Supporting Information (SI)

Inkjet-printed porous polyaniline gel as an efficient anode for microbial fuel cells

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Experiment section

Preparation of the inkjet-printed PANI/CP

The inkjet-printed PANI/CP was fabricated using a dual-nozzle Liquidyn Inkjet Print System (Yefu Co. Ltd., Shanghai). Two precursor inks were first prepared. Ink A is dissolving 0.286 g (1.25 mM) ammonium persulfate in 1 mL DI water, while ink B was prepared by mixing 0.921 mL (1 mM) phytic acid (50%, wt/wt in water, Aldrich), 0.458 mL (5 mM) aniline (purified by distilling) and 2 mL DI water. After cooling to 4 ^{o}C, these two inks were successively inkjet printed onto the carbon paper (TGPH-120, Toray Co. Japan), and the pattern was gelated to form a homogeneous PANI hydrogel thin film on the surface of the carbon paper within 3 minutes. To remove excess acid and by-products, the inkjet-printed PANI/CP was purified by immersing in DI water for an hour. Finally, a freeze-drying method was used to dry it. The content (C) of PANI printed on the carbon paper (0.5024±0.0092 mg cm^2) was calculated using $C = (m_1-m_0)/A$, where m_1 was the weight of carbon paper after printing, m_0 the weight of carbon paper before printing, and S the area of carbon paper.

Preparation of carbon paper modified with phytic acid-doped PANI and HCl-doped PANI.

The phytic acid-doped PANI was prepared according to our previous report,[1] while the HCl-doped PANI was prepared by a commonly used chemical oxidative polymerization.[2] The obtained phytic acid-doped PANI was mixed with poly(tetrafluoroethylene) solution (1 wt%) to produce a paste. The paste was then coated on the surface of carbon paper (1.5 cm × 1.5 cm) to form a uniform film. The content of PANI coated on the carbon paper equaled to that of inkjet-printed PANI/CP (0.5 mg cm^2). For carbon paper with HCl-doped PANI coating, the same procedure was used.

Characterization

The morphologies of the inkjet-printed PANI/CP and carbon paper were characterized using a field emission SEM (JEOL/JSM-6340F). FT-IR measurement was performed on a Perkin Elmer Spectrum BX FT-IR spectrometer. EIS tests were carried out using a CHI604E electrochemical workstation (Chenhua, China) with a conventional three-electrode system in 2 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ and 0.1 M KCl electrolyte. The inkjet-printed PANI/CP or carbon paper was used as the working electrode, while Pt wire and Ag/AgCl served as the counter and reference electrodes, respectively. All tests were conducted over a frequency range from 0.01 Hz to 100

KHz at open-circuit voltage with a perturbation signal of 5 mV.

Microbial culture

S.oneidensis MR-1 was cultured in a tube containing 15 mL of Luria-Bertani (LB) broth (10 g L^{-1} trypticase peptone, 5 g L^{-1} yesast exract, and 10 g L^{-1} sodium chloride) at 37 ^{o}C, with shaking at 150 rpm for 24 h. The cells were harvested by centrifugation (6000 rpm, 5 min) and re-dispersed in M9 buffer solution (22 mM KH_2PO_4, 42 mM Na_2HPO_4, 85.5 mM NaCl and 1.0 mM $MgSO_4$) with 5% LB broth. All solutions were sterilized before use.

SEM analysis of microbial biofilm on electrode

After 100 h incubation in MFC with bacteria culture, the electrodes were fixed by immersion in 2.5% glutaraldehyde solution for 1h and then dehydrated using a series of ethanol solution (25%, 50%, 75%, 95% and 100%). The samples were finally dried in air and coated with Au before the SEM characterization.

Phospholipids analysis for determining microbial biomass

After MFCs operation for 100 h, electrodes with biofilm were removed from the anode chamber and analyzed according to the procedure reported previously.[3] The absorbance at 610 nm was determined using a spectrophotometer (3600 Shimadzu, Japan). The concentrations of phosphate were calculated using the regression line from a standard curve. The total active biomass of electrodes was obtained by using the conversion factor of 191.7 μg of biomass-C per 100 mmol of phospholipid.

MFC construction and operation

H-shaped dual chamber MFCs separated by a proton exchange membrane (Nafion N117, Sigma-Aldrich, Singapore) were constructed in this study. After sterilization, 100 ml of M9 buffer solution containing bacterial culture was transferred to the anodic chamber, while the same volume of catholyte (50 mM $K_3Fe(CN)_6$ and 0.1 M KCl) was added into the cathodic chamber. The anodes are inkjet-printed PANI/CP and carbon paper (1.5 cm × 1.5 cm), and the cathode is carbon felt. The anode and cathode were then connected to a 1 KΩ resistor.

With the addition of substrate (lactate, 18 mM) to the anodic chamber, the cell voltage measurements across the resistor were recorded once every 10 minutes by an eDAQ-corder data acquisition system equipped with Chart software (Bronjo Medi, Singapore). When the MFC approached plateau, the polarization curves was obtained by switching resistors (50 Ω -100 KΩ). Power was calculated using P = IV, and current was calculated using I=V/R. The current and power outputs were normalized to the anode surface area, and the MFCs were operated at 30 ^{o}C.

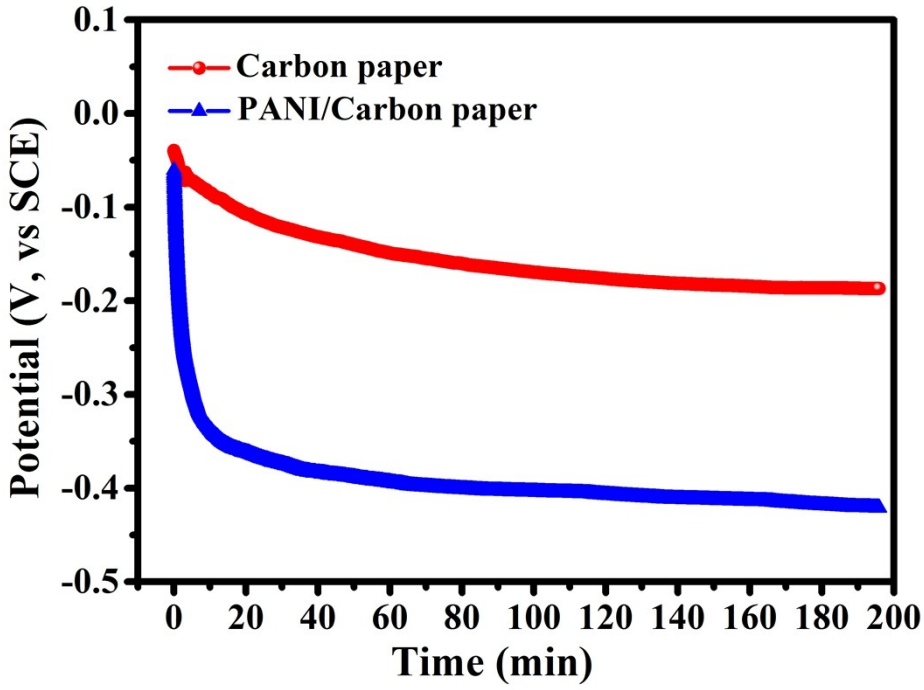

Fig. S1. Potential-time curve of different electrodes placed in a stirred anaerobic culture of *S. oneidensis* MR-1 in 25 ml of M9 buffer solution with 18 mM lactate.

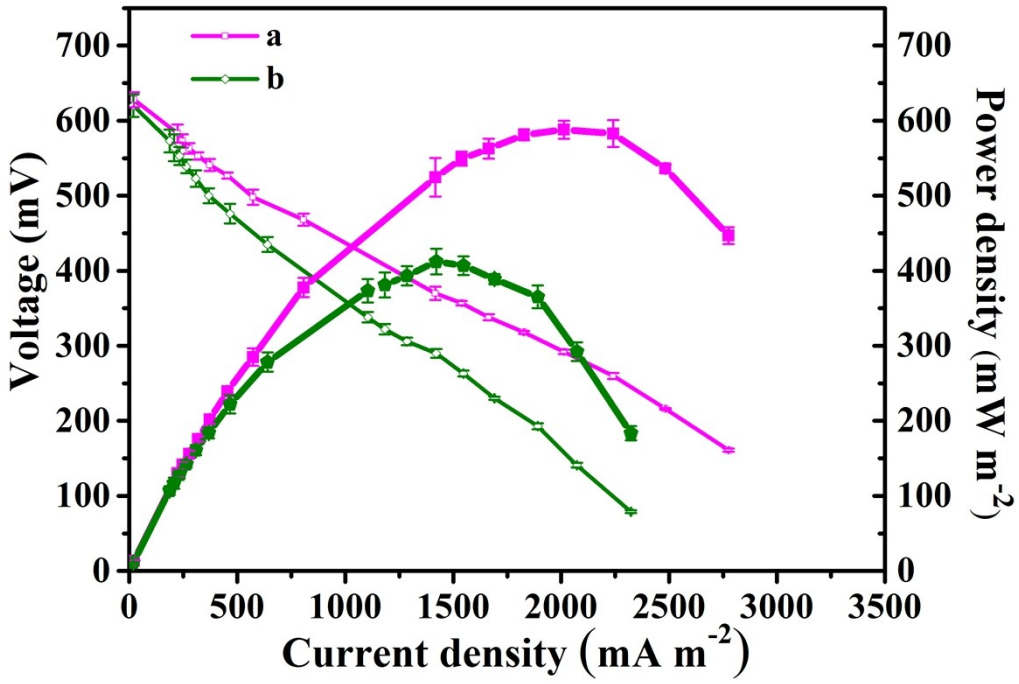

Fig. S2. Polarization curves and power density curves of MFCs equipped with different anodes: a) carbon paper modified with phytic acid-doped PANI and b) carbon paper modified with HCl-doped PANI.

Table S1. Comparison of the present result with literature data obtained using PANI based materials as anode electrode materials in MFCs.

Electrode	Anode material	Preparation method	Acid for PANI doping	Microbe	power density (mW m^{-2})	Reference
Carbon felt	PANI	chemical oxidative polymerization	HCl	*Saccharomyces cerevisiae*	460	4
Nickel foams	CNT/PANI	chemical oxidative polymerization	HCl	*Escherichia coli*	42	5
Graphite felt	PANI	electropolymerization	H_2SO_4	*Shewanella putrefaciens*	80	6
Graphite felt	CNT/PANI	electropolymerization	H_2SO_4	*Shewanella putrefaciens*	308	6
Graphite felt	PANI	electropolymerization	HCl	*Mixed bacteria*	134	7
Graphite felt	PANI/GO	electropolymerization	HCl	*Mixed bacteria*	183	7
Carbon cloth	PANI	chemical oxidative polymerization	tartaric acid	*Shewanella oneidensis*	490	8
Nickel foam	PANI	chemical oxidative polymerization	HCl	*Shewanella oneidensis*	70.8	9
Carbon felt	PANI	chemical oxidative polymerization	HCl	*Shewanella oneidensis*	145	9
Carbon cloth	PANI	chemical oxidative polymerization	HCl	*Shewanella oneidensis*	323	9
Carbon paper	**PANI**	**chemical oxidative polymerization**	**phytic acid**	**Shewanella oneidensis**	**693**	**This study**

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