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Supporting Information

Bifunctional bio-photoelectrochemical cells: a “trading” platform for simultaneous production of electric power and hydrogen peroxide

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Experimental procedures

Materials: Anatase Titanium dioxide (TiO_2, 99.8%), *meso*-tetrakis(4-carboxyphenyl)-porphyrin (TCPP, Dye content 75%), chenodeoxycholic acid (98%), tetraisopropyl orthosilicate (TPOS, 99%), and resorcinol (99%) were purchased from Aladdin Reagent. Tetraethyl orthosilicate (TEOS, 99%) and hydrofluoric acid (HF, 40 wt%) were bought from Xilong Scientific. α-Terpineol (98%) and ethyl cellulose (18-22 mPa·s, 5% toluene/isopropyl alcohol 80:20) were bought from Macklin Reagent. Glucose dehydrogenase (GDH, ≥200 U mg^{-1}) was purchased from Sigma-Aldrich. GDH solution was prepared by dissolving the powder into 0.025 M Tris-HCl at pH 8.0 to get an enzymatic solution with the concentration of 5 mg mL^{-1}. The single-sided indium tin oxide (ITO) and F-doped indium tin oxide (FTO) conducting glass were purchased from Huananxiangcheng, Hunan, China. All other chemicals of analytical grade were purchased from Beijing Chemical Reagent Corporation and used without further purification. Tris-HCl buffer solution (0.25 M, pH 8.0) containing 0.1 M KCl and phosphate-buffered saline (PBS, 0.1 M, pH 8.0) were respectively prepared as the anodic and cathodic supporting electrolyte. Ultrapure water (>18.25 MΩ cm) treated by Millipore Milli-Q was used throughout unless otherwise stated and all of the experiments were carried out at room temperature (20 ± 3°C).

Characterization: Morphology and structure characterizations were carried out with a PHILIPS XL30 ESEM field-emission scanning electron microscopy (SEM) at accelerating voltages of 5 kV (for MCHS and $SiO_2@SiO_2/C$ composite) and 10 kV (for TiO_2 and $TCPP/TiO_2$ electrodes). Transmission electron microscopy (TEM) and high-angle annular dark field (HAADF)-scanning transmission electron microscopy (STEM) images were obtained from a JEM-2010 apparatus operating at 200 kV, equipped with an energy-dispersive spectrometer (EDS). X-ray diffraction (XRD) data were recorded using a D8 ADVANCE (Bruker, Germany) X-ray diffractometer with Cu Kα radiation (λ= 1.5406 Å). X-ray photoelectron spectra (XPS) were acquired using a Thermo Scientific K-Alpha photoelectron spectrometer with an excitation source of Al Kα radiation. The Raman spectroscopy was performed with a LabRAM HR800 confocal

Raman microscope, analyzed using a 532 nm laser (20 s accumulation, averaged over 1 scan). The UV–Vis absorption spectra were detected with an Agilent Cary 60 (Varian) UV–Vis-near-infrared spectrometer. The UV-Vis diffuse reflectance spectra (DRS) were measured by PE-Lambda 35 (Perkinlmer, America). The Fourier-transform infrared spectroscopy (FTIR) measurements were performed using a VERTEX 70 Fourier-transform infrared spectrometer (Bruker, Germany) with diamond reflection crystal. Nitrogen adsorption isotherms were measured at 77.35K using an Autosorb iQ Station (Quantachrome). The samples were degassed under vacuum at 180°C for 10 h before analysis. Dynamic light scattering (DLS) measurements were carried out at 25°C on a Malvern Zetasizer Nano ZS instrument.

Electrochemical and photoelectrochemical measurements: To evaluate the performance of single electrodes, a standard three-electrode configuration was adopted. In all measurements, the prepared biophotoanode, cathode, and rotating ring-disk electrode (RRDE) were set as working electrodes. Platinum foil and Ag/AgCl (saturated KCl) electrodes were adopted as the counter electrode and reference electrode, respectively. For single electrodes and BPEC cell tests, equal electrode area ($S = 0.1256$ cm^2, $r = 0.20$ cm) was adopted to monitor the electrochemical performance. The two-chamber photoelectrochemical cell, designed by ourselves, was made of Teflon and plexiglass (transmittance 90%). The (photo)electrochemical experiments were performed with CHI 842C and CHI 660 electrochemical workstations. A 500 W Xe lamp (CHF-XM500W, Beijing Trusttech Co., China), coupled with a 420 nm cut-off filter, was used as a mimicking visible-light source (the irradiation intensity was 100 ± 2 mW cm^{-2}) for photoelectrochemical tests.

Preparation of the anode of BPEC cells: The TiO_2 paste was prepared by dispersing 450 mg anatase-phase TiO_2 nanoparticles and 225 mg ethyl cellulose into 2.5 mL α-Terpineol and then stirring overnight. TiO_2 films were coated onto FTO glass electrodes, which were pretreated with 40 mM $TiCl_4$ solution, by the doctor-blade method using four layers of perforated Scotch tape ($S = 0.1256$ cm^2, $r = 0.20$ cm) to guarantee the identical thickness. Then, the films were annealed at 450°C for 30 min under an air atmosphere. After being soaked in $TiCl_4$ solution at 70°C for 30 min, the TiO_2 electrode was sintered at 500°C for another 30 min. Subsequently, the TiO_2 electrode was immersed in 0.2 mM TCPP ethanol solution containing 1 mM co-adsorbent chenodeoxycholic acid overnight and then rinsed with ethanol several times to remove the loose dye molecules. After drying at room temperature, the TCPP/TiO_2 electrode was coated with 15 μL GDH solution (5 mg/mL) and stored at 4°C. Finally, 5 μL Nafion solution (0.5%) was deposited onto the GDH/TCPP/TiO_2 electrode for enzyme immobilization, and the biophotoanode was obtained.

Synthesis of mesoporous carbon hollow spheres: The mesoporous carbon hollow spheres (MCHS) were synthesized by the method previously described. Briefly, 10.8 mmol tetrapropyl orthosilicate (TPOS) and 1.2 mmol tetraethyl orthosilicate (TEOS) were added dropwise into a solution mixture containing 70 mL ethanol, 10 mL H_2O, and 3 mL ammonia (25 wt%) with stirring at room temperature. After 15 min, 0.4 g resorcinol and 0.56 mL formaldehyde (37 wt%) were added to the mixture solution and kept stirring for 24 h. The precipitates were separated by centrifugation, washed with water and ethanol several times, and dried at 60°C overnight. The precursor was then calcined in a tube furnace at 700°C for 5 h under an N_2 atmosphere. Finally, the MCHS were obtained by the removal of the SiO_2 template with HF (5 wt%) for 24 h.

Preparation of the RRDE and cathode of BPEC cells: Both of the electrodes were prepared by dispersing the MCHS in water, isopropyl alcohol, and 5 wt% Nafion solution with sonication for 60 min to get a homogeneous catalyst ink of ~ 3.14 mg mL^{-1}. Afterward, 4 μL of the ink was pipetted onto a glassy carbon disk (0.1256 cm^2 area, 0.1 mg cm^{-2} mass loading) and dried in the air before the RRDE test. As to the cathode of BPEC cell, 4 μL of catalyst ink was dropped cast onto the ITO substrate using perforated tape to control the electrode diameter as 4.00 mm.

Fabrication of BPEC cell: For the construction of the bio-photoelectrochemical cell, a GDH/TCPP/TiO_2 biophotoanode and an MCHS/CP cathode were arranged opposite each other and separated by a Nafion 115 membrane, which was filled with 10 ml 0.25 M Tris-HCl buffer solution and 10 ml 0.1 M PBS, respectively. Stainless steel chains and rubber washers were used for the stable fixation and leakproof seal of the two chambers (Fig. S9).

H_2O_2 quantification: The H_2O_2 concentration was detected by cerium sulfate ($Ce(SO_4)_2$) titration-based colorimetric method.[1] Early in the titration, the presence of Ce^{4+} can be easily observed by a yellowish solution color. While the product solution was added to the titration solution, Ce^{4+} would be bleached by H_2O_2 (equation (1)), therefore the H_2O_2 concentration could be quantified according to the consumption of Ce^{4+} measured by ultraviolet-visible spectroscopy at the wavelength of 317 nm.

$$2Ce^{4+} + H_2O_2 \rightarrow 2Ce^{3+} + 2H^{+} + O_2$$ * MERGEFORMAT (1)

To prepare the standard $Ce(SO_4)_2$ titration solution (1 mM), 33.224 mg $Ce(SO_4)_2$ was dissolved in 100 mL 0.5 M sulfuric acid solution (H_2SO_4). Afterward, to fit the linear range of the calibration curve, the stock solution was further diluted 10 to 100 times with 0.5 M H_2SO_4. In the standardized analysis process, 500 μL sample electrolyte was added to 5 mL 0.1 mM $Ce(SO_4)_2$ solution and measured by ultraviolet-visible spectroscopy. Based on the fitting calibration curve, the mole of H_2O_2 can be determined by the mole of consumed Ce^{4+} (equation (2)).

$$mH_2O_2 = 1/2 \times mCe^{4+}$$ * MERGEFORMAT (2)

Calculation: H_2O_2 selectivity ($H_2O_2\%$) and electron transfer number (n) of the MCHS on the RRDE could be calculated based on the current of disk and ring electrodes (equations (3) and (4)). The ring currents were recorded by applying a constant potential of 0.73 V (vs. Ag/AgCl, pH 8.0) on the Pt ring electrode.

$$H_2O_2(\%) = (200 \times I_{Ring}/N)/(|I_{Disk}| + I_{Ring}/N)$$ *MERGEFORMAT(3)

$$n = (4 \times |I_{Disk}|)/(|I_{Disk}| + |I_{Ring}|/N)$$ * MERGEFORMAT (4)

where I_{Ring} (A) is the Pt ring current, I_{Disk} (A) is the disk current and N is the collection efficiency (0.43 after calibration, Fig. S8).

To determine the practical H_2O_2 production of the MCHS catalysts at a customized H-cell, faraday efficiency (FE, %) could be calculated based on the equation (5):

$$H_2O_2(\mathrm{FE},\%) = {(2 \times M_{H_2O_2} \times V \times F)} \Big/ \int_0^t I(t)dt$$ * MERGEFORMAT

(5)

where M_{H2O2} is the concentration of the produced H_2O_2 (mol L^{-1}), V is the volume of electrolyte (L), F is the Faraday constant (96485 C mol^{-1}), and $\int_0^t I(t)dt$ is the total passed charge amount in chronoamperometry test.

Results and discussion

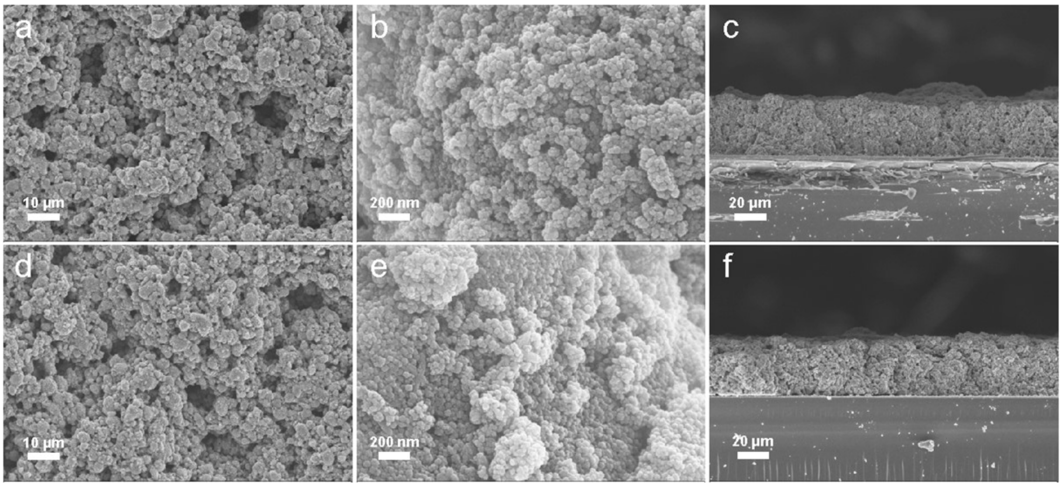

Figure S1. Top-view and cross-section SEM images of (a-c) porous TiO_2 and (d-f) TCPP/TiO_2 deposited on FTO.

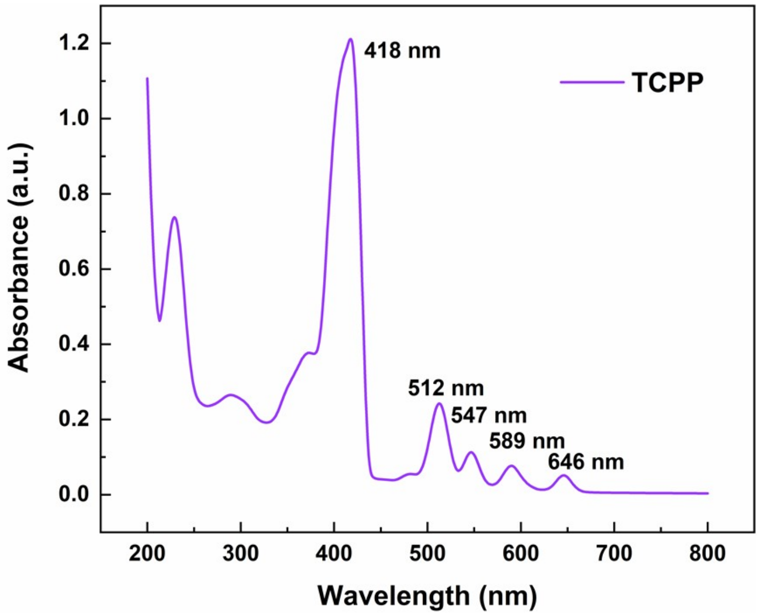

Figure S2. UV-Vis absorption spectrum of TCPP in ethanol solution.

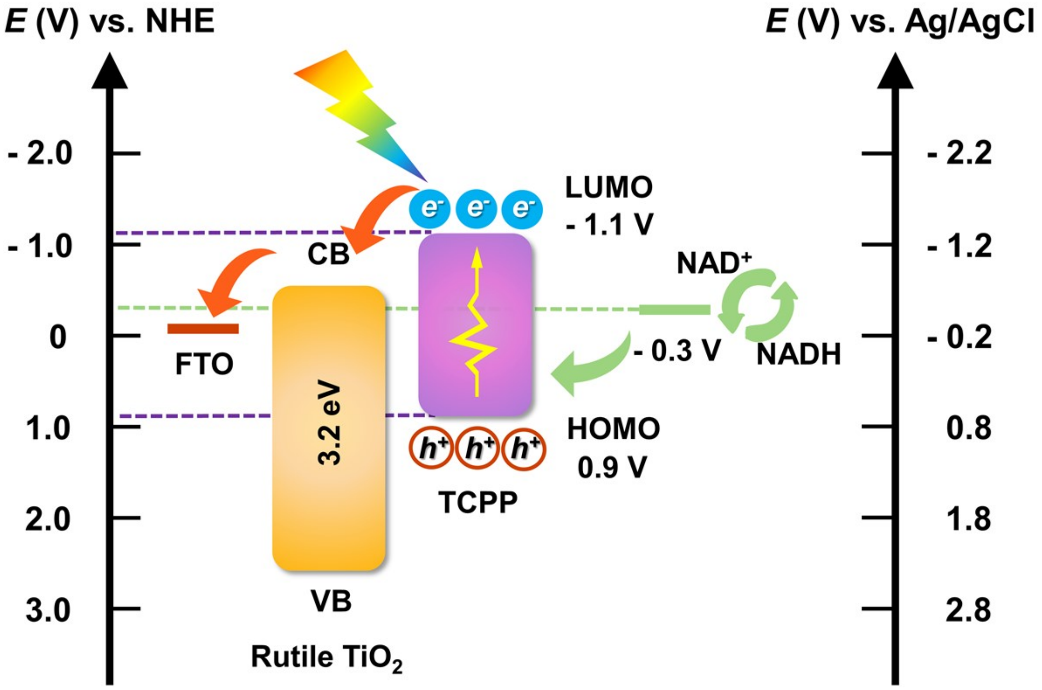

Figure S3. Schematic diagram of energy level and electron transfer in the TCPP/TiO_2 dye-sensitized photoanode.[2,3]

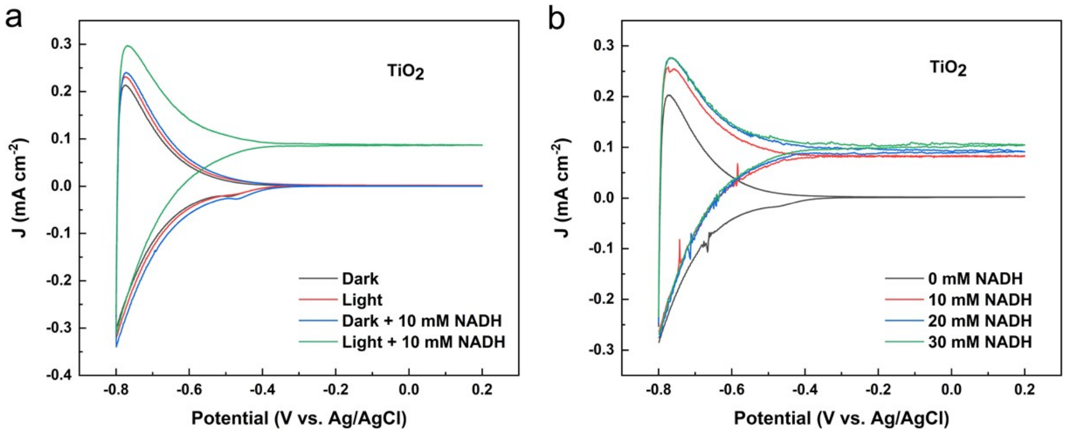

Figure S4. (a-b) Cyclic voltammogram (CV) curves of TiO_2 electrode measured in N_2-saturated 0.25 M Tris-HCl (pH 8.0) buffer solution. Light illumination intensity: 100 mW cm^{-2}, $\lambda>420$ nm; scan rate: 10 mV s^{-1}.

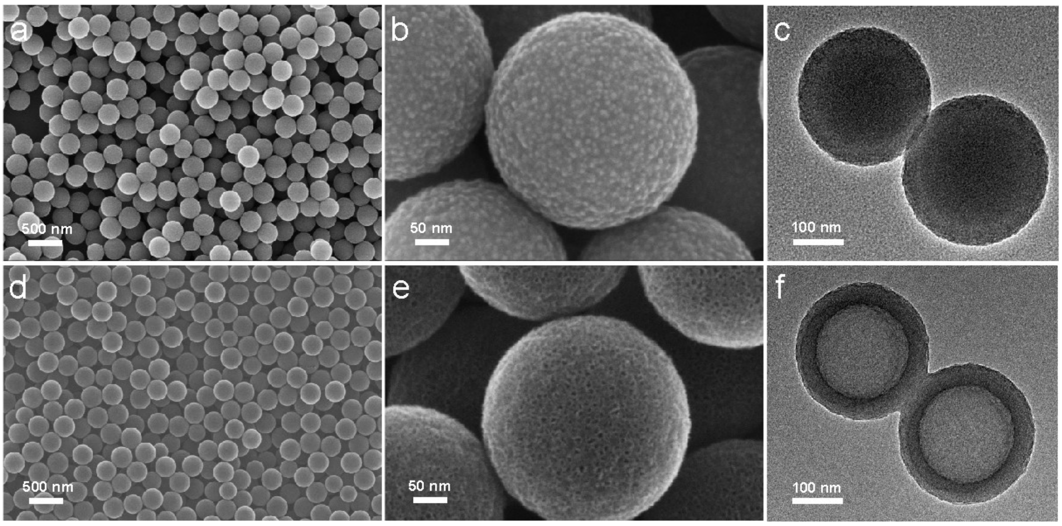

Figure S5. SEM images of (a-b) $SiO_2@SiO_2/C$ composite and (d-e) MCHS. TEM images of (c) $SiO_2@SiO_2/C$ composite and (f) MCHS.

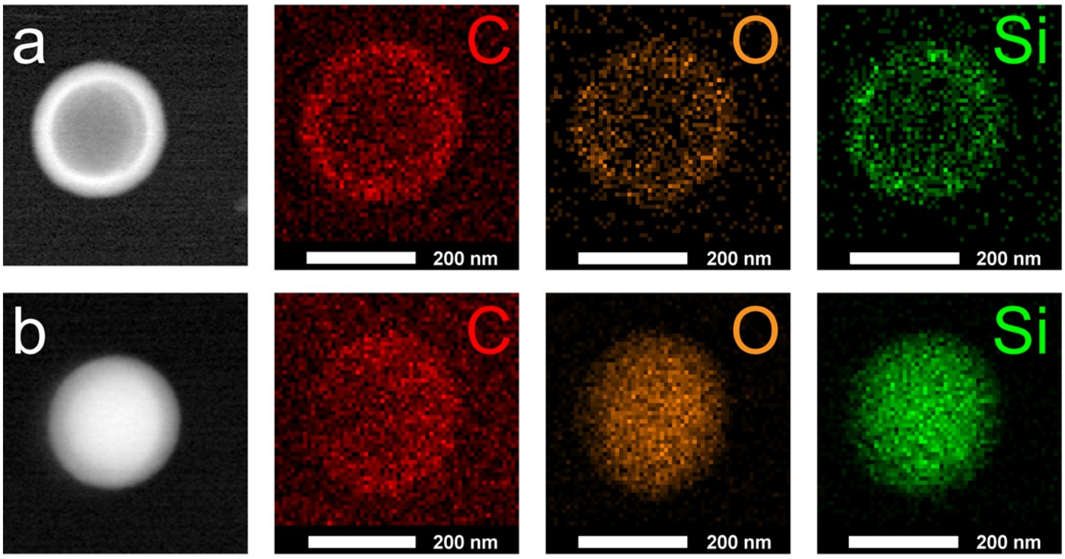

Figure S6. High-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDS) images of C, O, and Si elements in (a) MCHS and (b) $SiO_2@SiO_2/C$ composite.

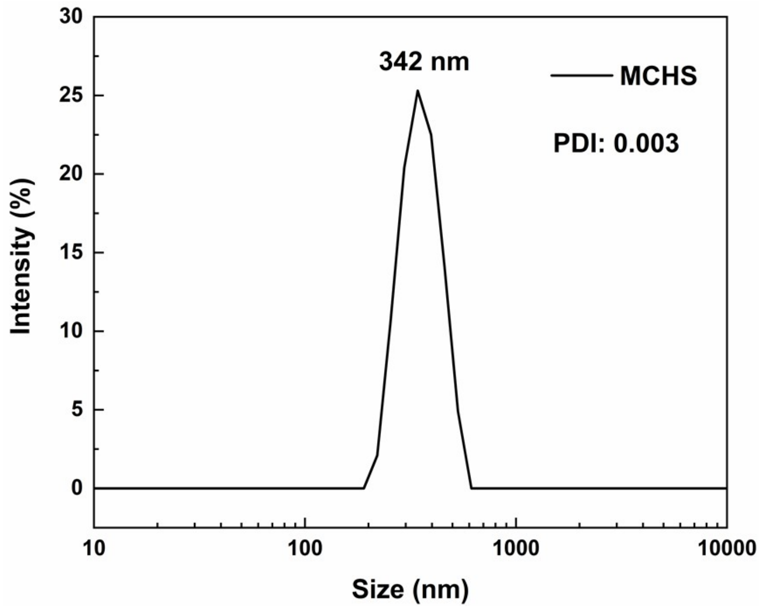

Figure S7. Dynamic light scattering (DLS) analysis of MCHS aqueous solution.

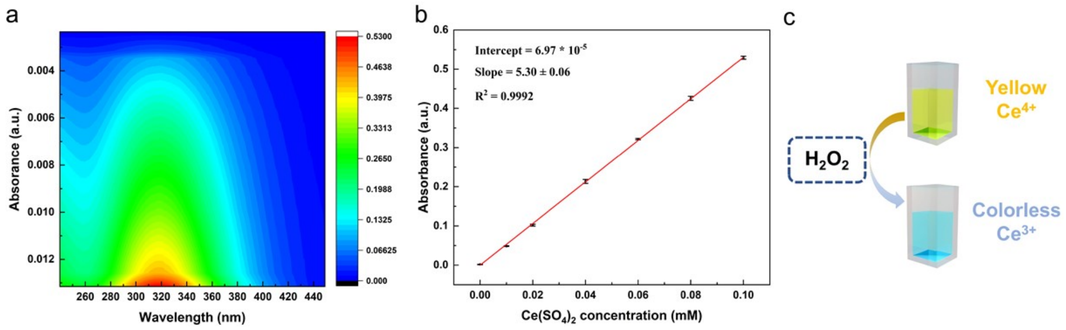

Figure S8. (a) Counter map of UV-Vis absorption spectra for cerium titration. (b) Calibration curve for the UV-Vis absorbance at 317 nm wavelength of $Ce(SO_4)_2$ solution in the concentration ranging from 0 to 0.1 mM. (c) Schematic diagram of cerium titration method.

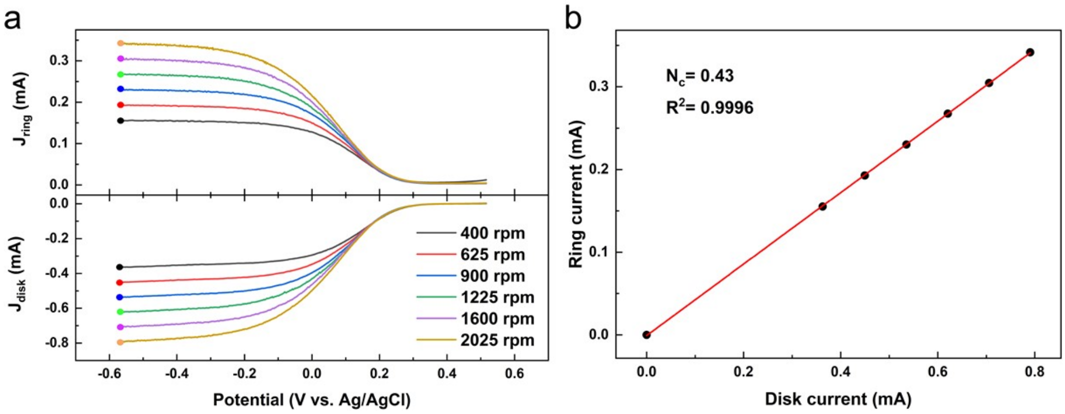

Figure S9. (a) Polarization curves for the bare glassy carbon rotating disk electrode with a Pt ring in N_2-saturated 0.1 M KOH containing 10 mM $K_3Fe(CN)_6$ at different angular velocities. The ring potential is fixed at 0.59 V vs. Ag/AgCl. Scan rate: 20 mV s^{-1}. (b) Linear fitting of the disk current and the ring current. The slope is the experimentally determined collection efficiency (N).

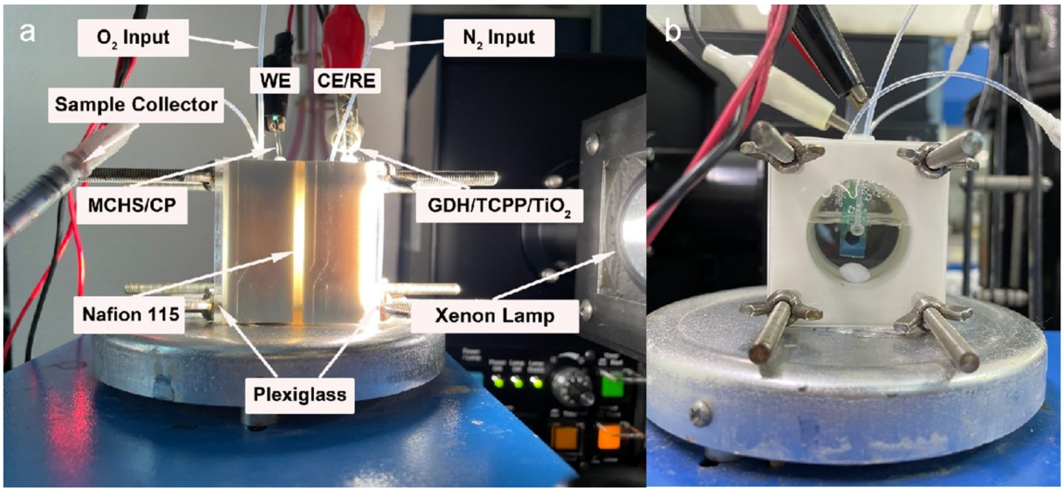

Figure S10. (a) Front view and (b) side view photographs of the BPEC system.

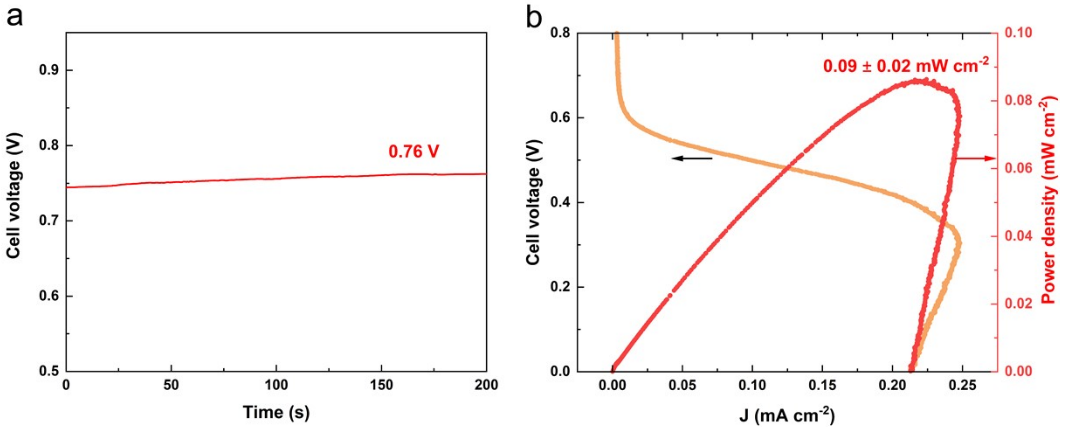

Figure S11. (a) Open-circuit voltage (V$_{oc}$) measurement of the BPEC cell. (b) Polarization curve and power density of glucose/O$_2$ BPEC cell with agitation applied in the anodic chamber.

References

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3 S. Zhang, Z. Liu, D. Chen, Z. Guo and M. Ruan, *Chem. Eng. J.*, 2020, **395**, 125101.