

Single wearable sensing energy device based on photoelectric biofuel cells for simultaneous analysis of perspiration and illuminance

*You Yu^{a, b}, Junfeng Zhai^a, Yong Xia^a and Shaojun Dong^{a, b, *}*

^aState Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, PR China;

^bUniversity of the Chinese Academy of Sciences, Beijing, 100049, PR China

Corresponding author: Prof. Shaojun Dong, Tel: +86-431-85262101, Email:

dongsj@ciac.ac.cn

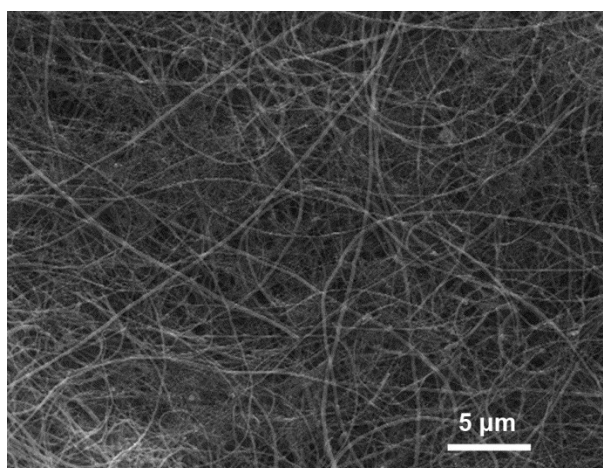


Figure S1. (A) The SEM image of the buckypaper.

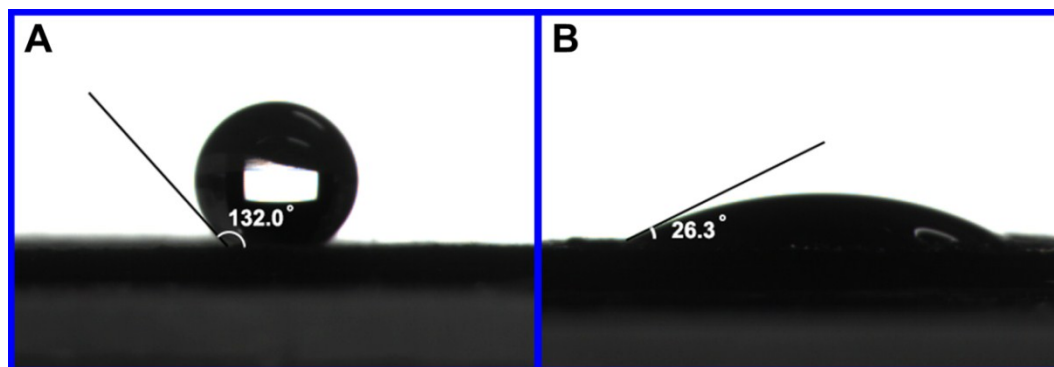


Figure S2. Contact angle images of buckypaper (A) and MDB-buckypaper (B).

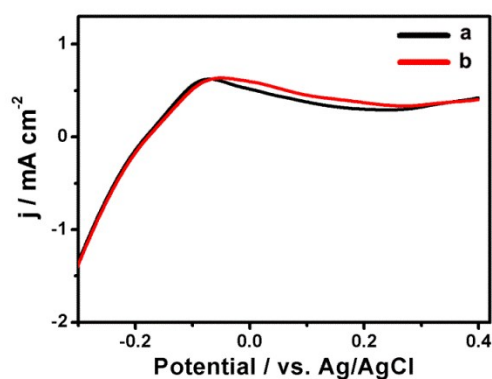


Figure S3. LSVs obtained at CS/MDB-buckypaper in 0.10 M PBS with (a) and without (b) 30 mM lactate. The scan rate is 20 mV s⁻¹.

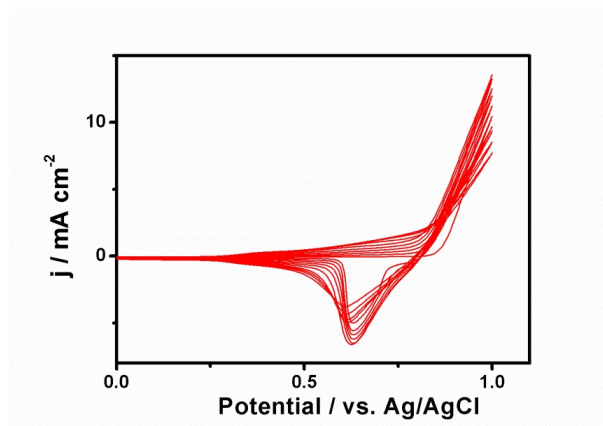


Figure S4. Cyclic voltammetric electrodepositions obtained in acetonitrile solution containing 50 mM TTh and 0.1 M LiClO₄. Scan rate: 50 mV s⁻¹.

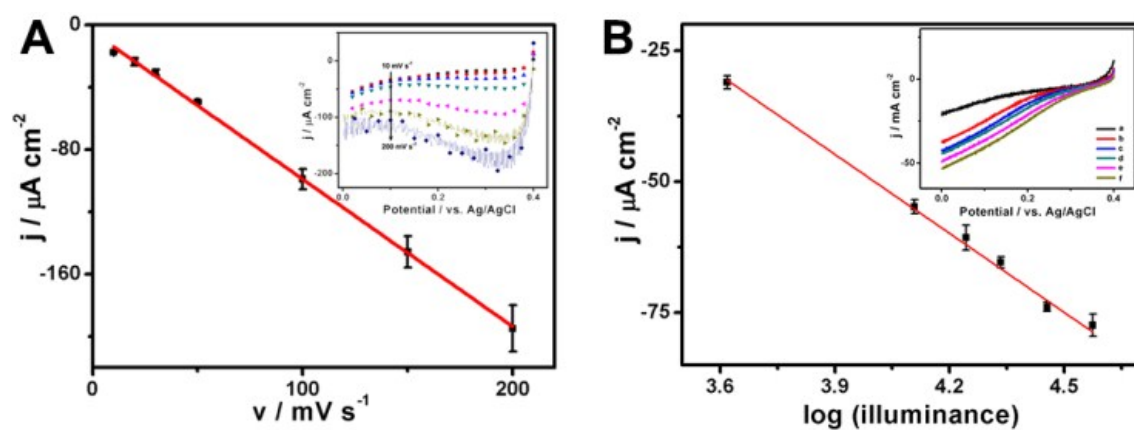


Figure S5. (A) Plots of peak current densities at 0.325 V versus scan rate from 10 to 200 mV s⁻¹. (Inset) LSV of pTTh photoelectrode obtained in PBS at scan rate 10, 20, 30, 50, 100, 150, 200 mV s⁻¹. (B) The linear function of the plot of current densities at 0 V versus the logarithm of illuminance. (inset) LSV of pTTh photoelectrode

response to illuminance of 4150 (a), 12830 (b), 17500 (c), 21600 (d), 28500 (e) and 37600 (f) Lux in 0.1 M PBS.

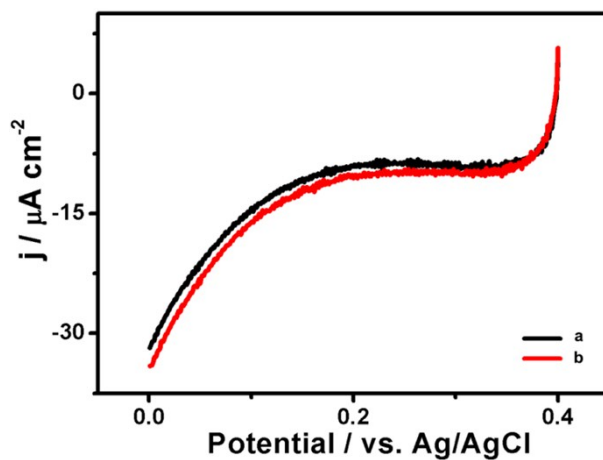


Figure S6. LSV obtained at the pTTh photoelectrode in PBS without (a) and with (b) 30 mM lactic acid under LED light illumination.

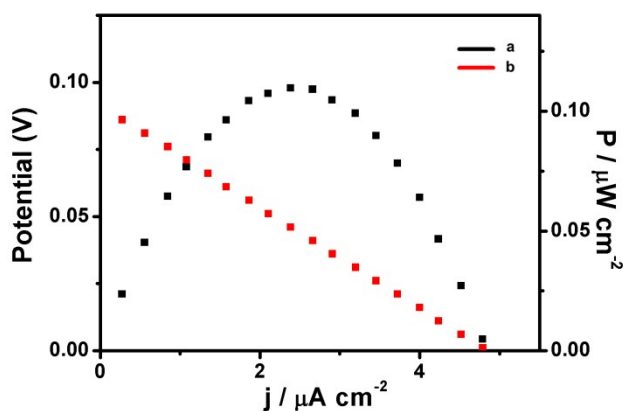


Figure S7. The power output (a) and the polarization curve (b) of the PBFC in the dark.

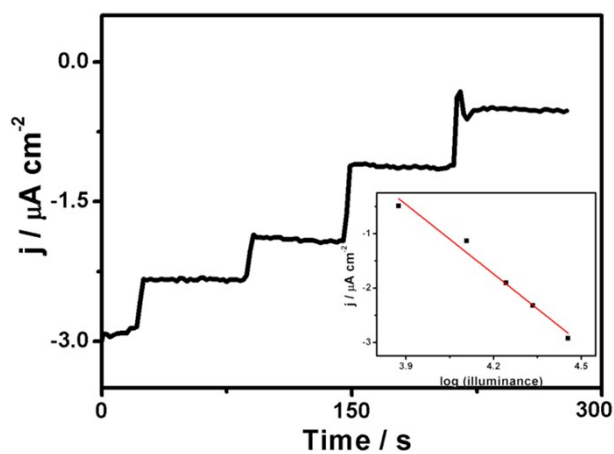


Figure S8. Current-time recording of short-circuit current for successive changes of

illuminance 7500, 12830, 17500, 21600 and 28500 Lux measured at 0 V in 0.10 M PBS contain 48 mM lactate. The inset is the plot of current density versus illuminance.

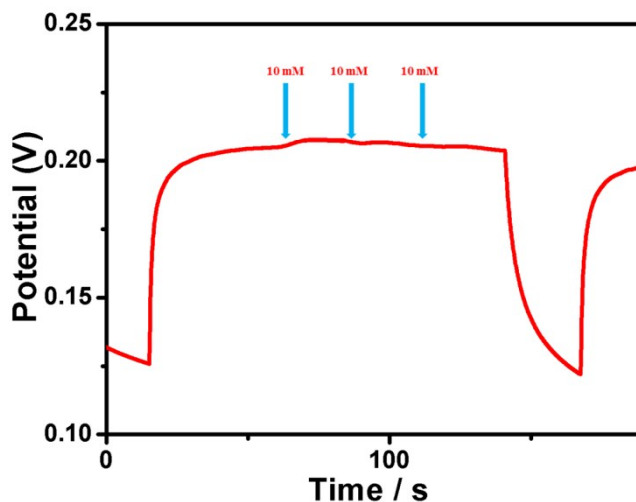


Figure S9. Open circuit potential-time recording of the PBFC response to successive additions of lactate concentrations. The experiment started in 0.1 M PBS (pH 6.0) containing 10 mM lactate under 4150/37600 Lux illuminance.

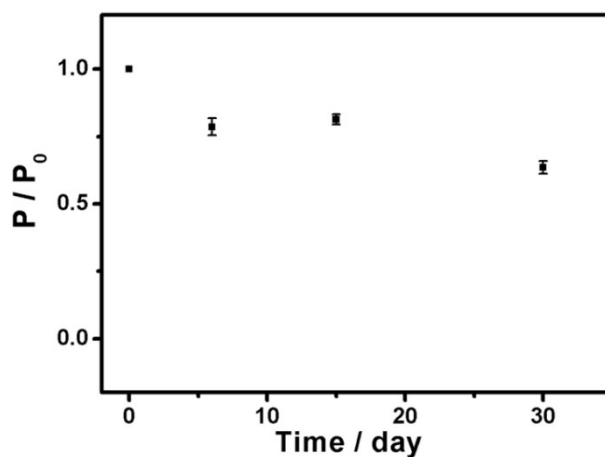


Figure S10. Stability of short-circuit current of PBFC stored at 4 °C in 0.1 M PBS with addition of 30 mM lactate at 0 V.

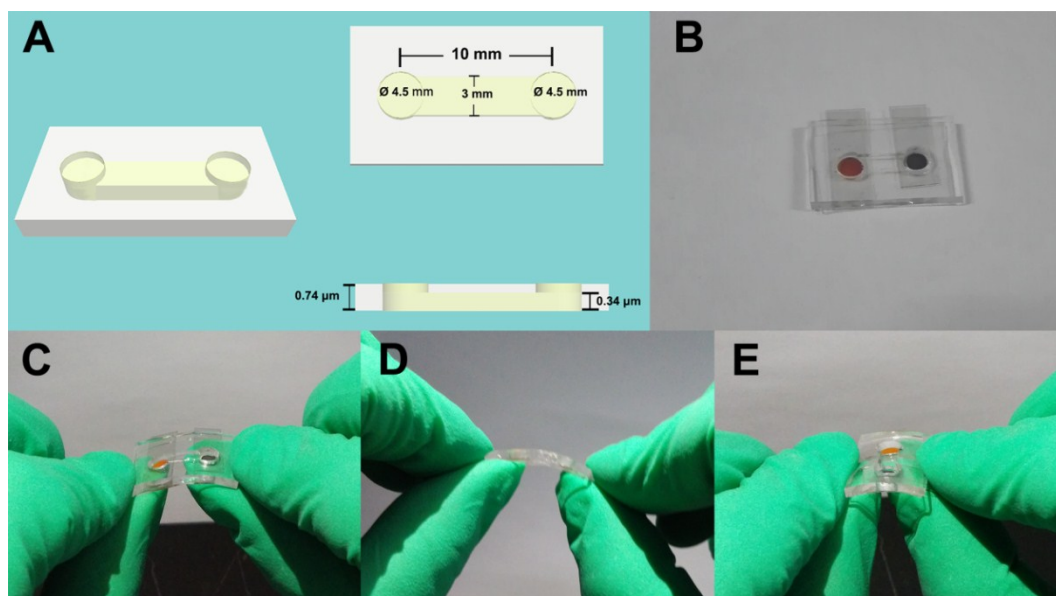


Figure S11. (A) Schematic illustration of the PDMS membrane with hollow channel. (B) Photos of the WSED. (C, D, E) Photos showed the WSED under mechanical strain tests including different directions of bending.

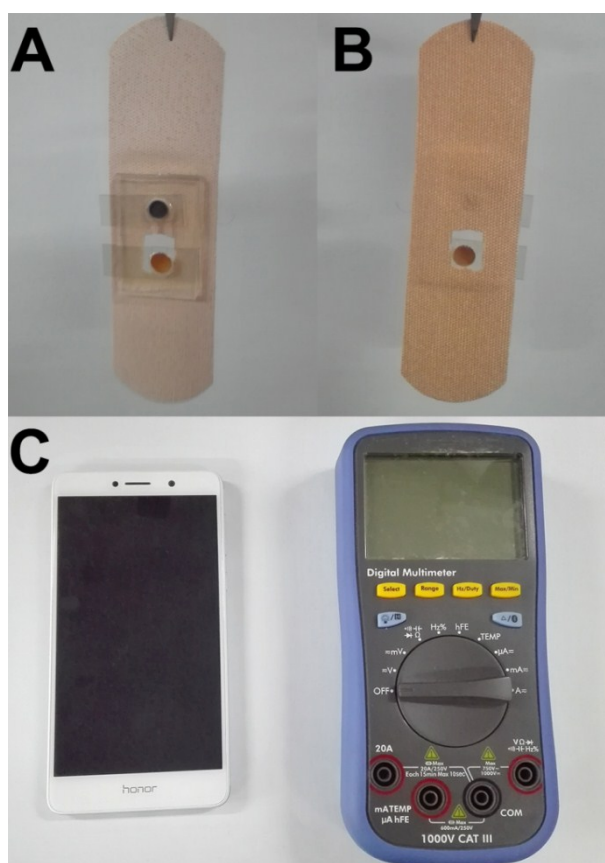
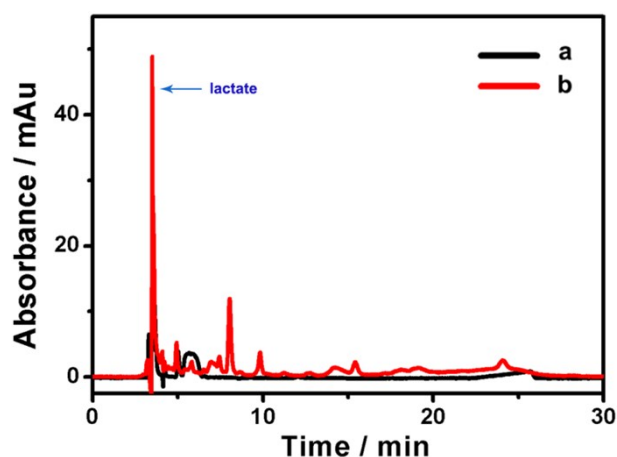


Figure S12. The photos about the back (A) and the front (B) of the WSED. (C) A multimeter contain a Bluetooth module (TI-CC2541) and a Bluetooth-enabled smartphone with the “battery test” App designed by authors.



	Retention time / min	Peak area / mAu·s
Standard simple	3.580	187.370
Sweat	3.512	326.242

Figure S13. Chromatograms of a standard simple of 1 mg mL^{-1} lactate (a) and the sweat sample (b). The diagram showed retention time and peak area of standard simple and sweat.

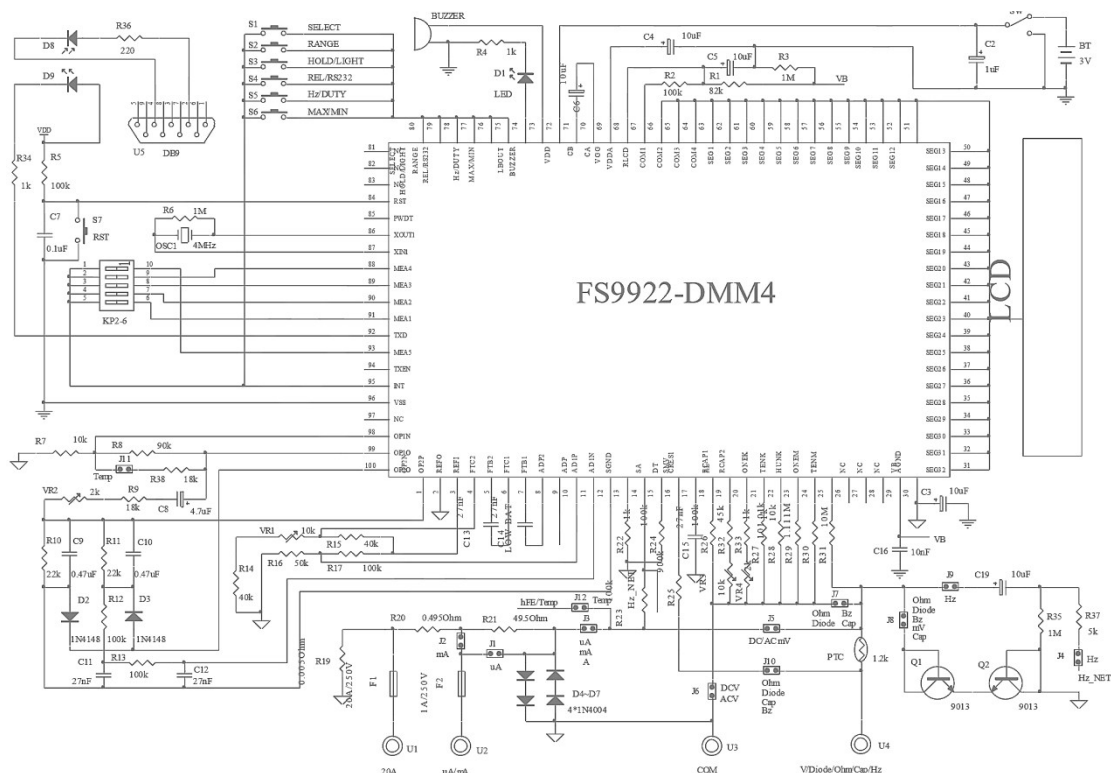


Figure S14. Schematic illustration for the multimeter (FS9922-DMM4).

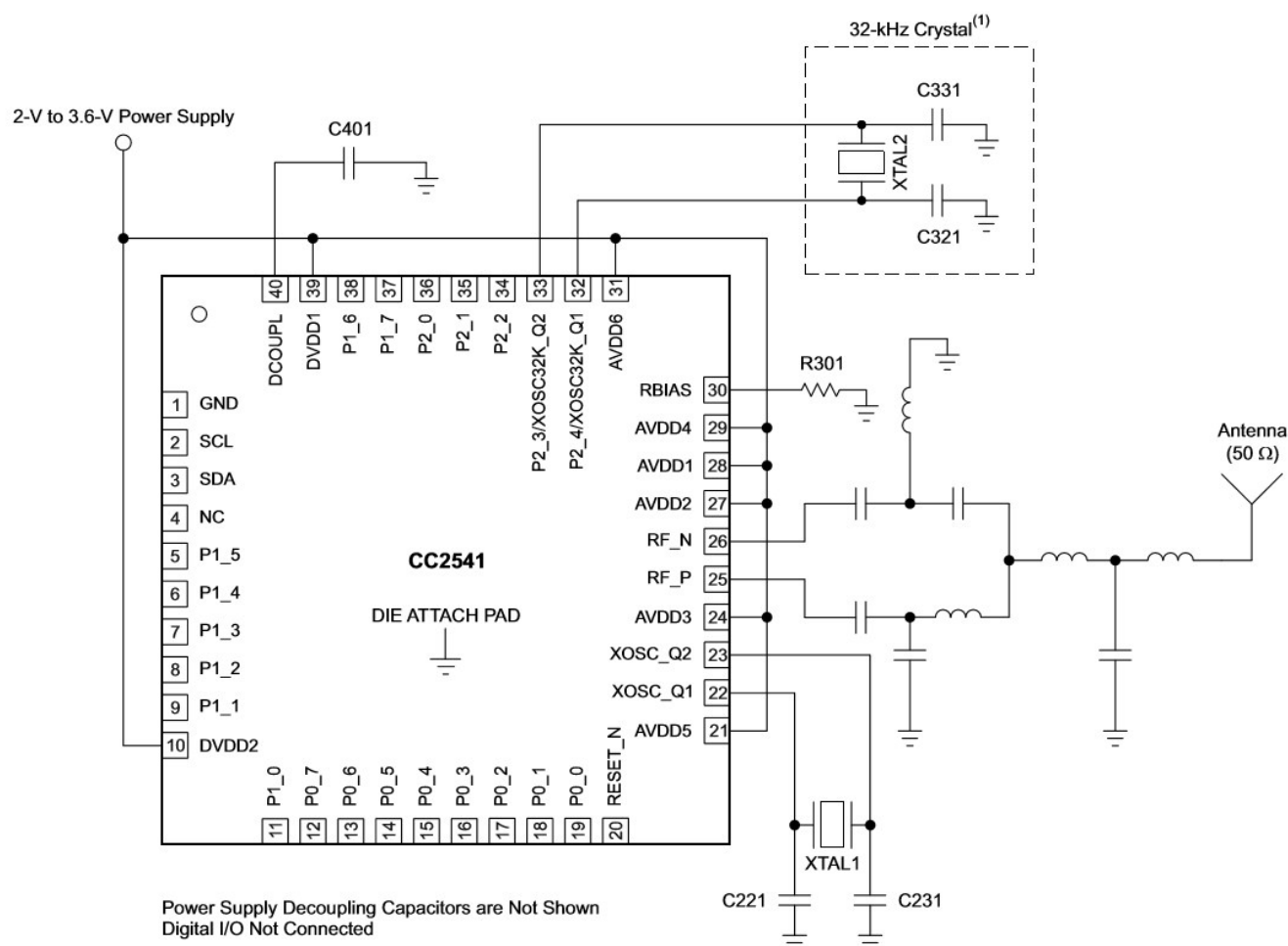


Figure S15. Schematic illustration for the Bluetooth module (TI-CC2541).

Experimental Procedures

Chemicals

2,2':5',2''-terthiophene (TTh) purchased from J&K Chemical Ltd. was used without pretreatment. Buckypaper was purchased from Nano Tech Labs, Inc. (Yadkinville, NC). LiClO₄, acetonitrile and lactic acid were purchased from Beijing Chemical Works, P. R. China. Chitosan, polydimethylsiloxane (PDMS) (10:1 w/w base:cross-linker), Meldola's blue, 1,1'-ferrocenedicarboxylic acid and LOD (E.C. 1.13.12.4, initial activity of 20 U mg⁻¹ from *Pediococcus* sp.) were obtained from Sigma and used as received. The single-sided indium tin oxide coated polyethylene

terephthalate (ITO-PET) electrodes ($15 \pm 2 \text{ } \Omega/\text{cm}^2$, light transmittance $> 76\%$) were bought from Kaivo Optoelectronic Technology Co., Ltd., China. A 0.10 M phosphate buffer solution (PBS, pH 6.0) was employed as the supporting electrolyte. All other chemicals were of analytical grade and all aqueous solutions were prepared with ultrapure water ($>18.25 \text{ M}\Omega \text{ cm}$) obtained from Millipore system.

Photoelectric biofuel cell assembly

In situ polymerization of TTh on ITO-PET electrodes proceeded in acetonitrile solution containing 50 mM TTh and 0.1 M LiClO_4 by the cyclic voltammetric electrodeposition. ITO-PET electrodes were coated by a PDMS membrane with a circular opening of 4 mm diameter aimed at maintaining the constant area. Cyclic voltammetric electrodeposition was performed of 10 circles from 0 V to 1.0 V at 50 mv s^{-1} to achieve pTTh/ITO-PET.

Buckypaper was immersed into 0.5 mM MDB for 24 h to achieve a hydrophilic electrode. Then MDB-buckypaper was cut into small circles of 3 mm diameters and adhered to ITO-PET electrodes with silver paint. $5 \text{ } \mu\text{L}$ $\text{Fc}-(\text{COOH})_2$ (5 mM) was pipetted onto the MDB-buckypaper and dried at room temperature. Then $5 \text{ } \mu\text{L}$ LOD (1 mg mL^{-1}) was coated on the buckypaper, which was dried at $4 \text{ } ^\circ\text{C}$ overnight and achieved LOD/MDB-buckypaper. After that, $5 \text{ } \mu\text{L}$ of 1% chitosan solution was spread onto the electrode surface to form a film (noted as CS/ LOD/MDB-buckypaper). The photoelectric biofuel cell was assembled by placing the as-prepared bioanode and photocathode in parallel into PBS (pH=6.0). The Xe lamp or LED was set facing to

the photocathode in order that the luminous beam could illuminate the whole photoelectrode surface.

Self-powered wearable sensing energy device

The as-prepared bioanode and photocathode were inset in parallel into PDMS membrane with a 29.34 mm³ channel to achieve a plane device (Figure S9B). This device was pasted in an adhesive bandage with a hollow rectangle just on the photocathode for the external illumination and then the device was set upon the forehead. To further fabricate a wireless WSED, the bioanode and photocathode were connected with a multimeter (FS9922-DMM4) with a Bluetooth module (TI-CC2541). A Bluetooth-enabled smartphone was used to record the data by an app designed by authors.

Apparatus

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 contact angle were measured by JC2000D1 (shanghai zhongchen instrument, China). Acchrom S6000 high performance liquid chromatograph was used for the quantitative analysis of target analytes. The light sources were a 300 W Xenon lamp (PLS-SXE 300, Beijing Trusttech Co. Ltd., China) with a UV-cut filter ($\lambda \geq 420$ nm) and a LED system with 4 white LED (0.5 W). 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