

Electronic Supplementary Information (ESI) for the Analytical Methods.

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Supplementary Information

Mercury ion-engineering Au plasmonics on MoS₂ layers for absorption-shifted optical sensors

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1. Experimental Sections

1.1. Materials

Molybdenum disulfide (MoS_2 crystalline powder, $< 2 \mu\text{m}$, 99%), tetrachloroauric acid (HAuCl_4) and mercury nitrate were obtained from Sigma-Aldrich Co. (USA). Sodium cholate (98%), Cetyltrimethyl Ammonium Bromide (CTAB), cadmium nitrate tetrahydrate and cobalt chloride hexahydrate were obtained from Aladdin Chemistry Co. Ltd. (Shanghai, China). Mercury nitrate was purchased from Sigma Aldrich (USA). Ethylene Diamine Tetraacetic Acid (EDTA), L-ascorbic acid (L-AA), manganese chloride and nickel chloride hexahydrate were obtained from Adamas-Beta Chemistry Co. Ltd. (Shanghai, China). Zinc nitrate dihydrate, Lead nitrate and calcium nitrate were obtained from KESHI Co. Ltd. (Chengdu, China). Sodium nitrate was obtained from Boyi Chemical Reagent Co. Ltd. (Chongqing, China). Ferrous chloride was obtained from Shanghai yuanye Bio-Technology Co., Ltd. Ferric sulfate was obtained from Shanghai Shanhai Engineering Group Experimental Factory no.2 (Shanghai, China). Other chemicals were of analytical reagent grade and used without further purified. Ultrapure water ($18.2 \text{ M}\Omega/\text{cm}$) was utilized throughout the whole experiment.

1.2. Instruments

Ultrasonic bath is KQ-400B from Kunshan Ultrasonic Instruments Co. Ltd. (Shanghai, China). Thermostatic metal bath (Tansoole, China) is employed to incubate the samples. The time-depending absorption spectra were recorded on a UV-2450 UV-vis spectrophotometer (Shimadzu, Japan). The most absorption spectra were recorded on the microplate reader (BioTek, USA). The centrifugation was utilized to collect the nanostructures (Thermo Fisher Scientific, USA). Transmission electron microscope (TEM), high-resolution TEM (HRTEM), and energy dispersive X-ray spectroscopy were performed by Tecnai TF30 (FEI, USA).

1.3. The Preparation of the Conjugated CTAB-Au(I) Mixture

Firstly, the stocking solutions, including CTAB (100 mM), HAuCl_4 (25 mM) and L-ascorbic acid (AA, 100 mM) were prepared. Then, A portion of 1.5 mL CTAB,

and 150 μL HAuCl_4 was mixed together in a sample bottle with the volume of 20 mL. After that, 7450 μL ultrapure water was added. In order to prepare the conjugated Au(I) solution, 900 μL AA was immediately added into the mixture.

1.5. The Preparation of Exfoliated MoS₂

The MoS₂ and sodium cholate was weighed and prepared to be 5 mg/mL and 1.5 mg/mL, respectively. Then, the solution was treated with ultrasonic bath for 12 h. The color changes of the solution from black to dark green indicted the formation of the layered MoS₂. Then, the purification of exfoliated MoS₂ nanosheets was conducted. The samples are treated with centrifugation at 3000 rpm for 30 min and the supernatant was collected in order to remove the large-size unexfoliated MoS₂ sediments. Lastly, the supernatant, containing exfoliated MoS₂ and the surfactant, was centrifugated at 10000 rpm for 30 min, and the sediments were re-dispersed into the pure water to obtain the liquid-exfoliated MoS₂ aqueous dispersions.

1.6. Hg²⁺ Detections Using the CTAB-Au(I) Solutions in the Presence and Absence of Exfoliated MoS₂

To begin with, 23 μL of MoS₂ was diluted to be 73 μL , which was stored in a small sample bottle. Then, a portion of 0.3 mL Hg²⁺ ions with different concentrations was added. Then, the whole sample was incubated for 30 min, for the conjugation of Hg²⁺ ions with MoS₂. After that, 1 mL of CTAB-Au(I) reaction solutions was added into the MoS₂ and Hg²⁺ ions mixture, and the system was further incubated for diverse times. In order to achieve the measurements, a portion of 200 μL reaction solutions was moved to the 96-well plate for absorption spectrum scanning (400-999 nm). As a control, the MoS₂ dispersions were replaced by the ultrapure water, and consistent operation was conducted for the measurements of Hg²⁺ ions in the absence of MoS₂.

1.7. The Interference of the Detections of Hg²⁺ Ions

The solutions of multifarious metal ions are prepared and diluted to be 1 mM, 100 μM and 1 μM , respectively. Then, Hg²⁺ with a concentration of 1 μM was totally mixed. The mixtures (0.3 mL) containing the co-existing compounds and Hg²⁺ were

collected, and the Hg^{2+} detections based on the CTAB-Au(I) solutions were conducted in the presence of MoS_2 .

2. Supplementary Figures

Figure S1

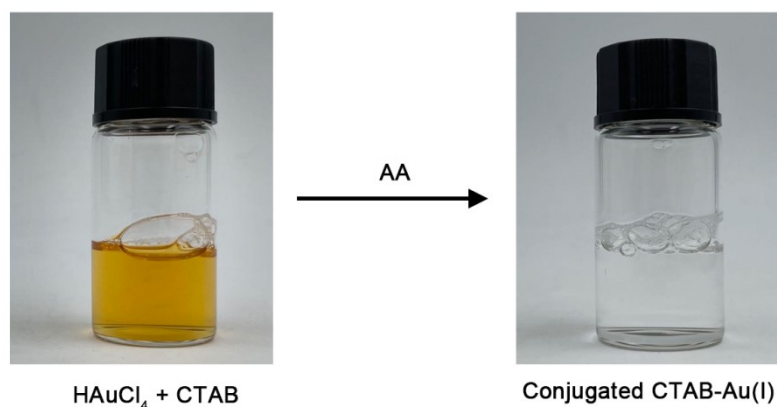


Fig. S1. The photos showing the mixture of H[AuCl₄] and CTAB solutions before and after the addition of AA.

Figure S2

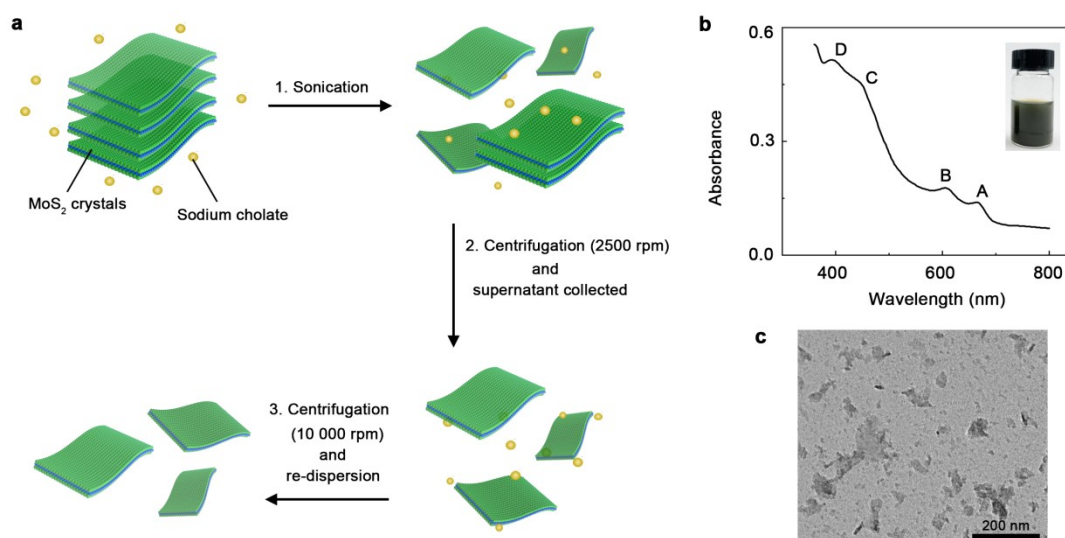


Fig. S2. (a) The scheme illustration showing the exfoliation and size separation of MoS₂ nanosheets. (b) The optical absorption spectrum of the exfoliated MoS₂ aqueous dispersion, exhibiting four characteristic A, B, C, D absorption peaks. (c) The TEM image of exfoliated MoS₂. The plane sizes of exfoliated MoS₂ are various from 30-100 nm.

Figure S3

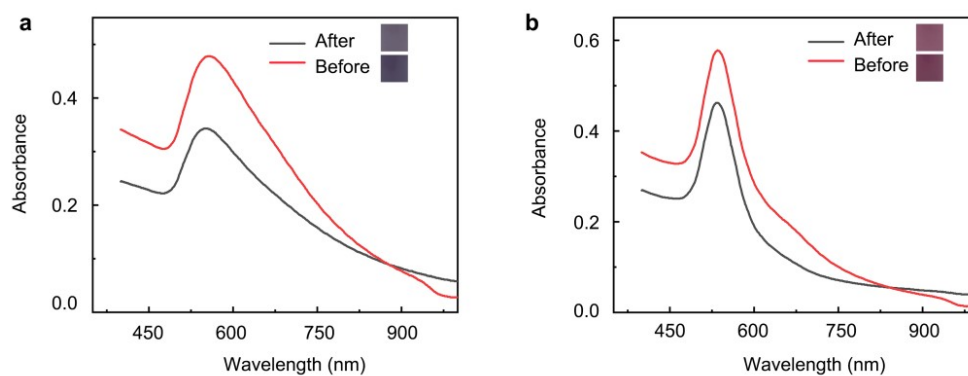


Fig. S3. The absorption spectra of Au-MoS₂ reaction products before and after the removal of CTAB via the centrifugation. The concentrations of Hg²⁺ ions were 100 nM (a) and 2 μ M (b), respectively.

Figure S4

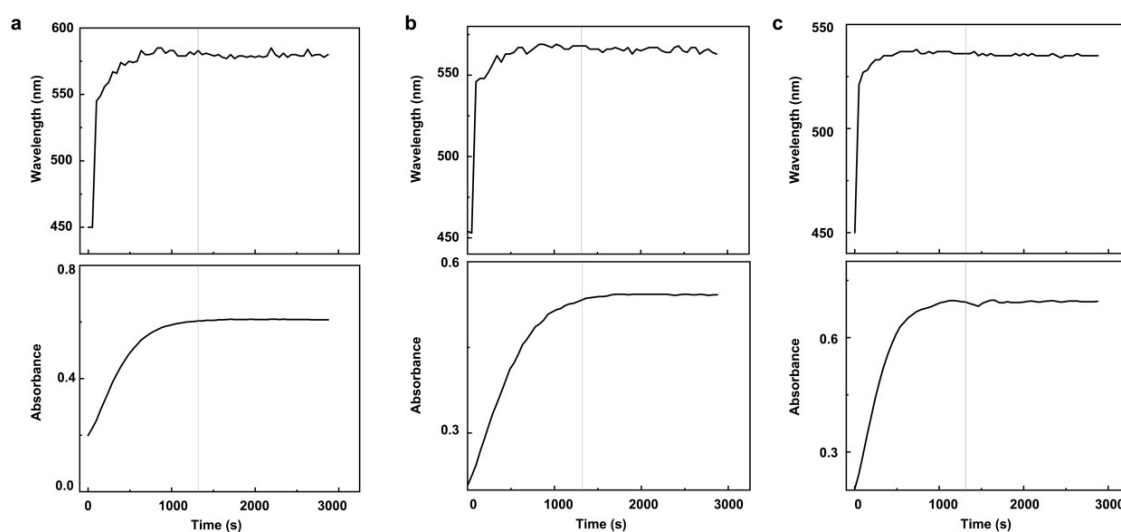


Fig. S4. Time-dependent changes of peak wavelengths and absorbance of MoS₂-CTAB-Au(I) reaction systems in the absence (a) and presence (b and c) of differential concentrations of Hg²⁺ ions (b: 100 nM, c: 2 μ M).

Figure S5

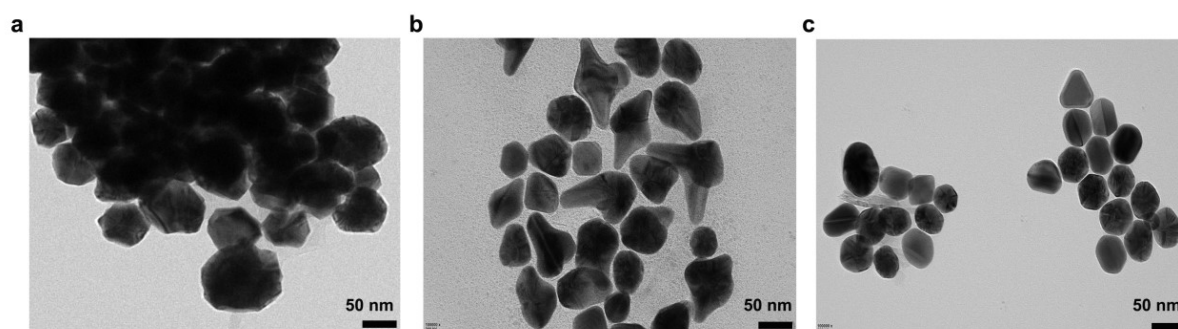


Fig. S5. The TEM images of final products of MoS₂-CTAB-Au(I) reaction systems in the absence (a) and presence (b and c) of differential concentrations of Hg²⁺ ions (b: 125 nM, c: 1 μM).

Table S1. The relative deviation caused by various chemical species at different ratios to Hg²⁺ ions. The concentrations of Hg²⁺ ions are 100 nM.

Species	Ratio	Relative Deviation	Species	Ratio	Relative Deviation
MnCl ₂	100:1	4.12%	Mg(NO ₃) ₂	1000:1	2.97%
NaNO ₃	100:1	4.12%	BaCl ₂	1000:1	2.97%
Pb(NO ₃) ₂	10:1	2.97%	Fe ₂ (SO ₄) ₃	1000:1	1.80%
Zn(NO ₃) ₂	100:1	5.81%	Ca(NO ₃) ₂	100:1	3.51%
Cd(NO ₃) ₂	100:1	2.97%	Co(NO ₃) ₂	100:1	4.12%
FeCl ₂	10:1	3.51%	EDTA	1000:1	4.91%
NiCl ₂	100:1	4.91%			