Electronic Supporting Information

A novel scattering switch-on detection technique for target-induced plasmon-coupling based sensing by single-particle optical anisotropy imaging

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Experimental Section

Materials

Hydrogen tetrachloroaute (III) trihydrate ($HAuCl_4 \cdot 3H_2O$), sodium citrate, sodium chloride (NaCl), dipotassium phosphate(K_2HPO_4), monopotassium phosphate(KH_2PO_4), hydroxylammonium chloride, glutathione (GSH, reduced), polyethylene glycol (PEG 400) were purchased from Sinopharm Chemical (Shanghai, China). Sodium hydrosulfide (NaHS) was obtained from Sigma-Aldrich. All reagents were AR grade and used without further purification.

Nanoprobe preparation and characterization

The 18 nm AuNPs were synthesized according to the classical Frens method. The obtained 18 nm AuNPs were then used as seeds for the preparation of 50 nm AuNPs using a seed-mediated growth method. In brief, 1.432 mL 18 nm AuNPs and 255 μL hydroxylammonium chloride (400 mM) were sequentially added into 18 mL DI water. After thoroughly mixed, 386 μL of 24.28 mM $HAuCl_4$ was gradually added into the mixture drop by drop in 30 min. The GSH@AuNPs were prepared by adding 5 μL GSH (1 mM) to 1 mL freshly prepared AuNPs under stirring at 600 rpm for 15 min. The prepared AuNPs and GSH@AuNPs were characterized with UV-visible spectroscopy (Shimadzu, UV-1800, Japan) and

transmission electron microscopy (JEM 1230, JEOL, Japan). The hydrodynamic radius and surface charge of the nanoparticles before and after modification were measured using a Zetasizer Nano ZS instrument (Malvern, UK).

Imaging apparatus

The imaging experiments were performed on a Nikon 80i upright microscope consisting of an oil immersion dark-field condenser (NA: 1.20~1.43) and a 40× objective (NA: 0.75). The original 100 W halogen tungsten lamp was replaced with a 1000 W professional studio flashlight (PN1000, JinBei Co., Shanghai, China), which features a flash duration time of 1/2000 s and a recharging time of less than 2 s. The polarizing optics is a DIC rotatable polarizer (Nikon, Japan) consists of a rotatable polarizer before the condenser and an analyzer before the detector. The detectors used in our experiment include a Neo sCMOS Camera (Andor, UK) and an Olympus DP72 color CCD camera (Japan).

Concept verification for H2S sensing by colorimetric assay

Typically, the concentration of NaCl solution for H_2S detection was optimized by testing the stability of the probes in salt solutions with various concentrations. By incubating the probes with a set of NaCl solutions with concentration ranging from 0 to 128 mM for 15 min, the nanoprobes were characterized with UV-visible spectroscopy. We also tested the effect of solution pH value (from 5 to 9) on probe stability. The detection time was selected according to reaction dynamics by monitoring the absorbance spectra of GSH@AuNPs incubated with 8 μM of NaHS For H_2S sensing in bulk solution, the concentration of NaHS ranged from 2 μM, 4 μM, to 20 μM. To further confirm the aggregation of nanoparticles induced by H_2S addition, the nanoprobes with or without the incubation of 10 nM H_2S were characterized with FLPDM and TEM.

H_2S sensing with FLPDM

For H_2S detection under FLPDM, the coverslips were carefully cleaned by using the piranha solution (H_2SO_4: H_2O_2 = 3:1) to remove organic residues, followed by sonication in ultrapure water for at least three times to remove excess dusts. Then the coverslips were incubated with 1 wt% PEG 400 for 30 min to prevent the nonspecific absorption of nanoparticles during the detection experiments. To investigate the selectivity, the following anions and thiols including Cl^- , Br^- , I^- , CO_3^{2-} , NO_3^- , $S_2O_3^{2-}$, SO_4^{2-} and cysteine with a same concentration of 10 μM were incubated with GSH@AuNPs and followed by the particle counting with FLPDM. For the quantitative detection of H_2S, the probe solution was incubated with NaHS

with final concentrations ranging from 0.1 nM to 100 μM. After reaction, 10 μL diluted sample was placed between two coverslips and detected under FLPDM. The images were processed with ImageJ software and the nanoparticle counts were obtained by using the particle analysis module.

Additional Tables and Figures

	Surface charge (mV)	Hydrodynamic diameters (nm)
Au NPs	-18.6	53.1
GSH-Au NPs	-28.0	63.3

Table S1. Surface charge and hydrodynamic size changes of the AuNPs before and after surface modification.

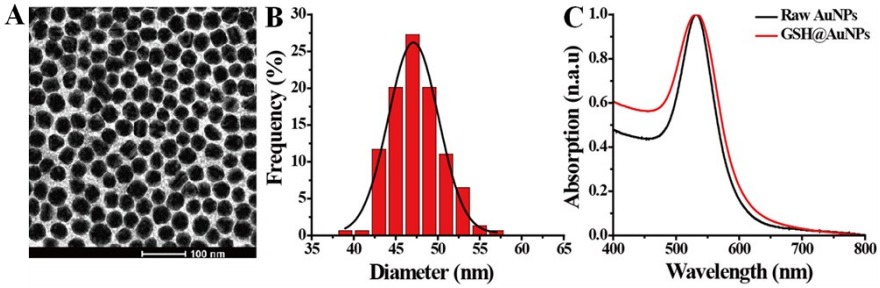

Fig. S1. Characterizations of the prepared GSH@AuNPs. Representative TEM image (A) and the size distribution (B) of the synthesized AuNPs. (C) Absorption spectra of raw AuNPs and GSH modified AuNPs.

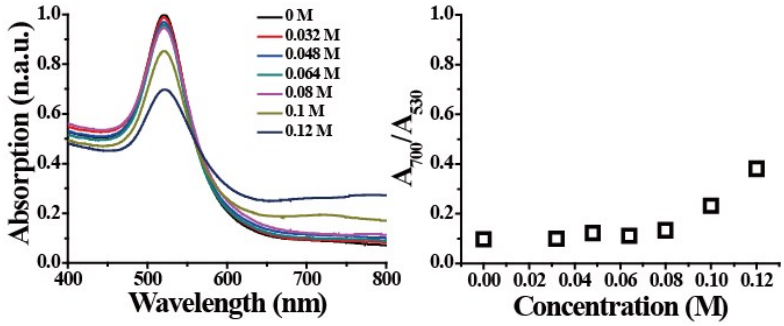

Fig. S2. Optimization of NaCl concentration used in the detection of H_2S. The GSH@AuNPs display well stability at a concentration of NaCl lower than 0.1 M.

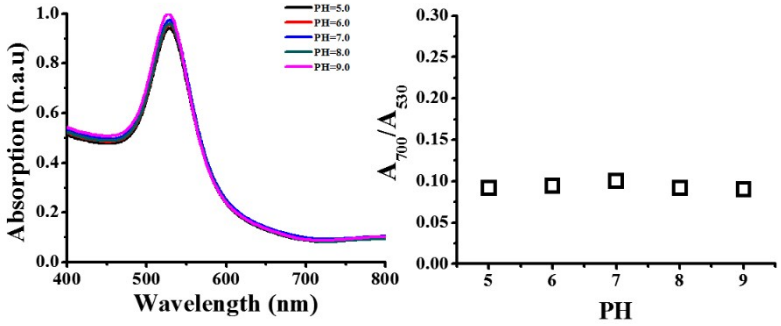

Fig. S3. The GSH@AuNPs display well stability in buffer solutions with pH values ranging from 5 to 9.

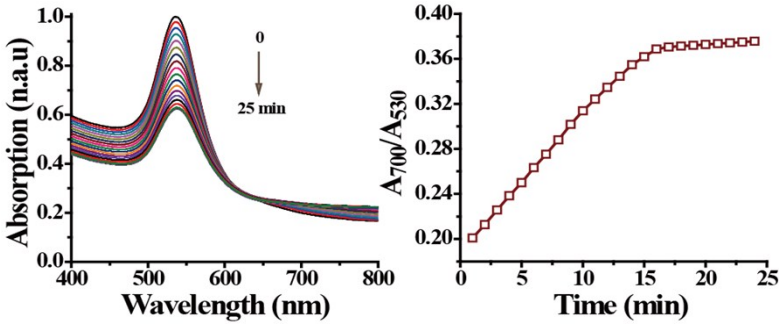

Fig. S4. Time course of absorption spectrum and relative absorption ratio changes of the GSH@AuNPs with the addition of 8 μM of NaHS.

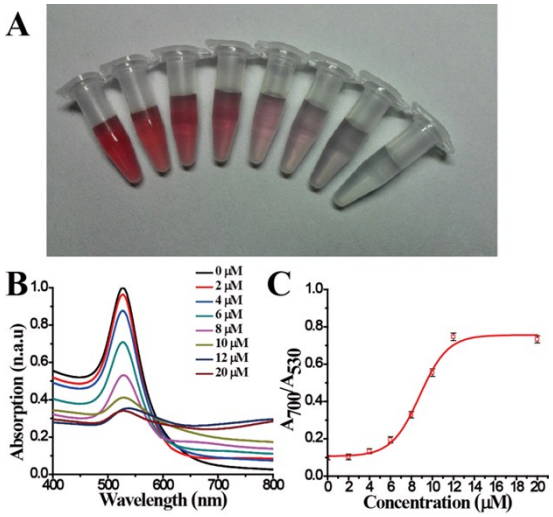

Fig. S5. Detection of H_2S with GSH@AuNPs as probes in bulk solutions. Digital photo (A), absorption spectra (B) and relative absorption ratio (C) of the GSH@AuNPs in the presence of H_2S at different concentrations from 0 to 20 μM.

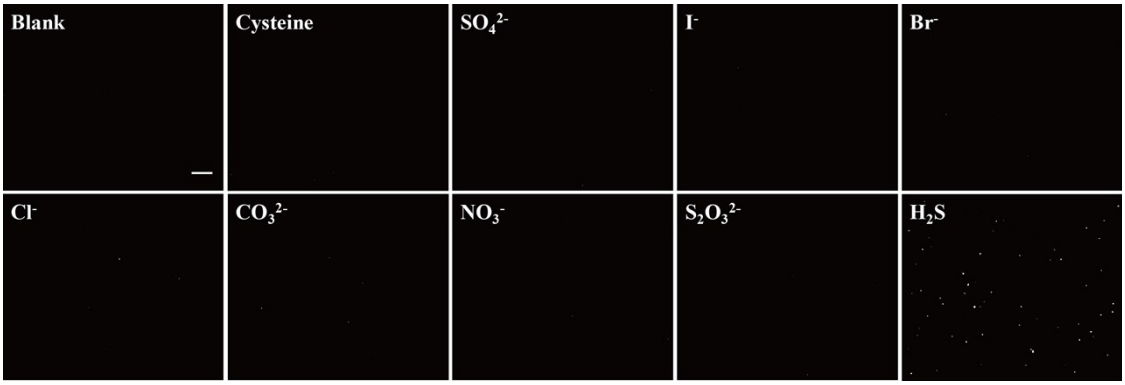

Fig. S6. Typical FLPDM images for studying the selectivity of GSH@AuNPs towards H_2S. The scale bar is 20 μm.

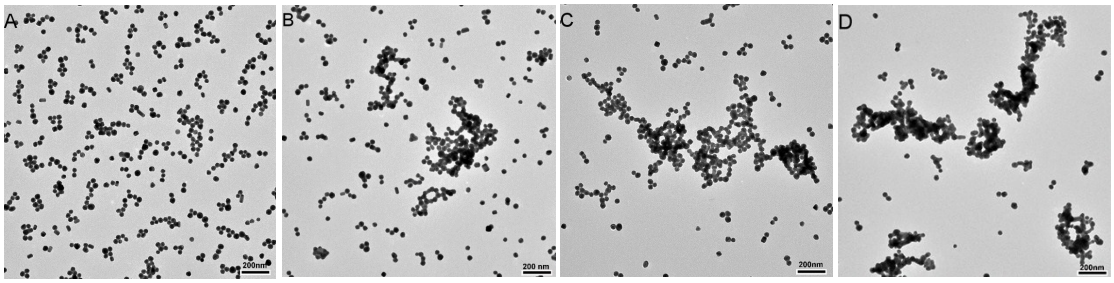

Fig. S7. Representative TEM images of GSH@$AuNP_S$ with the addition of H_2S at various concentrations. (A) 0.1 nM, (B) 10 nM, (C) 1 μM, (D) 100 μM.

Table S2. Comparison of this work with other available methods for particle-aggregation based sensing strategies.

Method	Principle	Background interference	Sensitivity	Ref.
Latex agglutination test	Latex agglutination	low	low	1
Colorimetric assays	Aggregation induced color change	high	middle	2
Dynamic light scattering	Aggregation induced size change	middle	high	3
Single particle counting	Aggregation induced number change	high	high	4
Scattering switch on	Aggregation induced symmetry change	free	high	This study

Reference.

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