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Cation exchange assisted synthesis of ZnCdSe/ZnSe quantum dots with narrow emission line widths and near-unity photoluminescence quantum yields

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Experimental

Chemicals

Cadmium oxide (CdO, 99.99%), zinc acetate ($Zn(AC)_2$, 99.99%), trioctylphosphine (TOP, 90%) were purchased from Macklin. Zinc acetate ($Zn(CH_3COO)_2$, 99.99%), n-Hexane (97%) and ethanol (99.7%) were purchased from Aladdin. Oleic Acid (OA, 90%), 1-octadecene (1-ODE, 90%) were purchased from Alfa Aescar. Selenium (Se, 99.99%, powder) was purchased from Sigma Aldrich.

Instruments

The absorption and PL emission data were collected on Horiba Duetta. Transmission electron microscopy (TEM) High-resolution scanning transmission electron microscopy (HRTEM) images were tested by performed using JEOL JEM-2100. High angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images were acquired by using a Thermo Fisher Scientific -Talos microscope. X-ray diffraction (XRD) patterns were recorded on a D/MAXRB X-ray diffractometer operated at 12 kW with Cu Kα radiation (λ = 1.5418 Å). Time resolved PL spectra were tested on JY HORIBA FluoroLog-3 fluorescence spectrometer with a 405 nm ps pulsed diode laser with a repetition rate of 1 MHz and pulse duration of 200 ps. Horiba Fluoromax spectrofluorometer with an integrating sphere (Quanta-φ) was used to measure the PL QYs.

Synthesis of ZnCdSe/ZnSe quantum dots

For a typical synthesis of the ZnCdSe/ZnSe quantum dots, 0.4 mmol CdO, 6 mmol zinc acetate, 7 ml oleic acid and 15 ml of 1-octadecene were loaded into a 50 ml flask degassed at 150 °C for 1 hour and then heated to 300 ^{o}C to form colorless solution under N_2 flow. At this temperature, 0.1 mmol Se-TOP (0.1 mmol Se dissolved in 0.5 ml TOP) was quickly injected into the solution. The reaction kept for 12 min. Then, a stock solution containing 2.5 mmol selenium dissolved in 1.25 mL TOP and 3.75 mL ODE was dripped into to solution at a rate of 2 ml/h. After that, the reaction kept for 30 min to obtain ZnCdSe/ZnSe QDs. The mixture was cooled down to room temperature and was centrifugation at 7000 rpm for 5 min followed by purifying with hexane and methanol, and then dispersed in octane.

Absolute photoluminescence quantum Yield (PL QY) measurements

The absolute PL QYs of the QD n-hexane solution samples were measured by using the methodology reported by de Mello et al..[1] Briefly, the PL QY η, is defined by

$$\eta = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} \tag{1}$$

The sample is placed in an integrating sphere, and excited with a monochromatic source of wavelength λ. Then the QD sample absorbance, A, is

$$A = \frac{L_b - L_c}{L_b} \tag{2}$$

where L_b is the integration of the scattered excitation light profile (λ) when the QD sample is diffusely illuminated; and L_c is the integration of the scattered excitation light profile when the QD sample is directly excited.

Using eqs. (1) and (2), we obtain the PL QY as

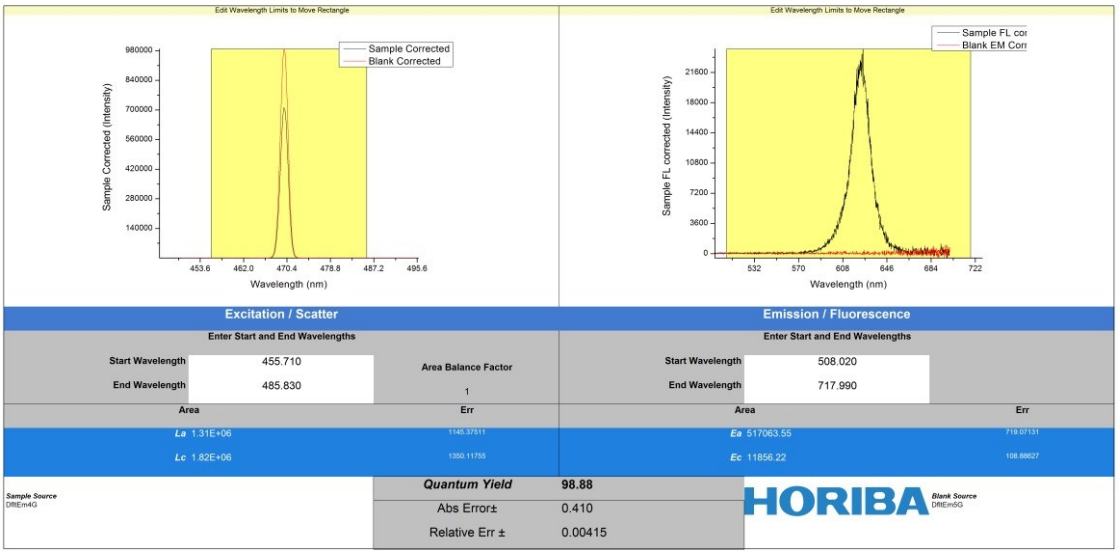
$$\eta = \frac{E_c - (1-A)E_b}{L_a A} = \frac{E_c - E_a}{L_a - L_c} \tag{3}$$

where E_c is the integrated luminescence of the QD sample under direct excitation, and E_b is the integrated luminescence of the QD sample under indirect illumination. L_a is the integrated excitation profile from a blank sample (pure n-hexane). E_a is the integrated luminescence from a blank sample (pure n-hexane).

Example

An example is given for CdZnSe/ZnSe (8 ML) QD solution excited at 470-nm light. The scattered 470 nm excitation spectra were recorded for both the blank cuvette containing only n-hexane (red line on the left, L_a),

and the QD sample (black line, L_c). Integration of the instrument-corrected incident beam's signal intensities I_1 and I_2 was performed from 455 to 485 nm. Next, the sample and blank's fluorescence spectral region intensities were measured under the same instrument conditions as the L_a and L_c. Integration of the emission-signal region I_3 for the blank (red line on the right, E_a) and I_4 for the QD sample (black line, E_c) was from 506 to 717 nm.



$$\eta = \frac{\int_{506}^{717} I_4 d\lambda - \int_{485}^{717} I_3 d\lambda}{\int_{455}^{485} I_1 d\lambda - \int_{455}^{485} I_2 d\lambda} = 98.88\%$$

Calculations for the shell growth

We first use the empirical formula of CdSe nanocrystal size (D) and first exciton absorption peak (λ) to obtain the diameter of the prepared core.[2]

$$D = (1.6122\times10^{-9})\lambda^4 - (2.6575\times10^{-6})\lambda^3 + (1.6242\times10^{-3})\lambda^2 - (0.4277)\lambda + 41.57 \quad (4)$$

Then the size of the CdSe cores is estimated to be D_0=4.6 nm (λ=601 nm), R_0=2.3 nm

The relationship between the extinction coefficient ε per mole of CdSe cores with the first exitonic absorption peak is described by the following formula

$$\varepsilon = 1600\Delta E(\mathrm{D})^3 \quad (5)$$

where ΔE is the transition energy corresponding to the first absorption peak and the unit is in eV.

The molar concentration of the prepared CdSe cores can be obtained by using Lambert-Beer's law

$$A = \varepsilon CL \quad (6)$$

where C is the molar concentration, L is the thickness of the cuvette (1 cm).

The amount of Cd/Se precursor for CdSe shell growth was calculated by using a previously reported density model.[3]

The molar concentration of the CdSe cores: $C=1.75\times10^{-5}$ mol/L

The volume of the core solution: V=22 mL.

The amount of CdSe core particles: $n_1=C\times V=165$ nmol

Lattice constant of zinc blende CdSe: a= 0.607 nm

The average thickness of one monolayer of CdSe: $d=\frac{\sqrt{3}}{3}a$ =0.35 nm

The volume of 1 ML CdSe layer:

$V_1=\frac{4\pi}{3}(R_1^3-R_0^3)$ = 2.72×10^{-26}m^3

$R_1=R_0+d=2.66$ nm

The density of zinc blende CdSe: $\rho=5.69 g/cm^3$

The mass of the 1 ML CdSe shell in one particle: $m=V_1\times\rho$

The amount of CdSe in one particle: n_2=m/M.W. (Molar weight, 191.36 g/mol)=8.085×10^{-22}/particle

The amount of Cd/Se precursor for the 1st ML CdSe growth: $A_1=n_1\times N_A\times n_2=0.08$ mmol

The second ML CdSe: $A_2=0.10$ mmol

The third ML CdSe: $A_3=0.13$ mmol

Theoretical calculation reveals that 3 ML CdSe needs 0.31 mmol Cd and Se precursors. In this work, the residue amount of the Cd precursor is about 0.3 mmol after nucleation. Therefore, we estimate that further adding of Se precursor could grow 3 ML CdSe.

The amount of Zn/Se precursor calculation for ZnSe shell growth:

The amount of CdSe particles: n_1= 165 nmol

The size of the CdSe particles: $R_0=3.36$ nm (After growth of 3ML CdSe)

Lattice constant of zinc blende ZnSe: a= 0.5669 nm

The average thickness of one monolayer of ZnSe: $d=\frac{\sqrt{3}}{3}a$ =0.327 nm

The volume of 1 ML ZnSe layer:

$V_1=\frac{4\pi}{3}(R_1^3-R_0^3)$ = 5.10×10^{-26}m^3

$R_1=R_0+d=3.69$ nm

The density of zinc blende ZnSe: $\rho = 5.26 g/cm^3$

The mass of the 1 ML ZnSe shell in one particle: $m=V_1 \times \rho$

The amount of ZnSe in one particle: $n_2=m/M.W.$ (Molar weight, 191.36 g/mol)$=1.86\times10^{-21}$/particle

The amount of Zn/Se precursor for the 1st ML ZnSe growth: $A_1=n_1\times N_A \times n_2=0.18$ mmol

The second ML ZnSe: $A_2=0.22$ mmol

The third ML ZnSe: $A_3=0.26$ mmol

4 ML ZnSe: $A_4=0.30$ mmol

5 ML ZnSe: $A_5=0.34$ mmol

6 ML ZnSe: $A_6=0.39$ mmol

7 ML ZnSe: $A_7=0.44$ mmol

8 ML ZnSe: $A_8=0.50$ mmol

The adding amount of Se precursor for 8 ML ZnSe shell growth:

$A=A_1+ A_2+ A_3+ A_4+ A_5+ A_6+ A_7+ A_8=2.63$ mmol

In our experiment, the second adding amount of Se precursor is 2.5 mmol, suggesting that the growth of about 8 ML ZnSe shell.

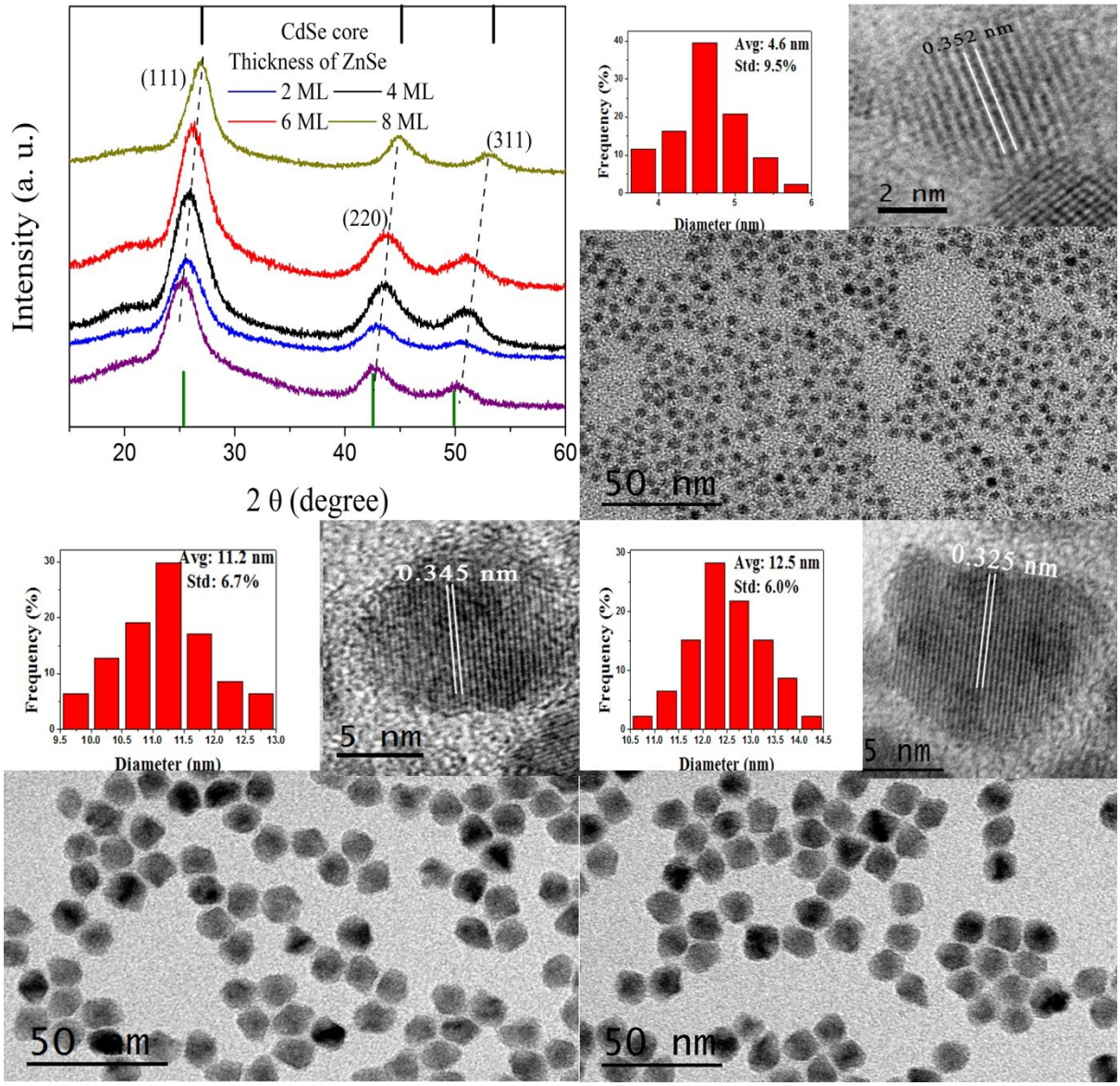


Fig. S1 (a) XRD patterns of the CdSe cores and the QDs with different thickness of ZnSe shells. (b) TEM images and size distribution of the CdSe cores. TEM and size distribution of the QDs with 6 ML ZnSe shell (c) and 8 ML ZnSe shell (d).

Three-exponential fitting:

$$I(t) = [a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) + a_3 \exp(-t/\tau_3)] \otimes F(t) \quad (7)$$

where I(t) denotes the decay signal, a represents the amplitude, τ_m is the lifetime, F(t) is the impulse response of the device. The average PL lifetime is estimated by using following formula.[4]

$$\tau = \frac{a_1\tau_1^2 + a_2\tau_2^2 + a_3\tau_3^2}{a_1\tau_1 + a_2\tau_2 + a_2\tau_3} \quad (8)$$

Goodness of fit calculation

Chi-square goodness of fit is used to find out how the observed value is significantly different from the expected value. Chi-square goodness of fit test examines how well theoretical calculated result fits the empirical data.

We compute the value of chi-square goodness of fit (χ_R^2) using the following formula:

$$\chi_R^2 = \sum_{i=1}^{n} \frac{(O_i - E_i)^2}{E_i} \tag{9}$$

where O_i is observed value, E_i is expected value.

R-square goodness of fit value (R^2) is also widely used parameter to measure how well that model explains the variance of the data. Generally, r-square values range from 0 to 1. Unlike chi-square χ_R^2, a higher r-square value R^2 indicates a better fit for the model.

In order to examine the reliability of our fit model, we also compute R^2 by using the following formula:

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (O_i - E_i)^2}{\sum_{i=1}^{n} (O_i - O_{ave})^2} \tag{10}$$

where O_{ave} denotes the average of the observed value.

All of the R^2 values are above 0.99 and show same trend as χ_R^2, suggesting that our fitting models are reliable.

Table S1. Kinetic parameters of the QDs obtained from theoretical fitting.

	a_1	τ_1(ns)	a_2	τ_2 (ns)	a_3	τ_3 (ns)	τ	χ_R^2	R^2
Core	0.68	1.80±0.01	0.53	7.45±0.04	0.20	23.6±0.1	3.97	0.68	0.9997
ZnCdSe/ZnSe(2ML)	0.59	6.21±0.04	0.55	19.4±0.08	——	——	8.9	0.37	0.9998
ZnCdSe/ZnSe(4ML)	1.01	15.43±0.05	—	——	——	——	15.4	1.08	0.9994
ZnCdSe/ZnSe(6ML)	0.99	14.33±0.04	—	——	——	——	14.3	1.05	0.9995
ZnCdSe/ZnSe(8ML)	1.01	11.41±0.04	—	——	——	——	11.4	0.90	0.9996
ZnCdSe/ZnSe(10ML)	0.37	5.1±0.1	0.64	13.3±0.1	——	——	7.3	0.64	0.9997

References

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