

Supplemental Information

Paper-Based Analytical Devices Relying on Visible-Light Enhanced Glucose/Air Biofuel Cells

Kaiqing Wu[†], Yan Zhang[†], Yanhu Wang[†], Shenguang Ge[‡], Mei Yan[†], Jinghua Yu^{*†},
Xianrang Song[§]

[†] School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, P. R. China

[‡] Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Jinan 250022, P. R. China

[§] Shandong Provincial Key Laboratory of Radiation Oncology, Shandong Cancer Hospital and Institute, Jinan 250117, P. R. China

*Corresponding author: Jinghua Yu

E-mail: ujn.yujh@gmail.com

Telephone: +86-531-82767161

Apparatus.

To investigate the stepwise-modified paper electrode, we measured the electrochemical impedance spectroscopy (EIS) of the modified paper electrode on an IM6x electrochemical station (Zahner, Germany). Scanning electron microscope (SEM) images and energy dispersive spectrometer (EDS) were obtained using a QUANTA FEG 250 thermal field emission SEM (FEI Co.,USA) and utilized to characterize the Au@Ag BMPs, bare paper, and modified paper. UV-vis absorption spectra were recorded on a UV-3101 spectrophotometer (Shimadzu, Japan). A 150 W Xe lamp (CHF-XM500) equipped with monochromator (CHF-300) (Beijing Changtuo.) was used to provide light for the cathode, and the incident light intensity was calibrated by a radiometer. Electrochemical measurements were performed on a CHI 660D electro-chemistry work station (Shanghai CH Instruments Co., China) with a new three-electrode system, which using Ag/AgCl (saturated KCl) electrode as reference electrode, platinum wire as auxiliary electrode and the modified PWE as the working electrode.

Reagents.

Tetrachloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, 1%, w/w), silver nitrate (AgNO_3), and ascorbic acid (AA) were purchased from Sigma-Aldrich Chemical Co. (USA). Polyvinyl pyrrolidone (PVP) was purchased from Alfa Aesar China Ltd. NaBH_4 was obtained from Shanghai Chemical Reagent Co. Ammonia hydroxide was purchased from Sinopharm Chemical Reagent Co., Ltd.

Fabrication of Origami Device.

The fabrication process consists of wax-printing, baking the wax-patterned sheet, screen-printing electrodes, cutting, and the whole fabrication process within 10 min on a paper sheet. Wax-printing has been drew attention in the applications of microfluidic paper-based analytical devices. The paper-based device (shown in Scheme 1A) was comprised of a single layer of bare paper (the black one,) and three layers of patterned rectangular papers with the same size (15.0 mm×15.0 mm), named as anodic tab (the blue one), reservoir tab (the red one), and cathodic tab (the green

one). The microfluidic origami electronic device consisted of three unprinted line and three circular hydrophilic zones. The diameter of circular hydrophilic zones on anodic tab, reservoir tab, and cathodic tab are 6 mm, 6 mm, and 8 mm, respectively. The zone of folding line, placed in the middle of each two tabs and unprinted, was used to ensure the hydrophilic zones are properly and exactly aligned after folding. The circle hydrophilic zones were designed for screen-printing carbon electrode on anodic tab and cathodic tab, respectively. Wax was used as the paper hydrophobization and insulation agent in this work. The progress of baking the wax-patterned sheet was operated on a digital hot plate set at 150°C. After melt the printed wax for 150 s, the wax would penetrate through the paper to form the hydrophobic and insulating patterns. Then, the as-prepared sheet was ready for printing electrode after cooling to room temperature. A disk-like carbon electrode (5.0 mm in diameter) was screen-printed onto the circle hydrophilic zones of anodic tab (Scheme 1B, Figure S1) and an arcuate carbon electrode was screen-printed onto the circle hydrophilic zones of cathodic tab (Scheme 1C, Figure S2).

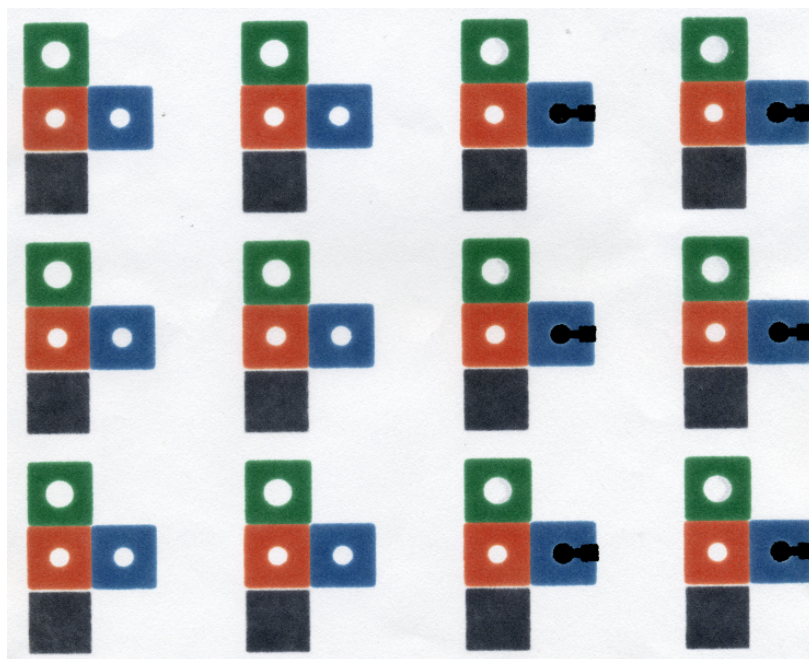


Figure S1. Right side of wax-printed VDBFCI after baking (the first and second columns) and screen-printing of carbon anodes (the third and fourth columns) on a paper sheet

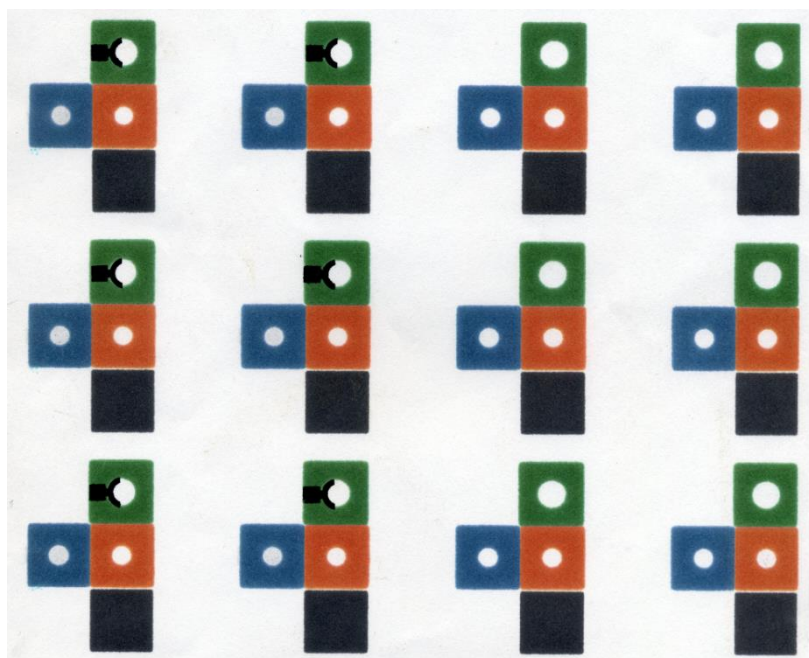


Figure S2. Reverse side wax-printed VDBFCI after baking (the third and fourth columns) and screen-printing of carbon anodes (the first and second columns) on a paper sheet

Preparation of the Au@Ag BMPs.

The Au@Ag BMPs were prepared through a simple kinetic controlled co-reduction route at room temperature according to the reported literature ¹. Briefly, 0.2 g of PVP was firstly added into 10 mL of AgNO₃ (2 mM) aqueous solution and stirred for 5 min, when the solution became clear, 2 mL of 2.8% NH₃·H₂O aqueous solution was injected into the above mixture and stirred for another 2 min at room temperature. Subsequently, 0.5 mL of HAuCl₄ aqueous solution was added. After 2 min, 1 mL of AA solution was added in under stirring. The solution color changed within 10 s. The products were washed with water and ethanol several times by centrifugation at 8000 rpm. Finally, the products were re-dispersed in 5 mL 10 mM PBS (pH 7.0) for further use.

Preparation of Au-PBAE and Au-PCE.

The gold nanocomposite modified paper bioanode electrode (Au-PBAE) and gold nanocomposite modified paper cathode electrode (Au-PCE) were fabricated through growth of an Au layer on the surfaces of cellulose fibers in the paper sample zone of PBAE/PCEThe Au layer enhanced the conductivity and enlarged the effective surface area of bare PBAE/PCE. Firstly, the suspension of Au seeds were prepared by using NaBH_4 as the reductant and stabilized with sodium citrate according to the literature². Then, 20.0 mL asprepared Au seeds solution were dropped into the paper sample zone of bare PBAE/PBCE. Then the origami device was equilibrated at room temperature for 1 h to optimize the surface immobilization of Au seeds on cellulose fibers. After rinsing with water thoroughly to remove loosely bound Au seeds, 20 μL freshly prepared growth aqueous solution of PBS (10.0 mM, pH 7.0) containing 1.2 mM HAuCl_4 , 2.0 mM cetyltrimethylammonium chloride and 7.2 mM H_2O_2 for seeds growth were applied into the Au seeded PBAE/PCE, and incubated at room temperature for 15 min. Subsequently, the resulting Au-PBAE/PCE was washed with water thoroughly. Thus a layer of interconnected Au on cellulose fibers with good conductivity were obtained, which were dried at room temperature for 20 min.

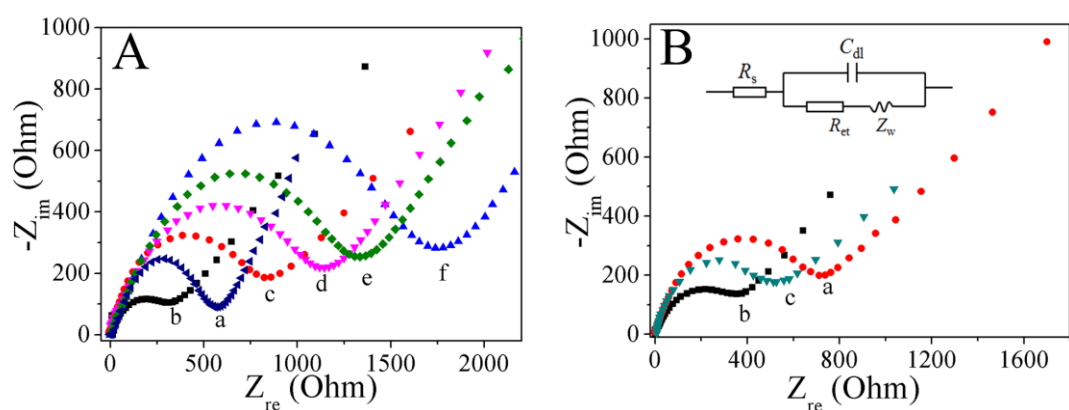


Figure S3. (A) EIS of PBAE with different surface condition in a background solution of 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution containing 0.5 M KCl: (a) bare PBAE, (b) Au/PBAE, (c) $\text{Ab}_1/\text{Au}/\text{PBAE}$, (d) $\text{BSA}/\text{Ab}_1/\text{Au}/\text{PBAE}$, (e) $\text{CA15-3}/\text{BSA}/\text{Ab}_1/\text{Au}/\text{PBAE}$, (f) electrode ‘e’ incubated with GDH-Au@Ag BMNPs- Ab_2 . (B) EIS of PBCE: (a) bare PBCE, (b) Au/PBCE, (c) $\text{pTTh}/\text{Au}/\text{PBCE}$.

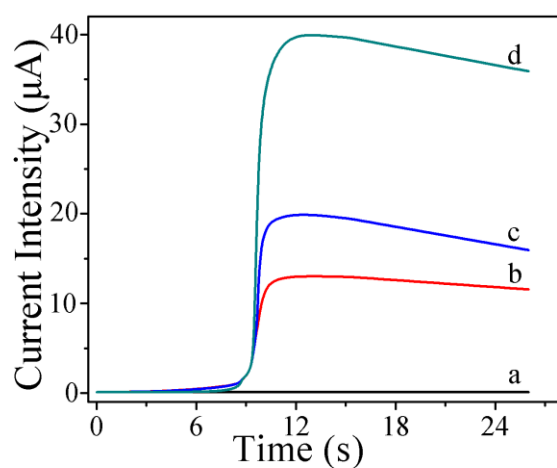


Figure S4. Current response of the VDBFCI using GDH-Au@Ag BMNPs (a,c,d) or GDH (b) as labels, $c_{\text{CA15-3}}$: 0 U mL^{-1} (a), 5 U mL^{-1} (b,c) and 20 U mL^{-1} (d).

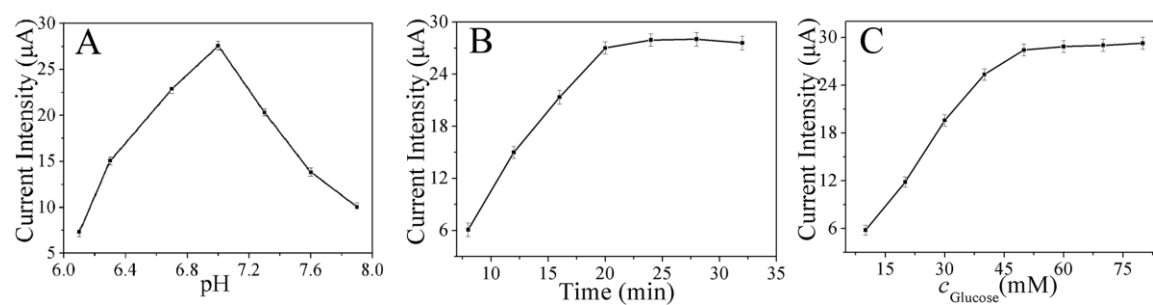


Figure S5. The effects of (A) pH, (B) incubation time, and (C) glucose concentration on the response of the VDBFCI to 15 U mL⁻¹ CA15-3.

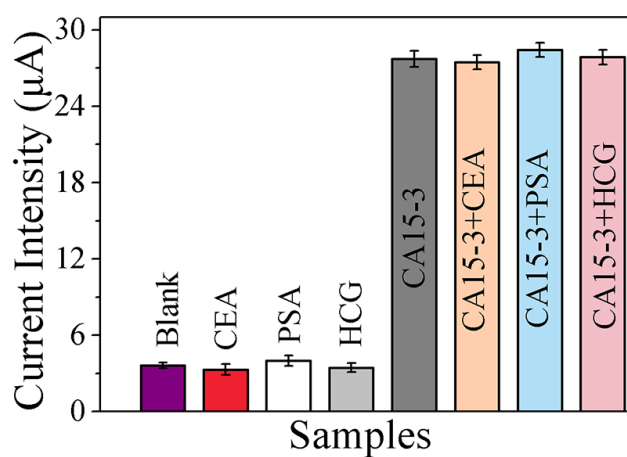


Figure S6. Selectivity of the proposed immunosensor toward: pure interference solution or CA15-3 containing the three interference solutions.

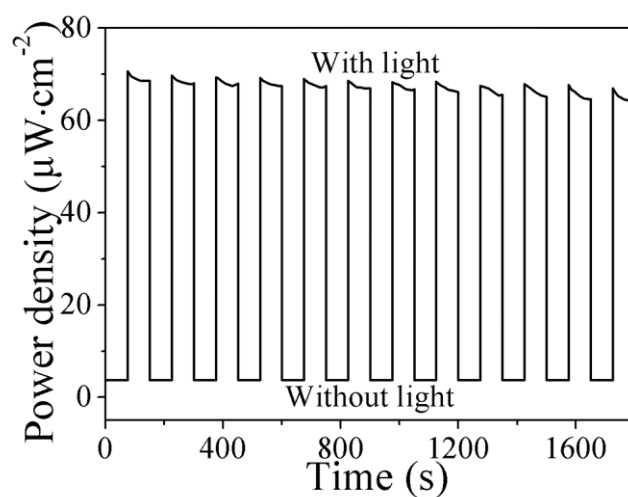


Figure S7. The power output cycle of the visible light enhanced BFCs with the illumination on and off.

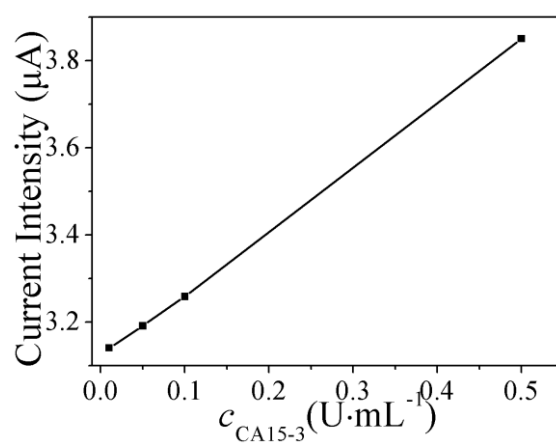


Figure S8. Relationship between current response of biofuel cell and concentration of CA15-3 in the as-prepared VDBFCI (The amplification of Figure 3) .

Optimization of the Amount of pTTh

The electrocatalytic oxygen reduction crucially depends on the amount of electro-polymerized pTTh, and therefore we optimized by investigating different polymerization charges and evaluating the behaviors of the obtained pTTh films towards oxygen reduction reaction. Samples were grown to varying charge densities, from 0.1 to 1 C cm⁻², by varying the polymerisation time with a constant current of 10mA cm⁻². As shown in Figure S9, the catalytic current increases with the amount of pTTh, and then reaches a maximum value at a charge density of 0.65 C cm⁻².

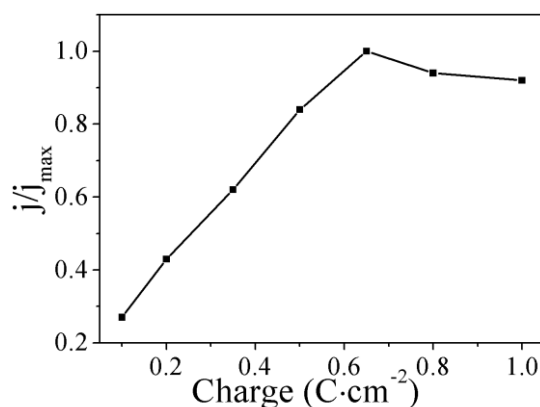


Figure S9. The catalytic current responses for different pTTh polymerization charge.

References

- (1) Li, W.Z.; Kuai, L.; Qin, Q.; Geng, B. Y. Ag–Au Bimetallic Nanostructures: Co-Reduction Synthesis and Their Component-Dependent Performance for Enzyme-Free H₂O₂ Sensing. *J. Mater. Chem. A* **2013**, *1*, 7111-7116.
- (2) Busbee, B. D.; Obare, S. O.; Murphy, C. J. An Improved Synthesis of High-Aspect-Ratio Gold Nanorods. *Adv. Mater.* **2003**, *15*, 414-416.