Electronic Supplementary Information (ESI):

# 3D Mesoporous Polysulfone-Carbon Nanotube Anode for Enhanced Bioelectricity Output in Microbial Fuel Cells

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***Fabrication of mesoporous polysulfone support matrix (MPPS)***

The porous substrate was prepared as follows: 20 g of polysulfone (MW=35,000) was dissolved completely in 75 g of N-methylpyrrolidone (NMP). While stirring continuously, 5 g of polyvinylpyrrolidone (PVP, MW=10,000) was added to the mixture to form a dope solution.[S1] The solution was then cast on a round glass substrate by a spin coating machine (SCS G3, Cookson Electronics) with spin speed at 100 rpm for 15 s. The coated substrate was immediately soaked in a mixture of dimethylformamide (DMF) and ethylene glycol (EG) (80/20 v/v.%) for 24 h to complete the porous formation process. Finally, the porous matrix was rinsed with plenty of DDI water followed by freeze treatment in liquid nitrogen for 5 min for curing and dense top surface removal.

***Preparation of SWCNT-coated MPPS***

A coating solution was first prepared by mixing, using an ultrasonic probe for 2 h, 0.125 g of SWCNT and 0.5 g of sodium dodecylbenzene sulfonate (SDBS) with 50 mL of DDI water.[S2] The obtained solution was transferred to a 100 mL-autoclave and a porous support sheet was dipped into it. The autoclave was placed in an oven at 80 °C for 48 h for infiltration. The coated

porous sheet was dried in a vacuum oven at 120 °C for 24 h. The process of coating and drying is repeated for 3 times to increase SWCNT loading onto the anode.

***Field Emission Scanning Electron Microscope***

The FE-SEM images were taken by a Field Emission Scanning Electron Microscope (JSM-6390LA, JEOL). Thin layers of platinum were coated on the surface of samples using an Auto Fine Coater (JSM) before observations. For biofilm characterization, the anode was first pretreated in 1% glutaric dialdehyde and then in ethanol solution with different concentrations (30, 50, 60, 70, 80, 90 and 100% of ethanol) before platinum coatings.

***Thermal analysis***

A thermo-gravimetric analyzer (Diamond TG/DTA, Perkin Elmer) was used to observe thermal stability and heat flow of the materials. The measurements were carried out under air at a heating rate of 10 °C $min^{-1}$ and a temperature range of RT-800 °C.

***Porosity calculation***

The support matrix's porosity, the fraction of total matrix volume that is porous, was estimated by the following equation

$$\emptyset_p = \left\{1 - \frac{w}{\rho.V}\right\} \times 100 \qquad (1)$$

where w, ρ, V stand for weight, density and volume of matrix, respectively.

***Conductivity measurement***

The conductivity of anodes was measured by sandwiching the sheets between platinum electrodes (1.2 cm x 1.2 cm). The measurements were carried out with a potential range from 0 to 30 mV. The conductance was estimated by the equation

$$\sigma = \frac{t}{RA} \qquad (2)$$

where t (cm), R (Ω) and A ($cm^2$) are thickness , resistance, and area of substrate, respectively.

***Electrochemical measurements***

The cyclic voltammetry analysis (CV) and electrochemical impedance spectroscopy (EIS) is performed in a three-electrode electrochemical cell with a counter electrode of platinum plate, a reference electrode of Ag/AgCl and a working electrode of either carbon cloth or SWCNT-coated MPPS.

***MFCs construction and operation***

A two-chamber cube shape (5.5cm x 5.5cm x 6cm) separated by a Nafion 117 membrane with a projected area of 4.9 $cm^2$ and equipped with a cathode of carbon cloth (2 cm x 2 cm) and the anode of SWCNT-coated MPPS (2 cm x 2 cm) was used to conduct the tests. A carbon cloth anode with the same dimensions was also used for comparison. While the anode medium consisted of M9 salt (8.8 g $L^{-1}$ $Na_2HPO_4.2H_2O$, 3 g $L^{-1}$ $KH_2PO_4$, 0.5 g $L^{-1}$ NaCl, 1 g $L^{-1}$ $NH_4Cl$, 1 mM $MgSO_4$, 0.1 mM $CaCl_2$), LB (10 g $L^{-1}$ peptone, 5 g $L^{-1}$ yeast extract and 5 g $L^{-1}$ NaCl) and 18 mM sodium lactate, the cathode medium contained 50 mM $Fe(CN)_6^{3-}$, 50 mM $K_2HPO_4$ and $KH_2PO_4$. Wild type *Shewanella MR-1* were first activated overnight and then amplified in LB medium to a steady state before inoculation. The inoculation was adjusted to a final OD600 of 0.4 for all of MFCs. All MFCs were operated under batch mode with a consistent resistance of 2 kΩ. 100 ml fresh medium was changed when the nutrient was depleted. The polarization tests were measured by varying loading resistance from 10 Ω to 5000 Ω. All MFC's performance tests were conducted in triplicates, and results had minor deviations. The results presented here are a typical one.

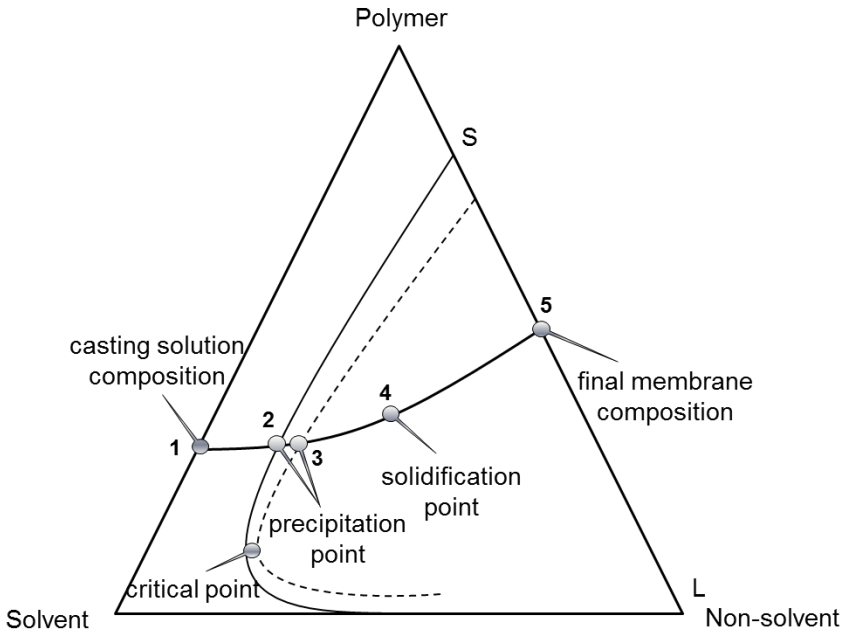


**Figure S1.** An illustration of the formation of porous polymers in phase inversion process.

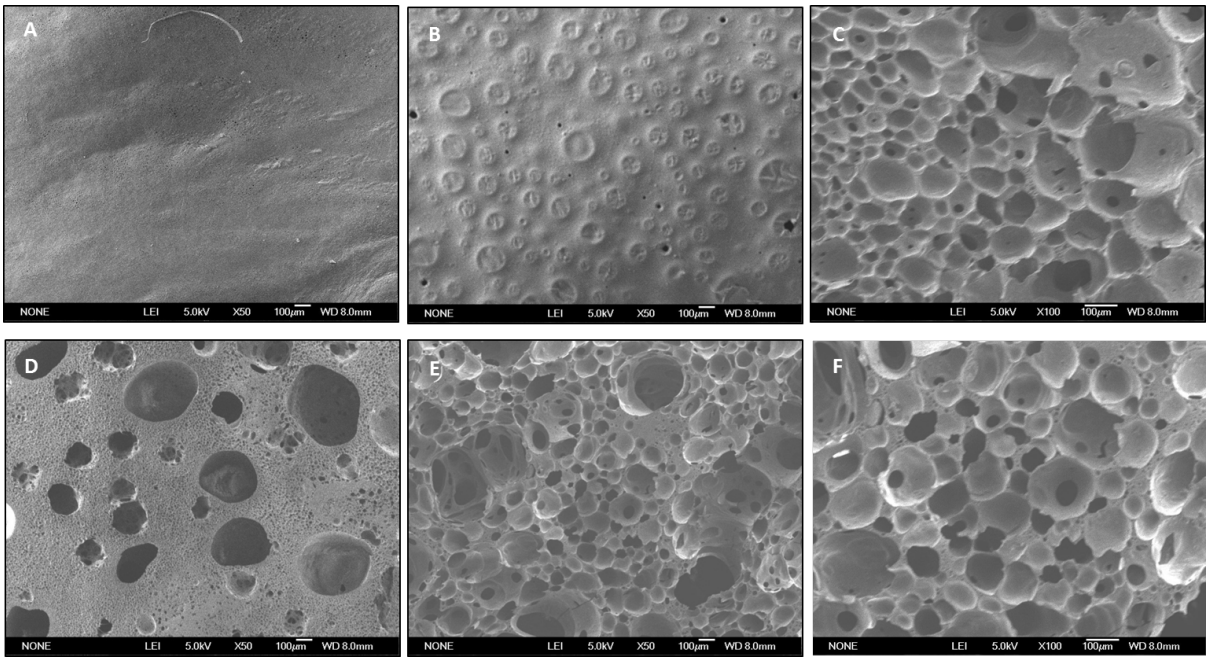


**Figure S2.** FESEM images of MPPS' surface, bottom and cross-section as synthesized (A), (B), and (C) and after treated in liquid nitrogen for 5 min (D), (E), and (F), respectively.

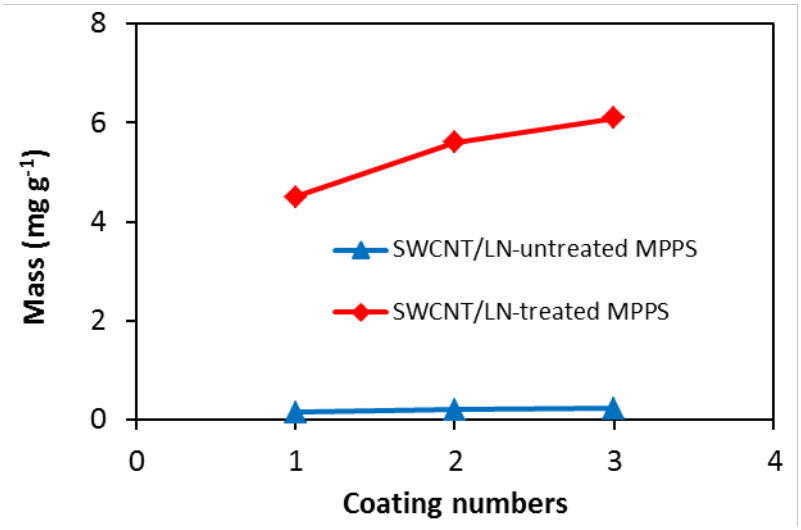


**Figure S3.** The loading of SWCNT onto MPPS with or without liquid nitrogen treated before with different numbers of coating during coating procedure.

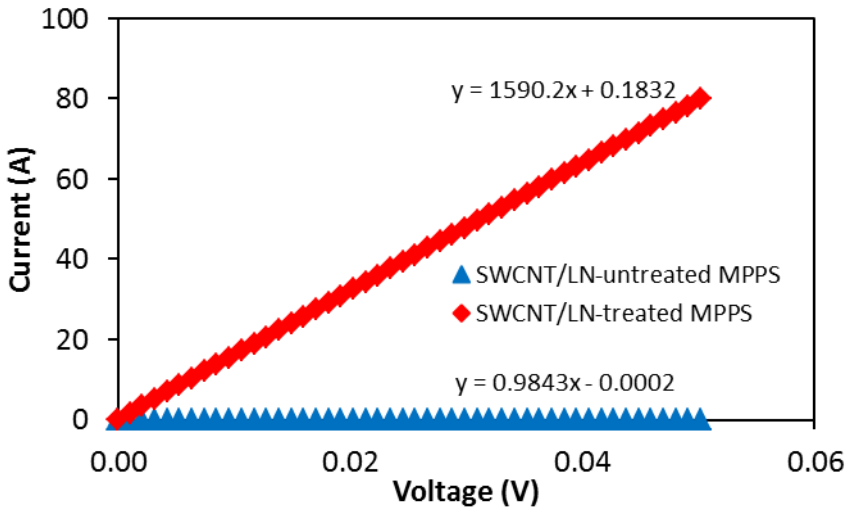


**Figure S4.** I-V curves of conductivity measurement of SWCNT-coated MPPS with PPSF treated and untreated by liquid nitrogen.

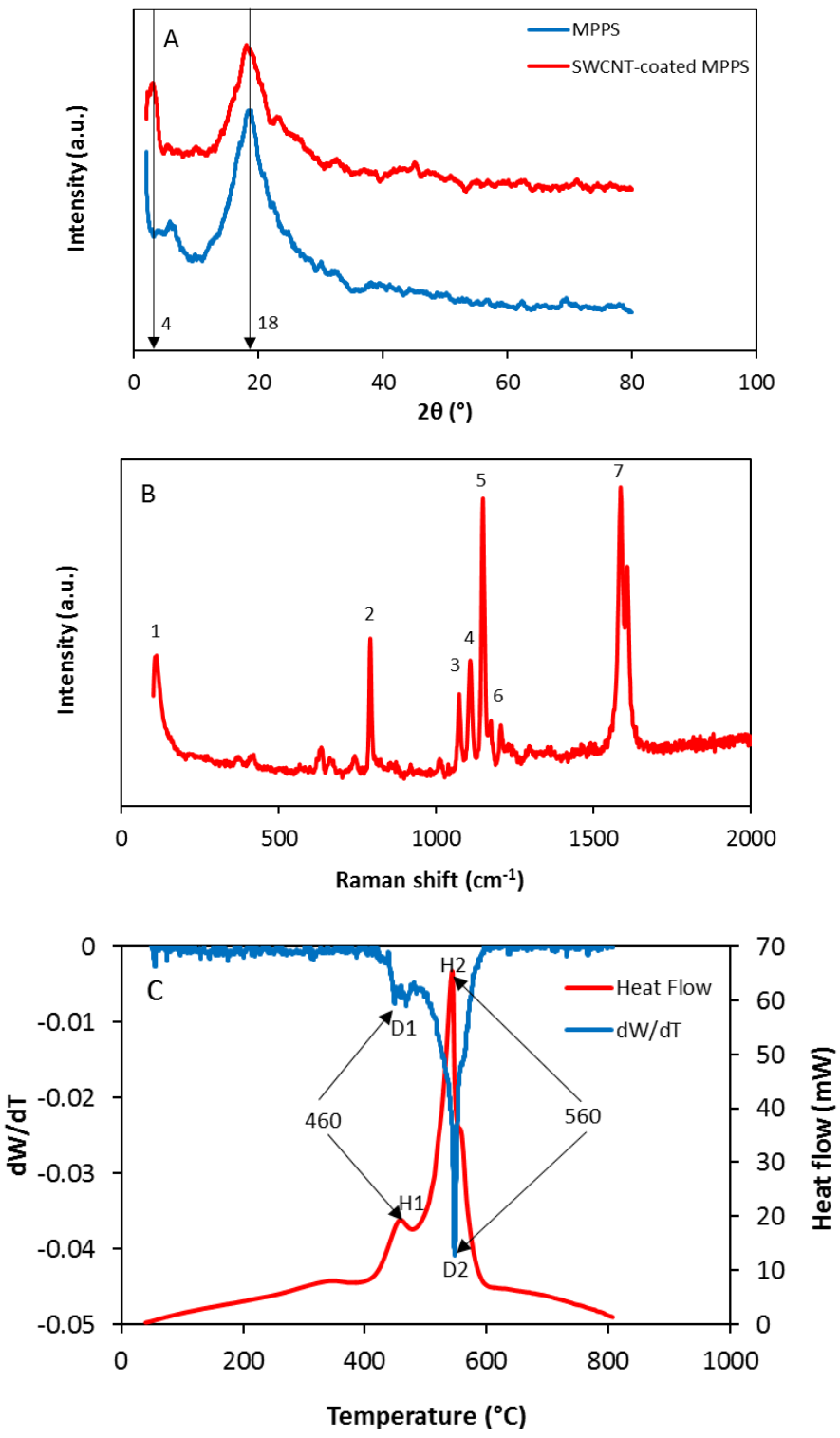


**Figure S5.** Physical properties of the SWCNT-coated MPPS anode. (A) XRD patterns. (B) Raman spectrum. (C) TGA/DTA curves.

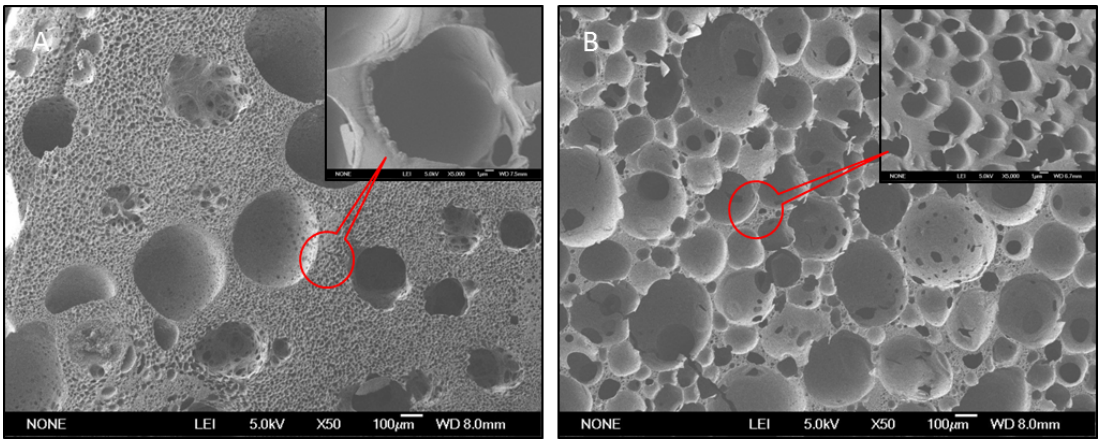


**Figure S6.** FESEM images showing micro-pores on top (A) and on bottom (B) of SWCNT-coated MPPS along with macro-pores. The inset images are for a high magnification.

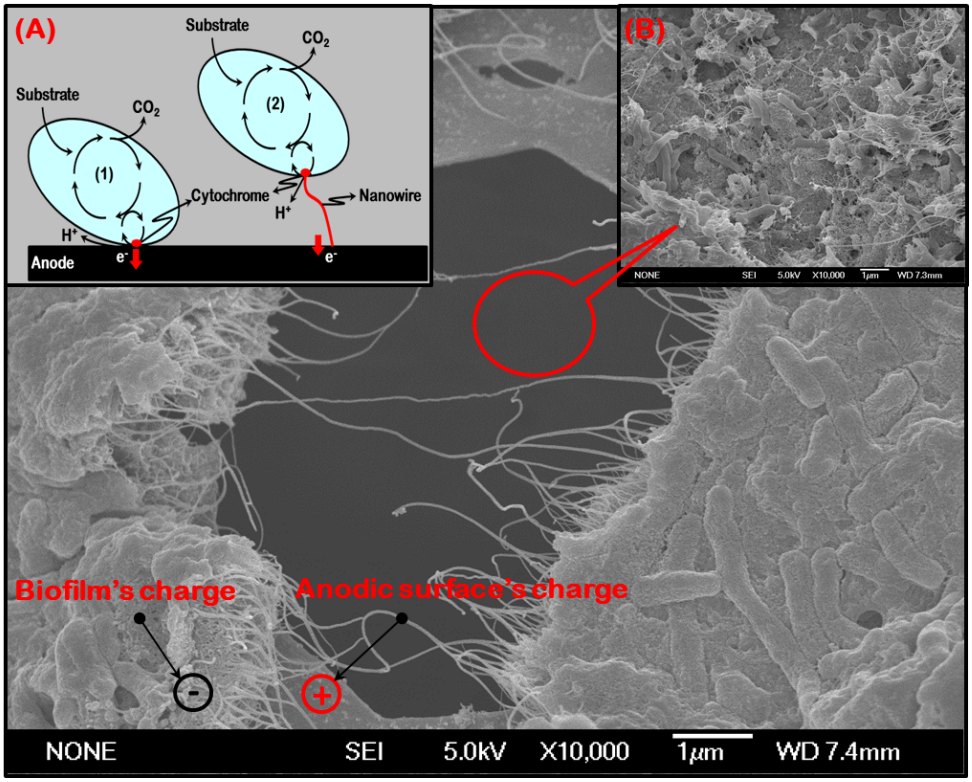


Figure S7. Biofilm formation on the anode of SWCNT-coated MPPS. (A) The mechanism of extracellular electron transfer via membrane-bound cytochromes. (B) Biofilms in mesoporous structure of the anode.

**References:**

S1 A. Rahimpour and S. S. Madaeni, *J. Membr. Sci.*, 2010, **360**, 371-379.

S2 X. Xie, M. Ye, L. Hu, N. Liu, J. R. McDonough, W. Chen, H. N. Alshareef, C. S. Criddle and Y. Cui, *Energy Environ. Sci.*, 2012, **5**, 5265-5270.