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Electronic supplementary information

Room-temperature method for coating ZnS shell on semiconductor quantum dots

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Experimental section

Materials

Cadmium oxide (CdO, 99.99%), zinc acetate ($Zn(Ac)_2$, 99.99%)、selenium powder (Se, 99.99%), hexamethyldisilathiane ($(TMS)_2S$, synthesis grade), oleylamine (OAm, 70%), oleic acid (OAc, 90%) were purchased from Sigma Aldrich. Myristic acid (MA, 98%), 1-octylamine (OA, 99%), trioctylphosphine (TOP, tech. 90%) were purchased from Alfa Aesar. 1-Octadecene (ODE, tech. 90%) was purchased from ACROS. Silver acetate, stearic acid, toluene, anhydrous hexane, and anhydrous methanol, anhydrous ethanol were purchased from China National Pharmaceutical Group Corporation.

Synthesis of CdSe nanocrystals

In a typical synthetic process, 0.35 mmol of CdO and 500 mg of stearic acid were added to a 25 mL 3-neck round-bottomed reaction flask, and heated to 150 °C until the CdO was completely dissolved. 1 mL of OAm, 0.5 mL of OAc and 6 mL of ODE were added to the reaction flask. After purged with argon at 60°C for 30 min, the mixture was heated to 280°C under argon flow. Then, the Se precursor (1.2 mmol Se dissolved in 3 mL of TOP) in the syringe was injected swiftly into the reaction flask under vigorous stirring. After the injection, the temperature of the reaction solution was set at 25 °C for the growth of CdSe nanocrystals. The as-prepared CdSe nanocrystals were purified by washing them with methanol and subsequently centrifuging. The precipitates of CdSe nanocrystals were redispersed in n-hexane or toluene.

Synthesis of Ag_2S nanocrystals

The Ag_2S nanocrystals were synthesized according to our reported method. In a typical synthetic process, 1.6 mmol of MA, 2.4 mmol of OA and 5mL of ODE were added to a 25 mL 3-neck round-bottomed reaction flask. 0.1 mmol of silver acetate powder was also added to the flask under stirring. After purged with argon at 60°C for 30 min, the mixture was heated to 110°C under argon flow. When the silver acetate was completely dissolved, the $(TMS)_2S$ precursor (0.05 mmol of $(TMS)_2S$ dissolved in 1.5 mL of TOP) in the syringe was injected swiftly into the reaction flask under vigorous stirring. After the injection, the temperature of the reaction solution was set at 90°C for the growth of Ag_2S nanocrystals. The as-prepared Ag_2S nanocrystals were purified by washing them with methanol and subsequently centrifuging. The precipitates of Ag_2S nanocrystals were redispersed in n-hexane or toluene.

The growth of ZnS shell on the CdSe and Ag_2S nanocrystals at room temperature without oxygen-free process

Preparation of Zn precursor solution (OAm-Zn^{2+}): 0.15 mmol of zinc acetate was dissolved in 1 mL of OAm and 2 mL of toluene

Preparation of S precursor solution (DDAB-S^{2-}): 3 mL of toluene containing 0.15 mmol of DDAB was mixed with 3 mL of 0.05 M aqueous Na_2S solution. After that, the S^{2-} anions were then transferred from water phase to toluene phase. The toluene phase was separated and used as sulfur precursor (DDAB-S^{2-}) in the further experiments.

In this procedure, 1 mL of OAm was added to 5 mL of the prepared CdSe or Ag_2S nanocrystals in a 50 mL 3-neck round-bottomed reaction flask. Then, 3 mL of Zn precursor solution and 3 mL of S precursor solution were synchronously added dropwise into the reaction flask under stirring at room temperature without oxygen-free process. The purification process of the as-prepared Ag_2S nanocrystals was similar with the process mentioned above.

Characterizations

JEM2010FEF (UHR) microscope with an acceleration voltage of 200 kV was used for transmission electron microscopy (TEM) imaging. The TEM samples were prepared by drying a hexane dispersion of the particles on copper grids coated with amorphous carbon film. The X-ray powder diffraction (XRD) patterns were obtained with Bruka D8 Advanced X-Ray diffractometer (Bruker axs) using Cu K-alpha radiation of wavelength 1.5406 Å, and the scan rate was 0.5 degree/min. Energy-dispersive X-ray (EDX) data were obtained by using JEM 2010 FEF (UHR) microscope equipped with EDX spectrometry (EDAX Inc.). Absorption spectra were recorded on UV-2550 spectrophotometer (SHIMADZU). Photoluminescence (PL) spectra were collected with the Fluorolog-3 fluorescence spectrophotometer (HORIBA JOVIN YVON INC.) equipped with photomultiplier tube (PMT) detector.

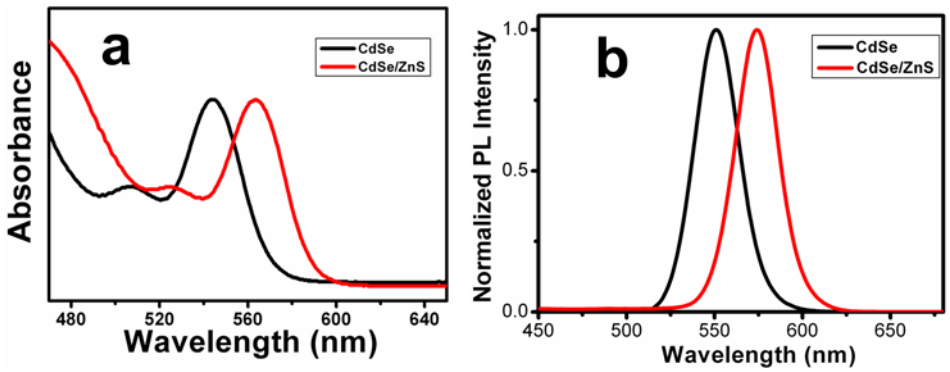

Fig S1. Absorption spectra (a) and the corresponding photoluminescence (PL) spectra (b) of CdSe QDs before (black line) and after (red line) coating ZnS shell at 150 °C. The ZnS shell was grown at 150 °C by using $Zn(Ac)_2$ and $(TMS)_2S$ as reactants. After coating ZnS shell, the PL peak and the corresponding absorption peak shifted from 551 nm to 575 nm and 545 nm to 564 nm, respectively.

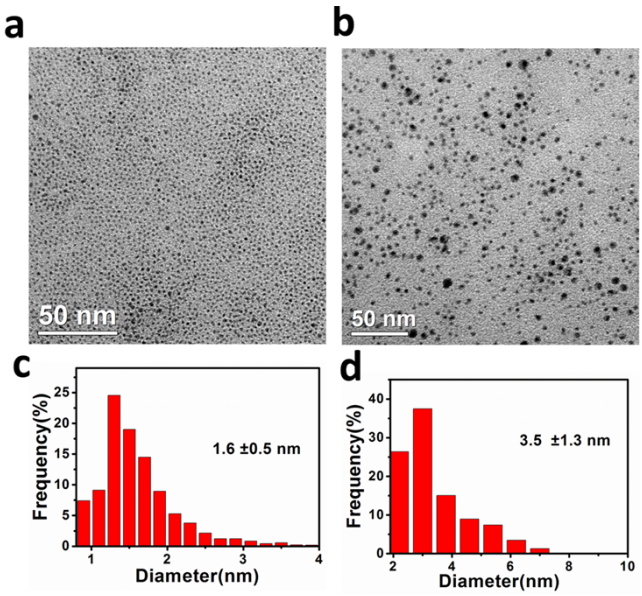

Fig. S2 TEM images of Ag_2S core (a) and Ag_2S/ZnS core/shell quantum dots (b), and the corresponding size distribution histograms (c, d).

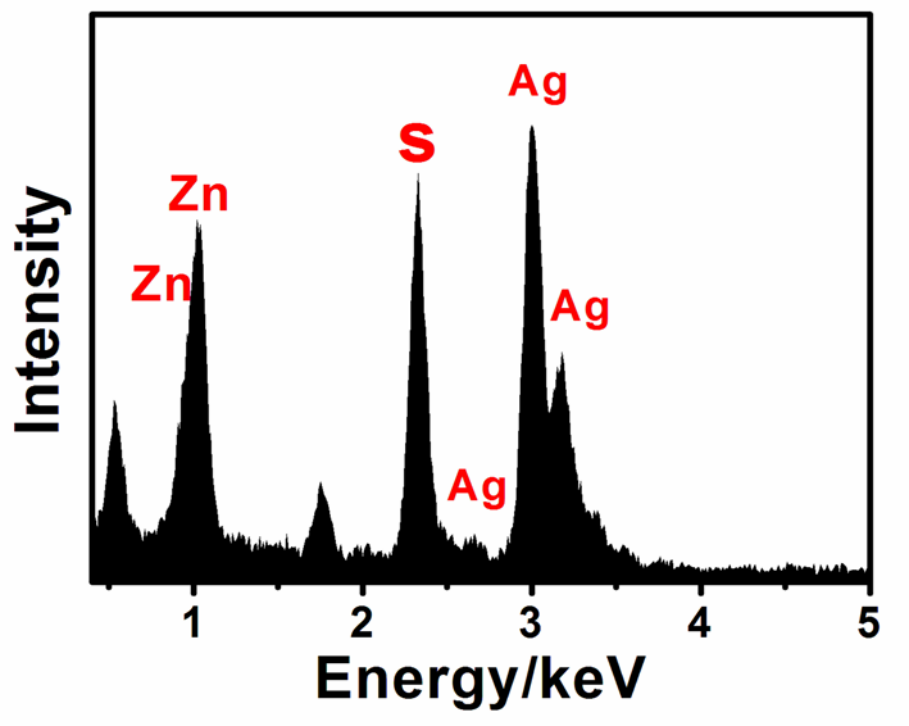

Fig. S3 EDX spectrum of the Ag_2S/ZnS core/shell quantum dots.

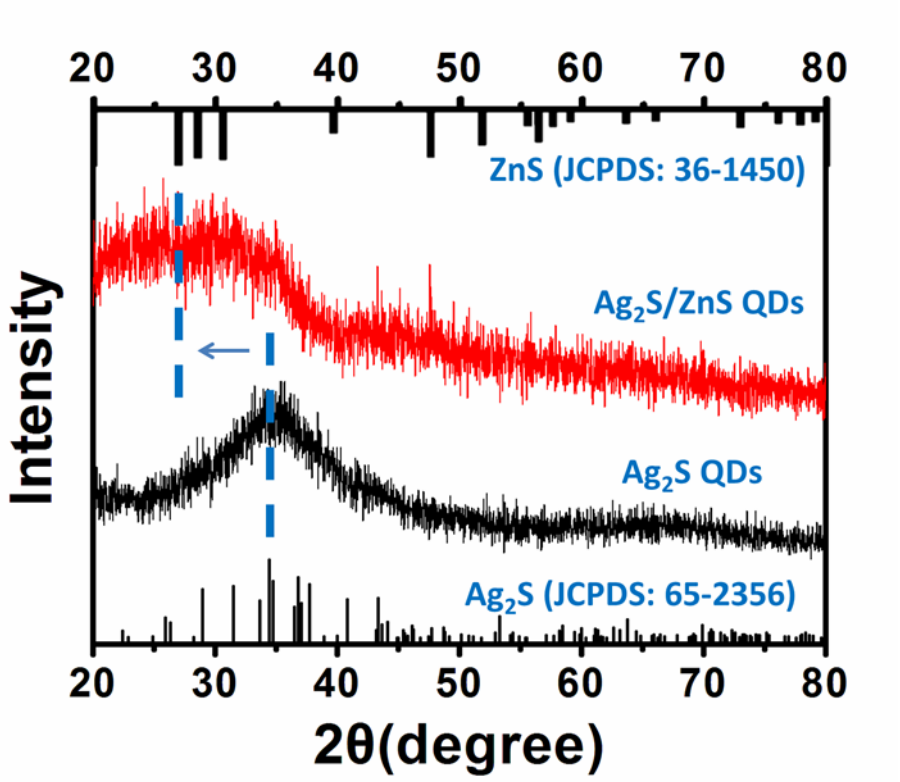

Fig. S4 XRD patterns of Ag_2S core and Ag_2S/ZnS core/shell quantum dots.