Supplementary Information

Construction of a Dual-signal Molecularly Imprinted Photoelectrochemical Sensor Based on Bias Potential Controlled for Selective Sensing of Tetracycline

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Materials

Zinc chloride ($ZnCl_2$), thiacetamide (CH_3CSNH_2, TAA), chloroauric acid ($HAuCl_4 \cdot 4H_2O$), potassium ferricyanide ($K_3[Fe(CN)_6]$), potassium ferrocyanide($K_4Fe(CN)_6$) and other reagents were obtained from Chengdu Kelon co., Ltd. Indium chloride tetrahydrate ($InCl_3 \cdot 4H_2O$) was purchased from Shanghai Macklin Biochemical Co. Ltd. Tetracycline (TC), aureomycin (AM), ciprofloxacin (CIP), kanamycin (KANA), gentamicin (GM), oxytetracycline (OTC), chloramphenicol (CAP) was supplied from Aladdin Reagent (Shanghai) Co. Ltd. The reagents used in the experiments were of analytical grade without further purification. Deionized water was used throughout this study.

Apparatus

The microstructure of the samples were obtained on a Hitachi S-4800 scanning electron microscope (SEM). Transmission electron microscopy images (TEM) were performed by a TF-20 microscope. The surface topography and the root mean square roughness were measured by employing SEM (FEI Nova NanoSEM 230) and AFM (BRUKER Dimension Icon). X-ray diffraction (XRD) patterns were tested by using a DX-2700 X-ray powder diffractometer with Cu Kα radiation at room temperature. The X-ray photoelectron spectroscopy (XPS) measurements were collected on a Nexsa photoelectron spectrometer with an Al Kα X-ray beam by Thermo Scientific. Ultraviolet visible (UV–vis) diffuse reflectance spectra were measured with a PerkinEImerLambda850 UV–vis spectrometer. Fluorescence (FL) spectra were carried out on a PerKinEImer LS55 fluorescence spectrophotometer with an excitation wavelength of 420 nm. All the electrochemical experiments and PEC signals were recorded on a CHI 650E electrochemical workstation.

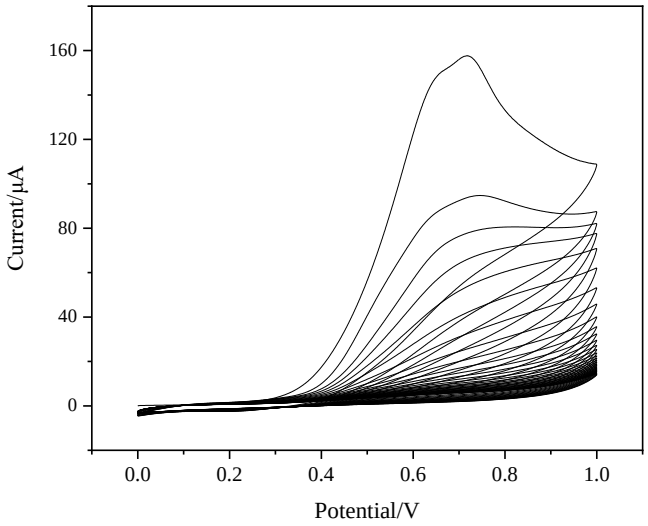

Fig. S1. Cyclic voltammogram curve of electropolymerization.

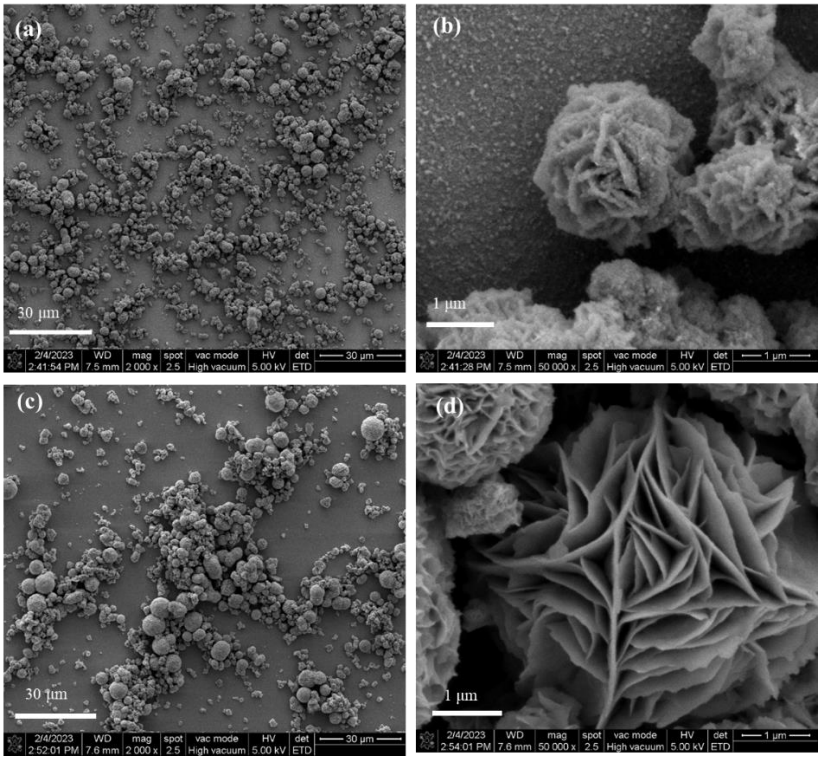

Fig. S2. SEM images of MIP (a) and (b), NIP (c) and (d).

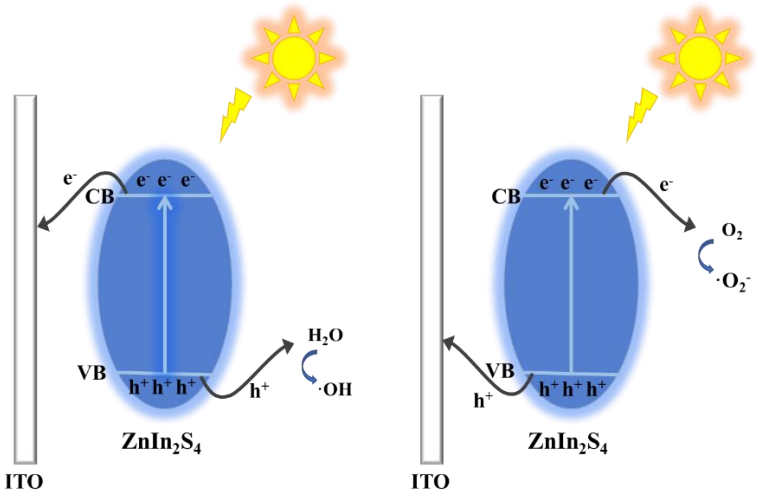

Fig. S3. The possible electron-transfer mechanism of $ZnIn_2S_4$ at 0.2 V and -0.3 V.

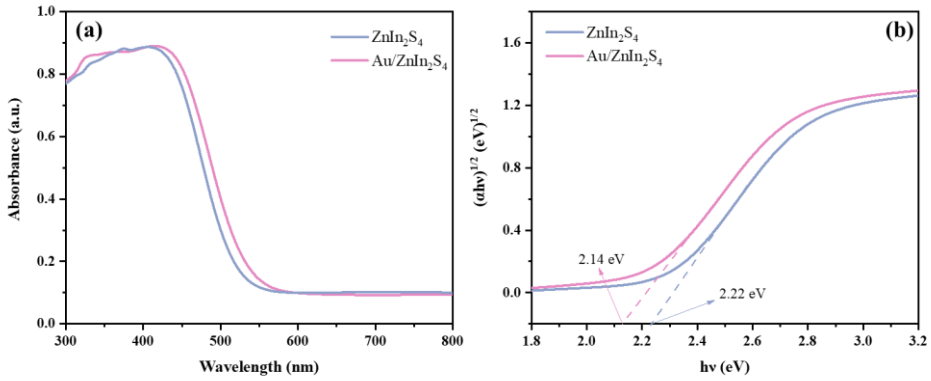

Fig. S4. UV-vis diffuse reflectance spectra (a) of $ZnIn_2S_4$ and Au/ $ZnIn_2S_4$; the band-gap energies (b) of $ZnIn_2S_4$ and Au/ $ZnIn_2S_4$ samples.

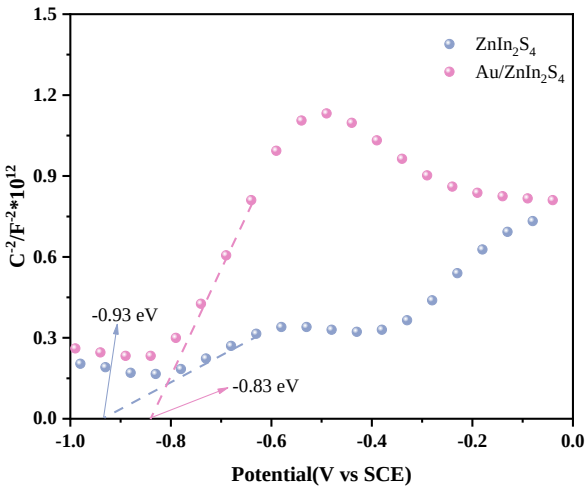

Fig. S5. M-S plots of $ZnIn_2S_4$ and Au/ $ZnIn_2S_4$ samples.

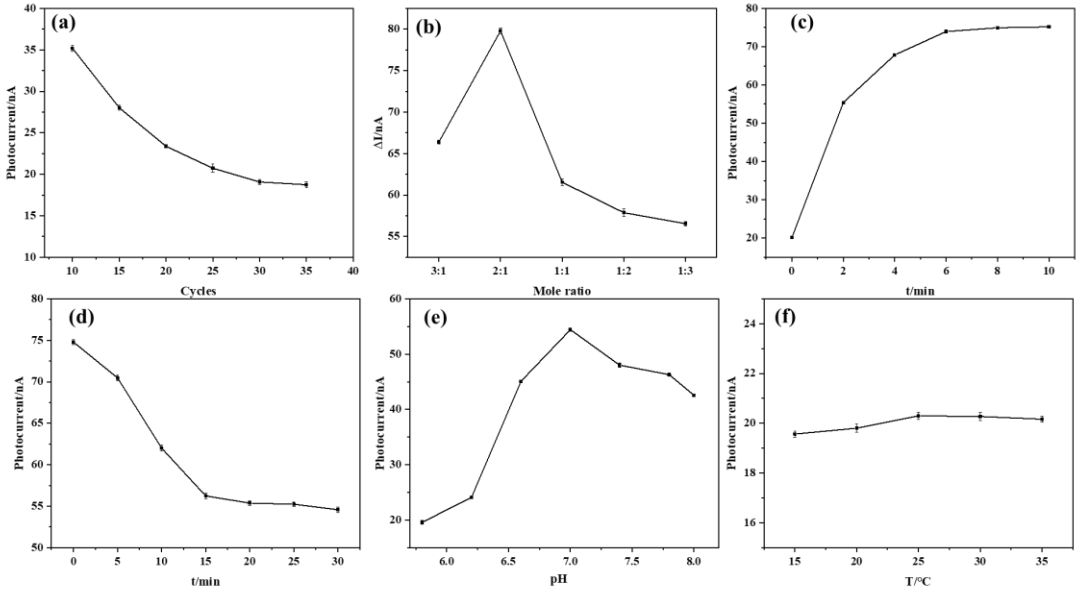

Fig. S6. Optimization of the number of polymerization circles (a); Optimization of molar ratio of functional monomer and template molecule (b); Optimization of elution time (c); Effect of incubation time (d); Effect of pH value of polymerization solution (e); Effect of experimental temperature (f).

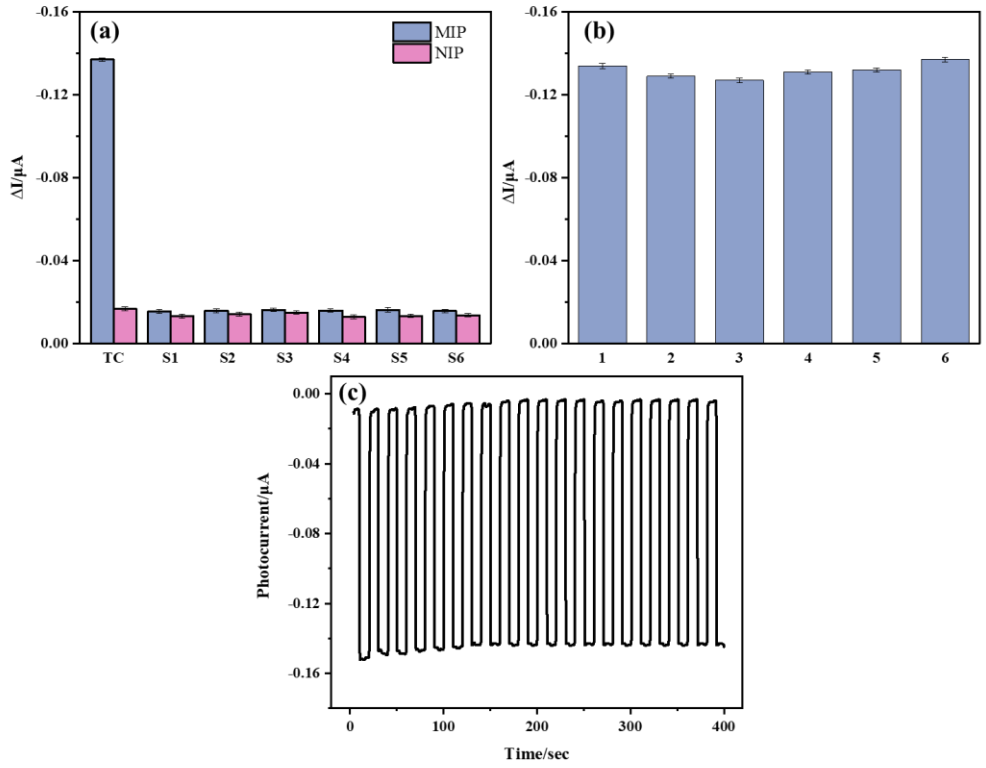

Fig. S7. Selectivity (a) of MIP-PEC and NIP-PEC sensor for TC and its analogues (S1-S6, AM, OTC, CAP, GM, KANA, CIP). Stability analysis (b) and reproducibility analysis (c) of MIP-PEC sensor. All the photocurrent tests were performed at a bias of -0.3 V.

Table S1. Anodic detection of TC in river water and milk sample.

Sample	Added(nM)	Founded(nM)	Recovery(%)	RSD(%)
River water	50	48. 9	97. 8	1. 94
	100	102. 4	102. 4	2. 85
	200	203. 2	101. 6	2. 93
Milk	10	9. 82	98. 2	2. 41
	20	19. 5	97. 5	3. 06
	50	53. 1	106. 2	2. 75

Table S2. Cathodic detection of TC in river water and milk sample.

Sample	Added(nM)	Founded(nM)	Recovery(%)	RSD(%)
River water	50	49. 2	98. 4	2. 31
	100	103. 6	103. 6	3. 15
	200	199. 1	99. 6	3. 02
Milk	10	9. 79	97. 9	2. 96
	20	19. 5	96. 8	3. 21
	50	51. 4	102. 8	3. 54