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Understanding Molecular Chemistry of Nanocrystals and Nanostructures: Precursor, Ligand, and Surface Chemistry

Weon-kyu Koh

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Understanding Molecular Chemistry of Nanocrystals and Nanostructures: Precursor, Ligand, and Surface Chemistry

Abstract
The aim of this dissertation is to understand the molecular chemistry of nanomaterials and to correlate their structures to their functions. The first part of this dissertation explores how we can use precursor chemistry to develop a synthetic approach to novel structures of nanomaterials. There will be a demonstration of morphology control in lead chalcogenide nanocrystals following an investigation of the precursor chemistry which gives valuable information on precursor decomposition during the crystal growth. At the same time, there will be a discussion about how we can understand structure-dependent properties of nanomaterials using advanced spectroscopic techniques. Well-established synthetic approaches discussed in the first part allow for the study of morphology-dependent optical properties of lead chalcogenide nanocrystals, including the shape-dependent electronic level structure of lead chalcogenide nanomaterials and the symmetry-dependent phonon modes of lead chalcogenide nanocrystals.

For the second part of this dissertation, I will address the importance of ligand and surface chemistry of colloidal nanomaterials. New ligand systems will be introduced which allow a variety of interesting studies in chemical, optical, and electrical analyses of nanomaterials. Especially flexible electronic devices using low temperature process of thiocyanate chemistry will be demonstrated for lead chalcogenide nanomaterials to show promising opportunities of these ligand systems. For the electronic transport in a 1-dimensional confined system, NWs-based field-effect transistors are studied with post-processed surface treatment. Investigating the role of chemical treatment reveals how the surface/interface chemistry of NWs affects the electronic transport in 1-dimensional confined nanostructures.

To sum up, this dissertation first focuses on the molecular chemistry of nanostructures to help understand the synthesis and ligand/surface chemistry of nanomaterials. This understanding then enables us to study the optical and electric properties of these materials with various morphologies and assembled structures. With the ability to control the size, shape, and composite materials of the individual building blocks, I hope this dissertation can aid in the formation of collective ensembles with tunable material properties and structures. The ultimate goal is the creation of nanomaterial-based devices with programmable performances.

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UNDERSTANDING MOLECULAR CHEMISTRY OF NANOCRYSTALS AND NANOSTRUCTURES: PRECURSOR, LIGAND, AND SURFACE CHEMISTRY

Weon-kyu Koh

A Dissertation in Chemistry

Presented to the Faculties of the University of Pennsylvania
In Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy

2011

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Abstract

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Weon-kyu Koh

Advisor: Prof. Christopher B. Murray, Ph. D.

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For the second part of this dissertation, I will address the importance of ligand
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Preface

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Chapter 1. Introduction

"I cannot tell my story without reaching a long way back." - Hermann Hesse, *Demian*

1.1. Semiconductor at Nanoscale: Quantum Confinement Effect

In solid state physics, a band gap is the spacing between the highest occupied energy band (valence band) and lowest unoccupied energy band (conduction band). In semiconductors, electrons can jump from the valence band to the conduction band by thermal excitation (phonon) or light absorption (photon) due to their small band gap. This process leaves an empty space in the valence band known as the ‘hole’.
The excited electron in the conduction band and its corresponding hole in the valence band form an electron-hole pair, which is called an ‘exciton’ that is bound by Coulomb attraction. The distance between the hole and electron of the exciton is called ‘exciton Bohr radius’. In a bulk semiconductor, the band gap is an intrinsic property of a given material; however, when the size of the semiconductor is smaller than the exciton Bohr radius, the exciton is physically confined in this scale. In other words, the band gap is increased as the size of the semiconductor is decreased along with the quantized energy levels of the conduction/valence bands. This is known as the quantum confinement effect. The band gap energy and particle size can be considered as a particle in a box: $E_g \sim 1/a^2$ (a: the radius of the particle).

Figure 1.1. Energy band diagrams for an insulator and a semiconductor.
Figure 1.2. (a) Bohr radius of an exciton and (b) the size effect of quantum confinement shown by the electronic structure.

Early studies of quantum confinement effect were investigated using thin semiconductor layers known as quantum wells, made by molecular beam epitaxy. Later, the theoretical and physical study of quantum wires and quantum dots expanded the understanding of the transition from bulk semiconductors to two-dimensional quantum wells (2D), one-dimensional quantum wires (1D), and zero-dimensional quantum dots (0D).
Figure 1.3. Illustration of quantum confinement going from bulk semiconductor
to quantum wells, wires/rods, and dots. In bulk semiconductors, electrons/holes
move in a continuous energy state, causing a band structure. In quantum
wells/wires/dots, the carriers are restricted to 2D/1D/0D, giving discrete band
structures of density of states (DOS).
1.2. Synthesis of Nanocrystals

Semiconductor nanocrystals (NCs), or quantum dots (QDs), have been synthesized by either the “top-down” method or the “bottom-up” method. In the “top-down” approach, NCs are grown by epitaxial techniques or ion implantation. The “bottom-up” approach involves a glass matrix used by Ekimov\(^3\) and using a colloidal solution used by Brus.\(^4\) Later, Murray et al. reported a solution process of growing cadmium chalcogenide NCs using an organometallic precursor, which opened many opportunities to develop high quality NCs of various materials such as CdSe, CdTe, CdS, ZnSe, ZnS, InAs, InP, PbSe, PbS, PbTe, and so on.\(^5\)\(^{10}\) In this dissertation, most NCs synthesis will be demonstrated based on Murray’s approach, using organometallic precursors in colloids.

The synthesis of colloidal NCs is based on organometallic precursors, organic surfactants, and high-boiling point solvents. At a high temperature, the precursors decompose to produce monomers and reach a supersaturation condition. Then nucleation is initiated to give NC growth. The important factors for NC growth are reaction temperature, concentration, and growth time. First, if the temperature is too high there will be secondary nucleation which gives broad size distribution of NCs. If the temperature is too low, NCs growth is not efficient and might give poor crystallinity and quality. Secondly, NC growth has “focusing” and “defocusing” regimes; high monomer concentration gives small critical size (the size of NCs at equilibrium between growing and shrinking) and monodisperse
size distribution (focusing). On the other hand, low monomer concentration gives large critical size and Ostwald ripening, causing polydispersion in the size distribution of NCs (defocusing).

![Figure 1.4. Schematic representation of the synthesis of PbSe NCs. The precursors are injected into the solution at the high temperature and NCs are formed with capped organic surfactant.](image)

As the shape control of NCs is important to understand their growth and adjust their optical and electronic properties, there have been numerous reports on the precise control of the shape of NCs by adjusting reaction conditions such as growth temperature, time, precursor, and surfactant. However, the morphology control of NCs is still challenging, and understanding their novel properties in optics and electronics is difficult due to the poor shape control of NCs and fluctuation of the resulting ensemble properties. One successful example of shape-controlled colloidal NCs is reported by Peng et al.\textsuperscript{11} They used
hexylphosphonic acid as a strong binding surfactant to induce anisotropic growth of elongated CdSe NCs.\textsuperscript{12}

\textbf{Figure 1.5.} Proposed growth mechanism of CdSe nanorods (NRs).

Another interesting example is oriented attachment, which was first reported by Penn et al.\textsuperscript{13} This is rather different than the previous surfactant-control approach, as it makes anisotropic nanostructures from individual particles by joining them at high energy surfaces. There have been other reports involving CdTe and ZnO, where they were assembled to make single crystal anisotropic nanostructures.\textsuperscript{14,15}
Figure 1.6. An example of oriented attachment: ZnO NCs and NRs.
1.3. Precursor Chemistry of Nanocrystals

The general process of NC formation is 1) decomposition of molecular precursors, 2) monomer formation, and 3) nucleation and crystal growth. Many studies have been done based on spherical NCs to understand this process. However, the process of NC formation is still not fully understood. Liu et al. proposed that the decomposition of Cd and Se precursors and transition state of TOP=E (trioctylphosphine, E=S, Se, Te) cleavage occur as shown in Figure 1.7.\(^{16}\)

![Chemical reaction pathway and hypothetical transition structure](image)

**Figure 1.7.** (a) Proposed reaction pathway for precursor conversion and (b) hypothetical transition structure for TOP=E cleavage.\(^{16}\)

Later, Steckel et al. pointed out that dialkyl phosphines are one of the impurities in technical grade of TOP that accelerate NC formation and change the decomposition mechanism of metal precursors.\(^{17}\) Also, Evans et al. reported that pure TOPSe does not react with metal precursors but dialkyl phosphine, an impurity of TOP, actually leads to NC formation via a metal-chalcogenide
complex (Figure 1.8). This example highlights the difficulty in understanding NC formation at the molecular level even for simple spherical NCs. This is mainly due to the instability of precursors and the complexity of reaction condition like precursor impurities.

![Proposed reaction mechanism for metal chalcogenide complex](image)

**Figure 1.8.** Proposed reaction mechanism for metal chalcogenide complex.¹⁸

Impurity effects of shape control for NCs have also been investigated by several groups. Peng et al. initiated shape control of CdSe NRs and related morphologies by pointing out the importance of an impurity in commercial trioctylphosphine oxide (TOPO),¹¹ while Wang et al. reported a similar issue on the synthesis of semiconductor nanowires (NWs) using a solution-liquid-solution (SLS) process.¹⁹ Houtepen et al. noticed that incomplete dried lead precursor produces branched structures of PbSe NCs,²⁰ and Smith et al. reported that the iodide impurity in
cetyltrimethylammonium bromide (CTAB) prevents gold NR formation.\textsuperscript{21} In many cases, impurities adsorb on to specific surfaces of NCs, changing their growth and resulting in anisotropic morphologies of the final products.

**Figure 1.9.** TEM images of CdSe NWs grown in TOPO without (left) and with (right) phosphonic acid impurities.\textsuperscript{19}

Another point on chalcogenide precursors is that most NCs have been synthesized with either phosphine-free chalcogenides\textsuperscript{22,23} or TOP/TBP(tributylphosphine)-based chalcogenides\textsuperscript{11,5}, implying that there would be many opportunities to study new phosphine chemistry for NC-based research. In chapter 2 and 3, the new phosphine chemistry of PbSe NCs will be demonstrated and discussed to understand the role of precursor chemistry on the morphology control for PbSe NRs.
Figure 1.10. TEM images and absorption spectra of Au NRs (left) and Au NCs (right) to show the effect of iodide impurities in CTAB.21
1.4. Surface Chemistry of Nanocrystals

The solution process of inorganic NCs has a promising advantage to fabricating a variety of solid-state devices. This becomes possible by adopting organic surfactants in NC synthesis through enhanced solubility and precise controllability of size and shape of NCs. One challenge in the organometallic synthesis of NCs is the preparation of water-soluble NCs or phase transfer of NCs into polar solvents, especially for biological applications. Because the syntheses of NCs are performed in organic nonpolar solvents, there have been many studies to control the surface chemistry of NCs to disperse them into aqueous mediums. These efforts include ligand exchange, bilayer formation, or polymer surfactant. Early ligand exchange was known to use thiol-based ligands like 11-mercaptoundecanoic acid, which has both a polar carboxylic acid and a thiol group. In particular, thiols are strongly bound to the surface of NCs, giving good stability in water for a short time. However, Aldana et al. reported that the thiol-based ligand can induce photochemical oxidation of NCs to decrease the stability of NCs in solution.24 There have been several alternative ways to overcome the instability of NCs in water/polar solvents such as bilayer formation25 and the usage of a phosphine oxide-based polymeric surfactant26. However, a large volume of outer surfactant is not ideal for electron transport, NC coupling to see various interesting solid state physics, and applications for optical/electronic devices.
Figure 1.11. (a) Scheme of the possible mechanism for photochemical oxidation of thiol-capped CdSe NCs. (b) Bilayer formation of oleic acid for water-soluble NCs. (c) Phosphine oxide-based water-soluble polymeric surfactant for various NCs.

Another challenge is that insulating surfactants prevent the further progression of interparticle coupling between NCs, which is critical for electronic transport and other applications. Recently Kovalenko et al. reported the molecular metal chalcogenide (MMC) system as a new ligand model of colloidal NCs, and also showed good conductivity of solid film NCs cooperated with MMC ligand.\textsuperscript{27}
Figure 1.12. (a) Sketch of a CdSe NC capped with Sn$_2$S$_6^{4-}$ ions. (b) Current-voltage scans for a film of dodecanethiol-capped 5 nm Au NCs (open circles) and for a film of the same Au NCs capped with (N$_2$H$_5$)$_4$Sn$_2$S$_6$ (black squares). Dashed arrows show the voltage scan direction.

Another issue is whether there are any methodological tools to understand surface chemistry of NCs by conventional spectroscopy and chemical analysis. Most surface analysis is based on bulk materials, which is quite challenging to understand a NC surface due to perturbation of analysis from strong coupling with core materials, surrounding medium, and surface defects. Sometimes this causes a controversy in the interpretation of data analysis: for example, the FT-IR analysis for ligand quantization in PbSe NCs $^{28,29}$. Thus it is critical to develop a good analytical method for understanding the surface chemistry of colloidal NCs.
1.5. Optics of Nanocrystals

Typical NCs are made with a size between 1 nm-10 nm, which proves difficult for the strong confinement of II-VI/III-V semiconductors due to the small hole Bohr radii. However, IV-VI semiconductors have strong quantum confinement, especially with lead chalcogenides that have small and similar electron/hole masses with large electron/hole Bohr radii. This allows lead chalcogenide NCs to have less effect on surface traps or defects. They also have simple non-degenerate conduction/valence bands, resulting in simple energy spectra.

Figure 1.13. Electronic structures of II-IV/III-V and IV-VI semiconductors for bulk and NC systems.
Figure 1.14. The absorption spectra and electronic band structure for CdSe and PbSe NCs.

The current theories for the electronic states of lead chalcogenide NCs are based on envelope function approaches\textsuperscript{30} and tight-binding methods\textsuperscript{31}. The envelope function approximation considers the NC as a truncated infinite crystal. It assumes that the NC wavefunction can be expressed as a product of the bulk semiconductor wavefunction and an envelope function that independently satisfies the physical NC boundary conditions. On the other hand, the tight-binding approximation treats the NC as an ensemble of the individual atoms. It assumes that the NC wavefunction can be expressed as a sum over the wavefunctions of the individual atoms compromising the NC when only accounting for nearest-neighbor interactions. These electronic structure
calculations have been very successful in providing accurate energies of higher exciton states as well as the lowest exciton, electron, and hole wavefunctions with the correct symmetries, and the interband dipole transition strengths and selection rules.

Still, there are several limitations for all current calculations in explaining the optical absorption spectra of lead chalcogenide NCs: the first is that the second optical transition has been assigned to either an S-P transition or a P-P transition, which is not clear yet.\textsuperscript{32,33} Another is that the direct energy gap occurs not at the center of the Brillouin zone (Γ), but rather at the 4 equivalent hexagonal face-centers (L). Therefore, the degeneracy of the electronic states is increased by factor of 4. This source of degeneracy in lead chalcogenides is expected to be lifted by coupling of the equivalent valleys, but this effect has not been clearly shown with experimental evidence.

In addition, phonon measurement of PbSe NCs will be addressed using Far-IR spectroscopy. A phonon is a quantized quasi-particle of the modes of lattice vibrations of crystal. There are two types of phonons. One is the acoustic phonon, where the two atoms on the unit cell vibrate along the same direction, either longitudinal or transverse acoustic phonon (LA or TA). Another is the optical phonon, where the two atoms on the unit cell vibrate in opposing motion, either longitudinal or transverse optical phonon (LO or TO). The optical phonon can be infra active and/or Raman active depending on the symmetry of objects; infra active phonon is a mode of vibration where positive and negative ions swing against each other, making a time-varying electrical dipole moment. Raman active
phonon is an optical phonon from indirect interaction with light through Raman scattering. There is another important phonon mode, a surface phonon, which is a collective lattice vibration mode associated with surfaces: this can be from an artifact of periodicity, symmetry, termination at the surface layer, and so on.

Figure 1.15. (a and d) Equilibrium positions of atoms. (b) Longitudinal acoustic vibration. (c) Longitudinal optical vibration. (e) Transverse acoustic vibration. (f) Transverse optical vibration.

In a cubic structure like PbSe, the radial mode has angular momentum $l_p = 0$, which is Raman active. When $l_p = 1$, there can be LO or TO or surface phonon which is Fröhlich mode and IR active, due to violation of translation symmetry. When $l_p = 2$, there can be an ellipsoidal mode that is Raman active.

Kigel et al. reported phonon modes of spherical PbSe NCs using Raman spectroscopy, where they found TA, TO, and LO modes (Figure 1.16a). In particular, phonon modes are quite sensitive to the morphology of objects, with aspect ratios and rod-morphology giving different trends in phonon modes. In an example of CdSe NR, LO depends on the diameter of rods and the surface phonon...
depends on the aspect ratio of rods (Figure 1.16b).\textsuperscript{35}

![Figure 1.16](image)

**Figure 1.16.** (a) Phonon mode of spherical PbSe NCs. (b) Surface phonon vs aspect ratio of CdSe NRs.
1.6. Overview of this Thesis

In this thesis, a broad range of topics is covered from synthesis of colloidal nanomaterials to optics and electronic transport of them either with individual component or with collective ensemble. The first goal of the work in this thesis is to understand on morphology control of NCs, especially lead chalcogenide system such as lead sulfide and lead selenide. Chapter 2 introduces a new type of precursor chemistry to control the morphology of lead chalcogenide nanomaterials, especially focusing on NR synthesis, with materials characterization using TEM, XRD, and steady-state spectroscopy.

Chapter 3 describes understanding precursor chemistry of lead chalcogenide nanomaterials, introduced in the previous chapter. Chemical analyses such as NMR and TGA-MS were combined with electron microscopy and optical spectroscopy to understand phosphine chemistry of Se precursors, implying small chemical species would affect both morphology of NCs and precursor decomposition during the crystal growth.

Chapter 4 describes the optical properties of lead chalcogenide nanomaterials studied in previous chapters, using steady-state, time-resolved, and far-IR (FIR) spectroscopy. Theoretical understanding of electronic structures and optical transitions in lead chalcogenide, and phonon measurement of anisotropic lead chalcogenide are included here.
Furthermore, chapter 5 describes new ligand systems of colloidal NCs, especially thiocyanate and its derivatives as compact surfactants on the surface of NCs. This new concept of surface chemistry allows us to understand more about optical and electrical properties of nanomaterials, by providing highly sensitive IR probe as well as enhancing coupling between neighboring NCs. Cubic PbS NC-based field-effect transistor on plastic substrates will be also demonstrated to open new opportunities for solution-processible flexible electronics.

The last goal is to understand electronic transport in 1D or 0D nanostructures, as described in Chapter 6. PbSe NWs field-effect transistor was studied to understand the control of electron and hole transport by chemical doping, especially careful treatment at interface of electrode/NW and on the surface of NWs allow us to investigate chemistry of doping process.

Chapter 7 will address future directions of my research to expand to various areas of precursor/surface chemistry, synthesis/assembly of nanomaterials, and their optic/electric properties with device application.
Chapter 2. Synthesis of Lead Chalcogenide Nanorods

"What I cannot create, I do not understand." - Richard Feynman

2.1. Introduction

Solution-process synthesis of NCs has been developed intensively for electronic, optical, and magnetic applications.\(^{36-39}\) In particular, the ability to control the morphology of semiconductor NCs has presented many research opportunities in understanding the fundamental properties of materials and developing electro-optical devices.\(^{12,40-44}\)

Lead selenide (PbSe) is a narrow band gap (0.28 eV, bulk) material that has small effective masses for both holes and electrons (~0.1 \(m_e\)), and a large exciton Bohr radius (23 nm).\(^{30,32}\) Although PbSe is interesting in semiconductor and IR applications, especially when its size and morphology can be controlled at the nanoscale, there have been few reports of anisotropic PbSe nanostructures. Previously, Cho et al. reported PbSe nanowires (NWs) made by oriented attachment,\(^9\) a process which makes anisotropic nanostructures from individual

particles by joining them to high energy surfaces.\textsuperscript{13-15} In their paper, PbSe NWs were synthesized at a higher temperature (250 °C) than PbSe NCs (150-170 °C) in order to enhance oriented attachment and to produce longer NWs; and the authors used tetradecylphosphonic acid or hexadecylamine as a co-surfactant to control the morphology of wires (straight or zigzag shape). However, optical properties of NWs are not easy to study due to the low NW solubility and large scattering, especially when surface traps exist. In addition, rapid wire formation (<1 min) at high temperature has prevented the detailed understanding of oriented attachment in the growth of PbSe structures, and has also made it difficult to modify the morphology and size of NWs. There have been other reports of anisotropic lead chalcogenide nanostructures such as PbSe nanorods (NRs) using Au-Fe\textsubscript{3}O\textsubscript{4} seeds,\textsuperscript{45} PbSe NWs using a Au/Bi catalyst,\textsuperscript{46} and PbS NRs using cationic exchange on CdS NRs;\textsuperscript{47} but none of them have shown a catalyst-free, one-pot synthesis of single-crystalline, anisotropic PbSe nanostructures.

Here we report a simple and high quality PbSe NR synthesis and their shape-dependent structural/optical properties. The key improvement reported here is controlled NR growth, enabled by the use of tris(diethylamino)phosphine selenide (TDPSe) instead of trioctylphosphine selenide (TOPSe). This makes possible NR growth of PbSe at lower temperatures on a longer time scale (150-170 °C, >2~3 min), so we could monitor a transition process of NR growth by TEM and absorption spectra. Details of the synthesis, along with structural analysis and optical properties of the PbSe NRs will be presented. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) were performed to support their
structures, and optical spectra showed how the morphology of lead chalcogenide crystals affects their quantum-confined electronic structures.
2.2. Experimental Section

2.2.1. Chemicals

All manipulations were carried out using standard Schlenk line techniques under dry nitrogen. Tris(diethylamino)phosphine (TDP, Aldrich, 97%), oleic acid (OA, Aldrich, 90%), 1-octadecene (ODE, Aldrich, 90%), squalane (Aldrich, 99%), amorphous selenium shots (Se, Aldrich, 99.999%), and lead (II) oxide (PbO, Aldrich, 99.9%) were used as purchased without further purification. Anhydrous ethanol, chloroform, acetone, hexane, and tetrachloroethylene (TCE) were purchased from various sources. To prepare 1.0 M stock solutions of TDPSe, 7.86 g of Se was dissolved in 100 ml of TDP.

2.2.2. Synthesis of PbSe Nanorods

Typically, 0.22 g of PbO was dissolved in 5 ml squalane in the presence of 1 ml OA. (Squalane can be replaced by ODE.) After drying under nitrogen at 150 °C for 30 min, the solution was heated to 170 °C and 3 ml of 1 M TDPSe solution in TDP were injected under vigorous stirring. Once the reaction finished, the reaction mixture was cooled to room temperature using a water bath. The crude solution was mixed with hexane and precipitated by ethanol. The precipitated NRs were isolated by centrifugation (at 5000 rpm for 3 min) and redispersed in chloroform or other organic solvents. Size-selective precipitation can be carried
out to obtain better monodispersity of NRs samples using chloroform/acetone or other solvent/nonsolvent pairs.

2.2.3. Sample Characterization

Powder X-ray diffraction (XRD), in-plane XRD, and transmission small angle X-ray scattering (TSAXS) were performed using Cu Ka1 radiation (λ=1.54 Å) from a Rigaku SmartLab at 40 kV and 30 mA. For XRD measurement, samples were prepared by depositing NCs or NRs solutions in hexane onto a Si substrate or a glass plate. For in-plane XRD measurement, the incident angle was typically 0.83 degrees. For TSAXS measurement, the 1 mm capillaries containing the NR solutions (~5% in toluene) were sealed and mounted perpendicular to the beam direction. The TSAXS fitting curve was simulated using NANO-Solver, Rigaku software. Transmission electron microscopy (TEM), high-resolution TEM, and energy-dispersive X-ray spectroscopy (EDX) were carried out by using a JEOL JEM 1400 and a 2010F at 120 and 200 kV, respectively. Samples for TEM images were prepared by dropping a solution on a 300 mesh carbon-coated copper grid and allowing the solvent to evaporate at room temperature. Absorption spectra were measured on a Shimadzu UV-3101PC spectrophotometer at room temperature. Emission spectra were recorded at room temperature with an infrared fluorometer equipped with a 200-mm focal length monochromator, a single mode fiber coupled laser (S1FC635PM, 635 nm, Thorlabs, Inc) as the excitation source, and an InGaAs photodiode detector (New Focus Femtowatt
model 2153). The samples were excited at a repetition rate of 20 kHz by nanosecond pulses of a Lumanova muFlare laser system frequency doubled to 532 nm. The sample was exposed to intensity levels well below one electron-hole pair per dot. Fluorescence was monitored with a Hamamatsu H10330A-75 PMT, and the output was fed into, and averaged, by a 1 GHz Oscilloscope. All optical experiments were carried out in the solvent TCE.
2.3. Synthesis of PbSe Nanorods, Assemblies, and Growth transition

Figure 2.1a shows a TEM image of typical PbSe NRs, with ~4 and 40 nm diameter and length, respectively. As shown in Figure 2.1b, the rod is single crystalline; here we can see the \{100\} facet, which is matched with the inset Fourier transform image. Interestingly, slow evaporation of PbSe NR solutions in chloroform or TCE allowed liquid-crystalline assembly (Figure 2.1c) and vertical alignment (Figure 2.1d), as shown in previous reports of CdSe NRs.\textsuperscript{11,48}
In order to investigate the process of PbSe NR growth, an aliquot of the reaction solution was taken at different time points and observed by TEM. At first, small particles were produced from the mixing of lead and selenide precursors (Figure 2.2a). Later, the aspect ratio increased rapidly, but the diameter increased slowly (Figure 2.2b and 2.2c).

**Figure 2.1.** (a) TEM image of typical PbSe NRs. (b) High resolution TEM image of individual PbSe NR. (Inset: FFT image of (100) face) (c) Liquid crystal assembly of PbSe NRs. (d) Vertical alignment of shorter PbSe NRs. (Inset: FFT image of hexagonally assembled NRs)
Figure 2.2. TEM images of different growth times (a) 30 sec, d=3.9 nm; (b) 2 min, d x L=3.8 x 21 nm; (c) 4 min, d x L=4.1 x 44 nm; (d) 8 min, d x L=5.7 x 35 nm. (d: diameter, L=length of rods) At stage (d), the actual products are a polydisperse mixture of rods and particles, so it is not suitable to compare the average length with that of other samples.

This can be confirmed by absorption spectra during rod growth, in which the
first exciton peak was shifted only slightly (Figure 2.3a). This corresponds to a slow increase in rod diameter, as the quantum confinement effect of anisotropic nanostructures mostly depends on the smallest length scale present. An example of this is the case of CdTe tetrapods with a similar length that showed diameter-dependent first exciton peak positions, while samples with fixed diameter showed almost identical first peak positions regardless of the length of the tetrapod branches. Another example is the case of PbSe NRs, for which samples with various diameters confirm that the first peak of the absorption spectrum depends mainly on the NR diameter (Figure 2.3b).

![Figure 2.3](image)

**Figure 2.3.** Absorption spectra of (a) different growth times (the same conditions as shown in Figure 2.2) and (b) different diameters of PbSe NRs. (Diameter/length of samples shown in (b) =4.0 x 16 nm, 4.8 x 26 nm, 5.5 x 41 nm)

After the reaction time represented in Figure 2.2c, the surface of the rods was
rough, and the products were polydisperse (Figure 2.2d). As reported in a previous paper, the rapid transition from small particles (Figure 2.2a) to NRs (Figure 2.2b) and attached particles (Figure 2.4) imply the possible mechanism of oriented attachment. This would occur in addition to Ostwald ripening, a commonly observed process in nanocrystalline semiconductor synthesis (Figure 2.2c and 2.2d).

Figure 2.4. TEM images of (a) zigzag, (b) T-shape, and (c) arrow structures of PbSe. (All scale bars are 5 nm.) Under different growth conditions for PbSe NRs (such as a different mole ratio of precursors or different temperature and time of growth), partially attached particles were observed. These show good examples of oriented attachment, where an individual particle keeps its own shape but forms a single crystal.
2.4. Structural Analysis using In-plane XRD and TSAXS

In wide angle X-ray scattering (WAXS), the diffraction peaks of PbSe NRs showed good agreement with those of spherical PbSe NCs; except for a slightly narrower (200) peak (Figure 2.5a and 2.5b). On a flat Si wafer, there is likely a similar mixture of NR orientations as observed on a TEM substrate. This mixture of orientations (standing up, lying down, and intermediate) gives rise to a diffraction pattern that reflects collective isotropy that is similar to that of individual PbSe spheres. However, because NRs are elongated, more of the NRs align parallel to the substrate than vertically (as shown in Figure 2.1c and 2.1d). In order to confirm the anisotropy of PbSe NRs, we took in-plane XRD with the same sample as used in Figure 2.5b and saw an enhanced (200) peak. This implies that NR growth is mainly in the <100> direction since an enhanced peak results from an increased number of lattice planes in the Bragg condition for diffraction (Figure 2.5c). Thus, an enhanced (200) peak can be understood in terms of NR growth in a favored direction and subsequent alignment on the substrate. This growth direction matches the result from a previous report, in which PbSe straight NWs showed only (200) and (220) peaks in XRD.\textsuperscript{9} Transmission small angle X-ray scattering (TSAXS) was also performed on PbSe NRs that were dispersed in toluene and then loaded into a capillary tube. The data in Figure 2.5d was fitted to a cylindrical model with a 6.8 nm diameter and an aspect ratio of 3.5. (The size of the NRs is 6 x 18 nm (diameter x length), measured by TEM.) The PbSe NR SAXS data deviate from the cylindrical model for angles below 2θ=1.0°, most
likely due to short-range correlations between NRs in the relatively concentrated conditions under which the SAXS measurements were made. These short-range correlations between NRs are similar to Jana’s report that Au NRs form small clusters under SAXS measurement conditions.  

Figure 2.5. (a) WAXS pattern of PbSe NCs. (b) WAXS pattern of PbSe NRs. (c) In-plane XRD pattern of PbSe NCs. (Inset: magnified XRD patterns of (111) and (200) peaks for (a)-(c); patterns normalized to the (111) peak.) (d) TSAXS pattern of NRs with fitting curve.
2.5. Conclusion

In this chapter, we demonstrated a simple, one-pot, catalyst-free synthesis of high quality PbSe NRs based on a new phosphine selenide precursor. Optical spectroscopy shows the shape-dependent anisotropic behavior of PbSe NRs as compared to that of spherical NCs (i.e., a larger Stokes shift and longer fluorescence lifetime). TEM and XRD confirmed that the PbSe nanorod was grown along (100) direction, as well as single crystalline of nanorods.
Chapter 3. Precursor Study of Lead Chalcogenide Nanorods

"Truth is ever to be found in simplicity, and not in the multiplicity and confusion of things." - Issac Newton

3.1. Introduction

Colloidal NCs have been investigated with good control of size and morphology, opening electrical and optical applications such as field-effect transistors and photovoltaics. However, the mechanism of NC growth was not fully understood because of the complexity of the colloidal system and the vigorous/air-sensitive synthesis conditions. Although several groups have demonstrated chemical analyses to understand the surface chemistry of NCs or the mechanism of NC growth, their studies have mostly focused on the spherical NC system. Another limitation involves the impurities of trioctylphosphine (TOP) or trioctylphosphine oxide (TOPO) which actually affect precursor decomposition, morphology, and properties of the products, making it difficult to understand the mechanism. Recently we reported the synthesis of PbSe nanorod (NR) using tris(diethylamino)phosphine selenide

(TDPSe) instead of commonly used TOPSe for spherical NCs while keeping other reaction conditions such as Pb oleate and temperature the same as for the synthesis of spherical PbSe NCs;\textsuperscript{54} this implies that the phosphine selenide precursor has an important role in morphology control. Given that most anisotropic Pb chalcogenide nanomaterials are understood as oriented attachment, which still cannot fully explain this precursor-dependent shape evolution;\textsuperscript{9,55} it is required to understand the importance of precursor chemistry to produce high quality anisotropic nanomaterials.

Here we studied the precursor decomposition of PbSe NRs using TDPSe and compared to TOPSe-based spherical PbSe NCs, with a focus on how different reaction temperatures and precursor conditions affect the decomposition of precursors. We performed $^{31}$P NMR experiments to compare the decomposition of TOPSe and TDPSSe to correlate with the morphologies of PbSe NCs, which are confirmed by absorption spectra and TEM. TGA/TGA-MS demonstrates the possible chemical species released during the reaction, and further control experiments support the additive effect this species using TEM and $^{31}$P NMR analyses. Details of the experiment, analysis result, and discussion will be presented.
3.2. Experimental Section

3.2.1. Chemicals

All manipulations were carried out using standard Schlenk line techniques under dry nitrogen. Triocetylphosphine (TOP, Strem, 97%), Tris(diethylamino)phosphine (TDP, Aldrich, 97%), oleic acid (OA, Aldrich, 90%), 1-octadecene (ODE, Aldrich, 90%), amorphous selenium shots (Se, Aldrich, 99.999%), and lead (II) oxide (PbO, Aldrich, 99.9%), lead acetate trihydrate (PbAc$_2$·3H$_2$O, Fisher, 99.999%), diphenylphosphine (DPP, Aldrich, 98%), Toluene-d$_8$ (Aldrich, 99.6%), CDCl$_3$, (Aldrich, 99.8%), trimethyl phosphate (TMP, Aldrich, 99%) were used as purchased without further purification. Anhydrous ethanol, chloroform, acetone, hexane, and tetrachloroethylene (TCE) were purchased from various sources. To prepare 1.0 M stock solutions of TOPSe or TDPSe, 0.786 g of Se was dissolved in 10 ml of TOP or TDP. To prepare neat TOPSe or TDPSe solutions, TOP or TDP and Se were combined by 1:1 mole ratio, and stirred overnight in a nitrogen filled glovebox.

3.2.2. Temperature Dependence of the Decomposition of Se Precursors

Typically, 0.22 g of PbO was dissolved in 5 ml ODE in the presence of 1 ml OA. After drying under nitrogen at 150 °C for 30 min, the solution was heated or cooled to desired temperature, and neat or 1 M Se precursor was injected under
vigorous stirring (1:1 mole ratio of Pb:Se). Aliquots of the reaction solution was taken from the reaction flask and monitored by absorption spectra or $^{31}$P{$^1$H} NMR spectra.

### 3.2.3. Free Phosphine Effect of the Decomposition of Se Precursors

The reaction condition was the same as temperature dependence experiment. When neat Se precursor was used, overall concentration was corrected for by the purity of the phosphine source by dilution with ODE.

### 3.2.4. Amine Effect of the Decomposition of TDPSe

For TDPSe and diethylamine mixture, 1 mmol of TDPSe and 1 mmol of diethylamine is mixed and diluted to 3 ml by ODE as a solvent. For Pb oleate, TDPSe, and diethylamine mixture, 0.22 g of PbO and 1 ml OA were added and diluted to 3 ml by ODE to keep the overall concentration.

### 3.2.5. Sample Characterization

Transmission electron microscopy (TEM) and high-resolution TEM were carried out by using a JEOL JEM 1400 and a 2010F at 120 and 200 kV, respectively. Samples for TEM images were prepared by dropping a solution on a 300 mesh carbon-coated copper grid and allowing the solvent to evaporate at room temperature. Absorption spectra were measured on a Cary 5000 UV-Vis-IR
spectrophotometer or QualitySpec Pro Vis/NIR Spectrometer at room temperature. All optical experiments were carried out in the solvent TCE. $^{31}\text{P}^{1}\text{H}$ NMR spectra were recorded on a Bruker DMX 360 NMR spectrometer, with proton decoupling. The chemical shifts (δ) are given in parts per million relative to an external standard H$_3$PO$_4$ (0 ppm) and an internal standard TMP (3.0 ppm). To quantize the ingredients of samples, 10 µl of TMP was added into 0.5 ml of aliquot then diluted to 1 ml by CDCl$_3$. NMR integration of each peak was compared to the given quantity of TMP. Thermogravimetric analysis was performed with a heating rate of 10 °C/min under N$_2$, on a Thermaladvantage Q600 thermal analyzer connected to a quadrupolar mass spectrometer (Pfeiffer Vacuum Thermostar GSD301T).
3.3. Temperature Effect

Figure 3.1 and 3.13 show that TOPSe-based synthesis at 50–60 °C,\textsuperscript{18} which was reported to form PbSe magic size clusters, decomposes more Se precursor than TDPSe-based synthesis at 50–60 °C. However, TDPSe-based synthesis decomposes more Se precursor than TOPSe-based synthesis under normal synthetic conditions of PbSe NCs (150~160 °C) based on \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectra.

![Plot for decomposition of Pb oleate and 1 M Se precursors in ODE (Pb:Se=1:1 by mole ratio). Dashed line shows conventional PbSe NC growth time limit with further growth providing poor monodispersity of NC products. Data was obtained from integration of \textsuperscript{31}P\{\textsuperscript{1}H\} NMR peaks which had less than 5% error (using TMP as an internal standard).](image)

**Figure 3.1.** Plot for decomposition of Pb oleate and 1 M Se precursors in ODE (Pb:Se=1:1 by mole ratio). Dashed line shows conventional PbSe NC growth time limit with further growth providing poor monodispersity of NC products. Data was obtained from integration of \textsuperscript{31}P\{\textsuperscript{1}H\} NMR peaks which had less than 5% error (using TMP as an internal standard).
This is confirmed by absorption spectra; at lower temperature, TOPSe-based synthesis gives peak evolution during the reaction time (Figure 3.2a), while TDPSa-based synthesis does not change the absorption spectrum at all (Figure 3.3a). It is possible that the larger cone angle of TDPSa suppresses the decomposition at low temperature by steric hinderance around the Se atom in contrast to the reported formation of magic size clusters using TOPSe.\textsuperscript{18} However, this does not explain why TDPSa-based synthesis shows more decomposition of precursor at higher temperature; this leads us to a further investigation of the free phosphine effect of precursor decomposition.

**Figure 3.2.** Absorption spectra of Pb oleate and 1 M TOPSe at (a) 50~60 °C and (b) 150~160 °C.
Figure 3.3. Absorption spectra of Pb oleate and 1 M TDPSe at (a) 50~60 °C and (b) 150~160 °C.
3.4. Free Phosphine Effect

While many metal chalcogenide NC syntheses use extra free phosphine in the Se precursor solution, most reports on the NC synthesis mechanism relied on neat phosphine selenide precursor for simplicity.\textsuperscript{16-18} Indeed, the TOPSe-based synthesis shows no evidence of an effect due to free TOP on their synthesis, as confirmed by TEM in Figure 3.4a and b. For TOPSe-based synthesis, we found that their synthesis from spherical products with or without extra free phosphine. However, we found that free TDP affects the morphology of PbSe NCs made with TDPSe; TEM shows that 1 M TDPSe makes PbSe NR but neat TDPSe produces isotropic particles or attached particles but without rod-morphology (Figure 3.4c and d). Absorption spectra also confirm the effect of free phosphine, showing similar quality of spectra for TOP-based synthesis (Figure 3.5a and b) but different pattern of spectra for TDP-based synthesis (Figure 3.5c and d). We also performed \textsuperscript{31}P\{\textsuperscript{1}H\} NMR to quantitatively compare the effect of free phosphine in PbSe synthesis at normal condition (150 ~ 160 °C). Neat TOPSe and 1 M TOPSe gives 12\% and 11\% decomposition of initial Se precursor, respectively (Figure 3.14a and b). Neat TDPSe gives 7\% decomposition of the initial precursor, which is similar to that of TOP-based synthesis (Figure 3.14c). However, 1 M TDPSe gives 38\% decomposition yield, implying that TDP accelerates the precursor decomposition (Figure 3.14d). Thus we can conclude that the presence of free TDP plays a critical role in the higher precursor decomposition and morphology control in PbSe NR synthesis.
Figure 3.4. TEM images of spherical PbSe NCs (a, 7.5 nm) with 1 M TOPSe vs. (b, 7.0 nm) with neat TOPSe, and those of PbSe NRs (c) with 1 M TDPSe (40 x 4 nm$^2$) and (d) with neat TDPSe. All reactions were done at 150 ~ 160 °C.
Figure 3.5. Absorption spectra of spherical PbSe NCs (a) with 1 M TOPSe vs. (b) with neat TOPSe, and those of PbSe NRs (c) with 1 M TDPSe and (d) with neat TDPSe. All reactions were done at 150 ~ 160 °C.
3.5. Possible Mechanism of Free Phosphine Effect

This section explores how free TDP in PbSe NR synthesis may play such an important role. Since the P-N bond of TDP is weaker than P-C bond of TOP, it is easily cleaved under various conditions such as nucleophile attack or EI-MS ionization.\textsuperscript{56-58} To confirm the release of amine, we monitored the decomposition of free phosphine in the TDPSe-based synthesis using TGA-MS. 1 M TDPSe in TDP solution shows a possible NEt\textsubscript{2}\textsuperscript{+} peak (m/z=72) during the heating process, which can be from either the release of NEt\textsubscript{2} or the fragmentation of vaporized TDP above 150 °C (Figure 3.6a and b). Running the same experiment with neat TDPSe solution, TGA-MS produces the NEt\textsubscript{2}\textsuperscript{+} peak at a higher temperature (above 220 °C) with much less ion intensity of mass decomposition than with 1 M TDPSe in TDP solution (Figure 3.6c and d). Considering that there is little amount of TDP in neat TDPSe solution, the peak at m/z=72 may be assigned as diethylamine released from either residual TDP or from evaporated TDPSe.
Figure 3.6. (a) TGA and (b) TGA-MS of 1 M TDPSe in TDP solution (Starting mass = 18.4020 mg). (c) TGA and (d) TGA-MS of neat TDPSe solution (Starting mass = 20.9930 mg).

The release of diethylamine at high temperatures from free phosphine can explain why TDPSe-based PbSe NR synthesis is not accelerated at lower temperature (Figure 3.1b and 3.3a), while free phosphine accelerates the precursor decomposition at higher temperature with the release of amine (Figure 3.1d and 3.3b). To confirm the amine effect of precursor decomposition, we mixed neat TDPSe and diethylamine by 1:1 mole ratio in ODE as a solvent at 50 ~ 60 °C. After 40 minutes, 21.9% of TDPSe was decomposed with diethylamine but less than 1% of TDPSe was decomposed without diethylamine (Figure 3.16). Also, the mixture of lead oleate, TDPSe, and diethylamine by 1:1:1 mole ratio in ODE as a
solvent at 50–60 °C results in the decomposition of TDPSe by 15.7%, while the same mixture without diethylamine causes the decomposition of TDPSe by 3.6% (Figure 3.17). It is well-known that amines can accelerate precursor decomposition and crystal growth for CdSe and InP NCs. Although the exact role of amines in the precursor decomposition and crystal growth is not yet fully understood as seen in the different effects of long chain amine additives for InP NCs described by Peng and Bawendi groups, our result with short chain amine indicates enhanced precursor decomposition. We speculate that the difference between the effects of long chain and short chain amines may be due to their differences in steric hindrance, with diethylamine being less sterically hindered and thus more activating.
3.6. The Role of Amine for the Morphology of PbSe

After confirming the effect of diethylamine for precursor decomposition, we checked its effect on PbSe morphology by adding a minimum quantity of diethylamine to the growth solution by diluting diethylamine in octadecene (ODE) solvent. Diethylamine was minimized by diluting in ODE because the direct injection of diethylamine into the reaction solution gave an uncontrollable reaction that immediately turned the solution black at the typical reaction temperature of PbSe NR (150~160 °C). For 1 mmol of PbO (0.22 g, same scale as the other reactions), 0.2 ml of 10% by volume of diethylamine in ODE was injected after injection of neat TOPSe or TDPSSe at 170 °C. The precursor decomposition with diethylamine is similar to the reactions without diethylamine: 10% for TOPSe and 3% for TDPSSe, respectively (Figure 3.15) In this case, we do not observe rate enhancement with added amine probably due to the small quantity of diethylamine, in which the mole ratio of Pb:diethylamine is ~1:0.2. However, the morphologies of final products are quite different by TEM; TOPSe-diethylamine produces more homogeneously attached particles (Figure 3.7a), and TDPSSe-diethylamine starts to provide thin and long rod-like products (Figure 3.7b).
Figure 3.7. TEM images of reaction products from Pb oleate and (a) TOPSe-diethylamine and (b) TDPSe-diethylamine at 150~160 °C for 5 min.

It is well-known that the amine group is weakly binding on the surface of PbSe NCs, especially on {111} facets. Oriented attachment is found in many cases, especially when the highly energetic facets are attached to minimize the surface energy of the particles by making a single crystalline. It is possible that released amine species from TDP could accelerate the attachment process by removing {111} facets of PbSe, especially when short-chain and low boiling point diethylamine is present in the growth solution. However, it is still critical to have TDPSe as a Se precursor to produce anisotropic PbSe nanorod, since TOPSe-diethylamine only enhances the attachment process to produce branched structures.
Figure 3.8. TEM images of reaction products from Pb oleate and neat TDPSe with the mole ratio of Pb:diethylamine = (a) 1:0.02 and (b) 1:0.6.

At reaction temperatures below 100 °C, the Pb oleate, TDPSe, diethylamine in ODE solution did not turn black and there was no PbSe product. This suggests that although NMR data show diethylamine increases the decomposition of TDPSe, it might be possible that triggering the intermediate to produce final PbSe requires higher growth temperatures than the decomposition temperature. With growth temperature at 100~110 °C, mainly tiny particles are produced both with and without diethylamine (Figure 3.9a). Interestingly, a small portion of disk-shaped PbSe was observed in TEM images when diethylamine was added during growth (Figure 3.9b), implying that diethylamine effect varies depending on growth temperatures.
Figure 3.9. TEM images of reaction products from Pb oleate and neat TDPS (a) without and (b) with diethylamine. The mole ratio of Pb:TDPS:diethylamine = 1:1:1.
3.7. Free Phosphine Effect of Anisotropic Growth for PbSe NRs:

Transfer Process of the Se Atom

In the previous chapters, we have described that both TDPSe and excess TDP are necessary for the growth of PbSe NRs. When we use neat TOPSe and excess TDP, or neat TDPSe and excess TOP, the products are neither spheres nor rods. Instead zigzag-type elongated structures are produced as shown in Figure 3.10.

![Figure 3.10](image)

**Figure 3.10.** TEM images of reaction products (a) from Pb oleate, neat TOPSe, and excess TDP, and (b) from Pb oleate, neat TDPSe, and excess TOP. Pb:Se:excess phosphine = 1:1:1 by mole ratio. Growth temperature = 150~160 °C and growth time = 3 min.

One possible explanation is that there is an exchange process of Se from one phosphine to another, giving a mixture of TOPSe and TDPSe with free TOP and TDP. When the same mole amount of TOPSe and TDP, or TDPSe and TOP in 1-
ODE are heated at 150 °C for 3 min, both mixtures produce a major portion of TOP/TDPSe with a minor portion of TDP/TOPSe (Figure 3.11). Thus both TOPSe/TDP and TDPSe/TOP mixtures would produce a similar morphology of PbSe NCs, as diethylamine can be released from both reactions and induce oriented attachment with elongated shape.

![Bar graph](attachment://graph.png)

**Figure 3.11.** NMR monitoring of neat TOPSe + TDP and neat TDPSe + TOP mixtures after heating at 150 °C for 3 min. Initial mixtures contained neat Se and excess phosphine by 1:1 mole ratio.
3.8. Conclusions

In conclusion, we studied the morphology of PbSe NCs by understanding precursor chemistry with an emphasis on how different phosphine selenide systems react to shape the final product. Temperature dependence of precursor decomposition implies the effect of steric hindrance for phosphine selenide precursors. TEM images and absorption spectra show consistent result that free phosphine is critical to induce anisotropic morphology of PbSe NRs. $^{31}$P NMR supports the effect of free phosphine for precursor decomposition of PbSe, and TGA-MS provides evidence of amine release from TDP. Further control experiment with adding amine species demonstrates possible origin of the morphology change in the growth of PbSe NC. We hope this report advances the understanding of both the fundamental science of phosphine chemistry and the chalcogenide-based semiconductor NC synthesis.
3.9. Appendix: Raw data for NMR spectra

Figure 3.12. $^{31}$P-$^{1}$H NMR of (a) 97% TOP, (b) 97% TDP, (c) neat TOPSe, and (d) neat TDPSn.
Figure 3.13. $^{31}$P{¹H} NMR spectra of the reaction solution with Pb oleate and various Se precursors at different temperatures: (a) 1 M TOPSe at 50–60 °C, (b) 1 M TOPSe at 150–160 °C, (c) 1 M TDPSe at 50–60 °C, and (d) 1 M TDPSe at 150–160 °C.
Figure 3.14. The decomposition of Se precursors monitored by $^{31}$P{¹H} NMR spectra at 150–160 °C for 5 min. Each spectrum shows initial (top) and final (bottom) peaks of corresponding Se precursors. (a) Pb oleate and neat TOPSe, (b) Pb oleate and 1 M TOPSe in TOP, (c) Pb oleate and neat TDPSe, and (d) Pb oleate and 1 M TDPSe in TDP.
Figure 3.15. The decomposition of Se precursors monitored by $^{31}$P{$^1$H} NMR spectra at 150~160 °C for 5 min in the presence of diethylamine (Pb:diethylamine=1:0.2 by mole ratio). Each spectrum shows initial (top) and final (bottom) peaks of corresponding Se precursors. (a) Pb oleate and neat TOPSe/diethylamine, (b) Pb oleate and neat TDPSe/diethylamine.
Figure 3.16. The decomposition of TDPSe monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at 50–60 °C for 40 min (a) in the presence of diethylamine (TDPSe:diethylamine=1:1 by mole ratio), (b) without diethylamine, and (c) initial peaks of corresponding TDPSe precursors.
Figure 3.17. The decomposition of Se precursors monitored by $^{31}\text{P}$$\text{^1H}$ NMR spectra at 50~60 °C for 40 min (a) in the presence of diethylamine (Pb:TDPSe:diethylamine=1:1:1 by mole ratio) and (b) without diethylamine. Each spectrum shows initial (left) and final (right) peaks of corresponding Se precursors.
Chapter 4. Optics: Anisotropy of Lead

Chalcogenide Nanocrystals*

"There is strong shadow where there is much light." - Johann Wolfgang von Goethe

4.1. Introduction

Solution-based chemical synthesis of semiconductor nanostructures has allowed tremendous flexibility in crystal morphology. After much work on zero-dimensional (0D) nanocrystals (NCs), attention is shifting to one-dimensional (1D) nanorods (NRs) and nanowires (NWs)\cite{63,64,12} and the variation of material properties in the transition from 0D to 1D. The electronic structure of these crystals is the foundation for understanding their properties. Previously, the electronic structure of 1D NCs has been modeled using a variety of methods, including effective-mass theories based on k·p Hamiltonians,\cite{65,67,42} pseudo potential techniques,\cite{68,70} tight binding models,\cite{71,72,31} and density functional theory.\cite{42,73,76} The relaxation of confinement in going from 0D to 1D goes hand-in-hand with an increase in the importance of Coulomb effects mediated through

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the NC’s dielectric environment.\textsuperscript{77} Lead chalcogenide (PbS, PbSe, PbTe) NCs offer unique advantages to study the interplay of these two effects. Their large exciton Bohr radii places them at the limit of strong confinement, while their large dielectric constants coupled with their mirror-like electron and hole spectra substantially reduce the Coulomb interaction in spherical NCs.\textsuperscript{78,30} However, in a 1D structure the Coulomb interaction can act primarily through the host medium, so it will not be screened as effectively as in 0D.\textsuperscript{66} Thus, the lead chalcogenides provide a unique system to study the transition from strong confinement to strong Coulomb binding as the length of the NC changes.

We calculate the spectra of 1D excitons including self-interaction corrections.\textsuperscript{79} Surprisingly, the calculations show that although the binding energy of excitons in the smallest NWs reaches 350 meV, the optical transition energies are not affected by the small dielectric constant of the surrounding medium and are almost identical to the transitions between non-interacting electron and hole subbands. The cancelation of the exciton binding energy and the self-interaction corrections to the electron and hole levels is a consequence of the almost mirror symmetry of the conduction and valence bands of PbSe. The theoretical results agree well with the measured absorption spectra of (100) PbSe NRs.

In Chapter 4.2, we examine optical electronic structures of anisotropic PbSe NRs by absorption spectra and compared to the theoretical calculation. Measurements of the size-dependent absorption spectra of colloidal PbSe NRs are presented, as well as the data from steady-state spectroscopy and time-resolved spectroscopy.
Using room-temperature energy-band parameters extracted from the optical spectra of spherical PbSe NCs, the theory provides good quantitative agreement with the measured spectra.

Furthermore, as the NC shape changes from 0D to 1D, the local-field factor (LFF) is increased, which relates an externally applied electric field to the internal field within the high dielectric constant NCs when immersed in a low constant medium. The local field effect plays a major role in many important physical phenomena such as surface-enhanced Raman scattering and far-infrared (FIR) spectra, and can drastically reduce optical nonlinearities. However, there is no systematic study on local-field effect of NRs, compared to many studies with metallic nanorods.

In Chapter 4.3, we study the local field effect in semiconductor NRs by measuring far-infrared (FIR) absorption spectra. The local field factors of PbSe NCs and nanorods are calculated by the dielectric function without the contribution of free carrier absorption. These are used to predict far-infrared absorption spectra and describe well the features measured in experiment. Increasing the aspect ratio leads to a splitting of the single Frohlich phonon mode in NCs into two modes parallel and perpendicular to the nanorod axis. The peak shift with increasing aspect ratio is very well matched with the calculated values. As a result of these calculations, the local field factor of long nanorods should cause a two order of magnitude enhancement of the nonlinearity compared to spherical PbSe NCs.
4.2. Optical Transition of PbSe NCs and NRs

First, we will compare the qualitative deference between the absorption spectra of NRs and spherical NCs. Figure 4.1 shows the absorption spectrum of 3.3 nm diameter x 12 nm length PbSe NRs along with that of 4.4 nm diameter spherical NCs, chosen to have a nearly identical first absorption peak. The spectrum of the NRs has fewer obvious features than the NC spectrum. The first peak in the NR spectrum has a broad high energy side, even though its narrower low energy side is nearly identical to that of the NCs. (inset of Figure 4.1). Both of these observations indicate the presence of more densely-spaced transitions in the NR spectrum, which have the effect of smoothing out the peaks. Interestingly, the second NC peak appears where there is a dip in the NR spectrum.

**Figure 4.1.** (a) Absorption spectra of PbSe NRs (blackline, vertically offset for clarity) and spherical PbSe NCs (redline) are compared. The inset shows detail of the first peak. (b) Emission spectra and fluorescence decays measured at the emission peak (inset) of the same two samples.
The broadening of the NR absorption peak seen in Figure 4.1 is connected with the dispersion of NR diameter and length. Our best PbSe NR samples have around 5% size distribution in radius, but a much larger 20% in length. This large length polydispersity will blur out many of the NR transitions in an ensemble, except for those that are roughly independent of length - specially, the lowest energy exciton for each pair of NW subbands. Fortunately, this is also the transition predicted to have the largest oscillator strength. The energies of the optical transitions of the ground exciton states practically coincide with the energies between non-interacting electron and hole subbands, even though their respective wave functions differ greatly. This greatly simplifies the interpretation of the absorption spectra of NRs. We performed second-derivative analysis on the absorption spectra to determine the transition energies accurately. To avoid the problems inherent in this method, only the peaks in the second-derivative spectra that correspond to obviously-visible peaks in the measured spectra were used.

Figure 4.2a has an example measured spectrum of a 3.9 nm diameter x 17 nm length PbSe NR that shows all five peaks, and the locations of all measurable peaks from all samples are shown in Figure 4.2b. The measured peaks are plotted vs. $D^{-3/2}$ following the similar graph in Koole’s paper. This power of the diameter is chosen to make the trend linear over the measured range, allowing rough extrapolation to bulk as $D^{-3/2} \to 0$. In this manner, the peaks originating from the L-point and Σ-point are easily distinguished.
Figure 4.2. (a) Example absorption spectra of a 3.9 x 17 nm PbSe NR. Inset shows the same data, but on a scale where the 5th peak is visible. (b) Peaks in 2nd derivative spectrum as a function of NR diameter (symbols), calculated allowed transitions (grey lines), simple parabolic effective mass calculation around the Σ-point (dashed grey line), and linear fits (colored dashed lines.)

The theoretical size dependence of the optical transitions in PbSe NRs is shown in Figure 4.2b by solid lines. The lowest two transitions agree well with the theory. The third predicted transition is not observed, possibly owing to its proximity to other strong transitions in our NR samples. The third and fourth peaks are strong transitions that do not appear to be associated with the L-point. Their energies extrapolate back to the Σ-point energy. The third peak is fit well by the same parabolic band model used to model spherical PbSe NCs, and thus we assign this transition to the lowest-energy excitonic state at the Σ point. Without more-detailed knowledge of the band structure there, we cannot predict the excited states with any accuracy. Thus, the identity of the fourth transition cannot be determined, but as the energies approach the same 1.65 eV bulk value, it is
reasonable to tentatively attribute it to a higher-energy exciton from the Σ point. Finally, the fifth peak was perhaps the strongest in the absorption spectra, but showed no size dependence. We tentatively ascribe this to a metal-complex transition on the surface of the NC based on its proximity to absorption peaks of Pb (II) complexes.\textsuperscript{86} The identities of these transitions are summarized in Table 4.1.

Table 4-1. Transitions observed in the absorption spectra of PbSe NRs

<table>
<thead>
<tr>
<th>Label</th>
<th>Assigned Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_1$</td>
<td>$1\Sigma^{h}<em>{1/2} \rightarrow 1\Sigma^{e}</em>{1/2}$</td>
</tr>
<tr>
<td>$P_2$</td>
<td>$1\Pi^{h}<em>{3/2} \rightarrow 1\Pi^{e}</em>{3/2}$ and $1\Pi^{h}<em>{1/2} \rightarrow 1\Pi^{e}</em>{1/2}$</td>
</tr>
<tr>
<td>$P_3$</td>
<td>Σ-point ground state</td>
</tr>
<tr>
<td>$P_4$</td>
<td>Σ-point excited state (?)</td>
</tr>
<tr>
<td>$P_5$</td>
<td>Surface metal complex mode</td>
</tr>
</tbody>
</table>

The fluorescence spectra and decays (Figure 5.1b) are nearly identical for NCs and NRs, with a slightly larger Stokes shift in the NRs along with a slightly broader peak. The ensemble quantum yield of the nanorods is around 15%, around half that of the NCs. This might indicate that the radiative lifetime of the rods is longer than that of the NCs, but it is also possible that the QY reflects an ensemble with 15% emitting and 85% non-emitting rods. Two effects would be expected to modify the radiative lifetime in nanorods. First, because the radiative lifetime is inversely proportional to the oscillator strength, the increased electron–hole correlation in NRs should decrease the lifetime compared to NCs. Second,
the effect of screening is reduced in NRs, which is believed to be the cause of the long lifetime in PbSe NCs.\textsuperscript{33} Approximating the NR as a dielectric prolate spheroid, the screening will substantially decrease along the rod axis, while slightly increasing along the other two axes, with an overall effect of a reduction in screening of the lifetime. Compared to a spherical NC of the same diameter, the larger oscillator strength and the reduced screening should each produce about a factor of 3 reduction in lifetime in NRs with typical aspect ratios. Together this amounts to almost an order of magnitude reduction, and should be measurable even considering other sample–related uncertainties. However, the measured lifetime (Figure 4.1b) is nearly identical in NCs and NRs. This discrepancy is not understood. It might be explained by a dark ground exciton state that controls the photoluminescence decay in PbSe NRs and NCs, with the same activation mechanism in both structures. To be thorough, the nonradiative rate must be determined, and completing this along with exploring this phenomenon is a topic of future work.

Figure 4.3. The size dependence of the transition energies in spherical PbSe NCs.
Experimental data are shown by symbols. The solid lines show the size dependence of optically allowed transitions calculated in a fully anisotropic effective mass model. The optically allowed transitions occur between the states of the same symmetry but opposite parity, and we label them by a symmetry type, which is common for both states. Open points indicate transitions originating from the L-point in the Brillouin zone, while half-open points are suggested to be from the Σ point as in Koole’s paper. The dashed line shows the size dependence of lowest confined level connected with the Σ point of the Brillouin zone.
4.3. Phonon Mode of PbSe Nanorods

In the Rayleigh scattering limit, the local field factor directly determines the FIR-active absorption spectrum of NCs or NRs dispersed in dielectric hosts through the following expression:

\[ \alpha_{abs} = \frac{n}{n_{host}} |f_{LF}|^2 \frac{4\pi k}{\lambda} \]  

(4.1)

where \( \lambda \) is the wavelength of the incident light, \( n_{host} \) is the refractive index of the host medium, \( n + ik \) is the complex refractive index of the NR, and \( f_{LF} \) is the local field factor of the NR. \( f_{LF} \) is a function of the aspect ratio (L/D) and dielectric ratio \( \varepsilon_{NR}/\varepsilon_{host} \) of the NR. The local field factor will have strong peaks in this spectral region due to the presence of the Frohlich optical phonon mode. And due to the dependence of the local field factor on the aspect ratio, these peaks will have shape dependent frequencies and strengths, making FIR absorption a particularly sensitive way to explore \( f_{LF} \).

To calculate \( f_{LF} \) for NRs, we need to know the complex frequency-dependent dielectric function of PbSe NRs, which we initially assume is the same as for bulk PbSe. This has been measured experimentally and fit to a classical oscillator model:

\[ \varepsilon_{PbSe}(\omega) = \varepsilon_\infty + \frac{(\varepsilon_{st} - \varepsilon_\infty)\omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\Gamma \omega} + \frac{\omega_p^2}{-\omega^2 - i\gamma \omega} \]  

(4.2)

where \( \varepsilon_\infty \) and \( \varepsilon_{st} \) are the static and high frequency dielectric constant, \( \omega_{TO} \) and \( \omega_p \) are the transverse optical (TO) phonon and plasma frequencies of bulk PbSe,
respectively. Γ and γ are damping factors of ionic and free carriers of bulk PbSe, respectively. The second term of Eq. (4.2) represents the contribution due to optical phonons and the third term is due to free carrier absorption. By choosing $\varepsilon_\infty = 23.4$, $\varepsilon_{st} = 250$, $\omega_{TO} = 45 \text{ cm}^{-1}$, $\omega_p = 880 \text{ cm}^{-1}$, $\Gamma = 20 \text{ cm}^{-1}$, and $\gamma = 40 \text{ cm}^{-1}$, the fitted result (solid and dotted blue lines) agrees very well with the experimental real and imaginary refractive indexes of bulk PbSe as seen in Fig. 4.5.

![Figure 4.4](image_url)

**Figure 4.4.** Log-log plot of n (real part of refractive index, open square) and k (imaginary part of refractive index, open circle) versus wavelength for bulk PbSe. The blue lines are the fitted results obtained by using Eq. (4.2). The green lines are the fitted results without the free carrier contribution, i.e. the third term of Eq. (4.2).
From the complex dielectric function of PbSe, the two local field factors (one perpendicular and one parallel to the rod axis) of PbSe NRs are calculated for different aspect ratios. The shape of the NR is approximated as a prolate spheroid to allow analytic solution. Figures 4.5a and 4.5b show the local field factors parallel and perpendicular to the long axis of rod, respectively. The calculated local field factor of a spherical PbSe NC (black line) has a single peak centered at 216 cm\(^{-1}\). As the aspect ratio increases, the local field factors split into two parts, parallel and perpendicular to the rod axis, moving the parallel peak to lower frequency and the perpendicular peak to slightly larger frequency. The peak shifts increasing the aspect ratio is displayed in Figure. 4.6 as blue lines.

![Graph showing local field factors of PbSe NC and NR for different aspect ratios](image)

**Figure 4.5.** The calculated local field factors of PbSe NC and NR for 1 (black), 2 (red), 3 (blue), and infinity (magenta) of aspect ratios. (a) and (b) correspond to the local field factors parallel and perpendicular to the long rod axis, respectively, and are calculated by using the dielectric function expressed with Eq. 4.2.
Figure 4.6. Frohlich phonon frequencies of PbSe NR versus aspect ratio. The blue and green lines represent the calculated peak shifts PbSe NR by using the dielectric function of Eq. (4.1) with and without free carrier absorptions, respectively. The open red circles represent the absorption peak positions inferred from the measured FIR spectra of PbSe NCs and NRs.

To test these expectations, the Fourier transform FIR spectra of PbSe NCs and NRs dispersed in hexane are measured at room temperature. Hexane was found to be highly transparent in the FIR between $15 - 350$ cm$^{-1}$. NC and NR solutions are loaded into a home-made 2.54 mm thick cell with 6 µm thick Mylar film windows. Figure 4.7a shows the typical absorption spectra of PbSe NCs and NRs dispersed in tetrachloroethylene (TCE). The diameters and lengths of NCs and NRs used in this work are determined from their TEM images and listed in Table 4.1. Figure 4.8a and 4.8b show the TEM images of the PbSe NCs and sample PbSe NR-4, and are representative of all samples. Similarly, the measured FIR spectra of the same samples are displayed in Figure. 4.6b.
Figure 4.7. (a) Typical absorption spectra of PbSe NCs (solid red line) and PbSe NRs (solid blue and green lines) in TCE. The diameters and lengths are determined from their TEM images. (b) the typical FIR spectra of PbSe NC and NR-3, 4 in hexane.

There is one peak in the FIR spectrum of the PbSe NCs centered at 134 cm$^{-1}$, but as the aspect ratio increases, the peak is split into two asymmetric peaks. As the aspect ratio is changed from 4.3 to 9, the high-frequency peak shifts from 140 cm$^{-1}$ to 144 cm$^{-1}$. In comparison, the low frequency peak moves from 105 cm$^{-1}$ to 81 cm$^{-1}$. The obtained peak positions (open red circles) are represented in Figure 5.6. These are sharply different from the expected calculated mode frequencies. As a result, we speculate that the band gap of NCs is too large for free carrier absorption at room temperature and that the actual dielectric function predicted by the Eq. (4.2) is not accurate. For PbSe NCs and NRs at room temperature, $E_g > 0.73$ eV, dramatically reducing the concentration of free carriers, and decreasing the plasma frequency. Thus we expect that the latter term Eq. (4.2) is effectively removed.
The predictions from this revised model are displayed as green lines in Figure 4.6, and show excellent agreement with the measured FIR peak locations. In addition, we calculate the FIR absorption spectra of PbSe NRs by inserting this revised dielectric function into Eq. (4.1). The calculated spectra are additionally broadened by assuming that the length of the NRs has a Gaussian size distribution of $\Delta L/L = 20\%$. The calculated spectra are displayed with the measured spectra in Figure 4.9. While the peak locations are very well reproduced, the ratio of the heights of the peaks is overestimated in all cases. Within our model, it is difficult to explain this. It would seem to say that the predicted ratio of local field factors is overestimated by a factor of $\sim 2^{1/2}$, but if this were correct, then the peak locations would also shift. So, it is likely that some other effect is causing this, perhaps that the shape of NR is more accurately modeled as a cylinder, not a spheroid.

**Figure 4.8.** Typical TEM images of PbSe (a) NC and (b) NR-4.
Table 4-2. Diameters, length, and aspect ratio of PbSe NCs and NRs.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Diameter (D) [nm]</th>
<th>Length (L) [nm]</th>
<th>Aspect ratio L/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbSe NC</td>
<td>5.0</td>
<td>N/A</td>
<td>1</td>
</tr>
<tr>
<td>PbSe NR-1</td>
<td>4.4</td>
<td>19</td>
<td>4.3</td>
</tr>
<tr>
<td>PbSe NR-2</td>
<td>3.9</td>
<td>17</td>
<td>4.4</td>
</tr>
<tr>
<td>PbSe NR-3</td>
<td>4.0</td>
<td>20</td>
<td>5.0</td>
</tr>
<tr>
<td>PbSe NR-4</td>
<td>4.0</td>
<td>37</td>
<td>9.0</td>
</tr>
</tbody>
</table>

This good agreement between the calculated and experimental FIR spectra gives us confidence that our model of the local field factor is correct in NRs. Thus, by using the value of the dielectric constant in the near-IR, we can estimate the shape-dependent enhancement of the $\chi^3$ nonlinearity. If all NRs are well aligned, we can only consider the local field factors along the long rod axis. In the near-IR, the local field factor of PbSe NC is ~0.2 but that of a PbSe NR with an aspect ratio of 9 is ~0.8. This leads over a 100x enhancement of the $\chi^3$ nonlinearity. Even in case of randomly oriented NRs, a 10x enhancement is still expected. This significantly increased nonlinearity will provide a huge opportunity to apply PbSe NRs to optical switching devices.
Figure 4.9. The calculated (red line) and measured (blue line) FIR absorption spectra of PbSe NRs studied in this work. For the calculation, Eq. (5.1) is used with the simplified dielectric function, i.e. the dielectric function neglecting the contribution due to the free carriers.
4.4. Conclusions

In Chapter 4.2, the electronic structures of lead chalcogenide NRs were measured and discussed for the origin of their anisotropy at the nanoscale. The absorption spectra of PbSe NRs have remarkable feature: the size dependence of the third and fourth absorption peaks is strong evidence that they originate from the Σ point were observed previously in the absorption spectra and in the hot carrier dynamics of spherical PbSe NCs. These observations provide clear experimental evidence that even in the smallest nanostructures, wave functions from distinct critical points (L and Σ, in the particular case) are not mixed if both their corresponding conduction-band minima and valence-band maxima are well-separated energetically. The predicted strong increase in electron-hole Coulomb interaction in PbSe NWs should have major implications for other properties. This enhancement should increase the rate of the nonradiative Auger recombination as well as the rate of the inverse process, impact ionization. A high rate of impact ionization or efficient multiple exciton generation, combined with good conductivity that might be expected in PbSe NWs, suggests that these structures may be promising for photovoltaic applications.

In Chapter 4.3, the local field factors of PbSe NC and NR are calculated by using a modified dielectric function without the contribution of free carrier absorption. These are used to predict FIR absorption spectra and describe well the features measured in experiment. Increasing the aspect ratio leads to a splitting of the single Frohlich phonon mode in NCs into two modes parallel and
perpendicular to the NR axis. The peak shift with increasing aspect ratio is very well matched with the calculated values. As a result of these calculations, the local field factor of long NRs should cause a two order of magnitude enhancement of the $\chi^3$ nonlinearity compared to spherical PbSe NCs.
Chapter 5 . Thiocyanate Ligand Chemistry of Nanocrystals

"What does not destroy me, makes me stronger." - Friedrich Nietzsche

5.1. Introduction

Nanocrystals (NCs), tiny collections of atoms with dimensions on the scale of 1 to 100 nm, are of tremendous technological interest both because their small size is compatible with efforts to miniaturize devices and also because they often exhibit size-tunable properties that differ significantly from those observed in bulk materials. Collections of interacting NCs comprised of metallic, semiconducting, ferromagnetic or ferroelectric materials, can be used for a variety of electronic, magnetic, optical and thermoelectric applications.\textsuperscript{36,38,39,89}

However a common problem in the fabrication of devices made from these materials is the necessity of stabilizing the particle with surface ligands to prevent aggregation and promote dispersibility in solvent, and which conventionally consist of organic surfactants, while simultaneously avoiding the undesirable effect of maintaining large inter-particle spacing and poor electronic conductivity between particles when condensed into NC-solids. One solution is direct deposition of NCs synthesized with capping ligands, followed by annealing or
exchange in the solid film with small ligands (e.g. pyridine, ethanediithiol or hydrazine). The main disadvantage is deposited films exhibit discontinuity (cracking) due to shrinkage and void space is left by removed ligands. Another approach is direct deposition of NCs synthesized with thermally labile capping ligands, followed by thermal degradation of the ligands. Still there is an issue that high process temperature is incompatible with many organic components, making it inappropriate for organic film devices. Also, degradation occurs at similar temperatures as the sintering of NCs leading to a loss of size-tunable properties of NCs. Early studies of direct deposition of NCs synthesized without capping ligands would be one choice only for developing inorganic “ink” as a precursor for thin-film fabrication. Drawbacks to this approach are that aqueous synthesis offers worse size and shape control of NCs, still requires high temperature post-process, and furthermore is not applicable to many of the materials described above. Talapin et al. reported new type of ligand system, where molecular metal chalcogenides (MMCs) allow NCs soluble in polar solvents such as DMF and even water. More importantly, they demonstrated enhanced coupling between NCs so it is much possible to fabricate inorganic thin film via solution processes of NCs at low temperatures. One drawback is MMCs cannot produce pure inorganic materials but inorganic composites of NCs and MMCs themselves.

Herein, we demonstrate the use of chalcogenocyanates (\(\text{A-C≡N}, \text{where A is S or Se}\)) as a new type of surface-capping group for NCs (Figure. 5.1). Chalcogenocyanate-capped NCs can be dispersed in a variety of solvents,
allowing for solution processibility and, when packed in a solid, demonstrate close interparticle spacing, and good electronic conductivity between particles. Furthermore the addition of the chalcogenocyanate to the NC surface is achieved under mild processing conditions, with relatively environmentally benign starting materials, at room temperature, without the requirement of an inert atmosphere and is thus compatible with a wide range of device fabrication modalities.

**Figure 5.1.** Cartoon of NC capping groups (a) before and (b) after exchange with SCN group.
5.2. Experimental Section

5.2.1. Synthesis of colloidal NCs

Monodisperse Au, Ag, CdS, CdSe, ZnSe, PbS, and PbSe NCs were synthesized according to literature methods or modified ones from them.\(^{96,59,97,8,98,15}\) As-synthesized NCs were washed twice by centrifugation with ethanol and then dissolved in hexane to form stable dispersions with concentrations ranging from 1 to 10 mg/mL.

5.2.2. Ligand exchange process of NCs

To prepare chalcogenocyanate-capped NC dispersions, 1% by weight of NCs in 5 mL of hexane solution is mixed with 1 mL of 1% by weight ammonium thiocyanate in acetone, and centrifuged to isolate thiocyanate-capped NCs. 5mL of DMSO is added to dissolve the NCs, forming a stable solution for further processes.

5.2.3. Characterization

Transmission electron microscopy (TEM) images were recorded using a JEOL-1400 TEM equipped with a SC1000 ORIUS CCD camera operating at 120 kV. The TEM sample was prepared by drop-casting a NC dispersion on a carbon-
coated copper grid followed by drying in air. FTIR spectra were acquired in the transmission mode using a Nicolet 8700 FTIR spectrometer and/or a Nicolet 6700 FTIR spectrometer with a Grazing-Angle Total-Reflectiom mode. The samples were prepared by drop-casting concentrated NC dispersions on double-polished Si substrates followed by drying in air to form a thin NC film. Dynamic light scattering (DLS) and \( \zeta \)-potential data were collected on a Beckman Coulter Delsa Nano-C system. TGA was conducted using a Thermaladvantage Q600 thermal analyzer with a heating rate of 10 °C/min under N\(_2\).

5.2.4. Electric measurement

For metallic NC films, a small aliquot of NCs capped with SCN ligand in DMSO solution is deposited on a Si wafer patterned with SU-8 photoresist. Solvent is removed under reduced pressure at 60° C, leaving behind a conductive NC film in the desired pattern. For semiconductor NC films, a highly n-doped Si wafer with a 250 nm thermal oxide is treated with 3-(mercaptopropyl) trimethoxysilane to form a thiol terminated surface. A monolayer is formed at the air-solvent interface by dropping a solution of NCs with oleic acid capping groups in hexane on an aliquot of acetonitrile using a method developed by Dong al.\(^9\) The monolayer is then transferred on to the substrate and the capping groups exchanged for thiocyanate by immersing the substrate in 1 % by weight ammonium thiocyanate in acetone for 1 min. The device is washed in pure acetone and the process repeated until three layers have been formed. 20 nm thick
Au patterns are vacuum deposited through a shadow mask on the surface of the particle-film to form the source and drain electrodes.
5.3. FT-IR spectroscopy of ligand exchange: qualitative and quantitative analysis of ligand

Most colloidal NCs have organic ligands, which generate organic/inorganic interface and strongly affect their physical and chemical properties. While the importance of ligands have been studied a lot to understand the growth of NCs or the solubility of NCs, there is a lack of understanding for organic/inorganic interface on the surface of NCs. Previously, Talapin and Nozik groups demonstrated FT-IR monitoring of quantifying ligands as an indirect way.\textsuperscript{28,27} Here we demonstrate FT-IR study of quantifying ligand exchange as a direct evidence. Figure 5.2a shows FT-IR data of SCN ligands of various NCs, which are consistent with literature values for metal-SCN stretching in Table 5.1.\textsuperscript{100,101}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Compounds & Zn(NCS)\textsubscript{4} & Cd(NCS)\textsubscript{4} & Cd(NCS)\textsubscript{2} & Pb(NCS)\textsubscript{2} \\
\hline
Wavenumber [cm\textsuperscript{-1}] & 2074 & 2100/2090 & 2100/2080 & 2050/2007 (+/- 50) \\
\hline
\end{tabular}
\caption{Literature values for IR stretching frequencies of CN groups}
\end{table}

Especially we compared SCN stretching frequencies of molecular metal-SCN compounds to those of NCs, implying there are two possible stretching modes of SCN with symmetric and antisymmetric manners. It seems that the splitting of two stretching modes is smeared out on the surface of NCs, probably due to fast tumbling/reorientation of SCN groups. Figure 5.3 show kinetics of ligand
exchange process for PbSe NCs, comparing the solvent effect of AcCN and acetone. Although acetone shows much faster exchange of SCN group than AcCN, both cases agree that diagnostic peak of SCN peak is increasing as C-H vibrational peak from original organic ligands is reducing. This confirms that SCN ligand actually replaces the original organic ligands quantitatively.

**Figure 5.2.** FT-IR spectra of (a) NC films and (b) model compounds after SCN ligand exchange. Peak observed in 2000-2200 cm$^{-1}$ region is diagnostic for the presence of the nitrile group. Denote that the frequency depends on binding metal and binding mode (through S or N atom).
Figure 5.3. Kinetics of ligand exchange for PbSe NCs. (a) 0.25% NH$_4$SCN in AcCN (b) 1% NH$_4$SCN in acetone after 30 sec. Diminishment of the peaks in the 2900 cm$^{-1}$ region indicative of removal of organic surfactants used during synthesis.

Another interesting observation is that once SCN-capped NCs are annealed at moderately high temperature, SCN peak is gone as shown in Figure 5.4. This annealing effect will be discussed later for more detail.
Figure 5.4. FT-IR of PbS NCs during thiocyanate ligand exchange.
5.4. Solution phase transfer of NCs

We have found that NCs of Au, Ag, CdSe, CdS, and heterostructures of CdSe/CdS, when treated with NH₄SCN, form homogenous solutions in the common and environmentally benign solvent DMSO, in addition to a small number of other polar solvents (Figure 5.5). Au or Ag NCs, when treated with NaSeCN, also form solutions in DMSO. Additional materials including ZnO and PbS form dispersible colloids in DMSO after treatment with NH₄SCN. Au NCs with -SCN or –SeCN ligands are stable for many days in DMSO.

![Image of Au, Ag, and CdSe NCs with DMSO and Hexane]

**Figure 5.5.** Photo images of Au, Ag, and CdSe NCs using SeCN for Au and Ag, SCN for CdSe. 2 vials of each group show before (left) and after (right) ligand exchange.

Interestingly, SCN-capped CdSe NCs showed solvent-dependent PL intensity as shown in Figure 5.6. Further quantitative PL measurement will be done later to
understand quenching of emission from SCN-capped CdSe NCs in various solvents. Absorption spectra of CdSe NCs show 11 meV red shift from the original peak when they form solid film on the substrate (Figure 5.7a); this is consistent to previous literatures that shorter ligand between NCs increase coupling between NCs causing red shift of excitonic peak.\textsuperscript{37,28,27}

![Image of CdSe NCs with UV illumination after ligand exchange in various solvents.](image)

**Figure 5.6.** Photo image of CdSe NCs with UV illumination after ligand exchange in various solvents.

Another part is Au NCs show purple color after SCN ligand exchange, which is also confirmed by UV-Vis absorption spectra of Au NCs before and after ligand exchange. (Figure 5.7) Oleylamine-capped Au NCs show characteristic peak of plasmon absorption at 520 nm, while SCN-capped Au NCs show broader peak maybe due to increased coupling between neighboring Au NCs. The SCN-capped Au NCs in DMSO are stable after 3 days, showing the same absorption spectrum. Thus, the broad peak of SCN-capped Au NCs doesn’t seem to be from aggregates of them, but rather from secondary bonding mode of SCN ligand to neighboring
Au NC through N atom; which will be investigated for more detail soon.

**Figure 5.7.** UV-Vis absorbance spectra of solutions of (a) CdSe NCs and (b) Au NCs before and after ligand exchange with thiocyanate. In black is the spectrum of hexadecylamine-capped Au NCs in hexane. In red and blue are the spectra of the thiocyanate-capped Au NCs in DMSO on the same day as the exchange (red) and 3-days after the exchange (blue)
5.5. Enhanced coupling of NCs: metals

We have demonstrated that thiocyanate-treated Au NCs, dispersed in DMSO, form highly conductive films on glass substrates upon removal of the solvent (Table 5.2). This conductivity, comparable to thin films of vacuum-deposited Au, is higher or achieved by lower process temperature than examples for Au NC films in the literature using polymer or short ligands.\(^\text{102,103}\)

**Table 5-2.** Sheet resistance of Au NCs at various annealing temperatures.

<table>
<thead>
<tr>
<th>Exposure Temp (°C)</th>
<th>(\rho) (avg)Ωxcm</th>
<th>(\rho) (st.dev.)Ωxcm</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>13.8</td>
<td>0.01</td>
</tr>
<tr>
<td>100</td>
<td>2.7</td>
<td>0.03</td>
</tr>
<tr>
<td>150</td>
<td>0.1</td>
<td>&lt; 0.01</td>
</tr>
</tbody>
</table>

To understand the effect of annealing for the conductivity of Au NCs, we studied XRD and TEM at various annealing temperatures. Figure 5.8 and 5.9 show that Au NCs capped with SCN sinter to increase their size above 100 °C as an annealing temperature. Interestingly, Au NCs without ligand exchange doesn’t show significant sintering in Figure 5.8d; this implies that SCN ligand is critical for low temperature annealing process.
Figure 5.8. XRD patterns of Au NCs annealed (a) 60 °C, (b) 100 °C, (c) 150 °C after SCN ligand exchange, and (d) 150 °C without ligand exchange. All processes were done for 20 min under vacuum or inert atmosphere.
Figure 5.9. TEM images of Au NCs (a) before SCN ligand exchange, (b) after SCN ligand exchange, and (c) after SCN ligand exchange and 100 °C annealing for 20 min.
5.6. Enhanced coupling of NCs: semiconductors

TEM images of PbS NCs (Figure 5.10) and PbSe NCs (Figure 5.11) compare the interparticle distance between NCs before and after ligand exchange, as well as reflection small angle X-ray scattering (RSAXS) data of PbS NCs and PbSe NCs (Figure 5.12) do.

**Figure 5.10.** TEM images of PbS NCs (a) before, (b) after SCN ligand exchange, and (c) after SCN ligand exchange following annealing at 150 °C for 20 min.
Figure 5.11. TEM images of PbSe NCs (a) before and (b) after SCN ligand exchange.

Interestingly, annealing process dramatically causes sintering between NCs to have much improved connectivity in NCs film, although in which individual NC loses its quantum confinement and ends up bulk inorganic film (Figure 5.14). This sintering effect can be supported by XRD patterns of PbS NCs at various annealing temperatures. As FT-IR data pointed out in Figure 5.4, SCN group would accelerate the sintering of PbS NCs but evaporate to leave pure inorganic film; this can open an important opportunity for low temperature solution process of NCs-based inorganic thin film materials.
Figure 5.12. Reflection small angle X-ray scattering (RSAXS) of (a) PbSe and (b) PbS NCs before and after ligand exchange.
Figure 5.13. TGA of (a) PbS and (b) PbSe NCs before and after ligand exchange.
We have demonstrated that the optical properties of CdSe NC films formed from thiocyanate capped particles exhibit evidence of enhanced interparticle electronic coupling, as expected for small interparticle distances (Figure 4.7a). Similarly, PbSe NCs capped SCN groups also show red shift of excitonic peak in absorption spectra. By monitoring the excitonic peak of NCs using FT-IR spectrometer, kinetics of ligand exchange and enhanced coupling between NCs is shown in Figure 4.15. The ligand exchange process is quite fast (< minutes) to get a close packing of NCs film, however there is NCs etching when the exchange process is more than hours, causing blue shift of the excitonic peak of NCs film.
Figure 5.15. Excitonic coupling in PbSe NCs during thiocyanate ligand exchange. ($\Delta E = -50$ meV)

A bottom-gate, top-contact field effect transistor employing thiocyanate-capped PbS has been realized by transferring successive layers of PbS capped with oleic acid, and exchanging the capping groups with thiocyanate in the solid film. The active layer demonstrates enhanced hole and electron mobility after annealing at 150 °C for 30 min relative to devices before annealing process (Figure 5.16). This is consistent with XRD and TEM data in which annealing process accelerates sintering of NCs to cause bigger grain boundary of NCs film. Especially low temperature of annealing process enables to fabricate devices made of polymer substrates, which is promising for low-temperature solution process based on inorganic NCs materials.
Figure 5.16. Output and transfer characteristics for PbS thin film FET. (a, b) pristine, p-type, mobility $7 \times 10^{-6}$ cm$^2$/Vs. (c-f) annealed at 150 °C for 30 min, ambipolar, mobility $2 \times 10^{-3}$ cm$^2$/Vs (hole) and $4 \times 10^{-4}$ cm$^2$/Vs (electron). Kapton film with 500 nm parylene as dielectric layer. W/L=3 mm/0.2 mm. All mobility values are calculated in the saturation regime.
5.7. Engineering Morphology of PbS NCs for Flexible Devices

It is interesting to examine the effect of morphology of NCs in charge transport. Here we compare the charge transport of cubic PbS NCs with spherical PbS NCs studied in the previous chapter. The same devices of cubic PbS NCs were fabricated using a similar process described in Chapter 5.6. The active layer demonstrates enhanced hole and electron mobility after annealing at 120 °C for 30 min relative to devices before annealing process (Figure 5.17, a–c). Especially this low temperature of annealing process enables to fabricate devices made of polymer substrates, which is promising for low-temperature solution process based on inorganic NCs materials. The best device of cubic PbS NCs show 0.2 cm²/Vs for hole transport and 0.5 cm²/Vs for electron transport, which are the best values comparing to previous reports of PbS devices using hydrazine treatment which reported ~0.1 cm²/Vs for only electron transport, and even comparable result with PbSe devices using hydrazine treatment (1.0 cm²/Vs for electron transport and 0.2 cm²/Vs for hole transport). Liu et al. studied PbSe NCs FET to conclude that the increase in mobility with NC size is caused by fewer hopping of carriers at a given distance through films of larger NCs, and by shallower trap states of larger NCs. Thus it is reasonable to see enhanced charge transport in cubic PbS NCs film, because they are quite bigger than typical PbS NCs (3–8 nm), and they can pack and sinter to form a continuous solid film as shown in Figure 5.18. With an ambipolar behavior of PbS NCs devices annealed at 150 °C, we fabricated CMOS-like inverters by connected gates of FETs as the input of the
inverter (Figure 5.17, d and e). These are the first reported flexible PbS NC circuit with promising gains ~ 22 for positive $V_{dd}$ and ~17 for negative $V_{dd}$.

**Figure 5.17.** Output and transfer characteristics for 11 nm cubic PbS thin film FET. (a~c) Annealed at 120 °C for 20 min, mobility $1.1 \times 10^{-1} \text{ cm}^2/\text{Vs}$ (hole) and
1.2 × 10⁻¹ cm²/Vs (electron). Kapton film with 500 nm parylene as dielectric layer. W/L = 2.25 mm/0.15 mm. (d and e) Transfer and gain characteristics of CMOS-like inverters constructed from ambipolar cubic PbS NC FETs annealed at 150 °C.

Figure 5.18. (a) High magnification and (b) Low magnification of PbS cubes after SCN treatment. (Inset TEM image: as-synthesized PbS cubes, scale bar 20 nm) SEM scale bars: (a) 100 nm and (b) 1 µm.

To optimize the annealing condition of PbS FETs, we compared various annealing temperatures as shown in Figure 5.19. For the hole and electron mobilities, higher annealing temperature induced higher mobilities even though the improvement was not so significant. Rather, current modulation of hole and electron transport is more critical to the annealing condition. Higher annealing temperature tends to reduce the current modulation of devices; probably due to surface oxidation or degradation of PbS NCs at higher temperatures even we did all processes in the glove box (< 10 ppm for both O₂ and H₂O). It is questionable and interesting to see whether it really involves molecular oxygen or other
oxygen-containing chemicals to get surface oxidation of NCs, which will be further investigated near future.

Figure 5.19. Annealing effect of cubic PbS FETs treated with SCN ligands. (a, b) Hole and electron mobilities of PbS FETs at various annealing temperatures. (c, d) Current modulation of hole and electron transport for PbS FETs at various annealing temperatures. The error bars show the standard deviation of 6 devices from 3 different batches of NCs.
5.8. Conclusions

In this chapter, we demonstrated a new type of surface and ligand chemistry for colloidal NCs, which allows benign and mild process for modifying the surface properties of NCs. Thiocyanate and related structures are unique due to their short interparticle distance between NCs, capability of phase transfer from nonpolar to polar medium of NCs, and possibility of low-temperature process for various devices such as micropatterning of metal electrodes, thin-film transistors, light emitting diodes, solar cells, and so on. Especially the strong vibrational mode of SCN and related structures is promising to develop a new type of surface analysis as IR probe molecules. Correlated with other analyses such as absorption/emission spectroscopy and X-ray techniques, this novel surface chemistry will open a new opportunity to understand interface between NCs and surrounding medium either in solution or in solid matrix/composite.
Chapter 6 . Interface Chemistry of Electronic Transport in Lead Chalcogenide Nanowires* 

"The scientific man does not aim at an immediate result... His duty is to lay the foundation for those who are to come, and point the way. He lives and labors and hopes." - Nikola Tesła

6.1. Introduction

Semiconductor nanowires (NWs) have motivated widespread interest to explore the fundamental physical properties of one-dimensional materials and their potential in a range of device technologies. In particular, PbSe is a high mobility, infrared absorbing semiconductor that exhibits strong quantum confinement in nanostructured materials due to its large Bohr exciton radius (a_{ex} \approx 46 \text{ nm}) and its uniquely large and similar electron and hole Bohr radii (a_e \approx a_h \approx 23 \text{ nm}).\textsuperscript{78} PbSe NWs promise low-cost and high performance field effect devices,\textsuperscript{106} thermoelectrics,\textsuperscript{107} energy efficient photovoltaics\textsuperscript{108} and photodetectors\textsuperscript{109}. However, unmasking the intrinsic properties of nanostructured materials and exploiting their characteristics in applications, requires their integration in device

architectures. For example, PbSe NW field-effect transistors (FETs) suffer from contact resistance, seen in previous reports by the sigmoidal I-V characteristics at low voltages.\textsuperscript{106} Forming Ohmic contacts to nanoscale materials is a general problem observed in a wide-range of materials systems and is critical to probing their fundamental electronic properties and to their device performance and scalability.

In bulk semiconductor devices, doping is used to engineer charge transport in the material and at device interfaces. While many groups have attempted to dope wet-chemically synthesized nanostructures by substitutional doping, it has been shown to be difficult to realize and control and it has been achieved only at low concentrations.\textsuperscript{110-112} Charge transfer at the surface of PbSe NCs and NWs upon exposure to organic compounds has been reported to provide an alternative route to dope nanostructured materials. Hydrazine has been reported to \textit{n}-dope PbSe nanostructures\textsuperscript{106,28,113} and improve device characteristics\textsuperscript{114} at typical concentrations of 1 M.\textsuperscript{106,28,113,37,91,115} Removal of hydrazine reverts the NC or NW FET behavior to \textit{p}-type.\textsuperscript{37} Other simple amines\textsuperscript{28} and ethanedithiol\textsuperscript{91} have also been used to modify nanostructures. However, the origin of the observed changes in carrier transport measured in FETs upon ligand exchange is not well understood. Here, we report low-resistance, bottom-contact ambipolar and unipolar \textit{p}- and \textit{n}-type PbSe NW FETs. We separate the contributions of charge transfer doping on carrier injection at the device contacts from carrier concentration modulation in the NW channel that give rise to the observed modifications in FET behavior.
In this chapter, PbSe NW FETs will be discussed to understand chemical doping of hydrazine on devices. In addition, PbSe NC FETs will be demonstrated as an example of flexible electronics. To avoid degradation of plastic substrate in chemical doping process, careful encapsulation process on the device will be discussed, following a CMOS inverter of ambipolar PbSe NC FETs.
6.2. Fabrication of PbSe Nanowire Field-effect Transistor

6.2.1. Materials

All manipulations were carried out using standard Schlenk-line techniques under dry nitrogen. Tri-
*n*-octylphosphine (further referred to as TOP, Aldrich, 90%), oleic acid (OA, Aldrich, 90%), diphenyl ether (Aldrich, 99%), amorphous selenium pellets (Aldrich, 99.999%), lead acetate trihydrate (Fisher Scientific Co.), and *n*-tetradecylphosphonic acid (TDPA, Strem, 97%) were used as purchased without further purification. Anhydrous chloroform and hexane were bought from Aldrich. To prepare a 0.167 M stock solution of trioctylphosphine selenide (TOPSe), 1.32 g of selenium was dissolved in 100 mL of TOP overnight by stirring.

6.2.2. Synthesis of PbSe Nanowires

The synthesis is based on previous report:106 Lead acetate trihydrate (0.76 g) was dissolved in 2 mL of OA and 10 mL of diphenyl ether. The solution was heated to 150 °C for 30 minutes under nitrogen flow in order to form a lead-oleate complex. The solution was then cooled to 60 °C and 4 mL of 0.167 M TOPSe solution was added slowly to prevent premature nucleation of PbSe. The combined lead-oleate/TOPSe solution was injected under vigorous stirring into a hot (250 °C) growth solution containing 0.2 g TDPA dissolved in 15 mL of
diphenyl ether. After ~50 seconds of heating, the reaction mixture was cooled to room temperature using a water bath. Once cooled, the reaction vessel (still under N₂) was transferred to a glovbox, where the crude solution was mixed with equal amounts of hexane, and the nanowires (NWs) were isolated by centrifugation at 4300 rpm for 5 minutes. The resulting precipitate (NWs) was redispersed in chloroform for further characterization.

6.2.3. Device Preparation

Devices were fabricated on an n-doped Si wafer with 250 nm thermally grown SiO₂. Electrodes were patterned using photolithography with a bilayer of Lift-off Resist (LOR3A from MicroChem) and S1813 (Microposit). Samples were exposed using a Karl Suss Mask aligner and developed in MF-319 (Microposit). The exposed sample was cleaned by a 3 minute O₂ plasma and metal was deposited by e-beam evaporation of 2 nm of Ti and 18 nm Au. Metal was subsequently lifted off using Remover PG (MicroChem). The fabricated devices were then put in a YES (Yield Engineering Systems) Oven, where the fabricated devices were first cleaned with an O₂ plasma and then vapor primed with hexamethyldisilazane (HMDS, Aldrich, 99.9%) for five minutes at 150 °C.
6.2.4. Nanowire Alignment

NWs were aligned across device structure having a channel length of 20 µm and channel width of 200 µm. The NWs were washed with ethanol and then chloroform to remove the HD-PVP polymer and organics, which was verified using a Nicolet 6700 FTIR equipped with a Harrick GATR. For $n$-type conversion of the $p$-type NW transistors, varying concentrations of hydrazine in acetonitrile was used. Electric-field directed assembly was carried out in an MBraun nitrogen glovebox and all solvents used were distilled and anhydrous.
6.3. Fabrication of PbSe NWs-based FETs

Transmission electron microscopy (Figure 6.1a) shows the synthesis produced single-crystalline PbSe NW samples approximately 10 nm in diameter and over 10 µm in length. Rigorous anhydrous conditions were used from synthesis to purification, fabrication, and characterization to prevent oxidation of the NWs, which has been observed in PbSe nanostructures.\textsuperscript{28,91,116-118} NWs were dispersed in octane:nonane at a 1:1 (vol:vol) ratio with several drops of 10 wt% solution hexadecane-graft-polyvinylprrolidone (HD-PVP) copolymer (\(M_n = \sim 7300\)) to improve the NWs’ dispersability. Hexamethyldisilazane (HMDS) primed n\(^+\) wafers with 250 nm thermally grown SiO\(_2\) were photolithographically patterned to define channel lengths of 20 µm and widths of 200 µm. NW solutions were dropcast under dc electric fields of \(10^4\) to \(10^5\) V/cm (Figure 6.1b), aligning NW arrays across the pre-fabricated bottom electrodes (Figure 6.1c, d).
Devices were then well-washed in both ethanol and chloroform to remove excess ligands, namely the oleic acid used in NW synthesis and the HD-PVP used to aid NW dispersion, which was verified by Grazing-Angle Total-Reflection FTIR spectroscopy (Figure 6.2). Removing excess ligands improved FET transport characteristics, whereas insufficient washing led to very poor FET current modulation.

Figure 6.1. (a) TEM of as-synthesized PbSe NWs. (b) Schematic of drop-casting NWs for electric field directed-assembly. (c) Schematic of PbSe NW FET after alignment. (d) SEM of PbSe NW FET.
Figure 6.2. GATR FTIR of PbSe NWs. (a) Oleic Acid, (b) HD-PVP, (c) PbSe NW solution dropcast on sapphire substrate with HD-PVP, (d) PbSe NW deposit with HD-PVP washed with ethanol, and (e) PbSe deposit with HD-PVP washed with CHCl₃.
6.4. Chemical Doping of PbSe NW FETs

As-synthesized PbSe NW FETs show ambipolar, but predominantly $p$-type behavior (Figure 6.3a). The sigmoidal, closely spaced $I_D-V_{DS}$ characteristics at low-voltages, known as “current crowding,” (highlighted in the inset Figure 6.3a) is a signature of high contact resistance, which limits the device on-current. Immersing these devices in 4 M hydrazine in acetonitrile (CH$_3$CN) for 24 hours converts the device behavior to predominantly $n$-type (Figure 6.3b). After hydrazine treatment, the $I_D-V_{DS}$ characteristics are linear at low voltages (inset Figure 6.3b) and the device on-current $I_D$ is increased by a factor of 40, consistent with forming a low resistance contact for electron injection. Pulling poor vacuum (30 mTorr) for an hour on the devices, removes the hydrazine and the NW FETs predominantly $p$-type characteristics are recovered (Figure 6.3c). In order to verify that all the hydrazine was removed, devices were also placed under high vacuum ($10^{-8}$ Torr) overnight and showed no difference in their characteristics from those pumped under poor vacuum. The predominantly $p$-type devices show linear $I_D-V_{DS}$ characteristics (inset Figure 6.3c) and increased on-current by a factor of 15, indicative of reduced contact resistance for holes then in the as-deposited NW FET behavior. We show that this process is repeatedly reversible as the NW FET can be converted from predominantly $p$- to $n$-type, retaining their linear $I_D-V_{DS}$ characteristics and high current levels, and back over multiple exposures to 4 M hydrazine and removal under vacuum (Figure 6.3d-g). Additionally, besides the as-aligned device, which shows high contact resistance
and low currents, all subsequent device characteristics, show consistent and reproducible $I_D-V_G$ characteristics, forming ambipolar, predominantly $n$-type FETs upon exposure to hydrazine and predominantly $p$-type FETs with vacuum removal of hydrazine (Figure 6.3h). The devices retain the same threshold voltage for electrons and holes when predominantly $n$- and $p$-type, respectively (Figure 6.4a). The reversibility in the NW FET characteristics has been measured over tens of device structures fabricated at different times on different wafers (Figure 6.4a and b).
Figure 6.3. $I_D-V_{DS}$ characteristics of PbSe NW FETs (a) as-synthesized and after (b) first immersion in 4 M hydrazine in CH$_3$CN, (c) pulling poor vacuum, (d) second immersion in 4 M hydrazine solution, (e) pulling poor vacuum, (f) third immersion in 4 M hydrazine solution, and (g) pulling poor vacuum. (h) $I_D$-
$V_G$ characteristics of the samples following the reversible conversion of FET behavior from predominantly hole to electron transport corresponding to: (—) Figure 6.3a, (—) Figure 6.3b, (—) Figure 6.3c, (—) Figure 6.3d, (—) Figure 6.3e, (—) Figure 6.3f and (—) Figure 6.3g.

**Figure 6.4.** Following the reversible conversion of a PbSe NW FET (a) threshold voltage for (—) electrons and (—) holes. (b) On-currents ($I_{ON}$) for (—) electrons and (—) holes. $I_D$-$V_{DS}$ characteristics of (c, d) predominantly $p$-type ambipolar devices and (e, f) predominantly $n$-type ambipolar devices.
6.5. Ambipolar behavior of PbSe NW FETs

While previous work on as-synthesized PbSe NW FETs showed only hole transport, these devices show evidence of electron transport in the $I_D-V_G$ curves, indicating ambipolar behavior (Figure 6.3h). Additionally, PbSe NC FETs have shown ambipolar transport when treated with ethanedithiol. Even after hydrazine treatment, the devices display ambipolar behavior when either predominantly $p$ or $n$-type. The $I_D-V_{DS}$ characteristics of ambipolar FETs show at high negative $V_G$ (Figure 6.4c, d) hole accumulation, at high positive $V_G$ electron accumulation (Figure 6.4e, f), and at moderate $V_G$ and high negative and high positive $V_{DS}$ both electron and hole accumulation in the FET channel. This is seen in particular by the nonlinear $I_D-V_{DS}$ characteristics as holes accumulate at the drain electrode at large positive $V_{DS}$ and moderate $V_G$ for predominantly $p$-type devices (Figure 6.4d). Conversely, electrons accumulate at the drain electrode at large negative $V_{DS}$ and moderate $V_G$ for predominantly $n$-type devices (Figure 6.4e).

The asymmetry in the on-currents ($I_{on}$) for both electrons and holes are only about one order of magnitude when operating both predominantly $p$- and $n$-type devices (Figure 6.4b), even after multiple cycles of hydrazine exposure and removal. The average majority carrier threshold voltage for electrons ($V_{th} = 28$ V) is less than the average threshold voltage for holes ($V_{th} = -35$ V) (Figure 6.4a), indicating that $V_G - V_T$ for electrons is greater than for holes, which is consistent with electron currents that saturate more readily than hole currents (Figure 6.4c-f).
Since PbSe NWs have a bandgap of only 0.56 eV, it would be likely to expect this material to exhibit ambipolar behavior at low doping because there are small barriers for both hole and electron injection. The predominantly $p$-type behavior may be attributed to a more favorable band alignment of the PbSe HOMO level with the work function of the gold contacts. The predominantly $n$-type behavior can be attributed to the influence of hydrazine, which can increase the electron affinity and ionization potential of the HOMO and LUMO levels of PbSe nanostructures, making the material more favorable toward electron injection.

After hydrazine treatment the devices all show fairly high off currents in the range of 1 to 10 nA. We estimated the expected off-current for PbSe NWs FETs with the 0.56 eV bandgap measured for the as-synthesized PbSe NWs by solving the effective density of states for a 1D system at room temperature ($T = 300$ K). An ~0.1 nA off-current is expected for a single PbSe NW across a 20 µm channel length, using the NW diameter of 10 nm as the channel width.

* Knowing the effective mass of the electron and hole ($m^*_e = m^*_h = 0.09$), mobility of holes ($\mu_h = 900$ cm$^2$/V•s) and electrons ($\mu_e = 1000$ cm$^2$/V•s), and the multiplicity ($M_c = 4$) for the conduction band minimum and valence band maximum both at the (111). Solving for current expected of a single PbSe nanowire 20 µm long and 10 nm diameter:

$$N_c^{1D} = \sqrt{\left(\frac{m^* kT}{2\pi \hbar^2}\right)} M_c = 2.78854 \times 10^6 \ 1/cm$$

Assuming the NW is intrinsic, the number of electrons ($n$) and holes ($p$) are equivalent to the intrinsic carrier concentration, $n_i$:

$$n_i = n = p = \sqrt{(N_c^{1D} N_v^{1D})} \exp(-E_g/2kT) = 55.1556 \ 1/cm$$

Therefore, the conductivity and resistivity can be calculated:

$$\sigma = ne\mu_e + pe\mu_p = 1.67673 \times 10^{-14} \ (cm^2/V) \ \ \rho = 5.96399 \times 10^{13} \ \Omega/(cm•A)$$

We estimate the 1D resistance and the current at 10V in an “off” device using Ohm’s law to be:

$$I = V/R = \frac{V}{l_{(dL)}} = 8.38365 \times 10^{-11} \text{ Amps} = 0.08387 \ \mu A/\text{wire}$$
Based on SEM images, which show tens to hundreds of NWs spanning sparsely the junction along its 200 µm width, it would be expected to have an off current in the range of 1 to 100 nA.
6.6. Selective Chemical Doping of PbSe NW FETs

6.6.1. Experimental Section

All e-beam resists and developers were degassed and used inside an MBraun nitrogen glovebox. An e-beam resist bilayer of 495 PMMA A4 (MicroChem) and 950 PMMA A4 (Microposit) was spin-cast and baked under nitrogen at 180 °C for 2 minutes for each layer. The PMMA coated device was secured in a jar under nitrogen in the glovebox and taken to the e-beam lithography tool, where the blocking layer was exposed. After exposure, the sample was developed in the glovebox with methyl isobutyl ketone in isopropyl alcohol (MIBK: IPA 1:3, Honeywell Burdick and Jackson). E-beam evaporation of the blocking layer was carried out in a nitrogen glovebox with an integrated evaporator, followed by lift-off with anhydrous acetone.

An Agilent 4156C parameter analyzer was in combination with a Karl Suss PM5 probe station was used to measure device characteristics. The source was grounded and a highly $n$-doped silicon wafer was used as a back gate electrode.

6.6.2. Discussion: Blocking Layer

In order to understand the origin of the reversible influence of hydrazine on the transport behavior of the NW FETs, an SiO$_2$ blocking layer was fabricated on top of 19 µm of the 20 µm NW channel to selectively dope 0.5 µm of the NW at the
NW-source and drain interfaces. All methods to fabricate the blocking layer were carried out in anhydrous conditions, as rigorously as possible. To achieve this structure, reversibly hydrazine treated and vacuum exposed NW FETs with predominantly $p$-type characteristics were used. Devices were coated with degassed PMMA e-beam resist, sealed in a vessel, and carried to the e-beam lithography tool to define the blocking layer. The resist development, SiO$_2$ e-beam evaporation, and lift-off to create the patterned SiO$_2$ blocking layer (Figure 6.5a and b), were carried out in a nitrogen-filled glovebox with an integrated evaporator. Control experiments were also performed at each processing step to ensure the integrity of the NW FETs remained unaffected throughout the fabrication process. The predominantly $p$-type characteristics remain unchanged when heated with and without PMMA at 180°C for a total four minutes (Figure 6.6a). There were no signs of NW sintering or growth, as verified by scanning electron microscopy, which is consistent with reported heat treatments of PbSe NC films that show electrical characteristics and conductivity that remain essentially unchanged from the as-made films when heated to 200 °C for an hour. The e-beam resist developer MIBK: IPA suppressed the device’s electron current (Figure 6.6b), but pulling high vacuum (10$^{-8}$ Torr) on the sample recovered the ambipolar behavior, as shown by the $I_D$-$V_G$ curve after SiO$_2$ evaporation.

The predominantly $p$-type, ambipolar FET behavior remained intact after fabrication of the blocking layer (Figure 6.5c). Immersing the device in 4 M hydrazine in CH$_3$CN for 24 hrs still converted the device to predominantly $n$-type
characteristics (Figure 6.5d). Upon removing the hydrazine under vacuum, the device regained its predominantly \( p \)-type behavior (Figure 6.5e). For predominantly \( n \)- and \( p \)-type FETs, the observed linear behavior in the \( I_D-V_{DS} \) curve at low voltage, which is followed by current saturation, indicates low resistance, high on-current FETs are maintained, and the current levels are similar to those for NW FETs without the blocking layer, upon exposure and removal of hydrazine. Figure 6.5f shows the \( I_D-V_G \) characteristics of the reversible transport behavior by modifying only the contact region. Different blocking layer lengths of 18 and 16 µm were also fabricated on top of the 20 µm channel, creating 1 µm and 2 µm gaps at the source and drain contact regions. The device current levels for the FETs when exposed to hydrazine and when hydrazine is removed, is invariant with the size of the gap at the electrodes, despite the exposure and removal of more of the NWs length to hydrazine.

### 6.6.3. Discussion: Hydrazine Doping

Many papers attribute the conversion of predominantly \( p \)-type PbSe NCs to predominantly \( n \)-type behavior on ligand exchange of the oleic acid with hydrazine.\textsuperscript{106,28,113,37,115,119} However, the exact role of hydrazine is not well understood. Hydrazine has been reported to remove only approximately 2-7% of the initial oleate surrounding these films based on FTIR spectra,\textsuperscript{28} while other groups suggest that hydrazine rapidly removes the vast majority of the oleic acid ligands on the surface of the NCs in the first five minutes based on AFM and
ATR-FTIR measurements. In FETs, single-crystalline NWs bridge the entirety of the junction, whereas transport in NC arrays is complicated by variations interparticle spacing and film cracking. The NW FETs allows separation between the role of ligand exchange on the PbSe nanostructures and on the PbSe-metal junction. Polarity switching of the majority carrier in FETs by selectively exposing the NW-metal junction, suggests at the lower 4 M hydrazine concentrations, energy level alignment at the metal-nanostructure contact governs the measured device behavior.

Hydrazine can transfer an electron to the NW, as has been reported in carbon nanotube FETs, forming $\text{N}_2\text{H}_4^+$, inducing a negative charge and forming an inward-pointing surface dipole. This surface dipole reduces the local metal work function to favor electron injection and suppress hole injection. Unlike carbon nanotubes, this process is reversible in PbSe nanostructures and once the sample is under vacuum for a period of time, the hydrazine is removed and the work function reverts to favor hole injection and suppress electron injection. However, using 4 M hydrazine, we were unable to achieve completely $n$-type unipolar devices. Therefore PbSe NW FETs were immersed in both 8 M and 12 M hydrazine in CH$_3$CN (Figure 6.6a) to see if the devices could be more strongly $n$-doped. Without a blocking layer present, immersing the device in 8 M hydrazine completely turned off the ambipolar behavior and converted the FET to fully $n$-type, shifting $V_T$ more negative. On the other hand, when exposing only the contacts to 8 M hydrazine (Figure 6.6b), the device characteristics were ambipolar, predominantly $n$-type. Both devices with and without blocking layers
treated in 8 M hydrazine can be reverted back to its predominantly $p$-type state under poor vacuum for an hour. Immersing the device in 12 M hydrazine ruined the devices, since hydrazine is a caustic base and has been shown to dissolve lead chalcogenides at high concentrations.$^{27,122}$ These results further illustrate the unique roles the contacts and the bulk of the NW channel have in modifying the FET behavior. At low to moderate doping densities, we see that contact modification dominates, determining the majority carrier injection type of the FET. At high doping concentrations, carrier density modification of the bulk of the NW channel becomes significant, similar to carbon nanotube FETs.$^{120,121}$ By controlling the hydrazine concentration used to charge transfer dope the NW FETs, it is possible to control the degree of electron transport seen in the device, ranging from ambipolar, predominantly $n$-type to unipolar $n$-type behavior.

6.6.4. Discussion: Ozone Treatment

In this study, rigorous anhydrous conditions were used, avoiding oxidation and enabling observation of both hole and electron currents (Figure 6.4a-f) in the NW FETs. Oxygen creates acceptor states in PbSe NCs,$^{123,124}$ causing the material to become strongly $p$-type, increasing the conductivity due to higher hole concentrations, and giving rise to a loss of gate modulation in FET devices.$^{28,117}$ However, controlled oxygen doping of PbSe FETs may serve to be advantageous for enhanced $p$-type characteristics. In order to better understand the role of oxygen, devices were treated under UV-ozone for varying times. Starting with an
ambipolar PbSe NW FET, we see a significant loss in electron current and a shift in the threshold voltage to more positive voltages even after a short 5 second UV-ozone exposure, and further improvement in the $p$-type characteristics for UV-ozone treatments up to 10 seconds (Figure 6.7c). Subsequent UV-ozone treatments longer than 10 seconds cause the predominantly $p$-type PbSe FET to degrade in performance, similar to what has been reported for PbS NCs in solar cells,\textsuperscript{125} and to suffer poor gate modulation. As a comparison, the contacts were selectively exposed to UV-ozone for varying amounts of time (Figure 6.7d). The electron current is not lost as readily as when the entire length of the NW was exposed to oxygen. Similar to the hydrazine, just by treating the contacts, the device characteristics can be modified, reflecting that the metal-semiconductor NW contact strongly dominates the FET device behavior. However, the electron transport can be recovered after re-immersing the devices in a 4 M hydrazine solution overnight. By controlling the UV-ozone exposure time over the entire NW, it is possible to control the degree of $p$-type behavior seen in PbSe FETs, ranging from predominantly $p$-type ambipolar to unipolar $p$-type.

6.6.5. CMOS Inverters of PbSe NW FETs

By taking advantage of the control we have over the PbSe device behavior, we fabricated bottom-contact inverters using a unipolar $p$-type FET (treated with 10 second UV-ozone) and a unipolar $n$-type FET (treated with 8 M hydrazine) (Figure 6.7e and f). The gates of the FETs were connected and used as the input
of the inverter. These are the first reported PbSe NW inverters which exhibit promising gains of ~8 for both positive and negative $V_{DD}$.

Figure 6.5. (a) Schematic of PbSe NW FET with top insulating SiO$_2$ blocking
layer. (b) SEM of blocking layer atop the PbSe NW FET and inset, higher resolution images. $I_D-V_{DS}$ characteristics of a NW device (c) with fabricated blocking layer, (d) treated in 4 M hydrazine, and (e) after pulling with poor vacuum. (f) $I_D-V_G$ characteristics following the conversion of the NW transport behavior when only modifying the NW-contact region corresponding: (—) Figure 6.5c, (—) Figure 6.5d and (—) Figure 6.5e.

![Graphs](image)

**Figure 6.6.** $I_D-V_G$ characteristics of PbSe NW FETs (a) heat control. (—) before heat and (—) after heating at 180 °C for 4 minutes in a glovebox. (b) step-by-step characterization of blocking layer fabrication. (—) original FET with no blocking layer and after (—) e-beam lithography, (—) development in MIBK:IPA, and (—) SiO$_2$ evaporation and acetone lift-off.
Figure 6.7. $I_D$-$V_G$ characteristics of PbSe NW FETs treated with (—) 4 M hydrazine and (—) 8 M hydrazine (a) without and (b) with a blocking layer. $I_D$-$V_G$ characteristics of PbSe NW FETs treated with UV-ozone for (—) 5 seconds, (—) 10 seconds, (—) 30 seconds and (—) 60 seconds (c) without and (d) with a blocking layer. (e, f) Transfer and gain characteristics of inverters constructed from unipolar $p$ and $n$-type PbSe NW FETs.
6.7. Conclusion

In summary, we report low-resistance, bottom-contact PbSe FETs with controllable and reversible device characteristics ($V_{th}$, $I_{on}$), ranging from oxygen treated unipolar $p$-type, ambipolar, to high hydrazine concentration treated unipolar $n$-type. Selectively treating the contacts with oxygen or hydrazine reversibly changes the predominant measured carrier to holes or electrons, suggesting the dominating role the metal-semiconductor NW contacts have on charge injection in these devices at low to moderate doping concentrations. At high doping concentrations, both hydrazine and oxygen manipulate carrier injection at the contacts and carrier density in the bulk of the PbSe NW channel. We demonstrate the importance of molecular charge transfer doping at the device interfaces in addition to the nanostructures’ surfaces in understanding charge transport and engineering device behavior. By taking advantage of the control we have over the carrier transport in PbSe NW FETs, we fabricated the first PbSe NW inverters that show the promise of these nanostructured materials in integrated circuits.
Chapter 7. Future Work and Concluding Remark

"Science never solves a problem without creating ten more." - George Bernard Shaw

7.1. Introduction to Future Directions

In this thesis, I described how structure of nanomaterials affects the function and properties of them as materials and devices, mainly focused on lead chalcogenides as narrow band gap semiconductors. Still, there are several interesting studies relevant to this topic, but not fully investigated yet, which I want to address as my future direction for further research area. I will introduce them as aspects of materials/precursor chemistry, ligand/surface chemistry, self-assembly, devices and measurements, and others in following sections.

7.2. Materials: Heterostructure and Mechanistic Study

Even I mainly focused on lead chalcogenides for my Ph. D. research, there are lots of other materials and complicated structures based on synthetic approaches of organometallic chemistry and solution process. For an example of photovoltaic
materials, there are many interesting materials such as $\text{Cu}_2\text{S}$, $\text{Bi}_2\text{S}$, $\text{In}_2\text{S}_3$, $\text{CuInS(Se)}$, $\text{SnS(Se)}$; and yet there are not many good reports on how to synthesize those materials with a good control of their size and shape. Also, multicomponent systems are getting popular because they could open a new area of designing materials property by combining semiconductor-metal or magnetic-semiconductor materials. Plasmonic-semiconductor or magnetic-semiconductor coupling is much related to new fields of optics, electronics, and magnetic devices as well as fundamental understanding of various solid state physics.

![TEM image of Au-PbS and PbS-Au multicomponents](image)

**Figure 7.1.** Au-PbS and PbS-Au multicomponents: (a) TEM image (b) EDX (c) XRD patterns

Another important area is to develop new precursor chemistry such as cheap, nontoxic, air-stable process. There are a lot of issues of irreproducibility in reported synthetic approaches to control size, shape, and composition of
nanomaterials. A few studies have been done with traditional chemical analysis using NMR, IR, Mass, and so on;\textsuperscript{16,17,19} however the recent paper of Krauss group demonstrate how much it is hard to understand the decomposition mechanism of NC precursors even for the simple spherical morphology. With more investigation about kinetic control of NC growth and oriented attachment, there are more and more interesting but not fully-understood topics in the synthesis of nanomaterials.

7.3. Surfactant Chemistry: Beyond Molecular Metal Chalcogenide

Most solution processes of NCs synthesis were done under nonpolar solvent, using bulky steric hindered surfactants as stabilizing reagents. Recently, Talapin group reported molecular metal chalcogenides (MMCs) as inorganic surfactants and they claimed this can stabilize NCs in polar solvent with quite short interparticle distance.\textsuperscript{27} Especially, close-packed NC film and assembly are very interesting for electronic application, due to their high conductivity without any insulating organic long chain surfactants. The traditional organic ligands are usually long alkyl groups, electronically insulating materials; thus short chain ligands such as hydrazine or ethanedithiol were introduced to exchange ligands and enhance conductivity of NCs thin film. However, hydrazine is highly toxic and ethanethiol smells quite bad, which are not easy to work with. Also, it’s necessary to exchange ligand molecules and remove previous long chain organic molecules, which is not reproducible or condition-sensitive. This also simplifies the device fabrication because ligand exchange is not necessary any more to
improve their conductivity by reducing NC spacing. Thus new types of ligand chemistry such as MMCs or thiocyanate groups introduced in Chapter 5 are quite interesting species because they suppresses the amount of insulating organic surfactant layer on the surface of NCs. Especially nontoxic and mild process of MMCs or thiocyanate chemsitry is quite interesting, because most plastic substrates for flexible electronics application are not compatible with highly reactive chemicals such as hydrazine. One of the promising area is NC-based electronics on flexible substrates such as FET, solar cell, or sensor applications. This will be addressed a little more in Chapter 7.6.

7.4. Assembly: Vertical Assembly of Nanorods

![Diagram of solar cell device using P3HT and CdSe nanorods](image)

**Figure 7.2.** (a) The ideal structure of solar cell device using P3HT and CdSe nanorods and (b) TEM images of vertical aligned CdS nanorods using electric field.

Since Alivisatos group proposed photovoltaic device structures based on vertical
aligned CdSe nanorods (Figure 7.2a), vertical alignment of nanorods has been interesting for both self-assembly and anisotropic properties of nanostructures. Early studies demonstrated external field-assisted nanorod assembly (Figure 7.2b), but there have been examples of vertical aligned nanorods without external force. One interesting paper is reported by Manna group, showing depletion attraction can induce vertical aligned nanorod assembly in solution. The idea is that when the nanorod solutions contain more and more additives, they will draw solvent away from the nanorods surface and depletion force will induce nanorods aggregation as shown in Figure 7.3.

Figure 7.3. The process of nanorods assembly in solution by depletion attraction.
7.5. Single Particle Measurement: Photocurrent in Nanogap

Figure 7.4. (a) Schematic of the nanogap device. Metal electrodes (3 nm of Ni and 30 nm of Au) separated by 20 to 30 nm are patterned on top of a 40 nm Si₃N₄ membrane that is supported by a Si wafer. (b) Optical image of the device with 12 electrode pairs.

Nanoelectronics based on colloidal semiconducting NCs is one of the promising technology, and it was successfully demonstrated to control the size, shape, and composition of the NCs. However, their surface properties and charge traps/defects are still not investigated with a good control of them. Electronic transport of NCs solid in film has been studied as a large scale device but it is quite challenging as a small scale device or a single particle measurement due to poor controllability of positioning them. Another challenge is addressed by recent paper of Banin group that electric switching phenomena of CdSe nanorods between nanogap, implying there could be similar charge-quenching process to
optical blinking. Our photocurrent experiment of PbSe NR is still preliminary, but we hope there could be more opportunities to overcome those challenges to achieve valuable scientific finding at nanoscale for photophysic, electronic transport, and device applications.

Figure 7.5. (a) TEM image of the Ni/Au electrodes separated by 20 nm prior to NC deposition. (b) TEM image of the same electrodes with PbSe nanorods.
7.6. Device: Flexible Electronics and Solar Cell

Flexible electronics is a technology for assembling electronic circuits by mounting electronic devices on flexible substrates. Its flexibility, lightweights, and space savings allow fabricating thin display devices, satellite powers, or stretchable robotic devices. There have been many demonstrations of organic
semiconductor FET on flexible substrates, which is based on solution-process such as spin-coating or self-assembled monolayer method. One direction is development of flexible electronics based on NCs, which provide both advantages of solution-processability and good electric properties as inorganic materials. Especially ink-jet printing or various solution process of NC ink would be promising for cost-down and easy fabrication.

**Figure 7.7.** Examples for flexible electronics: (a) An Olympus Stylus camera without the case, (b) a foldable keyboard, and (c) a flexible substrate for FET devices.
Since the photovoltaic effect was found by A. E. Becquerel in 1839, people have investigated the fundamental science and its application for solar cell. Especially the current energy consumption requires new energy resources, such as solar, wind, geothermal; of these renewable resources, solar energy shows the largest opportunity to solve increasing global demands. Air mass 1.5 (AM1.5) is the standard spectrum for the photovoltaic area, which is corresponding to the sun being at 42° and an integrated power density of 100mW/cm². The most common solar cells are based on Si, CdTe, CIGS (copper-indium-galium-sulfur or selenide) materials, which are only able to catch the visible range of sunlight. One third of the solar spectrum locates beyond 1000 nm, which requires developing infra-red active materials to maximize the photovoltaic efficiency.

![Figure 7.8](image.png)

**Figure 7.8.** The standard air mass (AM) 1.5 global solar spectrum. ETR is extraterrestrial radiation which is the amount of global horizontal radiation that a
location on Earth would receive if there was no atmosphere or clouds. Global Tilt displays spectral radiation from solar disk plus sky diffuse and diffuse reflected from ground on south facing surface tilted 37° from horizontal. Direct represents Direct Normal Irradiance nearly parallel (0.5° divergent cone) radiation on surface with surface normal tracking (pointing to) the sun, excluding scattered sky and reflected ground radiation. Circumsolar shows Spectral irradiance within ±2.5° field of view centered on the 0.5° diameter solar disk, but excluding the radiation from the disk.\textsuperscript{130}

NC-based solar cells have advantages of good tunability in band gap and band offset, solution-processability, and effective charge separation through large surface area. Recently there are promising results of NC-based solar cells,\textsuperscript{131-133} which could enlarge the field of NC electronics and photonics.

\textbf{7.7. Conclusion}

Overall, this thesis covers a whole variety of nanoscience from synthesis, precursor and surface chemistry, structure-dependent function of nanomaterials, self-assembly, and nanomaterial-based devices. Chapter 2 demonstrates a new methodology to control the morphology of lead chalcogenide NCs, which was further investigated to understand precursor chemistry in Chapter 3. This led to a study of the electronic structure and phonon modes of anisotropic NCs in lead chalcogenide, demonstrated in Chapter 4.
Chapter 5 introduces a new type of NC surface chemistry that allows for the phase transfer of NCs into polar solvents, formation of compact NC films to enhance coupling between neighboring NCs, and the introduction of reporter ligands to provide valuable information on the surface chemistry for NCs. Chapter 6 describes a study of electronic transport in anisotropic lead chalcogenide systems, especially focused on the importance of molecular charge transfer doping at the device interfaces. The direction of further research and investigation is discussed in Chapter 7, identifying the potential in these studies to better bridge molecular chemistry with nanomaterials/nanostructures.
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