

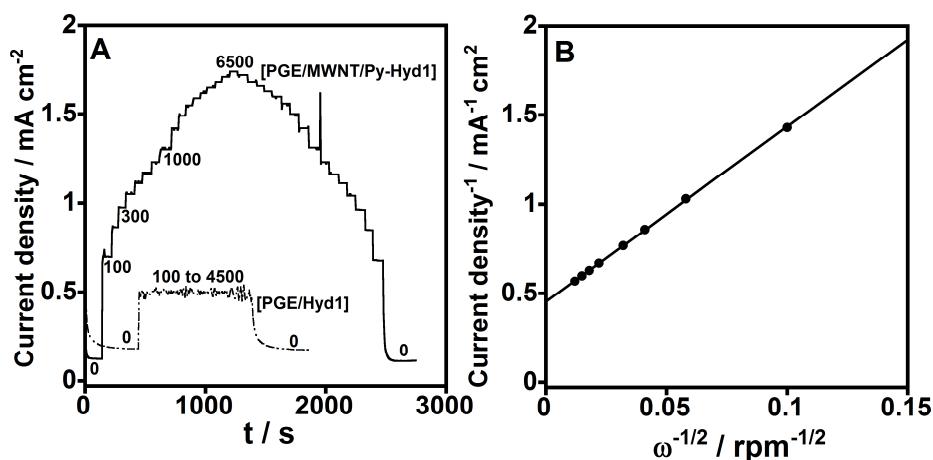
**Supplementary information for:**

**Order-of-Magnitude Enhancement of an Enzymatic Hydrogen-Air Fuel Cell based on Pyrenyl Carbon Nanostructures**

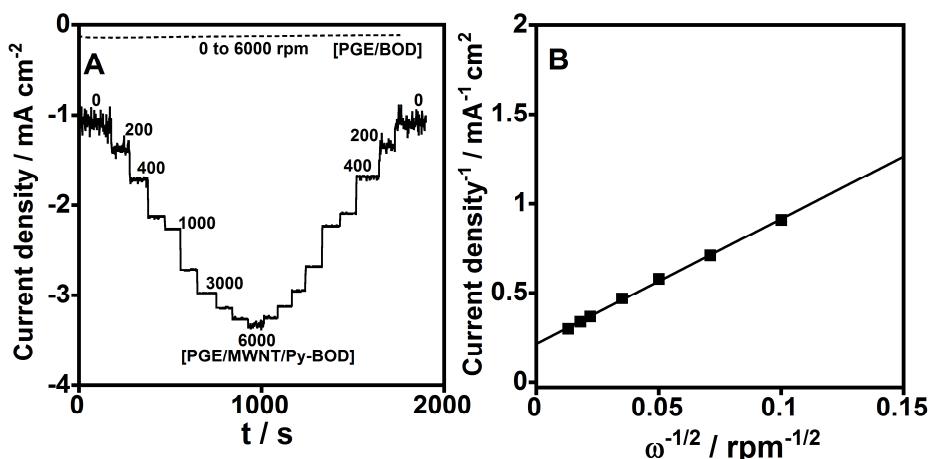
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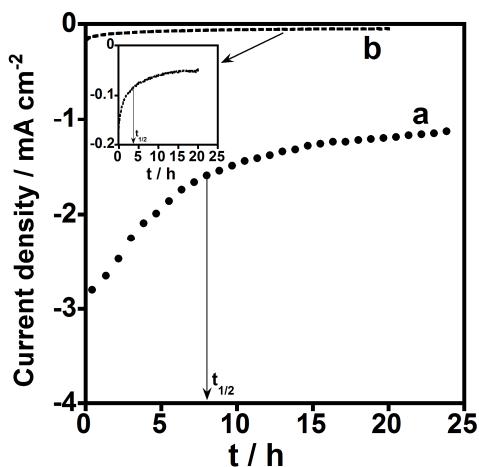
<sup>\*</sup> To whom correspondence should be addressed. E-mail: [fraser.armstrong@chem.ox.ac.uk](mailto:fraser.armstrong@chem.ox.ac.uk)



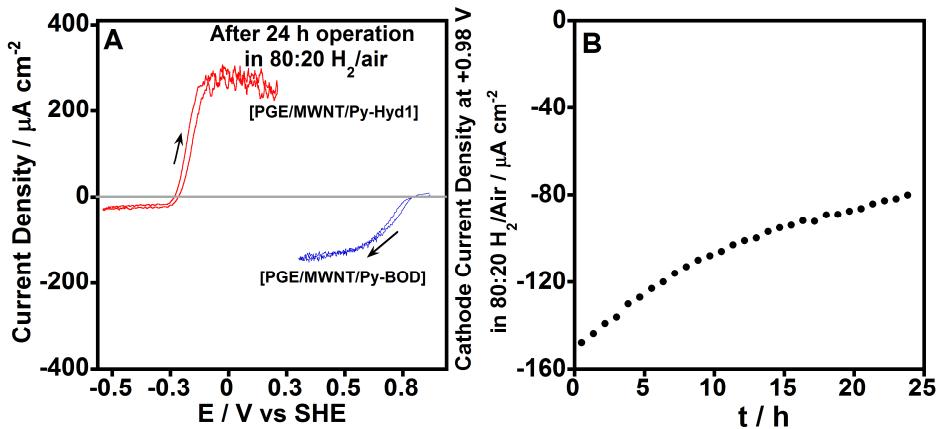
**Figure S1 (A)** Rotation rate dependence (in rpm) of the electrocatalytic current density for H<sub>2</sub> oxidation at a [PGE/MWNT/Py-Hyd1] electrode or Hyd1 simply adsorbed on polished PGE ([PGE/Hyd1]). Experimental conditions: 100 % H<sub>2</sub>, 25 °C, pH 6.0, potential -40 mV vs SHE. **(B)** Koutecky-Levich plot analyzing the H<sub>2</sub> oxidation current density by the [PGE/MWNT/Py-Hyd1] electrode, measured at -40 mV vs SHE.



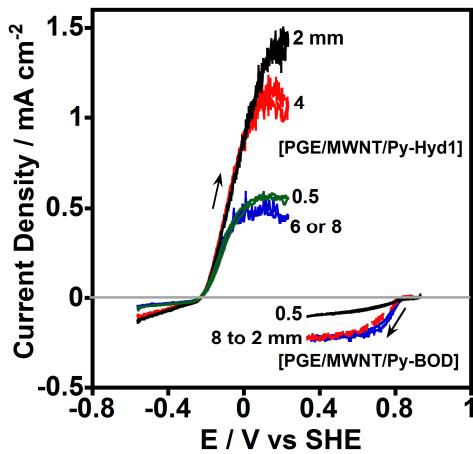
**Figure S2** (A) Rotation rate dependence (in rpm) of the electrocatalytic current density for  $O_2$  reduction at a [PGE/MWNT/Py-BOD] electrode or BOD simply adsorbed on polished PGE ([PGE/BOD]). Experimental conditions: saturated  $O_2$ , 25 °C, pH 5.0, potential +340 mV vs SHE. (B) Koutecky-Levich plot analyzing the  $O_2$  reduction current density by the [PGE/MWNT/Py-BOD] electrode, measured at +340 mV vs SHE.



**Figure S3** Stability measurements in saturated  $O_2$  for (a) a [PGE/MWNT/Py-BOD] electrode and (b) BOD adsorbed on polished PGE ([PGE/BOD]). Chronoamperometry was carried out at +340 mV vs SHE, 25 °C, pH 5.0, 2500 rpm. (Inset) Enlarged chronoamperometry trace of (b).



**Figure S4** (A) Voltammograms of a [PGE/MWNT/Py-Hyd1] anode and a [PGE/MWNT/Py-BOD] cathode after 24 h operation in the membraneless quiescent fuel cell, operated at an applied potential of 0.98 V in an 80:20 H<sub>2</sub>/air fuel mixture, pH 5.0, 25°C; (B) Current density vs time for the [PGE/MWNT/Py-BOD] cathode in the fuel cell at an applied constant potential of 0.98 V in an 80:20 H<sub>2</sub>/air fuel mixture, pH 5.0, 25°C.



**Figure S5** Voltammograms of a [PGE/MWNT/Py-Hyd1] anode and a [PGE/MWNT/Py-BOD] cathode at various separation distances (as denoted in the graph in mm) in the quiescent membraneless fuel cell through which an 80:20 H<sub>2</sub>/air fuel mixture was bubbled. Other conditions: 25 °C, pH 5.0.