Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Tailoring the Interfacial Structure of Colloidal "Giant" Quantum Dots for Optoelectronic Applications

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1. Experimental section

1.1 Materials: Trioctyl phosphine oxide (TOPO), trioctyl phosphine (TOP) (97%), Sulfur (100%), oleylamine (OLA), cadmium oxide (99%), oleic acid (OA), Rhodamine 6G, octadecene (ODE), and selenium pellet (≥99.999%) were obtained from Sigma-Aldrich Inc. Zinc nitrate hexahydrate (98%), sodium sulfide (Na_2S), sodium hydroxide, sodium sulfite (Na_2SO_3), hexane, toluene, methanol, acetone, ethanol and isopropanol (IPA) were obtained from Sinopharm Chemical Reagent Co., Ltd. Ti-Nanoxide BL/SC and TiO_2 pastes (20 nm and mixture of 20 nm and 450 nm) were bought from Sigma-Aldrich Inc. Transparent Fluorine doped tin oxide (FTO) coated conducting glass substrates with sheet resistance 10 Ω/square were bought from Pilkington glasses. All chemicals were used as purchased without any purification.

1.2 CdSe quantum dots (QDs) synthesis: TOPO (1 g) and $Cd(oleate)_2$ (0.38 mmol, 1 mL) in 8 mL of ODE were purged by N_2 at room temperature for 30 min. The reaction system was evacuated for 30 min at 100 °C, and then the temperature was raised to 280 °C. The Se powder (4 mmol) was dissoved in the TOP (4 mL), then the Se-TOP mixture was mixed with 3 mL of OLA, and 1 mL of ODE at room temperature. The mixture was quickly injected into the Cd-oleate suspension under vigorous stirring. The temerature of the mixture decreased quickly to 240 °C. After maintaining the reactionn at this temperature for 5 minutes, the reaction cell was quenched with cold water. Ethanol was added, then the suspension was centrifuged, the supernatant was removed and, finally, the QDs were dispersed in hexane.

1.3 Synthesis of core/shell QDs: Deposition of CdS layers on CdSe QDs was obtained by a successive ionic layer adsorption reaction (SILAR) approach. CdO was dissoved in oleic acid (OA) (molar ratio of 1:2) by heating the mixture to 240 °C for 30 min under vaccum with a final concentration of 0.2 M by adding octadecene (ODE). The S powder was dissoved in ODE with a final concentration of 0.2 M. The S/Se powder (molar ratio of 1:1) was dissoved in trioctyl phosphine (TOP) with a final concentration of 0.2 M. In detailds, in a round-bottom flask, OLA/ODE (5 ml/5 mL) and CdSe QDs ($\sim 2 \times 10^{-7}$ mol in 0.2 mL hexane) mixed and then the mixture was degassed at 110 °C for 30 min. The reaction flask was re-stored with N_2. Then the temperature was raised to 240 °C. The $Cd(OA)_2$ dispersed in ODE (0.25 mL, 0.2 M) was added dropwise and the mixture allowed to react for 1.5 h, followed by dropwise addition of 0.2 M S/ODE with same volume. The shell was further annealed for 10 min. All subsequent shells were annealed at 240 °C for ~10 min following the injection of sulfur and ~1 h following dropwise addition of the $Cd(OA)_2$ in ODE. Sulfur/$Cd(OA)_2$ addition volumes for shell addition cycles 1-12 were as follows: 0.25, 0.36, 0.49, 0.63, 0.8, 0.98, 1.18, 1.41, 1.66, 1.92, 2.2, and 2.51 mL, respectively.

For the synthesis of alloyed CdSe/$CdSe_xS_{1-x}$/CdS QDs, typically, OLA (5 mL) and ODE (5 mL) were mixed with 0.2 mL of CdSe QDs ($\sim 2 \times 10^{-7}$ mol in hexane), then the mixture was degassed at 110 °C for 30 min to evaporate the hexane. Subsequently, the temperature was raised to 240 °C under N_2 flow. The $Cd(OA)_2$ dispersed in ODE (0.25 mL, 0.2 M) was added dropwise to the mixture. After 1.5 h, the S/Se trioctyl phosphine solution was added dropwise to the reaction mixture with the same volume. The shell was further annealed for 10 min. S/Se and $Cd(OA)_2$ addition volumes for shell addition cycles 1-6 were as follows: 0.25, 0.36, 0.49, 0.63, 0.8, and 0.98 mL, respectively. The molar ratio of Se/S is 1:1. After 6-cycle growth of CdSeS alloyed shell, $Cd(OA)_2$/S precursors were used for further growth of the 6-cycle CdS shell. Sulfur/$Cd(OA)_2$ addition volumes for shell addition cycles 7-12 were as follows: 1.18, 1.41, 1.66, 1.92, 2.2, and 2.51 mL, respectively. The reaction was cooled to 20 °C by injecting cold toluene (-10 °C) to the reaction mixture. The purified QDs were dispersed in toluene for further characterization and device fabrication.

1.4 TiO_2 film preparation: FTO glass substrates were cleaned with ethanol and dried in a N_2 stream. A compact TiO_2 layer was spin coated on FTO glass substrates at 5000 r.p.m. for 30 s by using the solution Ti-Nanoxide, followed by annealing in air at 500 ℃ for 30 min and cooled down to room temperature. Subsequently a commercial TiO_2 paste, a blend of small anatase particles (~20 nm in diameter) and larger anatase particles (up to 450 nm in diameter) paste was deposited on the TiO_2 blocking layer by tape casting and dried in air for 15 min. The photoanodes were then fired on a hot plate at 120 °C for 6 min. The electrodes were subsequently sintered according to the following temperature profile: 325 °C /5 min, 375 °C/5 min, 450 °C/15 min and 500 °C 30 min with a ramp rate of 10 °C/minute. After cooling to room temperature, a TiO_2 mesoporous film (∼14 μm) was achieved.

1.5 Preparation of QDs-TiO_2 anode: QDs were deposited into mesoporous TiO_2 film by an electrophoretic deposition (EPD) method. Typically, a pair of TiO_2 films on FTO substrate were vertically immersed in the QD dispersion with a distance of 1 cm. A direct current bias of 200 V was applied for 120 min. The samples were rinsed three times with toluene and dried with N_2 at room temperature. The two-monolayers of ZnS capping layer were formed using the SILAR process.

2 Supporting Figures and Tables

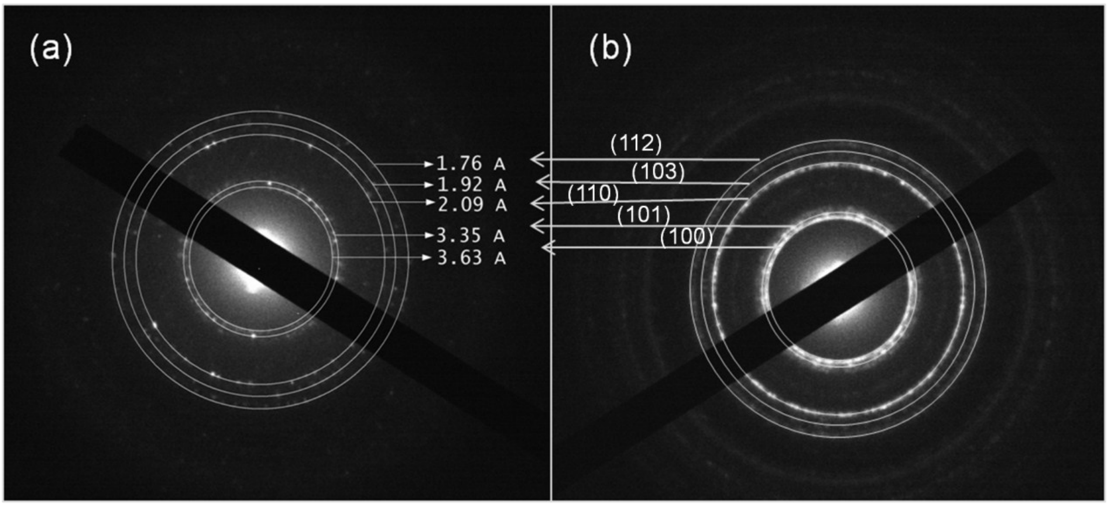

Fig. S1 The selected area selected-area electron diffraction patterns of “giant” CdSe/12CdS QDs (a), and CdSe/6CdSeS/6CdS QDs (b), indicating a wurtzite crystal structure.

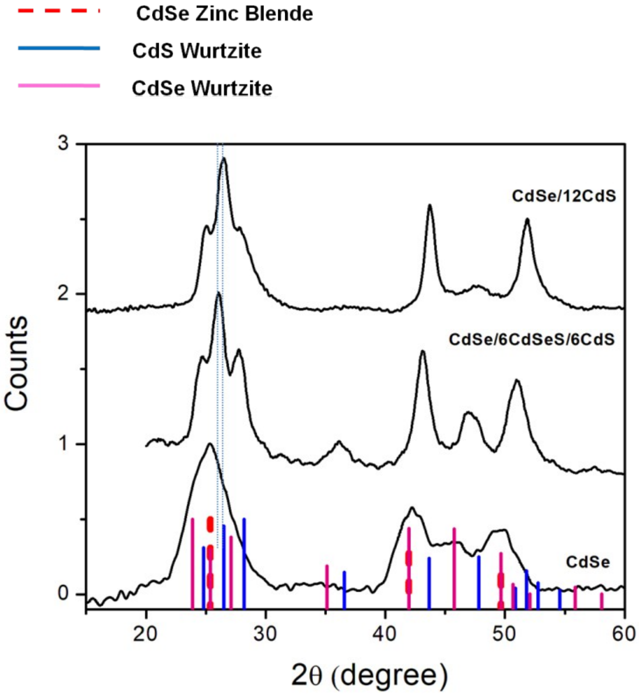

Fig. S2 X-ray diffraction patterns of CdSe QDs, “giant” CdSe/12CdS QDs, and CdSe/6CdSeS/6CdS QDs.

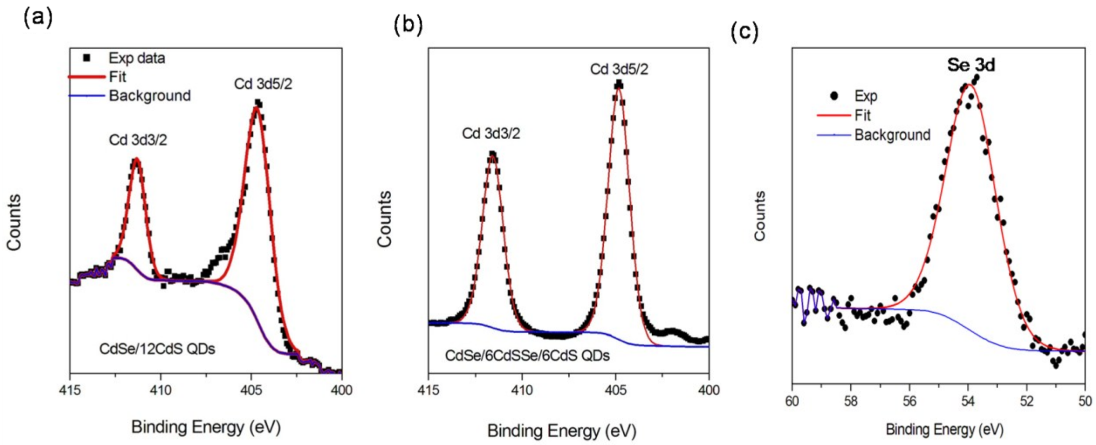

Fig. S3 High-resolution XPS Cd 3d and Se 3d spectra of the "giant" CdSe/12CdS QDs (a), and CdSe/6CdSeS/6CdS QDs QDs (b). (c) High-resolution XPS Se 3d spectra of the CdSe/6CdSeS/6CdS QDs QDs.

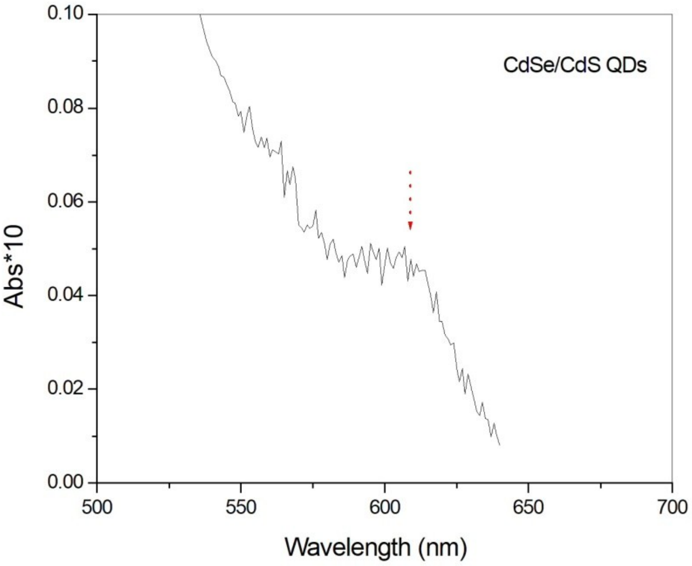

Fig. S4 Absorption spectrum of CdSe/CdS QDs in the range 500-700 nm.

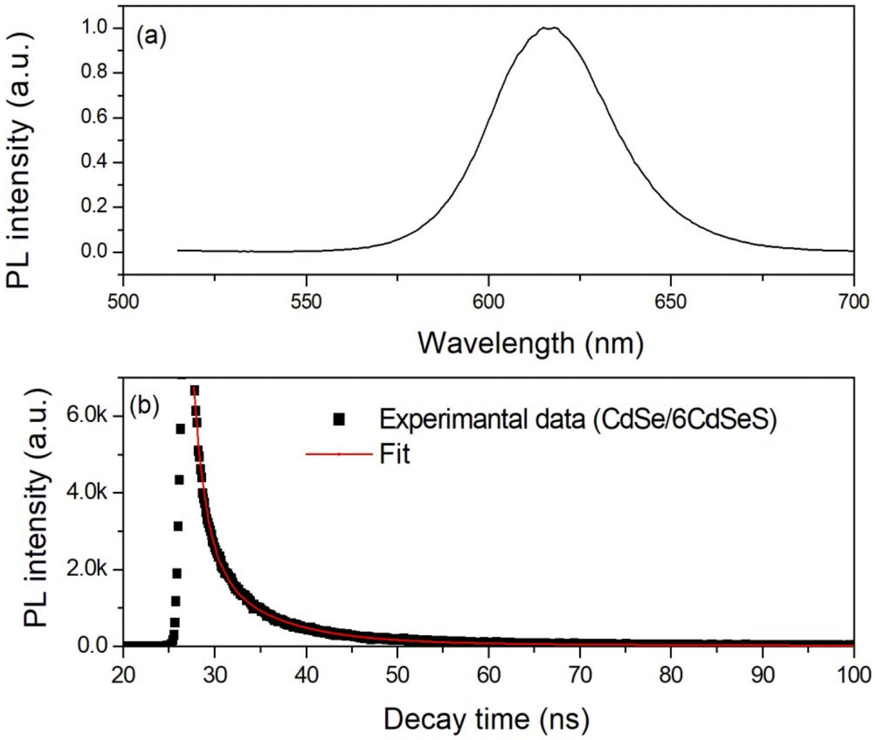

Fig. S5 (a) PL spectrum and (b) PL decay curves of CdSe/6CdSeS/6CdS QDs.