

Supplementary Material (ESI) for Chemical Communications

Facile Synthesis of Highly Luminescent UV-Blue Emitting ZnSe/ZnS
Core/Shell quantum dots by a two-step method

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Experimental Section

Materials

Selenium powder(99.95%), sodium borohydride (>96%), 3-mercaptopropionic acid (99%), oleic acid and sodium oleate were purchased from Sinopharm Chemical Reagent (Shanghai, China). Zinc acetate and thiourea were purchased from Guangcheng Chemical Reagent (Tianjin, China). All other reagents were of analytical grade and used without further purification. Ultrapure water with $18.2 \text{ M}\Omega \text{ cm}^{-1}$ (Millipore Simplicity, USA) was used throughout the experiments.

The synthesis of oleic acid-coated ZnSe QDs

Oleic acid-coated ZnSe QDs were synthesized by a modified liquid-solid-solution strategy. In a typical synthesis, 4 mmol of sodium oleate and 7 mL of oleic acid were dissolved in a mixture solution of 5 mL of deionized water and 20 mL of ethanol to form a transparent solution. Zinc acetate (0.5 mmol) dissolved in 5 mL of deionized water were added to this solution by stirring, and then 5 mL of fresh NaHSe aqueous solution prepared from NaBH_4 and Se powder (0.25 mmol) was injected into the

reaction system. The mixture was agitated for 10 min and then was transferred to a 50 mL autoclave. The autoclave was sealed and treated at 90-150 °C for 6 h., the reaction temperature depended on the desirable size of ZnSe QDs (90, 110, 125, and 150°C for the synthesis of ZnSe cores illustrated in the Fig.3, separately). Then the system was cooled down to room temperature naturally in air and the products (ZnSe QDs) were deposited at the bottom of the vessel. The as-prepared ZnSe QDs could be dispersed in the cyclohexane.

The synthesis of water-soluble ZnSe/ZnS QDs

First, the oleic acid-coated ZnSe/ZnS core/shell QDs were modified to become water-soluble through ligand exchange. In this process, the as-synthesized ZnSe QDs coated with oleic acid were dissolved in a appropriate amount of cyclohexane and treated with mercaptopropionic acid (MPA). The resulting mixture was shaken for 20 min under stirring. In this step, the cyclohexane solution gradually became turbid, as the original ligands (oleic acid) with a long hydrocarbon chain were replaced by MPA. The MPA-coated ZnSe precipitate was isolated by centrifugation and decantation. Excess MPA was removed by washing the precipitate with cyclohexane and centrifugation. Finally, appropriate amount 4 M NaOH aqueous solution was added to the precipitate, and then the QDs were dissolved into the water. In the next step, ZnS shell was deposited on the surfaces of the ZnSe cores in the aqueous solution using MPA as capping/stabilizing agent. A fresh aqueous solution (10 mL) containing zinc acetate and MPA was added into 80 mL ZnSe QDs colloidal solution by stirring (molar ration of Zn/MPA=5:1) and pH was adjusted to 11 with NaOH. The amount

of the zinc acetate was depended on the desirable shell thickness of ZnS and was calculated from volume ratio between the core and shell volumes using bulk lattice parameters of Zinc blende ZnS, which is based on the previous report¹ (the calculations of the precursors are stated below). After 30 min stirring, 10 mL thiourea aqueous solution was added into the solution (molar ration of Zn/S=1:1). The mixture was heated to 90 °C and then kept for 3 h under stirring, then ZnSe/ZnS QDs were obtained. The reaction was terminated by allowing the reaction mixture to cool down to room temperature. The obtained ZnSe/ZnS core/shell QDs was purified by centrifugation and decantation with the addition of acetone and ethanol. The excess ligand and unreacted precursors were removed by extensive purification prior to X-ray powder diffraction (XRD), X-ray photoelecctron spectroscopy (XPS) and transmission electron microscope (TEM) analyses. The quantum yield at room temperature was estimated using anthracene in ethanol (QY= 27%, emission range: 360-480nm)² as a reference sample.

Calculations of the precursors for the shell growth:

The size of ZnSe core: $D_0=3.3$ nm, $R_0=3.3/2=1.65$ nm

The amount of ZnSe particles: $n_0=1.5\times 10^{-7}$ mol

Lattice constant of Zinc blende ZnS: $a=0.5406$ nm

The volume of ZnS molecular: $V_{ZnS}=a^3/4=0.03950$ nm³

The average thickness of one monolayer of ZnS (d):

$$d = \frac{\sqrt{3}}{3} a = 0.5406 \times 1.732 / 3 = 0.312 \text{ nm, here, we take } d=0.31 \text{ nm}$$

The amount of Zn and S precursor for the 1 monolayer ZnS (1 ML):

The volume of the one ZnS monolayer: $V_1 = \frac{4}{3} \pi (R_1^3 - R_0^3)$

$$R_0=1.65 \text{ nm}, R_1= R_0+1 \times d=1.65+0.31=1.96 \text{ nm}$$

$$V_1=4 \times 3.14 \times (1.96^3 - 1.65^3) / 3 = 12.717 \text{ nm}^3$$

The amount of ZnS moleculars in one core/shell particle: $n_1=V_1/V_{\text{ZnS}}$

$$n_1=12.717 \text{ nm}^3 / 0.03950 \text{ nm}^3 = 322.0 \text{ (ZnS moleculars)}$$

The amount of Zn/S precursor for the 1 monolayer ZnS shell (**1 ML**):

$B_1 = (n_0 \times N) \times n_1 / N = n_1 \times n_2$; n_0 is the amount of ZnSe core particles, N is Avogadro constant.

$$B_1 = 1.5 \times 10^{-7} \text{ mol} \times 322.0 = 4.830 \times 10^{-5} \text{ mol} = 0.0483 \text{ mmol} \text{ (~} \mathbf{0.048 \text{ mmol}} \text{)}$$

$$\mathbf{2ML \text{ ZnS: } B_2 = B_1 + B_1 \times V_2 / V_1 = 0.048 + 0.048 \times (2.27^3 - 1.96^3) / (1.96^3 - 1.65^3) = \mathbf{0.114 \text{ mmol}}}$$

$$\mathbf{3ML \text{ ZnS: } B_3 = B_2 + B_1 \times V_3 / V_1 = 0.114 + 0.048 \times (2.58^3 - 2.27^3) / (1.96^3 - 1.65^3) = \mathbf{0.200 \text{ mmol}}}$$

$$\mathbf{4ML \text{ ZnS: } B_4 = B_3 + B_1 \times V_4 / V_1 = 0.200 + 0.048 \times (2.89^3 - 2.58^3) / (1.96^3 - 1.65^3) = \mathbf{0.310 \text{ mmol}}}$$

References

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G. Peng, *J. Am. Chem. Soc.*, 2003, **125**, 12567.

2 W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229.

