Electronic Supplementary Information (ESI):

## Nano-structured Textiles as High-performance Aqueous Cathodes for Microbial Fuel Cells

Xing Xie,<sup>*a*</sup> Mauro Pasta,<sup>*bc*</sup> Liangbing Hu,<sup>*b*</sup> Yuan Yang,<sup>*b*</sup> James McDonough,<sup>*b*</sup> Judy Cha,<sup>*b*</sup> Craig S. Criddle<sup>\**a*</sup> and Yi Cui<sup>\**b*</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, Stanford University, Stanford, California 94305, USA. E-mail: <u>ccriddle@stanford.edu</u>; Tel: +1-650-723-9032

<sup>b</sup> Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, USA. E-mail: <u>vicui@stanford.edu</u>; Fax:+1-650-725-4034; Tel: +1-650-723-4613

<sup>c</sup> Dipartimento di Chimica Inorganica, Metallorganica e Analitica "Lamberto Malatesta", Università degli Studi di Milano, Via Venezian 21, 20133 Milan, Italy.

## **Experimental details:**

*Electrode preparation.* The CNT-textile was fabricated through a simple and scalable dipping-drying process described previously in detail <sup>s1</sup>. A CNT-textile sheet with thickness of ~1 mm was cut into a 1 cm × 3 cm piece, and then treated with nitric acid (4 M, 2 hours) and glacial acetic acid (2 hours) successively before the Pt deposition. The acid treatment process increases the sample's hydrophilicity and produces oxygen-rich functional groups on the originally inert CNT surface to act as nucleating sites for Pt deposition <sup>s2, s3</sup>. The electrochemical deposition process was performed in a four-neck flask containing chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>, 0.019 M) and hydrochloric acid (HCl, 0.6 M) as electrolyte <sup>s2</sup>. The CNT-textile was the working electrode with only 1 cm × 1 cm dipped into the electrolyte. Two Pt meshes, one on each side of the CNT-textile, were used as counter electrodes in order to optimize the current lines and have a uniform Pt distribution on the whole current collector. The deposition was performed via a potentiostatic technique, fixing the potential at -0.6 V vs. a double junction Ag|AgCl|KCl (3.5M) reference electrode (RE) <sup>s2</sup>.

*Electrode characterization.* The morphologies of the electrode surfaces were investigated using a field emission scanning electron microscope (SEM, FEI XL30 Sirion). The Pt nanoparticles were also examined by a transmission electron microscopy (TEM, FEI Tecnai G2 F20 X-TWIN 200kV). Pt loadings were measured by an IRIS advantage inductively coupled plasma atomic emission spectroscopy (ICP-AES) system. The average sizes of Pt particles on different electrodes were calculated by the Debye Scherrer equation, based on the X-ray Diffraction (XRD) test results <sup>s2, s3</sup>. ECAS area was

characterized using an electrochemical method, in which the ECAS area was proportional to the hydrogen adsorption-desorption capability of the electrode <sup>s4</sup>. Oxygen reduction efficiencies were tested by performing linear staircase voltammetries (LSVs) at step-sweep rates of 10 mV per 10 seconds from 0.3 to -0.3 V vs. a double junction Ag|AgCl|KCl (3.5M) reference electrode and cyclic voltammetries (CVs) at scan rates of 10 mV s<sup>-1</sup> between -0.5 to 0.5 V vs. a double junction Ag|AgCl|KCl (3.5M) reference electrode was Pt foil, and the electrolyte was a phosphate buffer solution (see next section) simulating the working condition in aqueous-cathode MFCs <sup>s5</sup>. The electrolyte was saturated with oxygen under ambient pressure and temperature.

*MFC construction and characterization.* All cathode samples were investigated in an H-shaped two-chamber MFC with a CNT-textile anode (1 cm  $\times$  1 cm). The MFC was inoculated with domestic wastewater and has been operated for 6 months to obtain a mature biofilm on the anode. An anion exchange membrane (AMI-7001, Membranes International Inc., NJ) was used as the separator. The catholyte was a phosphate buffer solution (100 mM, pH 7) comprised of NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O (4.90 g L<sup>-1</sup>), Na<sub>2</sub>HPO<sub>4</sub> (9.15 g L<sup>-1</sup>), KCI (0.26 g L<sup>-1</sup>), and NH<sub>4</sub>Cl (0.62 g L<sup>-1</sup>) <sup>s5</sup>. The anolyte contains glucose (1 g L<sup>-1</sup>), mineral solution (12.5 mL L<sup>-1</sup>), vitamin solution (5 mL L<sup>-1</sup>), and the same PBS as that used for the catholyte <sup>s5, s6</sup>. The cathode chamber was continuously purged with air using a diffusion stone (flow rate ~0.1 L min<sup>-1</sup>). To evaluate the MFC performance, polarization curves were measured under a step-sweep rate of 10 mV per 10 seconds starting from the OCV value. The anode was the working electrode and the cathode was both counter electrode and reference electrode. Power and current densities were

normalized by the projected surface area of the cathode ( $2 \text{ cm}^2$ ). All experiments were conducted at room temperature.

## References

- S1. L. Hu, M. Pasta, F. L. Mantia, L. Cui, S. Jeong, H. D. Deshazer, J. W. Choi, S. M. Han and Y. Cui, *Nano Letters*, 2010, 10, 708-714.
- S2. K. Saminathan, V. Kamavaram, V. Veedu and A. M. Kannan, International Journal of Hydrogen Energy, 2009, 34, 3838-3844.
- S3. A. N. Golikand, M. Asgari, E. Lohrasbi and M. Yari, *Journal of Applied Electrochemistry*, 2009, **39**, 1369-1377.
- S4. S. Takenaka, H. Matsumori, H. Matsune, E. Tanabe and M. Kishida, *Journal of the Electrochemical Society*, 2008, 155, B929-B936.
- S. Oh, B. Min and B. E. Logan, *Environmental Science & Technology*, 2004, 38, 4900-4904.
- S6. W. E. Balch, G. E. Fox, L. J. Magrum, C. R. Woese and R. S. Wolfe, *Microbiological Reviews*, 1979, 43, 260-296.

## **Supplementary figures:**



Fig. S1 SEM images of a commercial CC-Pt cathode, (a-c) projective surface and (d) cross-section.



Fig. S2 CV results showing the stability of the CNT-textile-Pt cathode. Current densities were normalized by the projected surface area of the cathode (2 cm<sup>2</sup>). Fluctuations on the curve are caused by the continuous aeration of the electrolyte. Scan rate:  $10 \text{ mV s}^{-1}$ .



Fig. S3 Polarization curves of MFCs equipped with CNT-textile-Pt cathodes with different Pt loadings. Power and current densities are normalized by the projected surface areas of the electrodes  $(2 \text{ cm}^2)$ .



Fig. S4 XRD patterns of the CNT-textile-Pt and the CC-Pt.



Fig. S5 CV curves for the ECAS measurement. Electrolyte: 0.25 M  $H_2SO_4$ ; Scan rate: 20 mV s<sup>-1</sup>. The value of 210  $\mu$ C cm<sup>-1</sup> was used for determining the ECAS area from the desorbed hydrogen.



Fig. S6 SEM of carbon fiber with electrochemically deposited Pt nanoparticles.