# **Electronic supplementary information**

## A Potentiometric resolved ratiometric photoelectrochemical aptasensor

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Experimental section, synthesis procedures, X-Ray Diffraction, SEM of BiPO<sub>4</sub> NPs and BiPO<sub>4</sub>-rGO NCs, fabrication of PEC aptasensor, selectivity study of PEC aptasensor were in this supporting information.

### **Experimental Section**

**Materials and reagents.** Graphene Oxide (GO) was synthesized from natural graphene powder by a modified Hummers method.<sup>1</sup> Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O, ethylene glycol (EG) were purchased from Sinopharm Chemical Reagent Co., Ltd. OTA-Aptamer: 5'-GAT CGG GTG TGG GTG GCG TAA AGG GAG CAT CGG ACA-3', was purchased by Sangon Biotechnology Co., Ltd. (Shanghai, China). The oligonucleotides stock solution was prepared by dissolving the oligonucleotides in 0.1 M PBS buffer (pH 7.4, containing 0.1 M NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O and 0.1 M Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O) and was stored at 4 °C before use. Ochratoxin A (OTA), aflatoxin B1 (AFB1), fumonisin B1 (FB1) were obtained from Sigma-Aldrich. All reagents were used as purchased without further purification. Ultrapure water obtained from a Milli-Q grade water (18.2 Ω) in the study.

**Apparatus.** X-ray diffraction (XRD) was operated using a D8 ADVANCE diffractometer system equipped with Cu K $\alpha$  radiation (Bruker Co., Germany). Scanning electron microscope (SEM) was conducted with a JEOL JSM-6700 SEM technique (JEOL, Japan). PEC currents measurements were performed by a CHI 660B electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) in a standard three-electrode cell system which used the ITO as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum (Pt) wire as the counter electrode. All the PEC measurements were carried out in phosphate buffer solution (PBS) and a 500 W Xe lamp (CHF-XM35-500W, Beijing Chang tuo) was utilized as the visible light source with an intensity of 100 mW cm<sup>-2</sup>. Current-time (I–t)

method was used for the whole PEC experiments.

#### Preparation of pristine BiPO<sub>4</sub> NPs and BiPO<sub>4</sub>-rGO NCs

The synthesis procedures of BiPO<sub>4</sub>-rGO NCs were as follows. Firstly, 7.5 mg GO (the starting mass ratio of GO to BiPO<sub>4</sub>=0.1) was added into EG and the mixture was sonicated for 60 min to obtain homogeneous suspension. Secondly, 0.121 g of  $Bi(NO_3)_2 \cdot 5H_2O$  and 0.140 g NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O were added into the above suspension in turn with strring for 1 h, respectively. Thirdly, the resulting precursor suspension was sealed into a Teflon-lined autoclave and maintained at 160 °C for 12 h and it was allowed to cool to room temperature, and the product was centrifuged and washed with ultrapure water and alcohol for thrice. Finally, the compound was dried in a oven at 60 °C. Pure BiPO<sub>4</sub> NPs were also prepared under the same condition without the addition of GO sheets.

#### Progressively fabrication and detection process of photoelectrochemical aptasensor

First of all, the production of modified ITO electrodes, the resulting BiPO<sub>4</sub>-rGO NCs were dissolved in ultrapure water to obtain suspension and the ITO electrodes were placed in boiling water cotaining 0.1 M NaOH solution for 30 min, and then were ultrasonically cleaned in water and alcohol for 30 min. Next, 20  $\mu$ L of BiPO<sub>4</sub>-rGO NCs and BiPO<sub>4</sub> NPs suspension were dropped onto two adjacent areas of the ITO electrode with a fixed area of 0.5 cm<sup>2</sup> respectively and dried in room temperature to produce a BiPO<sub>4</sub>-rGO/BiPO<sub>4</sub> dual modified ITO electrode. Afterwards, 10  $\mu$ L of 1  $\mu$ M aptamer was dropped onto BiPO<sub>4</sub>-rGO NCs area. The ITO electrodes kept for 12 h at 4 °C and then

rinsed with binding buffer to remove the excess nonadsorbed aptamer. 10  $\mu$ L of OTA target was incubated on the aptamer-modified electrodes at room temperature for 30 min and the electrodes were subsequently washed with binding buffer solution and subjected to PEC measurements.

#### Characterizations of the resulting BiPO<sub>4</sub>-rGO NCs

X-Ray Diffraction showed the distinctions of phase structures of the resulting products, it was firstly investigated in Fig. S1. For the pure BiPO<sub>4</sub> NPs (curve a), several major diffraction peaks at 20=18.930°, 21.241°, 27.029°, 28.979°, 31.106°, 41.988°, and 46.187° were indexed to the (011), (-111), (200), (120), (012), (-103), and (212) pure monoclinic phase of BiPO<sub>4</sub> NPs(JCPDS 15-0767).<sup>2</sup> The positions of the diffraction peaks of BiPO<sub>4</sub>-rGO NCs (curve b) were the same as pure BiPO<sub>4</sub> NPs (curve a) without any impurity peaks, manifesting both samples were possessed of high crystalline quality and indicating the BiPO<sub>4</sub>-rGO NCs was prepared successfully. In addition, the characteristic peak of GO in the BiPO<sub>4</sub>-rGO NCs was not detected, demonstrating bulk GO was reduced to rGO and rGO sheets did not pile together. Fig. S2 shows the typical SEM imagess of the resulting BiPO<sub>4</sub>-rGO NCs (A) and BiPO<sub>4</sub> NPs (B). In Fig. S2A, it was apparent to observe that a large number of BiPO<sub>4</sub> NPs were uniformly distributed on the surface of rGO nanosheets. From the Fig. S2B, when the  $BiPO_4$  NPs without introduction with rGO nanosheets were re-dispersed in the ultrapure water, they were agglomerated due to the large surface-to-volume ratio of BiPO<sub>4</sub> NPs.<sup>3</sup> It demonstrated that BiPO<sub>4</sub> NPs attached to the rGO sheets presented a better dispersity which caused a better PEC performance.



Fig. S1 XRD of the BiPO<sub>4</sub> NPs (a) and BiPO<sub>4</sub>-rGO NCs (b).



Fig. S2 The SEM of the BiPO<sub>4</sub>-rGO NCs (A) and BiPO<sub>4</sub> NPs (B).

## Selectivity study of PEC aptasensor

The selectivity of this PEC aptamer sensor was evaluated by comparing the photocurrent of aptamer/BiPO<sub>4</sub>-rGO/BiPO<sub>4</sub>/ITO toward similar targets (AFB1, FB1). As showed in Fig. S3, the ratio of the difference value of the photocurrent in the presence of OTA at 0.41 V was maximal, it demonstrated this aptasensor was sensitive to OTA and showed weaker response to AFB1 and FB1, attributed to the specific interaction between

aptamer and OTA molecules.



Fig. S3 The ratio of  $\Delta I/I_0$ ,  $\Delta I$  was the difference value between the photocurrent in the presence of 50 ng·ml<sup>-1</sup> OTA, 200 ng·ml<sup>-1</sup> AFB1 and FB1 and aptamer/BiPO<sub>4</sub>-rGO/BiPO<sub>4</sub>/ITO at 0.41 V, I<sub>0</sub> was the photocurrent of BiPO<sub>4</sub>-rGO/BiPO<sub>4</sub>/ITO at -0.068 V bias voltage.



**Fig. S4** Photocurrent of BiPO<sub>4</sub>-rGO/BiPO<sub>4</sub> dual modified ITO electrode under -0.068 V (A) and 0.41 V (B) at two months ago and later.

## References

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