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Growth of Colloidal PbS Nanosheets and the Enhancement of Their Photoluminescence

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

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.¹⁴ 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.⁵ 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%.^{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.^{3,6-17} For cadmium salts (CdS, CdSe and CdTe), it is claimed that the anisotropic growth is driven by acetate salts.^{6,7,11} For ZnS, chelating

ligands – ethylenediamine – are thought to be critical in the formation of NS.¹⁸ For other materials such as PbS³ and SnSe,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.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).³

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.

The synthesis of PbS NSs follows a method similar to the one developed earlier.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 cosolvent 1,1,2-trichloroethane (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 cosolvent TCE is critical to the formation of NSs. When it is absent, no NS forms except QDs (Supporting information 1).

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Electronic Supplementary Information (ESI) available: Control syntheses without cosolvent TCE; PL and optical absorption of the products at reaction time of 0.5 minute; Atomic force microscopy – sample preparation and thickness measurements; Enhancement of PL of the PbS NSs after aging in toluene;; Spectrum of the light source in PL measurements. See DOI: 10.1039/x00xx00000x



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.

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 cosolvent. The products are then re-dispersed in tetrachloroethene for the photoluminescence-spectroscopy measurements.

Our PL measurements show very different PL spectra at different reaction times (Figure 2). 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, a 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 appeared. 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.

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 1a). At around 1 minute, both porous NSs and QDs appear (Figure 1b). At around 3 minutes, the number of QDs is significantly reduced. Instead, porous sheets form (Figure 1c). After 7 minutes of reaction time, the majority of the NSs become uniform while no isolated QDs are observed (Figure 1d).

The PL and TEM results are consistent based on the quantumconfinement 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 (a) 100 nm (c) 100 nm (d) 100 nm

Figure 1. 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.

nm as confirmed by high-resolution TEM imaging (Figure 1a, inset). QDs of this size have energy gap of 1.9 eV according to the fourband model (Figure 3).^{19,20} It predicts an optical absorption peak at around 655 nm, as confirmed by our measurement (Supporting information 2). The corresponding PL peak appears at 780 nm (Figure 2) due to Stokes shift. At 7 minutes reaction time, the product is mainly NSs. Their thickness is around 2.2 \pm 0.5 nm as measured by atomic force microscopy (Supporting information 3). According to our model developed recently (E_{gap} : energy gap in eV of the NSs; *L*: the thickness in nm of the NSs; $E_{gap}(\infty)$: energy gap of the bulk PbS at room temperature ~ 0.41 eV),¹

$$E_{gap}(L) = E_{gap}(\infty) + \frac{1}{0.99L + 1.18} , \qquad (1)$$

the energy gap is predicted to be 0.71 eV (Figure 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) 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), corresponding to the complicated structures (Figure 1b, 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

Journal Name

Page 2 of 5

Journal Name



Figure 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.

is nearly negligible at the reaction times of more than 3 minutes. This non-shifting but diminishing PL rules out the continuous 2Dgrowth 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 1c, 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



Figure 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).

COMMUNICATION

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 QDs²² and PbSe QDs.^{23,24} 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.

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. All the PL peaks are more redshifted 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 4a. 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.²⁵ It was attributed to enhanced acoustic phonon coupling in strongly quantum confined QDs.²⁶ 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 4b) after ten-month aging in toluene (Supporting information 4). 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.^{27,28} It is also noticed that the PL peaks of the aged NSs shift to shorter wavelengths (Figure 4b and Supporting information 4). The spectral blue-shift suggests a decrease of the average NS thickness, similar to the trend observed in colloidal PbS QDs.²⁶ The PbS NSs with an improved quality are important for further studies using transient PL and optical absorption spectroscopies.

Conclusions

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

COMMUNICATION

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.

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4 | J. Name., 2012, **00**, 1-3

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Journal Name

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