

Supporting Information

High Luminescent Core/shell QDs Based on Noninjection Synthesized CdSe QDs: Observation of Magic Sized CdSe Quantum Dots

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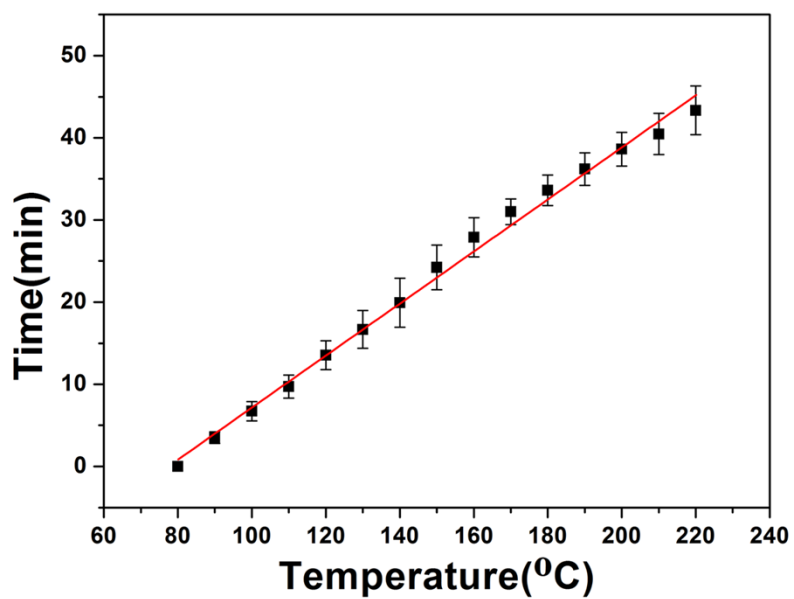


Fig. S1. Heating curve. Data point and error bars of the slopes showed correspond to the means and standard deviations of five independent measurements. Fitted red straight line is added to guide the eyes.

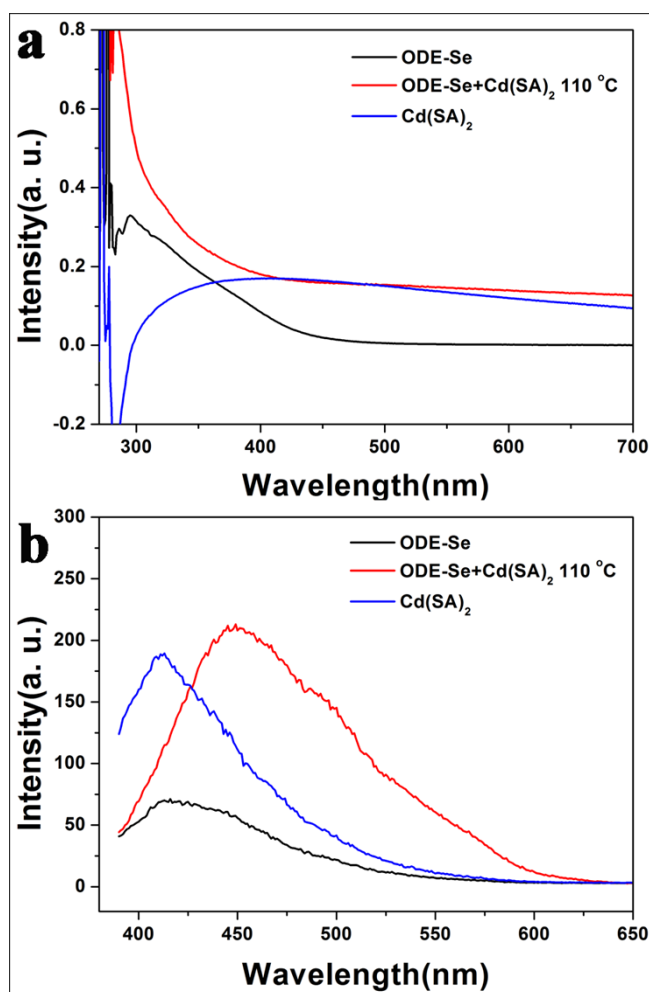


Fig. S2. Absorption a) and photoluminescent b) curves of ODE-Se, Cd(SA)₂ dispersed in ODE, ODE-Se and Cd(SA)₂ mixture has been shortly annealed at 110 °C. Diluter is toluene for all case. We can see that Cd(SA)₂ show strong luminescence at ~ 280 nm while ODE-Se has somewhat weak absorbance at short wavelength region. Cd(SA)₂ showed large absorbance but ODE-Se has fairly no absorbance at long wavelength. Absorbance curve of annealed ODE-Se and Cd(SA)₂ mixture can be seen as superposition of ODE-Se and Cd(SA)₂ curves at long wavelength region. But at short wavelength region, annealed mixture showed strong absorbance. As for photoluminescence (PL) curves, PL wavelength of the mixture is obviously red-shifted. Based on above phenomenon we conclude that ODE-Se and Cd(SA)₂ react with each other to form a transition state compound which was CdSe monomer.

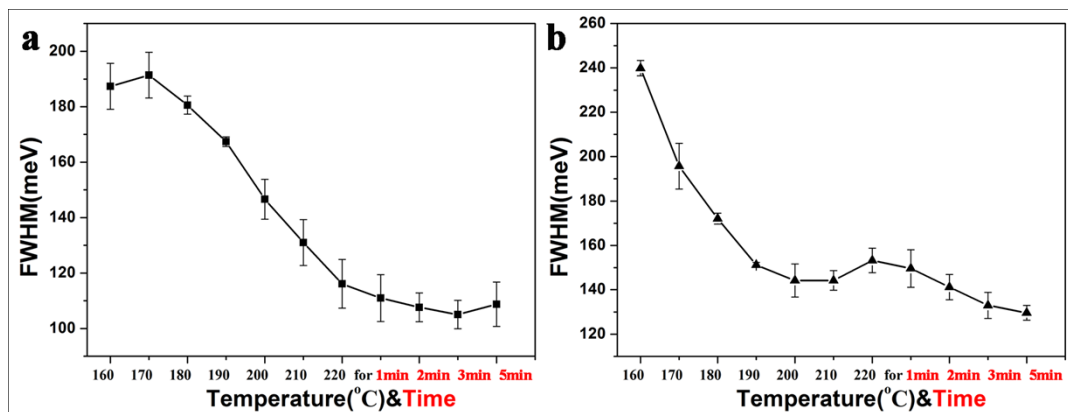


Fig. S3. Variation trend of FWHM for 2:3(a) and 3:2(b) Se/Cd feed molar ratios. The results in the two curves are means and standard deviations from three independent experiments respectively.

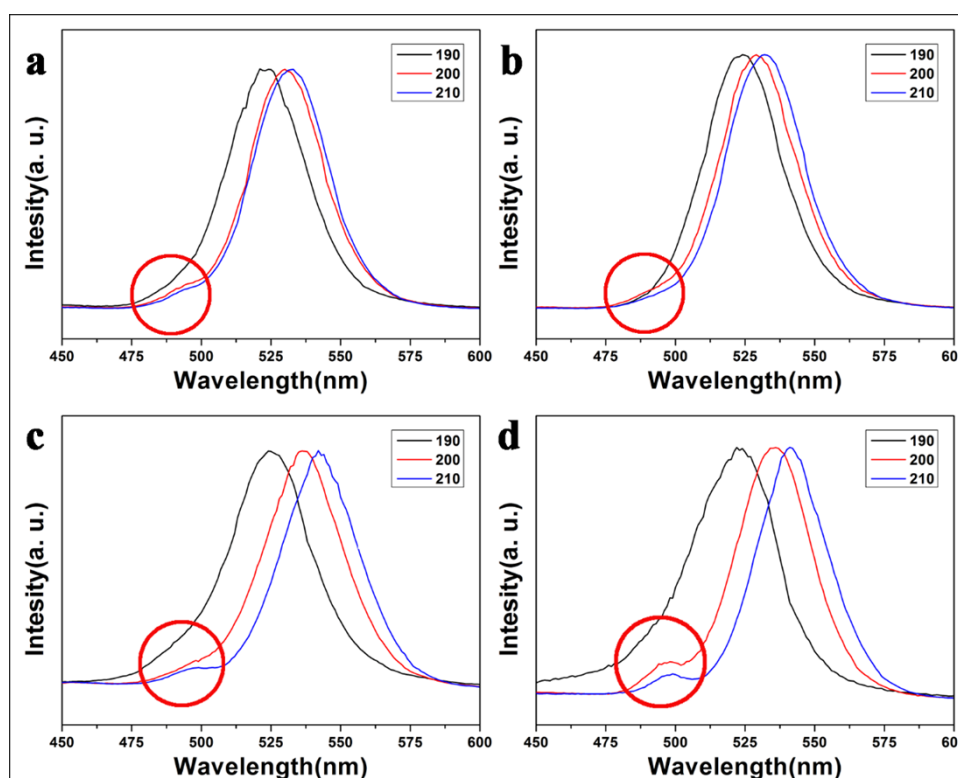


Fig. S4. Photoluminescent curves of samples obtained at 190 (black), 200 (red), 210 °C (blue) for Se/Cd feed molar ratios at a) 2:3, b) 2:4, c) 2:6, and d) 3:2. Red circle emphasize large energy tail. 200 °C curve of sample prepared at 2:4 has weakest tail while 200 °C curve of sample prepared at 3:2 showed strongest tail. Considering longest PL wavelength of sample prepared at 2:4 and shortest of sample prepared at 3:2 at the initial stage and inverse relation at the end of the reaction (table 1 in article), we conclude that the nucleation number is enormous for sample prepared at 2:4. So the growth of the crystal nucleus consume large amount of precursors thus lead to relative small degree of supersaturation and unobvious secondary nucleation. The generation of high energy tail is ascribed to secondary nucleation rather than cessation of growth because as reaction proceeding the tail tend to red-shift for all cases.

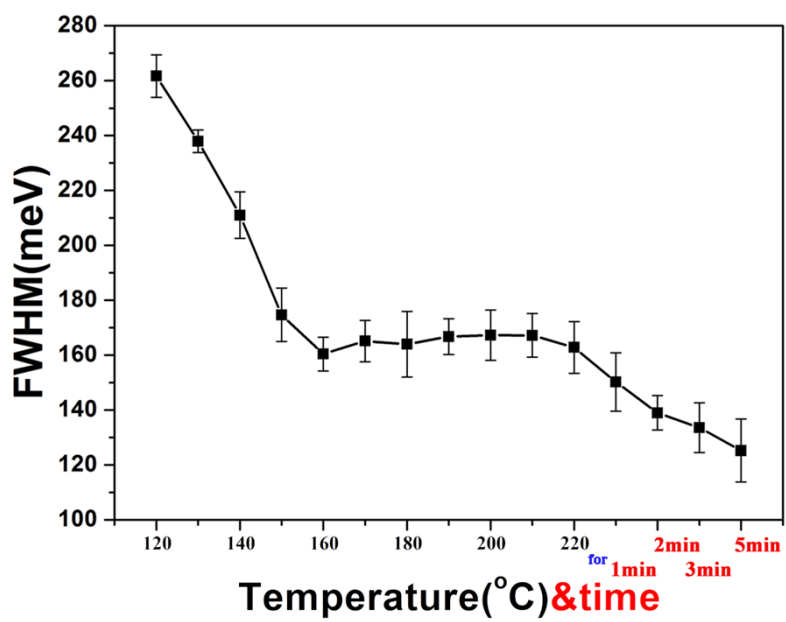


Fig. S5. Variation trend of FWHM for the verification experiment. The results are means and standard deviations from three independent experiments.

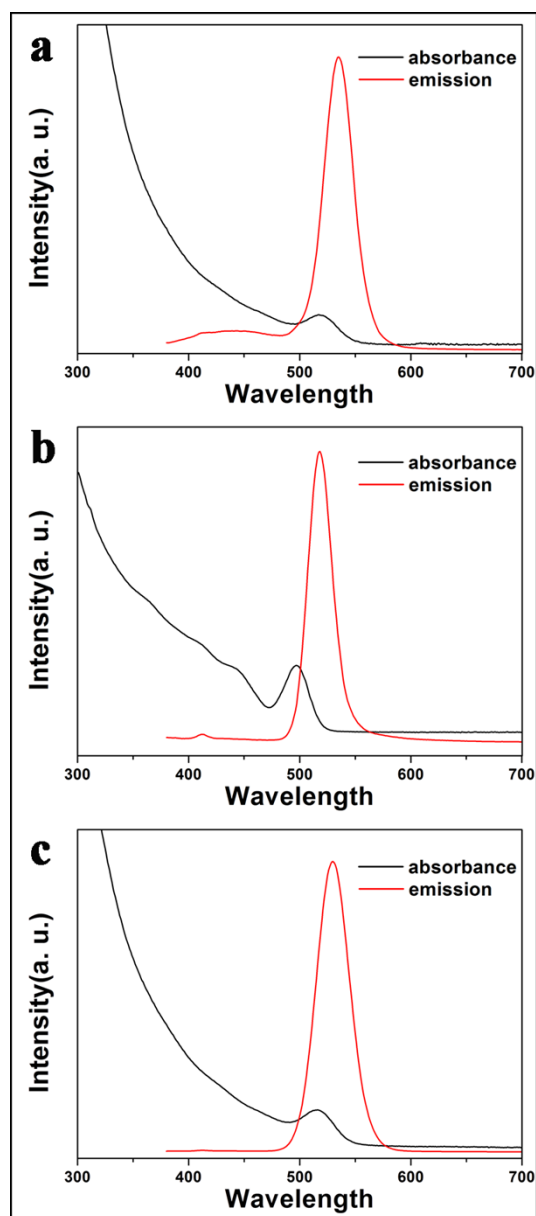


Fig. S6. Absorption spectra and photoluminescent spectra ($\lambda_{ex}=365$ nm) of a) CdSe/ZnS b) CdSe/ZnSe and c) CdSe/ZnSe/ZnS QDs with QY of 63, 6, and 74% , respectively.

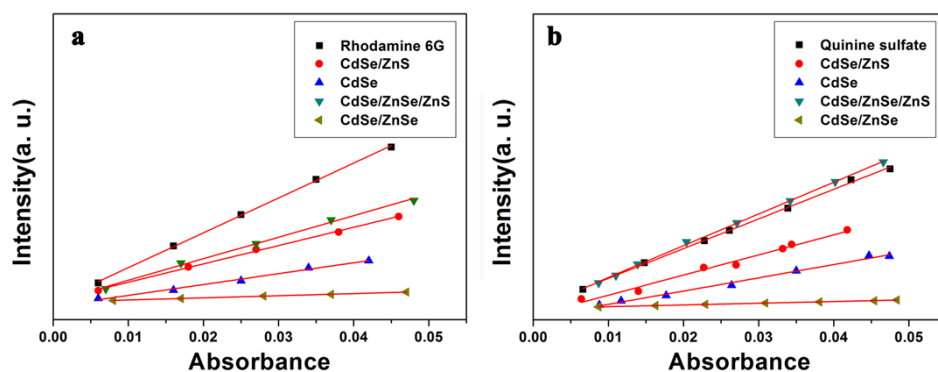


Fig. S7. Integrated fluorescence intensity vs absorbance of different samples.

Method details: Quinine sulfate emit in a similar region to our test sample whose wavelength range of the emission band is 380–580 nm, wavelength range can be used for excitation is 280-380 nm and QY is determined to be 55% in 0.1 mol/L H₂SO₄. So quinine sulfate is chosen as standard dye to determine QYs of QDs. Using well characterised rhodamine 6G (95% in ethanol) and quinine sulfate as reference, QYs of QDs were measured under excitation of 365 nm. Briefly, absorption and fluorescence spectra of reference solutions and QD solutions at different concentrations were recorded. The optical density at excitation wavelength (365 nm) of each measurement was between 0.01 and 0.05 to avoid self-absorption effects. At least five solutions with increasing concentrations of each sample were measured. The optical densities at 365nm and the integrated fluorescence intensities of each sample were then measured and processed as Fig. S7 shows. The PL QY of each QD sample was then calculated using the following equation:

$$QY_{QD} = QY_{Dye} \frac{Gra_{QD} \left(\frac{n_{QD}}{n_{Dye}} \right)^2}{Gra_{Dye}}$$

where Gra is the gradient obtained in the fitted line; n is the refractive indexes of the solvent; subscript QD and Dye represent corresponding sample measured.

Results:

Sample	QY ₁ (%)*	SD ₁	QY ₂ (%)	SD ₂	QY (%)	SD
CdSe	32	3	36	3	34	3
CdSe/ZnS	64	5	61	4	63	5
CdSe/ZnSe	5	1	7	1	6	1
CdSe/ZnSe/ZnS	75	7	72	3	74	6

*QY₁ corresponding to absolute value that is calculated using Quinine sulfate as the standard sample and QY₂ is calculated using R 6G as the standard sample; SD₁ is

corresponding standard deviation of QY_1 ; QY is the mean QY and SD is combined standard deviation calculated using the following equation:

$$SD = \sqrt{\frac{(n_1 - 1)SD_1^2 + (n_2 - 1)SD_2^2}{n_1 + n_2 - 2}}$$

where n_1 and n_2 denote number of data points in the two measurements; SD_1 and SD_2 respond corresponding standard deviation of the two measurements.

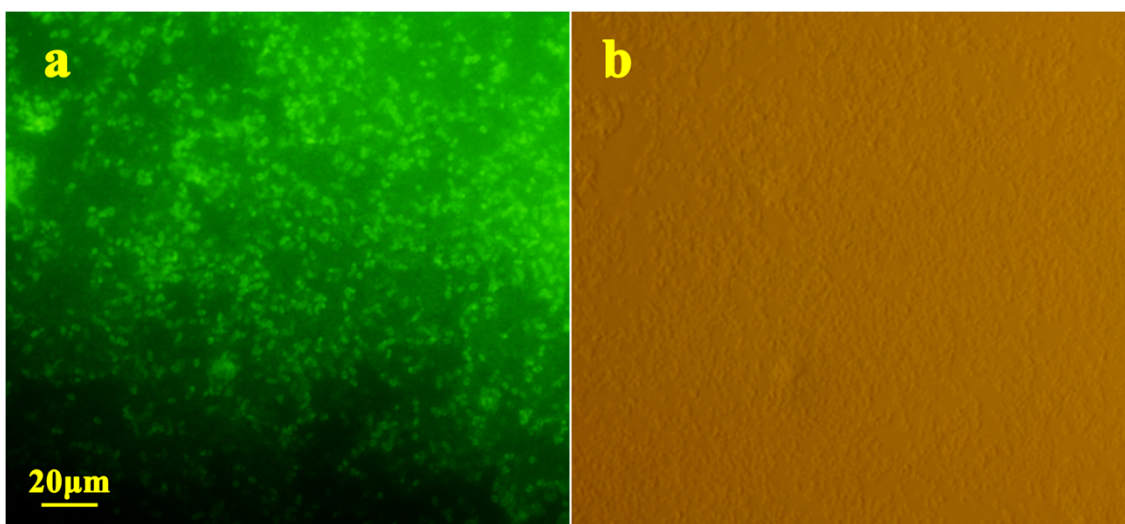


Fig. S8. Fluorescent images of *E. coli* O-157 conjugated with water soluble CdSe/ZnSe/ZnS QDs. (a) image in dark field; (b) image in bright field.

Phase transfer and bioconjugation: Briefly, 0.5 mL of Mercaptoacetic acid (MAA, 98%, Acros Organics) was dissolved in 5 mL of methanol and the solution was then adjusted to pH 8 with triethanolamine (AR, Sinopharm Chemical Reagent Co., LTD). 1 mL of MAA- triethanolamine solution was added to 5 mL of CdSe/ZnSe/ZnS QDs in toluene. Delamination was clear after mild stirring for 10 min. The upper colorless solution was decanted, and the QDs were precipitated out via centrifugation (19000 rpm, 15 min). The QDs were then resuspended in 1 mL of mixed phosphate (pH 6.86). After addition of 4 mg of EDC, the solution was vortexed for 15 min. Immediately after vortexing, the QDs solution was added to *E. coli* O-157 suspensions, and the mixture was mixed by hand-shaking and incubated for 45 min.

Atom measured	CdSe	CdSe/ZnSe	CdSe/ZnSe/ZnS
Cd in ppm	4.46	14.46	10.64
Zn in ppm	0	0.38	11.20

Table S1. ICP analysis result of CdSe, ZnSe and CdSe/ZnSe/ZnS.

Calculation:

Mass ratio is converted to molar ratio as follows:

For CdSe/ZnSe (3rd column)

$$\text{Zn: Cd} = (0.38/65.39):(14.46/112.40)$$

$$= 0.005811:0.128648$$

$$= 0.045$$

$$\text{Zn}/(\text{Zn}+\text{Cd}) = 0.045/(1+0.045)$$

$$= 0.043$$

$$= 4.3 \%$$

For CdSe/ZnSe/ZnS (4th column)

$$\text{Zn: Cd} = (11.20/65.39):(10.64/112.40)$$

$$= 0.171280:0.094662$$

$$= 1.809$$

$$\text{Zn}/(\text{Zn}+\text{Cd}) = 1.809/(1+1.809)$$

$$= 0.644$$

$$= 64.4 \%$$