### **Supporting Information**

# A self-powered aptasensor using the capacitor-amplified signal of a photofuel cell and a portable digital multimeter readout

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#### Experimental

#### Chemicals and apparatus.

STR, kanamycin (KAN), gentamicin (GEN) and doxycycline (DOX) were provided by Aladdin Reagent Co., Ltd. (Shanghai, China). Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, Na<sub>2</sub>WO<sub>4</sub>, HNO<sub>3</sub>, HAuCl<sub>4</sub>, trisodium citrate and other reagents of analytical grade were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Graphene oxide (GO) suspension was produced by Gaoxi Technology Co., Ltd. (Hangzhou, China). The STR aptamer, 5'-TAG GGA ATT CGT CGA CGG ATC CGG GGT CTG GTG TTC TGC TTT GTT CTG TCG GGT CGT CTG CAG GTC GAC GCA TGC GCC G-SH-3', was synthesized and purified by Sangon Biotech Co., Ltd. (Shanghai, China). Indium tin oxide (ITO) coated glass slides with a surface resistivity of 6–8  $\Omega$ /sq were purchased from South China Science & Technology Company Limited (Guangzhou, China). Doubly distilled water was used throughout the investigation.

The surface morphology was characterized by a SU 8010 field emission scanning electron microscope (SEM) (Hitachi, Japan). The crystalline phase was obtained on a Bruker D8 Advance X-ray diffractometer (XRD) (Darmstadt, Germany) with Cu Kα radiation, and the accelerating voltage and applied current were 40 kV and 40 mA, respectively. The UV-vis diffuse reflectance spectra (DRS) of Bi<sub>2</sub>WO<sub>6</sub> and G-Bi<sub>2</sub>WO<sub>6</sub> were conducted on a UV-3600 (SHIMADZU, Japan).

All electrochemical and PEC measurements were obtained on a CHI660A electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) at room temperature. A modified electrode, a saturated calomel electrode (SCE), and a platinum wire were employed as the working, reference and counter electrodes, respectively. Electrochemical impedance spectroscopic (EIS) analysis was performed in 0.1 M KCl solution containing 5.0 mM  $K_3Fe(CN)_6/K_4Fe(CN)_6$  at a bias potential of 0.2 V within the frequency range of 0.01 Hz to 100 kHz. The *V-I* curves of the cell were measured with

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galvanostatic polarization technique. The power output density curves (*P-I* curves) were obtained by plotting the power density ( $V \times I / A$ ) vs. the current (*I*), where A was the geometric area of the photoanode.

#### Preparation of G-Bi<sub>2</sub>WO<sub>6</sub> nanocomposites

Bi<sub>2</sub>WO<sub>6</sub> nanosheets were synthesized using a facilely hydrothermal process.<sup>1</sup> Briefly, Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.97 g, 2 mmol) was first dissolved in a nitric acid solution (1.2 mol L<sup>-1</sup>, 10 mL) to avoid hydrolysis of Bi<sup>3+</sup>. Then, a white precipitate was formed when a Na<sub>2</sub>WO<sub>4</sub> solution (0.05 mol L<sup>-1</sup>, 20 mL) was added dropwise into the above solution. The pH value of the suspension was adjusted to 7 with NaOH solution (4 mol L<sup>-1</sup>). After being stirred for 1 h, the suspension was transferred into a 50 mL Teflon-lined autoclave and then heated at 160 °C for 20 h. The obtained samples were collected and washed with water, dried at 60 °C in air.

Graphene was prepared by reducing commercial GO suspension using NaBH<sub>4</sub> according to previous description with slight modification.<sup>2</sup> A graphene suspension of 2 mg·mL<sup>-1</sup> was prepared by dispersing suitable amount of graphene in water with the assistance of ultrasonic agitation. The G-Bi<sub>2</sub>WO<sub>6</sub> nanocomposites were prepared by directly mixing the suspensions of Bi<sub>2</sub>WO<sub>6</sub> and graphene under ultrasonic agitation. Different weight contents of graphene in G-Bi<sub>2</sub>WO<sub>6</sub> nanocomposites were obtained by varying the mixture ratio of two suspensions.

#### Synthesis of Au nanoparticles (AuNPs).

Synthesis of AuNPs was based on a literature with slight modification.<sup>3</sup> Briefly, 2% HAuCl<sub>4</sub> mixed with 49 mL water was heated to boiling under reflux and stirring, and then 5mL of trisodium citrate (38.8 mM) was fleetly added. The solution turned from pale yellow to red-violet. The solution was kept under boiling for 20 min, and finally cooled to room temperature with stirring.

#### Electrode modification and construction of PFC.

Prior to modification, the tin-doped indium oxide (ITO) glass substrates were cleaned by successive sonication in acetone, mixed solution of ethanol, 2 M NaOH (v/v, 1:1) and water,

respectively. After being dried with nitrogen gas, the ITO glass substrates surface with an exposed geometric area of 0.1256 cm<sup>2</sup> was coated with 10  $\mu$ L of G-Bi<sub>2</sub>WO<sub>6</sub> suspension (4 g·L<sup>-1</sup>) and dried under an infrared lamp.

The PFC was constructed with the as prepared photoanode and a Pt foil cathode (1 cm  $\times$  1 cm), which separated into two chambers photoelectrochemical cell by a Nafion 117 membrane. The anolyte was 0.1 mol·L<sup>-1</sup> PB (pH 7.4) containing 2 mM AA while 0.1 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> was utilized as the catholyte. Moreover, the anodic chamber of the cell had a quartz window to allow the illumination from the light source on the anode. A portable violet laser pen with a power of 200 mW and an illumination diameter of *ca*. 3 mm served as the light source.

#### Fabrication of sensor and self-powered sensing of STR.

The circuit of the entire sensing system was assembled according to Scheme 1. At first, switches i and ii were turned on to charge the capacitor by PFC. After charging for 30 seconds, switch i was turned off while switch iii was turned on to allow the discharge of capacitor through the DMM. As a result, an amplified short circuit current ( $I_{sc}$ ) was displayed on DMM, but the signal changed quickly with discharging time. The DMM was connected with a computer through a cable to acquire all instantaneous data employed for plotting the  $I_{sc}$  curve accurately by software.

The G-Bi<sub>2</sub>WO<sub>6</sub>/ITO photoanode was coated with 8  $\mu$ L of AuNPs solution and dried under an infrared lamp. Then, the obtained AuNPs/G-Bi<sub>2</sub>WO<sub>6</sub>/ITO was incubated with 10  $\mu$ L of STR-binding aptamer solution (1  $\mu$ M) at 40 °C for 2 h to immobilize the aptamer on the electrode via Au-S bond. The ap/AuNPs/G-Bi<sub>2</sub>WO<sub>6</sub>/ITO electrode was rinsed thoroughly with water to remove any unbounded aptamer molecules. To perform the recognition between aptamer and STR, the ap/AuNPs/G-Bi<sub>2</sub>WO<sub>6</sub>/ITO was firstly incubated with 10  $\mu$ L of STR analytical solution with different concentrations at 40 °C for 2 h, followed by thoroughly rinsing with water. Finally, the electrode served as the photoanode of PFC, and the  $I_{sc}$  amplified by the capacitor was recorded.

#### **Results and discussion**

#### Materials characterization

The photoanode materials of G-Bi<sub>2</sub>WO<sub>6</sub> composites were prepared and characterized using SEM and XRD. The SEM image of Bi<sub>2</sub>WO<sub>6</sub> displays flower-like nanostructures assembled by nanosheets (Fig. S1). The XRD pattern of Bi<sub>2</sub>WO<sub>6</sub> shows five primary diffraction peaks at 28.30°, 32.80°, 47.16°, 55.84°, and 58.48° (Fig. S2), which are matched well with the (113), (200), (220), (313) and (226) planes of standard Bi<sub>2</sub>WO<sub>6</sub> (JCPDS 73-1126),<sup>4</sup> suggesting the high crystalline quality of Bi<sub>2</sub>WO<sub>6</sub>. For G-Bi<sub>2</sub>WO<sub>6</sub>, the morphology is not obviously changed (Fig. S3), because of the low content of graphene doped in the composites. Nevertheless, the doping of graphene in the composites is confirmed using the elemental mapping of G-Bi<sub>2</sub>WO<sub>6</sub> composites (Fig. S4). Moreover, the morphology of G-Bi<sub>2</sub>WO<sub>6</sub> decorated with AuNPs for the next step of immobilizing STR-aptamer on the photoanode was also characterized using SEM. As displayed in Fig. S5, many AuNPs are evenly distributed on the surface of G-Bi<sub>2</sub>WO<sub>6</sub> composites.

The light absorption ability of  $Bi_2WO_6$  and  $G-Bi_2WO_6$  was investigated using UV-vis DRS. As can be seen,  $Bi_2WO_6$  exhibits a strong absorption in ultraviolet region (curve a in Fig. S6). When  $Bi_2WO_6$  is doped with graphene, the absorption shows a significant enhancement in the visible region (curve b in Fig. S6). This result suggests that the doping of graphene in  $Bi_2WO_6$  promotes the visible light harvesting properties of the material.<sup>5</sup>

#### Real sample analysis

The feasibility of the proposed method for STR detection was evaluated in a real sample using the standard addition method. The lake water sample collected from Wuhan City was filtered through a 0.22  $\mu$ m membrane, and then diluted with PB (pH 7.4) for STR detection using the self-powered sensor under optimal conditions. Because no STR was detected in this lake water, different concentrations of STR were spiked to the sample. Fig. S12 exhibits the  $I_{sc}$  signal responses with these spiked samples. And Table S2 shows the analytical results of the proposed method for STR sensing in spiked water samples. The recoveries of STR are in the range of 95.7–102.2%. An average recovery of 98.9% reveals that the developed method is of good accuracy and reliability in practical applications.



Fig. S1. SEM image of Bi<sub>2</sub>WO<sub>6</sub>.



Fig. S2. XRD pattern of Bi<sub>2</sub>WO<sub>6</sub>.



Fig. S3. SEM image of G-Bi<sub>2</sub>WO<sub>6</sub> composites.



Fig. S4. Elemental mapping of  $G-Bi_2WO_6$  composites.



Fig. S5. SEM image of AuNPs/G-Bi<sub>2</sub>WO<sub>6</sub>.



Fig. S6. UV-vis DRS of (a)  $Bi_2WO_6$  and (b)  $G-Bi_2WO_6$ .



Fig. S7. Nyquist plots of (a)  $Bi_2WO_6/ITO$ , (b)  $G-Bi_2WO_6/ITO$ , (c)  $AuNPs/G-Bi_2WO_6/ITO$ , (d)  $ap/AuNPs/G-Bi_2WO_6/ITO$ , and (e)  $ap/AuNPs/G-Bi_2WO_6/ITO$  incubated with 50 nM STR. The EIS measurements were carried out in 0.1 M KCl containing 5.0 mM  $K_3Fe(CN)_6/K_4Fe(CN)_6$ .



Fig. S8. Polarization curves of (a)  $G-Bi_2WO_6/ITO$  in 0.1 M PB (pH 7.4) under photoirradiation and (b) Pt cathode in 0.1 M H<sub>2</sub>SO<sub>4</sub> saturated with air at 2 mV/s.



Fig. S9. Effect of graphene content in  $Bi_2WO_6$  on the photocurrent response.



Fig. S10. Effect of aptamer concentration on the  $P_{\text{Max}}$  of the fabricated PFC.



**Fig. S11.** Effect of charging time for the capacitor on the  $I_{sc-max}$  and voltage signals read out by DMM.



Fig. S12. The  $I_{sc}$  signal responses of the sensor toward lake water samples spiked with different concentrations of STR: 0.5 nM (samples 1-3); 10 nM (samples 4-6); 200 nM (samples 7-9).

Method	Linear range (nM)	Detection limit (nM)	References
Colorimetry	10 <sup>2</sup> -10 <sup>5</sup>	94	6
Photoelectrochemical aptasensor	0.1-50	0.033	7
Electrochemical aptasensor	30-1500	11.4	8
Fluorescence quenching aptasensor	-	47.6	9
Self-powered sensor	0.2-200	0.06	This work

## **Table S1** Comparison of different methods for STR detection.

Spiked (nM)	Found (nM)	Recovery (%)	RSD (%)
0	0	-	-
0.50	0.510	102.2	4.3
10.0	9.880	98.80	3.9
200	191.4	95.70	3.1

**Table S2** Determination of STR in lake water sample using the self-powered signal amplification aptasensor with standard addition method (n=3).

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