Supporting Information

Engineering amino-mediated copper nanoclusters with dual emission and assembly-to-monodispersion switching by pH-triggered surface modulation

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Experimental Section

Materials. Copper nitrate trihydrate [$Cu(NO_3)_2 \cdot 3H_2O$], L-cysteine (Cys), glutathione (GSH), cysteamine (CS), polyethyleneimine (PEI) and N-acetyl-L-cysteine were purchased from Sangon Biotechnology Co. Ltd. (Shanghai, China). Sodium hydroxide (NaOH, 96%) and Sulfuric acid (H_2SO_4, 98%) were acquired from Tianli Chemical Reagent Co., Ltd (Tianjin, China). Other reagents and solvents were all of analytical grade and obtained from Sigma-Aldrich. Deionized water was used for all of the experiments. All glassware was cleaned with aqua regia and rinsed with water before use.

Instrumentation. The UV-visible spectrum was recorded using a UV-Vis Cary 60 spectrophotometer at room temperature (Agilent, China). The fluorescence spectrum was studied using Hitachi F-7000 fluorescence spectrophotometer (Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) measurements were performed by using a VG Thermo ESCALAB 250 spectrometer. The transmission electron microscopy (TEM) images were acquired on a Tecnai G2 F30 S-TWIN. FT-IR spectrograms were received by a Nicolet iN10 MX & Is10 FT-IR spectrometer & microscope.

Synthesis of R-CuNCs@Cys and B-CuNCs@Cys. Cys aqueous solution (2 mL, 100 mM) mixed with Cu^{2+} aqueous solution (2 mL, 5 mM) at mole ratios from 20:1. The solution quickly turned from colorless to white suspension. Under 365 nm UV-light radiation, bright red emission of suspension was clearly visible, indicated the formation of luminescent R-CuNCs@Cys. R-CuNCs@Cys adjusted to pH=9-11, the solution became transparent, then stirred over 4 h. Eventually, a brown solution formed and showed blue emission under UV-light irradiation after dilution. The B-CuNCs@Cys also been prepared through microwave-assisted reaction by heated in a domestic microwave oven (800 W, Galanz). Regular intervals were needed every 20 s to avoid bumping and stirring was necessary during these intervals to ensure a homogeneous reaction. By keeping at irradiant heating for 4 min, B-CuNCs@Cys-containing powder was obtained. The as-synthesized R-CuNCs@Cys and B-CuNCs@Cys were stored at 4 °C in a refrigerator for further use. B-CuNCs@GSH, CuNCs@CS and CuNCs@PEI could use a similar preparation method.

Synthesis of R-CuNCs@GSH. GSH aqueous solution (2 mL, 50 mM) mixed with Cu^{2+} aqueous solution (2 mL, 10 mM) at mole ratios from 5:1. The solution quickly turned from colorless to white suspension. Under 365 nm UV-light radiation, bright red emission of suspension was clearly visible, indicating the formation of luminescent R-CuNCs@GSH. The as-synthesized R-CuNCs@GSH was stored at 4 °C in a refrigerator for further use.

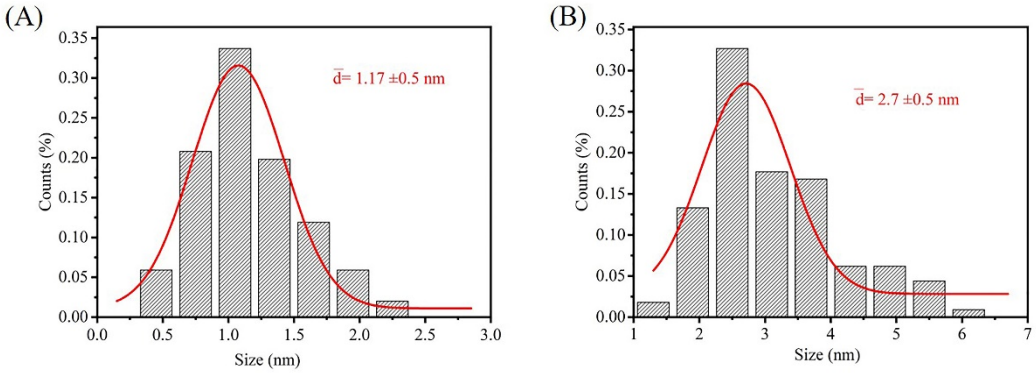

Figure S1. TEM size distributions of (A) R-CuNCs@Cys and (B) B-CuNCs@Cys.

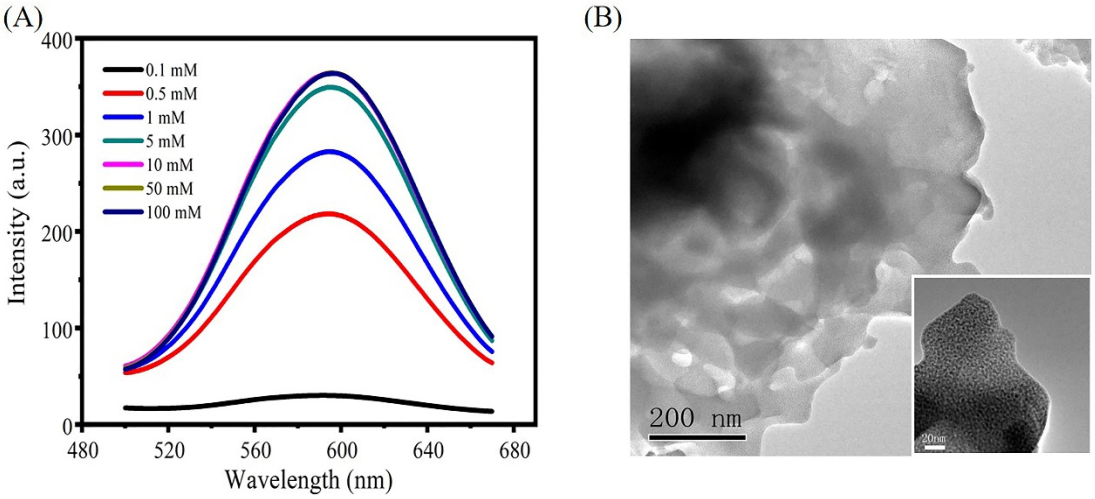

Figure S2. (A) Al^{3+}-induced emission spectra of R-CuNCs@Cys with different Al^{3+} concentration; (B) TEM images of R-CuNCs@Cys with 10 mM Al^{3+}. Inset: High magnification of TEM image (20 nm).

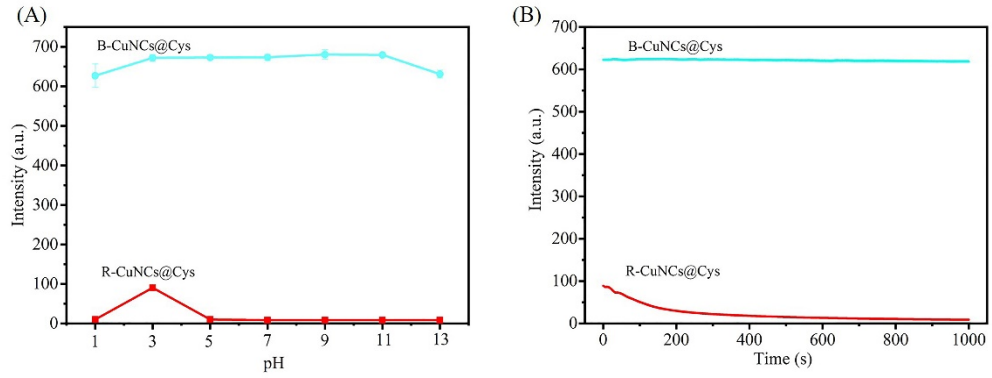

Figure S3. (A) Emission spectra at different pH and (B) Luminescence stabilities against continuous irradiation with a 150 W xenon lamp of R-CuNCs@Cys and B-CuNCs@Cys.

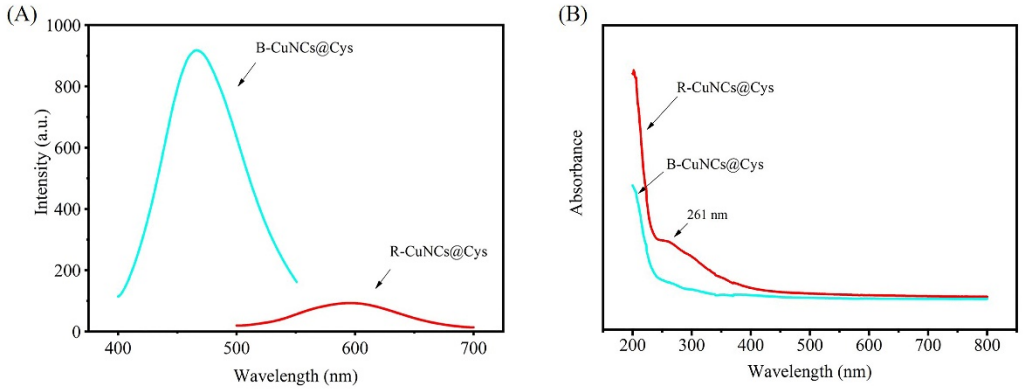

Figure S4. (A) Luminescence emission spectra and (B)UV-Vis absorbance spectra of R-CuNCs@Cys and B-CuNCs@Cys.

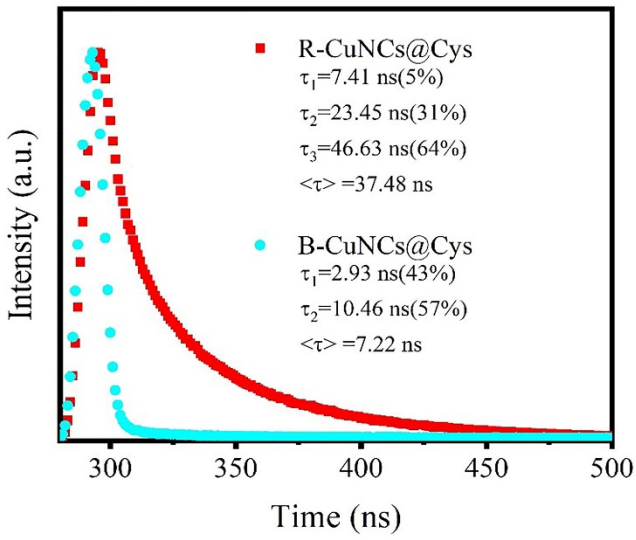

Figure S5. Emission lifetimes spectra of R-CuNCs@Cys and B-CuNCs@Cys.

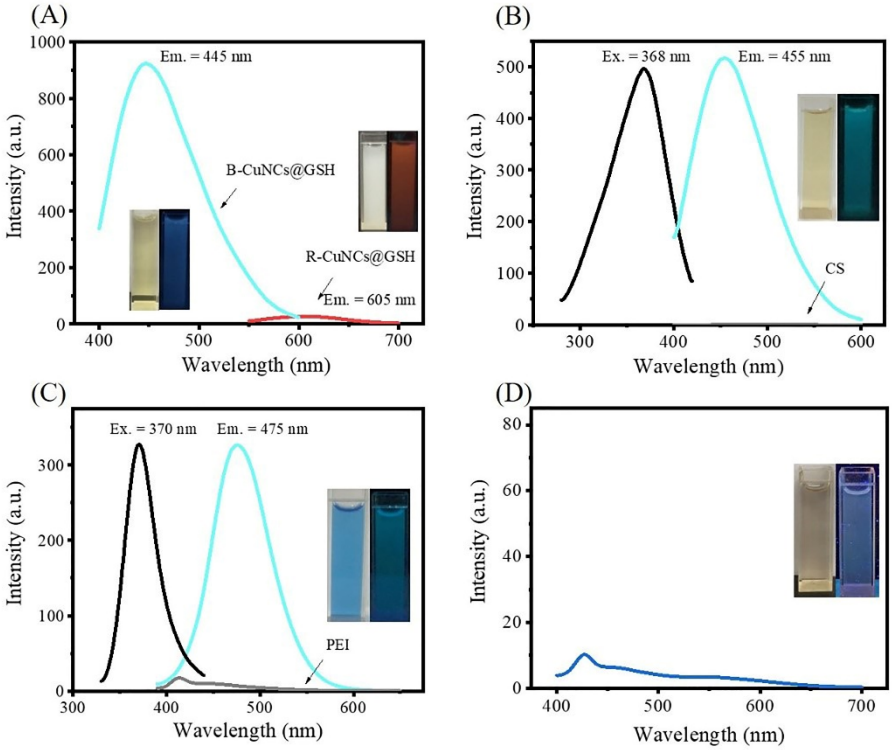

Figure S6. Luminescence spectra of (A)R-CuNCs@GSH (red line) and B-CuNCs@Cys (blue line); (B) B-CuNCs@CS (blue line) and CS (gray line); (C) B-CuNCs@PEI (blue line) and PEI (gray line); (D) CuNCs@NAC. All insets: photographs of CuNCs solution (under ambient and 365 nm light respectively).