Electronic Supplementary Material (ESI) for ChemComm.

A miniature origami biofuel cell based on a consumed cathode

You Yu [a,b], Yujie Han [a,b], Baohua Lou [a], Lingling Zhang [a], Lei Han [a], Shaojun Dong [a,b,*]

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

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

E-mail: dongsj@ciac.ac.cn

Material and methods

1. Chemicals

$MnSO_4 \cdot H_2O$ and $KMnO_4$ were purchased from Beijing Chemical Works. Single-walled carbon nanotubes (SWNTs) were purchased from Shenzhen Nanotech. Port. Co. Ltd., paraffin with ceresin was purchased from Sinopharm Chemical Reagent Co., Ltd. 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIMPF6) IL purchased from J&K Chemical Ltd. was used without pretreatment. β-D-(+)-glucose, chitosan (CS) 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. NAD^+ was purchased from the Gen-view Scientific Inc. Graphite flake (-325 mesh) was purchased from Alfa Aesar. Representative soft drinks (i.e., Nutri-Express, Coca Cola and Minute Maid grape juice) were obtained from a supermarket. A 0.10 M phosphate buffer solution (PBS) 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.

2. Modification of bioanode

SWNTs-IL-NAD^+ nanocomposites were prepared by hand-mixing SWNTs, NAD^+ and IL (BMIMPF6). Briefly, 2 mg SWNTs, 8 mg NAD^+ and 30 μL IL were mixed in an agate mortar and then ground for about 30 min to form a viscous gel. A 3 mm diameter of carbonfiber paper (CFP) was washed ultrasonically in ethanol and water for a few minutes and connected with 0.19 mm^2* 20 mm copper wires by silver paint (SEM image was shown in Figure S2). 1 mg SWNTs-IL-NAD^+ gel were immobilized on the CFP surface smoothly (noted as SWNTs-IL-NAD^+/CFP). 5 μL GDH (1 mg mL^{-1}) was coated on the SWNTs-IL-NAD^+/CFP, which was dried at 4 °C overnight and achieved GDH/ SWNTs-IL-NAD^+/CFP. After that, 10 μL of 1% CS solution was spread onto the electrode surface to form a film (noted as CS/GDH/ SWNTs-IL-NAD^+/CFP).

3. Synthesis of MnO_2-graphite flake cathode

For a typical synthesis of α-MnO_2, a 15 mL aqueous solution containing 0.2 g $MnSO_4$•H_2O and 0.5 g $KMnO_4$ was transferred into a 25 mL Teflon-lined stainless steel autoclave and kept at 140 ℃ for 12 h. The product was filtered, washed with distilled water, and then dried at 80 ℃ for 6 h in air. MnO_2 and graphite flake were mixed by different ratios and dissolved in ethanol (noted as MnO_2-GF). 10 μL MnO_2-GF (2 mg ml^{-1} of MnO_2) was coated on the CFP surface and achieved the MnO_2-GF/CFP cathode.

4. Fabrication of origami BFC device

Paraffin wax was used as the filter paper hydrophobization and insulation agent to

construct hydrophobic barrier on filter paper. Firstly, the filter paper was printed by the pattern as shown in Scheme 1B, which was design by Microsoft PowerPoint 2010. The patterned filter paper was immersed into the liquid paraffin wax at 100 ℃ and then cut as the pattern after cooling to room temperature. This origami was cut around the dotted lines on the four small rectangles to get hollow filter paper. Then the bioanode and cathode were placed at the blue circles onto the larger rectangle. The orange lines between rectangles were treated as folding lines for making further micro-channel of 0.82 cm^2 * 0.09 cm upon the electrodes. The origami was clamped by two microscope slides and binder clips. PBS containing biofuels was filled through the silicone tubes. When harvesting energy from soft drinks, the BFC employed biofuels with the mixture of 0.1 M PBS and soft drinks with a ratio of 1:1 (v:v).

5. 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 10-80º (2θ). Scanning electron microscopy (SEM) measurements and energy-dispersive X-ray image (EDX) were made on a XL30 ESEM with an accelerating voltage of 10 kV to determine the morphology of products. X-ray photoelectronspectroscopy (XPS) analysis was carried on an ESCALAB MK II X-ray photoelectron spectrometer.

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed with an electrochemical analyzer (CHI 832, Shanghai, China). The polarization curves (U-I) were achieved by the LSV measurement at scan rate 1 mv s^{-1}. A three-electrode system was used including a platinum flat as the counter electrode and the

Ag/AgCl (saturated KCl) as reference electrode, respectively. The operation of the biofuel cell was performed at 37 °C, other experiments were carried out at room temperature (22 °C).

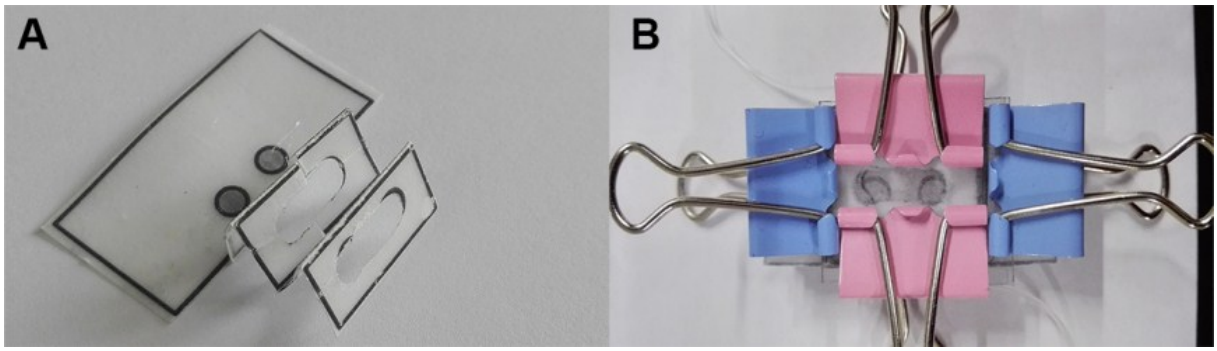

Figure S1. The photos showed the original origami (A) and the origami device without electrodes (B).

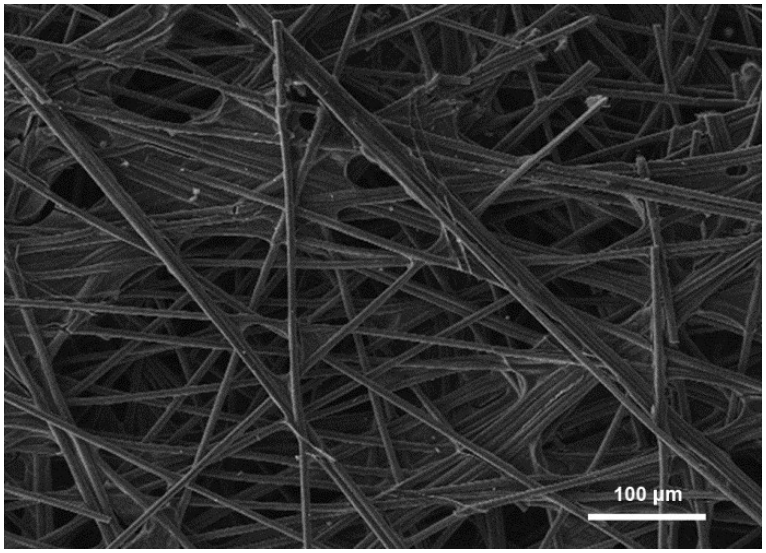

Figure S2. SEM images of the original carbonfiber paper (CFP).

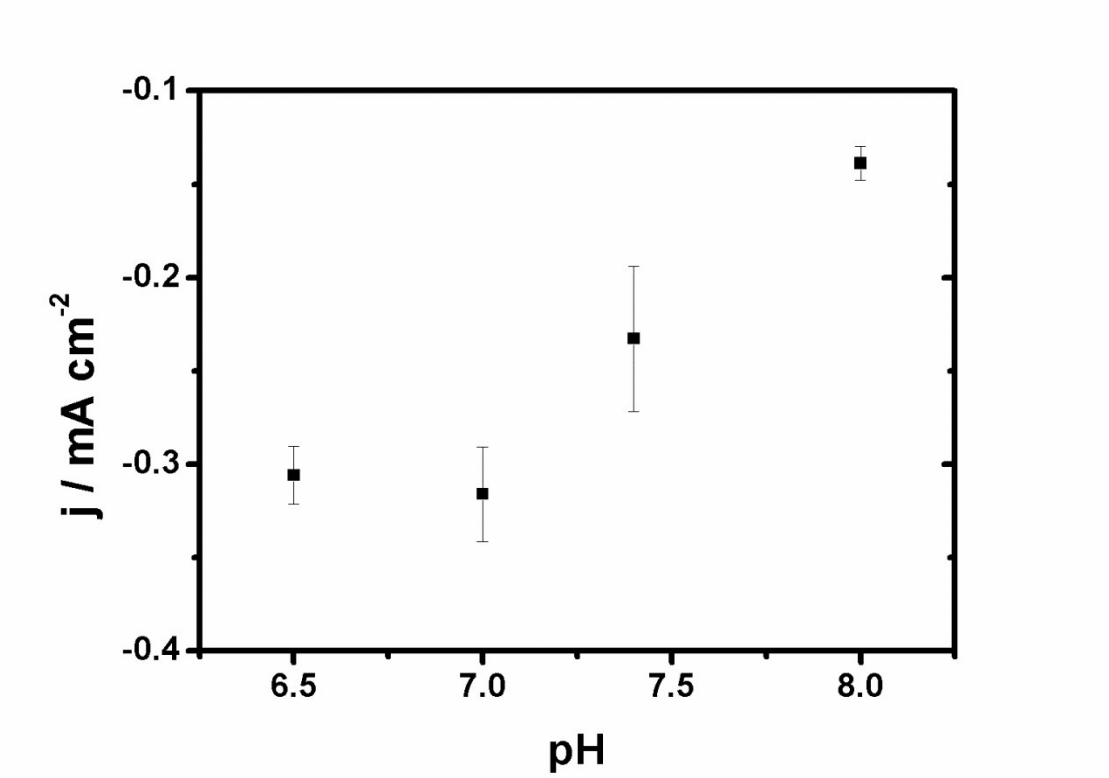

Figure S3. Current densities of the MnO_2-GF (1:2) cathodes obtained at 0.15 V in PBS with different pH.

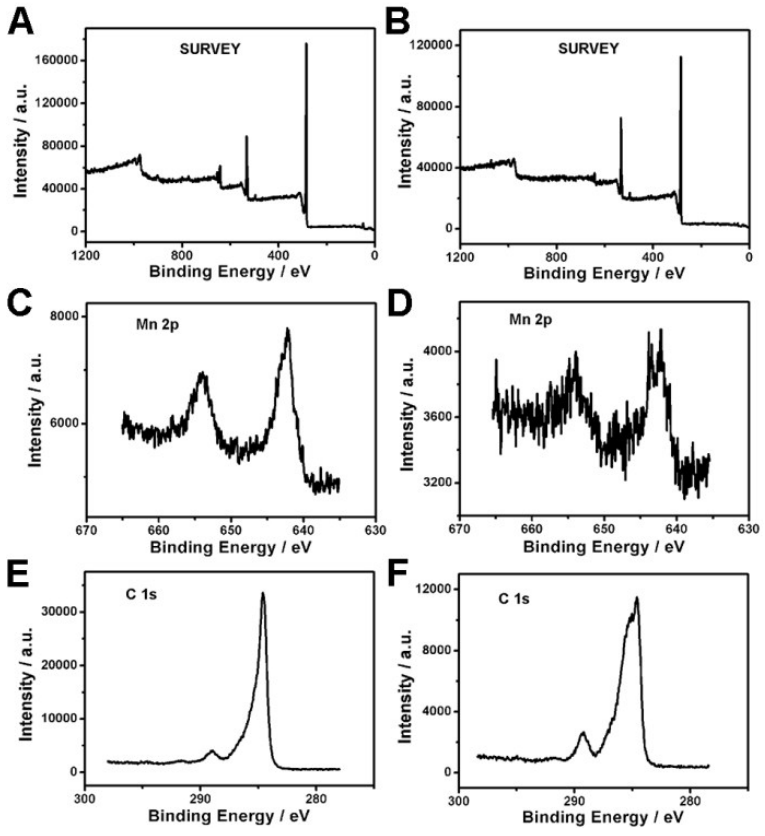

Figure S4. XPS spectra for MnO_2-GF cathode obtained before (A, C, E) and after (B,

D, F) discharging for 300 s at 0 V.

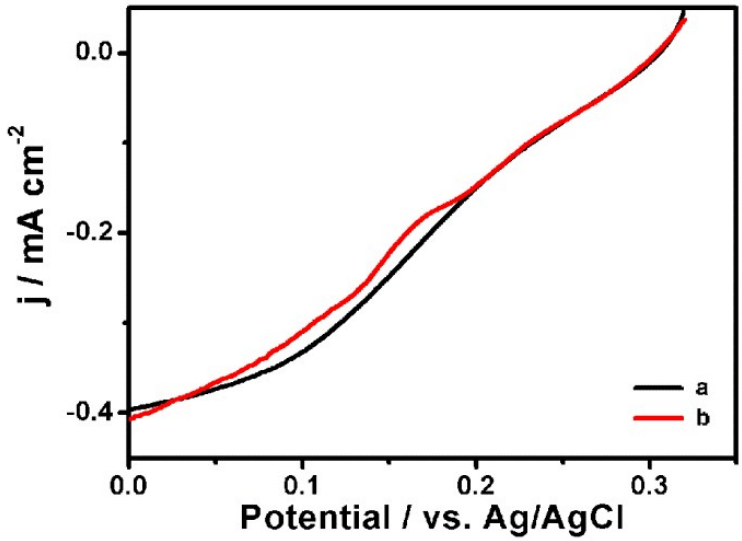

Figure S5. LSV recorded at the MnO_2-GF (1:2) cathode in PBS (pH 7.0) without (a) and with (b) 30 mM glucose.