

Supporting Information

Controlling synthesis and assembly of fluorescent AuAg alloy nanoclusters

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Experimental Section

Materials:

N-(2-mercaptopropionyl)glycine (MPC) was obtained from Aladdin Chemistry Co. Ltd. AgNO_3 , $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ and other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Water used throughout all experiments was purified with the Millipore system (18.2 M Ω). All glassware was washed with *aqua regia*, rinsed with ultrapure water and dried for use.

Apparatus and characterization:

UV-vis absorption spectra were recorded using a Cary 50 Scan UV-visible spectrophotometer (Varian, USA). Fluorescence emission spectra were collected with a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc. France) with excitation at 467 nm. The luminescence decay curves were measured by a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz) using a tunable laser (pulse width = 4 ns, gate = 50 ns) as the excitation (Continuum Sunlite OPO). Transmission electron microscopy (TEM) was carried out on a JOEL JEM-1011 at an acceleration voltage of 100 kV. High-resolution transmission electron microscope (HRTEM) was recorded on JEM-2100F operated at 200 kV. Scanning electron microscopy (SEM) was conducted using an XL30 ESEM FEG scanning electron microscope. X-ray power diffraction (XRD) pattern was recorded on a D8 Focus diffractometer (Bruker) with a Cu K α radiation source ($\lambda = 0.15406$ nm). X-ray photoelectron spectroscopy (XPS) was performed on ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with Al K α X-ray radiation (1486.6 eV) for excitation. IR spectra were collected with a VERTEX Fourier transform infrared spectrometer (Bruker). Matrix-assisted laser-desorption ionization time of flight mass spectrometry (MALDI-TOF MS) were obtained from Bruker autoflex III smartbeam MALDI-TOF/TOF-MS (Germany). The spectra were collected in positive-ion mode using the matrix sinapinic acid.

Synthesis of AgNCs:

In a typical synthesis, MPC (0.0612 g) was dissolved in water (7.5 mL) to form a clear solution. Then AgNO_3 solution (2.5 mL, 0.1 M) was added under stirring to form a cloudy yellow-white solution. After 2 min, NaOH (0.55 mL, 1 M) was introduced to make the mixture clear. Subsequently, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ aqueous solution (1.25 mL, 50 %) was added dropwise under vigorous stirring. The growth of AgNCs was allowed to process under stirring at 30 °C over about 3 days, accompanying with the solution colour from colorless to yellow and finally dark red-brown. After 10-fold dilution, the absorption peak at 466 nm (A_{466}) was approximately 0.5~0.6. The AgNCs were precipitated from the supernate by addition of

ethanol (20 mL), and washed with ethanol repeatedly through centrifugal precipitation. The product was dried by N₂ flow and collected as red-brown powder. The powder was dissolved in water (10 mL) for subsequent use.

Synthesis of Au/Ag alloy NCs by Galvanic Replacement Reaction:

The as-prepared AgNCs solution (2 mL) was added into water (17.7 mL), followed by addition of NaOH (24 μL, 1M). Then calculated volume of HAuCl₄ solution (40 mM, $V = 572.6 * A_{466}$ μL) was added under stirring. The galvanic replacement reaction was performed at room temperature for 12 h. The resultant yellow-brown solution was centrifuged at 10000 rpm for 30 min (Eppendorf centrifuges 5804R). The black precipitate was discarded. The yellow supernate was collected and then concentrated by rotary evaporator at 37 °C. The red concentrated solution was centrifuged at 14000 rpm for 2 h and the supernate was collected. The powder was obtained by evaporating the solvent by rotary evaporator at 37 °C.

Preparation of one-dimensional Au/Ag alloy NCs assemblies:

Self-assembly of Au/Ag alloy NCs nanowires was prepared with a modified sonication method (*Adv. Mater.*, 2012, **24**, 5227-5235). Typically, AgNO₃ solution (74 μL, 10 mM), MPC solution (74 μL, 10 mM), NaOH solution (20 μL, 2 mM) and the as-prepared Au/Ag alloy NCs solution (40 μL, 10 mg/mL) were orderly added to water (612 μL). The mixture was stirred for 1 h at room temperature, and then was sonicated for 2 h in an ultrasonic bath to produce the Au/Ag alloy NCs assemblies in solution.

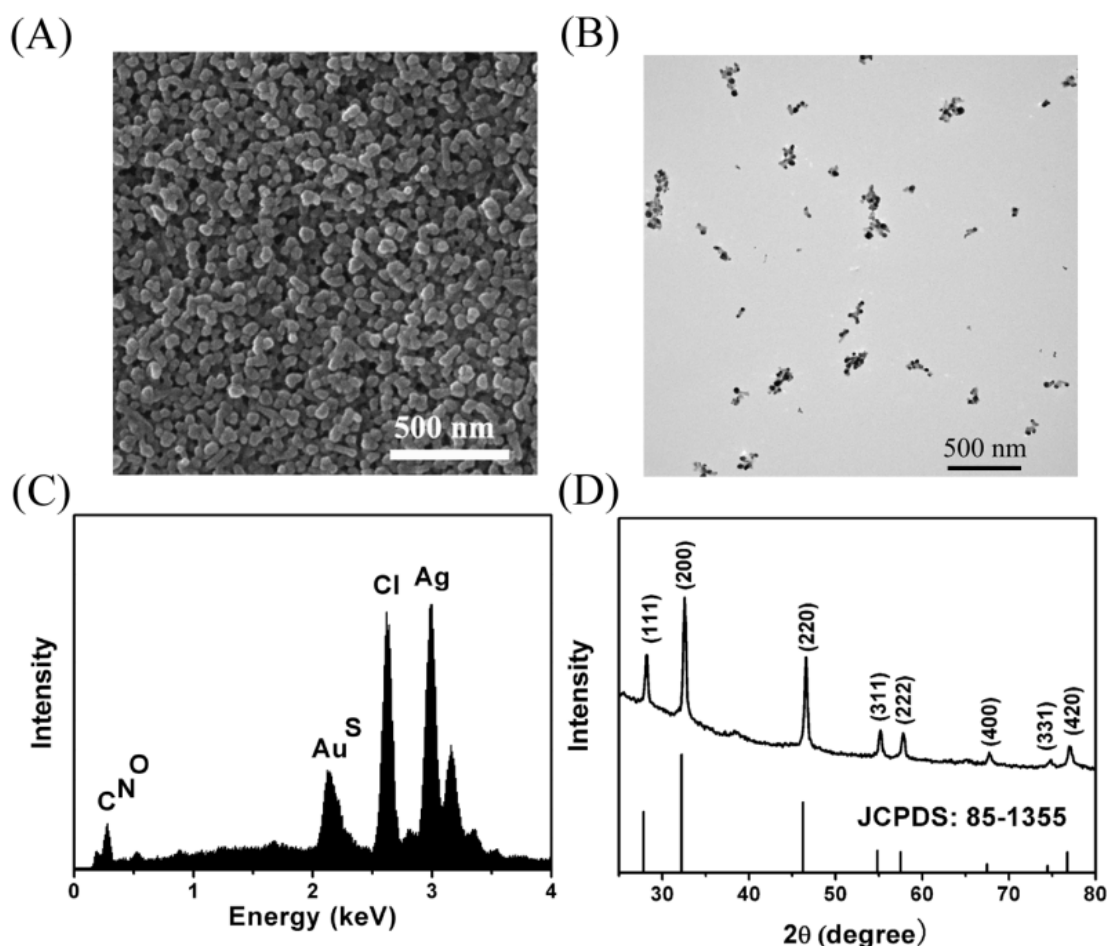


Figure S1. (A) SEM image, (B) TEM image, (C) EDX spectrum and (D) XRD pattern of the byproduct black precipitate during the synthesis of Au/Ag alloy NCs.

SEM and TEM images showed that the byproduct was nanoparticles with diameter of ca. 60 nm, which was encapsulated by thiolates (Figure S1A and S1B). Energy dispersive X-ray (EDX) analysis confirmed the presence of elements Ag, Cl, S, C, N and O in the products (Figure S1C). The element Au was from the substrate. Powder X-ray diffraction (XRD) (Figure S1D) was used to further investigate the crystal structure. The positions and relative intensities of all diffraction peaks matched well with AgCl (JCPDS Card No. 85-1355), suggesting the obtained byproduct were AgCl nanocrystals.

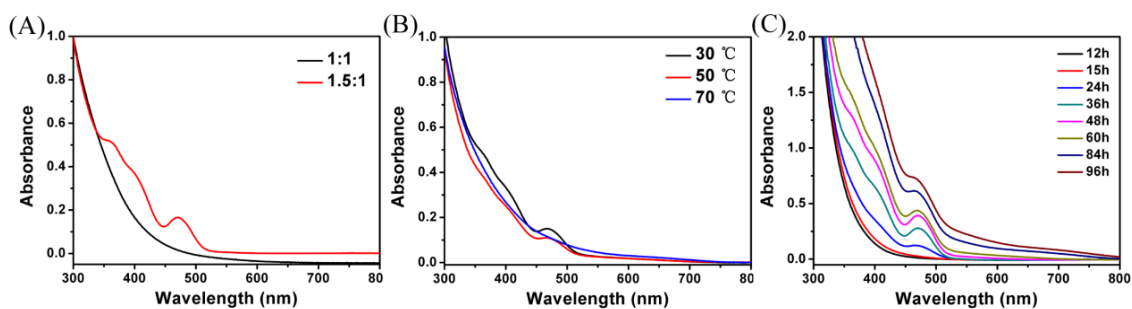


Figure S2. Evolution of the absorption spectra of AgNCs under different synthetic conditions: (A) molar ratio of MPC to AgNO₃; (B) temperature; (C) time.

Under the optimal condition (molar ratio of MPC to AgNO₃ at 1.5 and the temperature of 30 °C), the UV-vis absorption spectra of AgNCs exhibited distinct peaks. The evolution of the absorption spectra of AgNCs is shown in Figure S2C. The absorption peaks at 365, 408, 487 and 660 nm gradually appeared and enhanced as the reaction evolved.

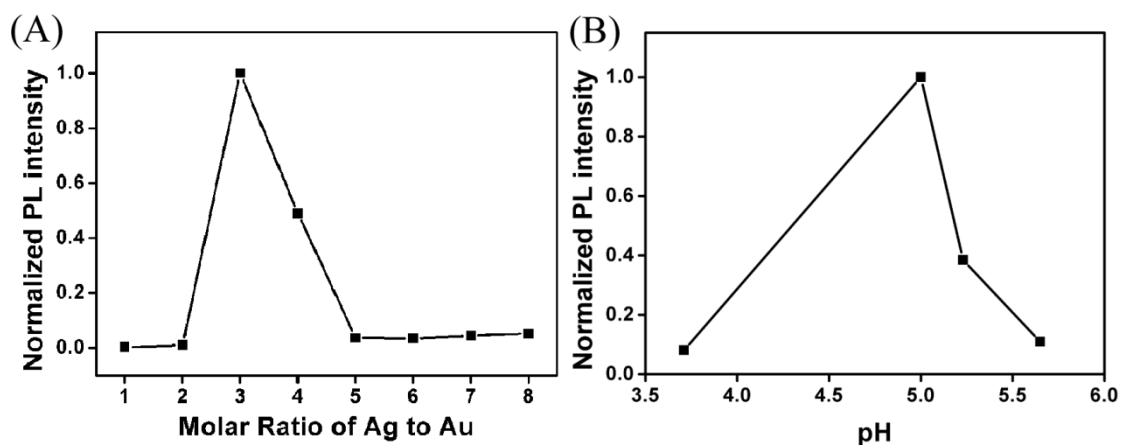


Figure S3. Normalized PL intensity of Au/Ag alloy NCs under different synthesis conditions: (A) molar ratio of AgNO₃ to HAuCl₄; (B) pH.

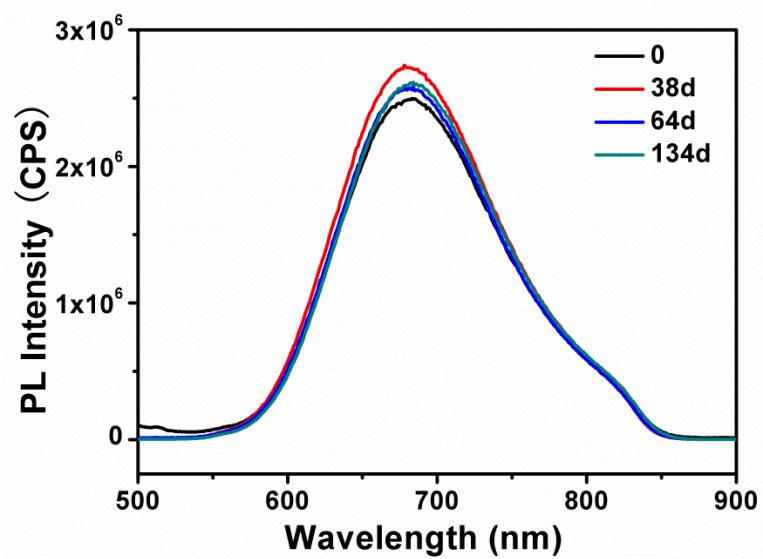


Figure S4. PL spectra of Au/Ag alloy NCs after storing at the temperature of 4 °C for different dates.

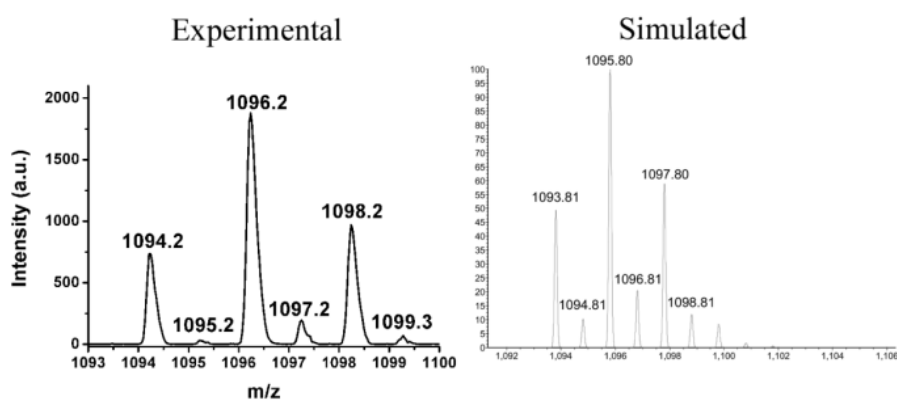


Figure S5. Experimental and simulated isotopic patterns of $[\text{Au}_2\text{Ag}_2\text{L}_3]^+$.

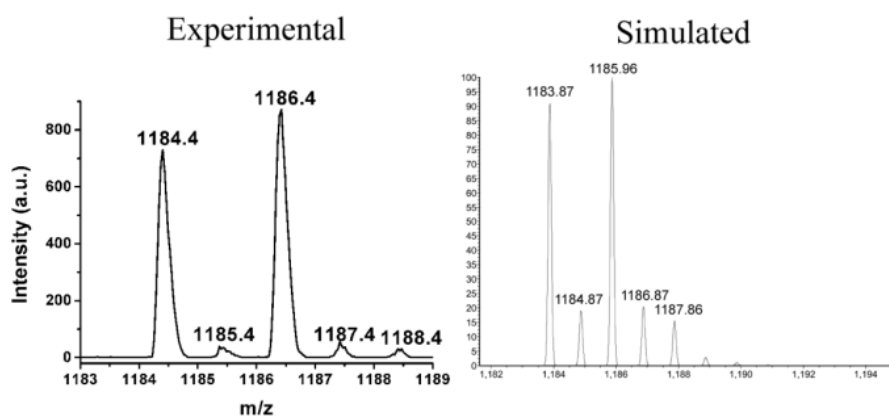


Figure S6. Experimental and simulated isotopic patterns of $[\text{Au}_3\text{AgL}_3]^+$.

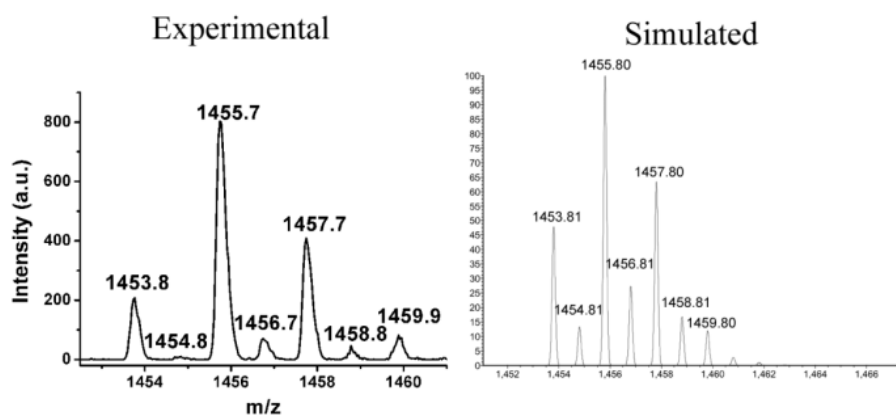


Figure S7. Experimental and simulated isotopic patterns of $[\text{Au}_3\text{Ag}_2\text{L}_4+\text{H}]^+$.

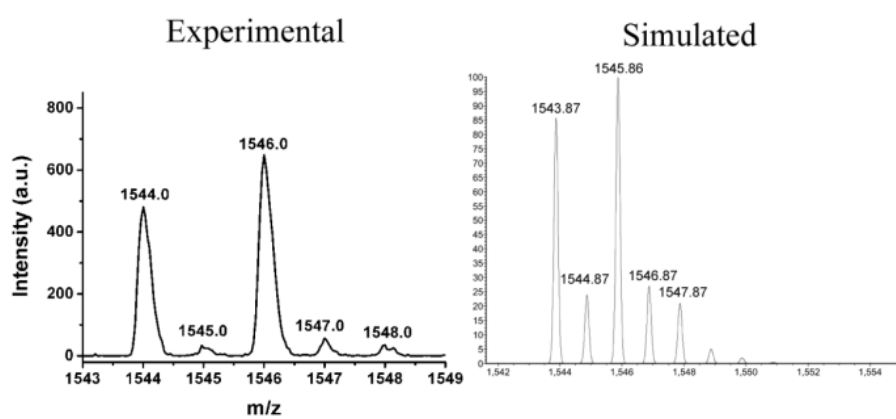


Figure S8. Experimental and simulated isotopic patterns of $[\text{Au}_4\text{AgL}_4+\text{H}]^+$.

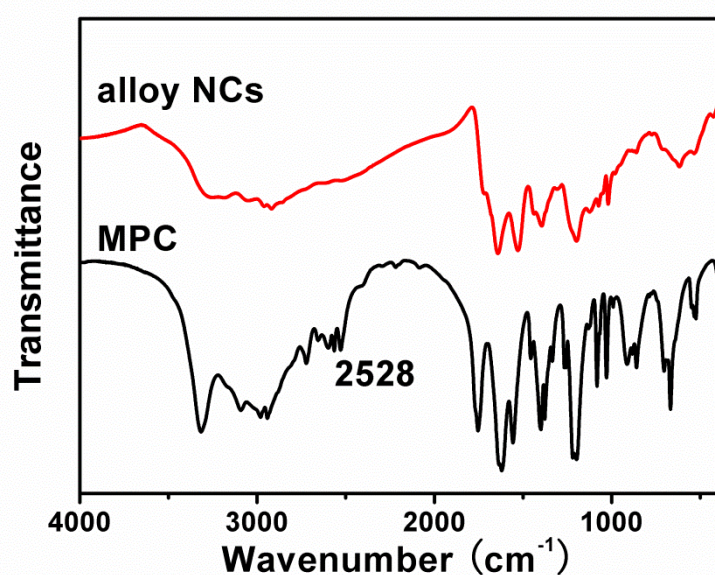


Figure S9. FTIR spectra of alloy NCs and the pure ligand MPC.

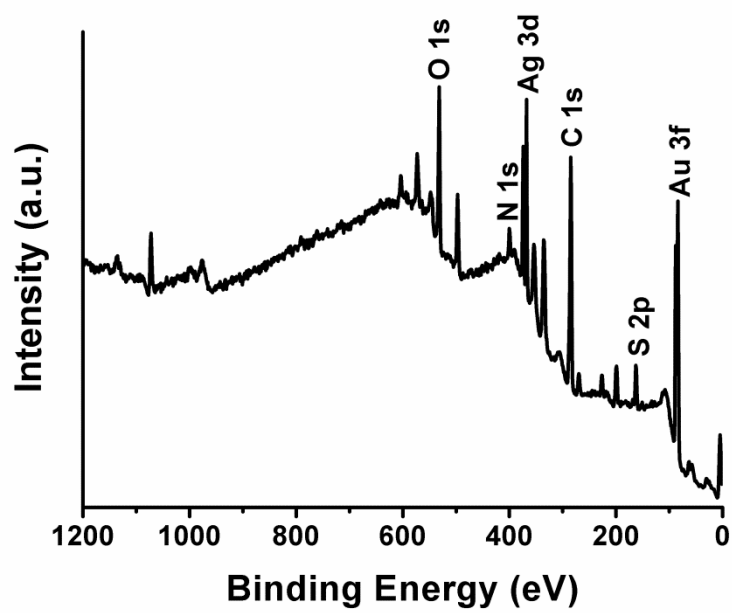


Figure S10. XPS survey spectrum of the Au/Ag alloy NCs.

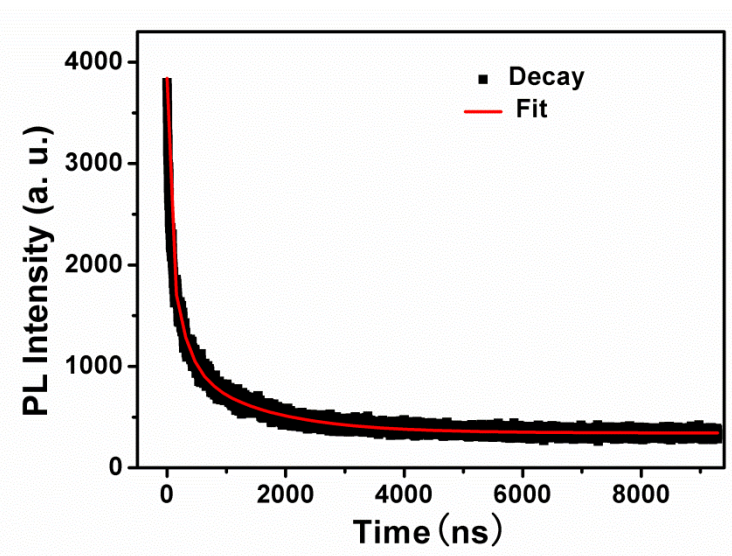


Figure S11. PL decay profiles of alloy NCs (λ_{em} = 680 nm) at the excitation of 467 nm. The fitted curve was overlaid on the experimental data.

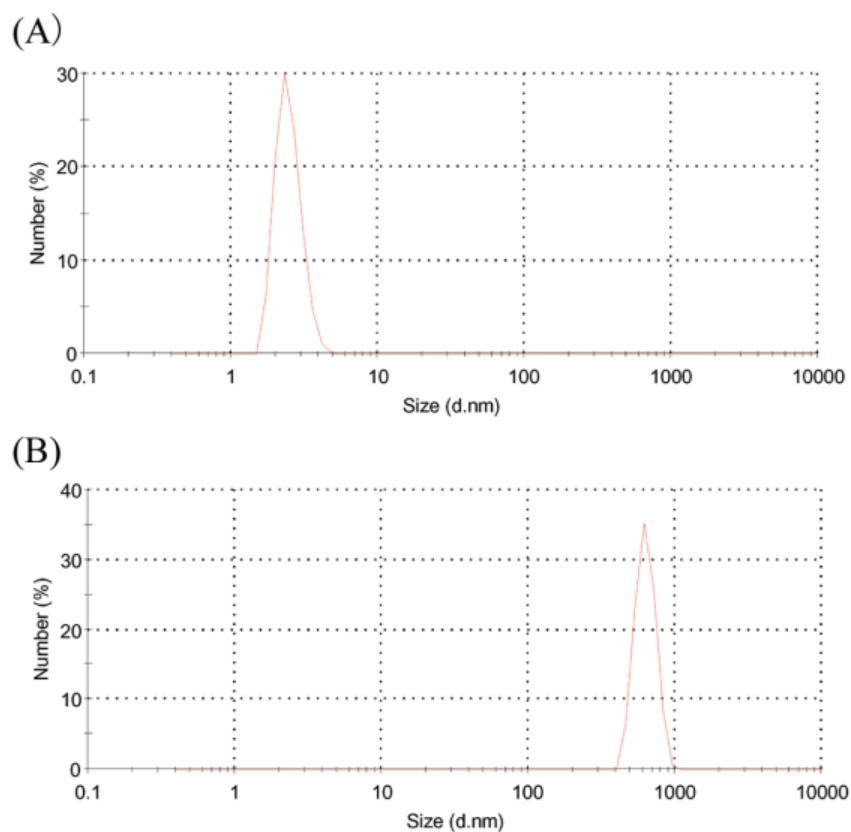


Figure S12. DLS measurements of Au/Ag NCs (A) and Au/Ag NCs assemblies.

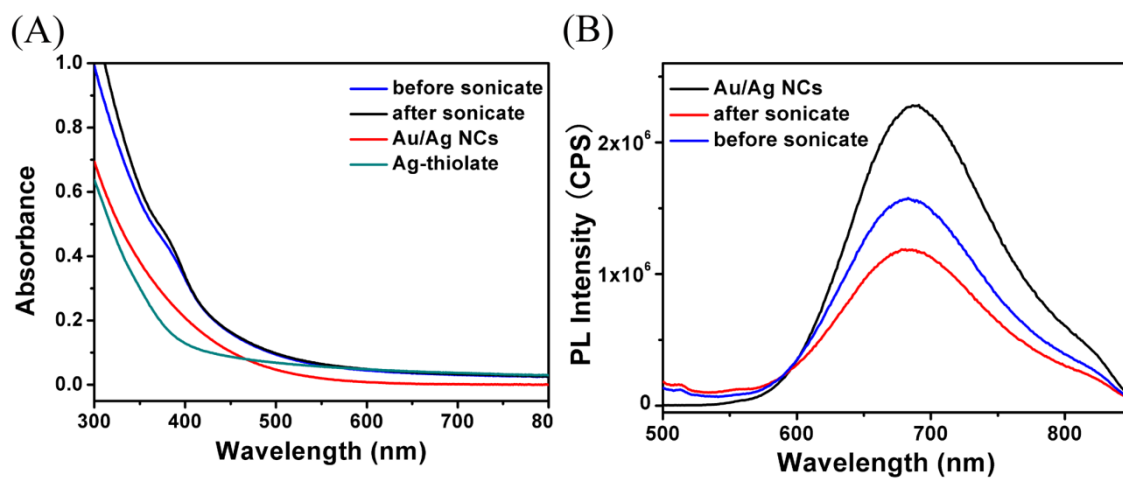


Figure S13. (A) Absorption spectra of the as-synthesized Au/Ag NCs and the mixture with Ag-thiolate before and after sonicate, as well as Ag-thiolate complex; (B) PL spectra of the as-synthesized Au/Ag NCs and the mixtures with Ag-thiolate before and after sonicate.

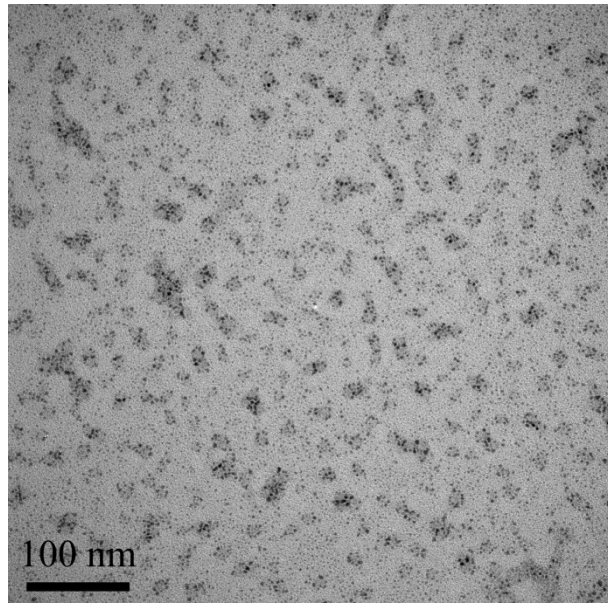


Figure S14. TEM image of 0.5 mg/mL Au/Ag alloy NCs and 0.25 mg/mL Ag-thiolate under sonication.