An Automatic Illumination Compensation Device Based on a Visible-Light-Driven Photoelectrochemical Biofuel Cell

You Yu [†, ‡], Yanchao Han [†], Miao Xu [†, ‡], Lingling Zhang [†, ‡], 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

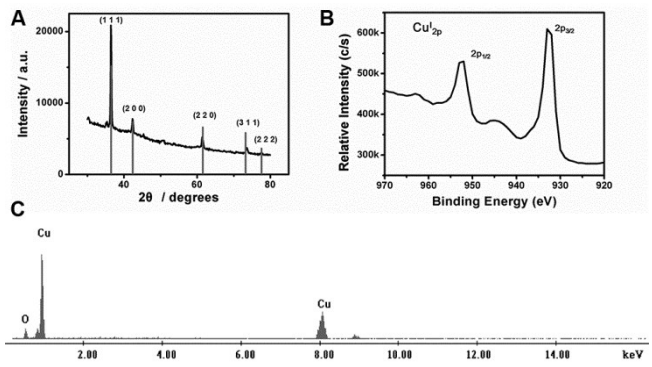

Figure S1 (A) Powder X-ray diffraction pattern of the Cu_2O film on ITO. The peaks are labeled with the standard cuprite reflections. (B) X-ray photoelectron spectra of Cu^{I}_{2p} of the sample of Cu_2O film. (C) Energy-dispersive X-ray image of the Cu_2O film.

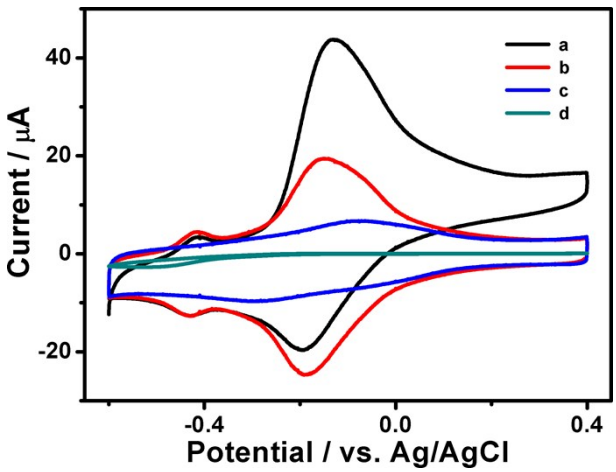

Figure S2 CVs recorded at the MDB-MWNTs/GCE with (a) and without (b) NADH (5 mM) , MWNTs/GCE (c) and bare GCE (d) in 0.1 M PBS, scan rate is 10 mV s^{-1}.

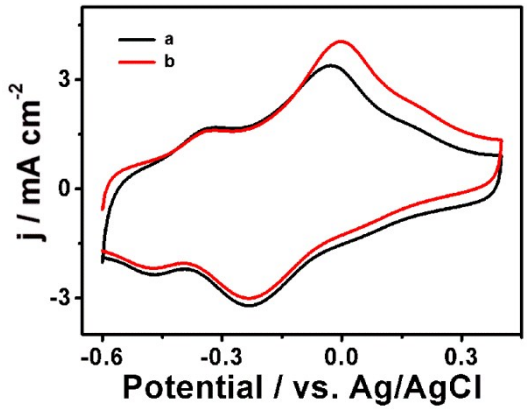

Figure S3 CVs showed the electrochemical oxidation of glucose at the Nafion/GDH/MDB-MWNTs/GCE in 0.1 M PBS containing 10 mM NAD^+ without (a) and with (b) 30 mM glucose, scan rate was 50 mV s^{-1}.

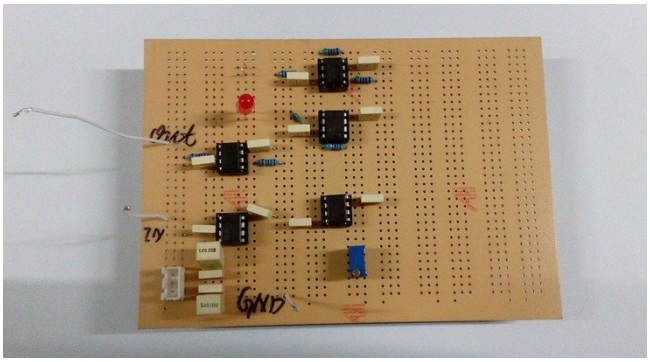

Figure S4 the photo of the illumination compensation device without a 9 V battery and the PBFC.

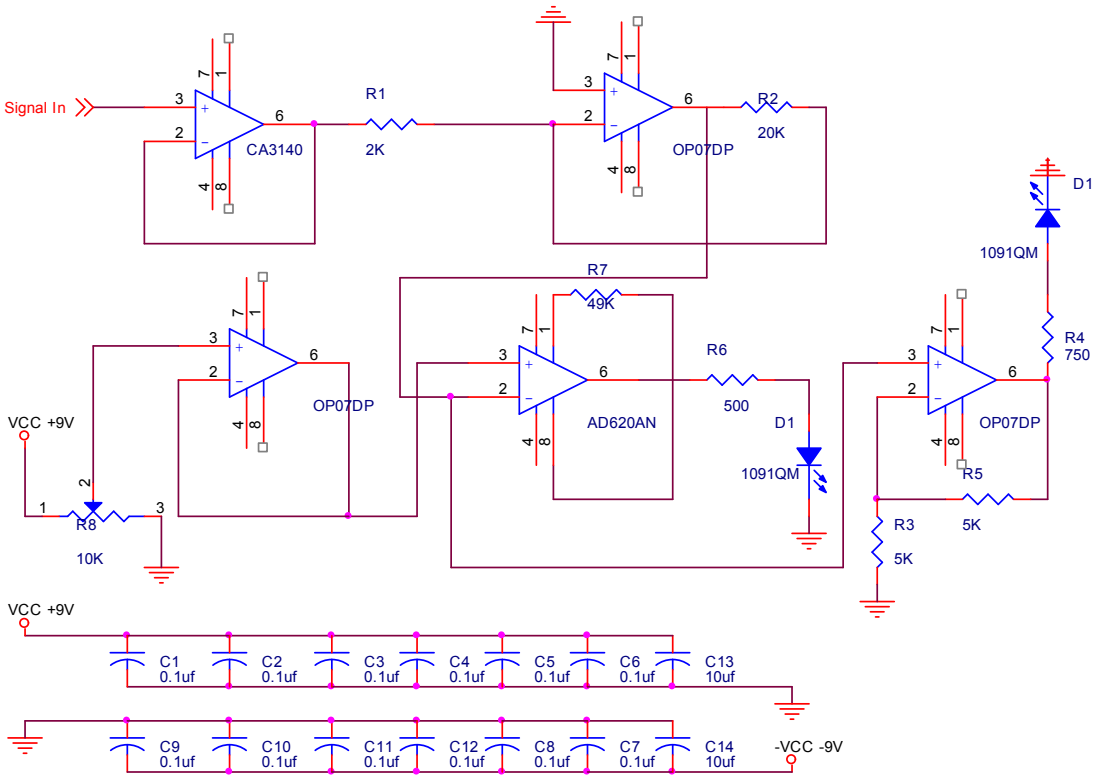

Figure S5 Schematic illustration for the electric circuit of the illumination compensation device.

Experimental section

Chemicals

Sodium hydroxide (NaOH), copper sulfate pentahydrate ($CuSO_4$•$5H_2O$) and lactic acid were purchased from Beijing Chemical Works, P. R. China. Multi-walled carbon nanotubes (MWNTs) (80% purity, diameter 20-50 nm) were purchased from Shenzhen Nanotech. Port. Co. Ltd. (Shenzhen, China). Nafion, β-D-(+)-glucose, Meldola`s blue (MDB) and glucose dehydrogenase (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. NADH and NAD^+ were purchased from the Gen-view Scientific Inc. The single-sided indium tin oxide (ITO) electrodes (30-60 Ω/cm^2, ~1.0 cm×5.5 cm) were bought from Nanbo Display Technology Co., Ltd., China. Glassy carbon (GC) was bought from Tokai Carbon Co., Japan. A 0.10 M phosphate buffer solution (PBS, pH 7.0) was employed as the supporting electrolyte. All other chemicals were of analytical grade and all aqueous solutions were

prepared with ultrapure water (>18.25 MΩ cm) obtained from Millipore system.

Photoelectrochemical biofuel cell

The Cu_2O photocathode was prepared by electrodeposition from aqueous solution of lactate-stabilized copper sulphate on ITO as the working electrode. Firstly, 0.02 M cupric sulfate and 0.4 M lactic acid were mixed in 25 mL solution. The pH of the cupric sulfate solution was adjusted to 11.0 by 1 M NaOH. The applied potential was kept at -0.2 V vs. Ag/AgCl in a 60 ℃ water bath and the electrodeposition time was 10-30 min. After that, it was rinsed with distilled water several times and dried in air.

GC (2.6 mm in diameter) was polished sequentially with 1.0 and 0.3 μm alumina slurry and washed ultrasonically in water and ethanol for a few minutes, respectively. MWNTs were treated by well-established methods with slight modification, MWNTs were dispersed in 30% HNO_3 and then refluxed at 140 °C for 24 h to acquire carboxylic group functionalized MWNTs. 10 μL of the MWNTs suspension (2 mg mL^{-1}) was spread onto a GC electrode (GCE) until dried, the electrode was immersed into 0.5 mM MDB for 30 min to achieve 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, 5 μL of 0.5% Nafion solution was spread onto the electrode surface to form a film (noted as Nafion/GDH/MDB-MWNTs/GCE).

The PBFC was assembled by placing the as-prepared bioanode and photocathode in parallel into 8 mL PBS (pH=7.0) containing 5 mM NAD^+ and 30 mM glucose. The Xe lamp was set facing to the photocathode in order that the luminous bean could illuminate the whole electrode surface.

Automatic illumination compensation device

The PBFC was inset into a device as shown in Figure S4, and the Xe lamp was set facing to the photocathode in order to make the performance of the PBFC change along with the variable ambient illumination.

Apparatus

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. X-ray photoelectron spectroscopy (XPS) analysis was carried on an ESCALAB MK II X-ray photoelectron spectrometer. 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).

Device fabrication

Electric circuit and device assembling. The electric circuit was connected according to **Figure 4B**. The main circuit contains a slide rheostat, an ad620 amplifier, two filter capacitors, three OP07DP amplifiers, a CA3140 amplifier, and a power supply (a dry battery) integrating in a

copper-clad plate. The photoelectrochemincal biofuel cell was inserted to the electric circuit. A LED was connected to the output as the lamplight.

Supplement information

In this work, the glucose catalysis on Nafion/GDH/MDB-MWNTs/GCE was more positive than the NADH catalysis on MDB-MWNTs/GCE. The Nafion layer prevented the electrons from glucose to the bioanode, and then had increased overpotential of the bioanode. On the other hand, the onset potential of the glucose/NAD^+ would be more positive by the increasing of the scan rate.