Title: Synthesis and properties of Au-Ag bimetallic nanoclusters with dual-wavelength emission†

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Supporting Information

1. Additional Materials and Methods

Materials and agents

Hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4 \cdot 4H_2O$) and Glutathione in the reduced form (GSH) were purchased from aladdin (Shanghai, China). Silver nitrate ($AgNO_3$) was purchased from Ling Feng Chemical Reagent Co., Ltd. (Shanghai, China). Ultrapure water (18.2 MΩ) was used in all experiments . All other chemicals were of analytical grade and used without further purification.

Apparatus

UV-visible absorption spectra were obtained by a UV2450 spectrophotometer (Hitachi, Japan). The PL spectra were acquired by an FLS920 fluorescence spectrometer (Edinburgh, UK). The high resolution transmission electron microscopy (HRTEM) micrographs were obtained by a JEM-2100 electron microscope (JEOL, Japan) operating at 200 kV. The fourier transform infrared (FTIR) spectra were recorded in the range of 500-4000 cm^{-1} using a NICOLET iS10 spectrometer (Thermo Fisher, America). The X-ray photoelectron spectroscopy (XPS) spectra were performed by a ESCALAB 250 spectrometer (Thermo Fisher, America).

Synthesis of highly luminescent Au-Ag NCs

The highly luminescent Au-Ag NCs were synthesized using a simple one-pot procedure. In a typical procedure, freshly prepared aqueous solutions of GSH (10 mL, 36 mM) and $AgNO_3$ (20 μL, 0.5 M) were mixed well under vigorous stirring. After stirring for 10 min, aqueous solution of $HAuCl_4$ (100 μL, 0.1 M) were added into the mixture solution. The mixture was then stirred at room temperature overnight. After stop stirring, the final solution was then incubated at room temperature for another 12 hours. Finally, the product was stored at 4 °C for further use.

Quantum yield measurement

Quantum yield (QY) is measured by the reference method. QY of the Au-Ag NCs was about 26% (Rhodamine B as a standard). The detailed experimental procedure is as follows:

1. Rhodamine B was chosen as the standard, the Φ_F value of which is 0.31 in water.

2. Different concentrations of the Au-Ag NCs and standards were prepared, all of which had absorbance less than 0.1 at their excitation wavelengths. So that the PL measurements with minimal errors due to the “inner-filter effect” were conducted.

3. Record the UV-vis absorbance spectrum and the PL spectrum of the chosen sample. Note down the absorbance and the integrated PL intensities at the excitation wavelength (λ_{ex}=320 nm), respectively. Similar spectral measurement procedure was taken for five selected samples of

different concentrations.

4. Plot a graph of integral PL intensity *vs*. absorbance. As shown in the Fig. S1, the slopes of standard and the test sample were obtained to calculate the QY by using the following equation:

$$\Phi_x = \Phi_{ST}\left(\frac{Grad_x}{Grad_{ST}}\right)\left(\frac{\eta_x^2}{\eta_{ST}^2}\right)$$

The subscripts *ST* and *X* denote standard and test sample respectively. Φ is the PL quantum yield. $Grad_x$ and $Grad_{ST}$ denotes the gradient from the plot of integrated PL intensity *vs*. absorbance for test sample and standard, respectively, and η is the refractive index of the solvent.

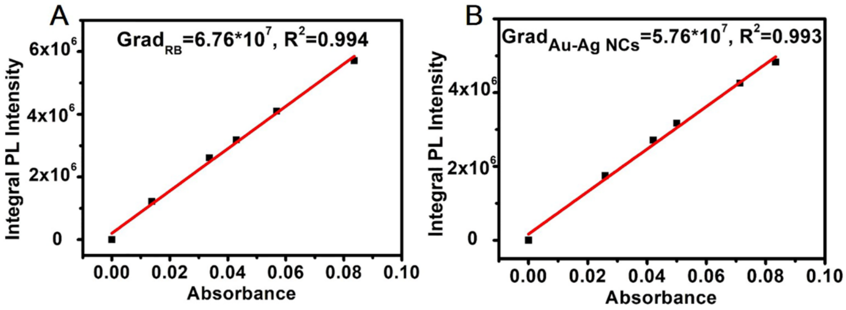

Fig. S1 Integral PL intensity and Absorbance of the Rhodamine B (RB) and Au-Ag NCs.

pH sensing

To evaluate selectivity, representative various 40 μM interfering substance including small molecules (Pro, Tyr, Gly, Trp, Asp, Cys, GSH), metal ions (Ni^{2+}, Co^{2+}, Mn^{2+}, Cd^{2+}, Mg^{2+}, Zn^{2+}, Ca^{2+}, Na^+, K^+) and anions ($H_2PO_4^-$, $Cr_2O_7^{2-}$, Cl^-, CO_3^{2-}, SO_4^{2-}, I^-, NO_3^-, Br^-) were added to the prepared Au-Ag NCs and the PL emission spectra were recorded. To evaluate the sensitivity of pH, different amounts of HCl/NaOH were added to the Au-Ag NCs to achieve different pH values (1.4, 1.9, 2.2, 2.4, 2.6, 2.8, 3.2, 3.8, 4.2, 5.1, 6.0, 6.8). We recorded the PL emission spectra of the pH adjusted product, respectively. To recover the PL emission of the Au-Ag NCs (pH=6.8), we added HCl to the non-emissive product to return the pH value of the solution back to 1.9 and made the solution stirred overnight.

Dissociation equilibrium of GSH in solution

$GSH^+ = GSH^\pm + H^+$, $pK_1(COOH) = 2.12$

$GSH^\pm = GSH^- + H^+$, $pK_2(COOH) = 3.59$

$GSH^- = GSH^{2-} + H^+$, $pK(NH_3^+) = 8.75$

$GSH^{2-} = GSH^{3-} + H^+$, $pK(SH) = 9.65$

2. Additional Figures and Images

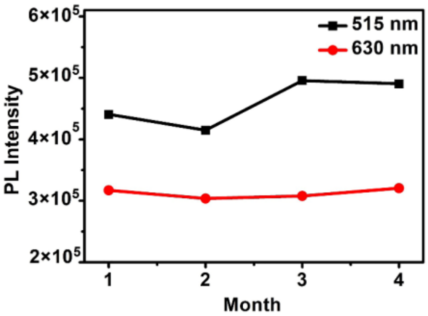

Fig. S2 Two PL emission intensities change of the Au-Ag NCs within four months.

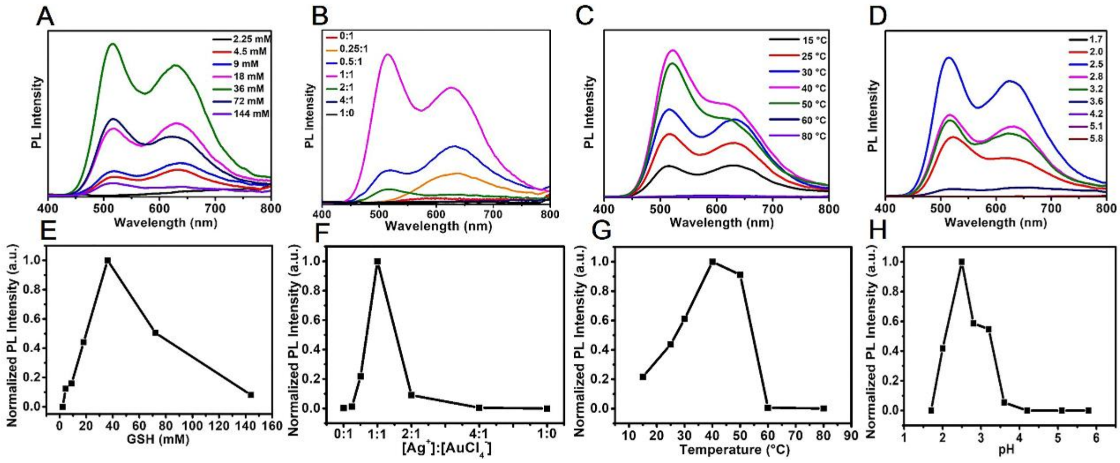

Fig. S3 PL emission spectra (λ_{ex} = 320 nm) of Au-Ag NCs prepared under different conditions. (A) Different concentration of GSH, (B) different [Ag$^+$]:[AuCl$_4^-$], (C) different reaction temperature and (D) different solution pH values. Optimal conditions for preparation of Au-Ag NCs by one-pot synthesis. The effects of (E) the concentration of GSH, (F) the [Ag$^+$]:[AuCl$_4^-$], (G) reaction temperature and (H) pH value on the PL emission intensities at 515 nm of Au-Ag NCs.

We choose the PL emission intensity at 515 nm as the reference standards to determine optimal conditions because the intensities of the two peaks show similar trend and same optimal value in different reaction conditions (Fig. S3, ESI†). Insufficient GSH leads to inadequate reduction of metal ions and poor stability of Au-Ag NCs while excessive GSH makes the decomposition of the NCs.[1] As expected, the PL emission intensity of Au-Ag NCs is enhanced with increasing concentrations of GSH in the range of 2.25 mM to 36 mM, and then decreases at higher concentrations (Fig. S3E, ESI†). Therefore, the optimal concentration of GSH is 36 mM. The [Ag$^+$]:[AuCl$_4^-$] is also explored for the subsequent experiments. As shown in Fig. S3F (ESI†), when [Ag$^+$]:[AuCl$_4^-$] is increased to 1:1, the strongest PL emission intensity is obtained. The finding indicates that the two emission wavelengths and the strong PL emission intensity of Au-Ag NCs are derived from the complex of Ag and Au. The PL emission intensity of Au-Ag NCs is increased with elevated temperature in the range of 15 °C to 40 °C, and gradually decreases when the reaction temperature is more than 40 °C (Fig. S3G, ESI†). We speculate that the high temperature is required to overcome the energy barriers of reduction of metal ions, increase the reaction rate and facilitate the structure optimization of MNCs.[2] When the temperature is less than 40 °C, the growth and aggregation of the NCs are dominated. By contrast, the NCs are gradually digested when the reaction temperature is higher than 40 °C. Considering the intensity and rationing of the two emission peaks comprehensively, we select 30 °C as optimized reaction temperature for Au-Ag NCs synthesis. The PL emission intensity of Au-Ag NCs is also dependent on the pH value of reaction solution, and reaches the maximum at pH 2.5 (Fig. S3H, ESI†). The surface charges of Au-Ag NCs can be varied through deprotonation/protonation of GSH, which might cause the change of the PL emission intensity in different pH values solutions.

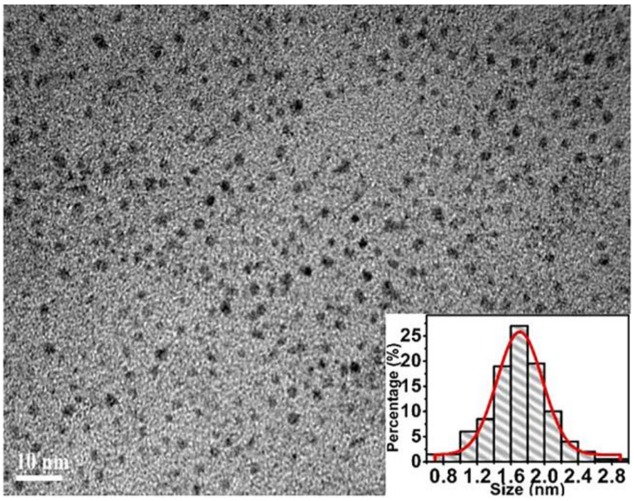

Fig. S4 HRTEM micrograph of Au-Ag NCs. The scale bar is 10 nm. The inset shows the size distribution.

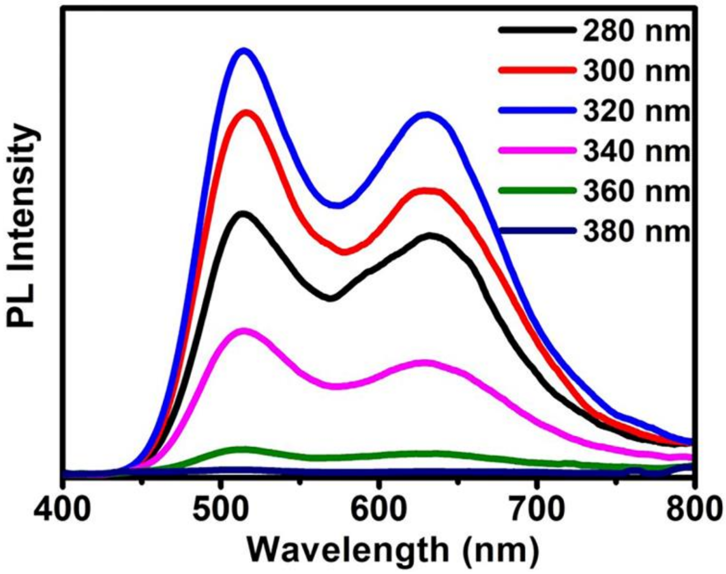

Fig. S5 PL Emission spectra of the Au-Ag NCs at different excitation wavelength.

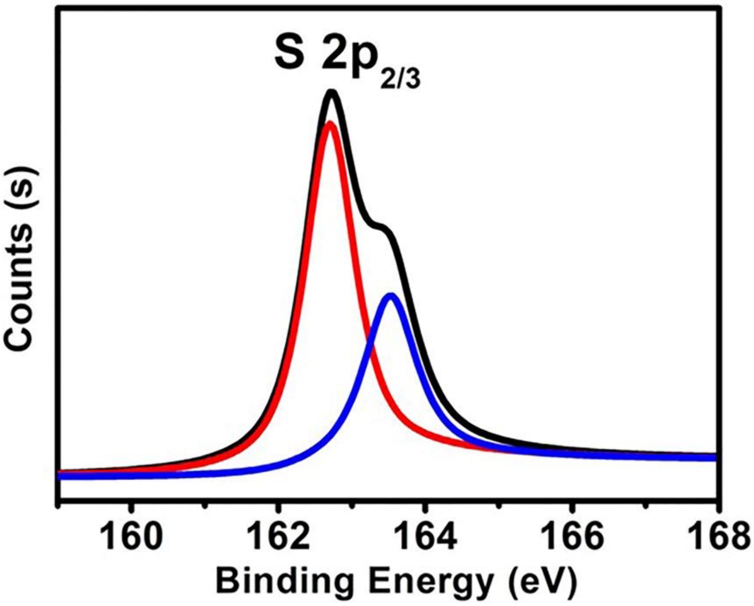

Fig. S6 XPS spectrum of S 2p for Au-Ag NCs.

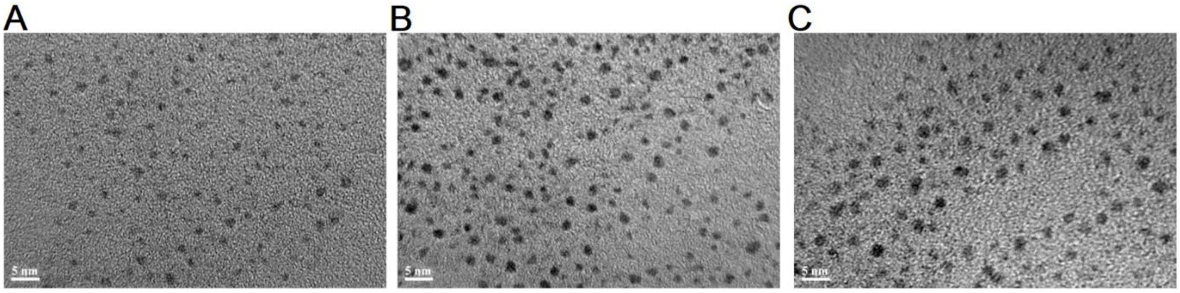

Fig. S7 HRTEM micrographs of Au-Ag NCs synthesized at different [Ag$^+$]:[AuCl$_4^-$]: A. 0:1, B. 0.25:1, C. 1:1.

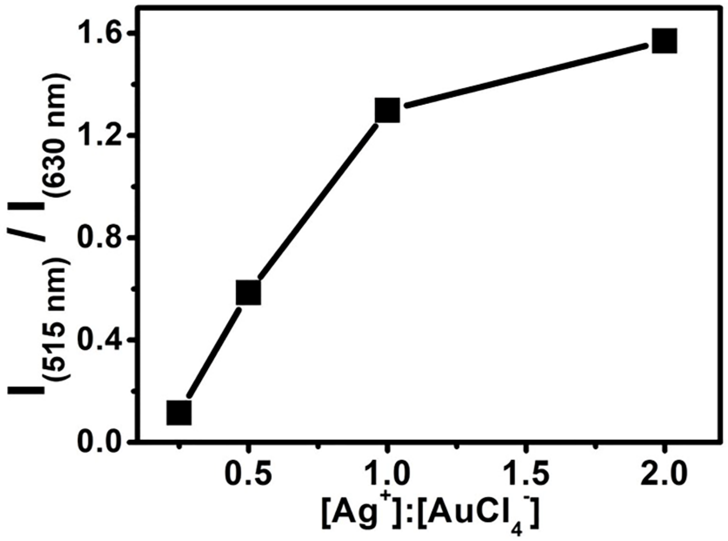

Fig. S8 The ratio of PL emission intensity at 515 nm with PL emission intensity at 630 nm ($I_{(515\ nm)}/I_{(630\ nm)}$) of Au-Ag NCs as a function of [Ag$^+$]:[AuCl$_4^-$].

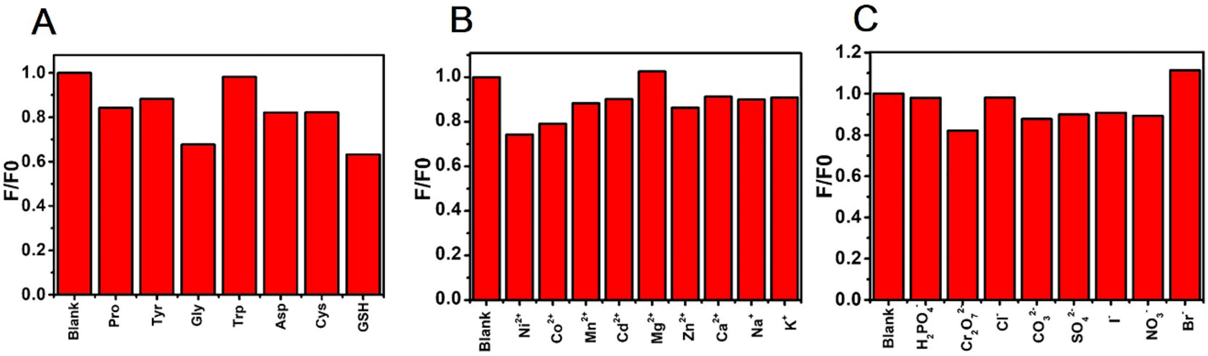

Fig. S9 PL emission intensity at 515 nm of Au-Ag NCs responses to interfering substances (A) amino acids, (B) metal ions and (C) anions. F0 means the PL emission intensity at 515 nm of Au-Ag NCs without interfering substance while F means the PL emission intensity at 515 nm of Au-Ag NCs with interfering substance.

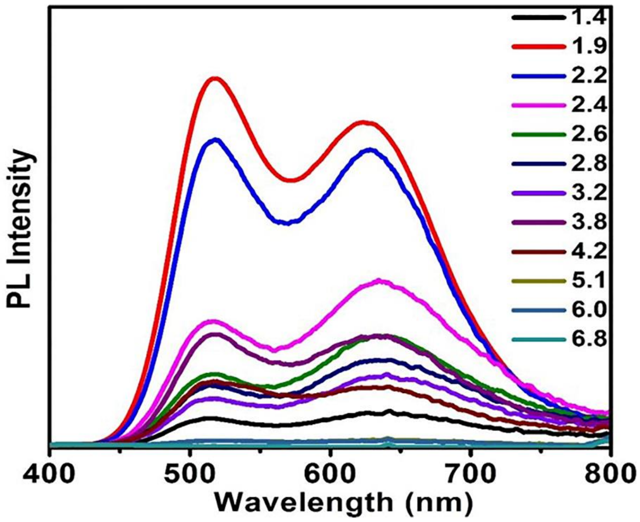

Fig. S10 The PL evolution (λ_{ex} = 320 nm) of Au-Ag NCs with pH changed.

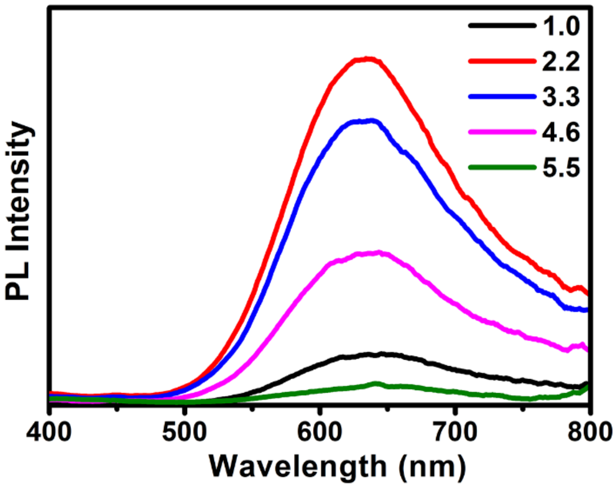

Fig. S11 The PL evolution (λ_{ex}=320 nm) of single emission Au-Ag NCs ($[Ag^+]$:$[AuCl_4^-]$ was 0.25:1) with pH changed.

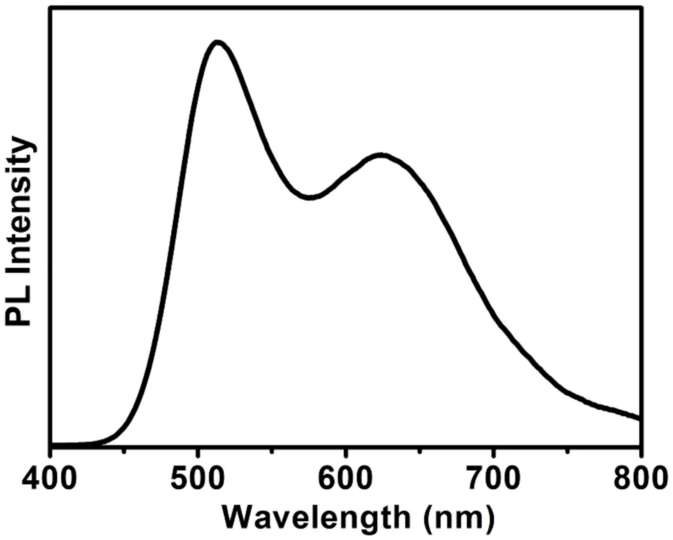

Fig. S12 PL emission spectrum of Au-Ag NCs when the pH of the solution was changed from 6.8 to 1.9.

Notes and references

1 Y. Lu and W. Chen, *Chem. Soc. Rev.*, 2012, **41**, 3594–3623.

2 Luo, Z., et al., *J. Am. Chem. Soc.*, 2014, **136**, 10577-10580.