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

Xiao Jin,a,b Kanlin Xie,b Tingting Zhang,b Huada Lian,b Zhenghe Zhang,b Bing Xu,b Dongyu Liab and Qinghua Lia,b*

a Key Laboratory of Clean Energy Materials Chemistry of Guangdong Higher Education Institutes, Lingnan Normal University, Zhanjiang 524048, P. R. China

b Key Laboratory of Environmentally Friendly Functional Materials and Devices, Lingnan Normal University, Zhanjiang 524048, P. R. China

E-mail: qhli@hqu.edu.cn (Q. Li)

Experimental

Chemicals

Cadmium oxide (CdO, 99.99%), zinc acetate (Zn(AC)₂, 99.99%), trioctylphosphine (TOP, 90%) were purchased from Macklin. Zinc acetate (Zn(CH₃COO)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 °C to form colorless solution under N₂ 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 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 \( \eta \), is defined by

\[
\eta = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}}
\]  

(1)

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

\[
A = \frac{L_b - L_c}{L_b}
\]  

(2)

where \( L_b \) is the integration of the scattered excitation light profile (\( \lambda \)) 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

\[
\eta = \frac{E_c - (1 - A)E_b}{L_a A} = \frac{E_c - E_a}{L_a - L_c}
\]  

(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\textsubscript{c}). Integration of the instrument-corrected incident beam’s signal intensities I\textsubscript{1} and I\textsubscript{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\textsubscript{a} and L\textsubscript{c}. Integration of the emission-signal region I\textsubscript{3} for the blank (red line on the right, E\textsubscript{a}) and I\textsubscript{4} for the QD sample (black line, E\textsubscript{c}) was from 506 to 717 nm.

Calculations for the shell growth

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

\[
D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + 41.57 \quad (4)
\]

Then the size of the CdSe cores is estimated to be D\textsubscript{0}=4.6 nm (\(\lambda=601\) nm), R\textsubscript{0}=2.3 nm

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

\[
\varepsilon = 1600\Delta E(D)^3 \quad (5)
\]

where \(\Delta E\) 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: \(C = 1.75 \times 10^{-5} \text{ mol/L}\)

The volume of the core solution: \(V = 22 \text{ mL}\).

The amount of CdSe core particles: \(n_1 = C \times V = 165 \text{ nmol}\)

Lattice constant of zinc blende CdSe: \(a = 0.607 \text{ nm}\)

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

The volume of 1 ML CdSe layer:

\[
V_1 = \frac{4\pi}{3}(R_1^3 - R_0^3) = 2.72 \times 10^{-26} \text{ m}^3
\]

\(R_1 = R_0 + d = 2.66 \text{ nm}\)

The density of zinc blende CdSe: \(\rho = 5.69 \text{ g/cm}^3\)

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) = \(8.085 \times 10^{-22} \text{/particle}\)

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

The second ML CdSe: \(A_2 = 0.10 \text{ mmol}\)

The third ML CdSe: \(A_3 = 0.13 \text{ mmol}\)

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: \(n_1 = 165 \text{ nmol}\)

The size of the CdSe particles: \(R_0 = 3.36 \text{ nm} \) (After growth of 3ML CdSe)

Lattice constant of zinc blende ZnSe: \(a = 0.5669 \text{ nm}\)

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

The volume of 1 ML ZnSe layer:

\[
V_1 = \frac{4\pi}{3}(R_1^3 - R_0^3) = 5.10 \times 10^{-26} \text{ m}^3
\]
\( R_1 = R_0 + d = 3.69 \text{ nm} \)

The density of zinc blende ZnSe: \( \rho = 5.26 \text{ g/cm}^3 \)

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

The amount of ZnSe in one particle: \( n_2 = m / \text{M.W.} \) (Molar weight, 191.36 g/mol) = \( 1.86 \times 10^{-21} \) /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:

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

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

\[ \tau = \frac{a_1 \tau_1^2 + a_2 \tau_2^2 + a_3 \tau_3^2}{a_1 \tau_1 + a_2 \tau_2 + a_3 \tau_3} \]  

\[ (8) \]
**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 ($\chi^2_R$) using the following formula:

$$\chi^2_R = \sum_{i=1}^{n} \frac{(O_i - E_i)^2}{E_i}$$  \hspace{1cm} (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 $\chi^2_R$, 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:

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (O_i - E_i)^2}{\sum_{i=1}^{n} (O_i - O_{ave})^2}$$  \hspace{1cm} (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 $\chi^2_R$, suggesting that our fitting models are reliable.

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

<table>
<thead>
<tr>
<th></th>
<th>$a_1$</th>
<th>$\tau_1$ (ns)</th>
<th>$a_2$</th>
<th>$\tau_2$ (ns)</th>
<th>$a_3$</th>
<th>$\tau_3$ (ns)</th>
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<th>$\chi^2_R$</th>
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<td>Core</td>
<td>0.68</td>
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<td>15.4</td>
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<tr>
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<td>7.3</td>
<td>0.64</td>
<td>0.9997</td>
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**References**