

Supporting Information

Photoelectrochemical aptamer sensor based on AgInS₂ and ZnS co-sensitized TiO₂ for detection of Hg²⁺

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1. Materials and reagents

Hydrochloric acid (HCl), tetrabutyl titanate, ethylene glycol, 3-mercaptopropionic acid, L-ascorbic acid (AA), nickel nitrate hexahydrate and thioglycolic acid (TGA) were purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). $\text{HAuCl}_4 \cdot 6\text{H}_2\text{O}$ was purchased from Alfa Aesar. $\text{In}(\text{CH}_3\text{CO}_2)_3$ was obtained from Tianjin ZhiYuan Reagent Co., Ltd. Silver nitrate (AgNO_3), $\text{Zn}(\text{Ac})_2$ and Na_2S was obtained from Sinopharm Chemical Reagent Co., Ltd (China).

Phosphate buffered saline (PBS, 0.1 M KH_2PO_4 and 0.1 M Na_2HPO_4) containing AA was used as an electrolyte for the PEC measurements. Indium tin oxide (ITO) glass was obtained from Zhuhai Kaivo Electronic Components Co., Ltd, China. Ultrapure water (Milli-Q, Millipore) used in all experiments was deionized to $18.25 \text{ M}\Omega \cdot \text{cm}$.

2. Apparatus

The PEC tests were obtained using a CHI760E electrochemical workstation, which was purchased from Chenhua Instrument Shanghai Co., Ltd, China. Meanwhile, a 100 W LED lamp of white light was used for an irradiation source. Scanning electron microscope (SEM) images and energy dispersive spectrometry (EDS) were obtained using a field emission SEM (Zeiss, Germany). X-ray diffraction (XRD) patterns were collected on a D8 advance X-ray diffractometer (Bruker AXS, Germany). UV-vis spectra were obtained on a Shimadzu UV-3600 Plus spectrometer (Japan). Electrochemical impedance spectroscopy (EIS) was examined using an electrochemical workstation (Zahner Zennium PP211, Germany) using $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as redox probe. Mott–Schottky measurement was conducted on electrochemical workstation (CHI760E

Chenhua Instrument Company, Shanghai, China) in 0.2 M Na₂SO₄ aqueous solution.

3. The synthesis method of AgInS₂

Silver nitrate (AgNO₃) (84.94 mg) and In(CH₃CO₂)₃ (291.95 mg) were dissolved in 50 mL of ethylene glycol and 610 μL of 3-mercaptopropionic acid was added. The mixture was purged with N₂ for 10 minutes to remove the oxygen. The mixture was heated at 150 °C for 30 minutes under N₂ atmosphere. After centrifugation and washing with water, the product was obtained by vacuum drying at 60 °C.

4. The synthesis method of Au nanoparticles

1 mL of 1% chlorauric acid solution was diluted to 100 mL in high purity water and boiled with magnetic agitation. After boiling, 2.5 mL 1% sodium citrate was added to the solution. After boiling until wine red, the solution is heated for another 5 minutes, cool at room temperature and set aside.

5. The characterization of TiO₂/AgInS₂/ZnS

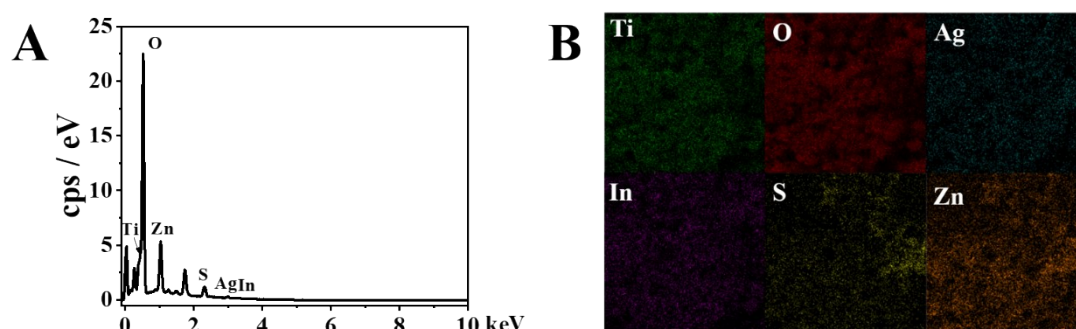


Fig. S1. EDS spectra (A) and the corresponding element mappings (B) of TiO₂/AgInS₂/ZnS.

6. The SEM image of NiCo-MOF and NiCo-MOF@Au

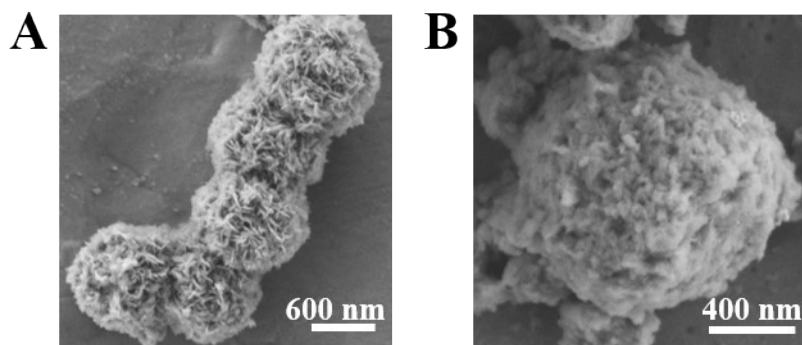


Fig. S2. SEM image of NiCo-MOF (A) and NiCo-MOF@Au (B).

7. Optimization of analytical parameters

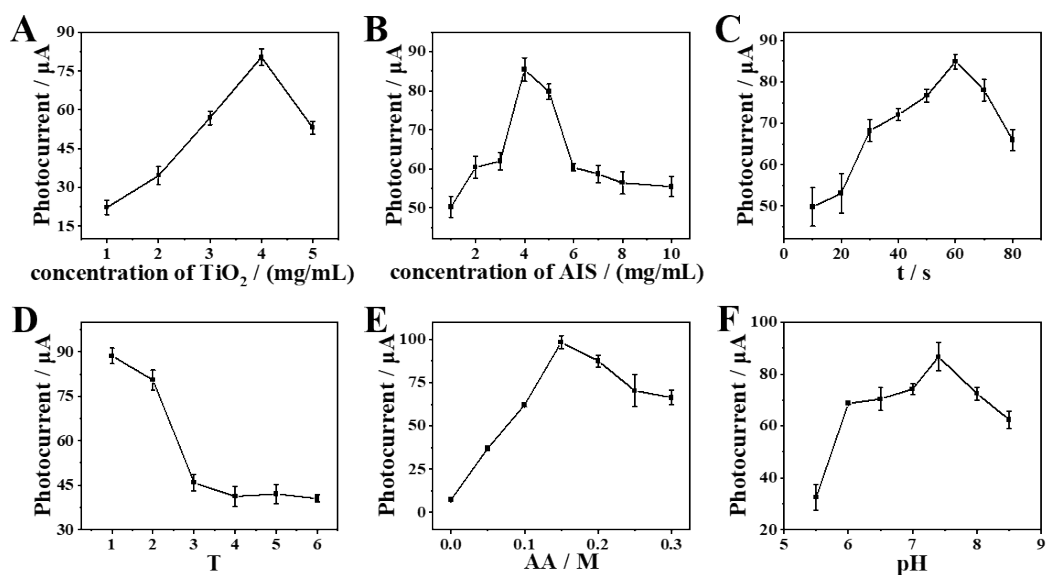


Fig. S3. Effects of the concentration of TiO_2 (A), the concentration of AgInS_2 (B), the SILAR time of ZnS (C), the SILAR cycle times of ZnS (D), the concentration of AA in the PBS buffersolution (E) and the pH value of PBS (F) on the photocurrent response of the ITO/ TiO_2 / AgInS_2 / ZnS electrode.

8. Comparison of various methods for Hg²⁺ detection

Table S1. Comparison of various methods for Hg²⁺ detection

Methods	Linear range	LOD	Reference
Self-powered nanosensor	10 nM-1 μ M	1.7 nM	1
Colorimetric sensor	40-1200 μ g/L	10 μ g/L	2
Fluorescence sensing platform	0.002-30 μ M	7 nM	3
Organic field-effect transistor sensor	1-60 nM	2.4 nM	4
Electrochemiluminescence assay	10 pM-100 μ M	2.9 pM	5
Colorimetric/fluorescence immunoassay	1 nM-30 μ M	1 nM	6
Photoelectrochemical aptasensor	1 mM-0.1 pM	34 fM	This work

9. Detection of Hg²⁺ in real water samples at different concentrations.

Taking tap water, lake water and untreated industrial wastewater in Jinan city as the research object, the application ability of this method in actual water samples was evaluated. Firstly, the collected samples were left to rest for 2 hours. The supernatant was centrifuged at 10,000 r/min for 10 min, and then filtered by 0.22 μ m filter membrane. The concentration of Hg²⁺ in the collected untreated industrial wastewater is 2.7 nM.

Table S2. Detection of Hg²⁺ in tap water different concentrations.

samples	the addition	AFS ^a	proposed	RSD ^b
	conten(nM)	(nM)	aptasensor ^a (nM)	(%, n=3)
Tap water	0.10	<0.20	0.11	3.0
	1.00	0.98	1.06	1.3
	10.0	9.97	10.03	2.8
Lake water	0.10	<0.20	0.10	1.5
	1.00	1.03	1.10	2.7
	10.0	10.07	10.10	2.9
untreated	0.10	2.86	2.87	1.5
industrial	1.00	3.77	3.73	1.9
wastewater	10.0	12.65	12.68	2.2

^aRepresents the average of three repeated measurements. ^bRepresents the relative standard deviation.

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