Supplementary Information for

## Preparation of Microvillus-like Nitrogen-Doped Carbon Nanotubes as the

**Cathode of Microbial Fuel Cell** 

Yan-Rong He<sup>a, b</sup>, Feng Du<sup>b</sup>, Yu-Xi Huang<sup>a</sup>, Li-Ming Dai<sup>b,\*</sup> Wen-Wei Li<sup>a</sup>, Han-Qing

Yu<sup>a,\*</sup>

<sup>a</sup> CAS Key Laboratory of Urban Pollutant Conversion, Department of Chemistry,

University of Science & Technology of China, Hefei, 230026, China

<sup>b</sup> Department of Municipal Engineering, Hefei University of Technology, Hefei,

230009, China

## **Experimental Section**

**Preparation of electrodes:** N-CNTs were grown on carbon cloth by using Ferrocene method with a dual-zone tube furnace, as described previously.<sup>1</sup> Pyridine containing 1 wt% ferrocene was fed into the preheater (200 °C) by an injection syringe pump at a feed rate of 25 mL h<sup>-1</sup>. Then, the reaction gas volatilized from the preheater was blown into the reactor by a purging gas mixture of H<sub>2</sub> (50 mL min<sup>-1</sup>) and argon (100 mL min<sup>-1</sup>). The carbon cloth was put in the middle of the reactor to be heated up to 750-850 °C for 10-15 min. Then, the furnace was cooled down to room temperature.

**Chemical analysis:** The morphology of the electrode samples was examined by scanning electron microscopy (SEM, JSM-7001F, JEOL Inc., USA). The Raman spectra were measured under ambient conditions using a micro-Raman spectroscopy system (Renishaw Co., UK) with a 514.5 nm argon-ion laser. The surface composition of the N-CNTs-carbon cloth was analyzed using an X-ray photoelectron spectroscopy (XPS) (ESCALAB 250, VG Instrument Ltd., UK) and curve-fitting software (XPSPEAK v4.1).

The electrochemical behaviors of the N-CNTs-CC and Pt/C-CC were examined using an electrochemical workstation (CHI 760E, ChenHua Instruments Co., China). All the electrochemical experiments were conducted in phosphate buffer solution (PBS, 50 mM, pH = 7.0) at ambient temperature (25 °C). The reference electrode was Ag/AgCl (saturated KCl, 0.197 V vs. SHE) and a Pt wire was used as counter electrode. Both the reference and counter electrodes were fixed with a 0.5 cm spacing from the working electrode. Tafel plots (log |current density|, mA cm<sup>-2</sup> versus overpotential, V) were recorded by sweeping the overpotential ( $\eta$ ) from 0 mV to 100 mV at 1 mV s<sup>-1</sup>, where  $\eta = 0$  is the open circuit potential (OCP) of the cathode vs. the reference electrode. Cyclic voltammetry (CV) analysis was performed from 0.4 to -0.5 V with a scan rate of 1 mV s<sup>-1</sup>.

MFC configuration and operation: Air-cathode cylindrical-shaped MFCs with a working volume of 110 mL and an electrode spacing of 3 cm were used (Fig. S1). Carbon cloth (3×3 cm<sup>2</sup>, CC6P20, Fuel cell Earth LLC Co., USA) was adopted as the anode. For the MFC start-up, the CC (30 wt% wet proofing, Fuel cell Earth LLC Co., USA) coated with Pt of 0.05 mg cm<sup>-2</sup> (GEL, GEFC Co., USA) was used as cathode as described previously. Bio-anodes were enriched under the same conditions before the experiments. After obtaining a parallel electricity generation the cathodes were replaced by the N-CNTs-CC ( $2 \times 2 \text{ cm}^2$ ), and a new Pt/C-CC with the same size was used for comparison. Fed-batch operation mode was adopted for the MFCs. The anode chambers of MFCs were filled with 100 mL acetate-laden synthetic wastewater, containing 310 mg NH<sub>4</sub>Cl, 130 mg KCl; 10 mg CaCl<sub>2</sub>; 20 mg MgCl<sub>2</sub>·6H<sub>2</sub>O; 2 mg NaCl; 5 mg FeCl<sub>2</sub>; 1 mg CoCl<sub>2</sub>·2H<sub>2</sub>O; 1 mg MnCl<sub>2</sub>·4H<sub>2</sub>O; 0.5 mg AlCl<sub>3</sub>; 3 mg (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>; 1 mg H<sub>3</sub>BO<sub>3</sub>; 0.1 mg NiCl<sub>2</sub>·6H<sub>2</sub>O; 1 mg CuSO<sub>4</sub>·5H<sub>2</sub>O; 1 mg ZnCl<sub>2</sub>; 1 g CH<sub>3</sub>COONa $\cdot$ 3H<sub>2</sub>O as substrate, in 1 L of 50 mM Phosphate buffer, pH = 7.0. The output voltage over a 1000  $\Omega$  resistor was automatically collected every hour using a

data acquisition system (2701, Keithley Instruments Inc., USA). The power densities of the cells were obtained from polarization curves by varying the external resistor from 10  $\Omega$  to 10000  $\Omega$  as the performance of MFC approached a steady state. The power density was calculated according to  $P = E^2/(VR)$ , where *E* is the external voltage, and *V* is the cell volume, and *R* is the external resistance.

The EIS analysis was conducted over a frequency range of 100 kHz to 0.01 Hz with the AC signal amplitude of 5 mV. For each measurement, the initial potential was set at the OCP. The anode and cathode potentials were detected for the MFC with a 1000  $\Omega$  external resistor versus Ag/AgCl reference electrode.

## References

 G. L. Zang, G. P. Sheng, Z. H. Tong, X. W. Liu, S. X. Teng, W. W. Li and H.-Q. Yu, *Environ. Sci. Technol.*, 2010, 44, 2715-2720.



- 1. MFC anode chamber, 110 mL
- 2. MFC anode, the apparent surface area was  $3 \times 3$  cm<sup>2</sup>
- 3. Proton exchange membrane
- 4. Air cathode, the apparent surface area was  $2 \times 2 \text{ cm}^2$
- Electrode spacing was 3 cm

Fig. S1 Schematic of the MFC setup