) of 2.7%, and a highly insulating band gap of 4.0 eV\(^\text{10}\). Early results and tests of MgSe nanomaterials have shown it can exist in rock salt (as seen in bulk) as well as wurtzite and zinc blende, which is encouraging for epitaxial growths on CdSe nanostructures.
References:


6) Talapin, D. V.; Nelson, J. H.; Shevchenko, E. V.; Aloni, S.; Sadler, B.; Alivisatos, A. P.


   Chem. 2013, 52, 2933.


Chapter 2:

Synthesis of Lead Sulfide Quantum Plates
Introduction

Herein we report the low-temperature synthesis of thin PbS quantum platelets (QPs) that exhibit large quantum-confinement effects. Their extinction spectra are well resolved and have features assignable to discrete quantum-well transitions. The QPs grow by a lamellar-template pathway, and their close proximity within the growth templates produces strong multi-quantum-well coupling.

Flat colloidal CdSe nanocrystals recently emerged that have discrete thicknesses corresponding to integer numbers of monolayers, and sharp absorption spectra assignable to quantum-well transitions.\textsuperscript{1,2} Their emission spectra are also sharp, and the photoluminescence (PL) efficiencies are high, in the range of 20-50\%.\textsuperscript{2,3} Epifluorescence imaging and spectroscopy established that photogenerated excitons are effectively delocalized over the entire volumes of the flat nanocrystals.\textsuperscript{3} The high PL efficiencies and exciton delocalization are due to the crystallographic flatness and dense, self-assembled monolayer passivation of the broad nanocrystal facets.\textsuperscript{4} Thus, flat nanocrystals having an extended length dimension should be capable of efficient energy and charge transport over \( \mu \)m to mm distances.

Flat colloidal semiconductor nanocrystals of a variety of compositions have now been prepared, including CdTe,\textsuperscript{6} In\textsubscript{2}S\textsubscript{3},\textsuperscript{7} CuInS\textsubscript{2},\textsuperscript{8} SnS,\textsuperscript{9} SnS\textsubscript{2},\textsuperscript{9} SnSe,\textsuperscript{10} SnSe\textsubscript{2},\textsuperscript{11} CuS,\textsuperscript{12} Cu\textsubscript{2}S,\textsuperscript{12} and FeS\textsubscript{2}.\textsuperscript{13,14} Of particular relevance to the present study is the report of ultrathin PbS nanosheets by Weller and coworkers.\textsuperscript{15}

The syntheses of flat colloidal CdSe and PbS nanocrystals are of two general types. One employs long-chain metal carboxylate or long-chain carboxylic-acid precursors and high reaction temperatures (\( \geq 170 \)°C for CdSe\textsuperscript{2} and 100 °C for PbS\textsuperscript{16}). The CdSe QPs prepared by
this method have zinc-blende structures. The second approach employs simple cadmium salts and long-chain amine solvents, is conducted at comparatively low temperatures (25 – 100 °C), and produces CdSe QPs and quantum belts (QB)s having wurtzite structures. The low-temperature, amine-solvent synthesis has been shown to proceed by a lamellar, amine-bilayer, mesophase-template mechanism, which produces the flat nanocrystal morphology.

The pathways leading to flat-nanocrystal morphologies by the high-temperature, metal-carboxylate/carboxylic-acid syntheses have not been fully resolved. Small nanoparticle intermediates were observed in the syntheses of both CdSe QPs and PbS nanosheets. Dubertret and coworkers determined that such CdSe nanoparticles served as seeds that were extended in two dimensions by monomer-supported lateral growth. Weller and coworkers presented compelling evidence that the PbS nanosheets formed by two-dimensional oriented attachment of the small, initially formed nanoparticle intermediates. However, the mechanistic factors imposing two-dimensional growth, as opposed to three-dimensional growth, have not been fully elucidated, and the possible role of a spontaneously formed lamellar-mesophase template has not been fully considered.

We noted that flat colloidal PbS nanocrystals had not yet been made by the long-chain amine-solvent method, and became interested in whether such a synthesis could proceed at a lower reaction temperature than that employed by Weller and coworkers. We now report the synthesis of crystalline PbS QPs in n-octylamine solvent at temperatures in the range of 25 – 40 °C. We provide strong evidence for the formation of a lamellar, amine-bilayer mesophase that templates the two-dimensional nanocrystal growth. Moreover, we re-examined the high-temperature, long-chain carboxylic-acid synthesis, and provide evidence that this pathway proceeds by a lamellar-mesophase template as well, which explains the two-dimensional growth
achieved by this synthesis. The results suggest that lamellar templating may be a more-general feature of flat colloidal nanocrystal growth.

In the course of this work, we noted an apparent discrepancy between the lamellar $d$ spacings measured in the amine-bilayer mesophases by TEM and low-angle XRD. Herein we propose that these differences result from elastic deformation of the mesophases in the high-vacuum environment of the TEM. Consequently, the ambient-pressure $d$ spacings should be measured by low-angle XRD or related ambient-pressure methods, as the TEM values will be enlarged by comparison.
Experimental

Materials: 1,2-Dichloroethane (DCE, 99%) was purchased from Taychemco, and Pb(OAc)$_2$·3H$_2$O from Strem Chemicals. 1,1,2,-Trichloroethane (TCE, 97%), thioacetamide (reagent grade, 98%), oleic acid (OA, technical grade, 90%), N,N-dimethylformamide (DMF, ≥ 99.8%), tri-$n$-octylphosphine (TOP, technical grade, 90%), diphenylether (Ph$_2$O, ≥99%), $n$-octylamine (99%), thiourea (≥ 99%), and polyvinyltoluene (PVT, avg. M$_w$ ~72,000, also known as poly(4-methylstyrene)) were purchased from Sigma-Aldrich. Oleic acid and TOP were stored at 0 ºC in a freezer. All other reagents were stored under ambient conditions. All reagents were used as received, without additional purification.

Analyses. UV-visible spectra were obtained from a Perkin-Elmer Lambda 950 UV/Vis spectrometer. Low- and high-angle XRD patterns were recorded on a Rigaku D/MAX A vertical powder diffractometer and a Bruker AXS D8 ADVANCE powder diffractometer, both using Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å). TEM images were obtained from a JEOL 2000FX microscope operating at 200 keV, and higher resolution (HRTEM) images from a JEOL JEM-2100F Field Emission STEM microscope operating at 200 keV.

Preparation of PbS Quantum Platelets in $n$-Octylamine. All synthetic manipulations prior to workup were carried out under dry N$_2$. Pb(OAc)$_2$·3H$_2$O (180 mg, 0.475 mmol) was dissolved in a mixture of OA (2.0 mL) and $n$-octylamine (3.0 mL) in a 50-mL Schlenk tube with magnetic stirring, yielding a clear, colorless solution. The tube was evacuated (500 mtorr) for 1h at room temperature, and back-filled with N$_2$(g). The stirring mixture was warmed to 40 ºC and a solution of thiourea (20 mg, 0.26 mmol) in $n$-octylamine (0.5 mL), also at 40 ºC, was injected into the flask. Stirring was immediately halted upon injection. The reaction mixture
appeared colorless for the first 5 min, after which a slow darkening to a brown suspension occurred. After 10 min the color darkened more rapidly, while remaining brown. The reaction mixture was removed from the heating bath after 12 min and diluted with a ~5:1 v/v toluene:methanol mixture (4 mL) to induce precipitation of the PbS QPs and centrifuged (≥2000 rpm) in order to separate the QPs from the unreacted precursor and reaction solvent. After workup procedure, concentrated PbS QPs appear as a reddish-orange suspension. For post-reaction UV-visible spectroscopy, this purification cycle was performed once; for TEM and post-synthesis XRD analysis the purification cycle was performed twice, to ensure a clean sample image.

**Preparation of a PbS QP Sample for XRD Analysis.** A PbS QP sample obtained as described immediately above was re-suspended in a small amount of toluene (~1 mL) and pipetted into a small-volume sample holder for XRD analysis, one drop at a time, until almost all of the toluene had evaporated. For atmospheric protection of the sample during data collection, 2 drops of PVT solution (10 wt% concentration in toluene) were added to the top of the almost-dry powder creating a thin film over the sample. A thin film was required to allow X-ray transmission and to minimize the background (centered around 25° 2θ) in the XRD pattern.

**In-situ UV-visible Monitoring of PbS QP Growth.** An *in-situ* study of PbS QP growth was conducted using a modified version of the above synthesis. Pb(OAc)$_2$·3H$_2$O (60 mg, 0.16 mmol) was dissolved in a mixture of *n*-octylamine (1.75 mL) and OA (0.75 mL) in a standard 3-mL quartz cuvette and lightly heated (40 °C) until the mixture became a homogeneous clear, colorless solution. A solution of thiourea (13 mg, 0.17 mmol) dissolved in octylamine (0.5 mL)
was injected into the cuvette and placed into a UV-visible spectrometer. A separate cuvette was prepared as a blank containing octylamine (2.25 mL) and OA (0.75 mL). An initial spectrum was recorded immediately (t = 0 min), and spectra were recorded at 10 min intervals thereafter, up to 180 min.

**Preparation of PbS Quantum Plates by the Weller synthesis.** In a typical preparation, Pb(OAc)$_2$·3H$_2$O (215 mg, 0.567 mmol) was weighed into a Schlenk reaction flask and dissolved in oleic acid (0.875 mL, 2.77 mmol), TOP (1.25 mL, 2.78 mmol), and Ph$_2$O (2.50 mL, 14.7 mmol), forming a clear, colorless solution. This mixture was degassed *in vacuo* for 3 h at 90 ºC with stirring, and backfilled with N$_2$. After backfilling with N$_2$, TCE (0.25 mL, 2.7 mmol) was added to the degassed solution. A mixture of thioacetamide (20 mg, 0.27 mmol) dissolved in TOP (1.50 mL, 3.34 mmol) was combined with DMF (0.125 mL, 1.6 mmol) in a vial at room temperature. The liquid components of the mixture were immiscible, and the vial was vigorously shaken immediately prior to loading the mixture into a syringe. The temperature of the Schlenk flask and contents was raised to 100 ºC, and then the thioacetamide solution in the syringe was injected into it. The mixture immediately darkened to an opaque, black color. Stirring at 100 ºC was continued for 5-20 min, and then the Schlenk flask was removed from the heating bath. Workup and purification were conducted using the procedure described in the *n*-octylamine synthesis above.
Results

**Low-temperature Synthesis of PbS Quantum Platelets.** Our initial goal was to develop a long-chain amine synthesis of flat, colloidal PbS nanocrystals that was analogous to the previously reported synthesis of CdSe QBs,\(^3\),\(^4\),\(^19\),\(^20\) QPs,\(^15\) and nanosheets.\(^2\),\(^18\) The precursors lead acetate (Pb(OAc)\(_2\)·3H\(_2\)O) and lead stearate were insoluble in \(n\)-octylamine at room temperature, forming milky-white suspensions. We found that the addition of oleic acid to Pb(OAc)\(_2\)·3H\(_2\)O in \(n\)-octylamine generated a clear, colorless mixture. Addition of thiourea to this mixture at room temperature resulted in color changes to light brown and then dark brown over the course of about 1 h, as the sample became opaque. A UV-visible spectrum of the sample obtained at this stage contained an absorption feature at a wavelength near 600 nm (2.07 eV). TEM images of the product after work-up contained crumpled, rolled, and aggregated sheets, presumed to be of PbS (Figure A1 in the Appendix).

The reaction time (12 min), temperature (40 °C), and precursor ratio (Pb:S = 1.8:1.0) were optimized according to eq 2-1, yielding the QPs shown in Figure 2.1. The TEM images revealed individual platelets having hexagonal to circular disk-like morphologies. Reactions conducted for longer periods yielded sheet-like structures exhibiting haphazard aggregation and crumpling.

\[
Pb(OAc)\_2 + \text{H}_2\text{O} + \text{S} \rightleftharpoons \text{NH}_2\text{C}\text{NH}_2 \xrightarrow{25 - 40 \, ^\circ \text{C}} \text{PbS} + 2 \text{HOAc} + \text{O} \rightleftharpoons \text{NH}_2\text{C}\text{NH}_2\]

(2-1)
Figure 2.1. A TEM image of PbS QPs prepared by eq 2-1 after a 12-min reaction time. Most of the QPs exhibited pseudo-hexagonal habits.

The QP images in Figure 2.1 are smooth with no evidence of a grainy texture. Because we did not observe PbS nanoparticle intermediates in the spectroscopic monitoring of our synthesis (see below and Figure 2.2a), the PbS QPs so prepared did not grow by oriented attachment as in the synthesis of Weller and coworkers, but rather likely by monomer attachment to the edges of the initially nucleated PbS QPs. Consequently, the QPs did not acquire the grainy texture that sometimes results from oriented-attachment processes.

The energy-dispersive X-ray spectrum collected in the TEM from a specimen of PbS QPs like those in Figure 2.1 was as expected for PbS (Figure A2). The spectral lines for Pb were clearly evident. However, the major S line, Kα (2.307 keV), falls beneath a major Pb line, Mα (2.345 keV), and was obscured. This makes the Pb:S ratio obscured at the very least. It can be noted that there is indeed some sulfur content, but the specific numbers were not available until
ICP-OES analyses were conducted by an outside facility (Galbraith Laboratories). The results of that experiment concluded that the Pb:S ratio is 1.89:1. This raises another interesting question about what the structure actually may be in a 1 nm thin platelet. Considering that even in bulk PbS the bond length from Pb-S is around 3 Å, this data implies that a plate could only be 3 or 4 monolayers thick. Such a thin nanoparticle may not have a stoichiometric ratio of cations:anions that would be common in bulk materials and even larger nanomaterials.

Another interesting note is that the Pb:S ratio is extremely close to the ratio of starting materials used (1.8:1 mol ratio). The plate as-synthesized plate may be closer to a stoichiometric ratio and surrounded on the surface by lead carboxylate salts passivating the surface. These surface lead species could simply be the unreacted lead that would find a local energy minima in the surface of a charged nanoplate.

Because of the air sensitivity of the PbS QPs, obtained from the synthetic workup as a rust-red powder, XRD data were collected (10 – 50° 2θ) on a sample protected by a thin polyvinyltoluene (PVT) film. The resulting XRD pattern (Figure A3) contained numerous broadened, but resolved reflections superposed on a broad background feature that was perhaps due to the very small thickness dimension of the QPs. The sharper reflections were indicative of the crystallinity of the QPs. Some of these reflections can be assigned to the low-angle pattern associated with the templated stacking of the QPs (see below). The remaining higher-angle reflections could not be assigned to a variety of bulk patterns of PbS in either the typical cubic rock salt structure, or in the high-pressure orthorhombic structure. They were also unassignable to the starting material Pb(OAc)2·3H2O. At most a trace amount of PbO may have been present as the litharge phase, as suggested by small features at 28.61 and 31.81° 2θ in the pattern, and presumably reflecting the air sensitivity of the extremely thin PbS QPs (see below).
In addition to attempts to index PbS to bulk rock salt and its previously observed orthorhombic (Cmcm) pattern, there are a number of other orthorhombic symmetries that have been observed in other IV-VI semiconductors in extreme conditions: the GeS structure and another orthorhombic structure based on a high pressure PbTe crystal (Figure A4). Both of these structures are based on the rock salt structure, but have been distorted to destroy the cubic symmetry and therefore have far more complicated powder diffraction patterns.

While both of these structures are much closer to matching our PbS QPs than bulk rock salt and the starting materials, they still do not account for all crystal reflections observed (minus the omitted low angle reflections), and fitting the structures to the QP powder pattern requires distortions of the unit cell that end up being wildly unrealistic: largely stretched out bond lengths (regular bonds greater than 3 Å), much larger cell volumes than the original rock salt structure (expansions of over 100%), and mismatching of a variety of lines in the observed pattern. The last point can be explained away with a simple explanation of the materials being examined, however. Systematic absences and missing peaks may be seen with an XRD powder diffraction experiment if there is a preferred orientation of the sample. With our PbS QPs (and QPs in general) we would expect that to be the case as the plates will lay mostly flat and perpendicular to the incident electron beam.

Lattice parameters in nanoplatelets and nanobelts have previously been observed to be alternatively contracted or expanded, shifting the corresponding XRD reflections to higher or lower 2θ, respectively. Such anisotropic distortions of the rock-salt or orthorhombic structure of PbS in the QPs may have been responsible for the mismatch of the observed pattern with those of the bulk phases. The observation of unassigned reflections below 2θ = 23° (the lowest position of the lines in the bulk phases) suggested lattice expansion in at least one dimension.
We have not yet successfully fit the XRD pattern to a distorted PbS crystal structure, but can safely assert that the structure is some type of distorted rock salt based on our XRD fitting and HRTEM images (see Figures A4 - A6), but distorted in what way and how much is still to be determined.

The eq 2-1 reaction was monitored by UV-visible spectroscopy, at 25 ºC to slow the reaction kinetics. Spectra were collected at 10-min intervals over 120 min (Figure 2.2a). The 610 nm (2.03 eV) feature emerged after 10 min, and continued to grow and shift to lower energy during the monitoring period. At 120 min, the feature had shifted to 640 nm (1.94 eV). An additional, higher-energy peak emerged at 420 nm (2.95 eV) after 20 min. This peak also shifted to lower energy during monitoring, to 500 nm (2.48 eV) at 120 min. The two peaks were assigned to the $1_e-1_h$ (lower-energy) and $2_e-2_h$ (higher-energy) quantum-well excitonic transitions, respectively ($h$ = hole, and $e$ = electron), on the basis of the reasoning given below.\textsuperscript{24}
Figure 2.2. UV-visible spectral data. (a) Extinction spectra recorded *in situ* during a PbS QP synthesis at 25 °C (eq 1) at various reaction times. The black spectrum (lowest in the stack) was recorded at 0 min, and each successive spectrum was recorded at increments of 10 min. (b) Peak position ($\lambda_{max}$) vs. reaction time for the high- and low-energy spectral features, assigned to the $n = 2$ and $n = 1$ quantum-well transitions in the QPs, respectively. (c) Data in part b shifted and rescaled on their energy axes to superimpose the curves corresponding to the $n = 1$ and $n = 2$ transitions.
Plots of peak position vs. time are given in Figures 2.2b and 2.2c. As a first approximation, we may ascribe the energetic shifting of the peaks during growth to changes in the effective thickness of the platelets. (However; in the Discussion we present a different physical model for the apparent changes in thickness.) If these features are indeed the $1_e-1_h$ and $2_e-2_h$ quantum-well transitions, then the shift in the higher-energy $\Delta E_2$ feature ($\Delta \Delta E_2$) should be four times that of the lower-energy $\Delta E_1$ feature ($\Delta \Delta E_1$), by eq 2-2 ($n^2 = 1$ vs. 4). The energy axis for the $n = 1$ data is expanded by a factor of four and the data shifted in Figure 2.2c to overlay the two energy-shift profiles, illustrating their similarity. The total shift $\Delta \Delta E_2$ is $0.49 \pm 0.05$ eV, which is slightly larger than four times the $\Delta \Delta E_1$ of $0.10 \pm 0.01$ eV. The lack of separate light- and heavy-hole bands in PbS results in a single transition at each of the $n = 1$ and 2 levels, as observed in Figure 2.2. Thus, the assignment of the Figure 2.2 features to quantum-well transitions is confirmed.

$$\Delta E_n = \left( \frac{h^2 n^2}{8L^2} \right) \left[ \frac{1}{m_e} + \frac{1}{m_h} \right]$$

(2-2)

**Elucidation of a Templated Growth Mechanism.** A precursor mixture of Pb(OAc)$_2$·3H$_2$O and $n$-octylamine in the ratio employed in the synthesis gained opacity and viscosity, and developed a gelatinous surface skin within 10 – 30 seconds of mixing. This mixture gave the low-angle XRD (LAXRD) pattern in Figure 2.3a. The sharp reflections indexed to a lamellar mesophase (Figure 2.4) having a $d$ spacing of $2.78 \pm 0.03$ nm. This $d$ spacing was close to those measured for other $n$-octylamine-bilayer mesophases \{[Cd(OAc)$_2$]$[n$-octylamine]$_2$\} ($d = 2.61$ nm),\(^3\) \{(CdSe)$_{13}$(n-octylamine)$_{13}$\} ($d = 2.64$ nm),\(^19\) \{CdCl$_2$(n-octylamine)$_2$\} ($d = 2.5$ nm).\(^20\)
and [(AgNO$_3$)$_x$($\text{H}_2\text{O}$)$_{0.87}$($n$-octylamine)$_{0.13}$] ($d = 2.74$ nm).\textsuperscript{25} The result established that the precursor was spontaneously organized into a lamellar-template structure having pseudo-planar reaction galleries containing the Pb$^{2+}$ ions.

Figure 2.3. Low-angle XRD patterns from the PbS QP synthesis. (a) A pattern collected from a mixture of Pb(OAc)$_2$·3H$_2$O and $n$-octylamine prior to initiation of the reaction. (b) A pattern collected from the washed and dried QP product after the reaction. The patterns were consistent with lamellar mesophases having periodicities of $d = 2.78 \pm 0.03$ nm (a, before) and $2.79 \pm 0.02$ nm (b, after).

Another low-angle XRD pattern (Figure 2.3b) was recorded of the dark-brown reaction mixture at the conclusion of the synthesis. This pattern also contained sharp reflections corresponding to a lamellar, amine-bilayer mesophase having a $d$ spacing of $2.79 \pm 0.02$ nm. Our observation of the low-angle patterns (Figure 2.3a, b) demonstrated that a lamellar, $n$-octylamine-bilayer mesophase persisted from before the PbS-forming reaction was initiated to beyond its conclusion. However, these results alone did not prove that the PbS QPs grew within the mesophase-template structures.
**Figure 2.4.** Schematic diagram of a lamellar amine-bilayer mesophase. The low-angle XRD data indicate a periodicity of $d = 2.8$ nm. The $n$-octylamine bilayer has a known thickness of for 1.8 nm. Thus, the hydrophilic layer in which PbS QP formation occurs has a thickness of 1.0 nm, and the resulting QPs also have thicknesses of 1.0 nm.

Consequently, the QP-growth process was monitored by TEM, by removing aliquots from the reaction mixture at various times in a synthesis conducted at 25 °C. Some aliquots were washed and some were unwashed prior to loading onto TEM grids. Figure 2.5 contains images collected from such aliquots. Figure 2.5a, an image of an unwashed sample removed at a reaction time of 20 min contained two kinds of features. The dark, pseudo-circular features are discussed below. Smaller, fainter, irregularly shaped features were also evident (see arrows in Fig. 2.5a). We surmised these to be individual, separated QPs, nucleated at random positions within the surrounding lamellar template, which obscured their resolution in the images. A better image of the irregular, presumed QPs was obtained from a washed specimen removed at 20 min (Figure 2.5b). The lateral dimensions of these features ranged from about 20 to 200 nm, which are equal to or surpassing the PbS bulk Bohr radius of 18 nm.

TEM images of lightly washed specimens removed from the reaction mixture at 60 min are given in Figure 2.5c and d. The images consisted of large (100 – 200 nm), pseudo-spherical globules. The globules contained both amorphous and mis-oriented, lamellar-textured domains.
within them (Figure 2.5c). We surmised that these globules also appeared in the 20-min images at smaller sizes as the dark, pseudo-circular features (Figure 2.5a, b). We concluded that after 60 min the PbS QPs had grown sufficiently in their lateral dimensions to begin to overlap spatially with one another within various template domains, producing the lamellar texture evident in the images.

**Figure 2.5.** TEM images taken from aliquots during a PbS QP synthesis at 25 °C after various reaction times. (a, b) at 20 min, (c, d) at 60 min, and (e, f) at 120 min. All samples were washed once prior to TEM analysis to preserve the template structure, except for that in part a, which was analyzed without washing.
The lamellar texturing was more evident and extensive in TEM images of lightly washed specimens removed from the reaction mixture at 120 min (Figure 2.5e, f). In these images, the amorphous regions appeared to have been largely filled such that lamellar texture was observed throughout the template globules. We interpreted the dark stripes within the globules to be PbS QPs (viewed on edge), which extensively filled the templates. The spacing between the centers of the dark stripes, measured in several regions of the images, was $d = 4.5 \pm 0.5 \text{ nm}$, significantly larger than the spacing of $d = 2.79 \pm 0.02 \text{ nm}$ obtained by low-angle XRD (see above). This discrepancy is addressed in the Discussion.

**Reinvestigation of the High-Temperature Synthesis.** As noted in the Introduction, we were particularly interested in the synthesis of PbS nanosheets reported by Weller and coworkers, conducted using a lead acetate precursor in an oleic-acid mixture at 100 °C.16 Clear evidence supporting nanosheet formation by a two-dimensional oriented attachment of PbS nanoparticles was presented. We were challenged to understand why the oriented attachment occurred in 2D to give nanosheets, rather than in 3D, and considered the possibility of a templated pathway related to that elucidated above.

Three of the components employed in the Weller synthesis were combined in the reported ratios,16 as described below. Neat oleic acid and lead acetate trihydrate were combined to give a viscous, clear, colorless solution. The addition of DMF produced a colorless, semi-opaque mixture having the consistency of applesauce. The low-angle XRD pattern of the mixture contained a series of sharp reflections corresponding to a lamellar mesophase having a $d$ spacing of $4.83 \pm 0.02 \text{ nm}$ (Figure 2.6a). This $d$ spacing was consistent with an oleate-bilayer mesophase analogous to the amine-bilayer mesophase in Figure 2.4.19 The result suggested the formation of a lamellar template under the conditions of the Weller synthesis.
Figure 2.6. Data obtained from the Weller synthesis.\textsuperscript{15,16,18} (a) A low-angle XRD pattern of a mixture of oleic acid, Pb(OAc)\textsubscript{2}·3H\textsubscript{2}O, and DMF in the synthetic ratios. (b) A TEM image at a reaction time of 30 s. (c) A TEM image at a reaction time of 2 min. (d) A TEM image at a reaction time of 5 min. (e) A TEM image at a reaction time of 10 min.

The growth of PbS nanosheets by the Weller synthesis at 100 °C was monitored by TEM. Aliquots removed from the reaction mixture at various times gave the TEM images in Figure 2.6b – 2.6e. Weller and coworkers reported the formation of PbS quantum dots within the first 50 seconds, and the formation of nanosheets on the timescale of 1 – 3 min. The images we collected from an aliquot removed at 30 s gave evidence of quantum dots clustered together in aggregate structures (Figure 2.6b). In the images of an aliquot removed at 2 min, the outlines of the nanosheets were developing as the quantum dots were engaged in the attachment process (Figure 2.6c). In a 5-min aliquot, the attachment process was nearly complete (Figure 2.6d), and in a 10-min aliquot tightly bundled stacks of mature nanosheets were clearly evident.
(Figure 2.6e). The progression of the images suggested formation of PbS quantum dots within lamellar templates, followed by their consequent 2D self-assembly into nanosheets entrained within the templates.
Discussion

**Disagreement of the Mesophase \(d\) Spacings Determined by XRD and TEM.** We were surprised to find such a large difference between the lamellar spacing of the PbS-QP amine-bilayer mesophase measured by XRD \( (d = 2.79 \pm 0.02 \text{ nm}) \) and TEM \( (d = 4.5 \pm 0.5 \text{ nm}) \), in which the TEM value was greater by a factor of 1.6. Consequently, we reviewed our previously published results on the \([(\text{CdSe})_{13}(n\text{-octylamine})_{13}]\) amine-bilayer mesophase,\(^{19}\) for which we now find a similar discrepancy that we failed to recognize earlier. The \(d\) spacings in \([(\text{CdSe})_{13}(n\text{-octylamine})_{13}]\) measured by XRD \( (d = 2.64 \text{ nm}) \) and TEM \( (d = 4.81 \pm 0.05 \text{ nm}) \) varied by a factor of 1.82. For comparison, we analyzed the published data of Hyeon and coworkers for a CdSe-nanosheet \(n\)-octylamine-bilayer mesophase \( (d = 3.3 \text{ nm by XRD and } 3.82 \pm 0.12 \text{ nm by TEM}),^{20}\) and a CdS-nanosheet \(n\)-octylamine-bilayer mesophase \( (d = 3.1 \text{ nm by XRD and } 3.46 \pm 0.05 \text{ nm by TEM}).^{27}\) Thus, such \(d\)-spacing discrepancies appear to be a general phenomenon in bilayer mesophases.

We next considered if the apparent \(d\)-spacing expansions in the TEM might correspond to deformations of the presumably soft mesophase materials. In our current example, the TEM images were recorded at chamber pressure of \(1.0 \times 10^{-5} \text{ Pa}\), which is 10 orders of magnitude below the ambient pressure at which the XRD data were recorded, and corresponds to a putative tensile stress on the mesophase of \(1.0 \times 10^1 \text{ GPa}\). By Hooke’s law, the strain (deformation) in a material is \(\varepsilon = \sigma/E\), where \(\sigma\) is tensile stress (in units of pressure), and \(E\) is Young’s modulus, or the modulus of elasticity (also in units of pressure).\(^{28}\) Given the apparent strain of 1.6 we measure from the TEM images of the PbS-QP amine-bilayer mesophase, and the presumed
tensile stress of $1.0 \times 10^1$ GPa, we calculate a Young’s modulus of $E = 6.3$ GPa for the organic-inorganic nanocomposite material.

This experimentally determined Young’s modulus may be compared to its predicted upper and lower bounds for such a nanocomposite. Platelet-reinforced polymer composites exhibit “rule-of-mixtures” elasticities, in which Young’s modulus scales with the volume fractions of the inorganic and organic components.$^{29,30}$ The upper bound to Young’s modulus may be expressed as eq 2-3,$^{29}$ where $E_{c,\text{upper}}$, $E_o$, and $E_i$ correspond to Young’s moduli of the composite, organic component (amine bilayer), and inorganic component (PbS QPs), respectively, and where $V_o$ and $V_i$ correspond to the volume fractions of the organic and inorganic components, respectively. The lower bound may be expressed as eq 2-4,$^{29}$ in which $E_{c,\text{lower}}$ is the elasticity in the direction normal to the PbS nanoplatelets.$^{28}$

$$E_{c,\text{upper}} = E_o V_o + E_i V_i \quad (2-3)$$

$$E_{c,\text{lower}} = \left(\frac{V_o}{E_o} + \frac{V_i}{E_i}\right)^{-1} \quad (2-4)$$

The Young’s modulus of PbS has apparently not been experimentally determined. We derive a value of $E_i = 72.1$ GPa from a theoretical value of Poisson’s ratio ($\mu = 0.224$)$^{31}$ and the experimental elastic moduli ($C_{11} = 124$ GPa and $C_{12} = 3.3$ GPa)$^{22}$ as detailed in the Supporting Information. We estimate the Young’s modulus for the amine bilayer from that of high-density polyethylene at $E_o = 1.1$ GPa,$^{30}$ as the elasticities in these two cases are governed by similar van der Waals interactions. The upper (eq 2-3) and lower (eq 2-4) limits derived from these elastic moduli are plotted as a function of PbS volume percent in Figure 2.7. Similar analyses producing Figure-2.7-like plots have been reported for polymer-clay nanocomposites.$^{32}$
The experimental volume fractions \( V_o = 0.65 \) and \( V_i = 0.35 \) are obtained from the layer thicknesses of the two components (Figure 2.4). Therefore, eq 2-3 yields an upper limit to Young’s modulus for the PbS-QP amine-bilayer mesophase of \( E_{c,\text{upper}} = 26 \) GPa, and eq 2-4 yields a lower limit of \( E_{c,\text{lower}} = 1.7 \) GPa. The experimental value of \( E = 6.3 \) GPa lies between these predicted limits, as shown by the plotted point in Figure 2.7.

![Plot of theoretical maximum and minimum values for Young's modulus vs. composition](image)

**Figure 2.7.** Plots of the theoretical maximum (eq 3, black line) theoretical minimum (eq 4, red curve) values for the Young’s moduli of PbS \( n \)-octylamine-bilayer mesophases as functions of composition. The experimental point at 35 volume % PbS corresponds to the value calculated from the TEM and XRD data (see the text).

Because strain is measured in the PbS-QP amine-bilayer mesophase in the direction normal to the PbS nanoplatelets, we should expect the observed value of \( E = 6.3 \) GPa to lie closer to the eq 2-4 lower limit of \( E_{c,\text{lower}} = 1.7 \) GPa, as we observe. However, note that all lamellar domains in the mesophase globules are not aligned with the same orientation. A larger component of the applied stress is transferred to the stiffer QPs in the misoriented domains, increasing the overall stiffness of the mesophase globules above the lower-limit value. Thus the observed value is somewhat higher than \( E_{c,\text{lower}} \), and appears to be reasonable.

We conclude that the generally observed discrepancies between the lamellar \( d \) spacings of bilayer mesophases measured by XRD and TEM result from tensile strain in the high vacuum of the TEM chamber. Such differences should now be expected. Moreover, the theoretical
magnitude of the strain may be approximated from Hooke’s law, the TEM chamber pressure, and eqs 2-3 and 2-4.

Interpretation of the Energetic Shifting of the Quantum-well Transitions During Growth. Figure 2.2 reveals a progressive shifting of the \( n = 1 \) and \( n = 2 \) quantum-well transitions to lower energies throughout the PbS QP growth process (see above). In typical semiconductor-nanocrystal-growth processes, such shifting is generally due to the increasing size of the nanocrystals \( (d \) in eq 2-2), and thus a weakening of the quantum confinement. However, in the present case the thickness of the PbS QPs is constrained to 1 nm by the surrounding lamellar template, which is presumably reached rapidly during the initial stages of growth. Moreover, the lateral dimensions of the PbS QPs have largely surpassed twice the bulk exciton Bohr radius in PbS of 18 nm\(^2\) after about 20 min (see Figure 2.5a and b), whereas the energetic shifting of the quantum-well transitions continues over the entire 120-min growth process. Thus, increasing QP dimensions would not seemingly explain the observed spectral shifting.

Instead, we propose that the shifting of the transitions to lower energies with time is due to the formation of a coupled-quantum-well system\(^3\) within the lamellar templates. The PbS quantum wells (QPs) in our PbS-QP amine-bilayer mesophases are 1.0 nm in thickness and separated by only 1.8 nm (the amine-bilayer thickness, Figure 2.4). As the bulk exciton Bohr radius for PbS is 18 nm, excitons are strongly confined in these very thin PbS QPs. Thus, exciton wave functions extend beyond a single QP, tunnel through the amine bilayers, and interact with adjacent QPs in the mesophase stacks.
Early in the growth process, the QPs nucleated at random positions within the templates are non-overlapping (Figure 2.8a, i), as suggested by Figure 2.5a and b, and are thus not coupled with one another. However, as growth proceeds, the degree of overlap increases (Figure 2.8a, ii), and becomes extensive as the templates fill (Figure 2.8a, iii). Thus, the extent of electronic coupling between the adjacent wells (QPs) continuously increases during growth, resulting in the delocalization of the exciton wave functions over multiple QPs, which lowers the energies of the corresponding \( n = 1 \) and \( n = 2 \) transitions (Figure 2.2a). The coupled quantum-well system also splits the quantum-well transitions into multiplicities equal to one less than the number of interacting wells.\(^{33}\) The transitions between these perturbed, closely spaced levels are not spectrally resolved, but contribute to the observed broadening of the absorption features.

**Figure 2.8.** Depictions of proposed template-growth pathways. (a) In an \( n \)-octylamine-bilayer mesophase; (i) nucleation of PbS platelets, which grow laterally within the template by monomer addition, (ii) lateral growth results in partial overlap of QPs within the template stacks, (iii) overlap becomes extensive as the QPs grow large in lateral dimensions. (b) In an oleate-bilayer mesophase;\(^{15}\) (i) PbS nanoparticles nucleate within the template, (ii) nanoparticles undergo oriented attachment within the 2D galleries of the template, (iii) oriented attachment results in the formation of PbS nanosheets.
Arguments Supporting a Templated Mechanism in the Weller Synthesis of PbS

Nanosheets. As noted above, the experimental evidence for the formation of PbS nanosheets in the Weller synthesis by the 2D oriented attachment of PbS nanoparticles is strong. Given that rock-salt PbS has a cubic crystal structure, the question is why the attachment occurs in 2D rather than in 3D. We argue here that evidence collected by us and by Weller and coworkers – before, after, and during the PbS synthesis – provide strong support for a lamellar-template mechanism.

We provide clear evidence here (Figure 2.6a) that three components of the Weller synthesis – Pb(OAc)$_2$·3H$_2$O, oleic acid, and DMF – spontaneously form a lamellar, oleate-bilayer mesophase at room temperature. Such a mesophase, present before the PbS synthesis is initiated, could template 2D oriented attachment within its planar reaction galleries. However, we note again that the mere observation of such an initial or starting mesophase is not proof of nanocrystals or nanosheets growing in a templated manner within it. Moreover, the Weller synthesis contained other components, including additional solvent, and was conducted at 100 °C, which are conditions that might disrupt or decompose a precursor-template structure. We may conclude only that the components employed in the Weller synthesis are capable of forming a lamellar precursor template.

Results reported by Weller and coworkers collected after PbS nanosheet formation by TEM and small-angle X-ray scattering (SAXS) provided strong evidence for periodic, nanosheet-bilayer stacking. TEM images of the product (Figure 1 in ref 15) clearly showed the nanosheets bundled into face-to-face stacks, as in our Figure 2.6e above. Weller and coworkers reported the highly anisotropic SAXS data (Figure 4 in ref 15) to be consistent with a PbS-
nanosheet, oleate-bilayer structure. Thus, lamellar bilayer mesophases were observed at the conclusion of the synthesis.

The results we obtained by TEM monitoring during the Weller synthesis were entirely consistent with those previously reported by Weller and coworkers.\textsuperscript{15} Nanoparticles formed at early times were observed to assemble into sheet structures and to finally yield the tightly bundled stacks of PbS nanosheets (Figure 2.6b-2.6e). Even at the early, nanoparticle stage, most of the PbS nanoparticles were assembled into loose aggregates (Figure 2.6b and 2.6c) having rough outlines comparable to those of the nanosheets ultimately formed. This observation strongly suggests that the PbS nanoparticles were formed and entrained within a common lamellar-template structure.

Therefore, the existence of a lamellar mesophase before, during, and after the synthesis, and the evidence for closely related precursor and product oleate-bilayer mesophases before and after, leads to the reasonable conclusion that the mesophases template the growth of the nanosheets and are responsible for their quasi-2D morphology. The mechanistic picture that emerges is diagrammed in Figure 2.7b. Nanoparticle assembly is confined to two dimensions by the surrounding lamellar template.
Conclusion

The low-temperature growth of PbS QPs at or near room temperature in an $n$-octylamine-bilayer mesophase template affords very thin (1-nm) QPs that exhibit strong quantum-confinement effects and well-resolved ($n = 1, 2$) quantum-well transitions in their extinction spectra. Spectral shifting observed during growth is attributed to increasing multi-quantum-well coupling among the adjacent, closely spaced QPs in the template bundles. The expansion of the lamellar $d$ spacing in the bilayer mesophase in the TEM is quantitatively analyzed as an elastic deformation occurring in the high-vacuum environment of the microscope.

A re-examination of the higher-temperature Weller synthesis of PbS nanosheets in an oleic-acid mixture provides evidence for a related lamellar-template growth pathway. As noted in the introduction, flat colloidal semiconductor nanocrystals have been prepared by two general methods, a lower-temperature long-chain amine synthesis and a higher-temperature carboxylate/carboxylic-acid synthesis. The results reported here demonstrate that both types of synthesis may proceed by lamellar-templated pathways. Given the other observations of templated pathways for flat colloidal semiconductor nanocrystals reported previously,1,3,4,8,19,25,27 a template mechanism should be suspected in any colloidal synthesis that produces flat nanocrystals.
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Chapter 3:

Updates to the CdSe Quantum Wire Synthesis
Introduction

A new synthetic procedure for the synthesis of CdSe quantum wires (QWs) has been formulated based on testing a range of variables in light of recent work done on the solvent trioctylphosphine oxide (TOPO) and its impurities, which were found to have substantial effects on wire growth.\(^1\) The new synthetic procedure modifies the acids used to dissolve the original cadmium precursor (CdO) as well as lowering the reaction temperature. The new reaction temperature is based on the size of the Bi catalyst nanoparticle (NP).

The solution-liquid-solid (SLS) method of synthesizing nanowires came about in 2001, with the advent of quantum wires coming shortly thereafter.\(^1\) These semiconductor wires are uniquely suited to carrying charges across long (1 \(\mu\)m +) distances, compared to other quantum nanomaterials, due to their one-dimensional nature. These nanowires are prepared by using a liquid metal catalyst particle in which the wire precursors are dissolved. A supersaturated solution of precursor species, dissolved in the catalyst particle, triggers a crystallization event, resulting in wire growth from the catalyst. Additional precursor species dissolve into the catalyst droplet, perpetuating the QW growth until the precursors are exhausted.\(^4\)

Quantum wires are noted as currently having much lower photoluminescence quantum yield (PLQY) than many other quantum nanomaterials (< 0.1\%),\(^5\) but can be modified post reaction to achieve much higher fluorescence efficiencies (~25\%).\(^6\) The PLQY measurement is of particular use to solar cells, and their mechanism of charge transfer. While direct fluorescence would not be harnessed in a solar cell, it is an indirect measure of the quality of the nanomaterials itself. Fluorescence occurs due to the radiative recombination of an excited electron-hole pair (also referred to as an exciton). A very high PLQY can imply that the quantum nanocrystals suffer
from few (or shallow) potential energy minima through the length of the crystal,\(^7\) and therefore can transfer their charges more effectively. This charge transfer is what will ultimately be harnessed by a solar cell, and if it is sufficiently high, the solar cell can harness more incoming energy with less wasted.

With the modification of the CdSe synthesis, our goal is to increase the PLQY to levels usable in a solar cell. While the PLQY has been increased (to around 1\%), it is still not suitable for use in a functional cell. Further work must be done to these materials in order to increase their efficiency as well as protect them from effects of prolonged exposure to intense light (photobleaching).\(^8\) A common method to protect nanomaterials is to grow a shell on the outside of these materials.\(^9\) While core-shell quantum dots are relatively commonplace these days,\(^9\) there has been only one epitaxially grown core-shell QW, and it retained the sensitivity to O\(_2\) from the atmosphere.\(^6\) To this end, we propose a model shell material that has previously been overlooked as an ideal CdSe shell: MgSe. MgSe has the smallest mismatch of any shell material for CdSe if looking to make a type-I core/shell material (see appendix). It also has a large band gap of 4.0 eV, which can insulate even the smallest of CdSe quantum crystals.
Experimental

Materials. Cadmium oxide (CdO, 99.99%, Sigma-Aldrich), magnesium oxide (MgO, 99%, Sigma-Aldrich), tri-\textit{n}-octylphosphine (TOP, technical grade, 90%, Sigma-Aldrich), amorphous selenium shot (Se, 99.999%, Alfa-Aesar), \textit{n}-tetradecylphosphonic acid (TDPA, 99%, Polycarbon Industries), and oleic acid (OA, technical grade, 90%, Sigma-Aldrich) were all used as described without any purification. Tri-\textit{n}-octylphosphine oxide (TOPO, 90%, Sigma Aldrich) was purified through distillation and recrystallization from acetonitrile.\textsuperscript{1} \textit{n}-Hexadecylamine (HDA, 90%, Aldrich) was vacuum distilled at 200 °C (0.1 Torr). \textit{Di-\textit{n}-octyl phosphinic acid (DOPA),\textsuperscript{10} and bismuth nanoparticles (Bi NPs)\textsuperscript{11} were synthesized using previously published methods. Tri-\textit{n}-octyl phosphine selenide (TOPSe) was made by saturating amorphous Se shot in TOP at room temperature in a glovebox under dry N\textsubscript{2} (g) and allowing it to sit overnight. All materials were stored at room temperature in a glovebox under dry N\textsubscript{2} (g).

Analyses. UV-visible spectra were obtained using a Varian Cary 100 Bio UV-visible spectrophotometer. Fluorescence measurements were taken on a Varian Cary Eclipse fluorescence spectrophotometer. TEM images were obtained using a JEOL 2000FX microscope operating at 200 keV.

Preparation of CdSe quantum wires using only phosphorus-based acids (new synthesis). All synthetic manipulations prior to workup were carried out under dry N\textsubscript{2}. CdO (12 mg, 0.093 mmol), DOPA (40 mg, 0.138 mmol), TDPA (12 mg, 0.043 mmol) and TOPO (5 g, 12.93 mmol) were mixed together in a 50 mL reaction flask with a stir bar in a glovebox. Separately, TOPSe (500 mg, 1.11 mmol), TOP (100 mg, 0.270 mmol), and Bi NPs (23 mg, 0.00092 mmol Bi) were pipetted into an injection vial. The flask and vial were removed from the glovebox and the flask
was heated to ~310 ºC using a salt bath (1:1 mole ratio of KNO$_3$:NaNO$_3$) with stirring. The flask was removed from heat once the solution changes color from opaque dark red to clear and colorless. The flask was placed in a second salt bath at 240 ºC and given time to equilibrate to the new temperature. The contents of the injection vial, kept at room temperature, were drawn up into a sterile syringe and injected into the heated flask and stirring was cut immediately. The solution changed from clear and colorless to dark black in ~45 seconds. At 5 minutes, the flask was taken out of the heat and given ~30 seconds to cool down, at which point most of the solution was poured into a storage vial to solidify and kept at room temperature, in the dark, until further use. The remaining sample left in the flask (~0.5 mL) was washed out with 1 mL of toluene and decanted into a test tube. The suspension was a light brown and very slightly opaque in appearance. The sample was then washed to purge unreacted precursors and extraneous reagents before analysis using a ~7:1 v/v toluene:methanol mixture (4 mL) to induce precipitation and centrifuged (≥1500 rpm) for 1 minute. The resulting supernatant was decanted and the sample was re-suspended in toluene. For UV-visible and fluorescence spectroscopy, one wash was performed; for TEM analysis, this washing was performed twice.

**Preparations of CdSe Quantum wires using Cd(oleate)$_2$ with phosphorus-based acids** (intermediate synthesis). All synthetic manipulations prior to workup were carried out under dry N$_2$. CdO (8 mg, 0.062 mmol), OA (100 mg, 0.354 mmol), DOPA (7 mg, 0.024 mmol), TDPA (7 mg, 0.025 mmol), and TOPO (5 g, 12.93 mmol) were mixed together in a 50 mL reaction flask with a stir bar in a glovebox. Separately, TOPSe (560 mg, 1.11 mmol), TOP (100 mg, 0.270 mmol), and Bi NPs (23 mg, 0.00092 mmol Bi) were pipetted into an injection vial.
Preparations of CdSe Quantum Wires using Cd(oleate)$_2$ (old synthesis). All synthetic manipulations prior to workup were carried out under dry N$_2$. CdO (5 mg, 0.039 mmol), OA (60 mg, 0.212 mmol), DOPA (6 mg 0.21 mmol), HDA (60 mg (50 mg, 0.21 mmol), and TOPO (5 g, 12.93 mmol) were mixed together in a 50 mL reaction flask with a stir bar in a glovebox. Separately, TOPSe (500 mg, 1.11 mmol), TOP (100 mg, 0.270 mmol), and Bi NPs (23 mg, 0.00092 mmol Bi) were pipetted into an injection vial. All synthetic procedure from here on is identical to the previous method, with the exception of reaction temperature. The secondary salt bath was set at 250-260 °C for this reaction.

Synthesis of MgSe Tetrapods. All synthetic manipulations prior to workup were carried out under dry N$_2$. MgO (20 mg, 0.50 mmol), OA, (400 mg, 1.42 mmol), and TOPO (5 g, 12.93 mmol), were mixed together in a 50 mL reaction flask with a stir bar in a glovebox. Separately, TOPSe (50 mg, 0.11 mmol), and TOP (225 mg, 0.61 mmol) were pipetted into an injection vial. The reaction flask was heated in a salt bath to ~300 °C, with stirring, to dissolve the MgO. Once the reaction solution changed from opaque white to a clear and colorless (sometimes it appeared a very dull brown), it was cooled to 260 °C in a second salt bath and left to equilibrate for a few minutes. The contents of the injection vial, kept at room temperature, were drawn up into a sterile syringe and injected into the flask at this temperature. No visible color changes occur during the reaction; after 60 m, the flask is removed from the salt bath and poured into a collection vial for storage. Washing procedure is similar to the one above with CdSe QWs. For
optical measurements, one washing procedure is done. For TEM, at least 2 washes are performed.

**Synthesis of CdSe Quantum Dots for Shell Addition.** All synthetic manipulations prior to workup were carried out under dry N$_2$. CdO (50 mg, 0.389 mmol), OA (250 mg, 0.885 mmol), and TOPO (5 g, 12.93 mmol) were mixed together in a 50 mL reaction flask with a stir bar in a glovebox. Separately, TOPSe (500 mg, 1.11 mmol) and TOP (100 mg, 0.270 mmol) were pipetted into an injection vial. The reaction flask was heated in a salt bath to ~310 °C to dissolve the CdO. Once the reaction solution changed from a dark red to clear and colorless, it was cooled to 160 °C in an oil bath and left to equilibrate for a few minutes. The contents of the injection vial, kept at room temperature, is injected into the flask at this temperature. The mixture changes to a yellow color and was reacted for 30 minutes before removing the flask from the heat source. The full sample was separated into 4 test tubes and left to dry. Each of these test tubes was weighed to calculate the theoretical amount of Cd atoms (the limiting reactant) present, assuming a 100% yield.

**MgSe Shell addition.** Each CdSe sample from the procedure above was weighed; based on the theoretical amount of Cd$^{2+}$ atoms in this mass (assuming 100% yield), a series of Mg(oleate)$_2$ solutions were made to add differing amounts of Mg$^{2+}$ to each sample, ranging from a 5:1 Mg:Cd to 100:1 Mg:Cd excess. Such high stoichiometries were chosen due to the relative stability of magnesium salts compared to cadmium. Each of the test tubes containing CdSe QDs were melted, suspended in toluene and washed with methanol once before the addition of Mg(oleate)$_2$. Each of the Mg$^{2+}$ soak solutions (containing 4.8:1, 19.7:1, 50:1, and 103.1:1 of
Mg:Cd) was allowed to react at room temperature for 3 days, after which time UV-visible spectra were taken of each sample.
Results

**Changes to the CdSe QW synthesis.** The goal for high PLQY CdSe QWs remains a core focus of our laboratory. At the time I began, the synthesis proceeded *via* a Cd(oleate)$_2$ precursor salt, which can work well in making nanowires as seen in Figure 3.1. The figure shows a representative sample of CdSe QWs and how they appear under the TEM: thin wires that will usually appear in bundles/aggregates upon drying on the TEM sample grid, and will appear in either straight (as shown) or wavy patterns.

![Figure 3.1](image)

**Figure 3.1.** TEM image of a bundle of CdSe QWs. These wires were grown with the “intermediate” synthesis (see above) using 8.8 nm Bi NP catalysts. The resulting wires are roughly 7.2 nm in diameter. With the CdSe Bohr radius being 5.6 nm,$^{12}$ each of these QWs is expected to exhibit quantum confinement effects, which can be seen later in this chapter.

When scrutinizing TEM images of these CdSe wires closely, striations are noticed in the wires as well as apparent changes in transparency. These are due to crystal imperfections in each of the wires. The striations, observed in the top of the figure above, illustrate the rapid changes...
in crystal structure between zinc blende (ZB) and wurtzite (WZ) occurring in the wire during SLS growth. The changes in transparency (noted by the dark regions of the wire) are due to twists in the wire, and the resulting “face” of the wire is more prone to absorbing the electron beam rather than transmitting.

The only issue with the Cd(oleate)$_2$ reaction is the precursor is just slightly too reactive to be the sole cadmium salt precursor used for QW growth. By comparison, a phosphonic acid (such as TDPA, see Figure 3.2) is polyprotic and will react with CdO in a 1:1 stoichiometry. The resulting Cd(TDPA) salt can be compared to a Cd(oleate)$_2$ salt and found to be more stable by the simple virtue of entropy. Therefore, the Cd(TDPA) salt is theorized to be less reactive than Cd(oleate)$_2$ and possibly more suitable for nanowire synthesis (see discussion).

![Figure 3.2](image)

**Figure 3.2.** Common acids used in CdSe QW synthesis. From left to right: Oleic acid, dioctylphosphinic acid (DOPA), and tetradecylphosphonic acid (TDPA). DOPA has two R groups attached to its central phosphorous atom, and, like other phosphinic acids, is monoprotic. TDPA contains only a single R group, and is, just as other phosphonic acids, a biprotic acid.

Early in 2009, we began experimenting with phosphinic acids (DOPA) and a variety of phosphonic acids (most notably TDPA). These additives eventually came to replace our use of HDA and OA in our synthesis. Primary amines have been observed to help increase PL levels in CdSe nanocrystals$^{13,14}$ and by adding it to the original synthesis we had hoped to eliminate a
post-reaction workup step. The reality of the HDA addition is a simple acid-base interaction with any or all of the acids used to react the CdO into a usable SLS precursor salt, drastically slowing down the reaction time (by increasing the dissolution time) and reacting away the very additive we sought to use to our advantage. The change in procedure to exclude HDA has since made all QW syntheses far more reproducible.

**Isolation of Variables Promoting PLQY.** Many variables were examined in an attempt to determine what influences the PLQY of CdSe QWs: CdO concentration, acid concentration, necessity of certain acids, reaction temperature, and dissolution of CdO under vacuum. All of these QWs were grown from the same size Bi NPs (8.8 nm), and as such will have similar diameters and, therefore, similar quantum confinement shifts in energies. All syntheses were modified from the “intermediate” synthetic method described above. Table 3.1 presents the summation of this experiment, specifically all of the fluorescence features as they relate to one another. In order to facilitate comparison, the fluorescence spectrum of each sample has been normalized using the extinction value at their respective first excitonic peak positions. As evidenced by the table, many of these variables do little to vary the ensemble QW fluorescence, with the exception of reaction temperature.

The bulk band gap for CdSe is 1.74 eV (712 nm)\(^{15}\) and each of these wires demonstrated a slight band gap shift towards higher energy, generally showing a \(\Delta E_g\) of 100 meV due to the effects of their quantum confinement.\(^3\) Shown below in Table 3.1, each of the variable CdO samples display little fluorescence variance, although lower concentrations of CdO show an especially decreased fluorescence, so \(\geq10\) mg CdO is recommended to ensure the highest PLQY.
When using the phosphorus-based acids exclusively instead of OA, the PL is increased slightly, but only marginally; the higher concentrations of DOPA appear to be beneficial in these cases.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative Peak Area (a.u.)</th>
<th>FWHM (meV)</th>
<th>Peak Position (eV)</th>
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<tbody>
<tr>
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<td>1.84</td>
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<tr>
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<td>2.96</td>
<td>97</td>
<td>1.83</td>
</tr>
<tr>
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<td>1.83</td>
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<td>127</td>
<td>1.85</td>
</tr>
</tbody>
</table>

Table 3.1. Fluorescence data for CdSe QWs. Peak integrations and full-width-half-maximum (FWHM) calculations were done in Origin. All integrations, with the exception of the two reactions carried out at 239 and 243 ºC were measured between 1.7 – 2.0 eV. These other two spectra were integrated from 1.75 – 2.05 eV.

The vacuum dissolution of CdO was carried out in an effort to eliminate any H₂O generated during the initial heating process, but instead quenched much of the fluorescence; a finding that
agrees with previous works. Very small amounts of H$_2$O, when vaporized and run over a sample of CdSe QDs, enhance the PLQY.$^{16}$ By eliminating all water generated by dissolving the CdO, the fluorescence is particularly inhibited.

When getting to the bottom of the table, we notice that the lowest temperature for synthesis gave, by far, the highest peak integration. Even considering that the FWHM is about 60% larger than the rest of the data, the integration is twice that of the average, indicating that the lower temperature makes more optically efficient QWs.

**MgSe exhibiting a variety of crystal structures.** MgSe in its bulk structure takes the form of rock salt. Rock salt, like zinc blende and wurtzite, is considered a close packed crystal structure, and they all contain a hexagonal close packed system with minor differences in the ion filling arrangement. MgSe has a unique distinction of having nanomaterials observed in all three of these arrangements, as shown in Figure 3.3. First, in Figure 3.3a, the standard rock salt structure is shown with a matching $d$ spacing for bulk MgSe (3.15 Å). In the next two images (Figures 3.3b and c), MgSe was observed in nanotetrapods, which are observed to be a zinc blende and wurtzite heterostructure. More images of the MgSe nanoparticles can be found in the appendix. This is especially interesting as MgSe is expected to undergo a phase transition only at very high pressures.$^{17}$
Figure 3.3. MgSe nanocrystals in various forms.  a) A rock salt nanocube with measured $d$-spacing of 3.15 Å.  b) The center of a MgSe tetrapod is seen here to be zinc blende.  c) A tetrapod arm of a MgSe crystal is wurtzite. Both b and c have measured $d$ spacings of 3.6 nm.

These MgSe tetrapods can be thought of as being based around a single zinc blende MgSe QD, with four wurtzite “arms” growing off the center body, which has been reported in CdSe as well.$^{18,19}$ This work is encouraging for attempts to grow a shell around any CdSe material, which has been seen to exhibit both zinc blende and wurtzite structures, even in the same nanocrystal.$^6$ By exhibiting the same crystal structures as CdSe, as well as having very closely matched lattice parameters to it (2.7% mismatch), MgSe is the ideal type-I shell material for any CdSe nanomaterial.

Attempts made at a CdSe/MgSe core shell QD system have yet proven unsuccessful. The resulting UV-visible spectra of each experiment showed a disappearance of the 1st excitonic peak originally taken from the CdSe QDs, indicating that the optical properties were being negatively affected by the Mg(oleate)$_2$ soak, or no movement/enhancement of PLQY features, indicating no positive changes to the core CdSe nanocrystal.
Discussion

**Temperature as the major variable for CdSe synthesis.** Using the data summed up in Table 3.1, we can observe a number of trends that suggest what we can do to modify the synthesis to increase the overall PLQY. First, the increasing amounts of CdO will increase the fluorescence, albeit by small amounts, and narrow the fluorescence peak width. This is most likely due to a low Cd$^{2+}$ concentration having detrimental or inconsistent effects rather than a higher Cd$^{2+}$ concentration effecting the reaction kinetics positively.

The introduction of DOPA to the synthesis has had positive effects on wire morphology and consistency of results since the first study was released in 2009, and it seems that using DOPA as the primary acid for dissolving the CdO works well for the wire morphology as well as its PLQY. DOPA is thought to be a more favorable surface passivating ligand than oleate or TOPO in this regard and increased concentrations of DOPA will passivate a wire surface more easily.

When observing the lower temperature syntheses, it should be noted that the fluorescence peak is widened, indicating that the diameter distribution is wider than in previous experiments, but the PL itself is overall higher. Due to the quantum confinement effects of very small semiconductor nanomaterials, a wide size distribution will generate a range of $\Delta E_g$ values from the bulk and therefore widen all of the optical features. This wide size distribution may be due to being slightly below the full melting point of the Bi catalyst NPs. The catalyst particles, if not completely molten, have been shown to create erratic wire growths, as shown below in Figure 3.4, if they even act as catalysts at all. Also shown in figure 3.4 is a cluster of unreacted Bi NPs that swell as they take in Cd$^{2+}$ and Se$^{2-}$ precursors, but will not generate a crystal nucleation
event. The Bi NPs used in the reaction below were originally 8.6 nm, and have swollen to 10-15 nm.

Figure 3.4. CdSe QWs grown at a low temperature. The TEM sample shown is populated with short, low quality wires of many different diameters as well as many unreacted Bi catalyst NPs, seen as the large black dots in the center.

If we take into account the extra width of the sample grown at 239 ºC (60% wider at FWHM), the ensemble emission of these wires are still around 40% brighter than the rest of the QWs made in this series. A brief number of follow-up experiments were conducted to arrive at the “new” synthetic method described in the experimental section for an ideal synthetic method for CdSe QWs.

Below, in Figure 3.4, we can see the culmination of all these effects on the PLQY of wire synthesis. Here we can easily see the changes made when modifying our variables studied above. The low temperature spectrum (blue line) shows the greatest change in overall fluorescence compared to the other two variables (The red and green lines). The black spectrum was taken after the conclusions were made and is the culmination of modifying the CdSe synthesis based on the results. Using all of these variables together begets fluorescence greater
than the sum of its parts, however the PLQY measured for the black spectrum is still only around 1%.

Figure 3.5. Relative fluorescence of CdSe QWs. These fluorescence spectra mark the relative changes in fluorescence when modifying certain variables. These variables (from the key) are: 10 mg CdO (essentially unchanged from the original synthesis), 40 mg DOPA (replacing OA with DOPA entirely), low temperature synthesis (CdSe QWs grown at 239 °C), and the last spectrum shows the fluorescence using all of these modified parameters in concert.

Viability of MgSe as a Shell Material. MgSe has extremely well matched theoretical values for affixing to a CdSe nanocrystal. In practice, it has proven to be a difficult material to grow evenly on CdSe QDs. CdS, shown below in Figure 3.5, is the widest use semiconductor shell for CdSe nanocrystals. Along with CdS, ZnS, ZnSe and ZnTe have also been studied for various effects on CdSe QDs.

CdS is an easy choice for a shell material in the case of CdSe due to the close relation both crystals have in size to one another. Both the conduction and valence bands of CdS sit outside those of CdSe (for bulk) and can insulate the exciton to within the core of a CdSe/CdS core/shell quantum nanomaterial. While all of these materials work well with CdSe QDs, the mismatch of
many of them (including CdS) remains too much for other nanomaterials in certain morphologies (a table of lattice mismatches for different materials is contained in the appendix). When making large morphology nanomaterials, such as wires, the extra length will begin to exacerbate the minor differences in lattice constants between crystals. A 4% strain, like that of CdS against CdSe, will be an entire unit cell in length difference when a QW is only 200 nm long. If we are to make 1-10 µm long wires and coat them with an epitaxial shell, there needs to be much closer lattice agreement between the core and shell materials. There may simply be maximum lengths for which a shell can coat certain core materials.

![Diagram of band gaps of selected semiconductors](image)

**Figure 3.6.** Relative band gap diagram of selected semiconductors. Each material is plotted relative to vacuum for direct comparison of valence and conduction bands relative to another. The colors chosen for each material are the visible color of their respective transitions, with the exceptions of ZnS and MgSe; 3.6 and 4.0 eV are both in the ultraviolet region and therefore not visible to the human eye.

If future experiments are to be attempted at a CdSe/MgSe system, more highly reactive Mg precursor needs to be used, perhaps even an organo-metallic compound if carboxylate salts are found to be just too stable for shell additions. During the Mg$^{2+}$ soaking experiments it should be noted that all samples were seen to fluoresce a pale blue color, which is has been observed to be
indicative of Mg(oleate)₂. This would suggest that the Mg²⁺ ion is not being taken up into the QW for shell growth, and more reactive materials need to be utilized.
Conclusion

A new synthetic procedure for making brighter CdSe QWs has been established by studying multiple reaction variables and determining their relative effects (if any) on the fluorescence of the sample. Based on these findings, the PLQY of our CdSe QWs has been enhanced and PLQYs of around 1% are now obtainable via the SLS method. The reaction temperature plays a larger role in the SLS growth of CdSe QWs than previously explored. While quality QWs can be made at a wide variety of temperatures using this method, the PLQY of the sample drop off very quickly with higher reaction temperatures. Therefore, the reaction temperature is now highly dependent on the size of Bi catalyst NPs used for wire growth.

Further modification of CdSe wires to increase the PLQY will likely rely on surface modification. It may be from growing an epitaxial shell (such as CdS or MgSe) or from other rearrangements of the surface due to ligand replacement/passivation. MgSe is presented here as the most ideal shell material for CdSe, but it comes with the difficulty of less-reactive Mg$^{2+}$ precursors. MgSe shows promise in the materials’ availability to grow in many different close-packed structures, but remains to be seen if they can be grown on any CdSe nanocrystals.
References


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Chapter 4:

CONCLUSION
The low-temperature growth of PbS QPs at or near room temperature in an n-octylamine-bilayer mesophase template affords very thin (1-nm) QPs that exhibit strong quantum-confinement effects and well-resolved \((n = 1, 2)\) quantum-well transitions in their extinction spectra. Spectral shifting observed during growth is attributed to increasing multi-quantum-well coupling among the adjacent, closely spaced QPs in the template bundles. The expansion of the lamellar \(d\) spacing in the bilayer mesophase in the TEM is quantitatively analyzed as an elastic deformation occurring in the high-vacuum environment of the microscope.

More experimentation is required in order to identify the role of the chlorocarbon additives used in other laboratories in their plate growths. If the mechanism for their involvement can be successfully found, the synthesis of thickness-tuned quantum plates can be exploited for optoelectronics such as solar cells.

A new synthetic procedure for making brighter CdSe QWs has been established by studying multiple reaction variables and determining their relative effects (if any) on the fluorescence of the sample. Based on these findings, the PLQY of our CdSe QWs has been enhanced and PLQYs of around 1\% are now obtainable via the SLS method. The reaction temperature plays a larger role in the SLS growth of CdSe QWs than previously explored. While quality QWs can be made at a wide variety of temperatures using this method, the PLQY of the sample will drop off very quickly with higher reaction temperatures. Therefore, the reaction temperature is now highly dependent on the size of Bi catalyst NPs used for wire growth.

Further modification of CdSe wires to increase the PLQY will likely rely on a heavy surface modification. It may be from growing an epitaxial shell (such as CdS or MgSe) or from other rearrangements of the surface due to ligand replacement/passivation. MgSe is presented here as the most ideal shell material for CdSe, but it comes with the difficulty of less-reactive Mg\(^{2+}\)
precursors. MgSe shows promise in the materials’ availability to grow in many different close-packed structures, but remains to be seen if they can be grown on any CdSe nanocrystals.

Future work in the arena of CdSe QWs will be based around surface chemistry of the wire. It may be another attempt at adding an epitaxial shell to CdSe QWs, or it may simply be an enhancement based on modifying the surface through ligand exchange. Both methods show promise, and for quantum wires in general, the only direction for the PLQY to go from here is up.
Appendix
Figure A1. TEM images of PbS QPs synthesized at room temperature (~25 °C) for 1 h. After growth for longer periods, platelets adopt extensively crumpled morphologies, and individual QPs are no longer distinguishable in the TEM images.
Figure A2. Energy Dispersive Spectroscopy (EDS) data from PbS QPs. (a) Full-range spectrum with peaks labeled by element. (b) Expansion of the region containing both Pb and S peaks, showing the spectral overlap. The labels are positioned at the energies for the corresponding S and Pb lines.
Figure A3. High-angle XRD data corresponding to PbS QPs. (a) Unmodified pattern collected from PbS QPs protected by a polyvinyltoluene film cast over the sample. (b) Polyvinyltoluene pattern (obtained without PbS QPs). (c) Background-subtracted pattern using an algorithm provided in the Bruker instrument software. The asterisks identify reflections belonging to the low-angle 00l reflections corresponding to the lamellar-mesophase architecture of the PbS QP assemblies.
Figure A4. Distorted rock salt structures seen in IV-VI crystals. a) The GeS structure as shown looking down the (001) axis. This structure has alternating compression and elongation deformations running along the [100] (horizontal) and [010] (vertical) directions. b) A PbTe structure observed at high pressures, shown looking down the (010) axis. Note the wave-like periodicity of the crystal plane in the [100] direction. Both of these structures show a loss in symmetry of the rock salt crystal system and could be similar to the structure exhibited in the PbS QPs.
Figure A5. High resolution TEM images of PbS QPs. a-b) Larger pan view of the plates and their crystalline nature. Due to the extremely thin dimension of the plates, they will bend in and out of focus due to the relative coarseness of the sample holder (carbon film on a Cu grid). c-d) Zoomed view from the same sample of QPs. From here we can take measurements of a square-like lattice parameter to be $d = 3.12 \pm 0.04$ nm. If the sample were strictly rock salt, this would indicate a relative expansion of the lattice of around 5%.
Calculation of $d$ spacings by Low-Angle X-Ray Diffraction (LAXRD)

Bragg’s law is rewritten as eq A-1. Ideally, the $y$-intercept value should be zero, but the inclusion of the $b$ parameter allows for an instrumental (or sample-height) offset. As an The low-angle diffraction data for the pre-synthesis Pb(OAc)$_2$-octylamine mixture (from Figure 2.3a) are plotted as $n\lambda$ vs. $2\sin(\theta)$, setting $n = l$ from the 00$l$ indices for each low-angle reflection. The data are fit by eq A-1, yielding a slope value of $d = 2.78$ nm, and a near-zero instrumental offset of 0.003 nm. The 2$\theta$ spacing ($\Delta 2\theta$) between adjacent low-angle reflections (Figure 2.3a) should be identical, and the standard deviation ($\sigma$) in the experimental values is the uncertainty in the measured 2$\theta$ values. This uncertainty is propagated to give the error in the $d$ spacing, in this case, $d = 2.78 \pm 0.03$ nm. The method described here was used to extract $d$ spacings from all LAXRD data obtained in this work.

$$n\lambda = d \ 2 \sin(\theta) + b \quad (A-1)$$

**Figure A6.** Low-angle XRD data from the Pb(OAc)$_2$·3H$_2$O-$n$-octylamine mesophase (Figure 3a) plotted as $n\lambda \ (= l\lambda)$ vs. $2\sin(\theta)$. The data are fit by eq A-1. The slope of the fit is the $d$ spacing within the lamellar mesophase.
Influence of chlorinated solvent on template

Figure A7. Low-angle XRD patterns corresponding to the Weller synthesis of PbS nanosheets (ref 15 in Chapter 2) containing additives used in their synthesis. (a) The pattern collected from a mixture of Pb(OAc)$_2$·3H$_2$O, oleic acid, and DMF in the proportions employed in the synthesis. This pattern may be indexed to a lamellar mesophase having a $d$ spacing of 4.82 ± 0.02 nm. (b) The pattern collected from a mixture of Pb(OAc)$_2$·3H$_2$O, oleic acid, DMF, and 1,2-dichloroethane (DCE) in the proportions employed in the synthesis. This pattern may be indexed to a lamellar mesophase having a $d$ spacing of 4.80 ± 0.05 nm, essentially identical to that in (a). Therefore, the DCE appears to play no special role in the formation or structure of the template.
Calculation of Poisson’s Ratio and Young’s Modulus for PbS

Young’s modulus $E$ may be obtained from the bulk modulus $K$ and Poisson’s ratio $\mu$ according to eq A-2. We obtained the bulk modulus of PbS from the experimental elastic moduli ($C_{11} = 124$ GPa and $C_{12} = 3.3$ GPa)\(^{21}\) according to eq A-3.\(^{2}\) An experimental value of Poisson’s ratio $\mu$ was not available, and so a theoretical value was calculated from theoretical values of Young’s modulus ($E = 94.416$ GPa) and the bulk modulus ($K = 56.957$ GPa) for PbS at ambient pressure ($P = 0$ GPa), by rearranging eq S2 ($\mu_{\text{PbS}} = 0.224$).\(^{3}\) This value may be compared to that of NaCl ($\mu_{\text{NaCl}} = 0.252$),\(^{53}\) which has the same rock-salt crystal structure. A hybrid experimental-theoretical value of Young’s modulus for PbS ($E = 72.1$ GPa) was obtained by substituting the derived values of $K$ and $\mu$ into eq S2.

\[
E = 3K(1 - 2\mu) \tag{A-2}
\]

\[
K = \frac{1}{3}(C_{11} + 2C_{12}) \tag{A-3}
\]
### Table A1. Lattice values and relative mismatch for all II-VI and III-V semiconductors

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<th>Material</th>
<th>WZ a (Å)</th>
<th>ZB a (Å)</th>
<th>WZ c (Å)</th>
<th>ZB c (Å)</th>
<th>Mismatch (%)</th>
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Note: Shaded values are preferred structure of bulk material @ 300K, 1 atm

* Bulk preferred structure for MgSe is rock salt

* * Bulk preferred structure for MgSe is rock salt
**Figure A8.** TEM images of MgSe nanomaterials. a) MgSe nanoprism, zoomed out from figure 3.3 to show the structure. b and c) MgSe nanotetrapods similar to the ones shown in figure 3.3. These tetrapods also contained small amounts of either nanorods or short nanobelts, such as those seen in the top left portion of part c.
References


(4) Reiss, P.; Protière, M.; Li, L. *Small*, 2009, 5, 154