Supporting Information

A novel label-free photoelectrochemical aptasensor for the sensitive detection of ampicillin based on carbon-coated Bi_2S_3 nanorods

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Experimental

1. Materials and reagents

Bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$) was supplied from Aladdin Chemical Reagent Company (Shanghai, China). Thioacetamide, ethylene glycol, glutaraldehyde and other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd (China). Glucose was provided by Shanghai Miura Chemical Co., Ltd. Chitosan was provided by Ark Pharm Co., Ltd (USA). Streptomycin (STR), kanamycin (KANA), oxytetracycline (OTC), lincomycin (LIN) and ampicillin (AMP) were provided by Sangon Biotech Co., Ltd (Shanghai, China). Cefprozil (CPZ) was purchased from Shanghai Macleans Biochemical Technology Co., Ltd. Amoxicillin (AMX), oxacillin (OXC), cefdinir (CFD) were purchased from Shanghai Myrell Chemical Technology Co., Ltd. The DNA aptamer for AMP and myoglobin (Mb) were synthesized by Shanghai Sangon Biotech Co., Ltd with the following sequence: 5'-NH_2-$(CH_2)_6$-TTT TGC GGG CGG TTG TAT AGC GG-3' ($K_d \approx 13.4$ nM)[1] and 5'-NH_2-$(CH_2)_6$-CCC TCC TTT CCT TCG ACG TAG ATC TGC TGC GTT GTT CCG A-3'. 0.1 mol L^{-1} phosphate buffered saline (PBS, pH 7.4) was employed as the supporting electrolyte and washing buffer. Bovine serum albumin (BSA, 96-99%) was obtained from Sigma-Aldrich Co., Ltd (USA). The other chemicals were of analytical grade and used without further purification. All aqueous solutions were prepared with twice-distilled water throughout the whole experiments. The real water samples were used only after simple filtration.

2. Apparatus

The morphology and structure of the samples were characterized by scanning electron microscopy (SEM) with a ZEISS GeminiSEM 300 scanning electron microanalyzer with an accelerating voltage of 5.00 kV. The morphology and composition of the samples were examined by transmission electron microscopy (TEM), high-resolution TEM (HR-TEM) operated at a JEM-2100F microscope. X-ray diffraction (XRD) analysis was performed on a Rigaku Dmax-2000 diffractometer (Bruker Co., Germany). X-ray photoelectron spectra (XPS) were acquired to determine the chemical compositions and valence states at a K-Alpha XPS spectrometer (SCIENTIFIC ESCALAB 250) with Al Kα X-ray radiation (1486.6 eV). Electrochemical impedance spectra (EIS) were recorded by the IM6e impedance measurement unit of Zahner workstation (Zahner, Germany).

3. Photoelectrochemical measurements

The PEC experiment was carried out on a PEC device equipped with a 5 W LED lamp (effective light density is about 700 μW cm^{-2}) with a wavelength of 450 nm as the excitation light source. Photocurrents were performed with a CHI 660A electrochemical workstation (China) in a three-electrode system: a modified electrode with a geometrical circular area (5.0 mm in diameter) as the working electrode, a Pt wire as the counter electrode and a saturated Ag/AgCl electrode as the reference electrode.

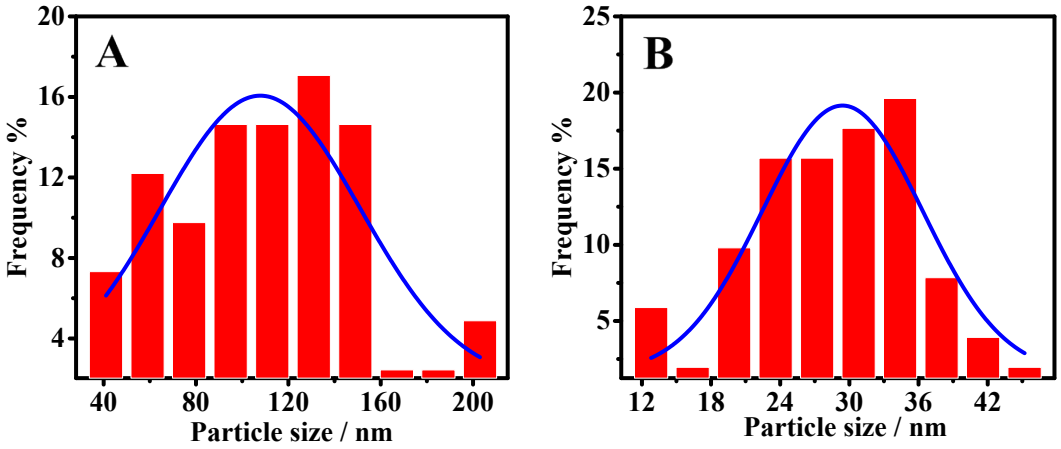

Fig. S1. The length (A) and width (B) size distributions of Bi_2S_3@C NRs.

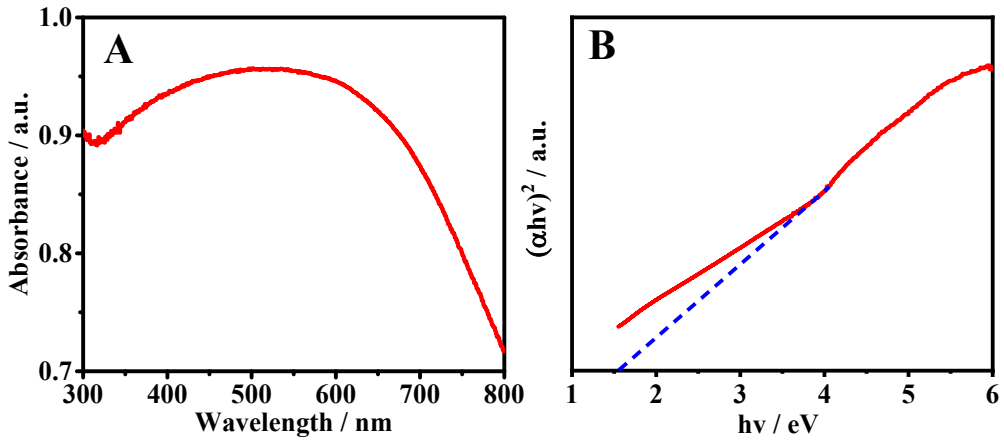

Fig. S2. UV-vis diffuse reflectance spectra (A) and the corresponding band gap energy (B) of Bi_2S_3@C NRs.

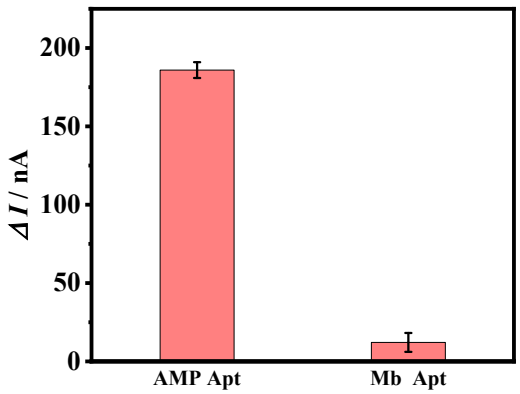

Fig. S3. The comparison of photocurrent response to AMP of the constructed aptasensor using AMP-aptamer and Mb-aptamer (C_{AMP} = 1.0 pg mL^{-1}).

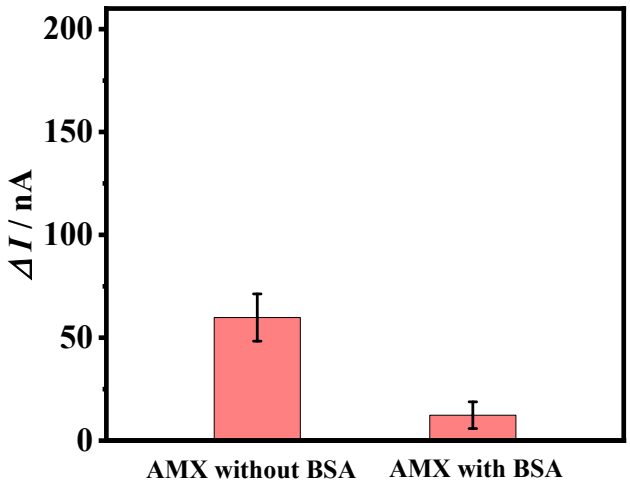

Fig. S4. Comparison of the photocurrent response to interferent-AMX of the aptasensor prepared with or without BSA blocking in the construction step (C_{AMX} = 1.0 pg mL^{-1}).

Table S1. Comparison of the developed method with those in the literature for the detection of AMP.

Method	Detection limit (ng mL^{-1})	Liner range (ng mL^{-1})	Reference
Colorimetric	10	25~1200	2
Fiber optic nanoplasmonic	0.74	4.0~4.0×10^{4}	3
Microwave electrodynamic resonator	4.0×10^{3}	4.0×10^{6}~5.0×10^{7}	4
FRET-enhanced nanoflares	0.65	1.8~20	5
Fluorescence	2.71×10^{-3}	0.01~0.20	6
Electromembrane microextraction followed by high-performance liquid chromatography	0.60	2.0~100	7
Colorimetric	2.60×10^{4}	6.0×10^{4}~1.0×10^{6}	8
PEC	1.01×10^{-4}	2.02×10^{-4}~4.03	9
Fluorescence	3.48×10^{-10}	1.0×10^{-5}~1.0×10^{-9}	10
PEC	5.01×10^{-5}	1.0×10^{-4}～5.0×10^{-3}	This work

Table S2. Detection of AMP in tap water and river water samples with the as-constructed aptasensor.

Samples	Added (fg mL^{-1})		Measured (fg mL^{-1})		Average (fg mL^{-1})	Recovery (%)	RSD (%, n=3)
Tap water	1000.0	919.23	1049.0	970.01	979.41	97.94%	6.68%
	500.00	565.79	514.84	544.83	541.82	108.36%	4.73%
	100.00	104.90	96.760	101.02	100.89	100.89%	4.04%
River water	1000.0	1043.3	1034.8	1110.4	1062.8	106.28%	3.90%
	500.0	525.05	506.87	516.54	516.15	103.23%	1.76%
	100.0	105.00	101.09	95.750	100.61	100.61%	4.62%

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