Electronic Supplementary Information (ESI)

Highly Bright Water-Soluble Silica Coated Quantum Dots with Excellent Stability

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Synthesis of CdSe/CdS/ZnS core/shell/shell QDs

Chemicals. oleylamine (OAm, 70%), 1-hexadecylamine (98%), 1-dodecylamine (>99%), oleic acid (99%), 1-octadecene (ODE, >95%) were obtained from Aldrich and used without further purification. All organic solvents such as hexane, dichloromethane, ethanol, methanol were of analytical grade and obtained from commercial sources and used as received. Deionized water was used throughout.

Synthesis of CdSe core QDs. CdSe core QDs were synthesized according to the method reported in a literature.[1] Typically, CdO (25.6 mg, 0.2 mmol), oleic acid (1.0 mL), TOPO (1.3 g), and ODE (4.0 mL) were placed in a 50 mL three-neck flask. The mixture was then heated to 320–330 ^{o}C under N_2 protection, and a colorless solution was obtained. After cooling to 315 ^{o}C, Se precursor solution (2.4 mL) made by dissolving selenium (79.0 mg) in TOP (4.0 mL) and ODE (6.0 mL) via supersonication was injected into the above solution. The reaction temperature was then set at ~270 ^{o}C for the growth of the CdSe core. During this process, different periods of heating time (10 s to 3 min) were used to adjust the desired size of the CdSe core because of the dependence of nanocrystal size on the reaction time. Finally, the reaction mixture was cooled to ~ 60 ^{o}C to obtain the CdSe core. The as-prepared CdSe core was further extracted by using 10.0 mL of hexane/CH_3OH (v/v, 1:1) as the extraction solvent to separate the CdSe core from byproducts and unreacted precursors, and then purified by centrifugation with the addition of acetone. The supernatant was discarded and the precipitate was re-dissolved in hexane for further using.

Stock solutions preparation. The Cd precursor solution (0.1 M) was prepared by dissolving CdO (128.4 mg, 1 mmol) in oleic acid (2.0 mL) and ODE (8.0 mL) at 160 ^{o}C. The sulfur precursor solution (0.1 M) was obtained by dissolving sulfur in ODE at 120 ^{o}C. The Zn

precursor solution (0.1 M) was prepared by dissolving $Zn(OAc)_2 \cdot 2H_2O$ (219.5 mg, 1 mmol) in ODE (10.0 mL) at 160 ^oC. Each stock solution was stored at room temperature.

Synthesis of CdSe/CdS/ZnS Core/Shell/Shell QDs. Oleic acid/OAm-capped oil-soluble CdSe/CdS/ZnS core/shell/shell QDs were prepared following the successive ion layer adsorption and reaction (SILAR) technique.[2,3] In a typical procedure, the obtained purified CdSe core in hexane solution, ODE (4.0 mL) and oleylamine (1.0 mL) were placed in a 50 mL flask, and then pumped down at room temperature for 20 min to remove the hexane and at 100 ^oC for another 20 min while flushing the reaction system twice with N_2. The reaction system was heated to 230 ^oC, and the Cd precursor stock solution was then injected into the above reaction mixture. After reacting for 10 min when the Cd precursor was fully deposited around the CdSe surface, an equimolar amount of S precursor stock solution was added into the reaction mixture for the growth of the CdS shell. After the first monolayer of CdS was deposited around the CdSe cores, another CdS shell was formed by adding Cd/S precursor solution alternately at approximately 10 min intervals. The volume of the precursor stock solution added in each cycle was the amount needed for a whole monolayer of CdS shell which was calculated from the respective volumes of concentric spherical shells with 0.35 nm thickness for one monolayer (ML) of CdS (e.g. 0.7, 1.0, 1.3 mL for the 1^{st}, 2^{nd}, and 3^{rd} ML, respectively). After the formation of CdS layers, the reaction temperature was set at 200 ^oC for the overgrowth of ZnS shell by adding the Zn/S precursor stock solution into the reaction system at intervals of 20 min. Aliquots of the sample were taken before a new cycle of injection to record their corresponding UV-vis and PL spectra. Finally, the reaction was terminated by allowing the reaction mixture to cool down to room temperature to obtain the desired CdSe/CdS/ZnS Core/Shell/Shell QDs. The prepared CdSe/CdS/ZnS QDs were purified by the similar procedure to that for CdSe core QDs.

References

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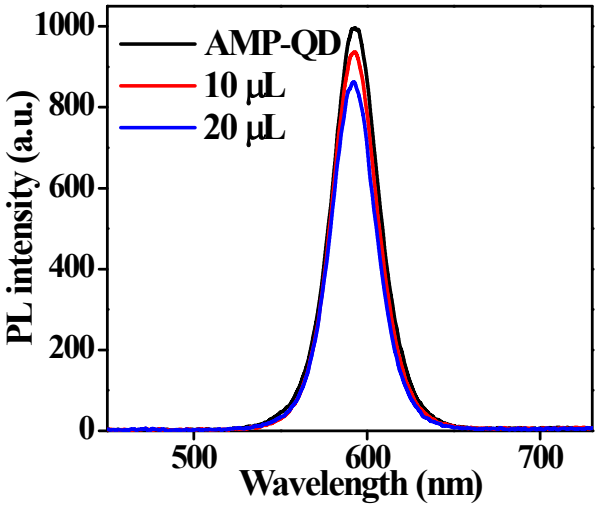

Fig. S1 The PL spectra of QD_{592} and corresponding $QD_{592}@SiO_2$ with the amounts of 10 μL and 20 μL of TEOS.

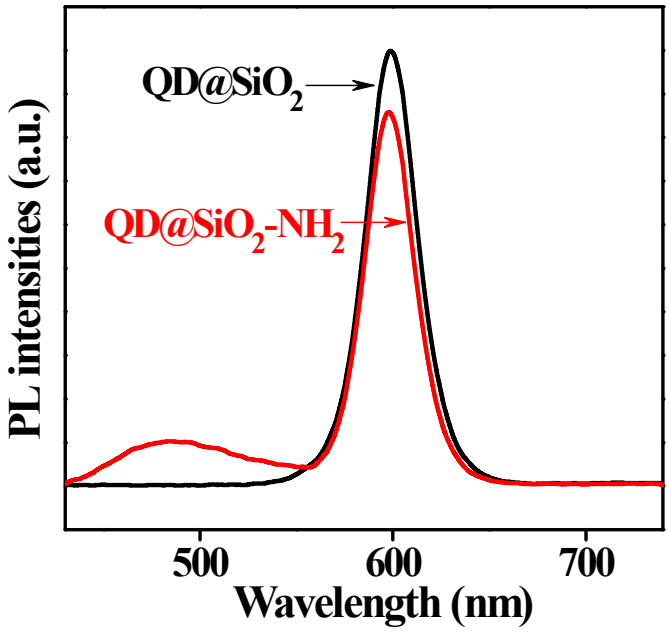

Fig. S2 PL emission (λ_{ex} = 390 nm) spectra of QD@SiO_2 and APTES grafting QD@SiO_2 with addition of fluorescamine. The appearance of PL peak at ~480 nm indicates the existence of amino groups on the APTES-QD@SiO_2 system.