Electronic Supporting Information (ESI) for

Highly specific colorimetric recognition and sensing of sulfide with glutathione-modified gold nanoparticle probe based on a anion-for-molecule ligand exchange reaction

Jia Zhang,[ab] Xiaowen Xu,[ab] and Xiurong Yang*[a]

[a] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, China

[b] Graduate School of the Chinese Academy of Sciences, Beijing 100049, China

*E-mail: xryang@ciac.jl.cn; Fax: +86 431 85689278

Contents:

1. Experimental

1.1. Materials

Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$), 3-mercaptopropionic acid and 11-mercaptoundecanoic acid were purchased from Sigma-Aldrich Co. (USA). Glutathione (GSH, reduced) and cysteine were purchased from Sangon Biotech Co., Ltd. (Shanghai, China). DL-Mercaptosuccinic acid was obtained from Acros Organics (USA). Sodium sulfide was obtained from Beijing Chemical Reagents Co. (Beijing, China). All other chemicals were analytical grade and used without additional purification. Phosphate buffer solutions (PBS) were prepared by varying the ratio of 0.01 M Na_2HPO_4 to 0.01 M KH_2PO_4. Milli-Q water (18.2 MΩcm) was used throughout the experiment. Unless specified, the experiment was conducted at 25 ± 1 ^oC.

1.2.Instrumentation

UV/vis absorption spectra were recorded with a Cary 50 UV/vis spectrophotometer (Varian). Photographs were taken with a Canon PSA490 digital camera (Canon). TEM images were acquired by using the Hitachi H-800 (Hitachi) transmission electron microscope operated at 200 kV. A filter paper was put under the carbon-coated copper grip when preparing samples to preclude the possibility of particle aggregation during drying. XPS samples on highly cleaned silicon wafers were analyzed by an ESCALAB MK II spectrometer (VG scientific). The electrochemical experiment was carried out on a CHI 660B electrochemical workstation (Shanghai Shenhua Apparatus) in a one-compartment cell by standard three-electrode systems. A Ag/AgCl (Sat. KCl) electrode was used as the reference electrode, a Pt foil as the counter electrode, and a glassy carbon electrode (GCE, Φ 3 mm) as the working electrode.

1.3.Synthesis of citrate-capped Au NP

The citrate-capped Au NP of an average 13 nm diameter was synthesized according to the Natan's method.[S1] 1 mL of 0.1 M $HAuCl_4$ was added with 190 mL of water and brought to a rolling boil with vigorous stirring. Then 10 mL of 38.8 mM trisodium citrate was rapidly added, and the solution kept stirring under heat for 10 min. The obtained ruby red solution continued to be stirred without heat for another 15 min. After cooling down to room temperature, it was stored at 4 ^{o}C before use. The concentration of the red AuNPs solution was determined to be ~7.2 nM by UV/vis spectroscopy, based on an extinction coefficient of 2.7×10^8 $M^{-1}cm^{-1}$ at λ = 520 nm for 13 nm AuNPs.[S2]

S1 K. G. Grabar, R. G. Freeman, M. B. Hommer and M. J. Natan, *Anal. Chem.*, 1995, **67**, 735.

S2 H. D. Hiller and C. A. Mirkin, *Nat. Protoc.*, 2006, **1**, 324.

1.4. Preparation of GSH-AuNP probes

For preparation of GSH-AuNP probes with designate ratios, in a typical experiment, 2 mL of citrate-capped Au NP solution was each added with 1.4, 3.5, 7.0,

14, and 28 μL of GSH stock solution (10 mM), denoted as *S*1, *S*2, *S*3, *S*4, and *S*5, respectively. After being stirred for 2 h at room temperature, each solution was then added with 2 mL of water. The solutions were stored at 4 ^{o}C for at least 48 h before the sulfide assay.

1.5. Detection of sulfide by the S2 sensor

The *S*2 probe was selected as sensor for sulfide. In a typical experiment, 100 μL of sensor solution was added with same volume of PBS buffer (pH = 6.0). Then it was incubated with different concentrations of sulfide and the solution was mixed homogeneously. Afterwards, NaCl solution (80 mM) was added to initiate the colorimetric responses. The absorbance spectra and the photographs were collected and taken after 10 min of interaction.

1.6. Modification of GCE by the GSH-AuNP after incubation with sulfide

300 μL of GSH-AuNP solution (probe *S*2) was mixed with the same volume of PBS (pH 6.0), and 9 μL of sulfide solution (1 mM) corresponding to a concentration of 15 μM was spiked to the buffered probe. After incubation for 10 min, the suspension was subject to centrifugation at 13500 r/m for 15 min. The red sediment was collected and resuspended in 50 μL of water. Before modification, the GCE was polished using 0.3 and 0.05 μm alumina slurries on a polishing cloth and then cleaned with sonication in water and ethanol for each 5 min. The obtained nanoparticle suspension was immobilized on the surface of GCE by spiking 10 μL of the new suspension and it was dried at room temperature.

2. Figures

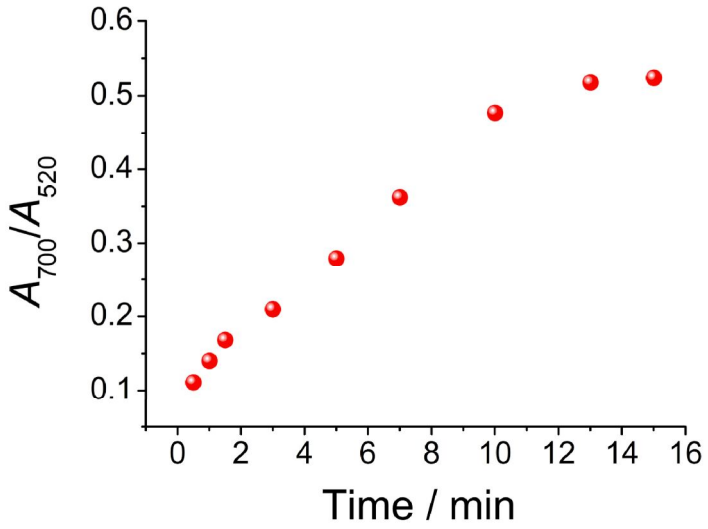

Fig. S1. Time-dependent absorption ratio for the *S*3 probe in PBS (pH = 7.0) in the presence of sulfide (10 μM) and NaCl (80 mM).

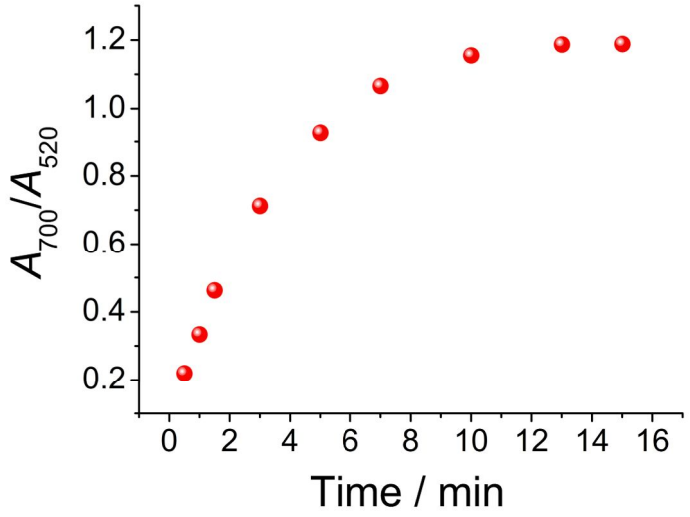

Fig. S2. Time-dependent absorbance ratio for the *S*3 probe in PBS (pH = 7.0) in the presence of 100 mM NaCl.

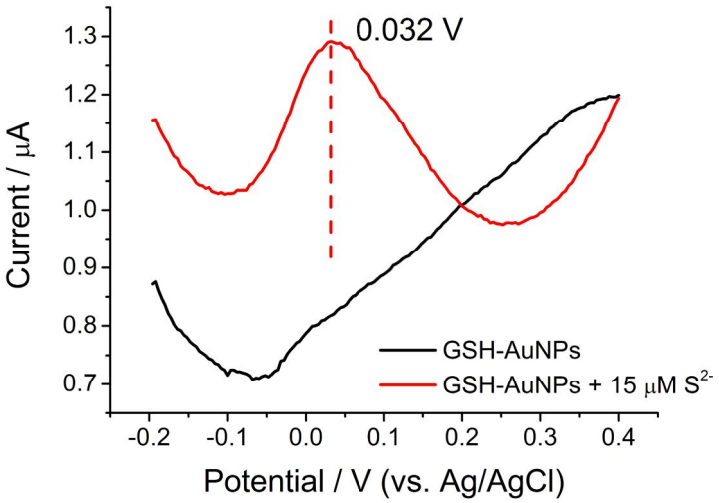

Fig. S3. Differential pulse voltammetric responses in PBS (10 mM, pH = 9.0) of GCE modified by bare GSH-AuNP and nanoparticle after interaction with 15 μM sulfide.

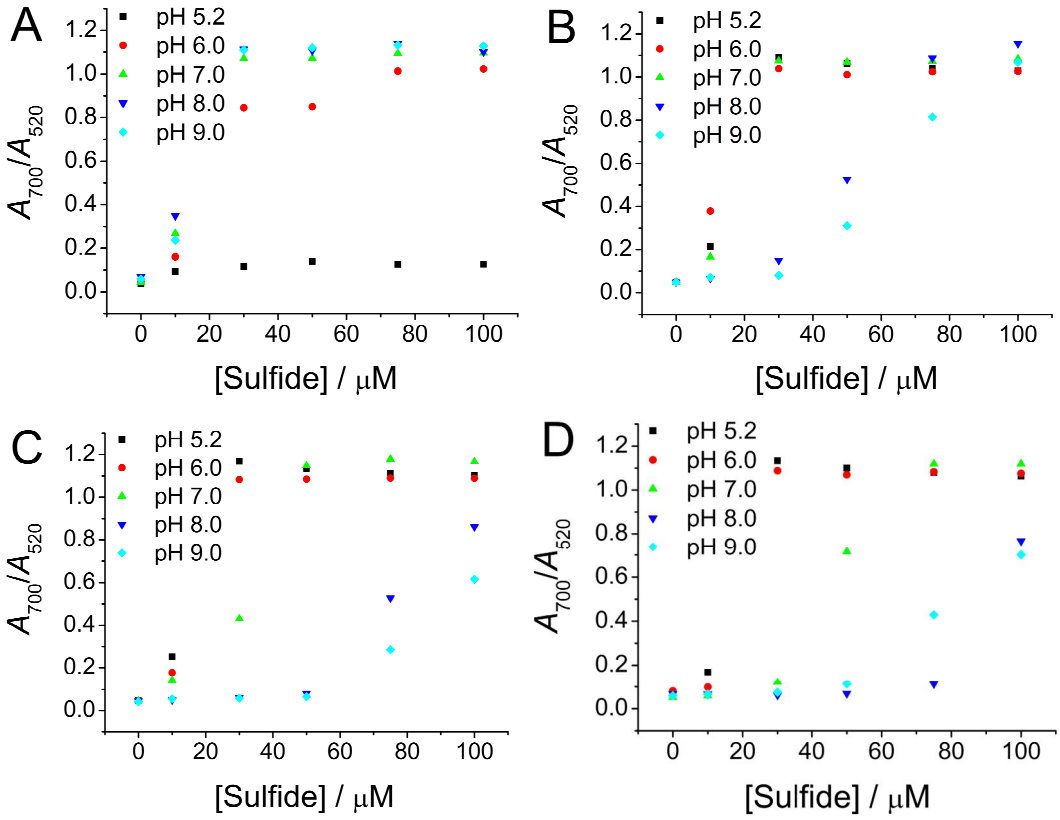

Fig. S4. The correlation of absorbance ratio with sulfide concentration under different pH values for (A) *S*1, (B) *S*2, (C) *S*4, and (D) *S*5 probe, respectively.

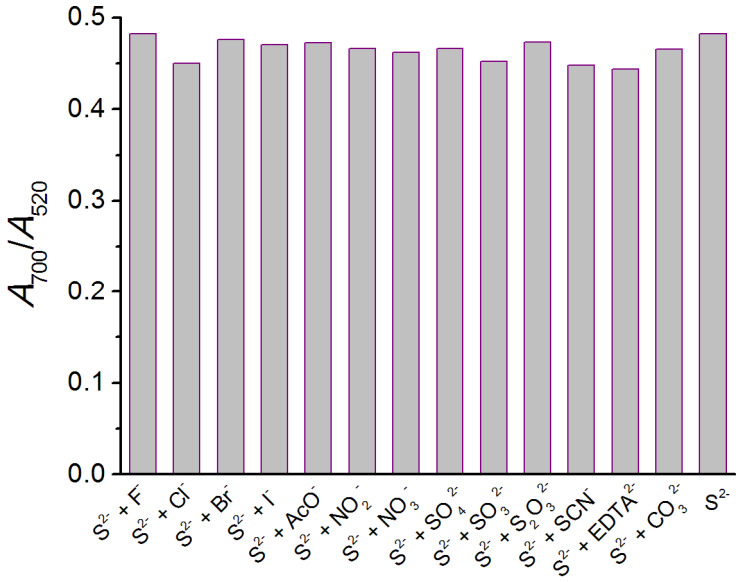

Fig. S5. Interference study of the sulfide sensor with incubation of sulfide (10 μM) and other individual anions (1 mM).