

Supplementary Material

Design and Optimization of Critical Raw Material-Free Electrodes Towards Performance Enhancement of Microbial Fuel Cells

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Materials

Iron (II)phthalocyanine (FePc), nitric acid (HNO₃), ethanol, Nafion solution (5 wt.%), and polytetrafluoroethylene - PTFE dispersion (60 wt.% in H₂O) were purchased from Sigma-Aldrich. Carbon Vulcan XC 72R and Black Pearls 2000 were supplied by CABOT Corporation. A stainless-steel mesh (304 woven wire # = 120, pore size = 0.125 mm), carbon paper 38-BC with a 325 µm thickness and 80% porosity was supplied by SGL Technologies GmbH, and carbon cloth ELAT 1400 with a 554 µm thickness and a 65% porosity was supplied Quintech.

Activation of the carbon black pearls and catalysts preparation

Activation of the BP with O-containing functional groups consisted of commercial powder (1g) treatment in nitric acid (50 mL, 65 wt.%) in a reflux system at 90 °C for 16 hours. Subsequently, the acidic suspension was centrifuged, washed in H₂O, and filtered until obtention of a 7 pH. The powder was dried overnight and ground overnight (T=70 °C) to facilitate impregnation with the precursors.

Electrochemical characterization: half-cell tests

The number of electrons transferred (n) and the yielding percentage of hydrogen peroxide (H₂O₂ %) were calculated following the equations (1) and (2), in which N is the ring collection efficiency (0.26).

$$n = \frac{4 \times |I_{Disk}|}{|I_{Disk}| + |I_{Ring}/N|} \quad (1)$$

$$H_2O_2(\%) = \frac{200 \times |I_{Ring}/N|}{|I_{Disk}| + |I_{Ring}/N|} \quad (2)$$

TG and XRPD results

Figure S1 reports the TG curves for the catalyst's precursors before the pyrolysis synthesis step. The TG curve for the activated carbon black pearls (BP, black curve) indicates two primary weight losses. The first one (10 wt.%), between 30 and 100 °C, for water desorption, with a 22 wt.% loss at the temperature range of 100 to 800 °C, which can be associated with the partial decomposition of the O-containing groups introduced in carbon black pearls during their activation [100], resulting in a final mass of 68 wt. %. The TG curve for iron phthalocyanine (FePc, red curve) indicates a first weight loss between 160-200 °C, which is related to the release of adsorbed water (6 wt.%). A second weight loss between 200 and 450 °C (20 wt.%) can be ascribed to a concomitant sublimation and phase transition of the FePc [101], followed by a third (19.8 wt. %, 450-650 °C) and fourth (12 wt.%, 650–800 °C) weight loss related to the fragmentation and carbonization of the macrocycle [74]. The residual mass of 42 wt.%. Four weight losses are observed for the catalyst precursor (blue curve): the first (25-100 °C) ascribed to the water desorption (6 wt.%); the second (200-250 °C, 8.7 wt.%), third (250-370 °C, 10.5 wt.%), and fourth (370-800 °C, 20.8 wt.%) weight loss, are related to decomposition of FePc and oxygen-containing groups from the BP, resulting in a residual mass of 54 wt.%. The different weight losses, as compared to those obtained for pristine FePc and BP, can be related to the π - π stacking interaction of the FePc macrocycle with the carbon support after the impregnation synthesis step [102] changing the temperature range at which the phase transition and decomposition phenomena take place, and promoting the integration of Fe- and N-based moieties in the carbonaceous matrix.

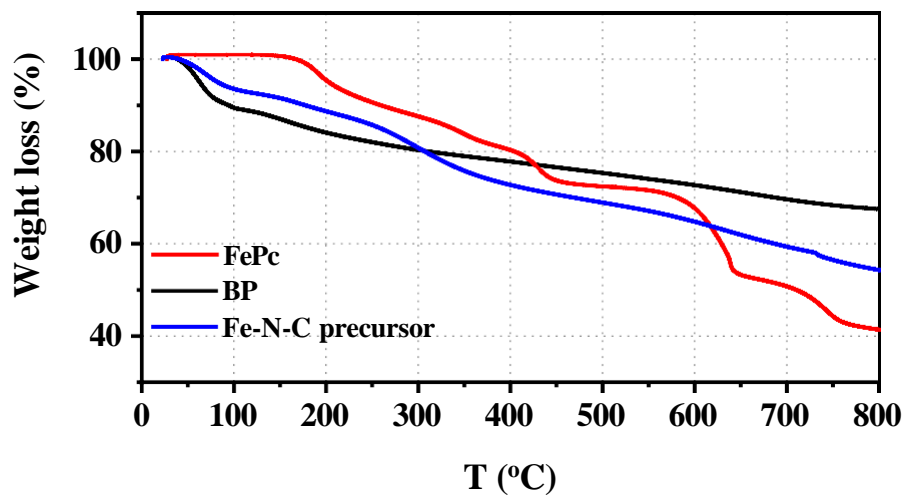


Figure S1. TGA curves of the catalysts precursors: (red) FePc, (black) O-functionalized BP, and (blue) Fe-N-C catalyst precursor.

Figure S2 shows the XRPD patterns for the pristine iron phthalocyanine (FePc) and the carbon black pearls (BP). The FePc (red) diffraction pattern is characterized by sharp peaks in between $2\theta = 10$ to 40° [103], while XRPD for BP indicates the diffraction peaks for graphitic carbon at $2\theta = 25^\circ$ and $2\theta = 43.6^\circ$, respectively typically observed for a carbonaceous matrix [104].

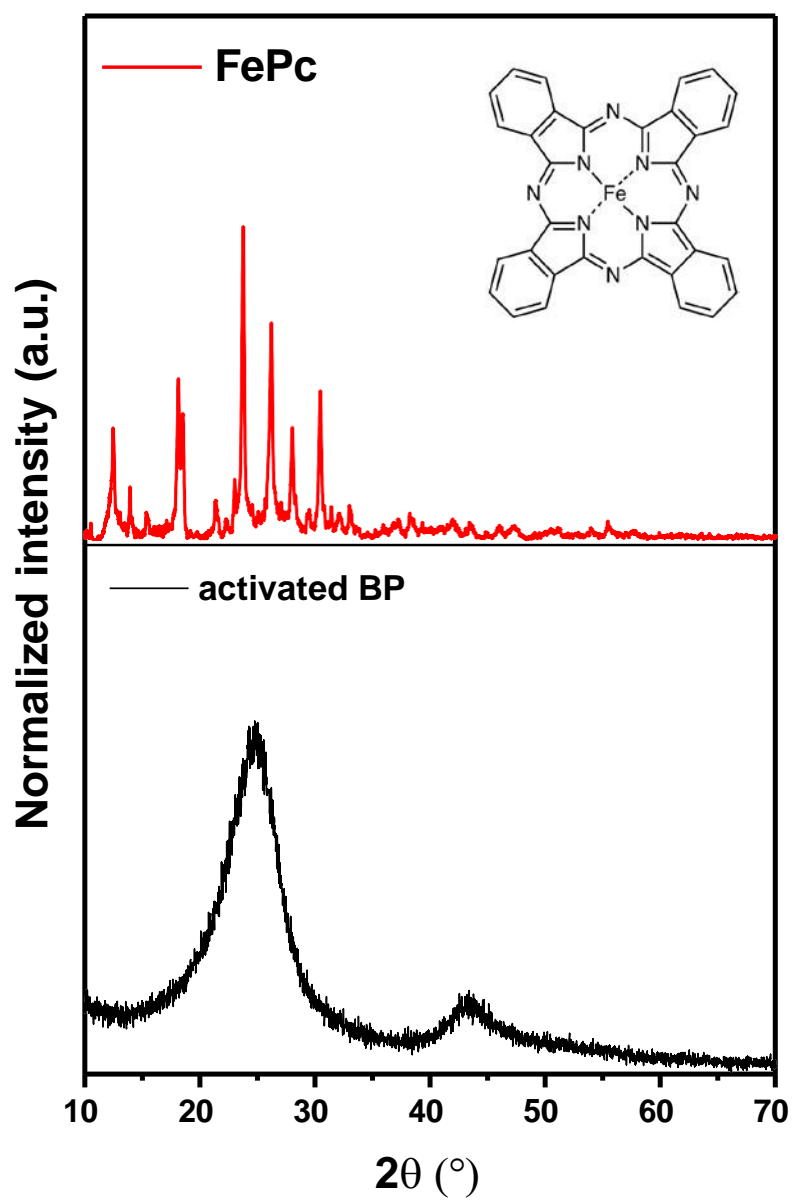


Figure S2. XRPD patterns for bare (red) Fe phthalocyanine and (black) activated carbon black pearls precursors.

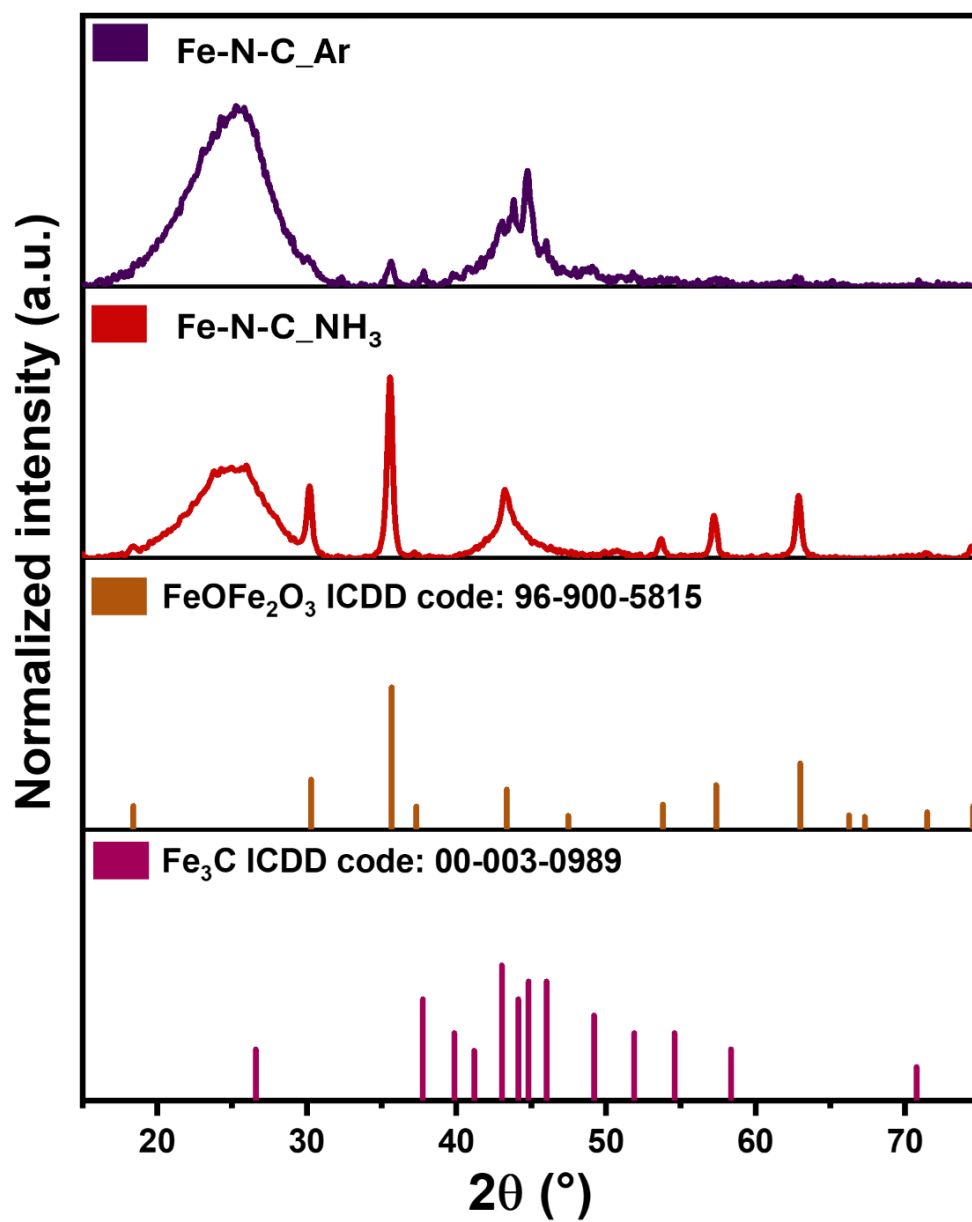


Figure S3. XRD patterns for the pyrolyzed samples.

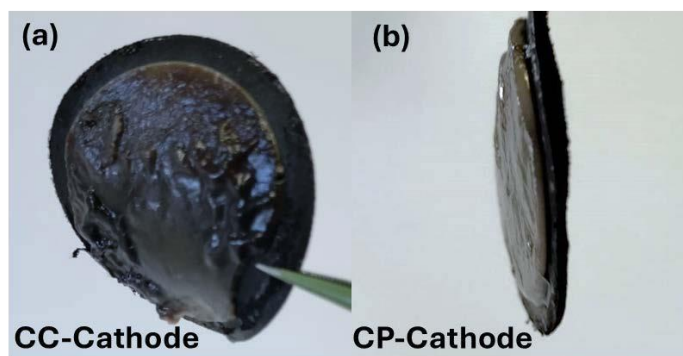


Figure S4. Pictures of the (a) CC-cathode and (b) CP-cathode after 90 days of MFC operation.

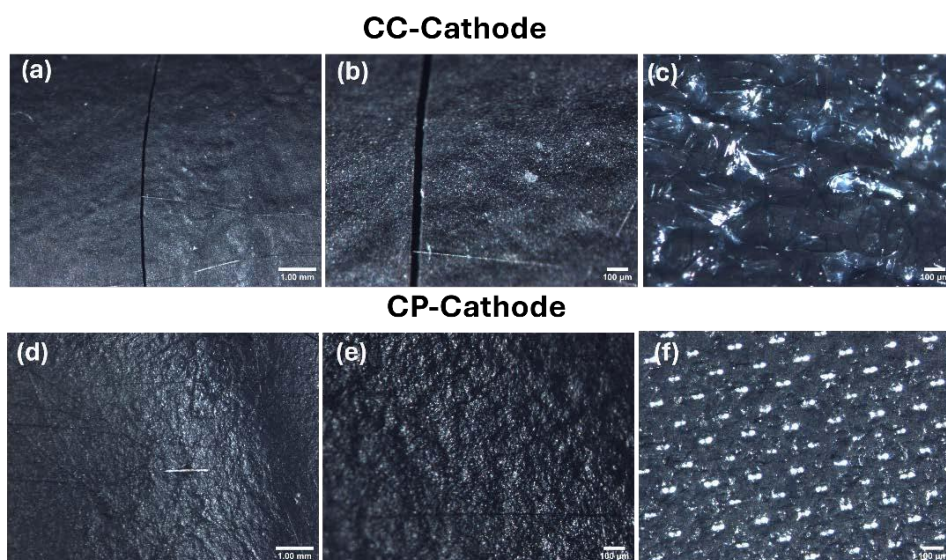


Figure S5. Optical micrographs of the catalyst layer of CC-cathode (a-b) and CP-cathode at different magnifications after 90 days of MFC operation. Optical micrographs of the GDL facing the air side of CC-cathode (c) and CP-cathode (f).