Supporting Information

Tri-n-octylphosphine-Assisted Successive Ionic Layer Adsorption and Reaction Method to Synthesize Multilayered Core/Shell CdSe/ZnS Quantum Dots with Extremely High Quantum Yield

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1. Experimental Section

1.1 Chemicals

Cadmium oxide (99.99%), selenium powder (99.5%, powder), sulfur (99.5%, powder), zinc oxide (99.99%, powder), oleic acid (OA, 90%), stearic acid (SA, 95%) were purchased from Sigma-Aldrich, USA. Trioctylphosphine oxide (TOPO, 95%), tri-n-octylphosphine (TOP, 97%), 1-octadecene (ODE, 90%), and octadecylamine (ODA, 90%) were obtained from J & K Chemical Reagent Company, China. All other organic solvents were purchased from J & K Chemical Reagent Company, China. All the chemicals were used as received without further purification.

1.2 Synthesis of CdSe core QDs

Highly fluorescent CdSe core were prepared by a modified procedure.1-4 For the preparation of orange CdSe core QDs with 590 nm emission, the mixture of 0.2 mmol of CdO, 0.8 mmol of stearic acid in a 25-mL three-neck flask was heated to 220 °C under argon atmosphere to obtain a colorless solution. After cooling to room temperature, 2.16 g of ODA...
and 8 mL of ODE were added into the flask, and reheated to 270 °C under argon atmosphere. At this temperature, a selenium solution made by dissolving 2 mmol of Se in 2 mL of TOP was swiftly injected. The growth temperature was then reduced to 250 °C for 5 min. The reaction mixture was allowed to cool to room temperature, and an extraction procedure was used to purify the nanocrystals from side products and unreacted precursors. This reaction generated CdSe QDs of about 3.7 nm in size with the first absorption peak of 575 nm.

For preparation of green CdSe core QDs with 570 nm emission and red CdSe core QDs with 615 nm emission, same procedures as above were employed except for the use of 0.65 g and 4.9 g of ODA, respectively.

1.3. Synthesis of the Core/Shell QDs

1.3.1. Preparation of the Shell Precursor Solutions

The zinc precursor solution (0.1 mol/L) was prepared by dissolving ZnO (2 mmol) in 16 mmol of oleic acid and 15 ml of ODE at 290 °C. The sulfur precursor (S-ODE) solution (0.1 mol/L) was prepared by dissolving sulfur in ODE at 130 °C. The sulfur precursor* (S-TOP) solution (0.1 mol/L) was prepared by dissolving sulfur in TOP at room temperature. All the precursor solutions were made under an argon atmosphere.

1.3.2. Calculations for the Amount of Precursors for the Injections

The amount of zinc and sulfur precursors required for each layer was determined by the number of the surface atoms of a given size of core/shell QD. The average thickness of one monolayer of ZnS was taken as 0.35 nm, and one additional layer growth would increase the
diameter by 0.7 nm.

For each injection, the calculated amount of injection solution was taken with a syringe using a standard air-free procedure. For example, in a typical experiment with $7.7 \times 10^{-5}$ mmol of 3.7 nm core, $3.3 \times 10^{-2}$ mmol of Zn and S precursors is needed for the growth of first-layer shell, and an additional $4.6 \times 10^{-2}$ mmol of Zn and S precursors is required for the growth of the second layer.

1.3.3. Preparation of Core/Shell QDs based on a TOP-SILAR Method

The TOP-assisted successive ionic layer adsorption and reaction (TOP-SILAR) procedure was used for synthesis of the core/shell QDs.

Orange CdSe QDs (3.7 nm in diameter, $7.7 \times 10^{-5}$ mmol of particles) dissolved in 2.5 mL of hexanes were mixed with 0.8 g of ODA and 4.0 mL of ODE in a 25-mL three-neck flask. The flask was pumped down to remove hexanes with a mechanical pump at room temperature for 30 min, followed by removing any residual air from the system at 100 °C for another 10 min. Subsequently, the system was switched to argon atmosphere and the reaction mixture was heated to 140 °C for the injections.

For the TOP activation procedure, 0.4 mL of TOP solution was injected as an activator, and the reaction mixture was further maintained at 200 °C for 30 min. After the activation, 0.33 mL of Zn injection solution (0.1 mol/L) was injected and maintained at 200 °C for 20 min.

For the growth of ZnS outer layers, without further purification, the temperature was decreased from 200 °C to 180 °C. Then 0.33 mL of S precursor solution was added.
consecutively via syringe to the reaction flask. The temperature was increased immediately to 220 °C for 60 min to allow in-situ growth of first ZnS monolayer, and then decreased to 140 °C.

After 0.4 mL of fresh TOP solution was injected, the temperature was increased immediately to 180 °C. The Zn and S precursor solutions (0.46 mL each) were added consecutively via syringe to the reaction flask at the interval of 10 min for the growth of second ZnS monolayer. Cycling of injection and growth continued for the increased monolayers of ZnS shell, and the amounts of subsequent injection solutions were calculated using the method described in 1.3.2. The reaction was terminated by allowing the reaction mixture to cool to room temperature. The final product was diluted by hexanes followed by a methanol extraction. The extraction procedure was repeated for three times, and the top hexane layer was stored.

Same procedures as above were employed to prepare green and red core/shell QDs, except for the use of different bare CdSe cores and the amounts of precursor for shell growth.

1.3.4. Synthesis of CdSe/ZnS Core/Shell QDs Based on Different Procedure

Orange CdSe QDs were used for synthesize the core/shell QDs according to a modified SILAR procedure.3,7

1.3.4.1 Typical SILAR Method using S-ODE as the S Precursor

Orange CdSe QDs (3.7 nm in diameter, $7.7 \times 10^{-5}$ mmol of particles) dissolved in 2.5 mL of hexanes were mixed with 0.8 g of ODA and 4.0 mL of ODE in a 25-mL three-neck flask.
The flask was pumped down to remove hexanes with a mechanical pump at room temperature for 30 min, followed by removing any residual air from the system at 100 °C for another 10 min. Subsequently, the system was switched to argon atmosphere and the reaction mixture was heated to 200 °C for the injections.

The Zn and S precursor solutions (0.33 mL each) were added consecutively via syringe to the reaction flask containing the CdSe cores at the interval of 10 min. The temperature was increased immediately to 240 °C for 60 min to allow the growth of first ZnS monolayer, and then decreased to 200 °C. Cycling of injection and growth were carried out by using the same process described in 1.3.3. The additional ZnS shells were grown by adding 0.46 mL (2nd layer) and 0.61 mL (3rd layer) of Zn and Se precursor solutions, sequentially. Purification of nanocrystals was carried out by using the same method described in 1.3.3.

1.3.4.2 Modified SILAR Procedure Using S-TOP as the S Precursor

The same procedure as 1.3.7.1 was employed except for the use of S-TOP in place of S-ODE.

1.3.4.3 Modified TOP-SILAR Procedure Using TOPO in Place of TOP

Orange CdSe QDs (3.7 nm in diameter, $7.7 \times 10^{-5}$ mmol of particles) dissolved in 2.5 mL of hexanes were mixed with 0.8 g of ODA, 2.0 g of TOPO and 4.0 mL of ODE in a 25 mL three-neck flask. The flask was pumped down to remove hexanes with a mechanical pump at room temperature for 30 min, followed by removing any residual air from the system at 100 °C for another 10 min. Subsequently, the system was switched to argon atmosphere and
the reaction mixture was heated to 200 °C for the injections.

The same procedure as 1.3.7.1 was employed for the further shell growth.

1.3.4.4 Modified SILAR Procedure Using a TOP Activated Core

For a typical reaction, orange CdSe QDs (3.7 nm in diameter, $7.7 \times 10^{-5}$ mmol of particles) dissolved in 2.5 mL of hexanes were mixed with 0.8 g of ODA and 4.0 mL of ODE in a 25 mL three-neck flask. The flask was pumped down to remove hexanes with a mechanical pump at room temperature for 30 min, followed by removing any residual air from the system at 100 °C for another 10 min. Subsequently, the system was switched to argon atmosphere and the reaction mixture was heated to 140 °C for the injections. 0.4 mL of TOP solution was injected as an activator, and the reaction mixture was further maintained at 200 °C for 30 min. After the activation, 0.33 mL of Zn precursor solution (0.1 mol.L$^{-1}$) was injected and maintained for 20 min at 210 °C to allow the growth.

The reaction was terminated by allowing the reaction mixture to cool to room temperature. The final product was diluted by hexanes followed by a methanol extraction. The extraction procedure was repeated for three times, and the top hexane layer was mixed with 0.8 g of ODA and 4.0 mL of ODE in a 25 mL three-neck flask. The flask was pumped down to remove hexanes with a mechanical pump at room temperature for 30 min, followed by removing any residual air from the system at 100 °C for another 10 min. Subsequently, the system was switched to argon atmosphere and the reaction mixture was heated to 200 °C for the injections.

The same procedure as 1.3.7.1 was employed for the further shell growth.
1.4. Optical Measurements

Absorption spectra were measured on a Lambda-25 spectrophotometer (PerkinElmer, USA). Fluorescence spectra were measured using a Hitachi F-4600 fluorescence spectrophotometer (Hitachi, Japan).

The fluorescence lifetime measurements were performed using an FLS920 Combined Steady State & Time Resolved Fluorescence Spectrometer. Time-resolved fluorescence decay spectra were obtained using a 470-nm pulsed diode laser.

Quantum yield (QY) of the QDs was determined by using the organic dye with a known QY as the standard at room temperature according to the reported method.\(^1,4,8-10\) As the QY values of R6G were independent of excitation wavelength,\(^8\) the QY data reported in this research were measured relative to Rhodamine 6G (R6G) at an excitation wavelength of 488 nm.\(^8,11\) The QDs in toluene and R6G in ethanol were optically matched at the excitation wavelength of 488 nm. Fluorescence spectra of QD and R6G were taken under identical conditions in triplicate and averaged. The absorbance at the excitation wavelength was kept at about 0.04.\(^8\) The integrated intensities of the emission spectra were corrected for differences in index of refraction and concentration. The QY was calculated according to eq 1.

\[
QY = \frac{QY_{\text{dye}} \cdot \left( \frac{S_{\text{QD}}}{S_{\text{dye}}} \right) \cdot \left( \frac{\text{Abs}_{\text{QD}}}{\text{Abs}_{\text{dye}}} \right) \cdot \left( \frac{n_{\text{QD}}^2}{n_{\text{dye}}^2} \right)}{S_{\text{dye}}} \quad (1)
\]

where \(QY_{\text{dye}}\) is the absolute QY reported for Rhodamine 6G (95% in ethanol),\(^1,8,10-12\) \(S\) is the integrated area under the fluorescence spectrum, \(\text{Abs}\) is the absorbance at 488 nm, and \(n\) is the refractive index of the solvent (toluene for QD, and ethanol for dye).
1.5 Transmission Electron Microscopy (TEM)

The TEM images were taken using a JEM-2010 transmission electron microscope (JEOL Ltd., Japan). All the samples were stored in toluene solutions. The nanocrystals were deposited onto ultrathin carbon film coated copper grids.

1.6 X-ray Powder Diffraction (XRD)

XRD patterns were obtained using a Bruker D8 X-ray diffractometer (Bruker, Germany). It was essential to remove the excess ODA ligands to obtain meaningful diffraction patterns. The highly pure nanocrystals were used for XRD measurement.

1.7 Size Measurement

The size distribution of QDs was measured by dynamic light scattering using Malvern Zetasizer Instrument (Malvern, UK).
References


Supporting Figures

**Fig. S1** Time-resolved fluorescence decay curves of CdSe/ZnS QDs with different shell thickness: 1 layer of ZnS shell (black), 3 layer of ZnS shell (red), 6 layer of ZnS shell (green), and 9 layer of ZnS shell (blue). All samples were excited at the wavelength of 470 nm, and the emission was detected at the maxima of PL spectra. The fluorescent lifetime was calculated to be 14.2 ns (1 layer), 17.3 ns (3 layer), 19.0 ns (6 layer) and 20.5 ns (9 layer), respectively.
Fig. S2 Normalized fluorescence spectra of CdSe/ZnS core/shell QDs synthesized by TOP-SILAR method with the increase of shell thickness: CdSe core (black), 1 layer of ZnS shell (red), 3 layer of ZnS shell (green), 6 layer of ZnS shell (blue), and 9 layer of ZnS shell (magenta). Their corresponding full-width at half-maximum (FWHM) is 24 nm, 26 nm, 27.5 nm, 28.5 and 30 nm, respectively.
**Fig. S3** Formation of isolated ZnS nanocrystals by using different synthetic procedures, as evidenced by the absorbance in the wavelength range below 500 nm: (a) the bare CdSe core; (b) the CdSe/ZnS QDs synthesized by TOP-SILAR method; (c) SILAR growth of CdSe/ZnS core/shell QDs using S-TOP as S precursor; (d) SILAR growth of CdSe/ZnS core/shell QDs using S-ODE as S precursor. The absorbance of the first exciton band is normalized.
Fig. S4 UV-vis and fluorescence spectra of CdSe/ZnS core/shell QDs synthesized by TOP-SILAR method (top) and the corresponding bare CdSe core (bottom) in n-hexane: (a) Green QDs with 570 nm emission; (b) orange QDs with 590 nm emission; (c) red QDs with 615 nm emission. Their corresponding full-width at half-maximum (FWHM) is 25 nm, 27 nm and 28 nm, respectively. The dashed lines (inset in b) are the corresponding SILAR growth of CdSe/ZnS core/shell QDs using orange CdSe core with 590 nm emission.