

Electronic Supporting Information

An Au@Ag Nanocube based Plasmonic Nano-sensor for Rapid Detection of Sulfide ions with high-sensitivity

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Experimental Section

(A) Materials and reagents

Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), silver nitrate (AgNO_3 , 99.8%), sodium borohydride (NaBH_4 , 96%), L-ascorbic acid (AA, 99%), cetyltrimethylammonium bromide (CTAB, 96%), and cetyltrimethylammonium chloride (CTAC, 99%), Sodium hydrosulfide (NaHS , 99%) were all purchased from Sigma–Aldrich and used as received. All chemicals were of analytical grade. During all experiments, all solutions were prepared with a Milli-Q ultrahigh-purity water system (Milli-Q, Millipore, US).

(B) Synthesis of Au@Ag NCs

A mature of Au@Ag NCs was synthesized according to the research group of Xia.¹ The Au seeds were prepared using a two-step procedure. First, we synthesized 2-3 nm Au nanocrystallites by adding ice-cooled 0.6 mL of NaBH_4 (0.01 M) solutions into a 10 mL mixed solutions which containing CTAB (10 mL, 0.1 M) and HAuCl_4 (0.25 mL, 0.01 M). After quick sufficient mixing, the 2-3 nm Au nanocrystallites solution was kept undisturbed at 27 °C for 3 h. Then, these Au nanocrystallites were allowed to grow into 10-nm Au seeds by adding 0.3 mL of 3-nm Au nanocrystallites in to grow solutions which containing 6 mL of HAuCl_4 (0.5 mM) solution, 6 mL CTAC (0.2 M) solution, 3 mL AA (0.1M) solution. And then 30-nm Au seeds could be successful Synthesized after several repeats with the protocol mentioned above. The Au@Ag NCs were formed by depositing Ag on the as-prepared 30 nm CTAC-Au seeds. In typical, 3 mL of AA (0.1 M) solution, 7 mL CTAC (0.2 M) solution and 3 mL of 30-nm Au seeds were sufficient mixed, then 0.6 mL of AgNO_3 (0.01 M)

solution were added to the mixed solutions by a syringe pump. The solutions were held at 60 °C for 3 h. Cubic Au@Ag nanocrystals were formed due to the conformal over-growth of Ag on the CTAC-Au seeds.² The edge lengths of the Au@Ag nanocubes (~50 nm) could be finely controlled by injecting certain volumes of AgNO₃ (0.01 M) into aqueous suspensions containing (13 mL) the same amount of Au seeds.

(C) Immobilizations of the PNPs onto the glass substrate

The indium tin oxid (ITO) glasses were chosen as the sensing substrate for dark-field imaging and individual nanoparticle LSPR scattering measurements. ITO glass substrate was cleaned by ultrasonic cleaning in soapy water, acetone, ethanol, ultrapure water for at least 1h, respectively. After drying under N₂ beam, the ITO substrates were stored in clean centrifuge tube for next using. Au@Ag NCs could be immobilized on the glasses surface by physical absorptions effect. The processed ITO glass immersing into diluted nanoparticles solutions for 30s, then followed removing superfluous Au@Ag NCs by washing ultrapure water and drying it under a weak stream of N₂.

(D) Experimental instrument

The DFM imaging and SPR scattering spectral was obtained by an inverted microscope (eclipse Ti-U, Nikon, Japan) equipped with a dark-field condenser ($0.8 < NA < 0.95$), a 60× objective lens, a 100 W halogen lamp, a true-color digital camera (Nikon DS-fi2) and a monochromator (Acton SP2300) equipped with a spectrograph CCD (PIXIS 400BR: excelon, Princeton Instruments) and a grating (grating density, 300 L/mm; blazed wavelength, 500 nm). The spectra were integrated as 15 s.

Transmission electron microscopy (TEM) images of the Au@Ag NCs were obtained with a Hitachi microscope operated at 100 kV (JEM-1400, JEOL, Japan). Extinction spectra of all the nanoparticles were recorded using a UV-VIS-NIR spectrophotometer (UV-3600, Shimadzu). Scanning electron microscope (SEM) images of Au@Ag NCs were measured by S-4800 (Hitachi). X-Ray Diffraction (XRD) patterns were acquired by Bruker D8 Advance diffractometer.

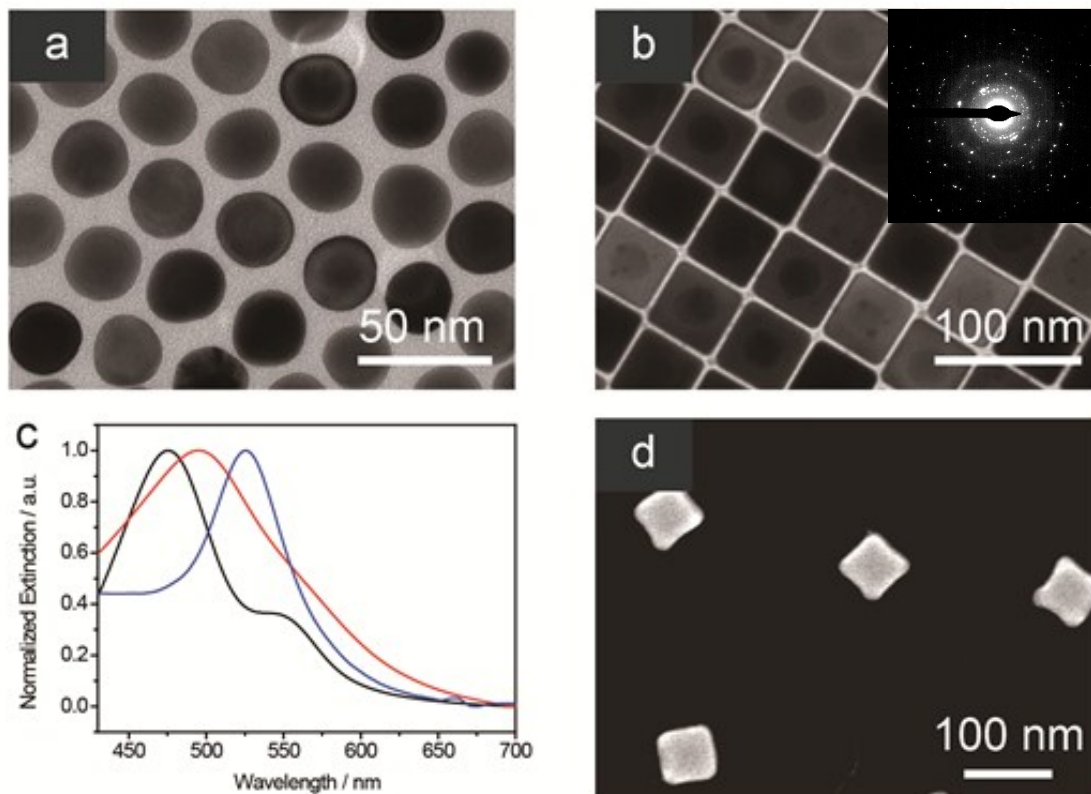
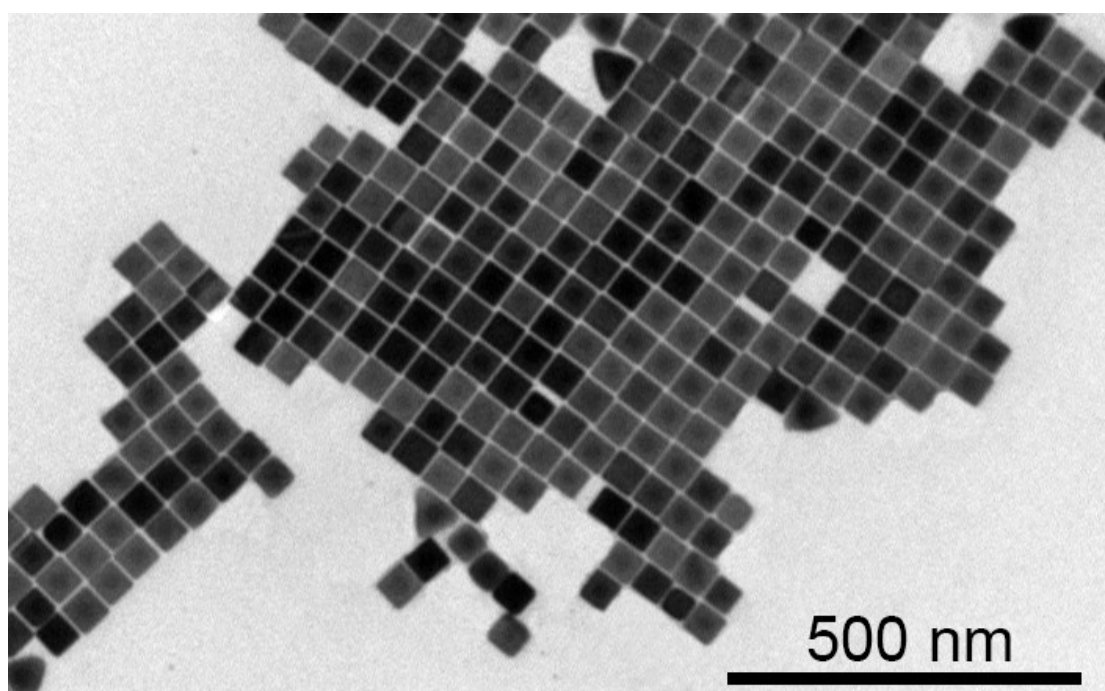


Fig. S1 (a) TEM image of 30 nm Au nanospheres. (b) TEM image of Au@Ag NCs. (c) Normalized extinction spectra of 30-nm Au NPs (blue), Au@Ag NCs (black) and Au@Ag@Ag₂S NCs (red). (d) SEM image of Au@Ag@Ag₂S core-shell after treatment by 1 μ M NaHS.



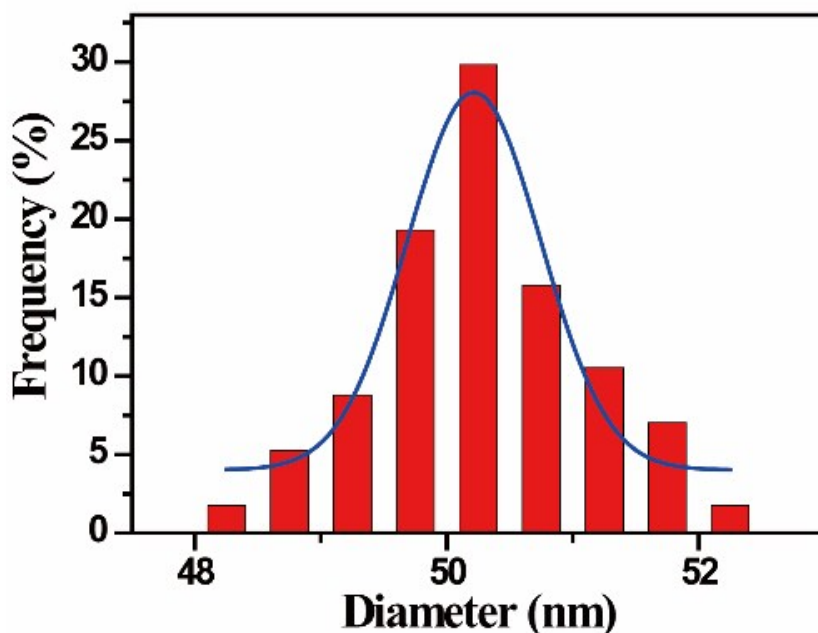


Figure S2 (a) TEM images of purified Au@Ag NCs. (b) Diameter distribution of Au@Ag NCs.

(E) Individual Au@Ag nanocube for sulfide ions detection

The true-color scattering images of AgNCs were taken using a 60× objective lens (NA = 0.8). The Au@Ag NC-functionalized glass slides were immobilized on a platform of dark-field microscopy. At first, the scattering spectrum of a selected single Au@Ag NC was recorded as the original spectrum. After different concentration of NaHS solutions were added on the glass slide, the peak position red-shifted continuously to longer wavelength, which indicated that sulfurization occurred on Au@Ag NC surface. With DFM, the color change images and time-dependent LSPR spectra shift of individual nanoparticle could be easily obtained. The scattering spectra from the single nanoparticle were corrected by subtracting the background spectra taken from the adjacent regions without Au@Ag NC and dividing with the calibrated response curve of the entire optical system. The spectra were integrated as 15 second.

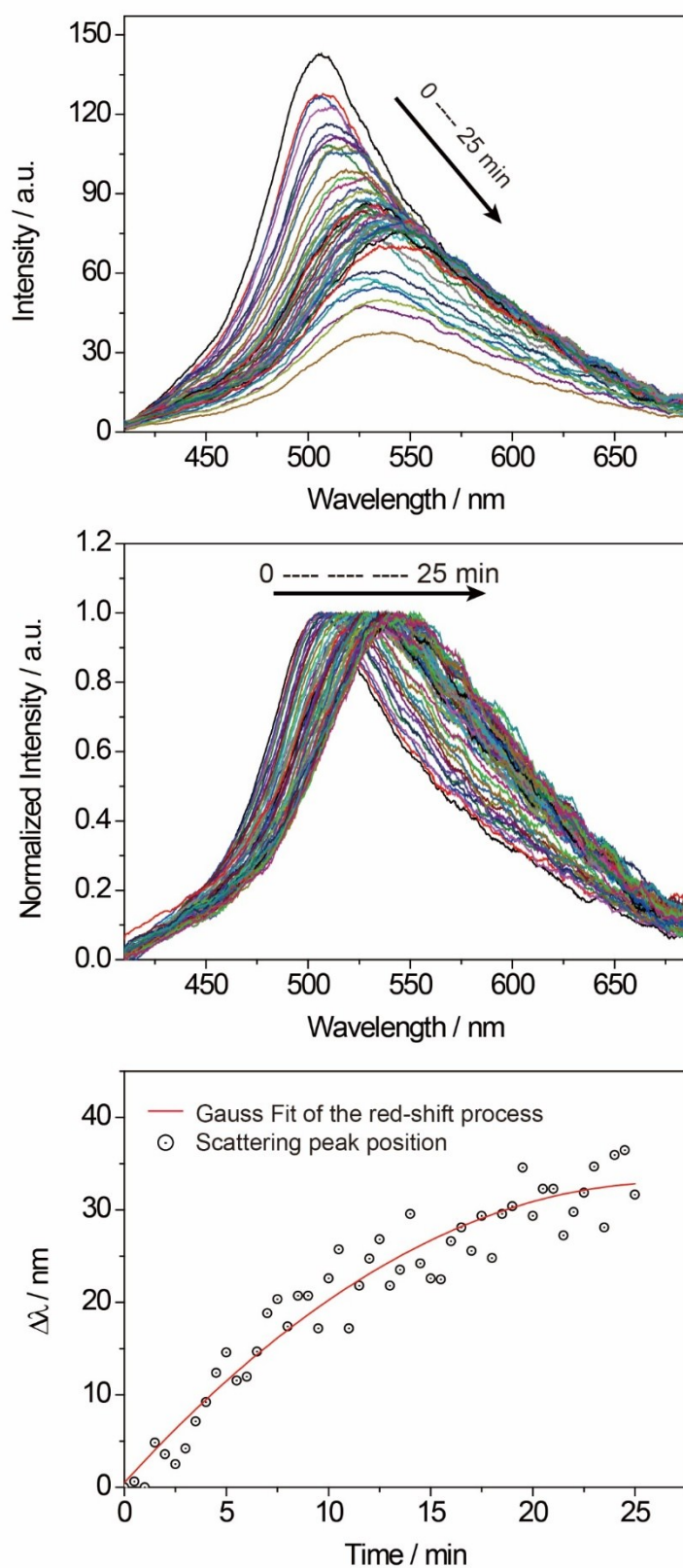


Figure S3. Original LSPR scattering spectra (a) and normalized LSPR scattering spectra (b) of individual Au@Ag NC react with 100 nM NaHS at different time, (c). The scattering spectra peak position at different time and the gauss fit of the $\Delta\lambda$ vs. the time.

Reference:

1. Y. Ma, W. Li, E. C. Cho, Z. Li, T. Yu, J. Zeng, Z. Xie and Y. Xia, *ACS nano*, 2010, **4**, 6725-6734.
2. Y. Tian, L. Zhang, J. Shen, L. Wu, H. He, D. L. Ma, C. H. Leung, W. Wu, Q. Fan, W. Huang and L. Wang, *Small*, 2016, **12**, 2913-2920.