Electronic Supplementary Information (ESI)
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Au nanoclusters-decorated WO_3 nanorods for ultrasensitive photoelectrochemical sensing of Hg^{2+}

Si Dai, Hui Huang, Shihan Liu, Wenfang Deng, Yueming Tan*, and Qingji Xie

Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

Email: tanyueming0813@hunnu.edu.cn

Instrumentation

Transmission electron microscopy (TEM) studies were performed on a TECNAI F-30 high-resolution transmission electron microscope. Scanning electron microscopy (SEM) studies were performed on a Hitachi S4800 scanning electron microscope. X-ray diffraction (XRD) pattern was obtained on a PANalytical X'pert Pro X-ray diffractometer using Cu Kα radiation, operating at 40 kV and 30 mA, with a scan rate of 4° min^{-1}. X-ray photoelectron spectroscopy (XPS) measurement was investigated using a PHI QUANTUM 2000 X-ray photoelectron spectroscopic instrument. Ultraviolet-Visible (UV-Vis) spectra were obtained on U3310 UV-Vis spectrometer (Hitachi, Japan). Fourier transform infrared (FTIR) spectrum was collected on Nicolet Nexus 670 Fourier transform infrared spectrometer. All electrochemical experiments were carried out on the CHI760E electrochemical workstation. All photoelectrochemical experiments were carried out on electrochemical workstation (ZENNIUM, ZAHNER-elecktrik GmbH & Co. KG, Germany) equipped with a controlled-intensity modulated-photospectroscopy setup (CIMPS, PP211, ZAHNERelecktrik GmbH & Co. KG, Germany). A white light lamp (WLC02, ZAHNER-elecktrik GmbH & Co. KG, Germany) with a visible-light filter (400-700 nm) was used as the light source.

Chemicals

Sodium tungstate, sodium chloride, mercury chloride, copper chloride, iron chloride, zinc chloride, cobalt chloride, potassium chloride, chromium chloride, calcium chloride, cadmium chloride, nickel chloride, hydrochloric acid and ascorbic acid (AA) were purchased from Sinophem Chemical Reagents Co. LTD. (Shanghai, China). Glutathione was purchased from Aladdin. $HAuCl_4 \cdot 3H_2O$, 4-chloro-1-naphthol were purchased from Sigma Aldrich. All

reagents are analytical pure and and used without further purification. Milli-Q ultrapure water (Millipore, ≥18 MΩ cm) was used throughout.

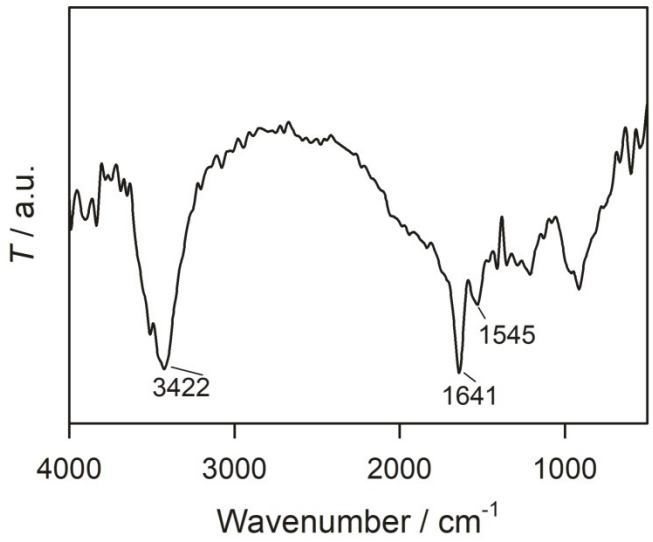


Fig. S1 FT-IR spectrum of AuNCs.

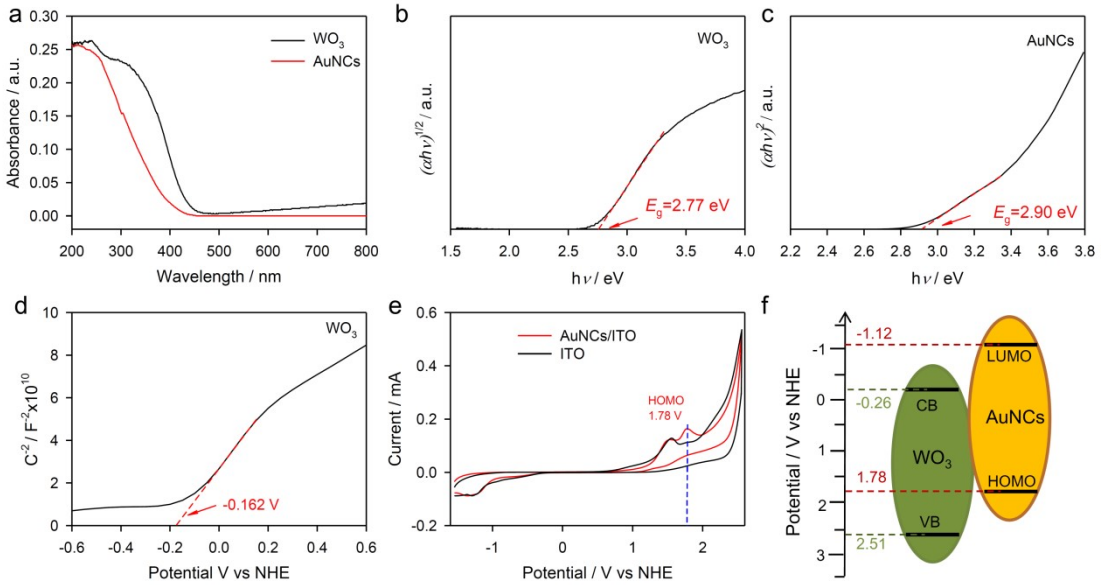


Fig. S2 (a) UV-vis diffuse reflectance spectra of WO_3 and AuNCs. (b) Plot of $(\alpha h\nu)^{1/2}$ versus hν for WO_3. (c) $(\alpha h\nu)^2$ versus hν for AuNCs. (d) Mott-Schottky plot of WO_3. (e) Cyclic voltammogram of AuNCs in degassed acetonitrile solution containing 0.1 M tetrabutyl ammonium perchlorate. (f) Illustration of energy-levels of AuNCs and WO_3.

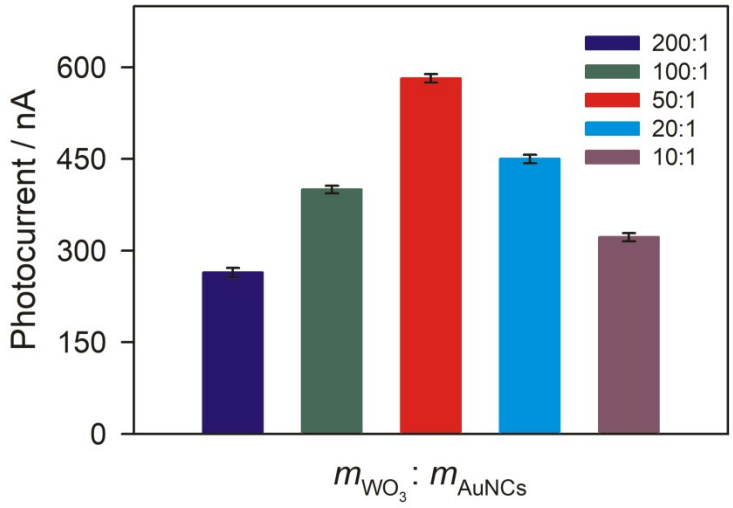
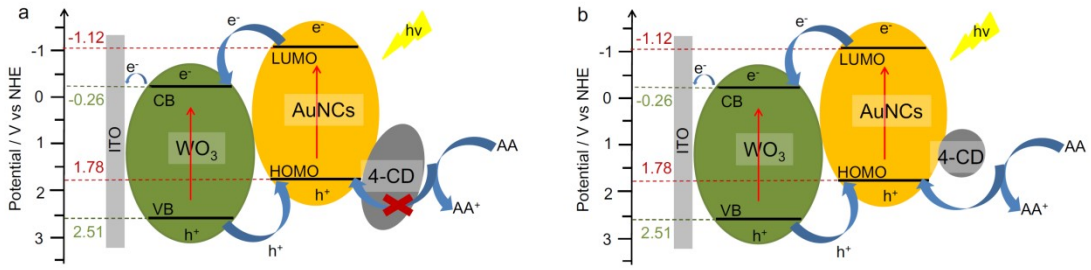


Fig. S3 Effects of weight ratios of WO_3 to AuNCs in WO_3/AuNCs on transient photocurrents of the prepared WO_3/AuNCs.



Scheme S1 (a) Charge transfer pathway of WO_3/AuNCs/ITO after 4-CN + H_2O_2 incubation. (b) Charge transfer pathway of WO_3/AuNCs/ITO after Hg^{2+} incubation and then 4-CN + H_2O_2 incubation.

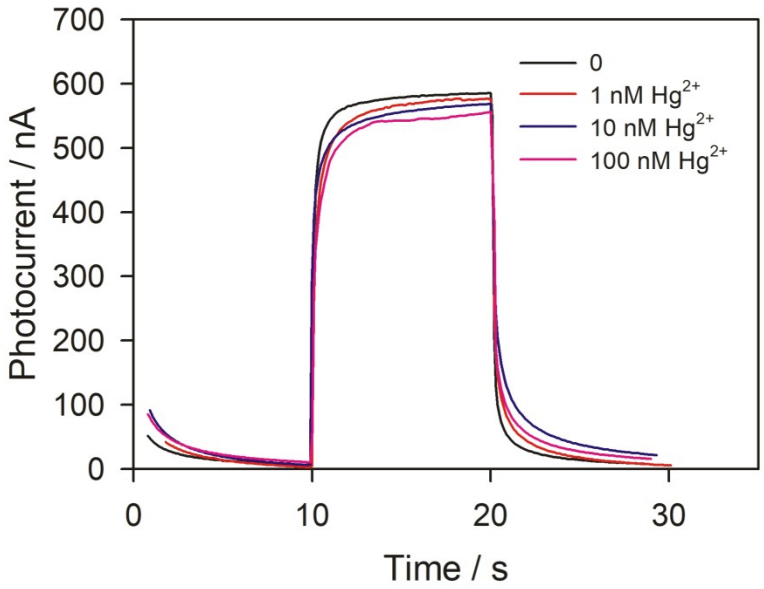


Fig. S4 Transient photocurrents of WO_3/AuNCs/ITO after the incubation with different concentrations of Hg^{2+}.

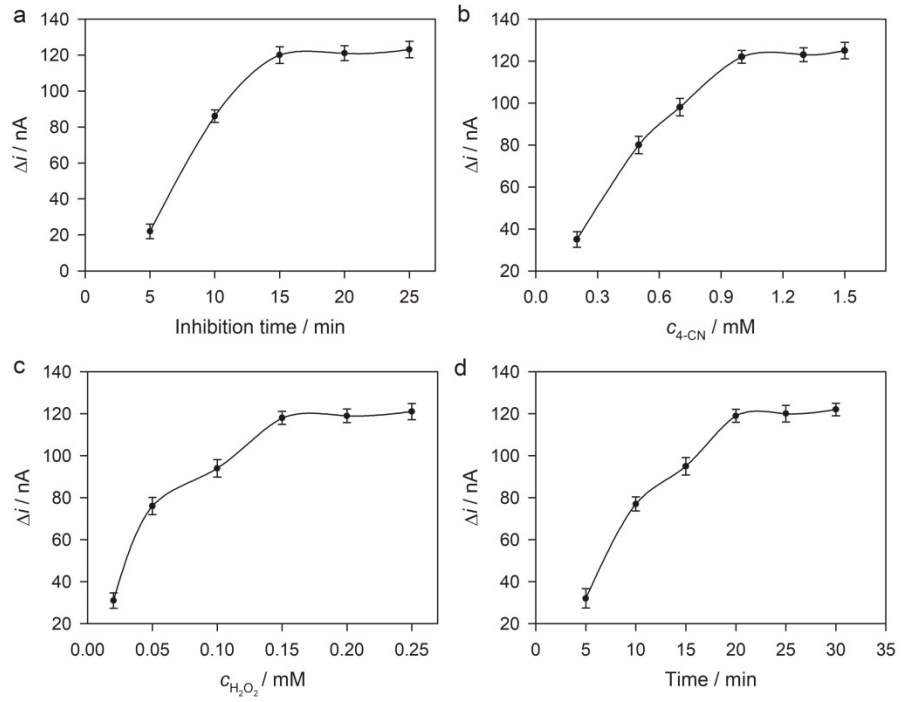


Fig. S5 Effects of (a) Hg^{2+} inhibition time, (b) 4-CN concentration, (c) H_2O_2 concentration, and (d) precipitation reaction time on photocurrent responses for detecting 10 nM Hg^{2+}.

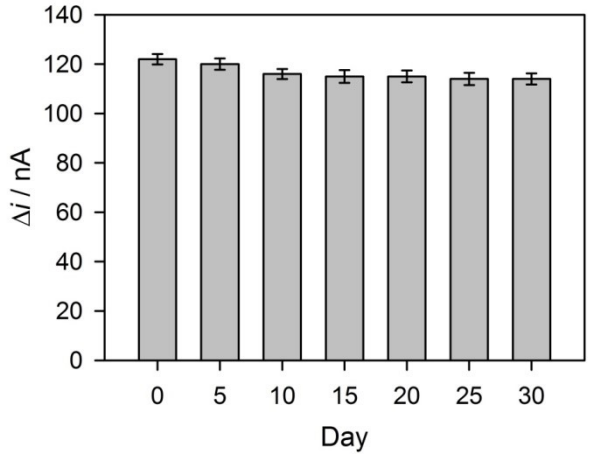


Fig. S6 Storage stability of the PEC sensor for detection of 10 nM Hg^{2+}.

Table S1. The comparison of the determination of Hg^{2+} in the literature.

Technique	Linear range (pM)	Detection limit (pM)	Ref.
Electrochemistry	1.0×10^4-1.0×10^6	5.8×10^3	1
Electrochemistry	1.0×10^2-1.3×10^5	30	2
Electrochemistry	5.0×10^2-5.0×10^6	2.3×10^2	3
Colorimetry	3.0×10^3-5.0×10^5	3.0×10^3	4
Colorimetry	2.0×10^4-2.0×10^7	5.0×10^3	5
Fluorescence	10-1.0×10^5	4.5	6
Fluorescence	100-1.0×10^5	65	7
Fluorescence	1.0×10^3-5.0×10^6	3.5×10^2	8
Fluorescence	1.0×10^5-6.0×10^6	3.8×10^3	9
Fluorescence	0-1.6×10^3	1.1×10^2	10
Surface-enhanced Raman scattering	1-10^3	0.4	11
Surface-enhanced Raman scattering	100-10^4	30	12
Photoelectrochemistry	1.0-2.0×10^3	1.0	13
Photoelectrochemistry	1.0-5.0×10^3	0.5	14
Photoelectrochemistry	1.0-5.0×10^4	0.2	This work

Table S2. Results of determination of Hg^{2+} in a river water sample.

Original (pM)	Added (pM)	Detected (pM)	Recovery (%)	RSD
	10.00	58.30	94.0	3.3
52.00	100.0	146.0	96.0	4.7
	1000	1092	104	1.1

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