

Figure S1. CV of TvLAC-functionalized MWCNT electrodes under O2 for (a) pristine MWCNTs, (b) naphthotate-modified MWCNTs and (c) anthraquinone-modified MWCNTs (0.1 mol L^{-1} Mc Ilvaine buffer pH 5, v = 10 mV s-1)



Figure S2. Stability of the *POXC*-functionalized MWCNT electrodes for (\blacksquare , blue) anthraquinone-modified MWCNTs and (\blacktriangle , red) naphthoate modified-MWCNT electrodes. Catalytic current densities were measured by one-hour chronoamperometry at $E_p=0.2$ V in stirred oxygen-saturated Mc IIvaine buffer pH 3



Figure S3. polarization (A, black) and power (
, blue) curves for the fuel cell based on a Pt/C anode and a pristine MWCNT cathode.

Materials and Methods

4-carboxylatonaphtyldiazonium tetrafluoroborate and 2-diazoniumanthraquinone were prepared as previously described.^[1] Sodium phosphate dibasic, sodium phosphate monobasic, 1-Methyl-2-pyrrolidinone (NMP), acetonitrile (MeCN), and laccase from *Trametes versicolor* (*TvL*AC, E.C. 1.10.3.2 r, 13.6 U mg⁻¹ solid) were purchased from Sigma Aldrich. POXC with an activity of 1000 U mg⁻¹ was produced and purified as previously described by Macellaro and coauthors.^[2] Commercial grade thin Multi-Walled Carbon Nanotubes (MWCNT, 9.5 nm diameter, purity > 95%) were obtained from Nanocyl. Carbon nanomaterials were used as received without any purification. When not used, the enzymes were stored at -80°C. All the reagents were used without further purification. All solvents were of analytical grade. Distilled water was passed through a Milli-Q water purification system.

Electrochemical measurements

The electrochemical experiments were carried out in a three electrode electrochemical cell using a Biologic VMP3 Multi Potentiostat. The MWCNT bioelectrodes were used as working electrodes. Pt wire was used as counter electrode and the Ag/AgCl (KCl sat) served as reference electrode. The experiments were conducted at room temperature. All potentials are given using Ag/AgCl as reference. All current densities are normalized towards the geometrical surface of the glassy carbon electrode (0.196 cm²) or the gasdiffusion electrode (0.07 cm⁻²). An oxygen concentration of 0.72 mmol L⁻¹ was measured in the electrolyte by using a Neofox Oxygen Sensing System from OceanOptics. All simulated curves were obtained via Origin Pro 9.0.

Preparation of the glassy carbon- modified MWCNT electrode

The working electrodes were glassy carbon electrodes (3 mm diameter). NMP dispersions of MWCNTs were prepared by 30 min sonication of 5 mg MWCNTs dispersed in 1 mL NMP until homogeneous black suspension was obtained. Then 20 μ L of the MWCNTs solution were drop-casted on a GCE or a GDE and NMP was removed under vacuum leaving a 5- μ m-thick film on the GCE.

Electrografting of aryldiazonium salts on MWCNT electrode

The aryldiazonium salts were electrografted onto MWCNT electrodes using a previously-described procedure.^[1] Electrografting was performed by performing 5 CV scans in a MeCN + 0.1 mol L⁻¹ TBAP solution in the presence of 2 mmol L⁻¹ of the aryldiazonium salt at a scan rate of 10 mV s⁻¹ under an inert atmosphere. The modified electrodes were then thoroughly rinsed with MeCN.

Functionalization of modified MWCNTs with POXC and TvLAC

The MWCNT electrodes were incubated in 20 μ L of a 0.2mg mL⁻¹ POXC in 0.1 mol L⁻¹ sodium phosphate buffer solution at pH = 7.6 for overnight at 4°C or with 20 μ L of a TvLAC solution (5 mg mL-1 in Mc Ilvaine buffer pH 5.0), overnight at 4°C. Electrodes were then rinsed with sodium phosphate buffer.

Electrochemical modeling of the CV curves

The electrocatalytic current (average of forward and backward scan) was modeled using the equation 1 (reproduced from ref ^[3]):

$$j = \frac{j_{lim}}{\beta do} \frac{e_1 - e_2}{1 + e_1} ln \frac{p e_1^{\alpha} + 1 + e_1}{\frac{k_{cat}}{k_{max}} e_1^{\alpha} + (1 + e_1) \exp(-\beta do)}$$
(1)

where $e_1 = \exp(nF/RT)(E-E^{\circ}_{Cu(T1)})$, $e_2 = \exp(-4F/RT)(E^{\circ}_{Cu(T1)}-E_{O2/H2O})$, $E_{O2/H2O} = 0.69V$ vs SCE at pH 7, α is the transfer coefficient, k_{cat} is the catalytic constant for the irreversible O_2 reduction catalysis and k_0^{max} is the electron transfer rate constant at the minimal distance between the electrochemical relay centre and the electrode. βd_0 is the ET tunneling factor accounting for ET rate dispersions. The electrocatalytic wave was well-fitted using n = 1.

	MWCNT	AQ-MWCNT	CN-MWCNT
βdo	26	5.0	5.3
k _{cat} /k ₀	0.24	0.86	0.20
Ĵlim	0.084	0.380	0.259
E _{cat}	0.523	0.577	0.579
R ²	0.86	0.999	0.997

Table S1. Fitting Parameters of simulated curves from figure 4A for MoBOD-modified MWCNT, AE-MWCNT and CN-MWCNT electrodes

Preparation of the Proton Exchange membrane fuel cell (PEMFC)

For the PEMFC setup, Nafion[®] membrane 212 was treated according to the standard procedure : 60 min in a 5 % (wt) H_2O_2 solution at 80 °C, 60 min in ultra pure water at 80 °C, and finally 60 min in an 8 % (wt) H_2SO_4 solution at 80 °C. After each treatment, the membrane was rinsed three times in ultra pure water in order to remove H_2O_2 traces. Nafion membrane was stored in ultra pure water before used. The PEMFC test cell was purchased from PAXITECH and consists in a 5 cm² hydrogen/air fuel cell with graphite bipolar plates and a serpentine gas flow design. Polarization and power curves were obtained by 30 s-galvanostatic discharges at room temperature under atmospheric H_2 gas pressure with humidified H_2 and air gas flows of 20 mL min⁻¹. At the cathode, only a 3 mm diameter surface of the GDL is in contact with the electrolyte, giving an equal surface area of 0.071 cm² at both the anode and the cathode. Commercial Pt/C GDE (diameter of 4 cm²) were used at the anode

REFERENCES

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