Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting information

One-step synthesis of water-soluble fluorescent copper nanoparticles for label-free detection of manganese ion

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Materials and Methods

Chemicals

Histidine, asparagine, aspartic acid, cysteine, glycine, proline, serine, tryptophan, and tyrosine were obtained from Acros Organics. 2-mercaptoacetic acid (MA), 3-mercaptopropionic acid (MPA), 4-mercaptobutyric acid (4MBA), 6-mercaptohexanoic acid (6MHA), 8-mercaptooctanoic acid (8MOA), and quinine sulfate were obtained from Sigma-Aldrich. $CuSO_4$, LiI, NaCl, $Ca(NO_3)_2 \cdot 4H_2O$, $CrCl_3 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $CoCl_2 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$, Na_2PdCl_4, $PtCl_2$, $CdCl_2 \cdot 2^1/_2H_2O$, $Hg(NO_3)_2 \cdot H_2O$ and $PbCl_2$ were purchased from Acros Organics. KCl and $MgCl_2 \cdot 6H_2O$ were purchased from Merck. All chemicals and solvents were analytical grade and used as-received without further purification. Ultrapure water (18.3MΩ) was purified through a Millipore system and employed for all experiments.

Apparatus

The fluorescence spectra were measured by a fluorescence spectrometer (AMINCO-Bowman, Series 2). Absorption spectra were measured by UV-vis spectroscopy (Hewlett-Packard, 8453). Absorption and emission measurements were conducted in 1 cm × 1 cm quartz cuvettes. The morphology and size of Cu nanoparticles were taken by high-resolution transmission electron microscopy (FEI, TECNAI G2) including EDS Spectroscopy, CCD Camera with Diffpack program. X-ray photoelectron spectra (XPS) were recorded on an X-ray photoelectron spectrometer (ULVAC-PHI, PHI Quantera SXM). Lifetime was measured by a self-assembled time-resolved laser spectrometer. The laser which was used in this experiment is Pulsed Q-switched Nd:YAG. The third harmonic of the laser (355 nm, FWHM = 10 ns) was used as excitation source. After excited, the signal emitted by sample was filtered by monochrometer (Acton Research Corporation SpectraPro-2150i). Then, the output was received by PMT (Hamamtsu model R928), digitized by a digitizer (LeCroy 9350A). And the collected data was fit by ns KinFit 4.0.1.

Preparation and purification of Cu nanoparticles

All glassware was washed with *aqua regia*, and rinsed with ultrapure water. In a typical experiment, an aqueous solution of $CuSO_4$ (90 µL, 50 mM) was added into a mixture solution of histidine (7.5 mL, 258 mM) and MPA (3 mL, 10 mM). The mixture was vortexed, and allowed to react without stirring for 48 h at 28 ℃. After the reaction has completed, the mixture was filtered with 0.22 µm filter membrane to remove the large aggregates. Lastly, the solution was purified by dialysis through a

semipermeable membrane (with 1000 MWCO) for 16 h to remove unreacted histidine, copper salts, and MPA. The final solution was stored at 4 ℃.

Quantum yield measurement

The relative quantum yield (QY) of Cu nanoparticles was measured using a reference compound quinine sulfate (dissolved in 0.1 M H_2SO_4). The formula below is used to calculate QY.

$$QY = \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{{\eta_R}^2} \times QY_R$$

Where QY is the abbreviation of quantum yield, I represents the integral area under the fluorescence spectrum, A is the absorbance of Cu nanoparticles aqueous solution at the excitation wavelength, and η is the refractive index of the solution. The subscript R represents the reference.

Detection of Mn^{2+} ions using fluorescent Cu nanoparticles

The as-prepared Cu nanoparticle solution (52 mg/mL) was mixed with various concentrations (0.25 μM to 250 μM) of manganese chloride. Next, the mixture was incubated in a water bath at 55 ℃ for 2 h. The fluorescence of the mixture was measured and recorded (λ_{ex}= 350 nm; $\lambda_{em,\ max}$= 449 nm). Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} were investigated, respectively.

Effects of pH

The Britton-Robinson (BR) buffers of various pH levels were mixed with the as-prepared Cu nanoparticles aqueous solutions. After vortexed, the mixture was incubated at room temperature for one day. Then, the fluorescence spectra were obtained and recorded by the fluorescence spectroscopy.

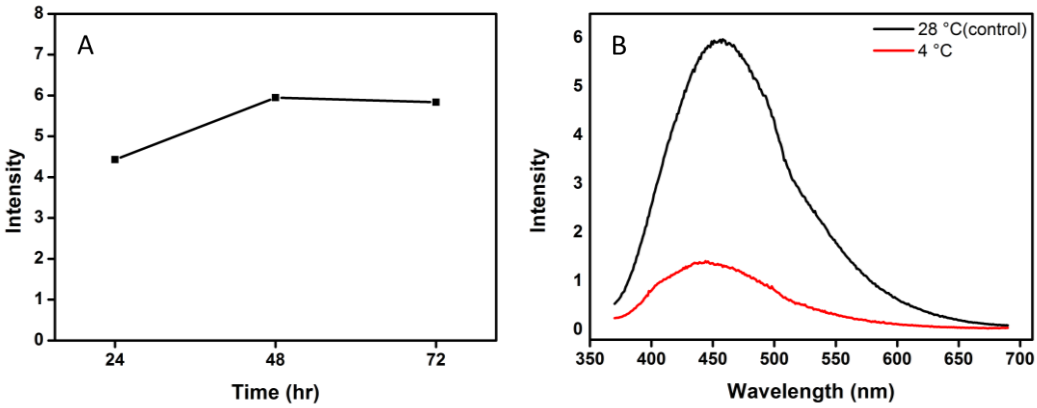

Fig. S1 The effect of (A) reaction time and (B) reaction temperature on the intensity of fluorescence. The fluorescence intensity was collected at 449 nm.

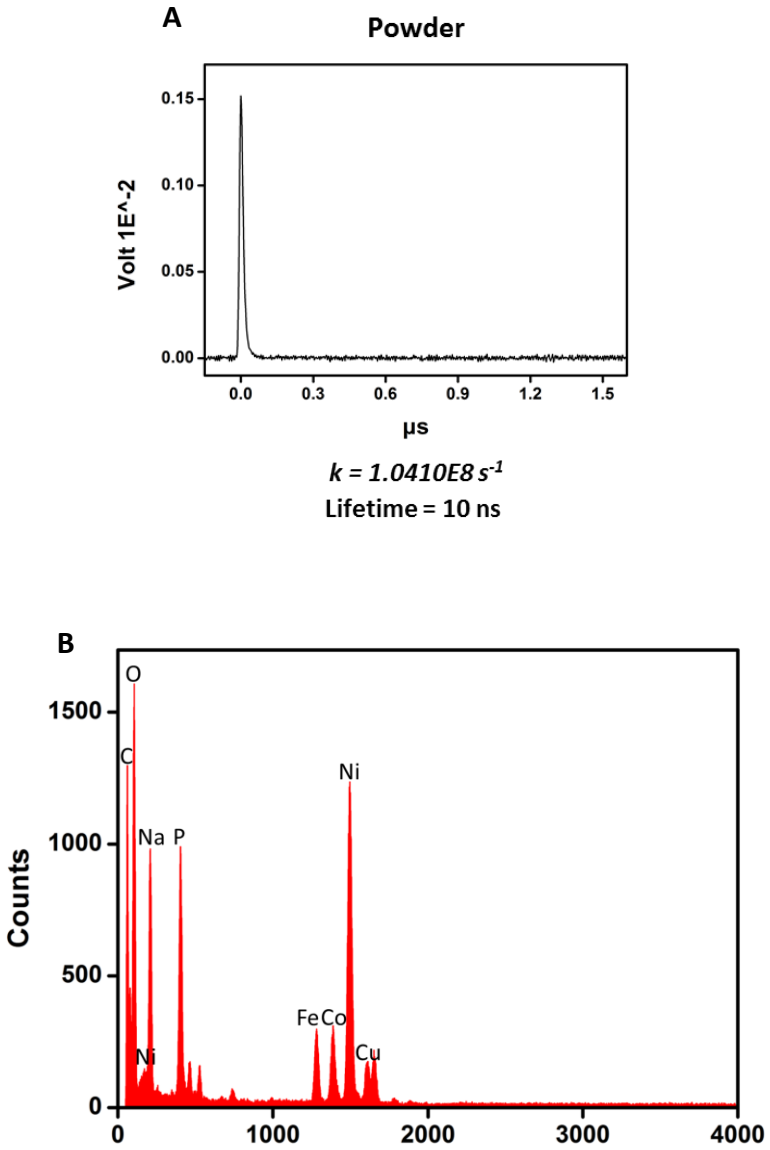

Fig. S2 (A) Fluorescence decay of the lyophilized powder of Cu nanoparticles (black line). (B) Energy-dispersive X-ray spectroscopy (EDS) of resulting Cu nanoparticle solution (Ni signals come from the nickel grid, and Fe and Co signals come from the background of the instrument.)

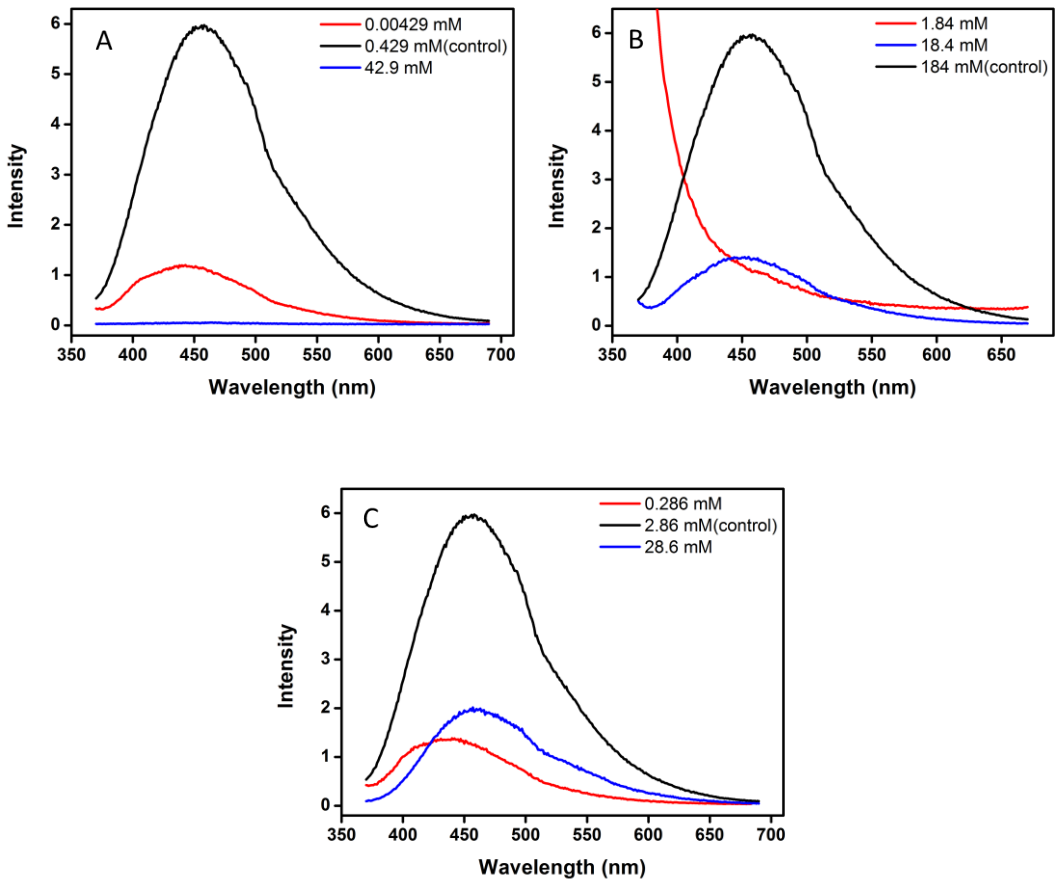

Fig. S3 The final fluorescence intensity of solutions containing different molar ratios of (A) Cu^{2+}, (B) histidine, and (C) MPA.

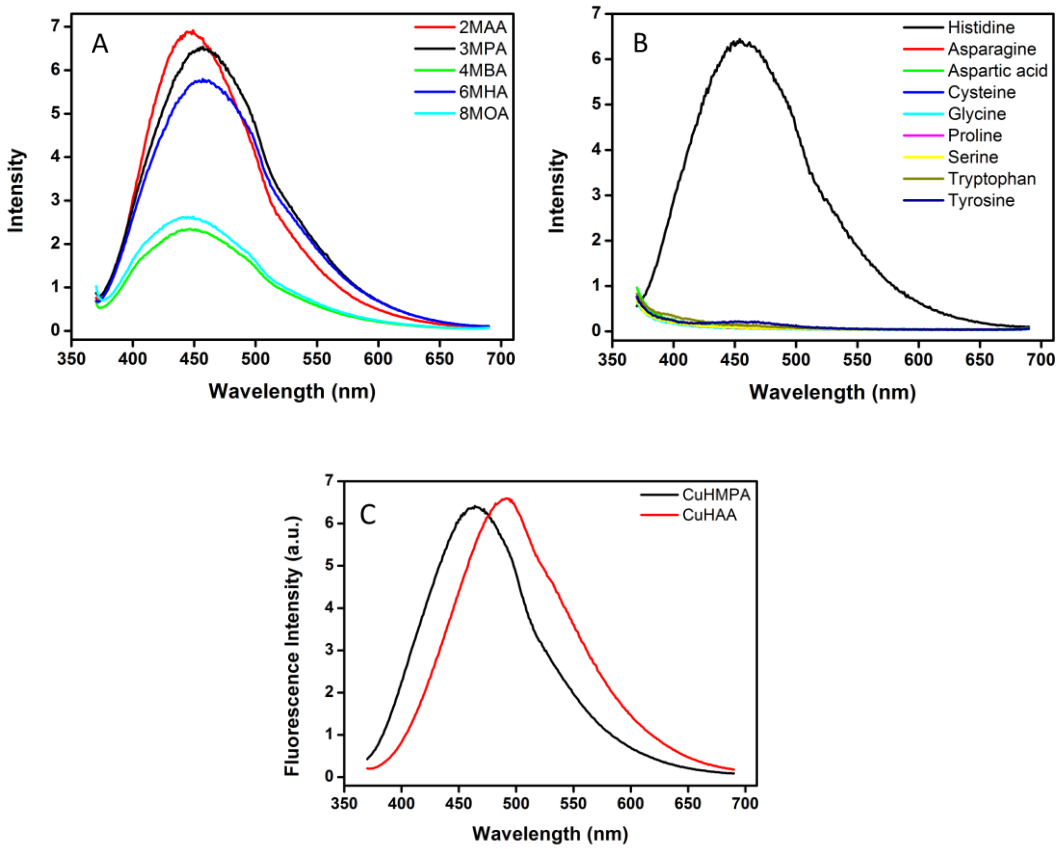

Fig. S4 (A) The effect of chain lengths on the final fluorescence intensity. (B) A variety of amino acids were used as a substitute for histidine in the synthesis of Cu nanoparticles. (C) Ascorbic acid was used as reducing agent in the synthesis of Cu nanoparticles.

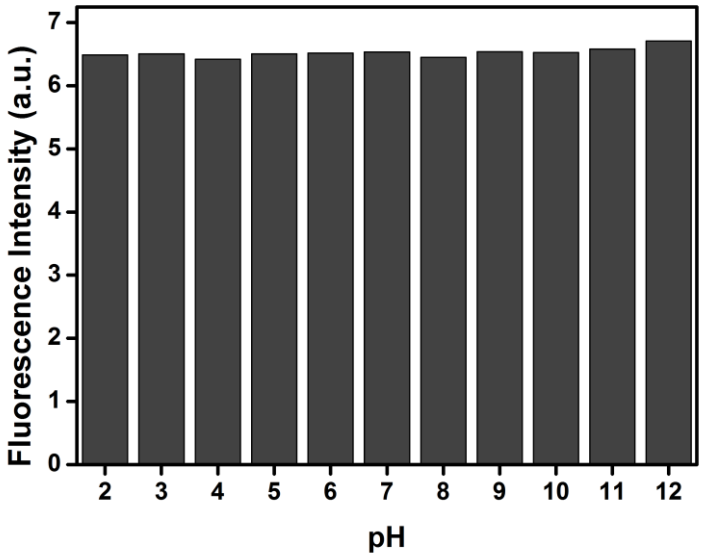

Fig. S5 The final fluorescence intensity of Cu nanoparticles at different pH values.