

## **Supporting Information**

### **Photofuel cell coupling with redox cycling as a highly sensitive and selective self-powered sensing platform for the detection of tyrosinase activity**

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## **Experimental**

### ***Reagents and Chemicals.***

Tyrosinase (from mushroom, 1380 U/mg) was purchased from Yuanye Bio-Technology Co., Ltd (Shanghai, China). Phenol,  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , and tris(2-carboxyethyl)phosphine (TCEP) hydrochloride were provided by Aladdin Reagent Co. Ltd. (Shanghai, China). Other reagents of analytical grade were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Phosphate buffer solution (PBS, 0.1 M) was prepared by mixing of the solution of  $\text{Na}_2\text{HPO}_4\cdot 12\text{H}_2\text{O}$  and  $\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$ . Doubly distilled water was used throughout the investigation.

### ***Apparatus and Procedures.***

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) are performed on a Nova NanoSEM 450 instrument (FEI, Netherlands) equipped with IE250X-Max50 EDS (Oxford, UK). X-ray diffraction (XRD) patterns were obtained Bruker D8 Advance X-ray diffractometer (Bruker Instruments, Darmstadt, Germany). The UV-visible absorption spectra were measured using a TU-1900 UV-visible spectrometer (Beijing Purkinje General Instrument Company, China).

Cyclic voltammograms (CVs), polarization curves, electrochemical impedance spectroscopy (EIS) and photocurrent curves were obtained on a CHI660A electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) in a conventional three-electrode system. A modified ITO or glass carbon electrode, a saturated Ag/AgCl electrode and a platinum wire were employed as the working, reference and auxiliary electrodes, respectively. EIS was performed in 5.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  aqueous solution with 0.1 M KCl as the electrolyte, within the frequency range of 0.01 Hz to 100 kHz and a bias potential of 0.23 V. A photocatalytic fuel cell (PFC) was constructed by using a two-compartment cell with a Nafion 117 membrane (Dupont Inc., USA) as separator. A violet laser pen (405 nm, 20 mW) with a circular illumination area (diameter  $\sim 3$  mm) was used as the light source. The  $V-I$

curves of the PFCs were measured with 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  $A$  represents the geometric area of the photoanode.

#### ***Preparation of g-C<sub>3</sub>N<sub>4</sub>-Bi<sub>2</sub>S<sub>3</sub> photoanode.***

Bulk g-C<sub>3</sub>N<sub>4</sub> was prepared by a typical pyrolysis of cyanoguanidine in air atmosphere<sup>1</sup>. Briefly, 5 g of cyanoguanidine was calcined in a muffle furnace at 220 °C for 2 h, and the sample was further heated to 350 and 550 °C and maintained for 2 and 4 h, respectively. The synthesized material was then rinsed with water to remove any unreacted precursor and dried overnight at 60 °C. To obtain g-C<sub>3</sub>N<sub>4</sub> nanosheets, the bulk g-C<sub>3</sub>N<sub>4</sub> powder was dispersed into isopropanol (3 g/L) and exfoliated under sonication for 16 h. The resulting suspension was centrifuged at 3000 rpm to remove the residual unexfoliated bulk g-C<sub>3</sub>N<sub>4</sub>, and the supernatant was further centrifuged at 10000 rpm, the obtained g-C<sub>3</sub>N<sub>4</sub> nanosheets was dried at 45 °C in a vacuum oven.

Bi<sub>2</sub>S<sub>3</sub> nanorods were synthesized via a solvothermal method with a little modification<sup>2</sup>. Briefly, 5.625 mmol of Na<sub>2</sub>S·9H<sub>2</sub>O dissolved in 30 mL water was added drop-wisely into 25 mL of glycol containing 3.75 mmol of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O under vigorous stirring, leading to the formation of a black solution. After adding 20 mL water containing 32 mmol of urea, the mixture was transferred into a 100 mL Teflon-lined autoclave and stirred at room temperature for 1 h. The autoclave was further sealed in a stainless-steel tank, and heated at 180 °C for 12 h. The product was washed three times with deionized water and ethanol, respectively, and dried at 60 °C overnight.

The g-C<sub>3</sub>N<sub>4</sub>-Bi<sub>2</sub>S<sub>3</sub> nanocomposites suspension was prepared by directly mixing aqueous dispersions of g-C<sub>3</sub>N<sub>4</sub> and Bi<sub>2</sub>S<sub>3</sub> with the aid of sonication. Prior to modification, the commercial ITO electrode (~7 Ω/cm<sup>2</sup>, Southern China Xiang Cheng Technology Co. Ltd.) was cleaned by successive sonication in acetone, mixed solution of ethanol and 2 M NaOH (v/v, 1:1), and pure water for 20 min. After being dried with nitrogen gas, the electrode with

an exposed geometric area of 0.071 cm<sup>2</sup> was coated with 7 μL of g-C<sub>3</sub>N<sub>4</sub>-Bi<sub>2</sub>S<sub>3</sub> suspension and dried at 60 °C in an oven, followed by rinsing with water to remove loosely adsorbed materials. The obtained modified electrode (g-C<sub>3</sub>N<sub>4</sub>-Bi<sub>2</sub>S<sub>3</sub>/ITO) was employed as photoanode for the construction of PFC.

#### ***Preparation of hemin-graphene modified cathode***

Hemin-graphene was prepared according to reported reference<sup>3</sup> with minor modification. Briefly, 300 mg of commercial graphene nanosheets (Xiamen Kaina nanotechnology Co., Ltd.) was pretreated with 50 mL of mixed acid solution containing 12.5 mL of sulfuric acid and 37.5 mL of nitric acid at 80 °C for 3 h. Subsequently, the mixture was collected by centrifugation, washed with deionized water for several times and dried at 60 °C. The obtained carboxylated graphene nanosheets (8 mg) was re-dispersed in 4 mL of 1.5 mM hemin methanol solution. The conjugation between hemin and graphene was performed under mild shaking for 2 hours. Afterwards, the hemin-graphene was centrifuged at 8000 r/min and washed with methanol for three times. The Hemin-graphene suspension were re-dispersed in 4 mL of DMF and stored at 4 °C for further use.

Prior to modification of the cathode, the glassy carbon electrodes (GCE, diameter 3 mm) were polished with 0.05 μm alumina slurry, rinsed thoroughly with doubly distilled water, washed successively with ethanol and distilled water under sonication and dried with a N<sub>2</sub> flow. Hemin-graphene modified electrode was prepared by coating 4 μL of hemin-graphene suspension on GCE and dried under an infrared lamp. The obtained modified electrode was marked as HG/GCE, which was employed as the cathode for the construction of PFC.

#### ***Construction of photofuel cell and self-powered sensing of Tyr activity***

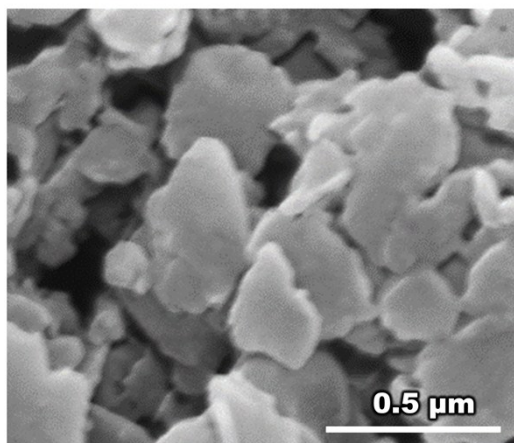
The PFC was constructed with the prepared g-C<sub>3</sub>N<sub>4</sub>-Bi<sub>2</sub>S<sub>3</sub>/ITO photoanode and HG/GCE cathode in a two-compartment photoelectric cell separated by a Nafion 117 membrane. In both chambers, 0.1 M PBS (pH 7.4) served as the supporting electrolyte, whereas the anolyte contained 0.1 mM phenol as zymolyte, different concentration of Tyr and 0.5 mM TCEP as

reductant. The enzymatic reactions were carried out at 25 °C. Moreover, a quartz window to allow the illumination from the light source on the anode was equipped on the anodic chamber. A portable violet laser pen with a power of 20 mW at 405 nm and a diameter of *ca.* 3 mm for the illumination area served as the visible light source.

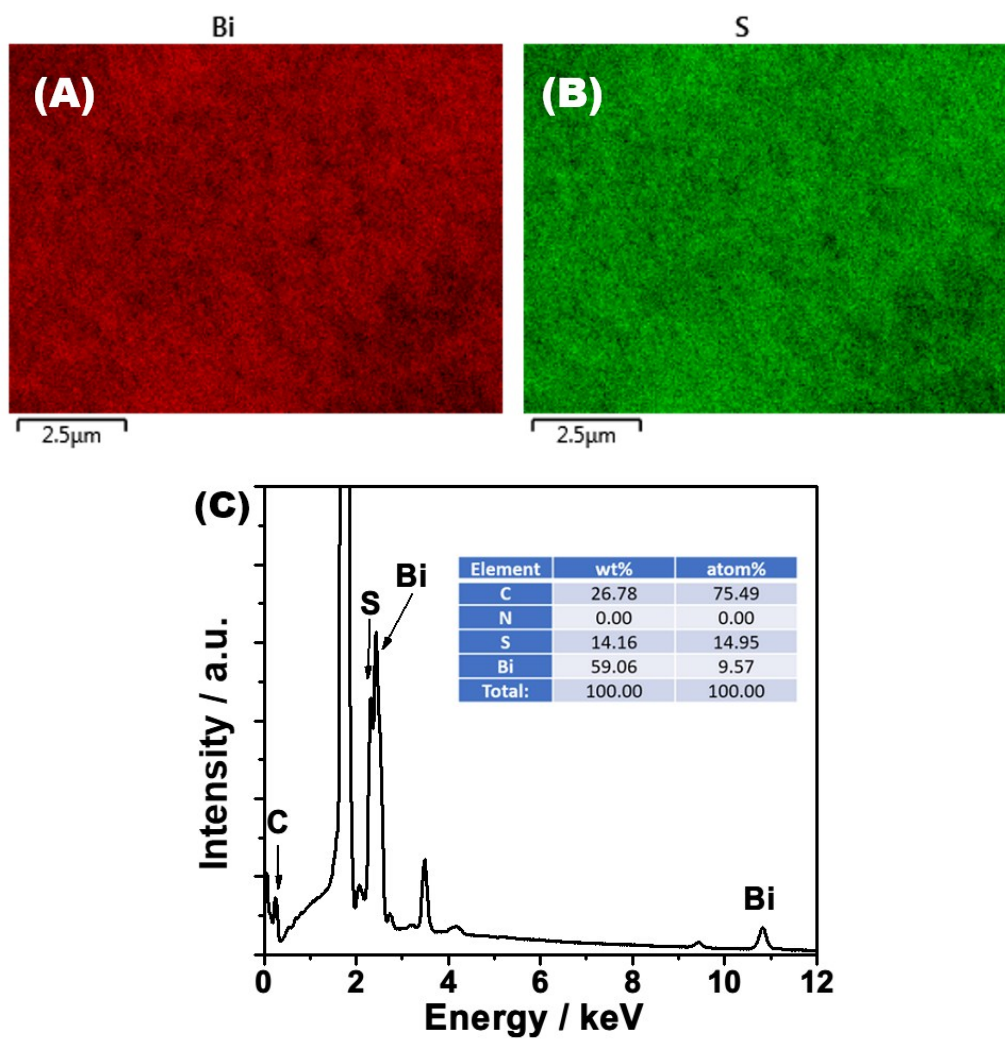
## **Results and Discussion**

### ***EDS analysis***

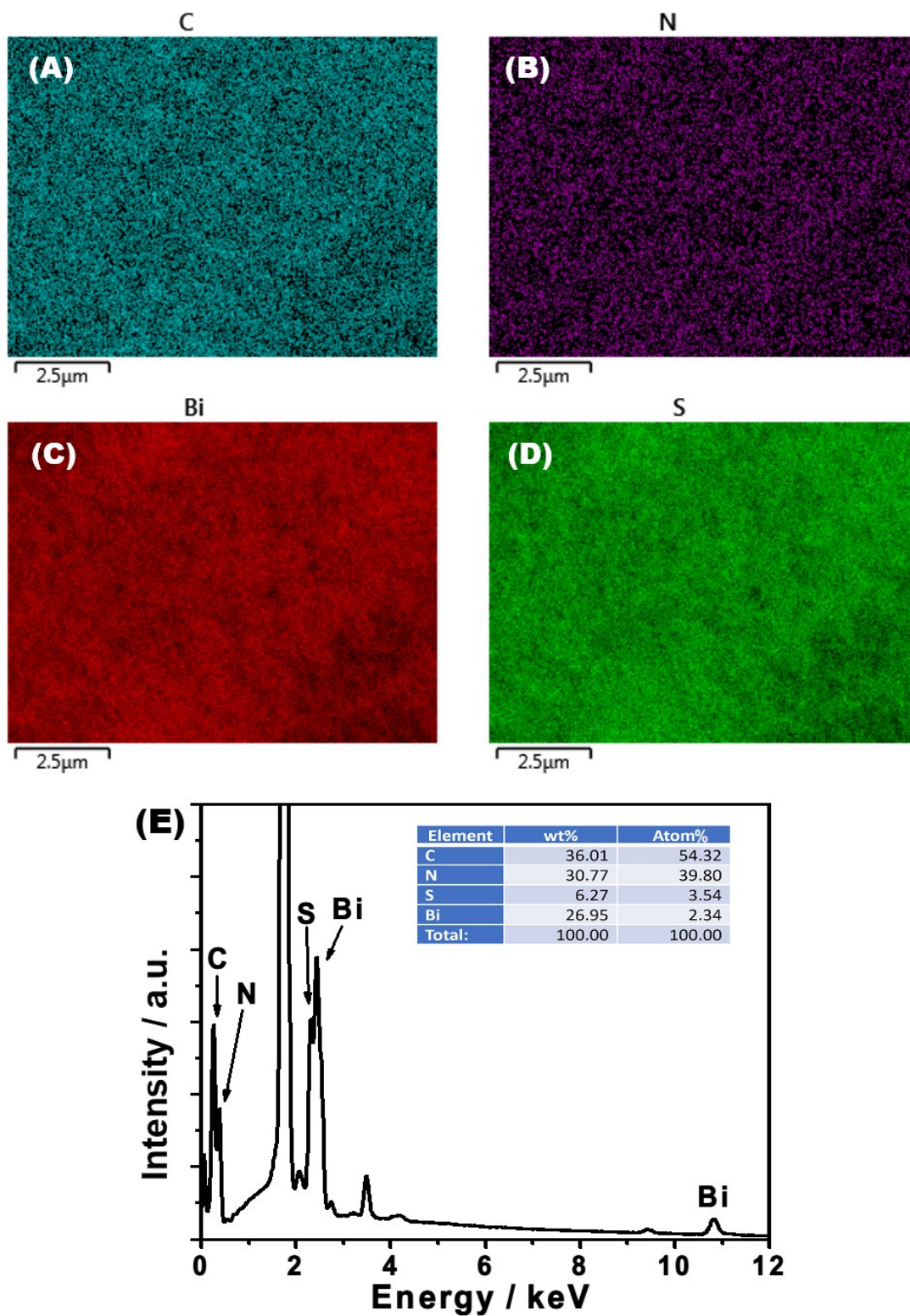
EDS mapping results of  $\text{Bi}_2\text{S}_3$  and  $\text{g-C}_3\text{N}_4\text{-Bi}_2\text{S}_3$  were collected and shown in Figure S2 and Figure S3, respectively. As can be seen from Figure S2, elements Bi and S distributed uniformly across the prepared  $\text{Bi}_2\text{S}_3$  sample (Figure S2A and S2B). For  $\text{g-C}_3\text{N}_4\text{-Bi}_2\text{S}_3$  nanoconposites, the EDS mapping results suggested the co-existence of elements C, N, Bi and S (Figure S3). For both samples, the atomic ratio of S:Bi obtained from EDS spectra was estimated to be *ca.* 1.5, which was in consistence with the molecular formula of  $\text{Bi}_2\text{S}_3$ . It should be noted that the high content of C in EDS spectra was aroused by carbon conductive adhesive which was used as substrate to fix sample for characterization.



**Figure S1.** SEM image of g-C<sub>3</sub>N<sub>4</sub>.

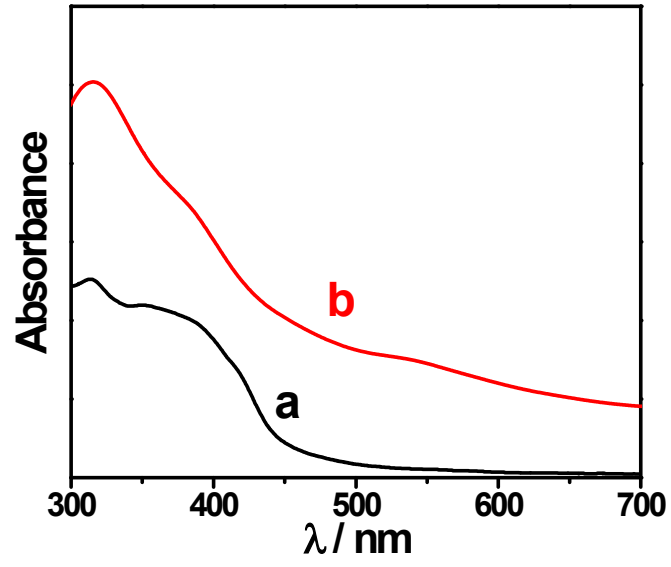


**Figure S2.** EDS mapping results of  $\text{Bi}_2\text{S}_3$ : (A) Bi element, (B) S element, (C) EDS spectrum of  $\text{Bi}_2\text{S}_3$ . The inset table shows relative content of elements.

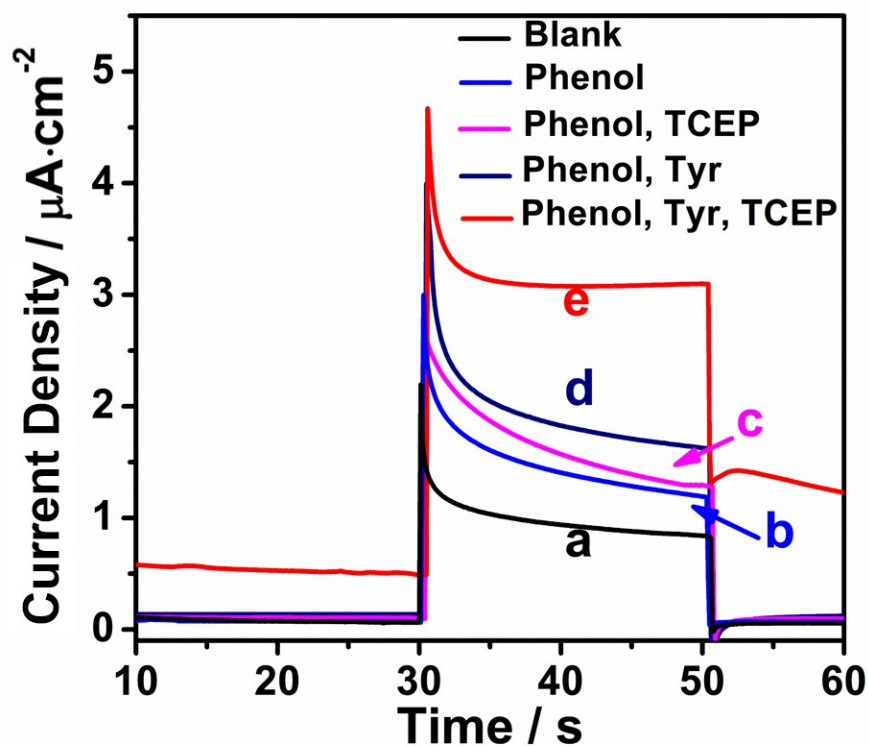


**Figure S3.** EDS mapping results of  $g\text{-C}_3\text{N}_4\text{-Bi}_2\text{S}_3$ : (A) C element, (B) N element, (C) Bi element, (D) S element. (E) EDS spectrum of  $g\text{-C}_3\text{N}_4\text{-Bi}_2\text{S}_3$ . The inset table shows relative content of elements.

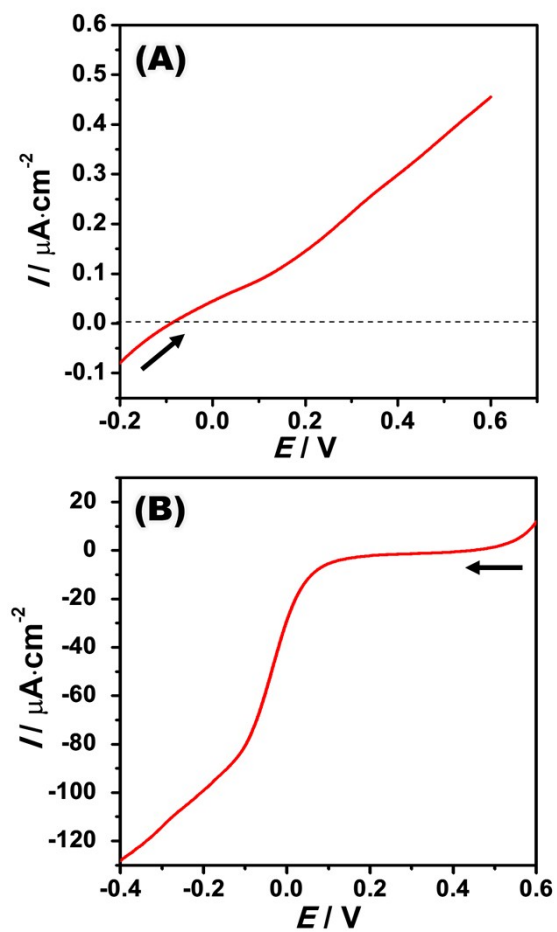




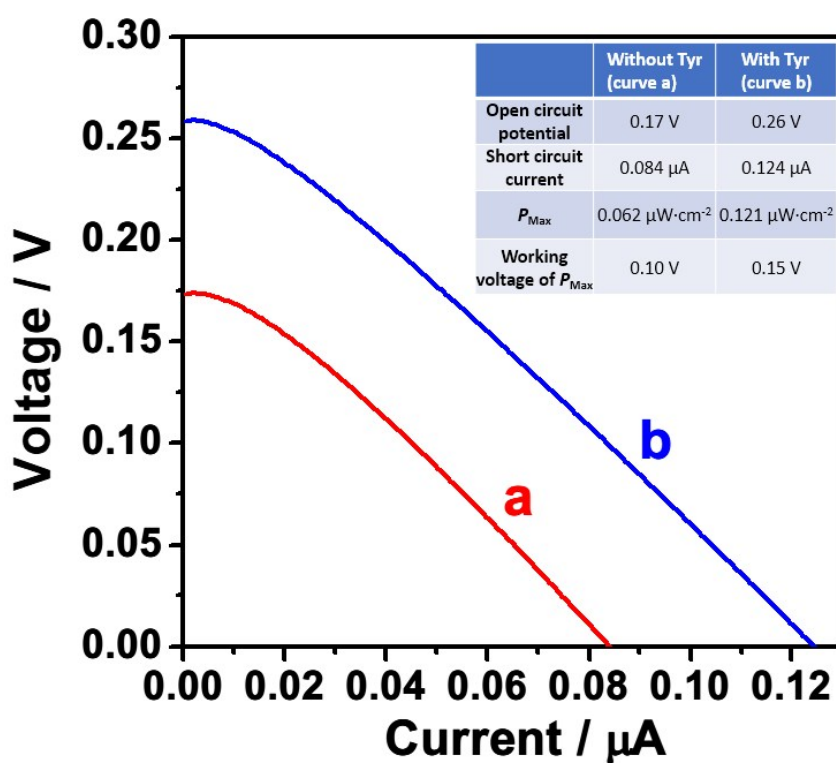
**Figure S4.** UV-visible absorption spectra of (a) g-C<sub>3</sub>N<sub>4</sub> and (b) g-C<sub>3</sub>N<sub>4</sub>-Bi<sub>2</sub>S<sub>3</sub>.



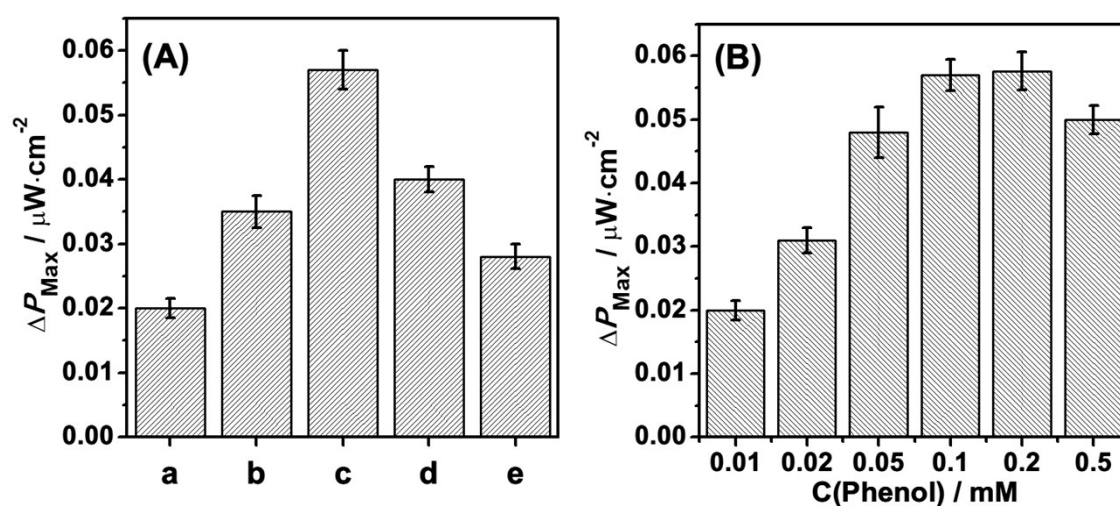
**Figure S5.** Photocurrent responses of  $g\text{-C}_3\text{N}_4\text{-Bi}_2\text{S}_3/\text{ITO}$  recorded in 0.1 M PBS (pH 7.4) containing different species: (a) blank PBS solution, (b) 0.1 mM phenol, (c) 0.1 mM phenol and 0.5 mM TCEP, (d) 0.1 mM phenol and 2 U/mL Tyr, and (e) 0.1 mM phenol, 2 U/mL Tyr and 0.5 mM TCEP at a bias potential of 0.2 V (vs. Ag/AgCl) under visible light illumination.



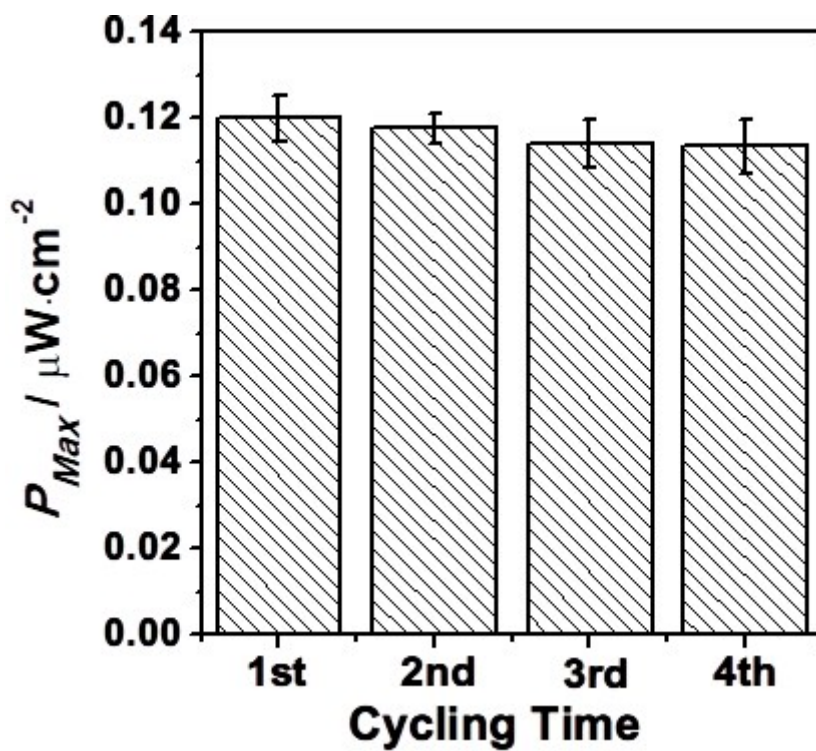
**Figure S6.** (A) Polarization curve of photoanode recorded in 0.1 M PBS in presence of 0.1 mM phenol, 2 U/mL Tyr and 0.5 mM TCEP under visible light irradiation at a scan rate of 2.0 mV/s. (B) Polarization curve of HG/GCE in air-saturated 0.1 M PBS at a scan rate of 2.0 mV/s.



**Figure S7.**  $V$ - $I$  curves of the PFC consisting of g- $\text{C}_3\text{N}_4$ - $\text{Bi}_2\text{S}_3$ /ITO photoanode and HG/GCE cathode recorded in PBS containing 0.1 mM phenol and 0.5 mM TCEP (a) without and (b) with 2 U/mL Tyr. The inset table shows some electrochemical parameters of the proposed PFC.



**Figure S8.** (A)  $\Delta P_{\text{Max}}$  responses toward 2 U/mL Tyr obtained from PFC constructed with different photoactive materials modified photoanodes: (a) 1.0 mg/mL g-C<sub>3</sub>N<sub>4</sub>, (b) 1.0 mg/mL g-C<sub>3</sub>N<sub>4</sub> and 0.5 mg/mL Bi<sub>2</sub>S<sub>3</sub>, (c) 1.0 mg/mL g-C<sub>3</sub>N<sub>4</sub> and 1.0 mg/mL Bi<sub>2</sub>S<sub>3</sub>, (d) 1.0 mg/mL g-C<sub>3</sub>N<sub>4</sub> and 1.5 mg/mL Bi<sub>2</sub>S<sub>3</sub>, and (e) 1.0 mg/mL Bi<sub>2</sub>S<sub>3</sub>. (B) Effects of phenol concentration on the  $\Delta P_{\text{Max}}$  responses toward 2 U/mL Tyr.



**Figure S9.**  $P_{Max}$  responses of the proposed PFC toward 2 U/mL Tyr under different running cycles. Error bars were derived from the standard deviation of three measurements.

**Table S1.** Comparison of various methods for Tyr activity evaluation.

Method	Linear range /U·mL <sup>-1</sup>	Detection limit /U·mL <sup>-1</sup>	Ref.
NHU-based fluorescent probe	0.05 - 50	-	4
Cyanine-based fluorescent probe	0.05 - 0.2	0.01	5
Gold nanoclusters-based fluorescent probe	0.5 - 200	0.08	6
Photoelectrochemistry	-	0.1 U	7
Ion-sensitive field-effect transistor devices	-	0.25 U	8
PFC-based self-powered sensor	0.01 - 5	0.005	This work

**Table S2.** Analytical results of Tyr activity in spiked diluted serum samples by the proposed method.

Spiked (U·mL <sup>-1</sup> )	Found (U·mL <sup>-1</sup> )	Recovery (%)	RSD (%)	Average recovery (%)
0	0	-	-	
0.1	0.106	105	3.4	
0.5	0.49	98.0	4.6	102.7
2.0	2.08	104	2.8	



## References

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