Effect of surface/interfacial defect on photo-stability of thick shell CdZnSeS/ZnS quantum dots

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EXPERIMENTAL SECTION

Materials

Cadmium oxide (CdO, 99.99%), 1-octadecene (ODE, 90%), Selenium (Se, 99.999%), zinc acetate (Zn(Ac)$_2$, 99.9%) and trioctylphosphine oxide (TOPO, 98%) were purchased from Alfa Aesar. Sulfur (S, 99.98%), Trioctylphosphine (TOP, 97%), oleic acid (OA, 90%) and zinc oxide (ZnO, 99.9%) were purchased from Sigma-Aldrich. All chemicals were used without any further purification.

Synthesis CdZnSeS/ZnS QDs with thin shell (3MLs)

The synthesis process was performed by following a modified literature method.$^{[1,2]}$ For a typical synthesis of thin shell CdZnSeS/ZnS core/shell QDs, 0.14 mmol of CdO, 3.41 mmol of ZnO, 15 mL of ODE and 7 mL of OA in flask were degassed at 100°C for 30min, then the solution was heated to 310°C. And then, an anionic stock solution, prepared by dissolving 2.2 mmol of Se and 2.2 mmol of S in 2mL of TOP, was rapidly injected to the above mixture and the alloy cores were prepared by reacting at that temperature for 10 min. Subsequently, 1.6 mmol of S dissolved in 2.4 mL of ODE was introduced into the core solution and the reaction was held for 12 min. Then, a Zn stock solution containing 2.86 mmol of Zn acetate dissolved in 2 mL of OA and 4 mL of ODE was quickly injected and subsequently a S stock solution containing 9.65 mmol of S dissolved in 5 mL of TOP was dropwisely introduced. After that, the thin ZnS shelling was performed at 270°C for 20 min. The as-reacted CdZnSeS/ZnS core/shell QDs were subjected to the repeated rounds of purification by centrifugation with excess acetone and the purified QDs were dispersed in 6 mL of TOP as the seeded QDs for further synthesis thick shell QDs.

Synthesis CdZnSeS/ZnS QDs with thick shell (11 and 17MLs)

We fabricated thick shell CdZnSeS/ZnS QDs by optimizing a “flash” synthesis method.$^{[3,4]}$ Briefly, ZnO and OA were mixed with 4 g of TOPO in a 50 mL three-neck flask. The reaction mixture was kept at 120°C for 1 h with argon and then heated to 330°C. After the solution became colorless, a mixture of seeded QDs dissolved in 1 mL of TOP (obtained using the synthesis method above) and sulfur powder in 2.2 mL of TOP was injected. The solution was reacted at 330°C for 7 min in all the synthesis processes, then the reaction was quenched by a
sudden drop of temperature. The thickness of the ZnS shell could be controlled by varying the amount of ZnO. The amount of OA was maintained with an excess of 4 mmol and the sulfur was in 3-fold excess compared to ZnO in all of the syntheses. The amount of ZnO precursor is 1.3 mmol and 2.3 mmol for CdZnSeS/ZnS core/shell QDs with 11MLs and 17MLs, respectively.

**Synthesis scheme exploration**

We make changes to the original synthesis method, changing only one condition at a time. Scheme A: Reducing the core growth temperature to 280°C; Scheme B: Increasing the core growth temperature to 340 °C (and changing the ODE to the corresponding amount of TOPO as the boiling point of ODE is much lower than that temperature); Scheme C: Changing the amount of ODE (15mL) at the beginning of the reaction to the limit of 1 mL; Scheme D: Adjusting the mole ratio of cation to oleic acid to 1:3 (1:6 in the original reaction) in the core reaction process; Scheme E: The original method. The specific results are shown in Figure S2 and Table S1.

**Spectro-electrochemical Measurements**

Indium tin oxide (ITO) coated glass slide (50 × 7 × 0.7 mm) was first covered with zinc oxide (ZnO) nanoparticles (NP) (Nanograde, ∼ 20 nm diameter) to avoid quenching of QD emission by fast charge/energy-transfer to ITO. The ZnO NP layer was deposited by dip-coating the glass/ITO substrate into an ethanol suspension of ZnO NPs (2 mg/mL, one dip for 10 s) and annealed at 150°C for 10 min in a nitrogen glovebox. The QDs were deposited onto the ZnO NP layer as a few-monolayer thick film by dip-coating from a dilute toluene solution (optical density of 0.08 at 500 nm; 2 dips for 10 s).

A three-electrode system was used for electrochemical measurements. The glass/ITO slide successively covered ZnO NPs and QDs was connected as a working electrode to the potentiostat, and the film was placed into a quartz cuvette filled with the electrolyte (0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile). Silver and platinum wires were used as quasi-reference and counter electrodes, respectively. All potentials reported in this work are measured relative to the quasi-reference silver electrode during staircase voltammetry scans (200 mV steps each lasting 14s). The film was excited at 400nm and the emitted light was collected with a Shimadzu RF-5301PC spectrofluorophotometer.
Preparation of QDs-based film

The preparation method of QD-based film followed the prepared process from Jang et al.\textsuperscript{[5]} First, the mass of green- and red- emitting QDs needed for a blue chip is calculated by theory calculation (see the section of theory calculation) and marked as $M_g$ and $M_r$, respectively. Then, 40-fold of $M_g$ (or $M_r$) green (or red) QD powder is mixed with 0.21g polymethylmethacrylate (PMMA) and 0.8 mL toluene solution and the mixture is sonicated until a clear and dense solution is obtained. Then the above mixed solution was poured on a glass plate, whose area is 40-fold of the blue chip area, and baked at 30°C for 24 hours at argon atmosphere to form a film. The QD-PMMA film is detached from the glass plate and then a PVP layer is covered by dip-coating from the PVP (polyvinylpyrrolidone)/ethanol solution prepared by dissolving 5 g of PVP in 10 ml of ethanol. The red-emitting and green-emitting QD-based films are adhered by the PVP solution to form a whole.

Characterization

Absorption and PL spectra were recorded using a Shimadzu UV3600 spectrophotometer and a Shimadzu RF-5301PC spectrofluorophotometer, respectively. The PL decay curves were measured with an Edinburgh F900 fluorescence spectrophotometer. X-ray diffraction (XRD) spectra were recorded on a D/max 2500 VL/PC diffractometer. Transmission electron microscopy (TEM) images were recorded on a Tecnai G2 Transmission Electron Microscope. The Absorption spectra, PL spectra as well as emission decay profiles are measured at room temperature.

Theoretical calculation of the mass of QDs

To simplify the calculation, we do not consider the light scattering (generally the light absorption is much larger than the light scattering) in the calculation process. When the blue light passes through the red- and green- emitting QD films, only the absorption and transmission processes are considered.

In general, when light propagates a distance $l$ through a QD-based film, the relationship between incident light $I_{in}$ and exit light $I_{out}$ can be described by:\textsuperscript{[6]}

$$I_{out} = I_{in} \exp(-\sigma_a N \nu l)$$

(1)
where $\sigma_a$ is the absorption cross section of the QDs and $N_V$ is the number of QD per unit volume. That is, the light transmittance $T$ can be expressed as:

$$T = \frac{I_{out}}{I_{in}} = \exp(-\sigma_a N_V l)$$

(2)

Then, the equation can be translated into:

$$N_V l = \frac{|\ln T|}{\sigma_a}$$

(3)

Actually, when $l$ is thin enough (such as a thin film), the left part $N_V l$ of Equation (3) is the total number of QD contained on a unit area. At this time, the total number of QD can be expressed as:

$$\frac{M}{m_{QD}} = \frac{|\ln T|}{\sigma_a}$$

(4)

where $M$ is the total mass of QD required per unit area, and $m_{QD}$ is the mass of a single QD. Thus, the total mass $M$ of QD required for a LED chip, whose light emitting area is $S$, can be expressed as:

$$M = S \cdot \frac{m_{QD}|\ln T|}{\sigma_a}$$

(5)

According to Equation (5), to obtain the total mass of the red- and green- emitting QDs, one only needs to know the mass of a single QD, the absorption cross section of the QD and the transmittance of the QD-based film.

The mass $m$ of a single QD can be calculated simply by equation (6), where $\rho$ is the density of the material and $V$ is the volume of the material.

$$m = \rho \cdot V$$

(6)

For red-emitting QDs (CdSe/CdS), we can know the size of the core and the thickness of the CdS shell by TEM measurement, and then we can get the volume of the core and the shell. By using the formula (6), the mass of a single red-emitting QD can be calculated. The same method can be used to estimate the mass of a single green-emitting QD. Due to the inaccurate density of the alloy core material during calculation, we estimate that the density of the alloy core material is $\sim 4.8 \times 10^3$ kg/cm$^3$, which is the median density of the ZnSe and ZnS bulk materials.
(Since the proportion of Cd in the synthesis of core is very small, we approximate the cores as the alloy ZnSeS cores).

The absorption cross section of the QD can be estimated by an empirical formula. The absorption cross section of the red-emitting QD at the excitation wavelength of 461 nm (the emission wavelength of the blue LED chip) is calculated as follows: First, the UV-Vis spectrophotometer is used to measure the absorption value of QDs (usually dispersed in toluene or hexane) at the first excitonic absorption peak and at the excitation wavelength of 461 nm. The extinction coefficient \( \varepsilon \) at the first excitonic absorption peak can be obtained using empirical formula (7), where \( D \) is the particle size of the QD. \(^7\)

\[
\varepsilon = 5837(D)^{2.65}
\]  

(7)

The molar concentration \( c \) of the QDs can be calculated by: \(^6,7\)

\[
c = \frac{A_\lambda}{\varepsilon L}
\]  

(8)

where \( A_\lambda \) is the absorption value at a certain wavelength, \( L \) is the path length (cm) of the radiation beam used for recording the absorption spectrum. In our experiments, \( L \) is fixed at 1 cm. The concentration of the QD solution can be obtained by substituting the absorption value of at the first exciton absorption peak. Then the extinction coefficient of the QDs near 461 nm can be obtained by substituting the corresponding absorption value to the formula (8).

The relationship between the extinction coefficient and the absorption cross section is established using empirical formula (9), where \( N_A \) is Avogadro’s number. \(^6\) Then the absorption cross section of the QDs near 461 nm can be obtained.

\[
\sigma_a = \frac{2304\varepsilon}{N_A}
\]  

(9)

Since there is no empirical formula for the concentration of CdZnSeS/ZnS QDs, we can only determine the volume of ZnS shell required for a single QD by TEM measurement, and then we can obtain the mole amount of ZnS. The mole amount of the precursor (such as Zn) consumed during the shell coating process is the total mole amount of ZnS required, so the number of QD generated in a one-pot reaction can be estimated, which means the concentration information of the QDs can be obtained. Using equation (8), the extinction coefficient of the green-emitting QDs near 461 nm can be calculated, and then the absorption cross section of the QD can be finally obtained using equation (9).
The transmittance of the red- and green- emitting QD-based films is calculated as follows: First, we can theoretically calculate the fluorescence proportion of red- and green- emitting QDs (recorded as $\alpha$ and $\beta$, respectively) in the power spectrum of a white LED (chromaticity coordinates of the reference white point are (0.313, 0.329) in Rec. 2020 wide color gamut standard). So the fluorescence proportion of the blue LED chip is $1-\alpha-\beta$. The light scattering process is ignored during calculation and only the transmission and absorption are considered. When the amount of the emitted red photons is $\alpha$, the actual number of photons required for red light is $\frac{\alpha}{\eta_r(\frac{hc}{\lambda_r})}$, and then the number of blue photons required for exciting red light is $\frac{\alpha}{\eta_r(\frac{hc}{\lambda_r})} \cdot \frac{hc}{\lambda_{LED} \eta_g} \cdot \frac{\lambda_{LED} \eta_r}{\lambda_{LED} \eta_r} \cdot \lambda_{r}\alpha$, the simplified result is $\lambda_{LED} \eta_g$. Similarly, the number of blue photons required for exciting green photon is $\lambda_{LED} \eta_g$.

Thus, the transmittance $T_1$ of the red-emitting QD-based film can be expressed as:

\[
T_1 = \frac{(1 - \alpha - \beta) + \frac{\lambda_{LED} \eta_g}{\lambda_{r}\alpha}}{(1 - \alpha - \beta) + \frac{\lambda_{LED} \eta_g}{\lambda_{LED} \eta_g} + \frac{\lambda_{LED} \eta_r}{\lambda_{LED} \eta_r}}
\]

(10)

where $\lambda_{g}$, $\lambda_{r}$ and $\lambda_{LED}$ is the peak wavelength of the green QDs, red QDs and blue LED chip, respectively, $\eta_g$ and $\eta_r$ are the PL QY of the green- and red- emitting QDs, respectively.

Then, the transmittance $T_2$ of the green-emitting QD-based film can be expressed as:

\[
T_2 = \frac{(1 - \alpha - \beta) + \frac{\lambda_{LED} \eta_g}{\lambda_{r}\alpha}}{(1 - \alpha - \beta) + \frac{\lambda_{LED} \eta_g}{\lambda_{LED} \eta_g}}
\]

(11)

The corresponding transmittances $T_1$ and $T_2$ can be obtained by bringing in various parameters. From the above derivation, we can obtain the total mass of the red- and green-emitting QDs ($M_r$=1.21×10⁻⁵ g and $M_g$=3.90×10⁻⁴ g, respectively) required for the preparation of the white LEDs.
Figure S1 Absorption spectra of CdZnSeS/ZnS QDs with different shell thicknesses.
Figure S2 TEM micrographs of CdZnSeS QDs from four different synthesis schemes. (a)-(d) correspond to scheme A to D.

Figure S3 Spectrally integrated PL intensity of CdZnSeS/ZnS core/shell QDs with 17MLs as a function of applied negative (blue squares) and positive (red circles) EC potential. $V_{EC}$ potential scanned from 0V to ±2.0 V and then back to 0 V.
Figure S4 Representative low-resolution (a) and high-resolution (b), (c) TEM images of CdZnSeS/ZnS (17MLs) core/shell QDs. The original image (Figure 1d in this paper) is included in the blue square (left panel) and the QDs marked with blue circles are those with dislocations. The marks named A, B, C and D in the high-resolution TEM are typical dislocations.

Figure S5 XRD patterns of CdZnSeS/ZnS (17MLs) QDs before and after illumination. Vertical lines indicate wurtzite and zinc blende ZnS bulk reflections.
Figure S6 Absorption and PL spectra of CdSe/CdS (10MLs) core/shell QDs. The inset show the TEM image of the sample. The emission wavelength is located at ~645 nm with a FWHM of ~28 nm. The average size of the QDs is about 11.2 nm.

Figure S7 Schematic of a white LED based on red- and green- emitting QDs.

Table S1 Peak wavelength, FWHM, particle size and size distribution of CdZnSeS QDs in different synthesis schemes.

<table>
<thead>
<tr>
<th>scheme</th>
<th>peak wavelength (nm)</th>
<th>FWHM (meV)</th>
<th>size (nm)</th>
<th>size distribution (%)</th>
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<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
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<tr>
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<td>493</td>
<td>598</td>
<td>535</td>
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<td>FWHM (meV)</td>
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<td>9.9</td>
<td>13.9</td>
<td>14.7</td>
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Table S2  PL peaks and FWHMs of a series of single QDs (CdZnSeS/ZnS QDs with 3MLs).

<table>
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<th>Sample number</th>
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<th>3</th>
<th>4</th>
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<tr>
<td>PL peak (nm)</td>
<td>520.9</td>
<td>512.5</td>
<td>517.5</td>
<td>511.8</td>
<td>518.5</td>
<td>519.7</td>
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<td>FWHM (meV)</td>
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<td>32.8</td>
<td>76.7</td>
<td>49.7</td>
<td>78.3</td>
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<td>8</td>
<td>9</td>
<td>10</td>
<td>11</td>
<td>12</td>
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<tr>
<td>PL peak (nm)</td>
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<td>520.5</td>
<td>521.2</td>
<td>523</td>
<td>519.4</td>
<td>527.1</td>
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<tr>
<td>FWHM (meV)</td>
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<td>52.2</td>
<td>86.7</td>
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<td>53.7</td>
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Table S3 Variations of CIE color coordinates, correlated color temperature (CCT) and luminous efficacy of the QD-based white LED as a function of forward current.

<table>
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<th>Forward current (mA)</th>
<th>CIE x</th>
<th>CIE y</th>
<th>CCT (K)</th>
<th>Luminous efficacy (lm/W)</th>
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<td>0.321</td>
<td>8706</td>
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References: