Supporting information

Photoenergy Storage and Power Amplification Strategy in Membraneless Photoelectrochemical Biofuel Cells

You Yu [†,‡], Miao Xu [†,‡], Shaojun Dong [†,‡,*]

[†] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin, 130022;

[‡] University of Chinese Academy of Sciences, Beijing, 100049

E-mail: dongsj@ciac.ac.cn

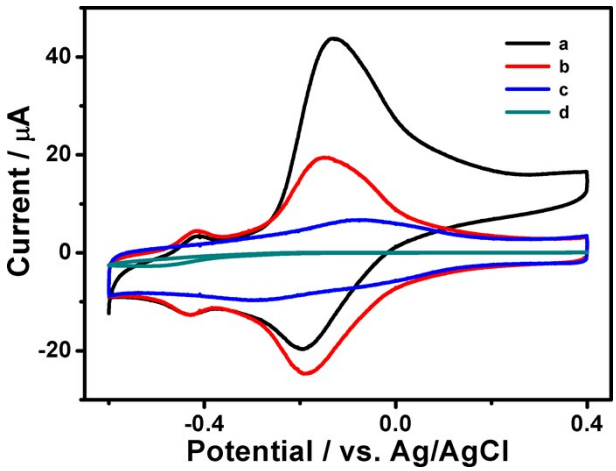

Figure S1 CV recorded at the MDB-MWNTs/GCE with (a) and without (b) NADH (5 mM) , MWNTs/GCE (c) and bare GCE (d) in 0.1 M PBS, scan rate is 10 mV s^{-1}.

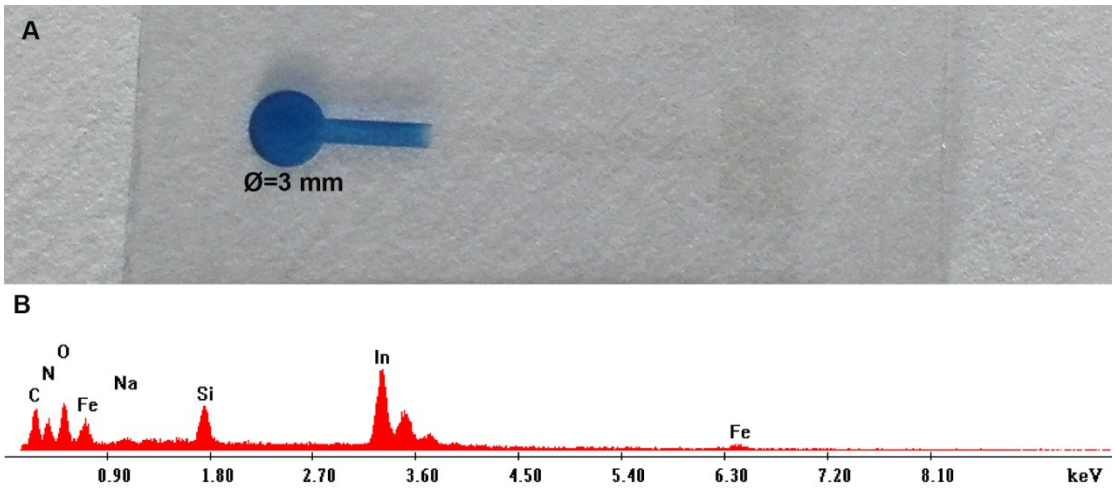

Figure S2 (A) The photo of the patterned PB electrode. (B) Energy-dispersive X-ray image of the PB electrode.

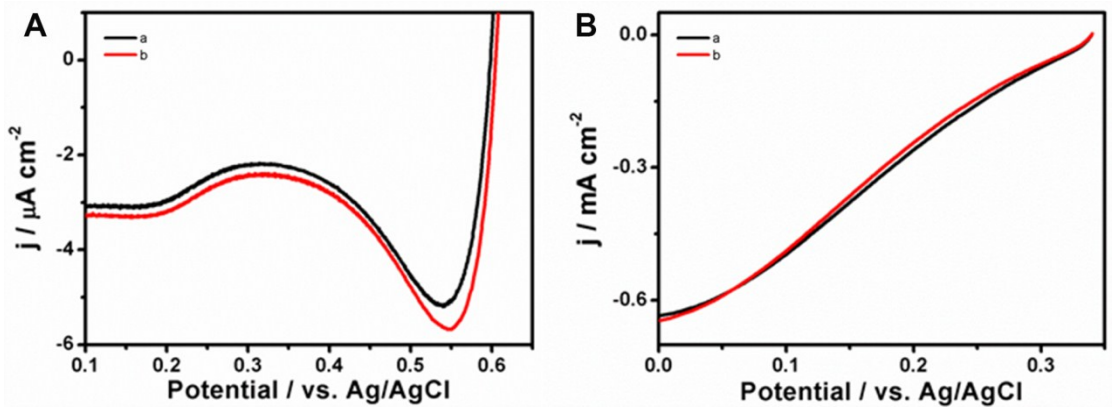

Figure S3 (A) LSV recorded at the $BiOI_{0.5}Cl_{0.5}$ in PBS (pH 6.0) under light illumination with (a) and without (b) 10 mM NAD^+ and 30 mM glucose; (B) LSV recorded at the PB in PBS (pH 6.0) with (a) and without (b) 10 mM NAD^+ , 30 mM glucose. Scan rate is 20 mV s^{-1}.

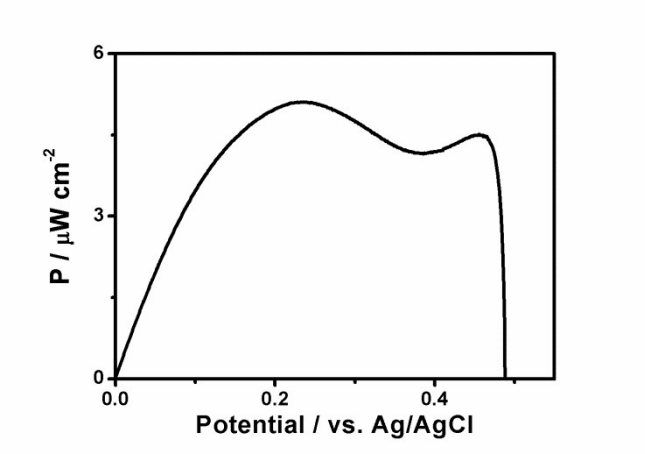

Figure S4. The power output of the PBFC assembled with PW and photoelectrode in the PBS containing 10 mM NAD^+, 30 mM glucose.

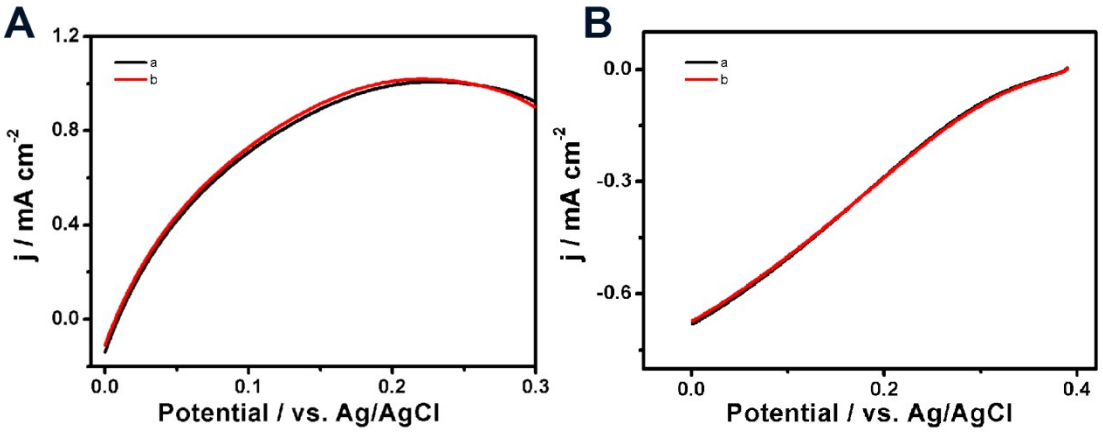

Figure S5 (A) LSV recorded at the PW in PBS (pH 6.0) under light illumination (a) or in the dark (b); (B) LSV recorded at the PB in PBS (pH 6.0) under light illumination (a) or in the dark (b). Scan rate is 20 mV s^{-1}.

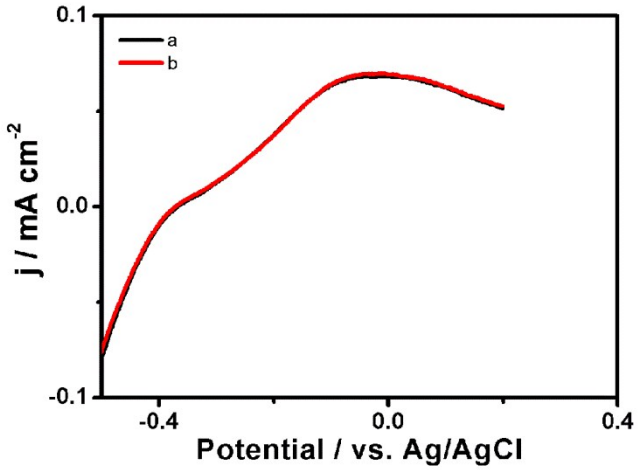

Figure S6 LSV obtained at the CS/denatured GDH/MDB-MWNTs/GCE in PBS containing 10 mM NAD^+ without (a) and with (b) 30 mM glucose. The scan rate was 20 mV s^{-1}. The bioelectrode was immersed into 3 M guanidine hydrochloride overnight aimed at the denatured enzyme modified electrode.

Table S1. Comparison of different photoelectrochemical biofuel cell.

Light sources	Anode	Cathode	P_{max} [μW cm^{-2}]	References
Visible light	GDH/tetraarylporphyrin sensitizer **S**/SnO_2	Hg/Hg_2SO_4	19	1
Visible light	GDH/porphyrin/TiO_2	Hg/Hg_2SO_4	37	2
Visible light	GDH/TCCP/TiO_2	Pt black	33.94	3
UV light	GDH/H_2-mesoporphyrin IX/TiO_2	Pt black	139	4
UV light	GDH/Zn-mesoporphyrin IX/TiO_2	Pt black	22	4
Visible light	GOx[a]/TiO_2/CdSe/carbonpaper	pt	40	5
UV light	TiO_2 nanotube array	BOD[b]/CNT-IL	36	6
Visible light	GOx/TTF-OMC[c]	Polyterthiophene	23.65	7
Visible light	GDH/MDB-MWNTs	PB/PW and $BiOI_{0.5}Cl_{0.5}$	160.3	This work

Experimental section

Chemicals

$K_3[Fe(CN)_6]$, $FeCl_3$, $Bi(NO_3)_3 \cdot 5H_2O$, KI, KCl, and nitric acid (HNO_3) were purchased from Beijing Chemical Works, P. R. China. P-Benzoquinone was obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Multi-walled carbon nanotubes (MWNTs) (80% purity, diameter 20-50 nm) were purchased from Shenzhen Nanotech. Port. Co. Ltd. (Shenzhen, China).β-D-(+)-glucose, chitosan (CS), Meldola`s blue (MDB) and GDH (E.C. 1.1.1.47, initial activity of 235.3 U mg^{-1} from Pseudomonas sp.) were obtained from Sigma and used as received. Guanidine hydrochloride, NADH and NAD^+ were purchased from the Gen-view Scientific Inc. A 0.10 M phosphate buffer solution (PBS, pH = 6.0) was employed as the supporting electrolyte for the best cyclic properties of PB/PW[9]. All other chemicals were of analytical grade and all aqueous solutions were prepared with ultrapure water (>18.25 MΩ cm) obtained from Millipore system.

Glassy carbon electrode (GCE, 2.6 mm in diameter, Tokai Carbon Co., Japan) was polished sequentially with 1.0 and 0.3 μm alumina slurry and washed ultrasonically in water and ethanol for several minutes, respectively. MWNTs were treated by well-established methods with slight modification, MWNTs were dispersed in 30% HNO_3 and then refluxed for 24 h at 140 °C to acquire carboxylic group functionalized MWNTs. 10 μL of MWNTs suspension (2 mg mL^{-1}) was spread onto a GCE to dry, then the electrode was immersed into 0.5 mM Meldola`s blue (MDB) for 30 min to achieved MDB-MWNTs/GCE. 5 μL GDH (1 mg mL^{-1}) was coated on the MDB-MWNTs/GCE, which was dried at 4 °C overnight and achieved GDH/MDB-MWNTs/GCE. After

that, 10 μL of 1% chitosan solution was spread onto the electrode surface to form a film (noted as CS/GDH/MDB-MWNTs/GCE).

Indium tin oxide (ITO) (surface resistance of 30-60 Ω cm^{-2}, Nanbo DisplayTechnology Co., Ltd.) was used as the working electrode. Prior to electrodeposition, the ITO was washed with acetone, ethanol and water in ultrasonic bath sequentially. The plating solutions were prepared as following: 0.338 g $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 0.4 M KI and 0.4 M KCl aqueous solution. Then 100 μL 4 M HNO_3 and 8 mL 50 mM p-benzoquinone were added to the above solution, respectively. The depositions were performed potentiostatically at −0.1 V at room temperature for 20 min. The patterned ITO electrodes (10.5 mm^2) were electropolymerized with PB in a freshly prepared solution containing 0.1 M KCl, 0.1 M HCl, 2.5 mM $K_3[Fe(CN)_6]$ and 2.5 mM $FeCl_3$ by applying a constant potential of 0.4 V for 480 s. The successful preparation of the PB film was confirmed by its obvious color and absorbance change. The modified electrodes were thoroughly rinsed with water to remove the physically adsorbed species, and then dried at 100 °C overnight.

The PBFC was assembled by placing the as prepared bioelectrode, PB film electrode and photoelectrode into 8 ml PBS (pH=6.0) containing 5 mM NAD^+ and 30 mM glucose. The Xe lamp was set facing to the photocathode in order that the light could illuminate the whole electrode surface, the PB electrode was set at right angles with the photoelectrode avoiding from the luminous.

The X-ray diffraction (XRD) measurements were performed on a D8 Focus diffractometer (Bruker) with Cu Kα radiation (λ = 0.15405 nm) in the range of 10-80° (2θ). Scanning electron microscopy (SEM) measurements were made on a XL30 ESEM with an accelerating voltage of 10 kV to determine the morphology of products. The light source was a 300 W Xenon lamp (PLS-

SXE 300, Beijing Trusttech Co. Ltd., China) with a UV-cut filter ($\lambda \geqslant 400$ nm). Cyclic voltammetry (CV), open circuit potential-time, chronoamperometry and linear sweep voltammetry (LSV) experiments were performed with an electrochemical analyzer (CHI 832C, Shanghai, China). The polarization curves were achieved by the LSV measurement at scan rate 1 mv s^{-1}. A three-electrode system was used including a working electrode, a platinum flat as the counter electrode and the Ag/AgCl (saturated KCl) as the reference electrode, respectively. The operation of the biofuel cell was performed at 37 °C, other experiments were carried out at room temperature (22 °C).

Notes and references

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