Growth of Colloidal PbS Nanosheets and the Enhancement of Their Photoluminescence

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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 ^{o}C. 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 ^{o}C. 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.

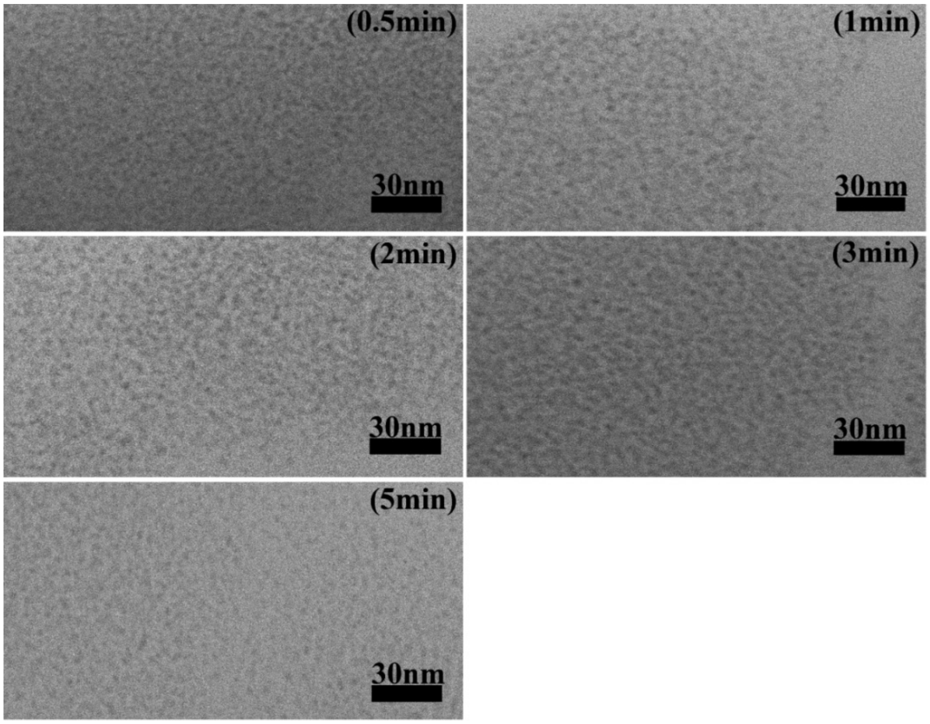


Figure S1, TEM images of the products at the reaction times of 0.5, 1, 2, 3, 5 minutes while the co-solvent 1, 1, 2-trichloroethane is absent.

2. PL and optical absorption of the products at reaction time of 0.5 minute

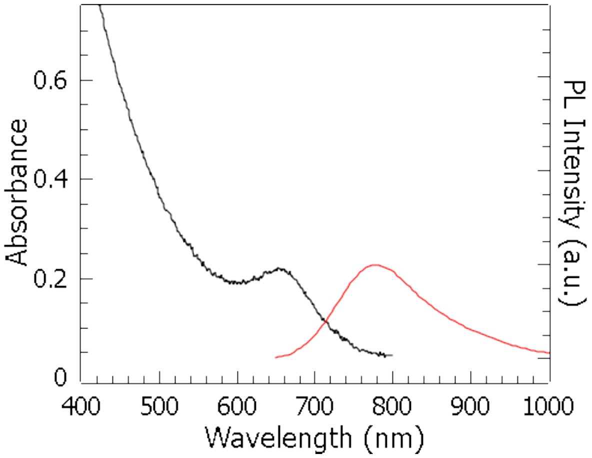


Figure S2. Optical absorption spectrum (black) and photoluminescence spectrum (red) of the product at the reaction time of 0.5 minute.

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.

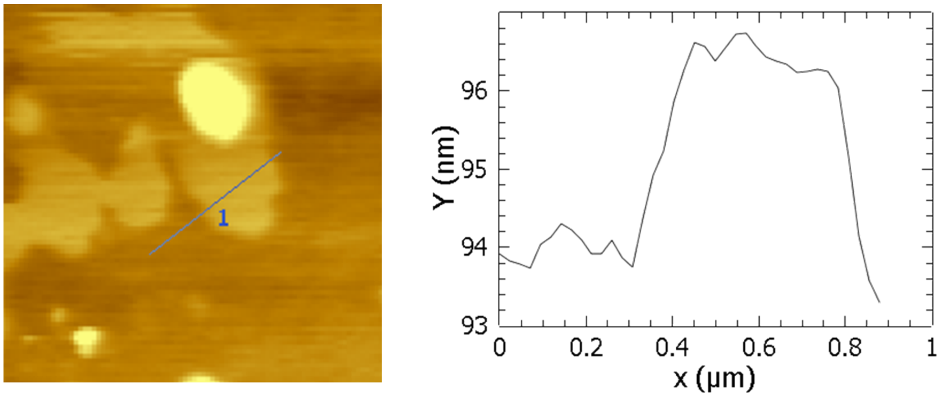
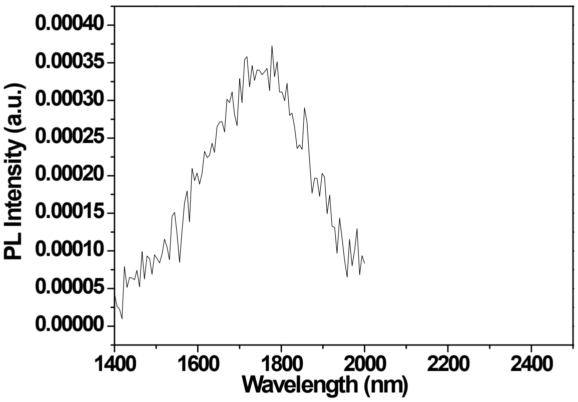


Figure S**3**. The AFM image and one height profile of the nanosheets.

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.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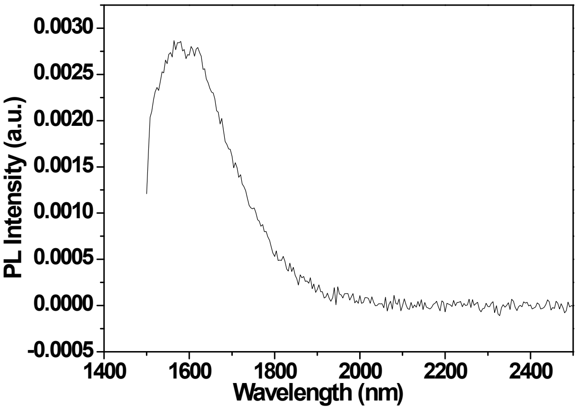
0.00030
0.00025
0.00020
0.00015
0.00010
0.00005
0.00000
1400
1600
1800
2000
2200
2400
Wavelength (nm)

(a)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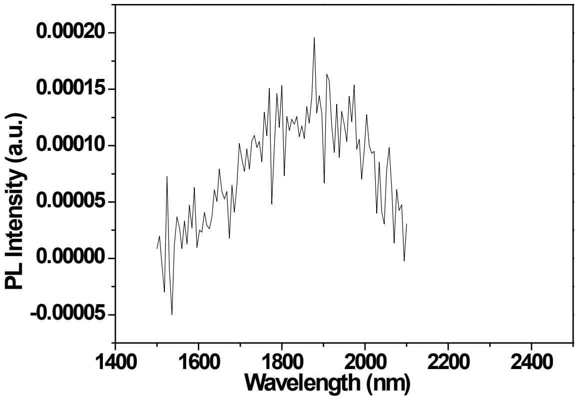
0.0015
0.0010
0.0005
0.0000
-0.0005
1400
1600
1800
2000
2200
2400
Wavelength (nm)

(b)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0.00000
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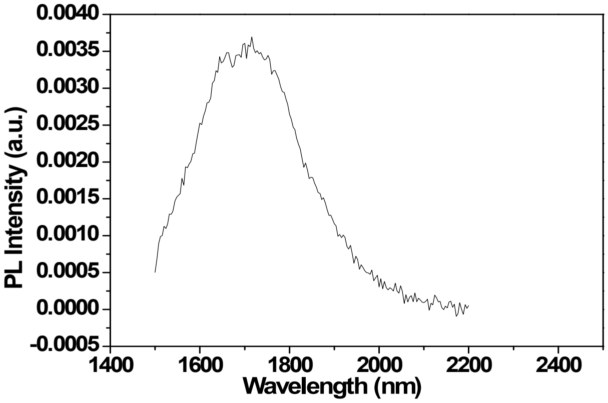
1600
1800
2000
2200
2400
Wavelength (nm)

(c)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0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
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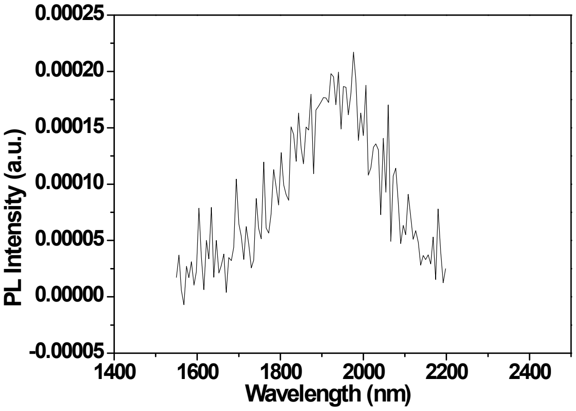
1400
1600
1800
2000
2200
2400
Wavelength (nm)

(d)


PL Intensity (a.u.)
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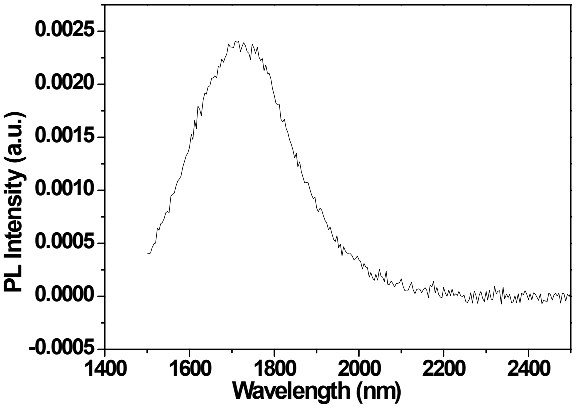
-0.00005
1400
1600
1800
2000
2200
2400
Wavelength (nm)

(e)


PL Intensity (a.u.)
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0.0015
0.0010
0.0005
0.0000
-0.0005
1400
1600
1800
2000
2200
2400
Wavelength (nm)

(f)

Figure S4. 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.

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.

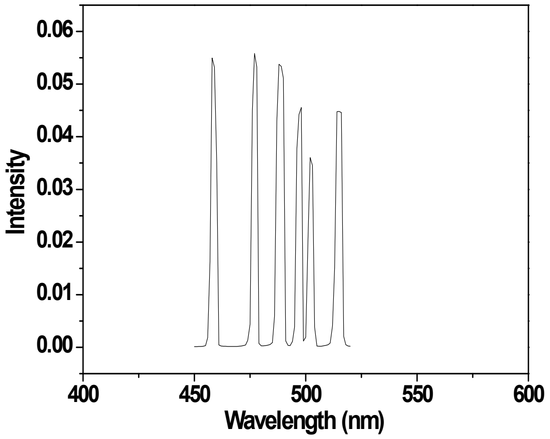

Figure S5. Spectrum the laser (Reliant laser from Laser Physics) used as the light source for PL measurements.