Supplementary Information

Graphenesupported α-MnO_2nanotubes as cathode catalyst for improved power generation and wastewater treatment in single-chambered microbial fuel cells

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Methodes

Membrane cathode assembly (MCA) preparation

The CEM (Nafion 117, DuPont, Wilmington, DE) was sequentially boiled in H_2O_2 (30%), deionized water, 0.5 M H_2SO_4, and deionized water (each for 1 h). In order to prepare a MCA, the CEM was hot pressed directly onto the composite catalyst loaded side of carbon paper by heating it to 125°C at 1780 kPa for 3 min (Moore Max Ton Hydraulic Press).

MFC test and operation

MFC test was carried out in fed-batch mode at a fixed external resistance of 100 Ω (except as indicated) and refilled at every 36 ± 2 h. sMFC consisted of an anode and cathode placed on opposite sides in a 0.6 cm thick acrylic (Plexiglass) cuboidal chamber of 6 cm length, 6 cm height and 2 cm width (empty anolyte volume of 60 mL). A schematic of sMFC cell is shown in Figure S1. The anode electrode was made of carbon cloth (projected surface area = 32 cm^2). The MCA was placed onto the opening face of the anode chamber. Provisions were made in the anode chamber for inlet, outlet, and wire input points (top) for electrical connection. Leak proof sealing was provided at the joints to maintain anaerobic microenvironment in the anode compartment and sealed carefully by epoxy sealant. Copper wire was used for electrical contacts.

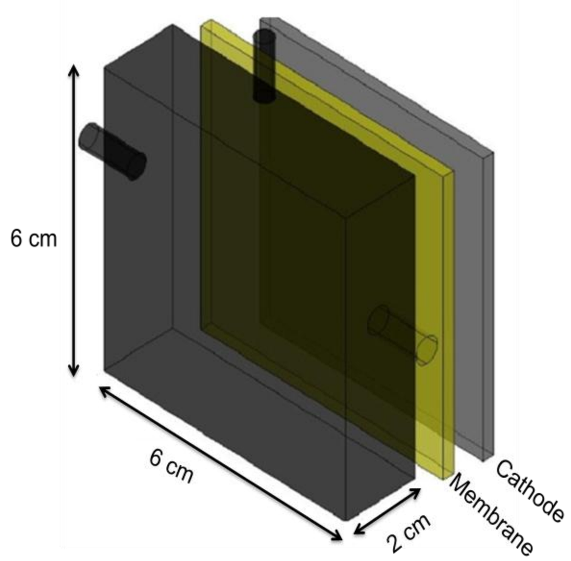

Fig. S1 Schematic of a single-chambered microbial fuel cell.

A synthetic wastewater containing acetate as a carbon source was used as anolyte throughout the study. The detail composition of anolyte was provided in our previous report.[1] The chemical oxygen demand (COD) of synthetic acetate wastewater was 3000 (± 10) mg/L for all the sMFC. The pH of the feed in all the sMFC was maintained at 7.0 by suitable alkalinity addition. Anaerobic consortia collected from bottom sludge of IIT Kharagpur's septic tank were used as parent culture (biocatalyst) for inoculating the anodic chamber. The inoculum sludge was sieved through 1-mm sieve, preheated at 100°C for 15 min and 1g/L 2-bromo ethane sulphonate (BES) was added to suppress the methanogen. Pretreated inoculum sludge was washed thrice (5000 rpm; 20°C) in saline-phosphate buffer (50 mM) [17.2 mM KH_2PO_4 and 32.8 mM K_2HPO_4 in 0.85% NaCl solution] and enriched in synthetic wastewater.

Analytical measurement and calculation

The cell potentials were measured at every 30 min interval using a data acquisition system (USB-6009, National Instruments, Texas, USA) and were recorded by a computer (NI LabVIEW based customized software, Core Technologies, India). The anode potential was measured by inserting a reference electrode (Ag/AgCl, saturated KCl; +197mV, Equip-tronics, India) into the anode chamber. The cathode potential was calculated from the measured cell voltage and anode potential. Polarization curves were obtained by varying external resistances from 90,000 to 30 Ω. Short circuit current (I_{sc}) was measured with a Mastech 6000 counts digital multimeter (Precision MASTECH Enterprises Co., Hong Kong). Volumetric current density was calculated as $i_d = V/RA$, where V (mV) is measured cell potential, R (Ω) is external resistance, and A (cm^3) is working volume of anolyte. Volumetric power density in MFC was calculated from P (W/m^3) = VI/A, where I (Amp) is measured cell current. The coulombic efficiency (C_E) was estimated (eq. S1) by integrating the measured current relative to the theoretical current on the basis of consumed COD.[2]

$$C_E = M_s I t_b / F b_{es} v_{An} \Delta c = 8 I t_b / F v_{An} \Delta c \qquad \text{(eq. S1)}$$

where 'F' = Faraday constant (96485 C/mol), 'I' = current generation at a particular external resistance (close circuit mode), 'Δc' = COD load removed in gram/L, 'v_{An}' = anolyte volume or substrate volume (L), t_b is batch time duration (s).

The internal resistance of the sMFC was calculated by the current interrupt method.[3] In the closed circuit mode, when the sMFC produced a stable current output (I) and potential (V), the circuit was opened causing a steep initial rise in the potential (V_R) followed by gradual increment. The steep rise is attributed to ohmic losses caused by the internal resistance (R_{int}) of the MFC and can be calculated using following equation (eq. S2)[4]

$$R_{\text{int}} = {V_R}/{I} \qquad \text{(eq. S2)}$$

COD measurements were conducted using standard methods (closed reflux method; American Public Health Association. 1998).2 COD values of the anolyte were measured using a COD measurement instrument (DRB200 & DR2800 Portable Spectrophotometer, HACH®, USA). The pH values were monitored using a desktop pH meter (pH510, Cyberscan, Singapore). Wastewater conductivities were measured with a conductivity meter (Electronics India), calibrated by using KCl solution.

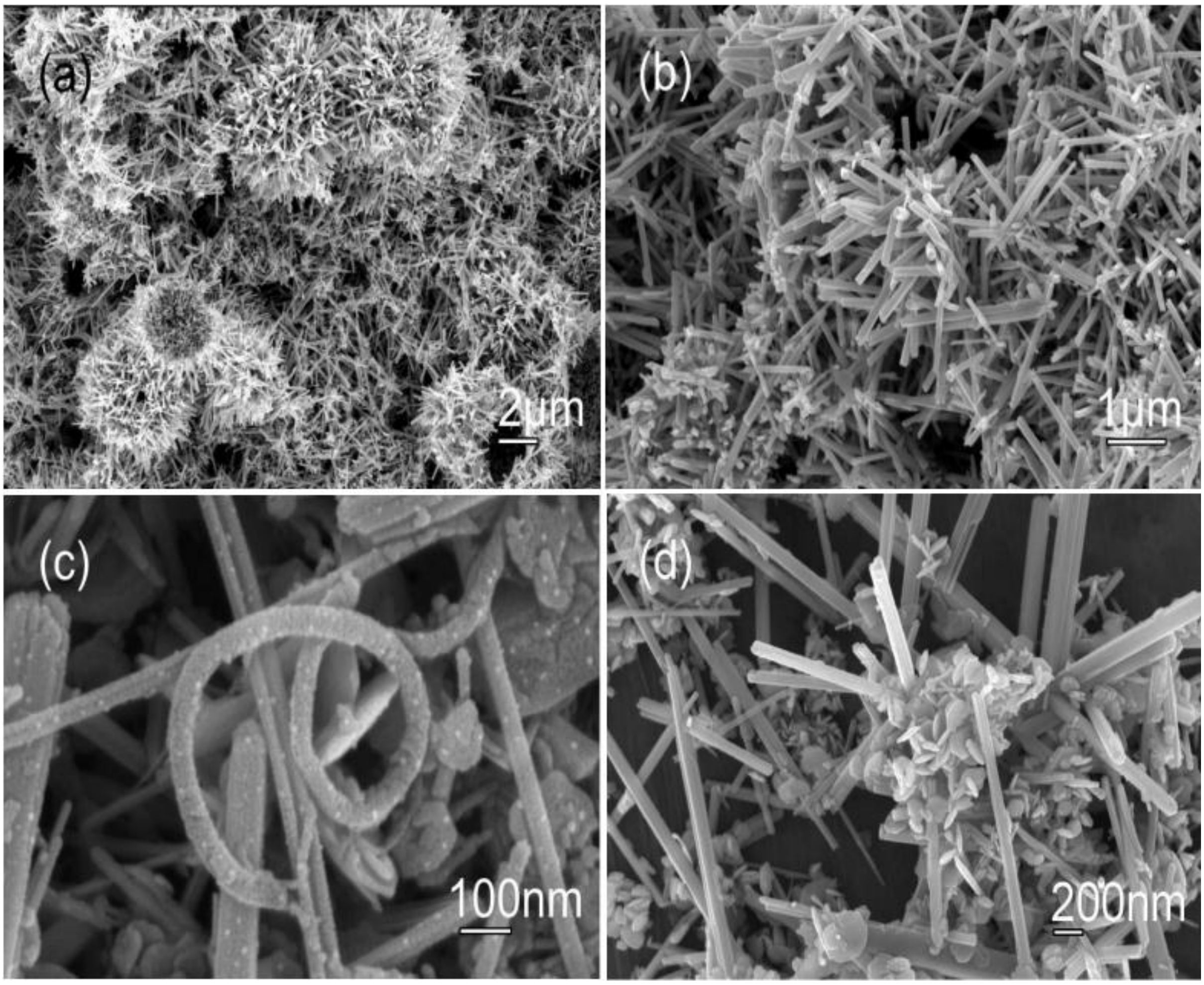

Fig. S2 FE-SEM images of (a,b) MnO_2-NTs, (c) MnO_2-NTs/MWCNTs composite and (d) MnO_2-NTs/graphene composite.

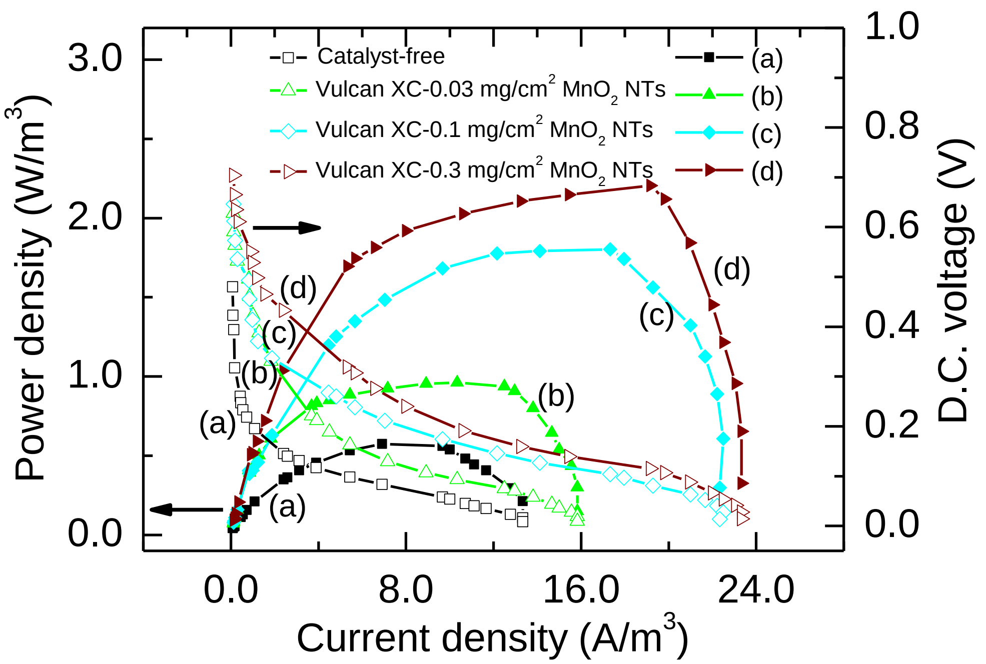

Fig. S3 Polarization plots of sMFC (power density and D.C. voltage as a function of current density) with MnO_2 NTs-Vulcan XC composite cathode loaded with (a) 0, (b) 0.03, (c) 0.1 and (d) 0.3 mg/cm^2 MnO_2-NTs.

Table S1:Effect of MnO_2-NTs loading in Vulcan XC-72 for air cathode in the sMFC.

MFC with catalyst loading	Catalyst-free cathode	0.03 mg/cm^2 MnO_2-NTs	0.1 mg/cm^2 MnO_2-NTs	0.3 mg/cm^2 MnO_2-NTs
Max. Open circuit potential (mV)	677	704	743	754
Max.Volumetric Power density (W/m^3)	0.57	0.93	1.77	2.2
Max. Coulombic efficiency (%)	5.0	6.3	8.3	8.4
COD removal efficiency (%)	69.23	70.10	77.34	78.70
Internal resistance (Ω)	172	154	118	108

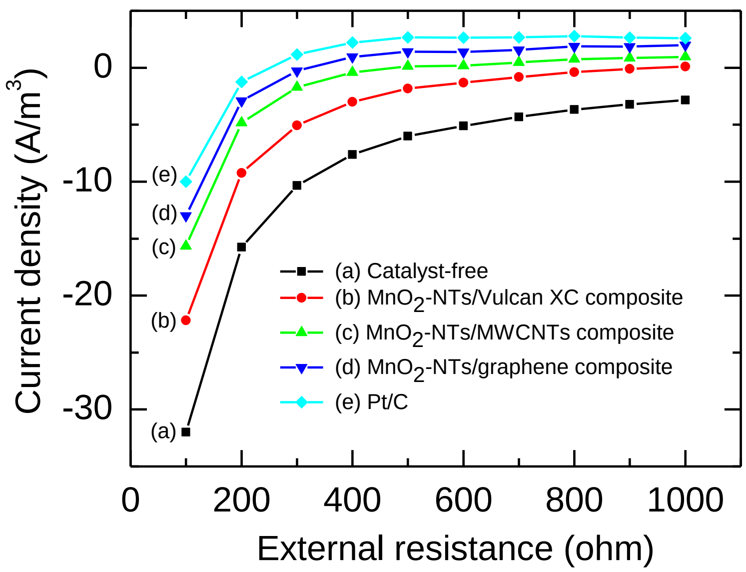

Fig. S4 Current density as a function of external resistance for the sMFC with (a) catalyst-free, (b) MnO_2-NTs/Vulcan XC, (c) MnO_2-NTs/MWCNTs, (d) MnO_2-NTs/graphene, and (e) Pt/C composite cathodes. Fixed quantity of catalyst (0.3 gm/cm^2 MnO_2-NTs or Pt) was loaded to different carbon support for comparison.

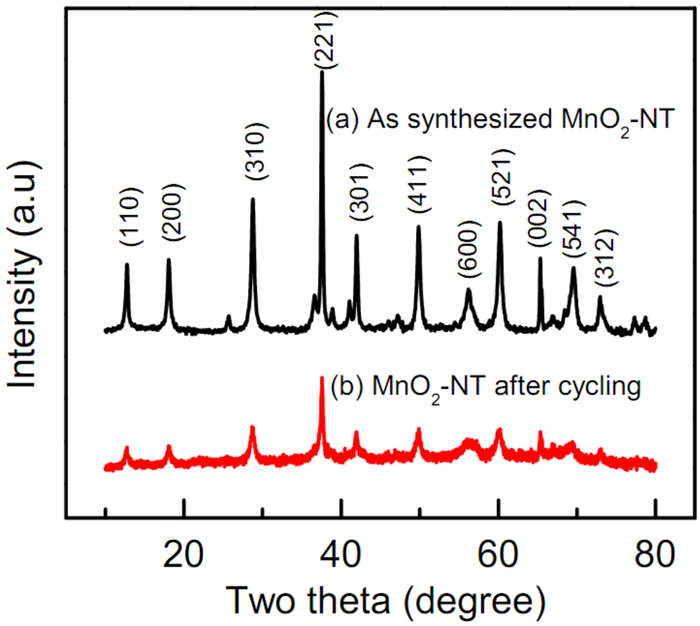

Fig. S5 XRD patterns of α-MnO_2-NTs (a) before and (b) after 20 electrochemical cycles. The phase of α-MnO_2-NTs remains same.

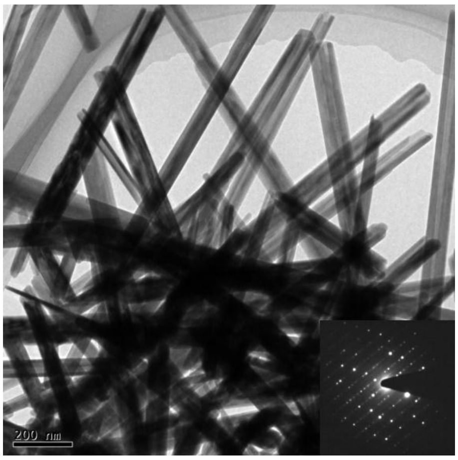

Fig. S6 TEM image of α-MnO_2-NTs after 20 electrochemical cycles. Inset shows SAED pattern.

References

1 M. M. Ghangrekar, V. B. Shinde, Simultaneous Sewage Treatment and Electricity Generation in Membrane-less Microbial Fuel Cell,*Water Sci. Technol.*2008, **58**, 37–43.
2 APHA Standard methods for the examination of water and wastewater: 20th Ed, American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC; 1998.

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4 S.Pandit, A. Sengupta, S. Kale, D. Das, Performance of Electron Acceptors in Catholyte of a Two-chambered Microbial Fuel Cell Using Anion Exchange Membrane. *Bioresour. Technol*.2011, **102**, 2736–2744.