ZERO-DIMENSIONAL AND TWO-DIMENSIONAL COLLOIDAL NANOMATERIALS AND THEIR PHOTOPHYSICS

Zhoufeng Jiang

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Committee:

Liangfeng Sun, Advisor

Anita Simic
Graduate Faculty Representative

Mikhail A Zamkov

H. Peter Lu
ABSTRACT

Liangfeng Sun, Advisor

Two-dimensional oriented attachment has been confirmed as the growth mechanism of PbS nanosheets by Horst Weller in 2010. By interrupting the growth of PbS nanosheets, we investigated the intermediate PbS products which include isolated PbS quantum dots, attached PbS quantum dots and porous PbS nanosheets. We linked the intermediate PbS products with their structure and optical properties by comparing the emissions from PbS quantum dots and emissions from PbS nanosheets. Meanwhile, we shield PbS nanosheets with a shell of CdS by cation exchange to improve their optical properties and tune their bandgaps. Furthermore, we found that PbS nanosheets can be completely converted into CdS nanosheets by cation exchange, while keeping the same morphology. Thus, we can compare their photophysics properties when they have the same quantum confinement dimensions. On the other hand, carbon nanodots have become a very promising nanomaterial for numerous bio-and optoelectronic applications since they have superior chemical stability and low toxicity compared to conventional inorganic semiconductor quantum dots. We investigated the origin of photoluminescence(PL) on citric-acid-derived carbon nanodots, particularly focusing on the excitation-dependent PL behavior. By conducting the absorption, PL and PL-excitation spectra, we succeed to observe the multi-emissive states of carbon nanodots.
To my parents and my future family
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CHAPTER 1 INTRODUCTION

1.1 Crystal growth mechanisms.

Colloidal semiconductor nanocrystal has received considerable attention due to many potential innovative applications such as catalysis\textsuperscript{1-5}, solar cell\textsuperscript{6-12}, biomedicine\textsuperscript{13-17}, light-emitting diode\textsuperscript{18-25}, lasing\textsuperscript{26-35} and so on. Compared to their bulk counterpart, they have novel optical, electronic and catalytic properties, which are closely related to their size and morphology. Therefore, it is important to synthesize high-quality nanocrystals to further explore their unique properties.

To synthesize high-quality nanocrystals, the understanding of their growth mechanism becomes significantly important. Traditionally, the nucleation and growth of nanocrystals can be described by LaMer’s burst nucleation theory\textsuperscript{36-37}, followed by the Ostwald ripening mechanism\textsuperscript{38} that is used to clarify the changing of nanocrystal sizes. According to LaMer’s theory, the nucleation and growth of nanocrystals can be separated into three stages\textsuperscript{39}: 1), the formation of supersaturation solution of free monomers. 2), the “burst-nucleation” occurs in the solution and the concentration of free monomers was greatly diminished. When the concentration of free monomers decreases to a critical value, nucleation process will stop. 3), after the ending of nucleation, the growth of nanocrystals was initiated with the diffusion of free monomers to the surface of crystal nucleus. The LaMer’s theory was shown in Figure 1. 1 where the concentration of solute was plotted as a function of reaction time. The numbers I, II and III represent three stages of LaMer’s theory: formation of supersaturation, “burst-nucleation” and the growth of crystal nucleus.
Ostwald ripening is a growth process of nanocrystals in solution, which describes the changing of size of the nanocrystals versus reaction time: i.e., the smaller nanocrystals will dissolve, and redeposit onto the larger nanocrystals as shown in Figure 1.2. Generally, the growth of nanocrystals by Ostwald ripening is caused by the variation of the solubility of nanocrystals that is dependent on the size of these nanocrystals. According to the Gibbs-Thomson relation in equation (1), the solubility of nanocrystals is partially determined by the size and the surface free energy of nanocrystals, leading to greater solubility for the smaller nanocrystals. Due to the higher solubility and surface energy of smaller nanocrystals, they will be consumed by larger size nanocrystals, making larger nanocrystals even bigger.

\[ C_r = C_b \times \exp\left(\frac{2\gamma \theta}{r K_b T}\right) \]  

(1)
Cr-solubility of nanocrystal; C_b-the bulk concentration of monomer in solution; γ-surface free energy of nanocrystal; θ-molar volume of bulk crystal; r-size of nanocrystal; K_b-Boltzmann’s constant; T-temperature.

![Schematic diagram of Ostwald Ripening.](image)

**Figure 1.** 2 Schematic diagram of Ostwald Ripening.

Accordingly, LSW theory was proposed by Lifshitz and Slyozov\textsuperscript{40} and Wagner\textsuperscript{41} to mathematically describe the kinetics of Ostwald ripening, where the size evolution of nanoparticles with time should obey the equation (2)\textsuperscript{42}:

\[
\frac{dr}{dt} = \frac{K_D}{r^2} \left( \frac{r}{r_{cr}} - 1 \right)
\]

Where \( K_D = \frac{2\sigma V^2 D C_0}{kT} \), \( r_{cr} = \frac{2\sigma V}{kT \ln S} \approx \frac{2\sigma V}{kT C_{cr} C_0} \); D is diffusion coefficient, r is radius of nanoparticle, V is molar volume, and C_0 is solubility of monomer; C is the monomer concentration; S=C/C_0; \( \sigma \) is the interphase free energy; K is Boltzmann constant; and T is temperature.

From equation (2), we can infer that there is a critical size of nanoparticle-\( r_{cr} \), beyond which the nanoparticle will grow up. Otherwise, its size will diminish and consumed by larger size nanoparticle.

Opposite to Ostwald ripening, digestive ripening, or size focusing, is another mechanism of growth process for nanoparticle in solution. In this case, nanoparticles with smaller size will
grow up at expense of larger size nanoparticles, a convenient way to achieve monodispersed nanoparticles (Figure 1.3).

**Figure 1.3** Schematic diagram of Digestive Ripening.

Until now, there are very few models that can clearly clarify the mechanism of digestive ripening. Lee et al.\textsuperscript{43} presented a theoretical model that can account for the self-assembled monodisperse state of nanoparticles, based on the assumption that nanoparticles are charged in solution with isotropic interfacial free energy. They proposed the growth rate of nanoparticle with radius \( r \)\textsuperscript{42-43}:

\[
\frac{dr}{dt} = \frac{D_f V_g C_0}{r K T} \left[ \mu(r)^* - \mu(r) \right] 
\]

\[
\mu(r) = V \left[ \frac{2\sigma}{r} - \frac{\varphi Z^2 q^2}{8\pi r^4} \right] 
\]

Where \( K \) is gas constant, \( D_f \) and \( C_0 \) are the diffusivity and solubility of nanoparticle in solution. \( V_g \) is the molar volume of nanoparticle, \( \mu(r)^* \) is the chemical potential of a critical particle in equilibrium with solution. \( \varphi = (4\pi \epsilon)^{-1} \), \( Z \) is the number of charges \( q \) of the particle, and \( \epsilon \) is the dielectric constant.

Oriented attachment is such a process that nanoparticles can be fused together with each other by atomic bonding on specific crystal facets. This mechanism is distinct from the classical
diffusion-controlled growth of nanoparticles in solution, i.e., Ostwald ripening\textsuperscript{44}. The oriented attachment mechanism has been explored since 1990s by Penn and Banfield\textsuperscript{45} and it provides a new route to produce nanoparticles with unique crystal morphologies and architectures\textsuperscript{46-53}. For example, lead sulfide (PbS) nanosheets have been firstly synthesized in solution through oriented attachment mechanism by Weller’s group in 2010, which clearly indicates the attaching process during the formation of PbS nanosheets as shown in Figure 1. 4 and Figure 1. 5.
In Figure 1. 4, the TEM image (B) shows an individual PbS quantum dot and TEM image (C) exhibits an aggregation of three PbS quantum dots which indicates the early stage of oriented attachment. With further attachment, the porous framework structure of PbS was formed due to large-scale attachments of PbS quantum dots. In the final stage of oriented attachment, uniform PbS nanosheets were obtained as shown in TEM image (E) with selected-area electron diffraction (SAED) pattern showing the single-crystalline structure. In Figure 1. 5, the diagram shows the formation of PbS nanosheets from PbS quantum dots by oriented attachment (route B), where larger size PbS quantum dots will be formed if without cosolvents in reaction (route A).
The alignment process and attachment mechanism were further explored by Li et al. in 2012. They investigated the oriented attachment of iron oxyhydroxide in a liquid cell that was installed inside high resolution transmission electron microscope. They found that the oriented attachment needs the matching of crystallographic orientation of nanoparticles and generally the attachment process occurs when nanoparticles rotate and approach to each other within the distance of less than 1 nm. It may take 10-100 seconds for nanoparticles to fuse together. Furthermore, they claimed that the coulomb interaction among nanoparticles may take responsible for the driving force of the orientation of two neighboring nanoparticles, while van der Waals interactions cannot be ruled out due to anisotropic polarizability.

Coalescence is very similar to the oriented attachment mechanism, except the crystallographic orientation of aligned nanoparticles. The coalescence mechanism does not require the crystallographic orientation of two attaching nanoparticles, while in oriented attachment mechanism nanoparticles will keep rotating until achieving crystallographic orientation between two nanoparticles. Zheng et al. revealed that platinum nanocrystals can grow either by monomer attachment from solution or by particle coalescence, resulting in a nearly monodisperse distribution of nanocrystals.
1.2 Passivation of PbS nanocrystals

Colloidal semiconductor nanocrystals or quantum dots (QDs) have already shown the significant potential in optoelectronic device application due to their attractive bandgap tunability and solution-processability\textsuperscript{12, 20-21}. However, the benefits of tunability and processability of QDs are seriously counterbalanced by the challenge of achieving superior carrier transport capability\textsuperscript{56}. For QDs solid film, there exists the insulating barrier due to the spacing among QDs, leading to the reduced carrier mobility because of the low efficient phonon-assisted tunneling mechanism\textsuperscript{57}. Furthermore, owing to the size effect of QDs, the large surface-to-volume ratio will contribute to the formation of electronic defects that will greatly enhance recombination loss and risk the charge collection. Two-dimensional single-crystal nanosheets have been proposed to reduce these hindrances, while preserving the quantum confinement in one dimension\textsuperscript{46-47, 49, 57-59}. As shown in Figure 1. 6, compared to the charge hopping among PbS quantum dots, charge mobility will be significantly improved on PbS nanosheets due to in-plane transportation.

![Figure 1. 6 Charge transport on PbS quantum dots and PbS nanosheets.](image)

On the other hand, ligand-assisted surface passivation has been confirmed to be an effective strategy to address these problems, as shown in Figure 1. 7. The typical class of surface ligands used for passivating QDs is organic molecules with single function group and a long hydrocarbon chain, e.g., oleic acid. This kind of organic ligands is the most common one used for nanocrystal
synthesis and they can help to form stable colloidal solutions. However, when incorporated with these long chain ligands, the QDs solid was characterized by highly insulating barrier, with conductivity of $10^{-12}$–$10^{-9}$ S/cm\(^6\). Thus, short chain organic ligands were put forward since they can diminish the spacing between QDs and improve electronic transport\(^{10-11, 61}\).

Figure 1. 7 PbS QD with organic and atomic passivation.

There are some other drawbacks by using these organic ligands such as, bulky size, vulnerability to oxidation and thermal degradation. Therefore, inorganic ligands, especially the metal chalcogenide complexes were suggested to replace organic ligands due to the impressive charge mobility enhancement and strong electrostatic repulsion that was required to achieve a stable colloidal dispersion\(^{62-64}\). Besides, Sargent group pushed the inorganic ligand concept further forward by using monovalent inorganic ligands that can be bonded to the cations on QD surface, which effectively enhance electronic transport and passivate surface defects in PbS QD film\(^5\).
Although ligand passivation strategy can increase charge transport efficiency and control QDs stability in solution, the trap states that were formed during QD synthesis cannot be removed by ligand exchange procedure and will act as fast non-radiative quenching channels for photon-generated excitons. One strategy to solve this problem is to grow a shell on the surface of QDs, resulting in the so-called core/shell heterostructure\textsuperscript{65} which can enhance photoluminescence quantum yield and thermal stability of QDs\textsuperscript{49,66-67}, as shown in Figure 1. Another solution could be the treatment of QDs with Triocetylphosphine(TOP) as capping ligands or reagent\textsuperscript{68}. For PbS QDs, oleic acid(OA) typically plays a role as reagent during synthesis and capping ligands that are preferentially bonded to lead atoms on PbS QD surface, which leaves the sulfur atoms unpassivated and forms hole trapping sites\textsuperscript{69}. After the treatment of TOP, the XPS measurements indicate that efficient bonding was established between TOP ligands and sulfur atoms on the surface of PbS QDs\textsuperscript{68-69}.

**Figure 1.8** Formation of PbS/CdS core/shell QD and NS.
1.3 Preparation of nanocrystals by cation exchange

Cation exchange is a process, where the cations in one ionic crystal are replaced by another kind of cations while the anionic framework is preserved\textsuperscript{70-71}. The exchange process occurs by exposing ionic crystals into new cations environment, either in solid or solution status. During the exchange process, the new cations will enter the ionic crystals by diffusion and the original cations will diffuse out of the ionic crystals, into the reaction solvent. As shown in Figure 1. 9 Schematic diagram of cation exchange, taking the reaction between PbS and Cd cations as an example., the Pb atoms in PbS ionic crystal were gradually diffusing out of parent crystal, while the Cd ions that were solvated in liquid environment were entering the crystals, occupying the Pb atom sites. The thermodynamic driving force of the cation exchange reaction is partially determined by the dissociation energy of Pb atoms in parent crystal and the solvation energy of Pb atoms into solvent\textsuperscript{70}. Generally, cation exchange reactions will be much easier going forward when the parent cations (e.g. Pb atoms in PbS ionic crystal) are preferentially solvated in reaction solvent than the environment cations.
Figure 1. Schematic diagram of cation exchange, taking the reaction between PbS and Cd cations as an example.

Due to the high specific surface area and nanometer-scale size of nanocrystals, the reaction kinetics have been dramatically enhanced with the cation exchange reaction at room-temperature and sub-second reaction time. Furthermore, the high surface energy of nanocrystals helps to reduce activation barrier and enable completely reversible cation exchange reactions. Thus, nanocrystals can be employed as reaction templates for synthesis of other nanocrystals and such a templated synthesis strategy has become an alternative to conventional routes for synthesis of specific ionic nanocrystals, especially when the chemical or physical properties of target nanocrystals cannot be obtained by conventional hot-injection method.
1.4 Photoluminescence mechanism of carbon nanodots

Carbon nanodots or carbon dots is a quite new class of carbon nanomaterials that was firstly discovered at 2004 by scientists when they were working on purification of single-walled carbon nanotubes\textsuperscript{81-82}. Generally, carbon dots have the quasi-spherical morphology with typical size of less than 10 nm. Chemically, it is usually made of carbogenic material as the carbon core and an outer shell that was composed of carboxylic or other functional groups\textsuperscript{83}, as in Figure 1.\textsuperscript{10} Carbon dots have many advantageous over traditional semiconductor quantum dots such as, easily functionalized to use in aqueous environment, highly resistance to photobleaching, high bio-compatibility and low toxicity. Therefore, they have already show the great potential in applications such as, sensing\textsuperscript{84-86}, light-emitting diode\textsuperscript{87-90}, drug delivery\textsuperscript{91-94}, and bio-imaging\textsuperscript{95-98}.

\begin{figure}[h]
\includegraphics[width=0.5\textwidth]{carbon_dot.png}
\caption{Diagram of carbon dot.}
\end{figure}

However, the origin and mechanism of excitation-dependent photoluminescence of carbon dots is still under debate\textsuperscript{99-101}. Current respectable mechanisms are: quantum size effect/conjugated sp$^2$ domains of carbon core, surface states due to the hybridization of carbon core and functional groups, and molecule states from fluorescent molecules on the surface or inner of carbon dots\textsuperscript{102}. 

\[ \text{HOOC-(CH}_2\text{-CH}_2)\text{n-CH}_3, \]
\[ \text{CH}_3\text{-CONH-(CH}_2\text{-CH}_2)\text{n-NH}_2 \]
\[ \text{.........} \]
Li et al. prepared carbon dots by electrochemical method, and revealed the strong dependence of photoluminescence properties with carbon dot size, where small size carbon dot exhibits UV light emission while the visible light emission and near-infrared emission are rendered by medium and large size carbon dots. Additional theoretical calculations were performed and the relation between HOMO-LUMO gap and size of graphitic fragments was established, where the energy gap will decrease with the increasing of fragment size. Therefore, Li et al. attributed the excitation-dependent photoluminescence of the as-synthesized carbon dots to the quantum size effect.

Carbon dots are usually attached with various functional groups on their surface, and these functional groups can be excited by certain excitation wavelength, leading to a series of emissive sites. Typically, the extent of surface oxidation can control the population of emissive surface defects, which may cause the red-shifting emission due to the hybridization of carbon bone and related functional groups. Mao et al. prepared carbon nanoparticles by the combustion soot of candles, where they obtained carbon nanoparticles with different emission wavelength by different surface oxidation. Similarly, Zheng et al. proved that the maximum emission wavelength was blue-shifted by chemically reducing carbon dots with NaBH4, while the reduced carbon dots can also be oxidized again by nitric acid and show a red-shifting emission around 520 nm from 440 nm that was typical emission wavelength for the reduced carbon dots.

Attached amine functional groups have been verified to affect the energy gap of surface state in carbon dots. Lin et al. revealed that the amine groups can increase the electron density owing to the presence of lone pair electrons in nitrogen of the amine group, resulting in the reduced energy gap between HOMO and LUMO for surface states in citric-acid-derived carbon dots. Jin et al. have observed the red-shifted emission spectra on graphene quantum dots with amine
groups, and they attributed it to the conjugation between lone-paired electrons on nitrogen and graphene layer. Even though the fluorescence mechanism of carbon dots is not completely understood yet, there is the well-accepted assumption that the origin of emissions is generally from the confined sp2 domains in carbon core and surface states which can be conjugated with sp2 domains and excited by energy transfer from carbon core\textsuperscript{107}.

Molecule states are different from the surface states: surface states in carbon dots are generally the emission centers that were formed due to the synergetic effect between functional groups and carbon core; however, molecules states are the emission centers of organic fluorophore, which can be on the surface or interior of carbon dots and fluorescence by following the Kasha-Vavilov rule. Krysmann et al\textsuperscript{108} investigated the photoluminescence behavior of citric-acid-derived carbon dots. They found that the carbon dots derived at low temperature-180°C exhibit intense photoluminescence spectrum with high quantum yield of ~50% due to organic fluorophore, while the carbon dots synthesized at higher temperature show the weak photoluminescence intensity and low quantum yield because the organic fluorophores were consumed in favor of the growth of carbon core, as shown in Figure 1. 11.
Figure 1.11 schematic representation of the emission characteristics of three photoactive species produced from the thermal treatment of mixture of CA and EA. Blue group-organic fluorophores; carbon core-black sphere; Blue bars-Photoluminescence component from organic fluorophore; Black bars-Photoluminescence component from carbon core. Reprinted with permission from ref.108. Copyright 2012 American Chemical Society.

Additionally, solvent relaxation has also been revealed to be the origin of the excitation-dependent photoluminescence spectra of carbon dots. Nandi et al.109 investigated the spectra behavior of carbon dots in solvents with different polarity, where they found that the energy states formed during the slow solvent relaxation should be responsible for the commonly observed red-shifting photoluminescence spectra.
1.5 References


CHAPTER 2 GROWTH OF COLLOIDAL PbS NANOSHEETS AND THE ENHANCEMENT OF THEIR PHOTOLUMINESCENCE


2.1 Abstract

Dual photoluminescence peaks observed during the synthesis of colloidal PbS nanosheets reveal their growth mechanism – two-dimensional attachments of the quantum dots. Well-grown nano-sheets show the photoluminescence linewidth of 95 meV at room temperature. Aged nanosheets in toluene have enhanced photo-luminescence with intensity improved by an order of magnitude.

2.2 Introduction

Quantum-dot (QD) based optoelectronic devices are limited by low current-density since the charge carrier transfer through the QD film is a low-efficiency hopping process. Making two-dimensional (2D) nanosheets (NSs) can significantly improve the in-plane charge transport while the quantum confinement remains in the direction normal to the plane. On the other hand, the anisotropic dielectric screening also enhances the Coulomb interaction of the excitons in the NSs, which is likely the cause of the high carrier multiplication efficiency. To explore further their novel properties, it is important to have high-quality NSs. However, the synthesis of PbS NSs is still in its early stage. The PbS NSs suffer from their low photoluminescence (PL) efficiency, in contrast to CdSe nanoplatelets which have high PL
quantum yields up to 50%.\textsuperscript{6,7}

To improve the quality of the PbS NSs, understanding their growth mechanism is an important step. Although colloidal syntheses of 2D NSs have been developed in the past decades, the mechanism of the NS growth is not yet well-understood.\textsuperscript{3,6–17} For cadmium salts (CdS, CdSe and CdTe), it is claimed that the anisotropic growth is driven by acetate salts.\textsuperscript{6,7,11} For ZnS, chelating ligands – ethylenediamine – are thought to be critical in the formation of NS.\textsuperscript{18} For other materials such as PbS\textsuperscript{3} and SnSe,\textsuperscript{13} the 2D attachment of QDs plays an important role in the formation of NSs. Particularly, Schliehe and co-workers have demonstrated that the PbS QDs attach to each other through \{110\} facets to form 2D NS.\textsuperscript{3} It is important to understand how the NSs are formed so that a better control of their morphology can be achieved. To investigate the growth mechanism, the reaction is usually stopped at different reaction times, and the products are taken out and imaged using transmission electron microscopy (TEM).\textsuperscript{3}

2.3 Experiments and discussion

In our recent research, PL spectroscopy has been used to study the growth of the PbS NSs and the improvement of their quality. It is demonstrated that the PL of the products are very different at different growth stages of the NSs. Dual PL peaks are observed at intermediate growth stages, indicating the coexistence of the QDs and the NSs. The PL peak corresponding to the QDs is non-shifting and its intensity decreases by growth time, while the PL peak corresponding to the NSs is red-shifting and its intensity increases by growth time. This unique feature of the PL indicates the dynamics of 2D oriented attachment of QDs toward NSs which is also confirmed by TEM measurements of the product at different growth stages. The PL linewidth of the NSs narrows by the growth time. The well-grown NSs have a linewidth (full width at half maximum) as small as 95 meV at room temperature. It is also discovered that the
PL intensity can be enhanced by an order of magnitude after the NSs are aged in toluene for several months. These results reveal a couple of general routes to improve the quality of the NSs.

2.3.1 Synthesis of PbS nanosheets

The synthesis of PbS NSs follows a method similar to the one developed earlier.\textsuperscript{1-3} In brief, a lead precursor is prepared by dissolving lead acetate trihydrate in diphenyl ether and oleic acid. The mixture is degassed and a co-solvent 1,1,2-trichloro-ethane (TCE) is added. Separately, the sulfur precursor is prepared by dissolving thioacetamide in N, N-dimethylformamide and trioctylphosphine under a nitrogen environment. After both precursors are ready, the sulphur precursor is then mixed with the lead precursor at 130 °C to grow PbS NSs. The co-solvent TCE is critical to the formation of NSs. When it is absent, no NS form, only QDs (S1, ESI†). To study the growth of the NSs, the reaction products are taken out at different reaction times and injected into cold toluene solvents to quench the reaction. The products are then precipitated through mixing with a non-solvent (e.g. methanol) and centrifuging to remove the unreacted precursors and the co-solvent. The products are then re-dispersed in tetrachloroethene for the photoluminescence-spectroscopy measurements.

2.3.2 Photoluminescence (PL) spectra of PbS products at different reaction times

Our PL measurements show very different PL spectra at different reaction times (Figure 2.1). The product extracted at 0.5 minute after mixing the lead and sulphur precursors shows a PL peak at around 780 nm, but no other PL peak at longer wavelengths. At 1-minute reaction time, two distinct PL peaks are observed: one is at 840 nm and the other is at 1420 nm. At 2 minutes reaction time, similar dual PL peaks are observed and the PL peak at the longer wavelength shifts to 1580 nm. At 3 minutes reaction time, the PL peak at short wavelengths is
nearly negligible while a strong PL peak at 1600 nm appears.

**Figure 2.** PL spectra of the products extracted at different reaction times: 0.5 minute (circles), 1.0 minute (squares), 2.0 minute (diamonds), 3.0 minute (solid line), 5.0 minute (dashed line) and 7.0 minute (dotted line). Inset, a zoomed in view of the PL peaks at long wavelengths for the products at the reaction times of 1 and 2 minutes.

After 3 minutes, the short-wavelength PL peak is nearly negligible and the long-wavelength PL peak shifts to 1720 nm. The intensity ratio of the long-wavelength PL to the short-wavelength PL increases significantly from 2 minutes to 3 minutes reaction time, indicating a dramatic change in the crystal morphology. The PLs at 5 minutes and 7 minutes reaction times have nearly identical peak wavelengths, indicating there is no major change in the energy gaps of the products.
2.3.3 Transmission Electron Microscopy (TEM) characterization of PbS products at different reaction times

The corresponding TEM images of the product at each growth stage are taken to reveal the change of the structures. At around the reaction time of 0.5 minute, the TEM image shows that the main products are QDs (Figure 2.1a). At around 1 minute, both porous NSs and QDs appear (Figure 2.1b). At around 3 minutes, the number of QDs is significantly reduced. Instead, porous sheets form (Figure 2.1c). After 7 minutes of reaction time, the majority of the NSs become uniform while no isolated QDs are observed (Figure 2.1d).
Figure 2. TEM images of the products after reaction time of (a) 0.5 minute, (b) 1 minutes, (c) 3 minutes, and (d) 7 minutes. (a) The main products are QDs. Inset, a HRTEM image shows a QD with diameter of 2.7 nm (scale bar 2 nm). (b) Attached and isolated QDs coexist. (c) QDs are barely seen while porous NSs formed. (d) Uniform and smooth NSs formed. Morie patterns observed at the overlap of two or more NSs, indicating a good crystallinity of the NSs.
2.3.4 Bandgap comparison between PbS nanosheets and PbS quantum dots

The PL and TEM results are consistent based on the quantum-confinement model developed for the QDs$^{19}$ and NSs.$^1$ The product at 0.5 minute reaction time is mainly QDs with diameter around 2.7 nm as confirmed by high-resolution TEM imaging (Figure 2.1a, inset). QDs of this size have energy gap of 1.9 eV according to the four-band model (Figure 2.3).$^{19,20}$
Figure 2.3  The energy gap dependence of a QD on its diameter calculated by 4-band model based on k·p theory (solid line),19,20 and the energy gap dependence of a NS on its thickness fitted from experimental data (dashed line).1 The solid circle indicates the QDs of 2.7 nm in diameter formed at the beginning of the reaction. The solid square indicates the NSs formed at the end of the reaction. The dotted line indicates the energy gap of a PbS bulk at room temperature.
It predicts an optical absorption peak at around 655 nm, as confirmed by our measurement (Figure S2.2, ESI†). The corresponding PL peak appears at 780 nm (Figure 2.1) due to Stokes shift. At 7 minutes reaction time, the product is mainly NSs. Their thickness is around 2.2 ± 0.5 nm as measured by atomic force microscopy (Figure S2.3, ESI†). According to our model developed recently (\(E_{\text{gap}}\): energy gap in eV of the NSs; \(L\): the thickness in nm of the NSs; \(E_{\text{gap}}(\infty)\): energy gap of the bulk PbS at room temperature ~0.41 eV),

\[
E_{\text{gap}}(L) = E_{\text{gap}}(\infty) + \frac{1}{0.99L + 1.18},
\]

the energy gap is predicted to be 0.71 eV (Figure 2.3). It is corresponding to a PL peak around 1750 nm (for NSs, the Stokes shift is negligible1). This is the same as what was observed in the PL spectra (Figure 2.2) within the experimental error. The thickness of the NSs (2.2 nm) is slightly less than the diameter of the QDs (2.7 nm), which is due to the surface reconstruction and filling of the gaps among the 2D attached QDs.3 At the reaction time between 0.5 minute and 7 minutes, the structures of the PL spectra are more complicated (Figure 2.2), corresponding to the complicated structures (Fig. 1b and 2c) of the intermediate products during the reaction. The PL peak at short wavelengths around 820 nm is nearly non-shifting from 0.5 minute to 2 minutes reaction time, indicating that the QDs do not grow by time. This feature during the formation of PbS QDs has also been observed and reported in the literature.3,21 The short-wavelength PL is nearly negligible at the reaction times of more than 3 minutes. This non-shifting but diminishing PL rules out the continuous 2D-growth model, since a continuously red-shifting PL peak would be otherwise observed. Starting at 1-minute
reaction time, a second PL peak at longer wavelengths appears. It starts at 1420 nm at 1 minute, shifts to 1580 nm at 2 minutes, 1600 nm at 3 minutes and 1720 nm at 5 minutes. The red-shifting of the long-wavelength PL peak is accompanied by the intensity-decreasing and vanishing of the short-wavelength PL peak, indicating the formation of the NSs through consuming of the QDs. The TEM images confirm this growth dynamics. At 1-minute reaction time, both QDs and NSs are observed. At and after 3 minutes, few QDs are observed in TEM images (Figure 2.1c and Figure 2.2d). The TEM images also reveal that the product changes from connected QD networks to porous NSs and finally to uniform NSs by reaction time. This explains the red-shifting of the long-wavelength PL peak. When the QDs are connected with each other, the wave functions of the electrons or holes are less confined since they extend to neighbour QDs. Consequently, the energy gaps decrease. This decrease of the energy gap is reflected in the red-shifting of the PL peak as reported for PbS QDs and PbSe QDs. For small QDs which have a diameter as small as 2.7 nm in our experiments, the energy-gap reduction is very significant. This explains the two distinguished peaks appeared in the PL spectra at the reaction time of 1 or 2 minutes. The quantum confinement decreases further when the gaps among the attached QDs are filled until uniform and smooth NSs are formed.

2.3.5 PL linewidth narrowing and enhancement of PL intensity

During the growth of the NSs, the PL linewidth narrows as well as the PL peak shifts toward longer wavelengths. To better understand this PL linewidth narrowing, another series of syntheses have been conducted. In these series of syntheses, the reactions are slightly faster than those shown in Figure 2.2. All the PL peaks are more
red-shifted than those shown earlier. These slight differences are commonly seen from one synthesis to the other, which are probably caused by slightly different reaction conditions in different syntheses. The products at the reaction time of 1, 3, and 7 minutes are analysed using PL spectroscopy. This width (full width at half maximum) of the PL peak narrows down from 150 meV (1-minute reaction time) to 95 meV (7 minutes reaction time) as shown in Figure 2. 4a.

**Figure 2. 4** (a) PL spectra of the products at the reaction times of 1 minute (squares), 3 minutes (diamonds) and 7 minutes (triangles). (b) PL spectra of the as-synthesized PbS NSs at the reaction time of 7 minutes (solid squares) with their PL intensity multiplied by 10 and the same NSs after aging in toluene for ten months (solid circles).

The corresponding ratio of the width to the central photon energy decreases from 19% to 15%. The origin of the PL linewidth remains an open question. The polydispersity of the thickness might contribute to the linewidth. Nevertheless, the linewidth of a single PbS QD was measured to be in the order of 100 meV. It was attributed to enhanced acoustic phonon coupling in strongly quantum confined QDs.
Since the PL linewidth of the NSs is close to that of a single PbS QD, it is likely the linewidth of 95 meV is an intrinsic width of the material. The dispersity of the thickness of NSs might not be the main contribution to the PL linewidth.

The as-synthesized PbS NSs have a low PL efficiency. It is probably due to the large lateral size of each NS which make the overall number of defects significantly large even when the defect density is low in each NS. The PL efficiency is significantly reduced since any defect in a single nanosheet can trap the excited charges and quench the PL. However, the PL intensity of the NSs is enhanced by an order of magnitude (Figure 2. 4b) after ten-month aging in toluene (Figure S2. 4, ESI†). The enhancement of the PL is likely due to the surface annealing which reduces the surface defects and trap sites, as observed in colloidal PbS QDs.\textsuperscript{27,28} It is also noticed that the PL peaks of the aged NSs shift to shorter wavelengths (Figure 2. 4b and Figure S2. 4, ESI†). The spectral blue-shift suggests a decrease of the average NS thickness, similar to the trend observed in colloidal PbS QDs.\textsuperscript{26} The PbS NSs with an improved quality are important for further studies using transient PL and optical absorption spectroscopies.

2.4 Conclusion

The non-shifting but diminishing PL peak at around 820 nm and the red-shifting peak from 1420 nm to 1720 nm observed during the reaction explain well the growth mechanism of the NSs. That is, the QDs formed at the beginning of the reaction do not grow afterward but attach to each other to form a two-dimensional sheet. The narrowing of the PL peak at long wavelengths also reveals that the porous NSs formed by QDs are getting smoother and more uniform in size as the gaps are filled and the surface atoms reconstruct. Aging of the NSs in toluene enhances their PL by an order
of magnitude as well as shifting the PL peaks toward shorter wavelength, which is attributed to the surface annealing. Well-grown NSs show PL linewidth about 100 meV at room temperature. The PL spectroscopy reveals the growth mechanism confirmed by TEM, and provides spectroscopic signatures of the NS growth. Due to the non-contact, non-invasive nature of the optical spectroscopy, it can also serve as an in situ approach to monitor the NS growth.
2.5 Supporting information

2.5.1 Control syntheses without cosolvent 1,1,2-trichloroethane

The lead precursor is prepared by dissolving lead acetate trihydrate (860 mg) in diphenyl ether (10 mL) and oleic acid (OA) (3.5 mL). The mixture is degassed for two hours at 85 oC. Then, the sulfur precursor is prepared by dissolving thioacetamide (0.012 g) in N, N-dimethylformamide (70 μL) and trioctylphosphine (930 μL) under nitrogen environment. After both precursors are ready, the temperature of the lead precursor is raised to 130 oC. The sulfur precursor is then injected into the flask to mix with the lead precursor, while the reaction solution is kept stirring. After 0.5 minute, 1 ml of the reaction solution is taken and injected into cold toluene. As the reaction proceeds, another four 1ml aliquots of reaction solution are also taken at 1, 2, 3, and 5 minutes then injected into cold toluene to quench the reaction. The products are dispersed in methanol and then precipitated via centrifugation. The precipitated NS/QD mixtures are then re-dispersed in toluene.
Figure 2. SF1, TEM images of the products at the reaction times of 0.5, 1, 2, 3, 5 minutes while the co-solvent 1, 1, 2-trichloroethane is absent.
2.5.2 PL and optical absorption of the products at reaction time of 0.5 minute

Figure 2. SF2 Optical absorption spectrum (black) and photoluminescence spectrum (red) of the product at the reaction time of 0.5 minute.

2.5.3 Atomic force microscopy – sample preparation and thickness measurements

Silicon wafers were cleaned by sonication in acetone, rinsed with methanol and distilled water, and dried by blowing with high purity nitrogen gas. To prepare the AFM sample of the NSs with their original OA capping ligands, the wafer was directly dipped into the NS solution for one hour, and then dried in air. To prepare the AFM sample of the NS with 3-mercaptopropionic acid (MPA) capping ligands, the wafers were dipped into a solution of acetonitrile dissolved with MPA (0.01 M) and then into a NS solution. The NSs were then attached to the substrate through the linker molecules MPA. The rest OA ligands were then replaced by short MPA ligands by dipping the film into the MPA-acetonitrile solution again. The excess MPA was then removed by dipping the substrate in acetonitrile.

AFM images were recorded in the AC mode under ambient conditions. A closed-loop multipurpose AFM scanner (Agilent 5500 SPM Microscope, Agilent technologies) and a VistaProbes AFM tip (Nanoscience Instruments) with 48 Nm⁻¹ spring constant and ~190
kHz resonant frequency were used in the measurements. The system was calibrated using standard grading sample for AFM. The average and standard deviation of the thickness are calculated through statistics of more than fifty height profiles. The measured thickness of the NSs is 2.2 ±0.5 nm.

![AFM image and one height profile of the nanosheets.](image)

**Figure 2. SF3** The AFM image and one height profile of the nanosheets.

2.5.4 Enhancement of PL of the PbS NSs after aging in toluene

After each synthesis, the PbS NSs were purified and dispersed in toluene and stored in a sealed glass vial. A small part of the NSs were taken out of the storage vial, dried by N2-purging and re- dispersed in 1,1,2,2-tetrachloroethane for PL measurement. The rest of the NSs were kept in toluene for 10 months and then a small part of the NSs were taken out for PL measurement in exactly the same way as before. The PL peaks from the NSs synthesized for 3, 5 and 7 minutes reaction times shift to shorter wavelengths after aging in toluene and the corresponding PL intensity enhanced by a factor of 9, 28 and 13, respectively. The PL spectrum of each sample was taken under the same condition. For each reaction time, the samples were prepared under the same parameters to ensure that NS concentration was nearly identical. The exciting light source, the spectroscopy system
and the detector remain the same for all the measurements. All the contributions to the uncertainty of the PL intensity are estimated to be less than 100%. Therefore, the enhancement of the PL by an order of magnitude can only be attributed to the improvement of the intrinsic quality of the NSs.
Figure 2. SF4 PL spectra of the as-synthesized PbS NSs after reaction time of (a) 3 minutes, (c) 5 minutes and (e) 7 minutes, and the same NSs [(b) 3 minutes, (d) 5 minutes, (f) 7 minutes] after aging in toluene for 10 months.
2.5.5 Spectrum of the light source in PL measurements

The spectrum of the excitation light source is shown below. Multiple laser lines are observed in the wavelength range 450 nm ~ 525 nm. This excitation laser light, however, is blocked by an optical long-pass filter before the light from the sample enters the spectrometer. This technique prevents the excitation light from interfering with the PL spectra.

Figure 2. SF5 Spectrum the laser (Reliant laser from Laser Physics) used as the light source for PL measurements.
2.6 References


CHAPTER 3 FEW-ATOM-THICK COLLOIDAL PbS/CdS CORE/SHELL NANOSHEETS


3.1 Abstract

Emissive PbS/CdS core/shell nanosheets are synthesized using a cation-exchange method. A significant blue-shift of the photoluminescence is observed, indicating a stronger quantum confinement in the PbS core as its thickness is reduced. High resolution transmission-electron-microscopy images of the cross sections of the core/shell nanosheets show atomically sharp interfaces between PbS and CdS. Accurate analysis of the thickness of each layer reveals the relationship between the energy gap and the thickness in the extremely one-dimensionally confined nanostructure. Photoluminescence lifetime of the core/shell nanosheets is significantly longer than the core-only nanosheets, indicating better surface passivation.

3.2 Introduction

Quantum confinement is the origin of the novel properties of quantum dots. However, three-dimensional confinement also hinders the charge transfer among the quantum dots, which limits the performance of the quantum dot-based electronic devices. In a two-dimensional (2D) structure, the charges within the 2D plane have high charge mobilities\(^1,\)\(^2\) while the one-dimensional quantum confinement is retained in the thickness direction. Consequently, the tunable optical properties and the high charge mobility are unified in a single structure. Among the artificial 2D materials, IV–VI nanosheets are particularly interesting. Due to the large exciton Bohr radii in lead salts, strong quantum confinement can be easily achieved.\(^3\) The small energy gaps of the IV–VI
semiconductors are also optimal to exploit carrier multiplication in solar cells. As recently demonstrated in colloidal PbS nanosheets, 4D structures of these materials can increase carrier multiplication efficiency which correlates with the enhanced electron–hole Coulomb interaction in the anisotropic structure. In addition, the spin–orbital coupling is strong in IV–VI materials. 6,7 When it interplays with quantum confinement in the 2D structure, a new class of material, topological crystalline insulators, can be created. 8 These materials have surface states that exhibit linear dispersion with a single Dirac cone, and charge transfer in the surface states is protected against backscattering by crystal symmetry. 9–11 These surface states can be more easily observed in 2D structures due to their large surface-to-volume ratio. 12–16 These novel properties are critical for low-dissipation devices, superconductors, and quantum computers. 17,18 So far, theoretical work has predicted that a series of 2D IV–VI materials including SnTe, 9,19 PbS, 9–11 PbSe, 8,9 and PbTe, 9,19 can be turned into topological crystalline insulators through tuning the thickness, 9 exerting a strain, 11 or applying an electric field. 10 These properties are mainly determined by size (quantum confinement), shape (anisotropy of spatial and dielectric confinement), and crystal heterostructures (strain). Creation of thickness tunable core/shell 2D nanosheets can partially address the challenges.

A wet-chemistry synthesis of colloidal nanosheets 1,20–26 followed by cation exchange will create such structures. The synthesized colloidal nanosheets are counterparts of the epitaxial quantum wells 27 but are free-standing and have low-cost (since no high-vacuum or high-temperature is needed for the synthesis). 28 In this Article, we report a facile synthesis of emissive PbS/CdS core/shell nanosheets with emphasis on the energy-gap tunability. We demonstrate that the energy gap of the PbS core can be systematically tuned from 0.75 to 0.93 eV through changing the reaction conditions. The tunable energy gap, while combined with the strong spin–orbit interaction in PbS, provides an opportunity to tune the topological property of the material. 8 High resolution
transmission electron microscopy (HRTEM) images of the cross-section of the nanosheets show clear crystal interfaces between PbS and CdS. It also provides an alternative method that can precisely determine the thicknesses of the PbS core and the CdS shell of the 2D heterostructure as well as the pure PbS nanosheets, while avoiding the effect of capping ligands or the fitting errors in the thickness determination using atomic-force microscopy or X-ray diffraction. It will help to resolve a debated problem, the energy gap dependence on the thickness of the nanosheets, which is partially due to the difficulty in measuring the thickness accurately. Photoluminescence lifetime of core/shell nanosheets is significantly longer than the core-only nanosheets, indicating a better surface passivation. The core/shell structures with improved surface properties are important for further multiple-exciton-generation study. The strain introduced at the interface of PbS and CdS alters the electronic structure of PbS and may create a topological crystalline insulator as theoretically predicted.

3.3 Experiments and discussion

3.3.1 Synthesis of PbS nanosheets and PbS/CdS core/shell nanosheets

The synthesis of PbS nanosheets (Supporting Information A) is based on the methods invented by Weller’s group and developed by others. After PbS nanosheets are synthesized and purified, a cation-exchange method is used to exchange the outer layer Pb ions with Cd ions to form a CdS shell surrounding the PbS core. In brief, cadmium oxide is mixed with oleic acid and heated under nitrogen to form cadmium oleate, which is then mixed with PbS nanosheets for the cation-exchange reaction. The reaction is stopped by adding cold hexane. The final solution is washed twice with toluene and finally dispersed in toluene (Supporting Information A). This method does not change the overall thickness of the nanosheets but rather reduces the thickness of PbS core (Figure 3. 1a).
Figure 3. 1 (a) Scheme showing the process of cation exchange for the PbS/CdS structure. The overall dimension of the sheet remains the same while the out-layers of the material turn into CdS. (b) Photoluminescence spectra from the nanosheets before (open circles) and after (solid circles) cation exchange showing the shift of the peak from 1760 to 1520 nm. (c) TEM image of the stacked original PbS nanosheets. Each nanosheet has a lateral size of a few hundred nanometers. (d) TEM image of the stacked nanosheets after cation exchange showing a similar morphology as in (c).

3.3.2 Structural and morphology of PbS nanosheets and PbS/CdS core/shell nanosheets

The transmission electron microscopy (TEM) images (Figure 3. 1c, d) and secondary-electron images (Supporting Information B) show that the morphology of the nanosheets remains the same after cation exchange. However, there is a significant blue-shift (Figure 3. 1b) of the photoluminescence (Supporting Information C), indicating the decrease of the thickness of the PbS core. Further energy-dispersive X-ray spectroscopy measurements show a clear Cd peak after cation exchanges (Supporting Information D). To learn the details of the heterostructure formed
in PbS/CdS nanosheets, it is essential to prepare the nanosheets standing on edge so that the cross sections of the nanosheets can be imaged using HRTEM. To achieve this goal, small lateral-size nanosheets having a width of around 20 nm are synthesized using a modified procedure (Supporting Information A). The narrow width of the nanosheet makes it easy for them to stand up on the TEM substrate (Figure 3. 2a).

**Figure 3. 2** (a) TEM image of PbS nanosheets showing both standing-up and lying-down nanosheets. (b) The HRTEM image of one standing-up nanosheet shows a single-crystalline structure with 12 layers of atoms in the thickness direction. (c) Diagram showing the arrangement of the atoms viewed in the \(\langle 110\rangle\) direction of the crystal. (d) In the thickness direction, the spacing between the neighbor atoms a is 0.297 nm, while in the orthogonal direction, the spacing between the neighbor atoms b is 0.42 nm. The angle \(\alpha\) is about 55°.

The HRTEM image (Figure 3. 2b) shows an array of dots which is the projection of the atoms in the nanosheets onto the substrate. This image reveals that the surfaces of the nanosheets
are nearly atomically flat. The standing-up PbS nanosheets show a single crystal structure with 12 atomic layers in the thickness direction. The thickness can be calculated by multiplying the lattice constant of PbS ($c = 0.594 \text{ nm}$) by the multiple of lattice constant the thickness spans (5.5), resulting in a thickness determination in this case of 3.27 nm. This thickness matches that obtained ($3.3 \pm 0.1 \text{ nm}$) using the calibrated HRTEM instrument (Supporting Information E). The dependence of the energy gap on the thickness of the PbS nanosheets is still under debate,$^{4,21,29}$ partially due to the difficulty of the thickness measurements. Since the nanosheets can be prepared standing-up on the substrate, their thickness can be accurately measured without ambiguity.

All of the observed cross sections of the nanosheets show the same facet as in Figure 3. 2b. For the projection of {110} facet of PbS crystal (Figure 3. 2d), the spacing between neighbor atoms in the (001) direction is $a = c/2 = 0.297 \text{ nm}$, while the spacing between the neighbor atoms (within the same plane) in the orthogonal direction (110) is $b = c/\sqrt{2} = 0.420 \text{ nm}$. The angle $\alpha$ (Figure 3. 2d) between the line of the same atoms and (110) direction is then 55° (Supporting Information F). All of the parameters $a$, $b$, and $\alpha$ as measured using HRTEM (Figure 3. 2c) match up with the calculated results above. This confirms the observed surface of the nanosheet edge has a {110} facet and the top/bottom surfaces of the nanosheet have a {001} facet. This result is consistent with the earlier 2D oriented attachment model$^{21}$ for the growth mechanism of 2D PbS nanosheets; i.e., the PbS quantum dots attach to each other through {110} facets, resulting in {110} facets at the edges of the nanosheets.

The same PbS nanosheets are used to synthesize PbS/CdS core/shell nanosheets. After cation exchange, the core/shell nanosheet shows atomically sharp interfaces between PbS and CdS (Figure 3. 3). The PbS core has about 8 atomic layers, indicating $\sim$2 atomic layers of PbS have
been turned into CdS on each side of the nanosheet, reducing the thickness of the PbS core to 2.1 nm as measured with HRTEM (Supporting Information E).

![HRTEM image showing sharp interfaces between the PbS core and the CdS shell.](image)

**Figure 3.** HRTEM image showing sharp interfaces between the PbS core and the CdS shell. The crystal structure of the CdS shell is similar to the PbS core. The lines are to guide the eyes to the array of atoms, making an angle $\alpha$ unique to the \{110\} facet.

The HRTEM image (Figure 3. 3) of the cross-section of the PbS/CdS nanosheet shows a \{110\} facet as in the original PbS nanosheet (Figure 3. 2c). At some locations, the crystal structure of the CdS shell remains nearly the same as the PbS core as in the case of core/shell PbS/CdS quantum dots,\(^32\) while it appears amorphous at other locations (Figure 3. 3). The PbS/CdS heterostructure is clearly revealed by the sharp contrast in the HRTEM image, which is due to the high atomic weight ratio Pb/Cd.

At the \{100\} facets (top/bottom surfaces) of the PbS nanosheet, the interfaces between PbS and CdS are nearly atomically flat, indicating that the cation exchange occurs uniformly from the surface into the bulk of the nanosheet. This differs from what was observed in PbSe/CdSe nanorods,\(^33\) for which a zigzag-shaped core terminated by \{111\} interfaces formed. The reaction
temperature is believed to play a key role in achieving uniform cation exchange. On the other hand, smaller surface to volume ratios in 2D sheets in contrast to 1D nanorods likely favor a uniform cation-exchange. Similar work by Dubertret and co-workers demonstrated that flat interfaces formed after cation-exchanges in PbSe/PbS, CdSe/CdS, and ZnSe/ZnS nanoplatelet.\textsuperscript{34} At the \{110\} facets (edge surfaces) of the PbS nanosheet, the CdS shells are significantly thicker than the shells at \{100\} facets and the PbS/CdS interface is less sharp (Figure 3. 3), which is likely due to the high reactivity of the \{110\} facets.\textsuperscript{21} The element mapping of the vertically aligned PbS/CdS core/shell nanosheets shows the same image for Pb, Cd, and S elements, and each of them overlaps with the high-angle annular-dark-field image (Supporting Information G). It reveals that the cation exchange occurs non-selectively. At this time, the resolution of the element mapping is not high enough to map out the elements layer by layer, but the element analysis over the ensemble of the nanosheets shows the molar ratio of lead (Pb) to cadmium (Cd) is around 2.4:1 (Supporting Information G). It is consistent with the HRTEM analysis: around 8 layers of PbS versus 4 layers of CdS.
3.3.3 Tuning thickness and bandgap of PbS nanosheets and PbS/CdS core/shell nanosheets

Figure 3.4 (a) The photoluminescence peak shifts from 0.75 to 0.80 eV after cation exchange for 3 min at 100 °C. It shifts to 0.83 eV after 15 min. After that, longer reaction times (60 and 120 min) do not shift the peak more but stabilize it between 0.84 and 0.85 eV. Further increase of the reaction temperature to 150 °C shifts the peak to 0.93 eV after an additional 60 min cation exchange. (b) Comparison of the energy-gap of the nanosheets (solid dots), the nanosheet model developed earlier (solid line)29 and PbS quantum dots (dashed line).35 The arrow indicates the data from PbS/CdS core/shell nanosheets obtained through cation exchange from the 3.3 nm thick PbS nanosheets (the rightmost dot).

The PbS/CdS nanosheets fluoresce in the infrared as the original PbS nanosheets,29 in contrast to nonemissive ZnSe/ZnS and PbSe/PbS core/shell nanoplatelets.34 Those nanoplatelets were created using two-step cation-exchange: CdSe/CdS to Cu2Se/Cu2S and then to ZnSe/ZnS or PbSe/PbS. The excess trap sites formed by the residue copper atoms were thought to quench the photoluminescence.34 Our emissive nanosheets help to determine the optical energy gap, since the Stokes’ shift is negligible for PbS nanosheets29 as well as for PbS/CdS nanosheets (Supporting Information H). The photoluminescence of the core/shell nanosheets shows a significant blue-shift
as compared with the original PbS nanosheets (Figure 3. 4a), indicating stronger quantum confinement due to the decrease of the core thickness after cation exchange. At 100 °C reaction temperature, the photoluminescence shift mainly occurs within 15 min after reaction. The shift is small beyond 15 min, indicating that the cation-exchange process is self-limiting at a certain reaction temperature (Figure 3. 4a). However, increase of the reaction temperature can further the cation exchange, resulting in more blueshift of the photoluminescence peak (Figure 3. 4a). So far, we have achieved tunability of the photoluminescence peak in PbS/CdS core/shell nanosheets from 0.75 to 0.93 eV, corresponding to the wavelength range from 1333 to 1653 nm. For the small-lateral-size PbS nanosheets, the optical energy gaps obtained from photoluminescence spectroscopy and the thicknesses obtained using HRTEM are plotted together in Figure 4b. The data points are slightly above the fitting curve obtained previously.29 The slightly larger energy gap is likely due to the additional confinement in the width direction since the width of the nanosheets is about 20 nm which is close to the exciton Bohr radius of PbS. After cation exchange, the decrease of the PbS thickness results in a larger energy gap. The relationship between the energy gap and the thickness is consistent with these obtained from core-only PbS nanosheets (Figure 3. 4b). As expected, the confinement energy in either the PbS nanosheets or PbS/CdS core/shell nanosheets is much less than in quantum-dots with the diameter equal to the thickness of the nanosheets. This is mainly due to the difference of 3D confinement (QDs) and 1D confinement (nanosheets).29

The average thickness of the PbS core (so is the CdS shell) can be precisely tuned by the reaction conditions. The accuracy of the thickness, as can be derived from the photoluminescence peak (Figure 3. 4), reaches a sub-nanometer level.
At a higher reaction temperature (150 °C), thinner (2.1 nm) PbS nanosheets can be nearly completely turned into CdS nanosheets. The photoluminescence peak around 1540 nm corresponding to the original PbS nanosheets disappears completely but a peak at 430 nm appears. Energy-dispersive X-ray spectroscopy confirms the amount of Pb in the product is negligible (Supporting Information I).

3.3.4 Photoluminescence lifetime of PbS nanosheets and PbS/CdS core/shell nanosheets

![Photoluminescence lifetimes of PbS and PbS/CdS nanosheets](image)

**Figure 3.5** Photoluminescence lifetimes of the PbS (solid circles) and PbS/CdS (open circles) nanosheets. Each lifetime is measured at the peak intensity of the photoluminescence, 0.75 eV for PbS nanosheets and 0.83 eV for PbS/CdS nanosheets. The solid lines passing through the data points are the fitting curves. The system response function (SRF) is also shown.

Creation of the core/shell structure also increases the lifetime of the photoluminescence (Supporting Information J) from the PbS core. The decay of the photoluminescence intensity from the nanosheets is not single-exponential. The 1/e photoluminescence intensity occurs at 4 and 7 ns for PbS nanosheets and PbS/CdS nanosheets, respectively (Figure 3.5). The nearly doubled decay
time in the core/shell nanosheets is likely due to a better surface passivation of the PbS core after cation exchange, instead of type II heterostructure (Supporting Information K). It is consistent with the improved photoluminescence intensity (normalized to absorption) from the core/shell nanosheets (Supporting Information L). Aging of the PbS nanosheets in toluene was demonstrated recently to improve the photoluminescence efficiency by an order of magnitude. The mechanism in this experiment is different, but both methods have significantly improved the optical properties of the nanosheets. The photoluminescence decay can be fitted well using double exponential functions, yielding a fast decay of 2.9 ns (core only) and 4.9 ns (core/shell) and a slow decay of 30 ns (core only) and 51 ns (core/shell). The nature of the double-exponential decay of the photoluminescence intensity is still under investigation. In contrast to PbS quantum dots, PbS nanosheets and their core/shell structures have much shorter photoluminescence lifetimes. It is likely that the reduced dielectric screening in the 2D structure shortens the lifetime, as demonstrated by Ithurria and coworkers on CdSe nanoplatelets. Surface defects can also shorten the photoluminescence lifetime by creating nonradiative decay channels. However, their effect can be reduced by surface-passivation methods, among which creating a CdS shell on the PbS core is an effective one, as demonstrated above.

It has been demonstrated that the strain between the PbS core and the CdS shell exists in PbS/CdS core/shell nanocrystals. It is expected that the strain also exists in PbS/CdS core/shell nanosheets, which will alter the electronic structure of the core, providing an additional parameter to tune the topological properties of the nanosheets. However, the strain effect is only significant at the PbS layers which are close to the PbS/CdS interface. We expect to see the effect when the PbS core has only one to two atomic layers. The range of the thickness tunability shown earlier
has not yet reached that region, so the electronic structure of PbS is still mainly determined by the thickness.

3.4 Conclusion

In summary, a facile synthesis of PbS/CdS core/shell nanosheets is developed. The core/shell heterostructure synthesized using cation-exchange methods has an increased energy gap and a longer photoluminescence lifetime. Proper preparations of standing-up nanosheets enable accurate characterizations of the core/shell crystal structures as well as their thicknesses. The HRTEM reveals that the interface between PbS and CdS is nearly atomically flat. It is expected that this method can be used to create thinner (less than 8 atomic layers) PbS sheets capped by CdS using thinner original PbS nanosheets and/or adjusting the reaction conditions. In these extremely thin core/shell nanosheets, novel electronic properties (e.g., topological properties) may occur as theoretically predicted. On the other hand, the improved optical properties are also important for further studies on the exciton dynamics in the 2D materials.
3.5 Supporting information

A) Synthesis procedures for PbS nanosheets and PbS/CdS core/shell nanosheets

The lead precursor is prepared by dissolving lead acetate trihydrate (860 mg) in diphenyl ether (10 mL) and oleic acid (3.5 mL) under nitrogen flow. The mixture is degassed for two hours at 85 °C. Then, 1 mL of 1,1,2-trichloroethane is added at the temperature 106 °C. Separately, the sulfur precursor is prepared by dissolving thioacetamide (0.012 g) in N,N-dimethylformamide (70 μL) and trioctylphosphine (930 μL) under nitrogen environment. After both precursors are ready, the temperature of the lead precursor is raised to 130 °C. The sulfur precursor is then injected into the flask to mix with the lead precursor, while the reaction solution is kept stirring. After five minutes, the reaction solution is then slowly cooled down to room temperature. The product is dispersed in toluene and then precipitated by centrifuging. The precipitated nanosheets are then re-dispersed in toluene.

To synthesize nanosheets with small lateral dimension, nitrogen flow is skipped during the preparation of lead precursors at the very beginning of the synthesis while other procedures are kept the same.

To synthesize PbS/CdS core/shell nanosheets, 1 gram of cadmium oxide (molar ratio Cd:Pb=23:1) is added to 6 mL of oleic acid and 16 ml of diphenyl ether. The solution is heated to 255 °C under nitrogen, and then cooled down to 155 °C. In another 3-neck flask, PbS nanosheets are kept under nitrogen at 100 °C. After the temperature reaches 155 °C, cadmium precursor is added to PbS nanosheets to react for 15 minutes, 30 minutes, 1 hour and 2 hours. After the reaction time, the final solution is added with cold hexane to stop the reaction and centrifuged at a speed of 2500 rpm for 5 minutes. The precipitated nanosheets are washed a few times with toluene and
finally dispersed in toluene. To learn the details of the cation-exchange process, different reaction conditions are used. For instance, higher reaction temperature 150 °C is used to create thinner PbS core; less cadmium oxide (0.022 gram, molar ratio Cd:Pb=0.5:1) is used to study the effect of Cd-ion concentration on the cation-exchange dynamics.

B) Secondary-electron microscopy images of nanosheets

Secondary-electron microscopy images of PbS nanosheets (a) and PbS/CdS core/shell nanosheets (b) were taken using the Hitachi HD-2300 Scanning Transmission Electron Microscope. The images show the same topographies of PbS nanosheets and PbS/CdS core/shell nanosheets that are both stacked.

![Secondary-electron microscopy images of nanosheets](image)

**Figure 3. SF1** Secondary-electron microscopy images of nanosheets

C) Photoluminescence (PL) measurements

The PL measurements are done using a home-built PL spectroscopy system. It includes an argon ion laser (Reliant 150M, Laser Physics), a monochromator (Acton SP-2357 Monochromator, Princeton Instrument) and an IR detector (PDA30G, Thorlabs). The spectral response of this apparatus is calibrated using a 20 W quarts-tungsten-halogen lamp (Newport Corporation). The
synthesized NSs dispersed in tetrachloroethene are transferred to a quartz cuvette (Starna Cells, Inc) for the PL measurements.

**D) Energy-dispersive X-ray spectroscopy (EDX)**

The energy-dispersive X-ray spectroscopy was measured in situ using an EDX detector mounted on the Hitachi HD-2300 Scanning Transmission Electron Microscope. The spectra show additional Cd peak after cation exchange.

![Energy-dispersive X-ray spectroscopy (EDX) of PbS/CdS nanosheets.](image)

**Figure 3, SF2** Energy-dispersive X-ray spectroscopy (EDX) of PbS/CdS nanosheets.

**E) Thickness measurements**

The thicknesses of PbS are measured using ImageJ (an open source image processing program designed for scientific multidimensional images) based on the HRTEM images of the cross-sections of the nanosheets. The statistical histograms of the thickness of the PbS nanosheets (a) and the thickness of the PbS core in PbS/CdS core/shell nanosheets (b) are shown below.
Figure 3. **SF3** Thickness measurements of PbS and PbS/CdS nanosheets.

F) Geometry of the \{110\} facet of PbS

\[ \alpha = \tan^{-1}\left(\frac{c}{b}\right) = \tan^{-1}\left(\frac{c}{(c/\sqrt{2})}\right) = 54.7^\circ \]

Figure 3. **SF4** Geometry of the \{110\} facet of PbS.

G) STEM and element mapping
The scanning/transmission electron microscope (STEM) characterizations were performed on 3 mm copper grids dispersed with the nanoparticles by using a FEI Talos F200 S/TEM, which was equipped with a field emission gun and was operated at an accelerating voltage of 200kV. X-ray energy dispersive spectroscopy analyses were conducted on the specimens in TEM by employing a FEI Super-X system including 4 silicon drift detectors for the fast-chemical composition measurements and elemental mapping (images below) of the PbS/CdS core/shell nanosheets.

Figure 3. SF5 Element mapping of PbS/CdS nanosheets.
The chemical composition measurements were done on three different locations of the sample (tables below), showing Pb to Cd ratio of 2.30, 2.54 and 2.50, respectively.

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H) Stokes’ shift

**Figure 3. SF6** Stokes’ shift of PbS nanosheets and PbS/CdS nanosheets.

The above figure shows the photoluminescence and absorbance for each for each sample:

(a) original PbS nanosheets, (b) PbS/CdS nanosheets after 3-minutes cation exchange at 100 oC,
(c) PbS/CdS nanosheets after 2-hours cation exchange at 100 oC, (d) PbS/CdS nanosheets after
additional 1-hour cation exchange at 150 oC. For each sample, the absorption edge is coincident with the photoluminescence peak, indicating the Stokes’s shift for the nanosheets is negligible.

The optical absorption measurements are done using a home-built system as mentioned in our earlier paper.1 It includes a quartz-tungsten-halogen lamp (Oriel 66187), an integrating sphere (Thorlabs IS200-4), a monochromator (Acton SP-2357, Princeton Instrument) and an IR detector (PDA30G, Thorlabs). The sample is prepared by dispersing the nanosheets in tetrachloroethene in a quartz cuvette (Starna Cells, Inc), and then being mounted inside the integrating sphere. Using the integrating sphere can significantly suppress the scattering light from the nanosheets so that the intrinsic absorption feature of the nanosheets can be revealed.

I) Nearly complete transformation of PbS nanosheets to CdS nanosheets

At a high reaction temperature (150 oC), thinner (2.1 nm) PbS nanosheets can be nearly completely turned into CdS nanosheets. The photoluminescence spectroscopy shows the peak (1540 nm) corresponding to the PbS nanosheets disappears completely while a peak at 430 nm appears. The photon energy of 430 nm emission is about 2.88 eV which is close to the energy gap (2.82 eV) of 2.1 nm CdS nanoplatelets demonstrated by Ithurria and coworkers.2

Figure 3. SF7 Nearly complete transformation of PbS nanosheets to CdS nanosheets.
The TEM shows the morphology of the nanosheets doesn’t change (figure above) but the in situ energy dispersive X-ray spectroscopy shows mainly Cd and S while the atomic percentage of Pb is negligible (figure below).

**Figure 3. SF8 EDX spectroscopy of PbS/CdS nanosheets.**

J) Photoluminescence lifetime measurements

Photoluminescence lifetime measurements were conducted via time correlated single photon counting (TCSPC) utilizing a Becker & Hickl Simple Tau SPCM 130-E/M photon counting module. Samples were excited via a 5 ps pulse from a Fianium photonic crystal fiber laser (SC400-2) at 5 MHz repetition rate; whereby an acousto-optical tuning filter was used to select the final output wavelength. The incident photon flux is ranging from $1 \times 10^{11}$ to $2 \times 10^{12}$ photons/pulse/cm$^2$). Radiative recombination events were detected using a Horiba iHR320 monochromator (900 g/mm – 850 nm blaze grating) and a Hamamatsu NIR PMT (H10330B-75). While photon detection was primarily performed at the peak wavelength of the sample PL spectra; samples with emission beyond the detection limit of the detector were observed at 1600 nm (long wavelength detection
TCPSC decay plots were fit to a bi-exponential decay function via iterative re-convolution with the measured system response function (SRF).

\[ y(t) = (SRF \ast f)(t) \]

\[ f(t) = A_1 \ast \exp\left(\frac{-t}{\tau_1}\right) + A_2 \ast \exp\left(\frac{-t}{\tau_2}\right) \]

K) Discussion of the energy levels among the core/shell structure

In a PbS/CdS core/shell structure, type II heterostructure is possible when the core is small enough and the shell is thick enough. However, in our PbS/CdS core/shell nanosheets, both core and shell are under significant quantum confinement so that it is unlikely to see type I behavior in our systems. Here is the rough estimation of the energy levels of core and shell. Assume it is in a quite extreme case where the core has two atomic layers (~0.593 nm) and the CdS shell has five atomic layers on each side (this makes total 12 atomic layers as in our experiment), the confinement energy is about 0.57 eV for PbS core according to our recent paper and 0.80 eV for CdS shell. Since the electron and the hole in PbS has nearly the same effective mass, the LUMO of the PbS nanosheet will shift from -4.45 V (bulk) to -4.17 V. This is already lower than the LUMO of bulk CdS (-4.15 V), and will be much lower than the LUMO of 5 layer of CdS shell due to quantum confinement. Therefore, it is unlikely to see type II behavior in our core/shell nanosheets.

L) Normalized photoluminescence intensity

To compare the photoluminescence efficiencies between the core-only nanosheets and core-shell nanosheets, both the photoluminescence spectrum and the optical absorption of each
sample are measured. Following the method developed by Friend et al., an integrating sphere is used to host the sample to measure the optical absorption at the excitation wavelength. The integrated photoluminescence intensity normalized to the optical absorption for each sample is compared. The ratio of the normalized photoluminescence intensity of core/shell nanosheets to core-only nanosheets is about 1.4:1.

References


3.6 References


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CHAPTER 4 PHOTLUMINESCENCE AND CATHODOLUMINESCENCE
SPECTROSCOPY OF CDS NANOSHEETS CREATED FROM PBS NANOSHEETS BY
CATION EXCHANGE

4.1 Abstract

CdS Nanosheets were synthesized through single cation exchange reaction. As the PbS nanosheets, the CdS nanosheets keep the same lateral size around 20 nm, while they exhibit distinct selected-area electron diffraction (SAED) patterns. Compared to the single photoluminescence peak (PL) of PbS nanosheets, CdS nanosheets exhibit a blue band with multi emission peaks. Cathodoluminescence of CdS nanosheets provides a red-shifted spectrum versus the dominant blue emissions in its PL spectrum.

4.2 Introduction

In the past decade, colloidal nanoplatelets of CdX (X=S, Se, Te) have been well developed and demonstrated superior optical properties, including high photoluminescence quantum yield\textsuperscript{1-3}, fast light emission\textsuperscript{4,5}, and low-threshold lasing\textsuperscript{6-11}. The infrared counterpart of this bright visible emitter – colloidal PbS nanosheets – is catching up\textsuperscript{12-17}. These two two-dimensional (2D) materials are very different in photophysics. It is interesting to compare their photo-physical properties side by side while keeping their morphology the same.

4.3 Experiments and discussion

4.3.1 Synthesis and structural characterization of CdS nanosheets and PbS nanosheets

Using cation exchange method, we can completely convert colloidal PbS nanosheets into CdS nanosheets. Both the CdS and PbS nanosheets have nearly the same morphology and good optical properties. However, due to the different composition their optical
absorption/emission spectra and their photoluminescence lifetimes are very different. Strong exciton peaks are observed in CdS nanosheets but they are absent in PbS nanosheets. There are emissive surface states exist in CdS nanosheets which are confirmed by cathodoluminescence spectroscopy and photoluminescence spectroscopy. However, emissive in-gap surface states in PbS nanosheets are not observed.

Figure 4.1 TEM images of PbS (a) and CdS (b) nanosheets. Insets give the corresponding SAED and the diagrams of lattice structure of (100) facet and (111) facet for PbS and CdS respectively; (gray sphere-Pb atom, pink sphere-Cd atom, yellow sphere-S atom).

As an alternative to conventional routes like hot-injection method, cation exchange process has already showed its potential on nanocrystal synthesis\textsuperscript{18-22}. The biggest advantage of cation exchange is that all cations in a nanocrystal can be replaced by another kind of cation, while the size and morphology of the nanocrystal can be preserved. This is particularly appealing to us because we can use nanocrystals as template to synthesize other nanocrystals of interest. Even though the lattice mismatch is less than 2\% between rock-salt structure PbS and zincblende structure CdS, the cation exchange reaction of Pb\textsuperscript{2+} to Cd\textsuperscript{2+} is more likely defined as self-limiting process which often results in core/shell heterogeneous structure\textsuperscript{23-26}. In this work, we obtained CdS nanosheets from PbS nanosheets by modified cation exchange method\textsuperscript{27-28}. PbS nanosheets
were firstly dispersed in 1-octadecene solution and degassed for 30min. CdS nanosheets were prepared by syringe injection of PbS nanosheets dispersed 1-octadecene solution into the Cd-oleate solution at 160°C and the cation exchange reaction were stopped when all the solution turned yellow color. The PbS nanosheets used for cation exchange has an average width 20 nm and length more than 50 nm (Figure 4. 1a). The dimensions of width and length are nearly the same after cation exchange (Figure 4. 1b), but the cations in the nanosheets are totally turned into Cd from Pb, as evidenced by Energy-dispersive X-ray spectroscopy (EDX) measurements (Supporting Information 7). Moire patterns appear in the overlapping areas of both PbS and CdS nanosheet, indicating good crystallinity of each. However, the selected-area electron diffraction (SAED) pattern changes from square (PbS) (Figure 4. 1a, inset at the left-bottom corner) to hexagonal (CdS) (Figure 4. 1b, inset at the left-bottom corner). This means the facet of nanosheets facing upward changes from \{100\} to \{111\}, as illustrated in the insets at the up-left corners in Figure 4. 1. This cubic-to-hexagonal transition of the crystal ordering has also been observed in the formation of PbS/CdS core/shell nanosheets. Colloidal CdS nanosheets obtained by thermal decomposition also show a hexagonal basal plane of (111) facet. The inset of SAED in both TEM images confirms the rock-salt structure of PbS nanosheets and zinc-blend structure of CdS nanosheets. The lower-resolution TEM images (Figure 4. SF1 and Figure 4. SF4) shows that the nanosheets flower contains nanosheets with standing-up and flat aligned positions which benefits the measurement of the thickness and lateral size of nanosheets.
4.3.2 X-ray powder diffraction (XRD) of CdS nanosheets and PbS nanosheets

![X-ray diffraction patterns of PbS (dashed line) and CdS (solid line) nanosheets.](image)

The standard diffraction patterns (vertical lines) of galena (PbS) and hawleyite (CdS) powders are inserted as references.

The powder X-ray diffraction (XRD) patterns of the PbS nanosheet and CdS nanosheet are shown in Figure 4.2. The crystal structure of PbS nanosheet was identified as the glena (rock-salt) structure (JCPDS card no. 05-0592), and only the (200), (220) and (311) diffraction peaks can be determined. This could be due to the texture effect of nanosheets that was vertically aligned to form the flower morphology.\(^1\) After cation exchange, the XRD pattern of the product was accredited to the zincblende structure of CdS (JCPDS card no. 65-2887). The (111) diffraction peak from the PbS nanosheets is missing, which is the most intense diffraction peak in PbS quantum dots (Figure 4. SF11). This is likely due to the fact that the typical nanosheets have only \{100\} and \{110\} facets, among which \{100\} facets count for the largest area (top and bottom surfaces) while the edge surfaces are \{110\} facets. The \{111\} facets are negligible\(^2\); Peak of (200)
is the most prominent peak in the diffraction pattern of PbS nanosheets, reflecting the aforementioned crystal structure. We also found that the most intense diffraction peak (200) in the XRD pattern of PbS nanosheet shifts to the diffraction peak (111) in the XRD pattern of CdS nanosheet, which means that the glena structure of PbS nanosheet was completely converted into the zincblende structure of CdS nanosheet. This is consistent with the transformation of SAED patterns on the basal plane of PbS nanosheet and CdS nanosheet. Recently, Lechner et al.\textsuperscript{3} quantify the crystal phases transition during cation exchange in the shell part of PbS/CdS core/shell quantum dots where they show a gradual transition of the intensity ratio of diffraction peak (200)/(111) in x-ray diffraction pattern. In their calculation, they identify the intensity ratio of one for the Rock-salt structure of pure PbS phase, and zero for the Zincblende structure of pure CdS phase. In our case, the intensity ratio (200)/(111) will go to infinite for PbS nanosheet since no diffraction peak (111) was identified in its diffraction pattern; however, the intensity ratio (200)/(111) will be zero for CdS nanosheet, matching very well with the value when their cation exchange process proceeds and pure zincblende phase were obtained. We also noticed that the XRD pattern of CdS nanosheet was shifted to lower angles side, which means there is lattice expansion. This probably can be explained by the excess Cd\textsuperscript{2+} with the Cd : S atomic ratio of 1.3:1(Figure 4, SF6)\textsuperscript{4}. 


4.3.3 Photoluminescence and absorption spectra of CdS nanosheets and PbS nanosheets

Figure 4.3 (a) Photoluminescence (dotted line) and absorption (solid line) spectra of PbS nanosheets. Inset, the photograph of the PbS nanosheet solution in a cuvette. (b) Photoluminescence (dotted line) and absorption (solid line) spectra of CdS nanosheets. Inset, a photograph of the CdS nanosheet solution in a cuvette under room light (left) and under UV excitation in dark (right).

After cation exchange, the color of the nanosheet solution changes from dark brown (Figure 4.3a) to yellow (Figure 4.3b, inset – left), indicating the energy gap of the material changes significantly. Under UV laser excitation, the CdS nanosheets show bright blue-color light emission while the light emission from the PbS nanosheets is not visible. Further optical spectroscopy measurements on PbS nanosheets demonstrate a photoluminescence emission peak and an optical absorption edge at 1.0 eV (Figure 4.3a). The optical absorption and emission of CdS nanosheet are mainly in the UV and visible photon energy spectra. However, the spectrum features are more complicated. Multiple peaks show up in both the absorption and emission spectra (Figure 4.3b). The possibility of photoluminescence from oleic acid (capping ligands for the nanosheets) or cadmium oleate (reactant for cation exchange) has been ruled out, while the assignment of absorption peak for CdS nanosheet sample can also be
excluded from the residue of oleic acid and cadmium oleate\textsuperscript{31}. Therefore, these peaks are from
the CdS nanosheets of different thickness.

4.3.4 Bandgap of CdS nanosheets and PbS nanosheets

The dependence of the energy gap on the thickness of the CdS nanosheets is well
described by the model of infinite one-dimensional potential wells:\textsuperscript{1,4,32-33}

\[ h\omega_e = E_g(bulk) + E_{p}^{h}(r) + E_{p}^{e}(r) + E_{(e-h)} = E_{g}(bulk) + \frac{\hbar^2}{8r^2} \left( \frac{1}{m_e} + \frac{1}{m_{hh}} \right) - 4 \cdot E_{bi} \]

\( E_{g(bulk)} \)-band gap energy of bulk CdS, =2.5eV;\textsuperscript{5,34} \( m_e \)-effective mass of electron,
=0.205\( m_0 \), \( m_0 \) is the mass of free electron, \( m_{hh} \)-effective mass of heavy hole, =5\( m_0 \);\textsuperscript{35} \( r \)-thickness of CdS nanosheet; \( \varepsilon_0 \)-permittivity of vacuum; \( \varepsilon \)-dielectric constant of CdS; \( E_{bi} \)-exciton binding energy of bulk CdS.

Using this model, we found that the thicknesses corresponding to the absorption peaks
at 3.1 eV, 3.3 eV and 3.5 eV are 1.64 nm (6 ML), 1.45 nm (5 ML) and 1.33 nm (4.5 ML),
respectively. These results are very close to those obtained using eight-band effective mass
model built by Efros and coworkers.\textsuperscript{4}
Since the thickness of nanosheets will be maintained during the cation exchange, we calculated the bandgap of PbS nanosheet by the thickness of CdS nanosheet (Figure 4. 4). we did the calculation of the bandgap of PbS nanosheet by the infinite 1D potential wells model (Table S4. 5), where the bandgap is far away from the experimental data in Figure 4. 3a at the two limits of the thickness. Meanwhile, we also tried another two methods to calculate the bandgap of PbS nanosheet. For the four-band model method, we found that the bandgap of PbS nanosheet is a little shifted to the higher energy side with respect to the absorption spectrum of PbS nanosheet in Figure 4. 3a. In another work, we fitted the dependence of bandgap versus thickness of vertical PbS nanosheet (red curve in Figure 4. 4). Following the fitting result, we calculated the bandgap of PbS nanosheet (data points with error bars in Figure 4. 4), leading to relatively lower values when compared to the four band model results. This probably is due to the diminished confinement.
strength from surface passivation of oleic acid. However, the PbS nanosheet with intermediate thickness of 1.45 nm has the bandgap of 0.99 eV, matching the band edge gap in the absorption spectrum of PbS nanosheet in Figure 4. Therefore, by different calculation methods, the calculated bandgap of PbS nanosheet shows the partial overlapping with experimental data from both the lower energy side and higher energy side, which validates the thickness of CdS nanosheet from its absorption spectrum. We also compared our data to the first-principle calculation results that was fitted from even-odd layer-dependent bandgaps, which indicates all overestimated bandgaps of first-principle calculation results, even though they show a well fitted data with four-band model.

In our synthesis, the as-synthesized CdS nanosheet exhibits very poor photoluminescence, which means the low quality of crystal structure of CdS nanosheet and the existence of defect sites that was introduced during the cation exchange. These structural defects were kinetically frozen at room temperature and will quench the PL by offering the nonradiative carrier recombination. However, they can be thermally activated and migrate to the surface of nanosheet. Thus, we processed the as-synthesized CdS nanosheet by thermal annealing at 100°C for 12 hours and a significantly enhanced photoluminescence has been obtained for the CdS nanosheet. (Figure 4.3). We also conducted the measurement of X-ray diffraction of CdS nanosheet before and after thermal annealing. Although the annealed CdS nanosheet shows enhanced PL, they keep the zincblende structure, while the FWHM of diffraction peaks on XRD pattern almost remains the same (Table S4.1). This can be explained by the critical temperature around 300 °C for CdS phase transformation from metastable cubic structure to stable hexagonal structure.
4.3.5 Photoluminescence lifetime of CdS nanosheets and PbS nanosheets

![Photoluminescence lifetime of PbS nanosheets (solid circles) and CdS nanosheets (solid squares).](image)

**Figure 4.5** Photoluminescence lifetime of PbS nanosheets (solid circles) and CdS nanosheets (solid squares).

Time-resolved photoluminescence studies were implemented on PbS nanosheet and CdS nanosheet. The PL decay profiles in Figure 4 show that the PL lifetime of PbS nanosheet is 64 ns, while the CdS nanosheet renders a much shorter 1/e lifetime of 1.6 ns. Compared to our previous work of flat PbS nanosheet\textsuperscript{29} which has the lateral size of \(\sim 1\) μm, the PbS nanoflower here with vertically aligned nanosheets presents much higher PL lifetime. The possible explanation was the much-reduced surface areas of a single nanosheet within PbS nanoflower due to limited width of \(\sim 20\) nm, which will accordingly lower the population of surface traps. Meanwhile, the CdS nanosheet has an average lifetime which is one order of magnitude smaller than that of CdS quantum dots.\textsuperscript{39-40} Due to the one-dimensional confinement of CdS nanosheet, the short lifetime of CdS nanosheet could be explained by the partially mixing of bright and dark exciton states.\textsuperscript{5}
Figure 4.6 Band edge and surface state photoluminescence lifetime of CdS nanosheet.

The photoluminescence decay dynamics were further investigated by comparison between the band-edge emission and the surface-states emission (Figure 4.6). Both two decay curves can be well fitted with biexponential decay function, and the fitted results were shown in Table S4.6. We found that the two PL decay curves share the same slow decay component around 35 ns, while the fast decay component indicates a little difference. This can also be seen in Figure 4.6, where the tail of two decay curves overlaps quite well and the fast decay component of surface state is a little steeper than that of band-edge. The slow component from surface state is 35 ns, which is the same as that from band edge emission (Table S4.6). For band-edge decay, the fast component should be resulted from the intrinsic free exciton recombination\textsuperscript{41-42}, while the slow component can be attributed to the delayed band-edge emission that was caused by phonon-assisted charge transfer from shallow trapped states\textsuperscript{43-44}. 
As shown in Table S4.6, the relative fractional intensity of the fast decay component dominates the band-edge decay profile, which means most of the emitted photons follow the band-edge decay route rather than trapped by shallow trapped states\(^45\). The fast component from surface state could be due to surface state related nonradiative process\(^42\), and this nonradiative decay contribution is of 22.4% fractional intensity, which is far less than the exciton recombination route. The slow component is from recombination of free exciton on CdS nanosheet. However, it has a long decay lifetime that is same as the slow decay component of band-edge emission. It may be due to the direct radiative decay from the trapped energy level.

4.3.6 Cathodoluminescence(CL) of CdS nanosheets

![Cathodoluminescence images](image)

**Figure 4.7** (a) SEM images of the CdS nanosheets. (b) – (d) The corresponding cathodoluminescence images in three spectral ranges: (b) red, (c) green and (d) blue. (e) Cathodoluminescence image of all colors; Each bar represents 2 μm.

Cathodoluminescence has been used to combine with electron microscope to identify and localize specific optical and structural property with nanoscale resolution\(^46-48\). Here, CL was used to reveal the luminescence center and map their spatial distribution. As in Figure 4.7, the SEM image of CdS nanosheet shows that CdS nanosheet tends to aggregate in flower morphology with random sizes. Although the CL intensity differs among the nanosheet flowers, a high degree of correspondence has been achieved between the CL and SEM images, which
indicates that the CL emissions are from the whole CdS nanosheets ensemble (Figure 4. SF1). From the CL image in Figure 5, we can see that CL of CdS nanosheet can be obtained in wide spectrum range of red(a), green(b) and blue(c), where the red and green CL could be attributed to the extrinsic CL of surface states of CdS nanosheet while the blue CL was the intrinsic CL due to band-to-band transition of CdS nanosheet.\(^{49}\)

However, we noticed that the red CL dominates the whole CL images (Figure 4. 7), which is different from the PL spectrum with PL peak at 435 nm (Figure 3b). Ding et al.\(^{50}\) revealed that the light emission of surface states exhibits more sensitivity to the excitation of charge-injection than that of photon-injection in Si nanocrystals. Meanwhile, they also found that the difference in electrogenerated chemiluminescence(ECL) and PL generally results from the more contribution from the surface state in ECL spectra of CdSe nanocrystal.\(^{51}\) Since CL is the light emission due to the irradiation of electron beam, the emerging of red CL in our CdS nanosheet could be attributed to the more contributions from surface states rather than band-to-band transition that takes an advantage in PL spectra. For a fair comparison between PL and CL, we also measured the PL and absorption spectra of CdS nanosheet in film status (Figure S8) because the CL emissions were collected from CdS nanosheet sample in film status. It was found that the PL spectrum of CdS nanosheet film generally overlaps with the PL spectrum of CdS nanosheet solution with major blue emission (Figure 4.SF9b), which indicates that the main red CL (Figure 4. 7e) should not be due to the improved long range excitonic and carrier transport between thinner and thicker CdS nanosheet.\(^{52}\)

Cation exchange method has been used to fabricate shell structure to passivate the surface of PbS nanosheet\(^{13, 29}\) and PbS quantum dots\(^{24, 27-28, 53-54}\). Combining TEM images (Figure 4. 1) with X-ray powder diffraction measurement (Figure 4. 2), we can conclude that
the anionic crystal structure of PbS nanosheet was preserved during the fast exchange of Pb cations with Cd cations, which also has been proofed by other research groups in quantum dots and nanorods. Dubertret group has synthesized PbS or PbSe/PbS nanoplatelets by the template of CdS or CdSe/CdS nanoplatelets through sequential cation exchange reaction. However, no PL could be observed on these samples which is probably due to residue of copper atoms that was used as intermediate material for cation exchange. In our case, we directly obtained CdS nanosheet from PbS nanosheet without copper cation exchange process. To the best of our knowledge, it is the first time that CdS nanosheets were directly synthesized with the template of PbS nanosheet by cation exchange, while converting the infrared-emitting PbS nanosheet into CdS nanosheet with visible PL.

Many research works have been done to assign various emissions of CdS to certain defects. The green band in CL measurements can be attributed to S interstitials, while the red band can be assigned to S vacancies. In our case, the CdS nanosheet shows a broad surface state emission peak centering at 708 nm, extending into green color and near infrared range (Figure 4. SF9). Due to the excess amount of Cd ions, it is of higher probability to generate S vacancies rather than Cd vacancies that will cause infrared emission. Therefore, the broad surface state emission is centering around 708 nm with tail into infrared range.

When dispersed in organic solvent, the exciton binding energy of PbS nanosheet is expected to be 30–80 meV, which is larger than the thermal energy at room temperature. That means the absorption spectrum of PbS nanosheet should exhibit a sharp excitonic peak because the electrons and holes are in tightly bound status. However, the absorption edge of PbS nanosheet in Figure 4. 3a was a plateau rather than a sharp peak, which should be resulted from inhomogeneity of the thickness of PbS nanosheets. This is consistent with our thickness
statistics of PbS nanosheet in another work. However, for CdS nanosheet in Figure 4. 3b, even though they have the same thickness dispersity as the PbS nanosheets, we found that the CdS nanosheet shows the multiple sharp excitonic peaks, corresponding to CdS nanosheets with various thicknesses.

4.4 Conclusion

In summary, PbS nanosheet was completely converted into CdS nanosheet by cation exchange method. During cation exchange, the crystal structure was transformed from rock-salt to zincblende for PbS nanosheet and CdS nanosheet respectively, with the basal plane turning from (100) facet into (111) facet. The optical measurements show the PL was shifted from infrared range for PbS nanosheet to visible range for CdS nanosheet. The CL measurements confirmed that the emission centers were uniformly dispersed on CdS nanosheet and the difference between PL spectra and CL spectra of CdS nanosheet indicates the extra contribution from surface states in CdS nanosheet.
4.5 Supporting information

4.5.1 Synthesis of vertical PbS nanosheets

The lead precursor is prepared by dissolving lead oxide (506 mg) into diphenyl ether (10 mL) and oleic acid (1.8 mL) in a 3-neck flask. The mixture is kept stirring at 110 °C until the whole solution turns transparent. Then the mixture is heated to 100 °C and degassed until no foam appears. The solution shows pale yellow color after degassing. A chloroalkane solvent (1 mL) is added to the solution at the temperature 4 °C lower than its boiling point. Separately, the sulfur precursor is prepared by dissolving thioacetamide (12 mg) into N, N-dimethylformamide (70 µL) and trioctylphosphine (930 µL) under nitrogen environment. After both precursors are ready, the temperature of the lead precursor is set to a desired one. The sulfur precursor is then injected into the flask containing the lead precursor which is vigorously stirred. The solution turns dark by time. After a few minutes, the reaction solution is then slowly cooled down to room temperature. The final solution is washed twice with toluene and then precipitated by centrifuging. The precipitated nanoribbons are then re-dispersed in toluene.

4.5.2. Synthesis of CdS nanosheets by cation exchange

1.0 g (7.8 mmol) amount of CdO, 6 mL (19 mmol) of oleic acid, were heated to 255 °C under Nitrogen until all of the CdO had dissolved. The clear solution was cooled to 160 °C under Nitrogen flow to remove water. Then, the PbS nanosheets dispersed in 1-octadecene solution was degassed by Nitrogen flow for 30 min. Immediately after the temperature of the Cd-oleate solution was stable at 160 °C, the PbS nanosheets solution was added via syringe with stirring. The reaction was stopped when all the solution become yellow color. Final products were cooled by mixing with toluene, and CdS nanosheets were isolated and washed twice with toluene and then precipitated by centrifuging. The precipitated CdS nanosheets are then re-dispersed in toluene.
4.5.3 Cathodoluminescence of CdS nanosheets in scanning electron microscope

The cathodoluminescence measurement was implemented on detector of ChromaCL Gatan Inc. The CL detector was mounted on the Hitachi S-2700 SEM Scanning Electron Microscope.

**Figure 4. SF1** cathodoluminescence(CL) and corresponding SEM images of CdS nanosheets

**Figure 4. SF2** cathodoluminescence(CL) images of CdS nanosheets split in channels: Blue(Left), Green(middle), Red (Right).

4.5.4 Structural characterization of vertical aligned PbS nanosheets and CdS nanosheets.

**Figure 4. SF3** TEM image of Vertical aligned and Flat aligned PbS nanosheets
Figure 4. SF4 TEM image of Vertical aligned and Flat aligned CdS nanosheets after cation exchange

4.5.5 Heating treatment of CdS nanosheets after cation exchange

The as-synthesized CdS nanosheets were dispersed in 1-Octadecene and kept in flask with N2 flowing for 12 hours at 100°C.

Figure 4. SF5 (Left) Photoluminescence spectrum of CdS nanosheets with laser excitation of 445nm. (Right) Optical Absorption spectra of vertical CdS nanosheets with/without annealing.

In figure 4.SF5, the absorption spectrum of CdS nanosheets shows more exciton peaks after annealing treatment. The possible reasons could be the removal of the surface states during annealing. Moreover, for the absorption peak of 7 monolayer, there is a 20nm blue-shifting of the
peak after annealing which probably is due to the self-narrowing effect of CdS nanosheets during annealing.5

4.5.6 Parameters of diffraction peaks on XRD patterns of CdS nanosheets before and after thermal annealing at 100 °C.

<table>
<thead>
<tr>
<th>No.</th>
<th>2-theta (deg)</th>
<th>d (ang.)</th>
<th>Height (counts)</th>
<th>FWHM (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26.388876</td>
<td>3.377145</td>
<td>7539.0182</td>
<td>3.04037</td>
</tr>
<tr>
<td>2</td>
<td>44.005764</td>
<td>2.059964</td>
<td>265.28649</td>
<td>3.04037</td>
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<tr>
<td>3</td>
<td>51.383285</td>
<td>1.776775</td>
<td>60.566356</td>
<td>3.04037</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>2-theta (deg)</th>
<th>d (ang.)</th>
<th>Height (counts)</th>
<th>FWHM (deg)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>26.413199</td>
<td>3.371579</td>
<td>4996.9637</td>
<td>2.97888</td>
</tr>
<tr>
<td>2</td>
<td>44.90(3)</td>
<td>2.055(14)</td>
<td>83(9)</td>
<td>3.0(3)</td>
</tr>
<tr>
<td>3</td>
<td>51.664275</td>
<td>1.767770</td>
<td>46.477858</td>
<td>2.97888</td>
</tr>
</tbody>
</table>

Table 4. ST1 Parameters of diffraction peaks on XRD patterns of CdS nanosheets before and after thermal annealing at 100 °C.

4.5.7. Energy-dispersive X-ray spectroscopy (EDX)

The energy-dispersive X-ray spectroscopy was measured in situ using an EDX detector mounted on the Hitachi HD-2300 Scanning Transmission Electron Microscope. The spectra show the nanosheets still keep the same morphology while the Pb was replaced by Cd peak after cation exchange.

Figure 4. SF6 EDX spectroscopy of CdS nanosheets
Figure 4. SF 7 EDX spectroscopy of PbS nanosheets

<table>
<thead>
<tr>
<th>Atomic ratio (%)</th>
<th>CdS nanosheets</th>
<th>PbS nanosheets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S K</td>
<td>43</td>
<td>51.8</td>
</tr>
<tr>
<td>Pb K</td>
<td>0</td>
<td>48.2</td>
</tr>
<tr>
<td>Cd L</td>
<td>57</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4. ST2 Atomic percent of CdS nanosheets and PbS nanosheets from EDS spectrum.

4.5.8 Lifetime Measurement

The PL lifetime measurements were performed using a time-correlated single-photon counting setup utilizing SPC-130 single-photon counting PCI card (Becker & Hickle GmbH), picosecond diode laser operating at 400 nm, as an excitation source (Picoquant), an id50 avalanche...
photodiode (Quantique). The frequency of the light was 10 MHz (optical power of 0.84 mW). The minimum pulse width is 49 ps. The laser response time is 40 ps.

4.5.9. Multi-peak fitting of PL spectra of CdS nanosheets Solution and CdS nanosheets Film.

![Multi-peak fitting of PL spectra of CdS nanosheets Solution and CdS nanosheets Film](image)

**Figure 4. SF 8** Multi-peak fitting of PL spectra of CdS nanosheets solution and film.

4.5.10. Assignment of peaks on Absorption spectrum of CdS nanosheets and Calculation of thickness of CdS nanosheets.

<table>
<thead>
<tr>
<th># of MLs in CdS NS</th>
<th>Confinement Energy in Literature</th>
<th>Absorption Peaks</th>
<th>d-thickness of NS</th>
</tr>
</thead>
<tbody>
<tr>
<td>7ML</td>
<td>2.839eV</td>
<td>2.91eV</td>
<td>1.91nm</td>
</tr>
<tr>
<td>6ML</td>
<td>2.996eV</td>
<td>3.1eV</td>
<td>1.64nm</td>
</tr>
<tr>
<td>5ML</td>
<td>3.244eV</td>
<td>3.29eV</td>
<td>1.45nm</td>
</tr>
<tr>
<td>(4ML~5ML)</td>
<td>-</td>
<td>3.46eV</td>
<td>1.33nm</td>
</tr>
<tr>
<td>4ML</td>
<td>3.643eV</td>
<td>3.65eV</td>
<td>1.23nm</td>
</tr>
</tbody>
</table>

**Table 4. ST3** Assignment of peaks on absorption spectrum of CdS nanosheets and calculation of thickness of CdS nanosheets.
<table>
<thead>
<tr>
<th>Thickness of CdS NS</th>
<th>Confinement Energy by our model</th>
<th>Confinement Energy in Efros’ paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>7MLs-2.04nm</td>
<td>2.846</td>
<td>2.839eV</td>
</tr>
<tr>
<td>6MLs-1.75nm</td>
<td>3.012</td>
<td>2.996eV</td>
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<tr>
<td>5MLs-1.45nm</td>
<td>3.299</td>
<td>3.244eV</td>
</tr>
<tr>
<td>4MLs-1.16nm</td>
<td>3.807</td>
<td>3.643eV</td>
</tr>
</tbody>
</table>

Table 4. ST4 Comparison of confinement energy of CdS nanosheets calculated by our model to that by Efros’ Group.

In Efros’s paper, the correlation of energy gap of CdS nanosheet and its thickness or the numbers of monolayers (MLs) was established using eight-band effective mass model. They suggested the number of MLs of 4, 5, 6, and 7 to the energy of electron/heavy-hole (H) and electron/light-hole (L) transitions of 3.643eV (H)-3.746eV (L), 3.244eV (H)-3.321eV (L), 2.996eV (H)-3.047eV (L) and 2.839eV (H)-2.888eV (L). In energy gap calculation, we also chose 2-dimensional limit-(4*Ebi, Ebi is exciton binding energy of bulk CdS) as coulomb correction, regardless of the effect of thickness. The validity of our model has been testified in Table-S2, where confinement energy calculated by our model matches quite well with the values in Efros’ paper. Thus, we assigned the absorption peaks in Figure 4.3b at 2.91eV (H), 3.1eV (H), 3.29eV (H) and 3.65eV (H) (a small bump) to CdS nanosheet with MLs of 7, 6, 5 and 4. For the absorption peak at 3.46eV, it could be due to the band transition of CdS nanosheet with thickness between 4 and 5 MLs. This assignment has also been reinforced since our PbS nanosheet has the thickness range of 1.5±0.8 nm. The peaks at 3.04eV and 2.86eV in PL spectrum can be due to the emission of 6 and 7 MLs CdS nanosheet. Interestingly, we noticed a tail following the main emission peak of 7ML CdS nanosheet extending to the bandgap of bulk CdS, which was also observed in Peng’s group where they accredited it to closing to the bulk bandgap of CdS.
Confinement energy of PbS nanosheets

Since the thickness of nanosheets is not changed during cation exchange, we can calculate the confinement energy of PbS nanosheets from the thickness of CdS nanosheets. In this calculation, we use the same method in the reference.\(^7\)

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Bandgap (Infinite 1D potential wells model)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.91nm</td>
<td>0.57eV</td>
</tr>
<tr>
<td>1.64nm</td>
<td>1.21eV</td>
</tr>
<tr>
<td>1.45nm</td>
<td>1.89eV</td>
</tr>
<tr>
<td>1.33nm</td>
<td>2.47eV</td>
</tr>
<tr>
<td>1.23nm</td>
<td>3.10eV</td>
</tr>
</tbody>
</table>

Table 4. ST5 PbS nanosheets - Bandgap vs Thickness.

4.5.11. CdS nanosheets in film status VS solution status

![Image](image1.png)

**Figure 4. SF 9** (Left) Photoluminescence spectrum and Absorption spectrum of CdS nanosheets in film status by excitation of 337nm laser. (Right) Surface state PL spectra of CdS nanosheets in film status excited by 445nm laser. The sharp peak around 1.4eV is the higher order diffraction of laser beam.
Figure 4. SF10 PL and Absorption spectra of CdS nanosheets in film and solution status.

<table>
<thead>
<tr>
<th>Origin of PL</th>
<th>A1 (weighting factor - A1*( \tau_1 ))</th>
<th>A2 (weighting factor - A2*( \tau_2 ))</th>
<th>(\tau_1)/ns</th>
<th>(\tau_2)/ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band edge</td>
<td>1.06(88.5%)</td>
<td>0.005(11.5%)</td>
<td>1.27</td>
<td>35</td>
</tr>
<tr>
<td>Surface state</td>
<td>3.57(35.3%)</td>
<td>0.17(64.7%)</td>
<td>0.91</td>
<td>35</td>
</tr>
</tbody>
</table>

Table 4. ST6 Fitted results of photoluminescence decay curves. Weighting factor of each decay time was calculated by the equation$^{4,8}$:

\[
\frac{A_i\tau_i}{\sum_{i=1}^{n} A_i\tau_i} \quad (n\text{-number of decay channels})
\]
4.5.12. X-ray power diffraction pattern of PbS quantum dots.

![X-ray power diffraction pattern of PbS quantum dots.](image)

**Figure 4. SF 11** X-ray power diffraction pattern of PbS quantum dots.

4.5.13 References


4.6 References


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42. Liu, X.; Zhang, Q.; Xing, G.; Xiong, Q.; Sum, T. C., Size-Dependent Exciton Recombination Dynamics in Single CdS Nanowires beyond the Quantum Confinement Regime. The Journal of Physical Chemistry C 2013, 117 (20), 10716-10722.


CHAPTER 5 PHOTOLUMINESCEENCE MECHANISM OF CITRIC ACID-DERIVED CARBON DOTS

5.1 Abstract

Light-emitting mechanism of carbon dots were studied. The photoluminescence spectra of carbon dots have two different components: the excitation-independent component in the short wavelength, and the excitation-dependent component in the longer wavelength. The absolute quantum yield of carbon dots dispersed in Polyvinyl alcohol is around 15% when the excitation wavelength is less than 425 nm, but decreases continuously when the excitation wavelength increases. The decay lifetimes of the carbon dots also show an abrupt change at excitation wavelength 425 nm. Time resolved photoluminescence was implemented from 31K to 291K to study the photoluminescence decay dynamics of carbon dots, resulting in the continuously decreasing of the lifetime as the temperature increases.

5.2. Introduction

Fluorescent semiconductor quantum dots have generated broad promising applications including biological labeling and solid-state lighting. Nanometer-size carbon dots which are the counterparts of silicon nanoparticles now light up. They are non-toxic, abundant, stable and bio-compatible. Although the typical photoluminescence quantum efficiency of carbon dots is not high yet, they are non-blinking\(^1\) and have large two-photon absorption cross section\(^2\) which are favorable for one-photon or two-photon bio-imaging.

There are two schools of fabrication methods for carbon dots: top-down, bottom-up. Top-down method starts from bulk carbon, and using laser\(^3\) or electrochemical oxidation\(^3\) to break down the carbon into small pieces which have the size in nanometer scale. Graphene fragment carbon dots exhibit size tunable optical properties\(^4\). The bottom-up method starts from organic molecules
and using chemical reaction, pyrolysis method to fabricate carbon dots, pioneered by Giannelis groups\textsuperscript{5}. Following this direction, we can make mass production of carbon dots. Using these carbon dots, we investigate their optical properties and discovered an abrupt change of the photoluminescence lifetime as the excitation wavelength is scanned from UV to visible region. This abrupt change indicates a change of light emission mechanism of the carbon dots.

5.3 Experiments and discussion

5.3.1 Synthesis of Carbon nanodots

The method of synthesis of C dots is adopted from a previously reported method with some modification\textsuperscript{6}. In a typical synthesis; a mixture of citric acid or acetylenedicarboxylic acid were mixed with ethanolamine under constant magnetic stirring to get a mole ratio of amine to acid of 3: 1 or 2: 1. After homogeneous mixing the reaction mixture was heated to above 70\degree C to get a syrupy suspension which is pyrolyzed directly in a furnace at temperature more than 180\degree C. The black product is highly water soluble and is used for different spectroscopic and microscopic analysis.

5.3.2 Transmission Electron Microscopy(TEM) of carbon nanodots

After dialysis, the unreacted precursors were filtered out. The carbon dots exhibit quite uniform size under electron microscope (as shown in Figure 5. 1). No lattice structure was observed from the carbon dots. They are basically amorphous.
5.3.3 Absorption and photoluminescence spectra of carbon nanodots

The optical absorption spectrum of the carbon nanodots is shown in Figure 5. 2, which shows an absorption maximum at 340 nm. According to the previous reports\textsuperscript{6}, the absorption peak at 340 nm is accredited to the n-\(\pi^*\) transition of the carbonyl group. For the shoulder after the absorption peak and the broad tail extending over to the visible spectrum, they could originate from other functionalized surface groups of carbon dots.

Figure 5. 1 Transmission Electron Microscope (TEM) image of carbon dots.

Figure 5. 2 UV-Vis spectrum of carbon nanodots.
A remarkable optical property of carbon dots is the excitation-dependent fluorescence, which violates the Kasha-Vavilov rule. In Figure 5.3, the fluorescence spectra of carbon dots show the typical two types of the trending to the excitation process: the excitation-independent component in the excitation wavelength from 275 nm to 400 nm, and the excitation-dependent component in the excitation wavelength from 425 nm to 550 nm, which clearly indicates the two different photoluminescence mechanisms. For the independent part, the photoluminescence of carbon dots residents around 450 nm. In the previous work\(^7\), the dual emission mechanisms have been attributed to the presence of organic fluorophores for the excitation-independent range and carbogenic cores for the excitation-dependent range.

The energy gap calculation of Carbon dots is determined by using Gaussian software. Where the hybrid DFT calculation method B3LYP is used with basis set 6-31G*. The calculation shows the energy gap of 3.33 eV. The Homo energy level is -4.471 eV and LUMO energy level is -1.134 eV. This value agrees with the maximum intensity at excitation wavelength of 375 nm.
**Figure 5.3** Excitation independent and dependent photoluminescence spectra of Carbon nanodots

In Figure 5.3, it shows the PL spectra of the carbon dots excited by different wavelength. When excited by laser below 310 nm, the carbon dots exhibit PL around 375 nm. For excitation above 310 nm, the PL peak was red-shifted to 450 nm and it shows an excitation-independent PL spectrum until the excitation of 410 nm. Particularly, with the excitation of 380 nm, the carbon dots achieve maximum PL intensity. With further increasing the excitation wavelength, the PL
spectra show the red-shifting trend with declining intensity until 490 nm. For the excitations above 510 nm, the PL spectra still show the red-shifting trend but with enhanced PL intensity.
Figure 5. 4 Excitation independent and dependent photoluminescence spectra of Carbon dot in water.
Figure 5. 4 shows the PL spectra of carbon dots dispersed in water. For excitation below 300 nm, the PL was located around 375 nm. With increasing excitation wavelength, the PL spectra were red-shifted until 460 nm. Furthermore, the PL spectra show the gradual red shifting trend with increased excitation length, which cannot be explained by ground state stabilization by H-bonding between the edge state on carbon dots and protic water molecule. Interestingly, for excitation between 370 nm and 390 nm, the PL spectra were fixed around 460 nm. For excitation above 410 nm, the PL spectra show the excitation-dependent trend where the PL peaks were red-shifted with decreasing intensity.

5.3.4 Excitation-dependent quantum yield and photoluminescence lifetime of carbon nanodots

As shown in Figure 5. 5, the quantum yield of carbon dots varies with the excitation wavelength. The quantum yield generally shows two stages with the increasing of excitation wavelength: when excited from 275 nm to 400 nm, the quantum yield of carbon dots fluctuates between 12.8% and 19.3%; while for the range of 425 nm to 550 nm, the quantum yield keeps decreasing from 18.8% to 0.34%, which also indicates the existence of two different photoluminescence mechanisms.
Figure 5. 5 Excitation dependent Photoluminescence Quantum Yield of carbon nanodots

The photoluminescence lifetime of the carbon-dots dispersed in PVA changes depending on the excitation wavelength (Figure 5. 5). It clearly indicates two different stages of the photoluminescence Lifetime with excitation wavelength where the 1st stage is around 6 ns with excitation wavelength from 275 nm to 400 nm and the lifetime of 2nd stage is ~1 ns after a sudden rising to 9.5 ns. The intrinsic photoluminescence lifetime was calculated and reveals the two stages trending. For the photoluminescence excitation-independent part, the intrinsic photoluminescence lifetime shows a continuous declining trend from 55 ns to 30 ns. However, after the sudden rising of 78 ns, the intrinsic photoluminescence lifetime falls to 9 ns with a growing trend from 9 ns to 28 ns. Recently, the exciton lifetime of partially reduced graphene oxide(GO) was demonstrated to be dependent on the reduction time where the larger size sp² domain will be formed with longer reaction time⁹. The increase of the intrinsic photoluminescence lifetime with the emission wavelength may originate from the larger size sp2 domain in the carbogenic core which also cause
the red-shifting of the photoluminescence spectra and the decreasing of the photoluminescence intensity due to their energy gaps.

**Figure 5.6** Excitation dependent photoluminescence Lifetime of PVA (Polyvinyl alcohol) dispersions of Carbon nanodots.

The temperature-dependent Time-Resolved Photoluminescence Lifetime (TRPL) shows the faster decay curves with the increasing of the temperature from 31 K to 291 K (Figure 5. 7(a)), which means the more contribution from the nonradiative decay process of carbogenic core of carbon dots. In Figure 5. 7(b), the average carrier lifetime calculated from the temperature-dependent TRPL measurements features a continuously decreasing trend from 4.2 ns to 2.9 ns when increasing the temperature. From the temperature-dependent decay curves of figure 6, the photoluminescence relaxation dynamics of carbon dots reveals multiexponential from low temperature to room temperature, which is quite different with the conventional semiconductor QD that usually shows the mono-exponential decay trace at low temperature.\textsuperscript{10}
Figure 5. (a) Temperature-Dependent TRPL for the carbon dot sample from 35 K to 291K.

(b) Estimations of average carrier lifetime from bi-exponential fits for the data.
The XPS measurements was carried out to confirm the presence of amide groups. In Figure 5. 8, the characteristic peaks of carbonyl group, amide nitrogen and carbonyl oxygen were located at 288.2 eV, 400 eV and 532.1 eV, respectively.

Figure 5. 8 X-ray photoelectron spectroscopy (XPS) of carbon nanodots.
Meanwhile, the FTIR spectrum of carbon dots was also collected and support the existence of amide functional groups (Figure 5. 9) with their vibrational fingerprints centered at 1550 cm⁻¹ of N-H in-plane bending, 1636 cm⁻¹ of C=O stretching of the amide bond, and 3300 cm⁻¹ of N-H stretching.

**Figure 5. 9** FTIR spectra of (a) ethanolamine, (b) citric acid, (c) CNP180, (d) PL-CNP180, (e) CNP230, (f) CNP300, (g) CNP400 and (h) ox-CNP400. Peaks that correspond to functional groups mentioned in the text are noted and identified. (The abbreviations used are: CNP, Carbon nanodot; ν, stretching; β, in plane bending.)⁷
5.3.5 Photoluminescence excitation (PLE) spectra of carbon nanodot

Figure 5. 10 PLE spectra of carbon dot film.

Photoluminescence excitation spectroscopy can tell the correlation of the optical emission and absorption, which is suitable to study the carbon dots that have a broad emission spectrum. In figure 10, excitation spectra of carbon dots film show the evolution of PL intensity contributions from different PL sources. For the PL with wavelength less than 420 nm, the excitation peaked at
275 nm which is likely due to the $\pi-\pi^*$ transition in carbon core or aromatic structure of. For the PL during the range of 410 nm to 500 nm, there is still the contribution from the $\pi-\pi^*$ transition, while the contribution from the other PL source around 375 nm is gradually increasing. When the PL wavelength goes up to 510 nm, another PL source around 450 nm is showing up and its contribution keeps increasing while the contribution from 375 nm PL source keeps decreasing, which means there is a red shifting of the PL sources with red-shifting emission peaks. For the PL above 600 nm, the PL contribution of 450 nm PL source has a declining trend, while the PL contribution around 575 nm dominates.
Figure 5.11 PLE spectra of carbon dot dispersed in water.

Figure 5.11 shows the excitation spectra of carbon dot dispersed in water. For PL under 380 nm, there is only one PL source around 275 nm due to the $\pi$-$\pi^*$ transition. For PL above 380 nm, there is still PL contribution from $\pi$-$\pi^*$ transition, while another red-shifting PL contribution is rising around 375 nm. Interestingly, for PL above 430 nm, the PL contribution around 375 nm dominates. Compared to carbon dot film, the carbon dot in water sample only exhibits two PL
sources of 275 nm and 375 nm, while the other two PL sources in carbon dot film is not present in its water counterpart.

The abrupt change of the photoluminescence lifetime at excitation wavelength of 425 nm is a strong indication that there are two different emission mechanisms. This is consistent with the result of excitation-wavelength dependent photoluminescence spectra. The low-temperature experiments show that the photoluminescence lifetime increases as the temperature decrease. This may indicate there are phonon-assisted exciton decays. Further experiments including temperature dependent photoluminescence spectroscopy will be carried out to obtain a better picture of the light-emitting mechanism of the carbon dots.

5.4 Conclusion

The photoluminescence studies including spectra, quantum yield and lifetime reveal the light-emitting mechanism of carbon dots. They are important to further our understanding of the carbon dots and to provide the knowledge for their future applications.
5.5 References


