Supplemental files

Highly efficient detection of ciprofloxacin with a self-powered sensing device

based on Au NPs/g-C₃N₄ micron tube and 3D Ni-doped ZnIn₂S₄ thin film

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1. Materials and reagents

All reagents were used directly without any more purified. The ultrapure water was acquired from Millipore system (18.2MΩ.cm). Melamine, Nafion (5 wt.%), rhodamine B (RhB), 4-hydroxybenzoic acid (4-HBA), methyl orange (MO), 4-aminobenzoic acid (4-ABA)), Ethylene diamine tetraacetic acid (EDTA), glacial acetic acid, methanol, ethanol, ZnSO₄·7H₂O, NiCl₂·6H₂O, NaH₂PO₄·2H₂O and Na₂HPO₄·12H₂O were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Tris(2-carboxyethyl)phosphine (TCEP), Thioacetamide (TAA), 6-Mercaptohexanol (MCH), tris (hydroxymethyl) aminomethane (Tris), NaCl, MgCl₂, KCl were the products of Sigma-Aldrich (St. Louis, MO, USA). AuCl₃·HCl·3H₂O, ciprofloxacin (CIP), bisphenol A (BPA) and InCl₃·4H₂O were purchased from Yien Chemical Technology Co., Ltd (Shanghai, China).

TE binding buffer solution consists of 50 mM Tris-HCl solution (pH 7.4), 0.1 M NaCl, 5 mM MgCl₂, 0.2 M KCl and 1.0 mM EDTA, and the Tris-HCl solution (pH 7.4) was prepared by adjusting the pH of Tris solution to 7.4 with HCl (1 M), which was sterilized in a high-temperature sterilization pot for later use. The probe solution was obtained by dissolving moderate TCEP in TE binding buffer solution. The high-performance liquid chromatography-purified Single-stranded DNA (ssDNA) aptamer with the following sequences was selected according to previous research ¹: 5'-Thiol-ATACCAGCTTATTCAATTCGATGGTAAGTGAGGTTCGTCCCTTTAATAAACTCGATTAGG ATCTCGTGAGGTGTGCTCTACAATCGTAATCAGTTAG-3' (Sangon (Shanghai, China))

2. Equipment

The 3D micromodel was fabricated by the micro-Arch S240 printing system (BMF Precision

Tech Inc., Shenzhen, China). The morphologies and structures of photoactive materials were inspected by Scanning electron microscopy (SEM, MIRA4 from TESCAN). The diffuse reflectance spectra were measured by the spectrophotometer (Hitach U4100 UV Spectrometer) with fine BaSO₄ powder as reference. The X-ray diffraction (XRD) was used to analyze crystal phase of the samples. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Fisher ESCALANB 250Xi spectrometer. The photoluminescence (PL) spectra were obtained by a Hitachi-7000 fluorescence spectrometer. The inductively coupled plasma mass spectrometry (ICP-MS) results were conducted on an Agilent 7900 ICP-MS. The electrochemical impedance spectroscopy (EIS) was carried out on an electrochemical workstation (CHI 660E) with a three-electrode system in 0.1 M KCl solution containing 5 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] mixture as a redox probe. The open-circuit potential (OCP) curve was measured by placing the photoelectrodes in the one-compartment cell. The V-I curve was obtained with galvanostatic polarization technique and the P-I curve was obtained by plotting the power density (V×I/A) vs the current, where A was the geometric area of the photoanode.

3. Experimental procedure

3.1 Synthesis of Au nanoparticles modified g-C₃N₄ micron tube

The photoreduction method was used to accelerate the reduction and adhering of Au nanoparticles (NPs) on the surface of $g-C_3N_4$ micron tube. In brief, the obtained $g-C_3N_4$ hollow tubular powder was dissolved in 80 mL methanol/water solution (20 wt.%) under ultrasonic for 10 min, then the mixture solution was magnetic stirred for 20 min. After that, 400 µL HAuCl₄ solution (1 wt.%) was slowly dripped into the above solution under dark conditions and continuously stirred for 60 min. Then the

mixture solution was continuously stirred for 60 min under a Xenon arc lamp irradiation. Finally, the Au NPs modified $g-C_3N_4$ micron tube was obtained after washing and dried at 60 °C for 10 h, marked as Au NPs/g-C₃N₄ tube. The Au NPs/g-C₃N₄ micron tube composites modified FTO electrode was prepared through the classic drop-casting technique ². In general, a certain amount of Au/g-C₃N₄ material was dissolved in nafion/ethanol (the proportion of nafion and ethanol is 7:3, v : v) mixture, and after sonicated continuously for ~60 min, the photoanode modified by Au/g-C₃N₄ was successfully prepared by annealing at 200 °C for 7 min.

3.2 The real photos of the procedure of fabricating Ni-doped ZnIn₂S₄ thin-film modified photocathode with different electroactive area



Fig. S1. The real photos of the fabrication procedure from FTO conductive glass to Ni-doped $ZnIn_2S_4$ thin-film modified photocathode with different electroactive area. (a), The FTO conductive glass (1×2 cm), Ni-doped $ZnIn_2S_4$ thin-film modified FTO (b) after hydrothermal reaction, (c) with an electroactive area of 1 cm², (d) with an electroactive area of 0.5 cm² and (e) with an electroactive area of 0.25 cm².

3.3 Possible formation mechanism of Ni-doped ZnIn₂S₄ photocathode

Based on the results of SEM, a possible formation mechanism of Ni-doped $ZnIn_2S_4$ thin-film modified FTO with three-dimensional (3D) reticulate structures is proposed as follows: The TAA plays as a chelating agent in the above hydrothermal reaction process, forms metal complexes including $Ni(TAA)^{2+}$, $Zn(TAA)^{2+}$ and $In(TAA)^{3+}$.(Eqs.(1), (2) and (3))³.

$$Ni^{2+}TAA \longleftrightarrow [Ni(TAA)]^{2+}$$
(1)

$$Zn^{2+}+TAA \longleftrightarrow [Zn(TAA)]^{2+}$$
 (2)

$$In^{2+}+TAA \longleftrightarrow [In(TAA)]^{3+}$$
 (3)

Meanwhile, TAA can contribute S to the reaction.

$$4CH_3CSNH_2 + H_2O \quad \blacktriangleleft \quad \textcircled{H}_3CONH_2 + H_2S \tag{4}$$

$$H_2S \leftarrow HS^-+H^+$$
 (5)

$$HS^{-} \longleftarrow H^{+} + S^{2-} \tag{6}$$

Therefore, the total reaction equation is shown below:

$$xNi^{2+}+(1-x)Zn^{2+}+2In^{3+}+4CH_{3}CSNH_{2}+4H_{2}O \rightarrow Ni_{x}Zn_{1-x}In_{2}S_{4}+4CH_{3}CONH_{2}+8H^{+}$$
(7)

4. Discussion

4.1 ICP-MS results

Table S1. Summary of ICP-MS results of Ni doping concentration (wt.%)

Commission 1 and	Addition amount of NiCl ₂ ·6H ₂ O	Measured value of Ni concentration	
Samples	(mmol)	(ICP-MS) (wt%)	
Ni-doped ZnIn ₂ S ₄ -1	4	1.2 %	
Ni-doped ZnIn ₂ S ₄ -2	6	1.6 %	
Ni-doped ZnIn ₂ S ₄ -3	8	2.0 %	
Ni-doped ZnIn ₂ S ₄ -4	10	2.7 %	
Ni-doped ZnIn ₂ S ₄ -5	12	3.0 %	

4.2 XPS

X-ray photoelectron spectroscopy (XPS) was performed to explore the surface chemical status of g-C₃N₄ nanotube, Au NPs/g-C₃N₄ nanotube, ZnIn₂S₄ and Ni-doped ZnIn₂S₄-3. The full scan spectrum displayed in Fig. S1 and Fig.S2 verified the presence of each element in Au NPs/g-C₃N₄ nanotube and Ni-doped ZnIn₂S₄-3 respectively. The high-resolution spectra of Au 4f, C 1s, N 1s, and O 1s were displayed in Fig. S1, while In 3d, Zn 2p and S 2p were displayed in Fig. S2. the Au 4f XPS spectrum showing two typical peaks at 83.02 and 86.80 eV ascribed to Au 4f_{7/2} and Au 4f_{5/2} respectively, which are well defined in relation to the metallic Au^{0 4}. It is noted that the XPS spectrum of Zn 2p in Nidoped ZnIn₂S₄-3 was deconvoluted into two peaks, the one peak at 1023.40 eV and the other peak at 1045.20 eV are corresponded to Zn 2p_{3/2} and Zn 2p_{1/2} respectively ⁵, which are shift to higher binding energy than those of ZnIn₂S₄-3. Meanwhile, the S 2p XPS spectrum shown that the binding energies of S $2p_{1/2}$ (161.20 eV) and S $2p_{3/2}$ (162.30 eV) in Ni-doped ZnIn₂S₄-3 are higher than those of ZnIn₂S₄-3, whereas the binding energies of In 3d in the two materials are almost identical. These changes can be attributed to the selectively doping of Ni at the sites of tetrahedral Zn rather than In sites ⁶. However, the typical peak of Ni 2p was not obvious because of its low content.



Fig. S2 (A) The full scan XPS spectrum of $g-C_3N_4$ micron tube and Au NPs/ $g-C_3N_4$ micron tube, (B-E) High-resolution XPS of Au 4f, C1s, N 1s and O 1s of $g-C_3N_4$ micron tube and Au NPs/ $g-C_3N_4$ micron tube



Fig. S3 (A) The full scan XPS spectrum of $ZnIn_2S_4$ and Ni-doped $ZnIn_2S_4$ -3, (B-D) High-resolution XPS of In 3d, S2p, Zn 2p in $ZnIn_2S_4$ and Ni-doped $ZnIn_2S_4$ -3

4.3 The OCP signal under intermittent illumination



Fig. S4 The OCP signal under intermittent illumination

4.4 Optimization of experimental conditions for PEC detection



Fig.S5. The effect of (A) Au wt.% in Au NPs/g-C₃N₄ tube composites; (B) pH value of PBS electrolyte solution; (C) concentration of aptamer in TCEP solution (pH 7.4); (D) incubation time with CIP

4.5 Calculation of the limit of detection (LOD)

The limit of detection (LOD) was calculated from $3\sigma/s$, where 3 is the measurement times of blank samples, σ is the standard deviation of the blank response and s is the slope of the calibration

$$\sigma = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2},$$
 w

curve. The computational formula of σ is: $\sqrt{1-\frac{1}{i=1}}$, where n=3. As for the proposed sensor, the calculated results of σ and s were 8×10⁻⁶ and 0.0008, therefore, the obtained determination of limit is 0.03 ng/mL.

4.6 Recovery and precision analysis of proposed sensor for detection of CIP in real samples

Table S2. Recovery and precision analysis of proposed sensor for detection of CIP in real samples

Sample	Added (ng/mL)	Content [mean ± SD(RSD%), n=3, ng/mL]			
		PEC aptasensor	Recovery (%)	HPLC-UV	Recovery (%)
Sewage 1	0	$6.25 \pm 0.10(1.64)$			
	100	$112.90 \pm 2.82(2.50)$	106.65	$107.58 \pm 2.54 (2.50)$	
	1000	$1086.06 \pm 36.93 (3.40)$	107.98	$1059.64 \pm 55.31 (5.22)$	95.21
	2000	$2056.40 \pm 58.60 (2.85)$	102.25	$2048.35 \pm 66.37 (3.24)$	97.04
	3000	$3156.33 \pm 133.20 (4.22)$	105.05	$3128.25\pm80.71(2.58)$	100.69
Sewage 2	0	$15.18 \pm 0.23 (1.51)$			
	100	$115.88 \pm 3.87 (3.34)$	100.70	$110.25 \pm 1.23 (1.12)$	
	1000	$1086.52 \pm 43.79 (4.03)$	107.14	$1054.33 \pm 44.60 (4.23)$	94.40
	2000	$2075.36 \pm 75.75 (3.65)$	103.01	2041.86 ± 66.16 (3.24)	96.58
	3000	$3182.65 \pm 143.86 (4.52)$	105.58	$3126.59\pm90.05(2.88)$	100.54
Milk 1	0	$3.758 \pm 0.04 (0.98)$			
	100	$101.06 \pm 1.18(1.17)$	97.30	$105.45 \pm 0.94 (0.89)$	
	1000	$1086.3 \pm 21.83 (2.01)$	108.06	$1045.29 \pm 25.51 (2.44)$	93.98
	2000	$2043.18 \pm 93.58 (4.58)$	102.00	$2015.86 \pm 103.21 (5.12)$	95.52
	3000	$3128.46 \pm 120.76 (3.86)$	104.16	$3104.52 \pm 116.11 (3.74)$	100.00
Milk 2	0	$1.25 \pm 0.01(1.07)$			
	100	$96.25 \pm 2.18 (2.26)$	95.05	$105.64 \pm 1.25 (1.18)$	
	1000	$987.55 \pm 30.02 (3.04)$	98.63	$1024.63 \pm 51.64 (5.04)$	91.90
	2000	$2015.64 \pm 84.25 (4.18)$	100.72	$2002.56 \pm 50.87 (2.54)$	94.85
	3000	$3117.25 \pm 141.83 (4.55)$	103.87	$3059.86 \pm 94.24 (3.08)$	98.47
Milk 3	0	$6.25 \pm 0.08 (1.28)$			
	100	$105.08 \pm 4.57 (4.35)$	98.83	$99.64 \pm 1.13 (1.13)$	
	1000	$1053.33 \pm 21.38 (2.03)$	104.16	$1059.64 \pm 29.35 (2.77)$	96.00
	2000	$2064.86 \pm 75.99 (3.68)$	102.93	$2098.56 \pm 60.65 (2.89)$	99.95
	3000	$3125.68 \pm 145.34 (4.65)$	103.98	$3198.65 \pm 111.31(3.48)$	103.30
Milk 4	0	$5.03 \pm 0.06 (1.11)$			

100	102.54± 2.18(2.13)	97.53	$100.64 \pm 1.35 (1.34)$	
1000	$1021.88 \pm 31.17 (3.05)$	101.68	$1068.72 \pm 30.89 (2.89)$	96.81
2000	$2043.84 \pm 74.40 (3.64)$	101.94	2024.63 ±77.95(3.85)	96.20
3000	$3094.25 \pm 130.58 (4.22)$	103.11	$3058.93 \pm 114.40 (3.74)$	98.61

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