

Electronic Supplementary Information

For

Aggregation-Induced Emission Property of Hydrothermally Synthesized **Cu-In-S** Quantum Dots

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Experimental Section

Chemicals. All reagents were commercially available and used without further purification unless special statement. 3-mercaptopropionic acid (MPA) was purchased from Aladdin Chemistry Co., Ltd (Shanghai, China). $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$, thiourea and other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Water was **deionized water**.

Synthesis of **Cu-In-S quantum dots.** 1.5×10^{-3} mol of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 1.0×10^{-3} mol of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ were dissolved in **100 mL of** water. Then **0.25 mol** of MPA was added into the solution under vigorous stirring. A yellow emulsion was formed. NaOH (2M) was then added dropwise into the mixture to adjust the pH of ~ 12.0 and the emulsion was dissolved. Then 50mmol of thiourea was added into the solution. After 10min of stirring, the mixture was transferred into a Teflon-lined stainless steel autoclave and maintained at 210°C for 15min. After the autoclave cooled down, the CIS QDs were precipitated by adding ethanol and washed with ethanol for several times. The product was dried and stored in drying condition for long-term preservation.

Apparatus and Characterization. UV-vis absorption and photoluminescence (PL) spectra were recorded by a Shimadzu UV-2100 photo spectrometer and a Hitachi F-4600 spectrofluorometer, respectively. Fourier transform infrared spectroscopy (FTIR) spectra of KBr powder-pressed pellets were recorded on a Shimadzu FTIR-8400S. Transmission electron microscopy (TEM) images were taken on a JEOL JEM-2100 microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 spectrometer with Al K α X-ray radiation (1486.6 eV) for excitation. A SGW WAY-2W abbe refractometer was used to measure the refractive index of different solvents. X-ray Diffraction (XRD) spectra were recorded by a Thermo-Fisher XTRA. ZETA potential spectra were measured by Malvern Zetasizer Nano.

AIE effect of the CIS QDs. To test the effect of viscosity on PL intensity, 200 μL CIS QDs solution (about 5mg/mL) or 200 μL of Rhodamine 6G (Rh 6G, about 10^{-4} mg/mL) were added in a 2mL EP tube. Then added 1800 μL of different fractions glycerol/water mixture into the EP tube and vortexed thoroughly and then transferred for PL measurement.

To study the solvent-induced aggregation property of QDs, 200 μL CIS QDs solution (about 5mg/mL) and 1800 μL of different fractions DMSO/water mixture were added into a 2mL EP tube. Then the solution was vortexed thoroughly and then transferred for PL measurement.

To study cation-induced aggregation property of QDs, different kinds of metal ion (3mmol/L) were respectively added into CIS QDs aqueous solution (2mg/mL).

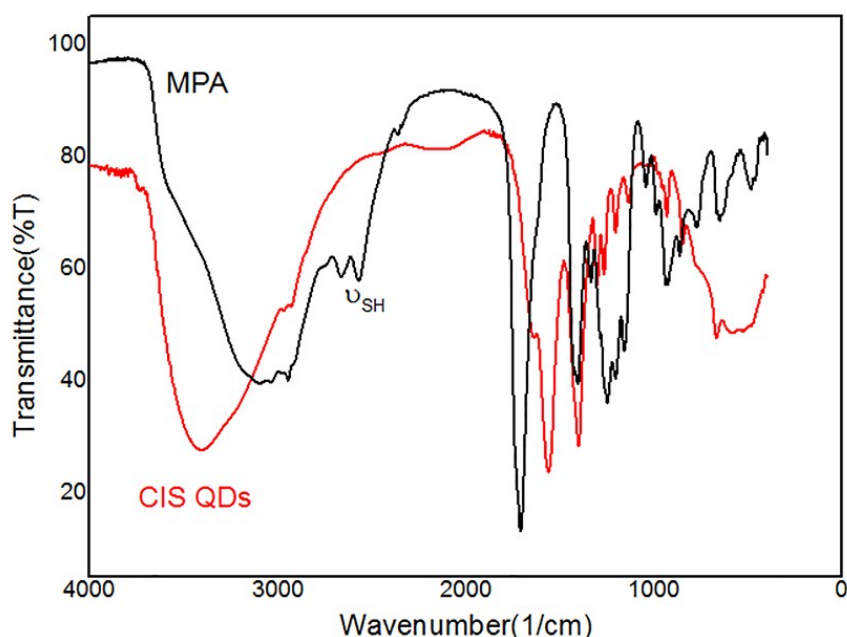


Figure S1 FTIR spectrum of the CIS QDs and MPA. a strong wide peak at 3400 cm^{-1} indicating the presence of O-H, while the peaks at 1569 and 1141 cm^{-1} exhibited characteristic absorption bands of C=O and C-O stretching vibrations, respectively, which proved the existence of carboxyl groups on the surface of CIS QDs. Peaks at 2970 cm^{-1} , 2929 cm^{-1} and 1406 cm^{-1} in FT-IR were attributed to the stretching vibration and bending vibration of C-H. The peak at 2574 cm^{-1} that corresponds to the S-H stretching vibration of MPA disappeared in the CIS QDs, indicating that the MPA cap on the QD surface through metal-S bonding¹.

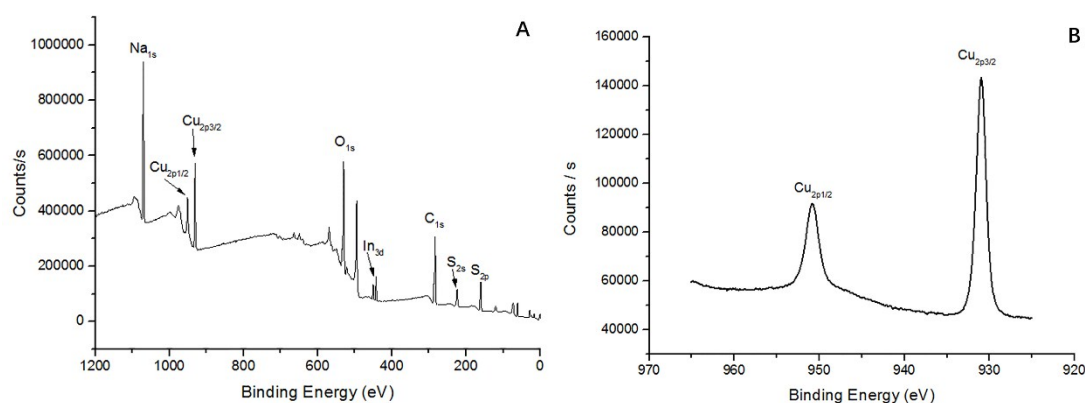


Figure S2 A) XPS spectrum of CIS QDs, peaks at 1070, 951, 931, 530, 451 (and 443), 283, 224 and 160 eV were attributed to the Na1s, Cu2p1/2, Cu2p3/2, O1s, In3d, C1s, S2s, S2p, respectively. B) amplify Cu2p electrons. The binding energies of Cu2p1/2 and Cu2p3/2 are observed at 951 and

931 eV peaks are consistent with that of Cu^+ reported¹⁻³. No satellite peak around 942eV confirms the absence of Cu^{2+} . Peaks at 495 eV was Sn, an impurity that is difficult to remove in raw material $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$.

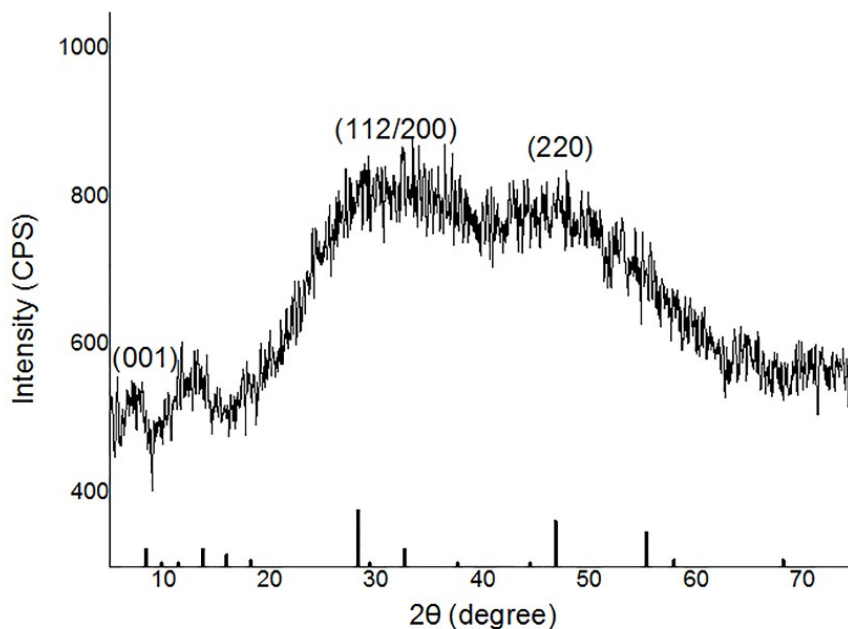


Figure S3 XRD pattern of the CIS QDs. Four relatively broad peaks appearing around 8° , 14° , 28° , 47° , which were in their expected lattice planes (001), (112/200), and (220), were indexed to the appropriate reference pattern (JCDPS #15-0681). So the chalcopyrite tetragonal structure of as-synthesized CIS QDs could be confirmed.

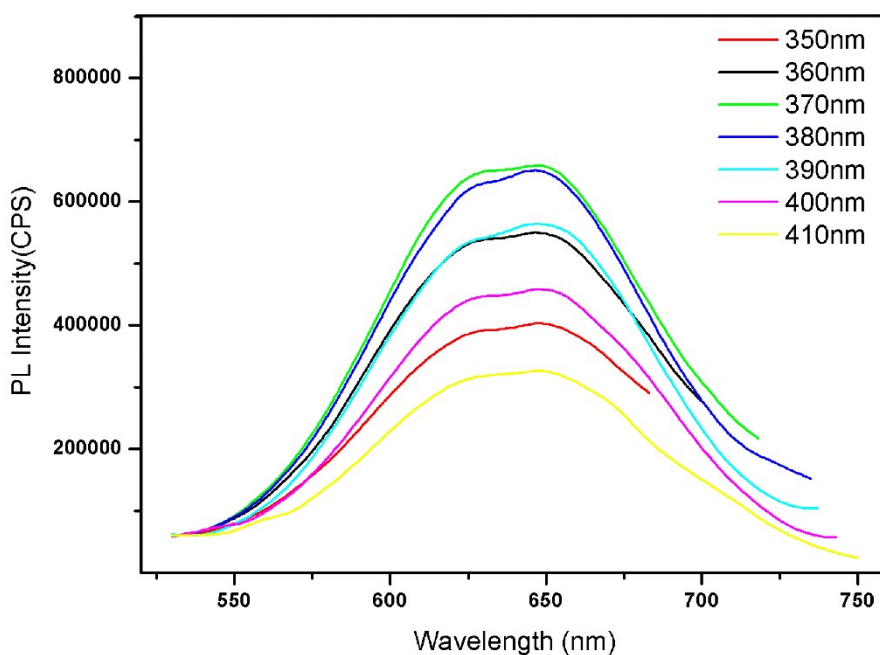


Figure S4 The PL spectra of the CIS QDs (dissolved in 70 vol.% DMSO) excited by different

excitation wavelengths. PL emission peak was independent from excitation wavelength.

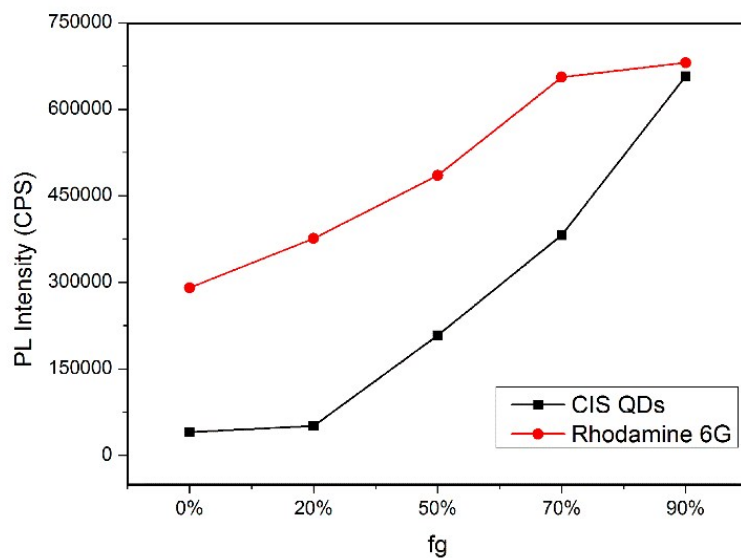


Figure S5 Plots of PL intensity of CIS QDs and Rh 6G versus fg. Compared fg=90% and 0%, the PL intensity of CIS QDs enhanced for about 16-fold while Rh 6G was 2.3-fold.

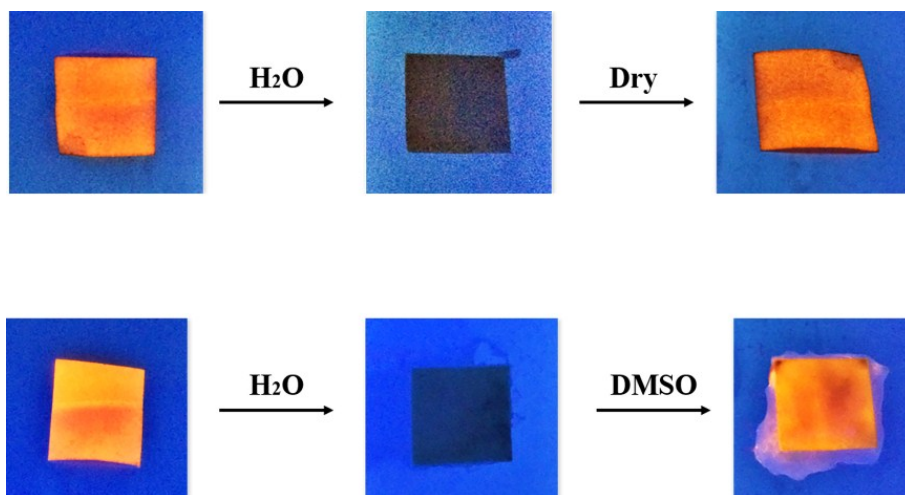


Figure S6 Digital photos of the CIS QDs in the solid state (vacuum dried on a paper carrier) and their “turn off” and “turn on” under UV light. Addition of water to aggregated CIS QDs resulted in the re-dispersion of the QDs and quenched of PL, and the CIS QDs can be “turned on” through vacuum drying or adding DMSO.

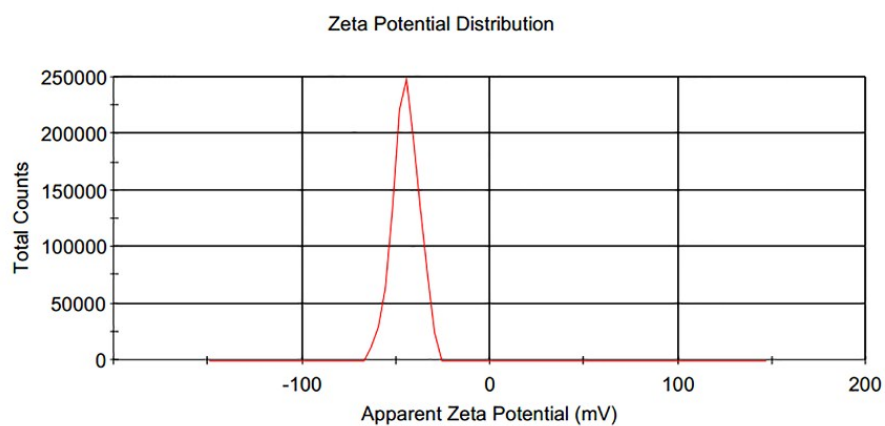


Figure S7 ZETA potential of CIS QDs aqueous solution was -44.6.

Notes and references

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