

Supporting Information

Near-infrared emitting Cu-In-Se/ZnS core/shell quantum dots: aqueous synthesis and sulfur source effects

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Experimental Section

Chemicals. Copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, Aldrich, $\geq 99.0\%$), indium(III) chloride tetrahydrate ($\text{InCl}_3 \cdot 4\text{H}_2\text{O}$, adamas, 97%), L-glutathione (GSH, Aldrich, $\geq 98.0\%$), sodium citrate dihydrate (Aldrich, $\geq 99.0\%$), selenium (Aladdin, $\geq 99.999\%$), Sodium borohydride (NaBH_4 , adamas, 98%), methionine (Met, adamas, 99.0%), thioglycolic acid (TGA, Aldrich, $\geq 99.0\%$), and sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, Aladdin, $\geq 99.99\%$) were used as received. Other reagents include ethanol, HCl, and NaOH of analytical grade from Sinopharm Chemical Reagent Co. Ltd. were used as received. Millipore ultra-pure water (Milli-Q water, resistivity of 18.2 $\text{M}\Omega \cdot \text{cm}$) was utilized in all the experiments.

Synthesis of CISE core QDs. Typically, for synthesizing CISE QDs, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.0125 mmol), $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ (0.0375 mmol), sodium citrate dihydrate (0.15 mmol), and GSH (0.125 mmol) were firstly dissolved into 20 mL ultrapure water in a 50-mL flask under magnetic stirring, to form a homogeneous solution with the pH value kept at about 4~5. The Se solution (0.06 mmol) was prepared by dissolving Se powder and NaBH_4 (0.141 mmol) in 300 μL H_2O under magnetic

stirring at room temperature with the protection of inert gas. It was then injected into the reaction mixture under magnetic stirring. The resultant solution was heated to boiling and kept for 2 h.

Synthesis of CISE/ZnS core/shell QDs. Following the aforementioned procedures for synthesizing CISE seeds, the reaction solution was cooled to 80°C. Without applying the purification procedure, a stock solution (with the pH adjusted to 4~5 by NaOH) containing 0.05 mmol ZnCl₂ and 0.05 mmol GSH was introduced into the reaction system, followed by the addition of 0.05 mmol Na₂S. Then the solution was kept at 80°C for 2 h to proceed the ZnS coating. Afterwards, the solution was cooled to room temperature. The resultant QDs were precipitated by ethanol ($V_{\text{ethanol}}: V_{\text{sample solution}} \sim 5:1$), collected by centrifugation for 10 min at 8000 rpm, washed with ethanol for three cycles, and finally redispersed in water for further experiments.

For synthesizing CISE/ZnS QDs with organic sulfur precursor, Na₂S was replaced by the same molar amount of GSH, TGA, or Met respectively, while the other reaction conditions were maintained the same.

Spectroscopic characterization. Steady-state UV-Vis absorption and Photoluminescence spectra were recorded at room temperature on a Shimadzu UV-2600 UV-Vis spectrophotometer and an Edinburgh instrument FLS980 spectrometer (with NIRPMT R5509 detector), respectively. The excitation wavelength for all steady-state PL spectra was 530 nm. Time-resolved photoluminescence spectra were measured on a FLS980 spectrometer, with a picosecond pulsed diode laser (EPL-450) as a single wavelength (450 nm) excitation light source for the time-correlated single-photon (TCSP) counting measurements. The absolute PL quantum yield (QY) of the QDs was determined by a Hamamatsu instrument C9920-02G spectrometer with the excitation wavelength of 530 nm.

Structural and compositional characterization. Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) images of the QDs were taken on a JEM-F200 electron microscope at an acceleration voltage of 200 kV. The particle size was determined by averaging at least 300 particles per sample by Image J. The hydrodynamic sizes of the QDs were determined by a Malvern Zetasizer Nano at

25°C. The Fourier transform infrared (FTIR) spectra were acquired by using a FT/IR-410 Fourier transform infrared spectrophotometer (JASCO, Japan). Powder X-ray diffraction (XRD) pattern of the particle sample was recorded on a Regaku D/Max-2500 diffractometer under Cu $K\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Thermo-VG Scientific ESCALAB 250Xi spectrometer with a monochromatic Al $K\alpha$ X-ray source. Thermogravimetric Analysis (TGA) was measured using a Mettler Toledo TGA/DSC1 1600.

Supplementary Results

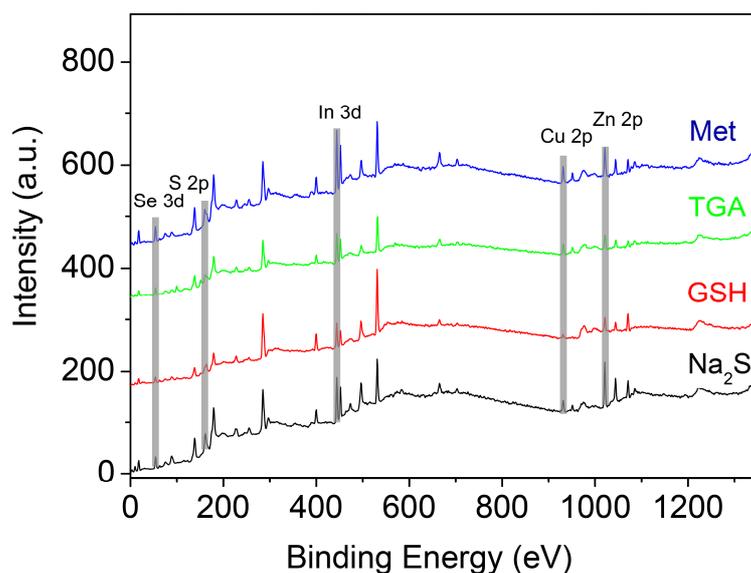


Fig. S1 XPS spectra of CISE/ZnS QDs prepared by different sulfur precursor.

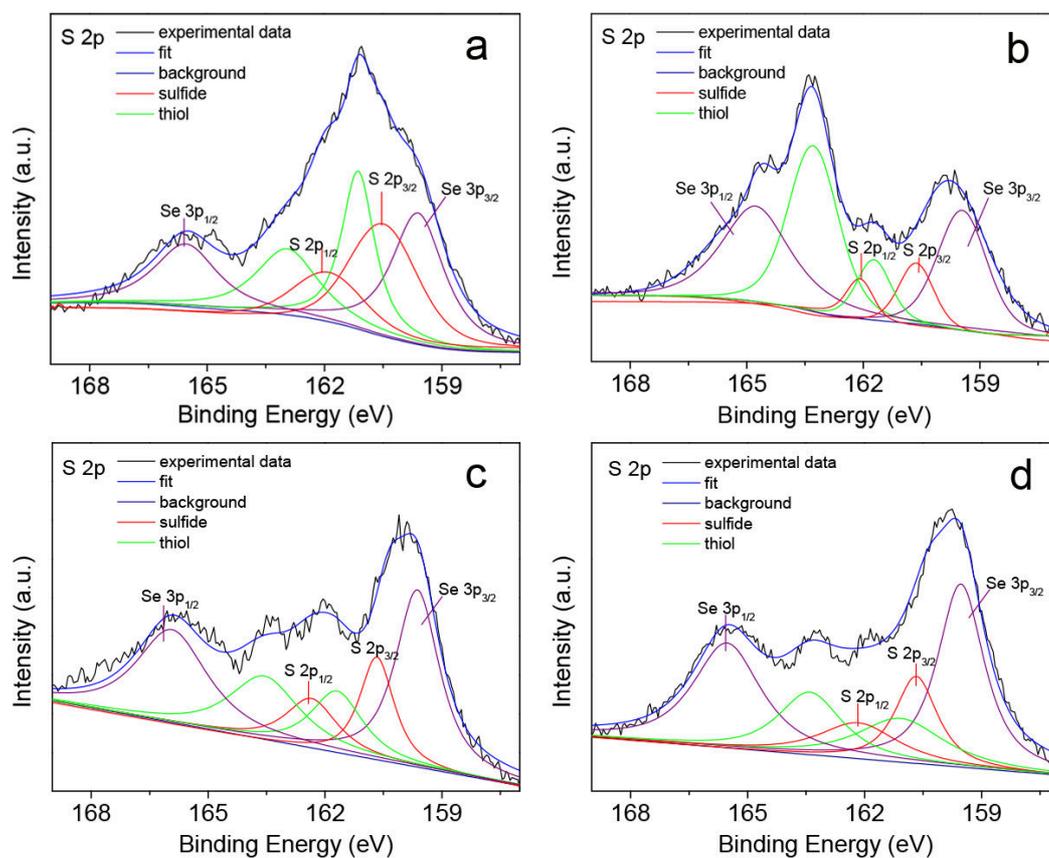


Fig. S2 High-resolution XPS signals including experimental and fitting results of S 2p for the sample prepared by Na₂S (a), GSH (b), TGA (c), and Met (d).

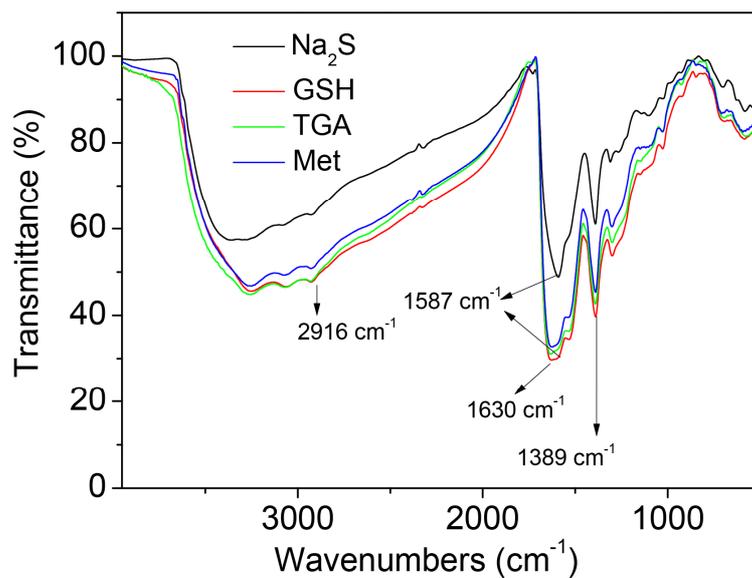


Fig. S3 FTIR spectra of CISE/ZnS QDs prepared by different sulfur precursor.

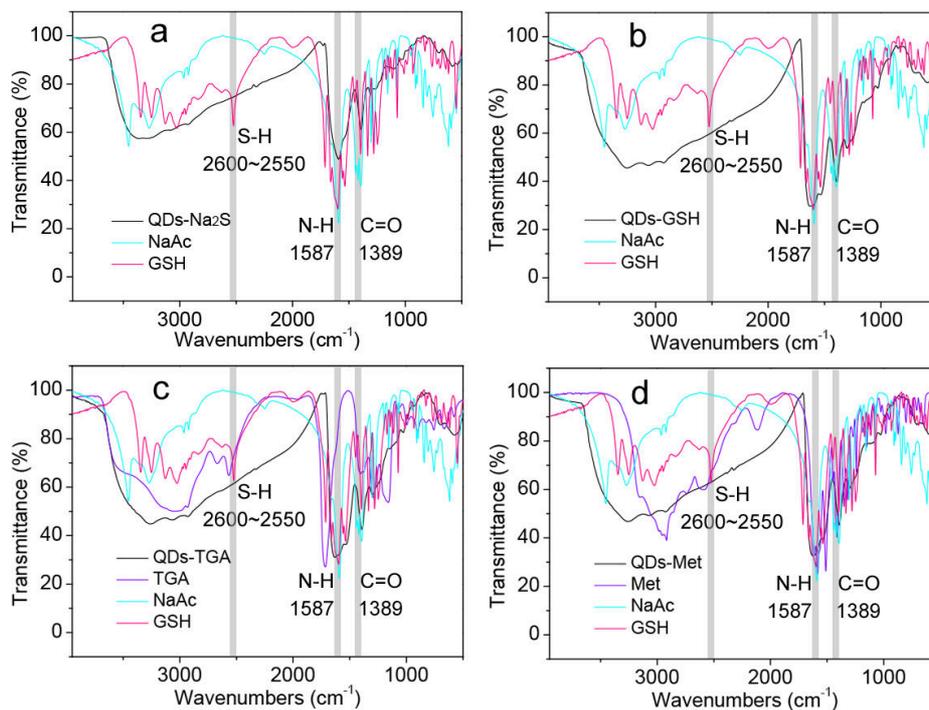


Fig. S4 Comparison of FTIR spectra of CISE/ZnS QDs prepared by different sulfur precursor: (a) Na₂S, (b) GSH, (c) TGA, and (d) Met, and corresponding surface ligands.

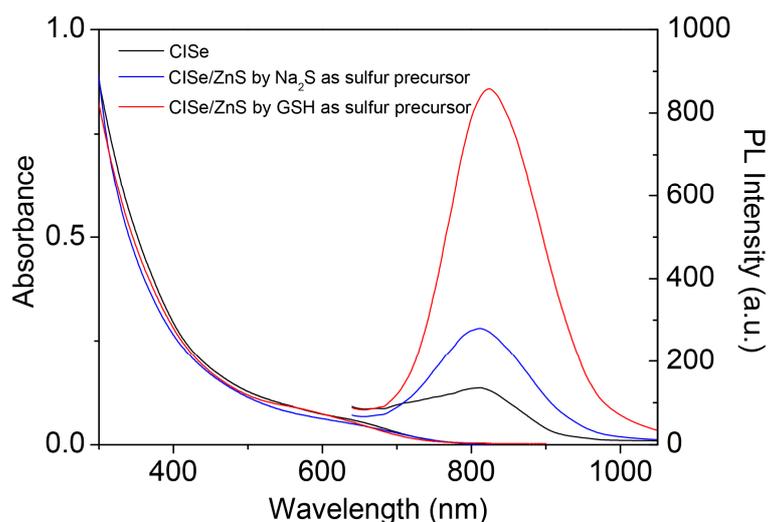


Fig. S5 UV-Vis absorption and PL spectra of different QDs. The excitation wavelength is 530 nm.

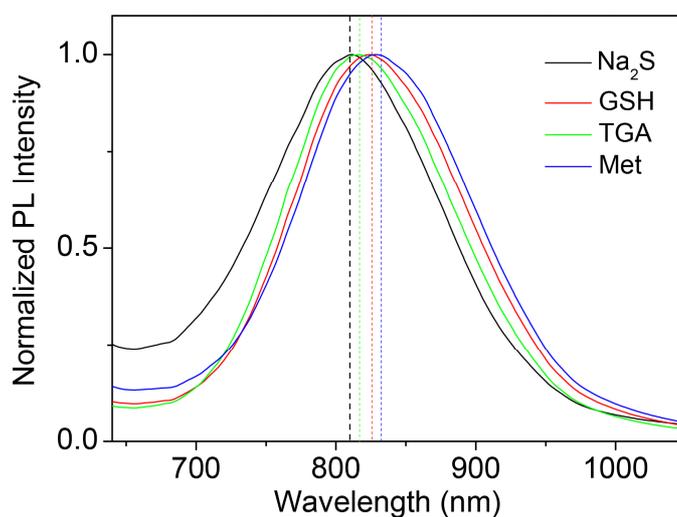


Fig. S6 Normalized PL spectra of CISE/ZnS QDs prepared by different sulfur precursor. The excitation wavelength is 530 nm.

Time-resolved photoluminescence (TR PL) measurements

The PL decay curves were fitted using a multi-exponential function¹:

$$I(t) = \sum_{i=1}^n B_i \exp(-t/\tau_i), \quad \sum_{i=1}^n B_i = 1 \quad \text{S(1)}$$

In this expression, τ_i represent the decay time constants, and B_i represents the normalized amplitudes of each components, n is the number of decay times. Because the photoluminescence decays for all the QDs are best fitted using a double

exponential function ($n = 2$), the amplitude weighted average decay lifetime τ_{avg} of the entire fluorescence decay process was calculated with the form:

$$\tau_{\text{avg}} = \frac{\sum B_i \tau_i^2}{\sum B_i \tau_i} \quad \text{S(2)}$$

The normalized lifetime-amplitude product is given as:

$$f_i = \frac{\tau_i B_i}{\sum \tau_i B_i} \quad \text{S(3)}$$

In this expression, f_i represents the relative time-integrated contribution of each respective process to the overall number of emitted photons (i.e., the emission intensity measured in steady state PL spectra).

The PL decay-fitting data for all curves are summarized in **Table S1**.

Table S1 The parameters for multi-exponential fitting of the PL decay curves in Fig. 1c, i.e., normalized amplitude B_i , time constant τ_i and their normalized products f_i , goodness-of-fit parameter χ^2 , together with the emission peak wavelength.

	λ_{em} [nm]	B_1	B_1 [%]	f_1 [%]	τ_1 [ns]	B_2	B_2 [%]	f_2 [%]	τ_2 [ns]	τ_{avg} [ns]	χ^2
Na₂S	809	532.4	80.50	32.70	12.90	128.9	19.50	67.30	109.6	78.04	1.196
GSH	824	634.5	82.36	44.94	64.92	135.9	17.64	55.06	371.3	233.6	1.095
TGA	816	573.2	76.88	37.71	51.50	172.4	23.12	62.29	282.9	195.7	0.933
Met	830	607.1	77.69	34.84	27.41	174.3	22.31	65.16	178.6	125.9	1.222

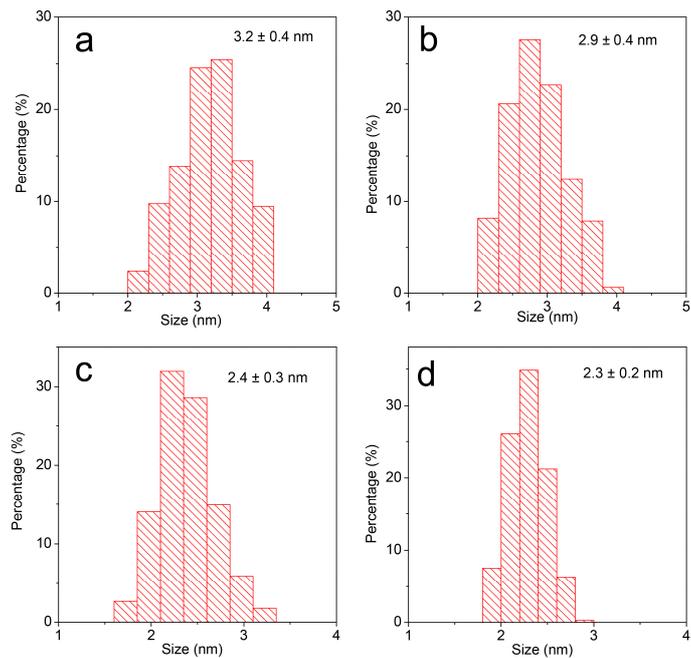


Fig. S7 Size histograms of CISe/ZnS QDs prepared by different sulfur precursor: (a) Na_2S , (b) GSH, (c) TGA, and (d) Met.

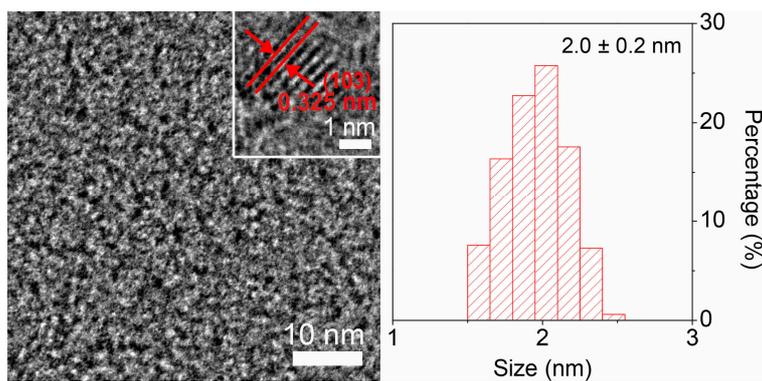


Fig. S8 TEM image of CISe core QDs together with the size histogram. The inset shows the HRTEM image of CISe core QDs.

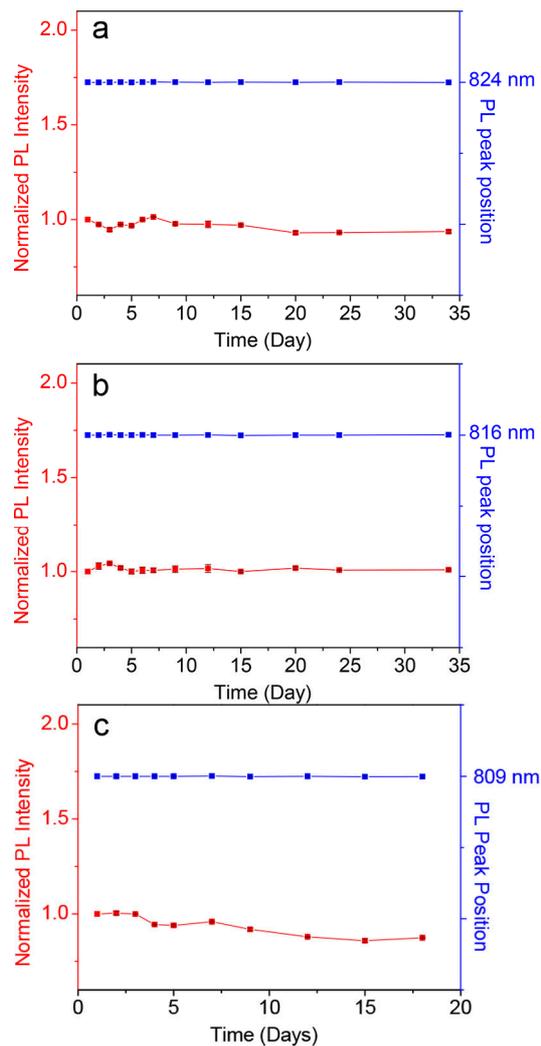


Fig. S9 Temporal evolutions of the PL intensity and peak position of CISE/ZnS QDs prepared by GSH (a), TGA (b), and Na₂S (c). The excitation wavelength is 530 nm.

Reference

- 1 Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Springer: New York, 2006.