Supporting inforamtion for

Metal coordination functionalized Au-Ag bimetal SERS nanoprobe for sensitive detection of glutathione

Experimental section

Materials

Hydrogen Tetrachlorocuprate ($HAuCl_4 \cdot 4H_2O$), silver nitrate ($AgNO_3$), sodium citrate, ferrous chloride ($FeCl_2$), copper chloride ($CuCl_2$), sodium chloride (NaCl), potassium chloride (KCl) and calcium chloride ($CaCl_2$) were purchased from Shanghai Chemical Reagent Company. Glutathione, neocuproine, ascorbic acid (AA), glucose and all the amino acids (99%) were obtained from Sigma-Aldrich (USA). Millipore water purification was used to produce ultrapure water (18.2 MΩ cm).

The synthesis of Au-Ag NBs

Typically, 1 mL of $AgNO_3$ (1 mM) was added into 99 mL deionized water within rounded bottom flask of 250 mL, after the solution was heated to boiling during vigorous, adding 4 mL sodium citrate (1% wt) to above solution. The boiling solution was keep heating for 30 min continuously to fabricate the Ag colloids. The 3 mL Ag colloids was dispersed in 10 mL of water containing PVP (1 mg/mL) in a 50 mL flask under magnetic stirring for 10 min. Then 1 mL $HAuCl_4$ (1% wt) aqueous solution was added into the flask dropwise under magnetic stirring. The solution was stirring for another 10 min until the color of the system became stable.

The preparation of Nc-Cu^{II} solution and UV-vis adsorption spectra

1mL copper (II) chloride solution (1 mM) was added into the 2 mL neocuproine (Nc) solution (1mM, pH=6-7). The different concentration GSH solution (1 mL) ranging from 0.05-10 mM was mixed with above Nc-Cu^{II} solution (3 mL) for UV-vis adsorption measurement.

Fabrication of Au-Ag NBs/Nc-Cu^{II}

The resulting Au-Ag colloids were centrifuged at 7000 rpm for 10 min, and then resuspended in deionized water for the subsequent fabrication of the nanoprobe. Under continuous mild stirring, the prepared Nc-Cu^{II} complex solution (1.0 μM, 1mL) was dropwise added into the colloidal Au-Ag (10 mL) to produce Au-Ag NPs/Nc-Cu^{II} nanoprobe, which facilitated the uniform distributions of Nc-Cu^{II} on the Au-Ag colloids surfaces. After 10 min, the physical adsorption or excess complex has been removed from the Au-Ag colloids through two times centrifugation (7000 rpm, 5 min).

Instrument Characterization

Transmission electron microscopy (TEM) images were recorded by a JEOL 2010 high resolution transmission electron microscope. UV-vis adsorption spectra were recorded using a Shimadzu UV-2550 spectrophotometer (Japan). SERS measurements were performed with Raman microscopy spectrometer (Lab RAM HR800, HORIBA Scientific Japan) equipped with 532, 633 and 785 nm laser. The Raman spectra of GSH were recorded with 532 nm laser with 1 mW and 50× objectives (1.5 μm^2 spot). The aperture is 100 μm slit and SERS spectra is the range of 400-2000 cm^{-1}.

SERS measurements

The centrifuged or concentrated Au-Ag/Nc-Cu^{II} colloids has been added on the Si wafer for drying and subsequent analytical detection. After the GSH with different concentration dropping on the dry nanoprobe, the corresponding SERS spectra have been collected with 532 nm laser and 2s time of integration.

Figures :

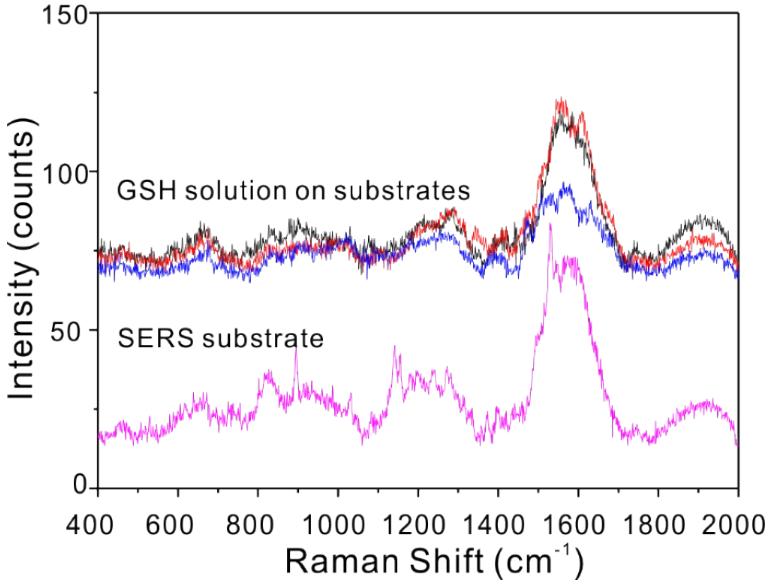

Figure S1: The SERS spectra of Au-Ag NBs background and GSH solution (2 mM) on substrates.

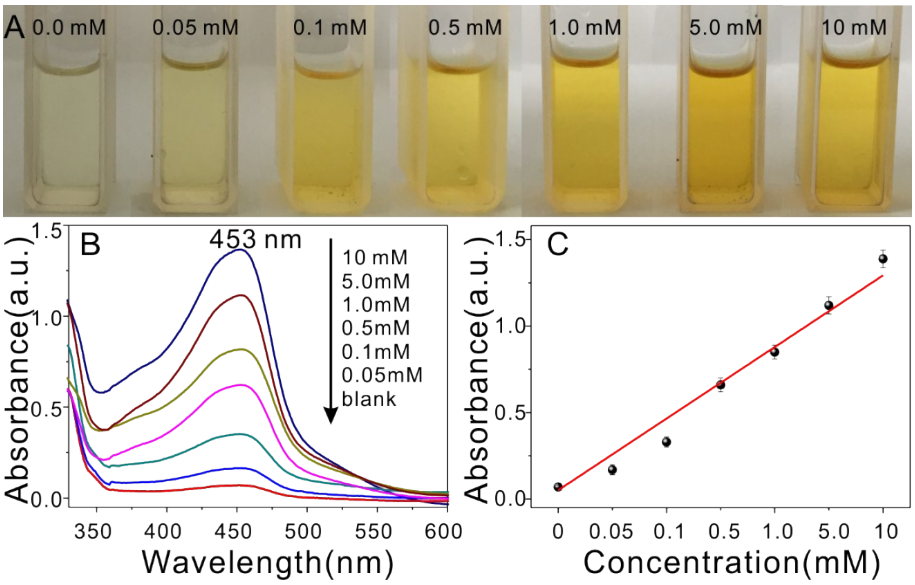

Figure S2: (A and B) The optical images and UV-vis spectra of Nc-Cu^{II} solution (1 mM) with alteration of GSH concentration. (C) Plots of absorption intensity versus GSH concentration based on maximum absorption at 453 nm.

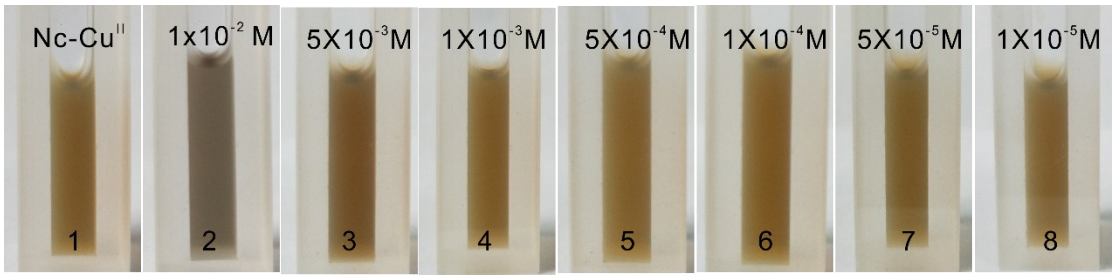

Figure S3: (No.1) The optical images of Au-Ag colloids modified with Nc-Cu^{II} (1 μM) and (No.2-8) the addition of GSH with different concentration into Au-Ag colloids modified with Nc-Cu^{II}.

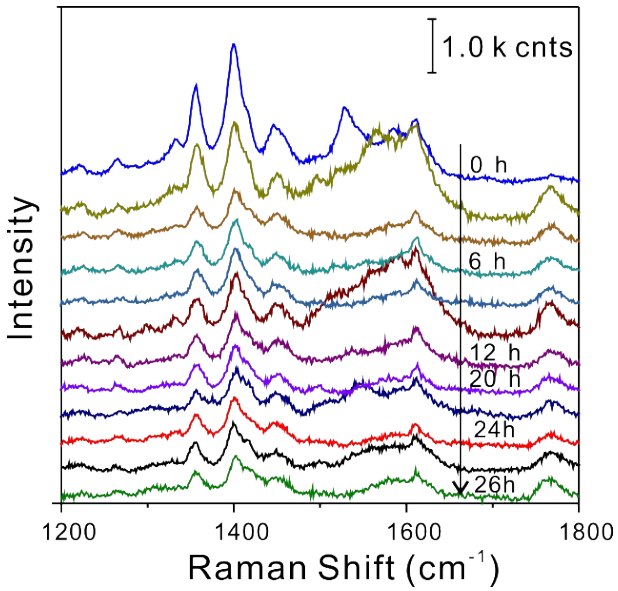

Figure S4: The alteration of SERS spectra of Nc-Cu^{II} complex coated on Au-Ag NBs with different storage time.

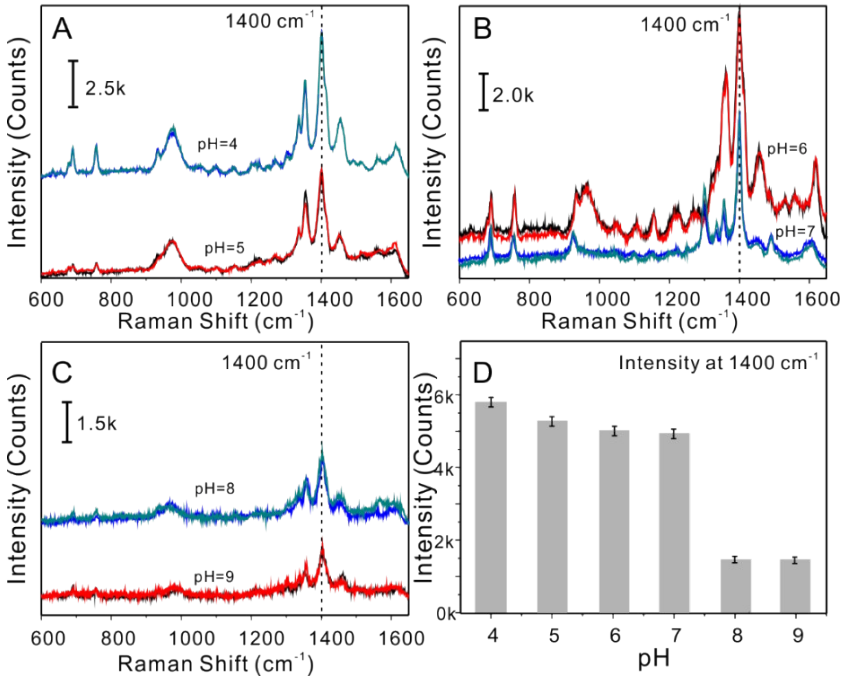

Figure S5: (A-C) The SERS spectra of nanoprobe Au-Ag NPs/Nc-Cu^{II} with alteration of pH. (D) Plots of SERS intensity at 1400 cm^{-1} versus different pH condition.

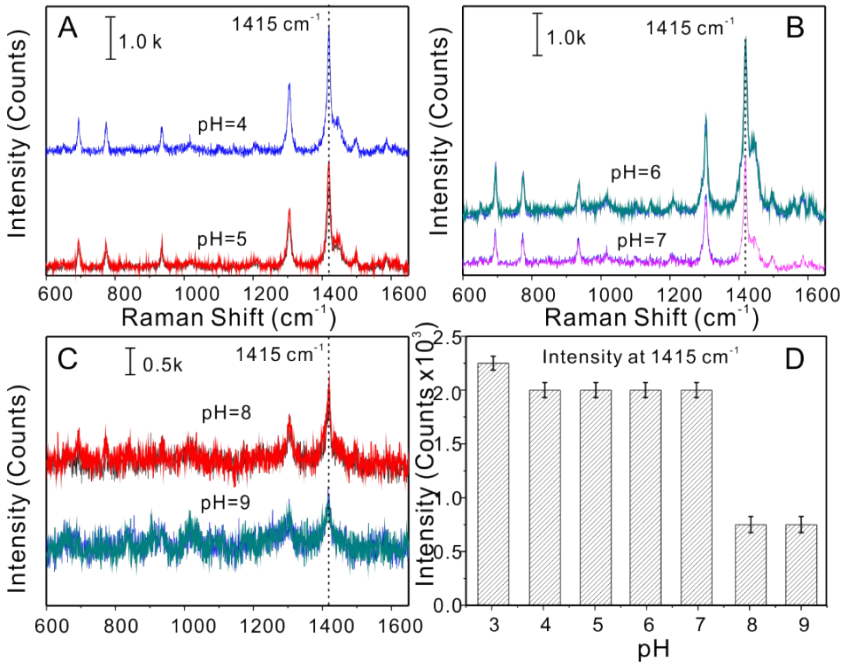

Figure S6: (A-C) The SERS spectra of nanoprobe Au-Ag NPs/Nc-Cu^{II} in the presence of GSH under different pH conditions. (D) The SERS intensity histogram of 1415 cm^{-1} under different pH conditions.

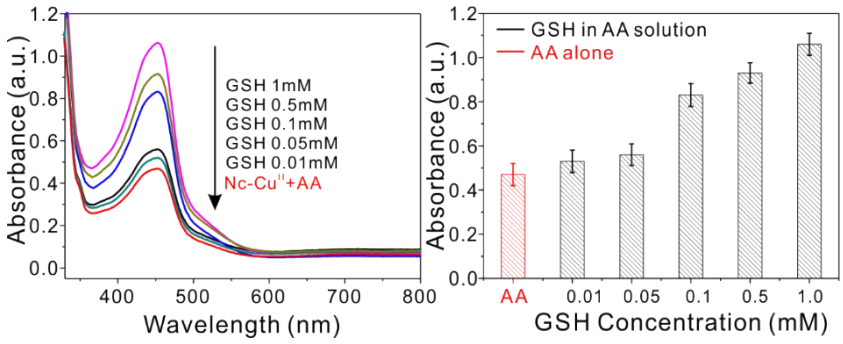

Figure S7: (A) The UV-vis spectra of Nc-Cu^{II} with different concentration of GSH in the AA (1 mM) solution. (B) The alteration of intensity at 453 nm based on the spectra in A.

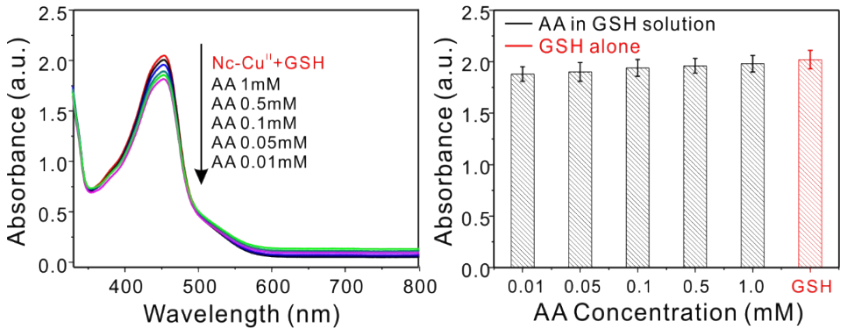

Figure S8: (A) The UV-vis spectra of Nc-Cu^{II} with different concentration of AA in the GSH (1 mM) solution. (B) The alteration of intensity at 453 nm based on the spectra in A.

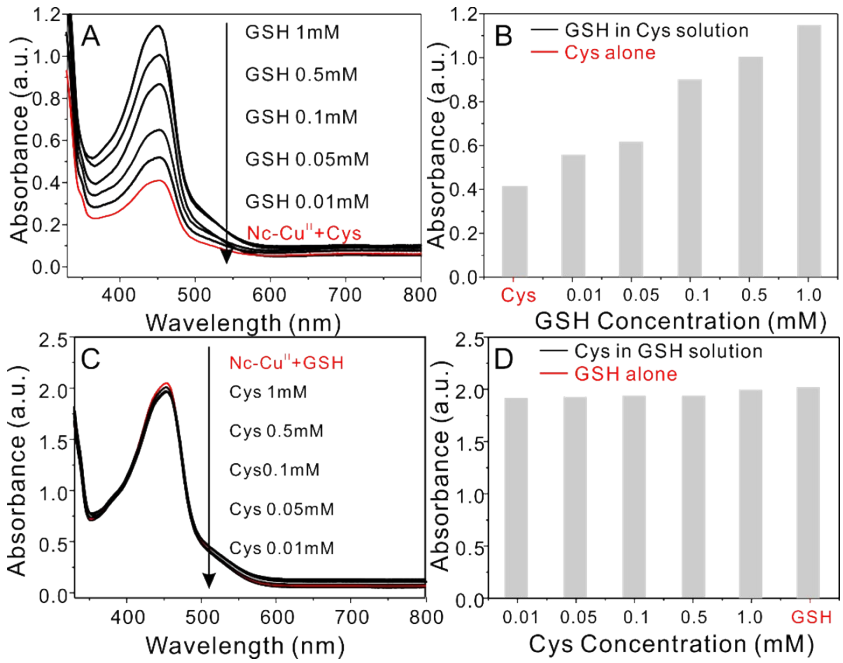

Figure S9: (A) The UV-vis spectra of Nc-Cu^{II} with different concentration of GSH in the Cys (1 mM) solution. (B) The alteration of intensity at 453 nm based on the spectra in A. (C) The UV-vis spectra of Nc-Cu^{II} with different concentration of Cys in the GSH (1 mM) solution. (D) The alteration of intensity at 453 nm based on the spectra in C.