

Supporting Information

Label-Free Detection of Sulfide Ions Based on Fluorescence Quenching of Unmodified Core-Shell Au@Ag Nanoclusters

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Materials and Apparatus

Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, >99.9%) and sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, >98%) were obtained from Shanghai Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Silver nitrate (AgNO_3 , >99.8%) was purchased from Nanjing Chemical Reagent Co. Ltd. (Nanjing, China), and bovine serum albumin (BSA) was purchased from Shanghai Sangon Biological Co. Ltd. (Shanghai, China). Phosphate buffer solution (PBS, pH 6.0-8.0, 50 mM) was prepared by varying the ratio of Na_2HPO_4 to NaH_2PO_4 . All chemicals and solvents were of analytical grade and were used without further purification. Deionized water was used throughout.

UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer (Tokyo, Japan). The Fluorescence spectra (FL) were performed on a Fluoromax-4 fluorescence spectrofluorometer (Horiba, U.S.A.). Transmission electron microscopy (TEM) measurements were conducted on a JEM-2100 transmission electron microscope (JEOL Ltd.). Cyclic voltammetry (CV) measurements were carried out with a CHI 660B electrochemistry workstation (CH

Instruments, Shanghai) with a conventional three-electrode system. The modified Pt disk electrode (diameter: 3 mm) was used as working electrode, a saturated calomel electrode (SCE) as reference electrode, and a Pt wire as counter electrode. The working electrodes were prepared by spreading 6 μL of 2 mmol/L Au NCs or Au@Ag NCs on the surface of the Pt disk electrode, respectively, dried and then kept in dark for use.

Synthesis of core-shell Au@Ag NCs

All glassware was washed with aqua regia (HCl/HNO₃ volume ratio = 3:1), and rinsed with ethanol and ultrapure water. (*Caution: aqua regia is a very corrosive oxidizing agent, which should be handled with great care.*) First of all, the Au NCs were synthesized according to the literature.¹ Briefly, the HAuCl₄ solution (5 mL, 10 mM, 37 °C) was added to BSA solution (5 mL, 50 mg/mL, 37 °C) under vigorous stirring for 5 min, then NaOH solution (0.5 mL, 1 M) was introduced, and the reaction was allowed to proceed under vigorous stirring at 37 °C for 12 h. The as-synthesized Au NCs (11 mL) were dialyzed in a dialysis bag (retained molecular weight: 3500 Da) for 24 h until the Au NCs solution showed pH 7. In a typical experiment,² the as-synthesized Au NCs (10 mL, 5 mM, 37 °C) were mixed with aqueous AgNO₃ solution (2.5 mL, 10 mM, 37 °C) for 5 min, followed by the addition of NaOH solution (50 μL , 1 M). The reaction was conducted under vigorous stirring at 37 °C for 24 h and the core-shell Au@Ag NCs prepared by this method show strong red fluorescence.

Detection Procedure

Typically, the binding of S^{2-} ions to 200 μM Au@Ag NCs was conducted at room temperature for a few seconds in 5 mM pH 7.4 phosphate buffer solution. The final volume of the mixture was adjusted to 500 μL with ultrapure water. Then the samples were placed in quartz cuvettes with a 5-mm path length to record absorption and fluorescence spectra with water as a reference.

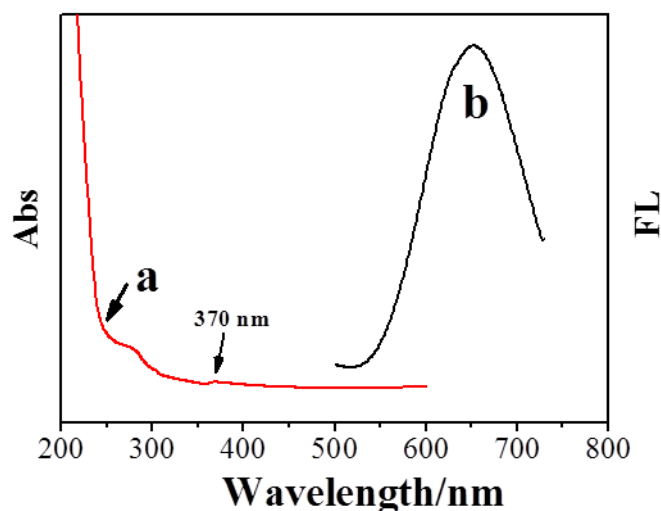


Fig. S1 UV/Vis absorption (a) and emission (b) spectra of the core-shell Au@Ag NCs. λ_{ex} : 370 nm; λ_{em} : 650 nm.

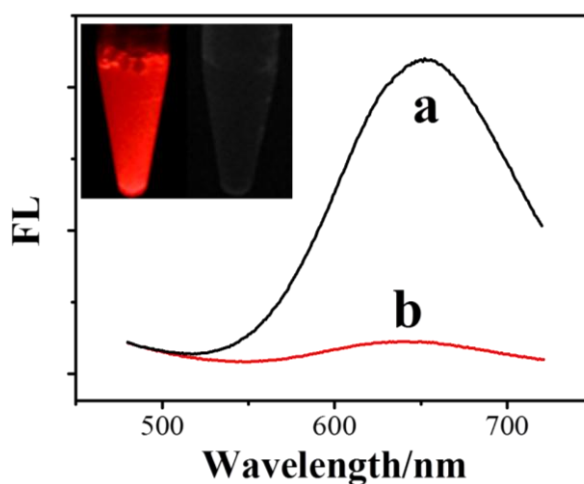


Fig. S2 Photoemission spectra ($\lambda_{\text{ex}} = 370$ nm) of Au@Ag NCs (200 μM) in the absence (a) and presence of S^{2-} ions (b, 700 μM). Inset: the corresponding fluorescence photographs under UV light (365 nm).

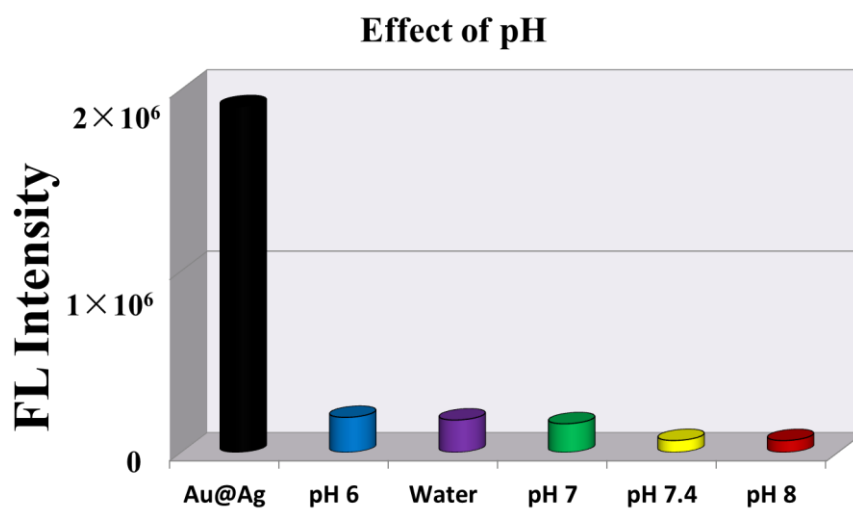


Fig. S3 pH-dependent changes in fluorescence Au@Ag NCs (40 μM) in the presence of S^{2-} (100 μM). Inset: Plot of the fluorescence intensity vs. different pH solution.

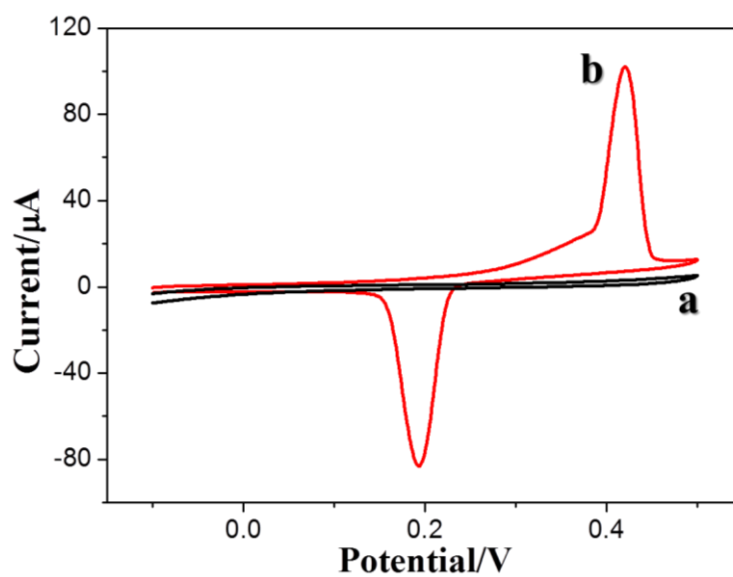


Fig. S4 Cyclic voltammograms of Au NCs (a) and Au@Ag NCs (b) films modified Pt electrodes in 0.1M PBS (pH 7.0) within the potential range of -0.1 ~ 0.5 V at a scan rate of 50 mV/s.

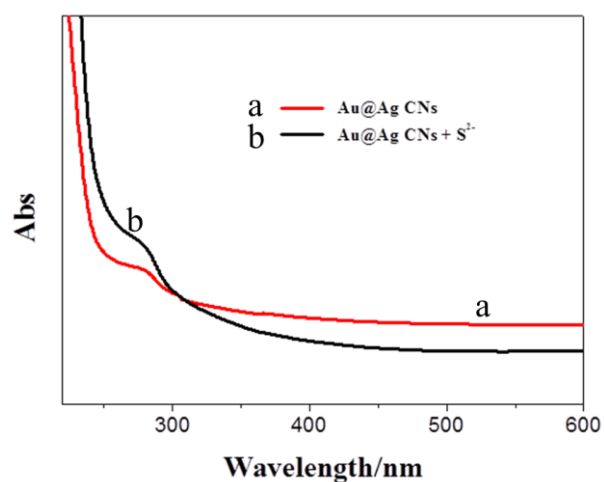


Fig. S5 UV/Vis absorption spectra of Au@Ag NCs without (a) and with (b) 600 μM S²⁻ ions.

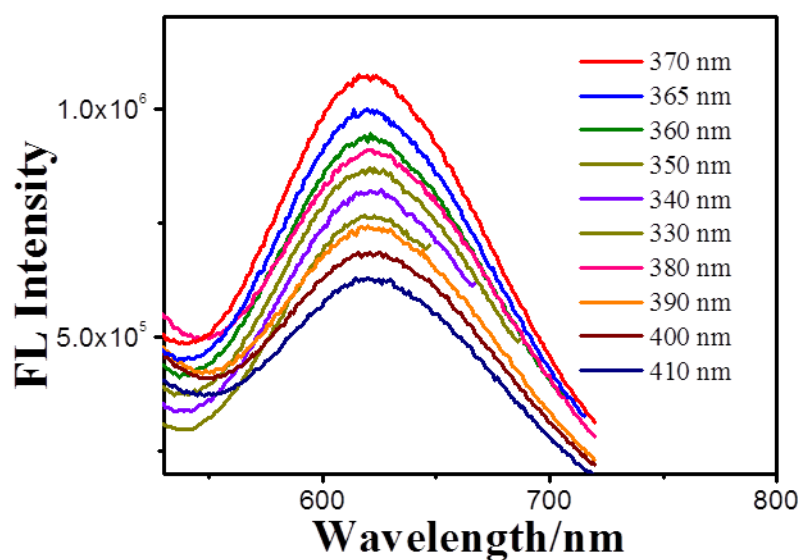


Fig. S6 Fluorescence spectra of the Au@Ag NCs with 600 μM S²⁻ ions at different excitation wavelengths from 330 to 410 nm.

References

- 1 J. Xie, Y. Zheng and J. Y. Ying, *J. Am. Chem. Soc.*, 2009, **131**, 888-889.
- 2 J. Xie, Y. Zheng and J. Y. Ying, *Chem. Commun.*, 2010, **46**, 961-963.