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Preparation of Photostable NIR Luminescent Glass with Quantum dot-Layered Double Hydroxide Composites

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1. Materials

Lead(II) acetate trihydrate, cadmium acetate hydrate, zinc oxide, zinc nitrate hexahydrate, aluminum nitrate nonahydrate, octadecene (ODE) (technical grade, 90%), bis(trimethylsilyl)sulfide ($(TMS)_2S$) (synthesis grade), trioctylphosphine (TOP) (technical grade, 90%), and oleic acid (OA) (technical grade, 90%), lipoic acid, sodium borohydride were purchased from Sigma-Aldrich. Aqueous ammonia solution (28.0-30.3 wt%), sodium chloride (NaCl), and 5 M hydrogen chloride (HCl) solution were obtained from Samjeon Pure chemicals. Formamide was purchased fromJunsei Chemical Co., Ltd. All chemicals were used without further purification.

2. Synthesis of PbS/CdS core/shell QDs

2.1 Synthesis of PbS QDs

All manipulations were performed using the standard Schlenk line technique. In a typical synthesis of 5.0 nm-sized PbS QDs, lead precursor solution was prepared as follows. Lead(II) acetate trihydrate (2.5 mmol) in a mixed solvent of 10 mmol oleic acid and 10 mL octadecene was degassed in a three-neck round bottom flask for 30 min under vacuum at 100 °C. Then the solution was heated at 180 °C for 1 h under a N_2 atmosphere. After the solution turned transparent, it was cooled to 100 °C and degassed for 30 min to remove acetic acid. For the sulfur precursor solution, 0.25 mmol $(TMS)_2S$ was mixed with 2 mL TOP solution in N_2 atmosphere, and loaded in syringe. The lead precursor solution was heated to 120 °C under a N_2 atmosphere, and the sulfur precursor solution was quickly injected into the lead precursor solution. The temperature was maintained for 2 min. The reaction was quenched by the quick injection of 10 mL cold toluene. To prepare 3.6 nm-sized PbS QDs, the reaction temperature was changed to 105 °C and other procedures remained the same. Before characterization, the final product solution was purified and by centrifugation with the addition of methanol and toluene. (crude solution:toluene:methanol = 1:4:35 (v/v%)) The black precipitate acquired after centrifugation was washed with methanol three times and re-dispersed in hexane.

2.2 Cation Exchange from PbS QDs to PbS/CdS core/shell QDs

The cation exchange process for thin shell of CdS on PbS QDs was a modification of Zhao's method[1]. 6 mmol of CdO, 9 mL (24 mmol) of oleic acid, and 20 mL of ODE were heated to 255 °C under N_2 purging until all of the CdO had dissolved to yield 0.2 M cadmium oleate solution. The solution was cooled to 100 °C under N_2 gas atmosphere, and degassed under vacuum to remove remaining water molecules. Then 200 nmol of purified PbS QDs was dispersed in 35 mL of ODE and degassed under vacuum at room temperature (RT), and 5 mL of 0.2 M cadmium oleate solution ([Cd]/[PbS QD]=5000) was added. The reaction solution was stirred at 30 °C for 30 min. Every 15 min, the temperature of reaction solution was increased stepwise by 5 °C. To produce monolayer CdS shell, the solution was typically heated to 50 °C, and annealed at that temperature for 15 min, then the reaction flask was cooled to RT. An aliquot of known volume of final product was extracted and diluted in toluene to calculate the extinction coefficient of PbS/CdS QDs on the basis of the number of PbS QD present. PbS/CdS QD solution was precipitated and purified with centrifugation with methanol, acetone, and toluene. (crude solution:toluene:methanol:acetone=2:3:30:10 (v/v%)) The brown precipitates acquired after centrifugation was washed with methanol 3 times. The purification step was repeated at least twice to eliminate unreacted precursors and surfactants.

3. Ligand Exchange of PbS/CdS QDs

The oleic acid surfactants of crude QDs were replaced with hydrophilic ligands by using lipoic acid (LA). The total amount of ligands was 10^5 times the number of QDs. To reduce the disulfide bond of LA to a dithiol group, 1 mmol LA in 2 mL deionized water was reduced by adding 2.2-equimolar amount of sodium borohydride and vigorously stirred for 20 min at RT. Purified QDs (10 nmol) in 1 mL chloroform were mixed with the solution of reduced LAs, and stirred vigorously for 1 hours at 50 °C. During the exchange of surfactants, QDs were transferred from chloroform to aqueous phase. After ligand exchange, the aqueous phase was extracted and degassed at RT under vacuum to remove the residual chloroform. QD aqueous solution was filtered with 0.2 μm membrane filter to clear away aggregates. To remove excess ligands, QD solution was dialyzed by using Amicon 50 kDa MW cutoff centrifugal filters.

4. Measurement of Photoluminescence Quantum Yield (PL QY) of QD

Absolute photoluminescence quantum yield (PL QY) of NIR-II emitting QD film was calculated using an integrating sphere (Labsphere) and wavelength-calibrated Si and InGaAs detectors, Si and InGaAs CCD. The optical setup and calculation has been reported previously[2]. We neglected the reabsorption effect in this measurement. The sample was excited at 828 nm with bandwidths of 20 nm from a Xenon lamp dispersed by a monochromator. Liquid sample was held in micro cell (light path 10 mm x 2 mm, 104.002F-QS, Hellma); and solid QD glass film sample was measured as coated on 15 mm x 15 mm soda lime glass.

5. Preparation of QD-LDH composites

5-1. Preparation and exfoliation of layered double hydroxides

Zinc nitrate hexahydrate (12 mmol) and 4 mmol aluminum nitrate nonahydrate were dissolved in 1 L of deionized water. Then 20 mL aqueous ammonia solution (28.0-30.3 wt %) was added. The mixture solution was stirred for 48 h at RT, then centrifuged to remove the solvent and collect the precipitated layered double hydroxide (LDH) powder. The LDH powder was dried in an oven at 60 °C for 12 h. CO_3^{2-} ions were deintercalated from the as-prepared LDHs by the salt-acid method[5]. First, 0.2 g of LDH powder was dispersed in 200 mL of 1 M NaCl and 3.3 mM HCl aqueous solution. The aqueous solution was stirred for 12 h at RT under a rigorous flow of N_2 gas to remove the dissolved CO_2 gas. The product was gathered by centrifugation, and then dried in an oven at 60 °C. 0.1 g of the product powders was dispersed into 100 mL of formamide in a flask, which was purged with N_2 gas, then sealed. The solution was stirred vigorously for 48 h. To remove the unexfoliated LDH powders, the suspension was centrifuged at 2000 rpm for 10 min, and then the sediment was discarded.

5-2. Formation of QD-LDH composites

Exfoliated LDH (20 mL) suspension was centrifuged at 15000 rpm for 20 min. The supernatant was removed and the sediment was mixed with 1 mL of 10 μM DHLA-capped QDs. The mixture was vortexed for 1 h at RT, then centrifuged. The supernatant was discarded and the sediment was dried in an oven at 60 °C.

6. Preparation of QD-LDH-As_2S_3 composites

The glass precursor of As_2S_3-propyl amine was prepared using Kovalenko's method[3]. Solid As_2S_3 (2.1 g) was added to 10 mL propyl amine under N_2 gas. The mixture was thoroughly mixed using a magnetic stir bar for 2 days. The mixture solution was filtered with 0.45-μm membrane filter under N_2 gas to remove the insoluble impurities also. In typical fabrication process, 1.0 mL of As_2S_3-propyl amine solution which contained 495 mg of As_2S_3 glass precursor was mixed with 8 mg of QD-LDH composites which possessed ~8 nmol of QD, and drop-casted onto silica glass substrate that had been pre-washed in piranha solution. The mixture was heated at 60 °C for 1 h, 90 °C for 1 h, and 130 °C for 1 h under vacuum. To change the QD content, the amount of QD-LDH varied from 2, 8, 16 mg and mixed with 1.0 mL of As_2S_3-propyl amine solution, which resulted in the QD-LDH-As_2S_3 composites with different QD content of 0.06, 0.28, and 0.42 wt% measured by inductively coupled plasma atomic emission spectroscopy. As a control experiment without LDH protective layer, 40 nmol of oleate-coated PbS/CdS QDs were mixed with 1.0 mL of As_2S_3-propyl amine solution. This mixture was heated in the same way as above.

7. Characterization

UV-VIS absorption spectra were measured using a Hewlett-Packard Agilent 8453 Spectrophotometer. Fluorescence change was recorded using a HORIBA Jobin Yvon Fluorolog3 InGaAs CCD, which was excited by 828 nm wavelength light from a Xenon lamp. Transmission electron microscope (TEM) images were obtained using a JEOL JEM-2100 and JEOL JEM-2100f. X-ray diffraction pattern was collected with RIGAKU JAPAN D/MAX-2500/PC. Hydrodynamic size and zeta potential of colloidal nanoparticles were measured using a Malvern zetasizer Z and S.

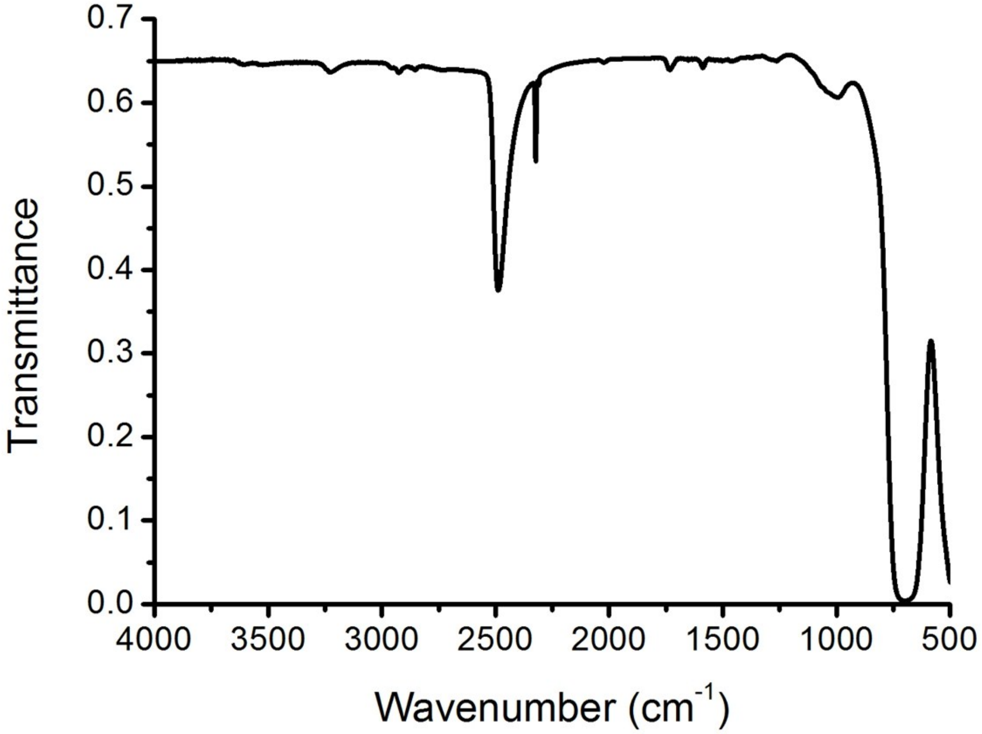

Figure S1. Fourier-transform infrared spectroscopy (FT-IR) data of As_2S_3 glass only.

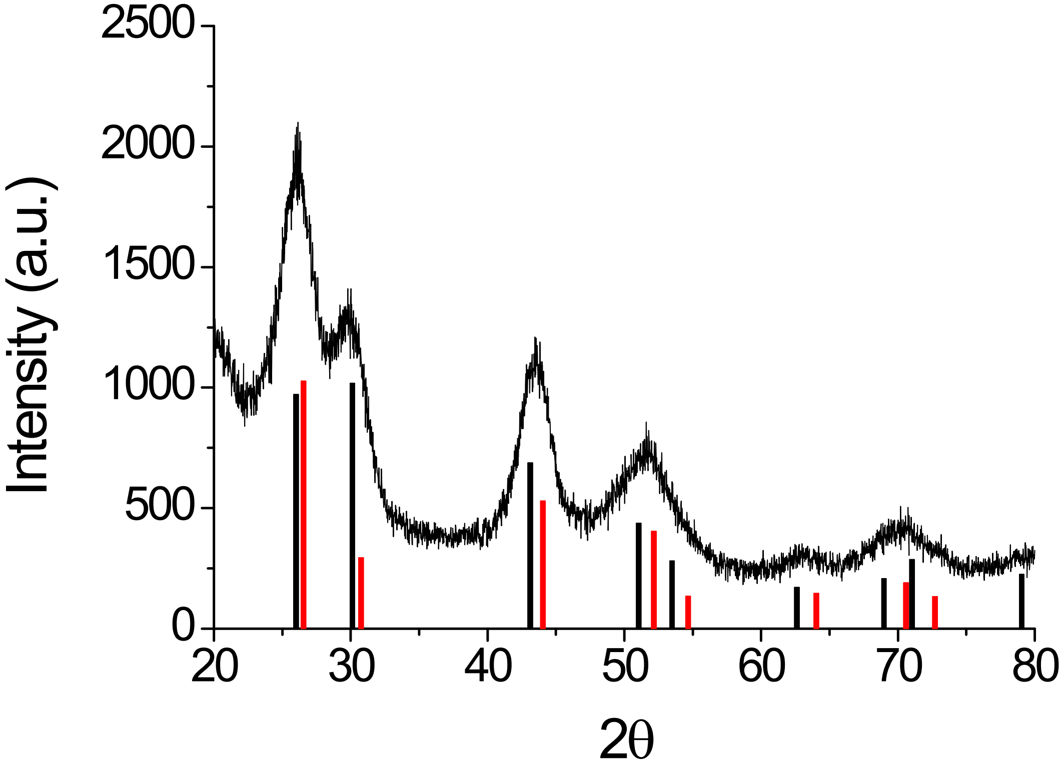

Figure S2. X-ray diffraction pattern (XRD) of PbS/CdS QDs. Vertical bars (bottom) correspond to reference data of the rock-salt cubic crystalline structure of PbS (black) and zinc blende structure of CdS (red) (JCPDS file No. 01-078-1054 and No. 10-454, respectively).

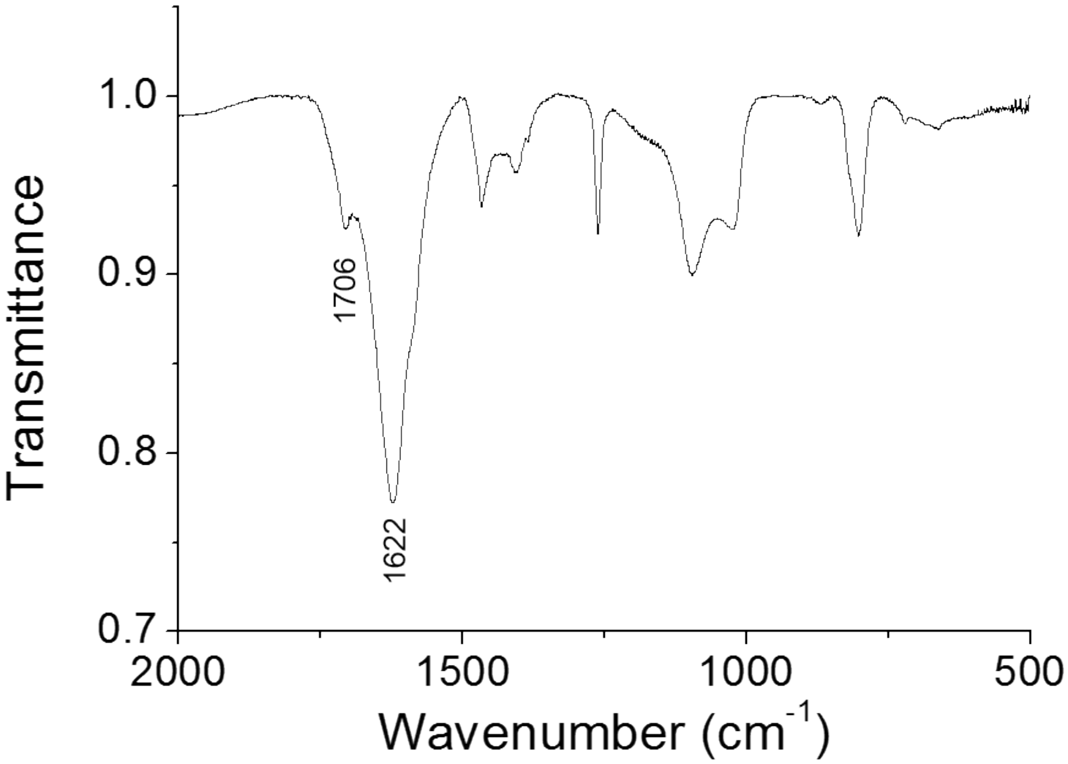

Figure S3. FT-IR spectra of hydrophilic PbS/CdS QDs coated by dihydrogen lipoic acid. Vibration mode of C=O bond in carboxylic acid can be found at 1706 cm^{-1}. The peak at 1622 cm^{-1} resulted from the bending mode of residual water molecules.

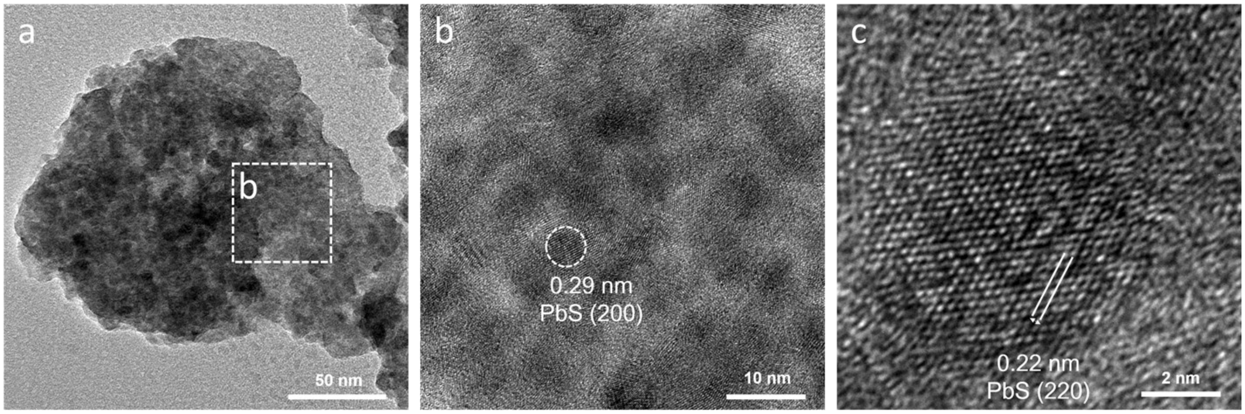

Figure S4. (a) TEM images of PbS/CdS QD-LDH composites. (b) Magnified area of the dotted rectangular region in (a). Diameter of the dotted circle in (b) is 5 nm. (c) The lattice fringes of (200) and (220) facet of rock salt PbS crystalline structure in LDH clearly showed the existence of PbS/CdS core/shell QDs.

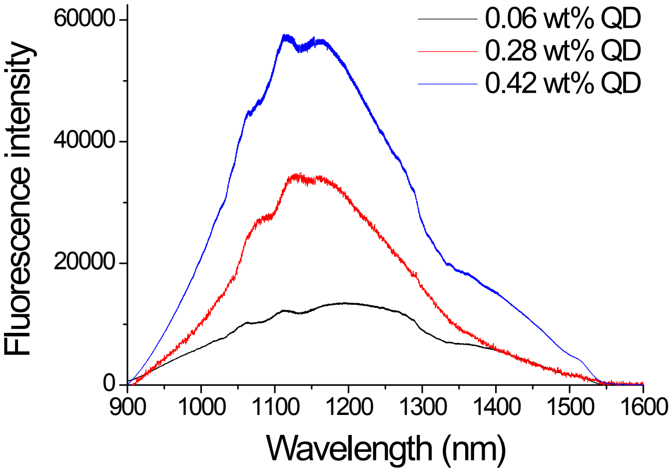

Figure S5. FL spectra of QD-LDH-As_2S_3 glass films with different loading percentage of QD from 0.06 to 0.42 wt%.

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(2) Hatami, S.; Wurth, C.; Kaiser, M.; Leubner, S.; Gabriel, S.; Bahrig, L.; Lesnyak, V.; Pauli, J.; Gaponik, N.; Eychmuller, A.; Resch-Genger, U. *Nanoscale* **2015**.

(3) Kovalenko, M. V.; Schaller, R. D.; Jarzab, D.; Loi, M. A.; Talapin, D. V. *J. Am. Chem. Soc.* **2012**, *134*, 2457.