Supporting Information

A Facile Synthesis of FeS/Fe_3C Nanoparticles Highly Dispersed on in-Situ Grown N-Doped CNTs as Cathode Electrocatalyst for Microbial Fuel Cells

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Experimental methods

Preparation of FeS@NCNTs-700: Iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, 1.05 g) was ground with thiourea (CH_4N_2S, 0.95 g). The resulting mixture was then transferred into a quartz ark and calcined in a tube furnace under N_2 atmosphere for 3 h at 700 °C to obtain FeS. To obtain NCNTs, iron nitrate (1.05 g) and melamine (5 g) were mixed and calcined in N_2 atmosphere for 3 h at 700 °C and then the resulting sample was treated with 2 M HCl to remove Fe_3C. FeS@NCNTs-700 was obtained by grounding the resultant FeS and NCNTs.

Preparation of Fe_3C@NCNTs-700: Fe_3C@NCNTs-700 was synthesized in the same way as Nano-FeS/Fe_3C@NCNTs-700, but without adding thiourea.

Formulation of phosphate buffered saline (PBS): PBS contained disodium hydrogen phosphate anhydrous (Na_2HPO_4, 4.21 $g \cdot L^{-1}$), sodium dihydrogen phosphate anhydrous (NaH_2PO_4, 2.13 $g \cdot L^{-1}$), potassium chloride (KCl, 0.13 $g \cdot L^{-1}$) and ammonium chloride (NH_4Cl, 0.31 $g \cdot L^{-1}$). The pH of the resulting solution is 7.0.

Formulation of acetate culture solution (1 $g \cdot L^{-1}$): Acetate culture solution contained anhydrous sodium acetate (CH_3COONa, 1 $g \cdot L^{-1}$), disodium hydrogen phosphate anhydrous (Na_2HPO_4, 4.21 $g \cdot L^{-1}$), sodium dihydrogen phosphate anhydrous (NaH_2PO_4, 2.13 $g \cdot L^{-1}$), potassium chloride (KCl, 0.13 $g \cdot L^{-1}$), ammonium chloride (NH_4Cl, 0.31 $g \cdot L^{-1}$), vitamin solution (12.5 $mL \cdot L^{-1}$) and mineral solution (12.5 $mL \cdot L^{-1}$). The pH of the resulting culture solution is 7.0.

Preparation of cathode: 17.5 mg of 20 wt% Pt/C or Nano-FeS/Fe_3C@NCNTs-700 were mixed with 15 μL of deionized water, 116.7 μL of Nafion solution and 58.4 μL of anhydrous ethanol and sonicated for 10 min. Then the slurry was applied uniformly on the carbon cloth with a diameter of 4 cm and air-dried for 24 h.

Measurements of power density: The power density of the MFCs was measured in a two-electrode configuration, where the cathode of MFC was served as the working electrode and the anode was as the counter and reference electrodes. The MFCs were discharged under constant resistor till the voltage of MFC dropped below 0.02 V. Then the resistor was removed and 15 mL of solution was replaced with fresh one. After 6 h of resting, LSV was performed from open circuit potential to 0 V relative at a scan rate of 1 mV s^{-1}.

Theoretical calculation method: The (114) crystal plane of FeS and the (031) crystal plane of Fe_3C were selected to calculate the adsorption energy of FeS and Fe_3C because these are the preferred exposed crystal planes of FeS and Fe_3C in Nano-FeS/Fe_3C@NCNTs-700. Spin-polarization density functional theory (DFT) calculations based on the first-principles[1, 2] were performed within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE)[3] formulation. The projected augmented wave (PAW) potentials[4, 5] were applied to describe the ionic cores with taking valence electrons into account and using a plane wave basis set with a kinetic energy cutoff of 450 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10^{-5} eV. A geometric optimization was

considered convergent when the energy change was smaller than 0.02 eV $Å^{-1}$. During the relaxation, the Brillouin zone with a 2 × 2 × 1 Gamma centered grid was used. The 20 Å vacuum layer was normally added to the surface to eliminate the artificial interactions between periodic images. In the k-plot optimization, two of Fe_3C structure, 2 × 2 × 1 and 3 × 3 × 1 had been considered. It was found that the energies of these two structures were -743.093 eV and -743.111 eV, and the corresponding adsorption energies with O_2 were -1.824 eV and -1.828 eV, respectively. These values are almost the same and the 2 × 2 × 1 structure was used for k-point optimization in this work for saving calculation time.

Experimental results

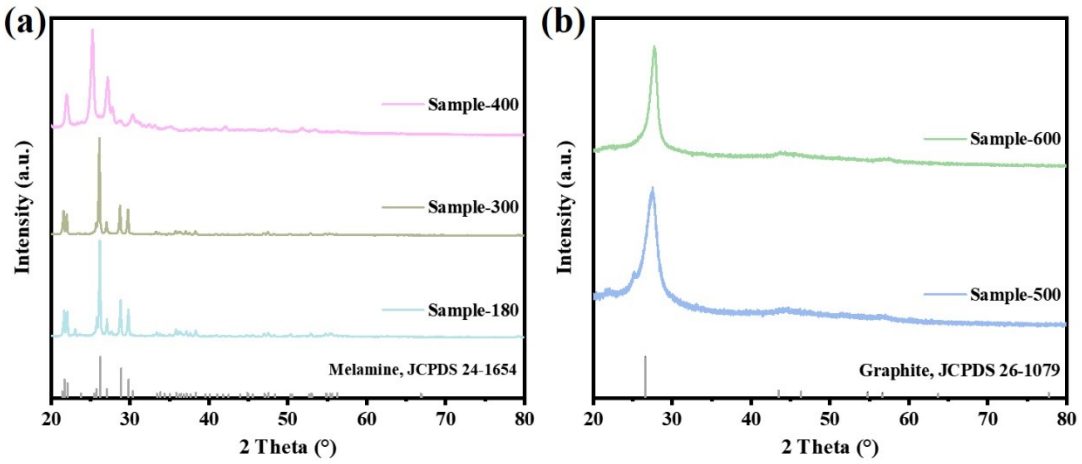

Fig. S1 XRD of samples carbonized at (a) 180 °C, 300 °C and 400 °C as well as (b) 500 °C and 600 °C.

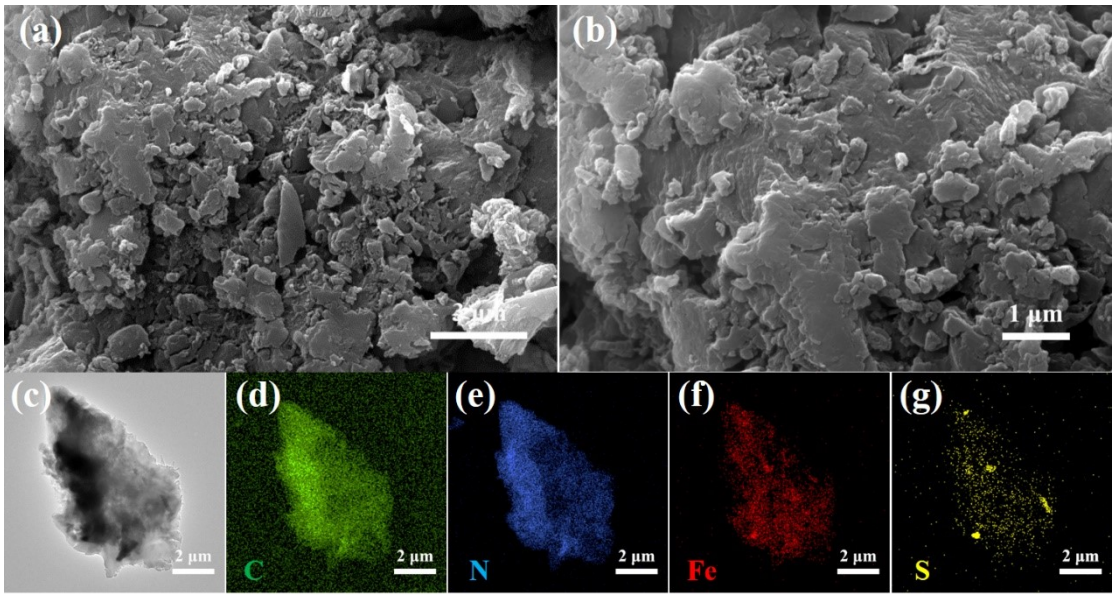

Fig. S2 (a, b) SEM images at different magnifications, (c) TEM image and (d-g) EDS elemental mappings of sample carbonized at 500 °C.

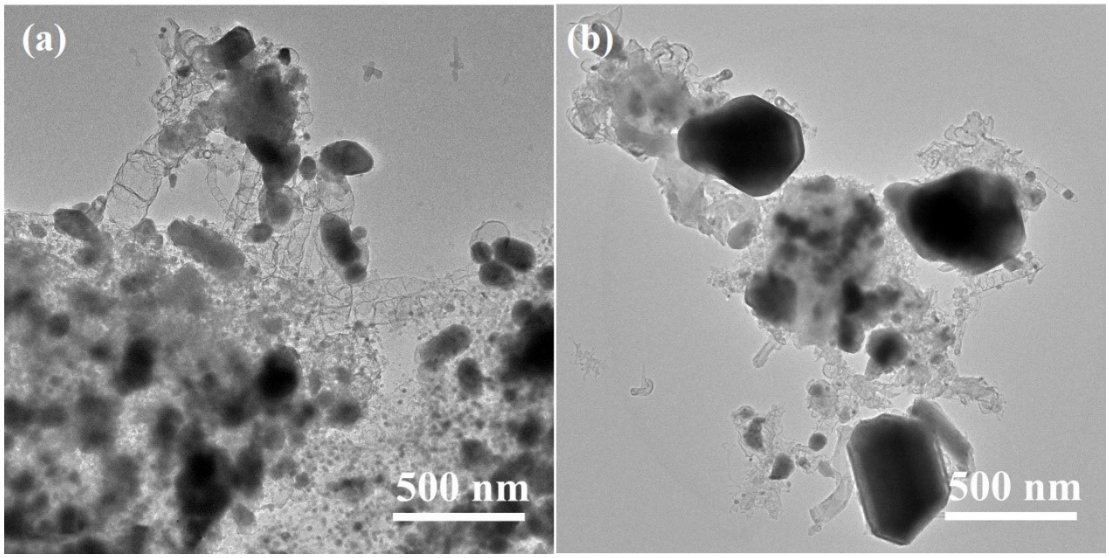

Fig. S3 TEM images of (a) Nano-FeS/Fe_3C@NCNTs-800 and (b) Nano-FeS/Fe_3C@NCNTs-900.

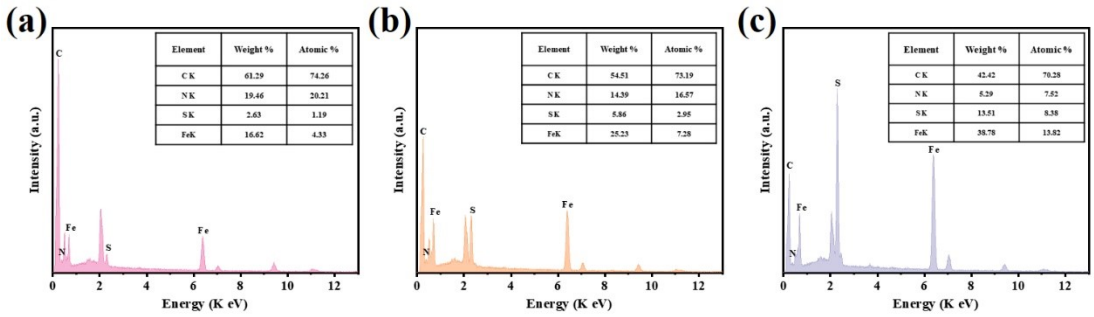

Fig. S4 Energy-dispersive X-ray spectra (EDS) of Nano-FeS/Fe_3C@NCNTs carbonized at (a)700 °C (b) 800 °C and (c)900 °C.

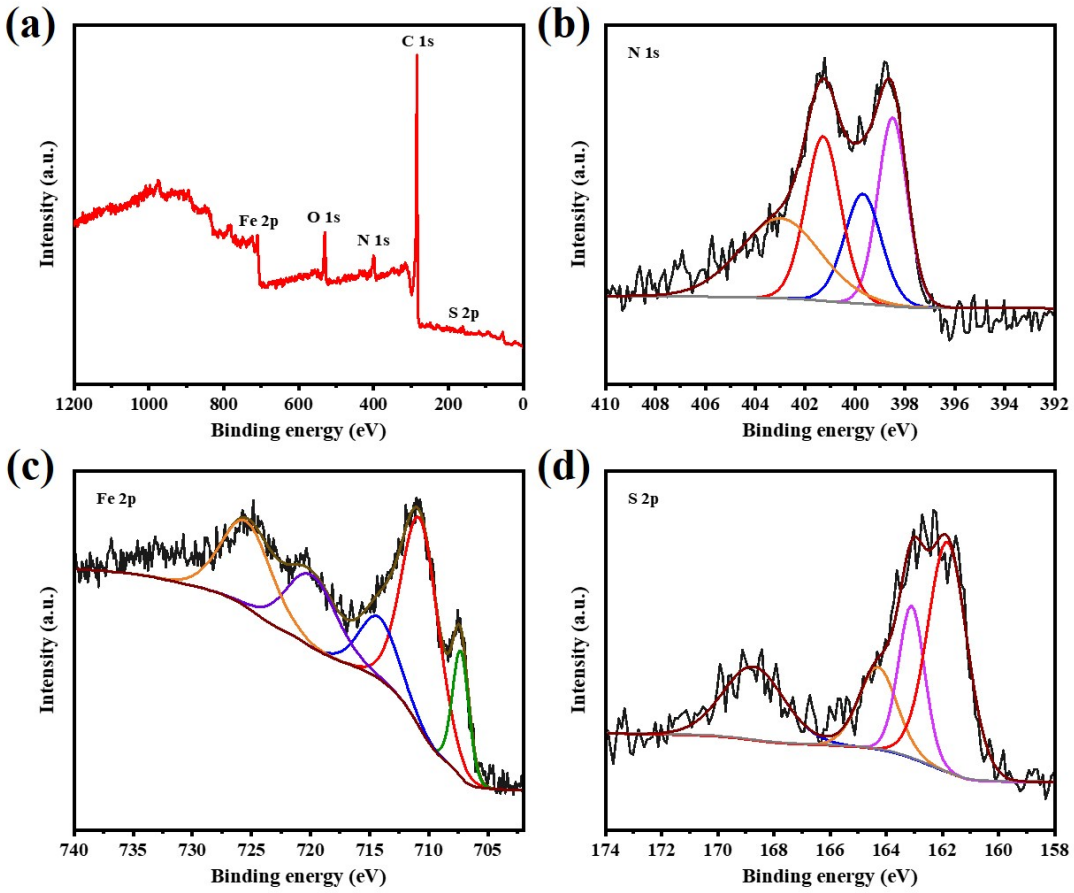

Fig. S5 (a) XPS survey spectrum of Nano-FeS/Fe_3C@NCNTs-800, and high resolution XPS spectra of (b) N 1s, (c) Fe 2p, (d) S 2p for Nano-FeS/Fe_3C@NCNTs-800.

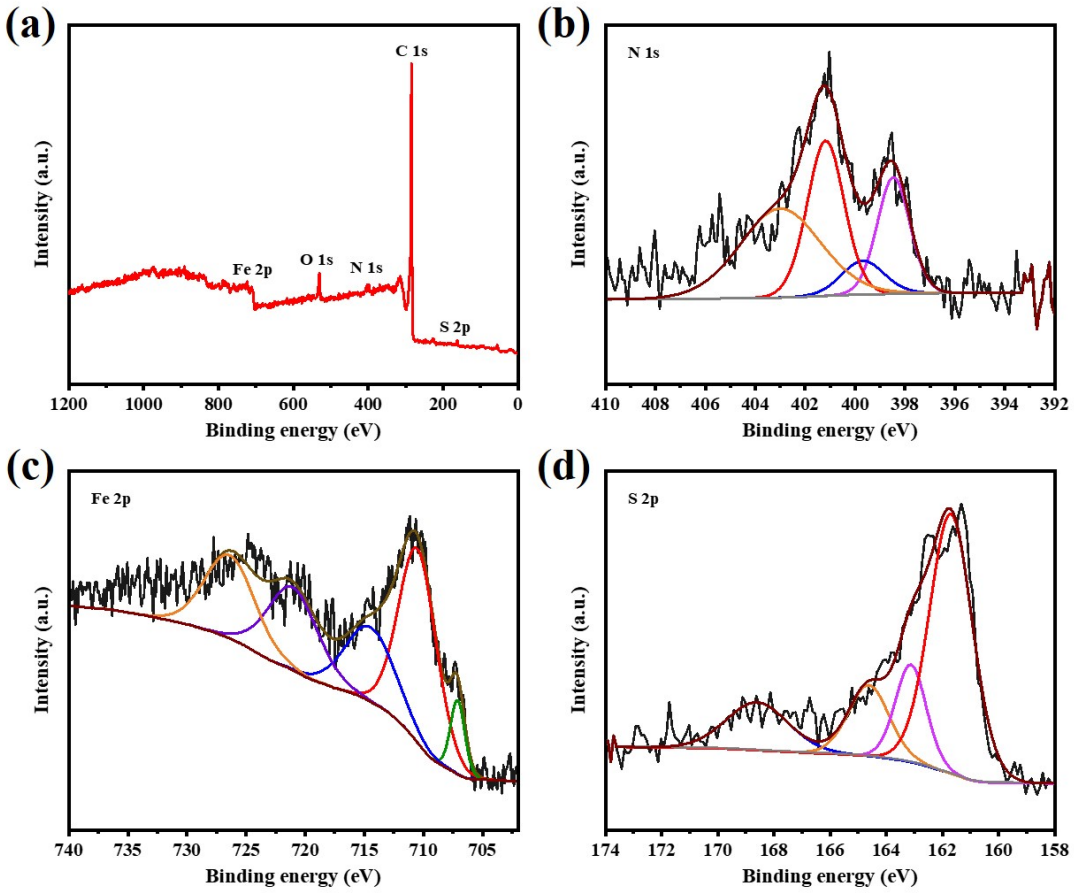

Fig. S6 (a) XPS survey spectrum of Nano-FeS/Fe_3C@NCNTs-900 and high resolution XPS spectra of (b) N 1s, (c) Fe 2p, (d) S 2p for Nano-FeS/Fe_3C@NCNTs-900.

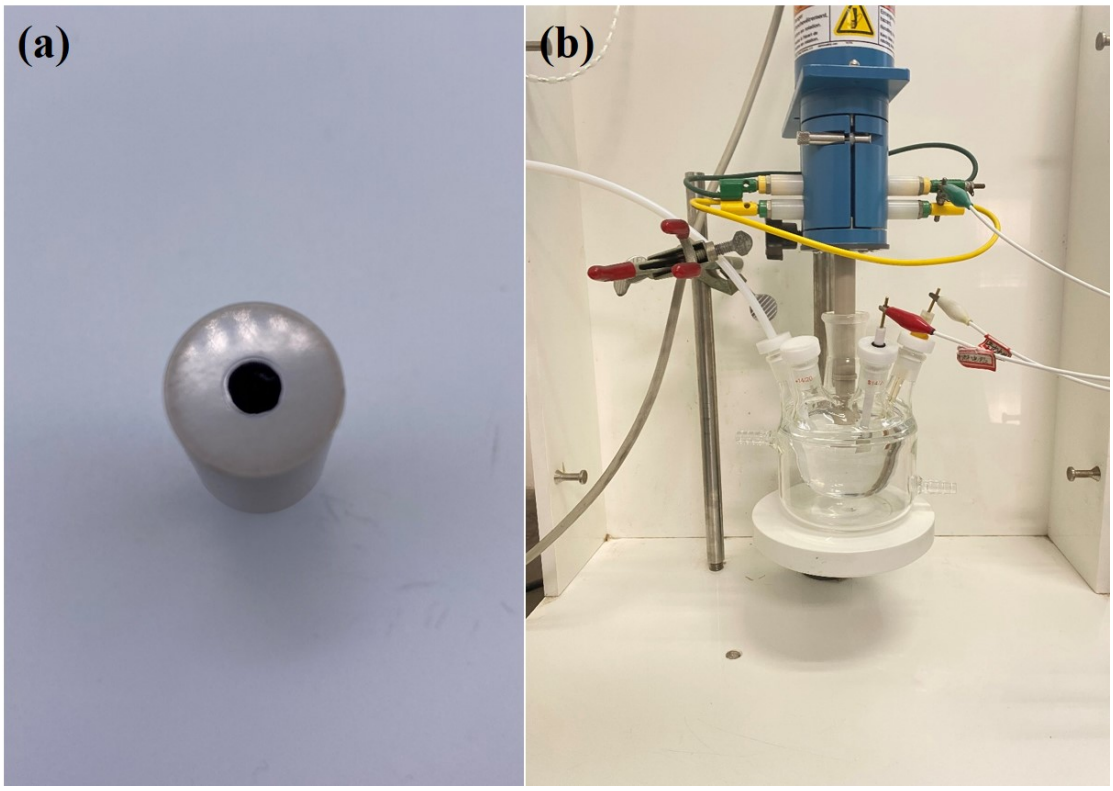

Fig. S7 Digital images showing (a) samples directly attached to the glassy carbon electrode and (b) the test device of rotating disk electrode.

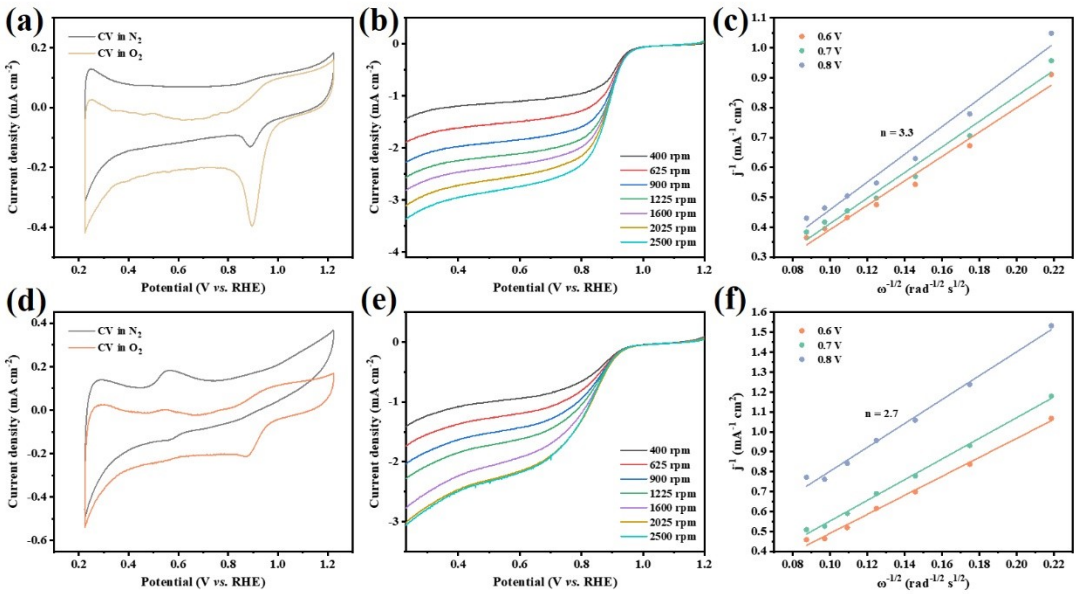

Fig. S8 (a) Cyclic voltammograms in N_2- and O_2-saturated 1 M KOH solution with a scan rate of 5 mV s^{-1}, (b) ORR polarization curve of Nano-FeS/Fe_3C@NCNTs-800 and (c) corresponding K-L curves in O_2-saturated 1 M KOH solution at various rotation speeds, (d) cyclic voltammograms in N_2- and O_2-saturated 1 M KOH solution with a scan rate of 5 mV s^{-1}, (e) ORR polarization curve of Nano-FeS/Fe_3C@NCNTs-900 and (f) corresponding K-L curves in O_2-saturated 1 M KOH solution at various rotation speeds.

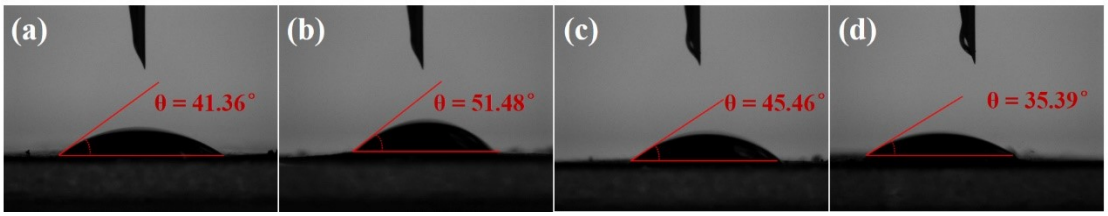

Fig. S9 Contact angles of (a) Pt/C, (b) FeS@NCNTs, (c) Fe_3C@NCNTs and Nano-FeS/Fe_3C@NCNTs with 1 M KOH solution.

Table S1. Resistances obtained by fitting electrochemical impedance spectra at open circuit potential.

	Pt/C	Nano-FeS/Fe_3C@NCNTs-700	FeS@NCNTs-700	Fe_3C@NCNTs-700
R_{ohm}（Ω）	5.393	5.321	7.793	5.48
R_f（Ω）	0.49592	1.915	4.022	0.72193
R_{ct}（Ω）	3167	8507	395.1	26244

Table S2. Resistances obtained by fitting electrochemical impedance spectra at 0.42 V vs. RHE.

	Pt/C	Nano-FeS/Fe_3C@NCNTs-700	FeS@NCNTs-700	Fe_3C@NCNTs-700
R_{ohm}（Ω）	5.385	5.483	8.095	5.442
R_f（Ω）	0.50133	1.694	3.52	0.82297
R_{ct}（Ω）	8443	7154	2800	9641

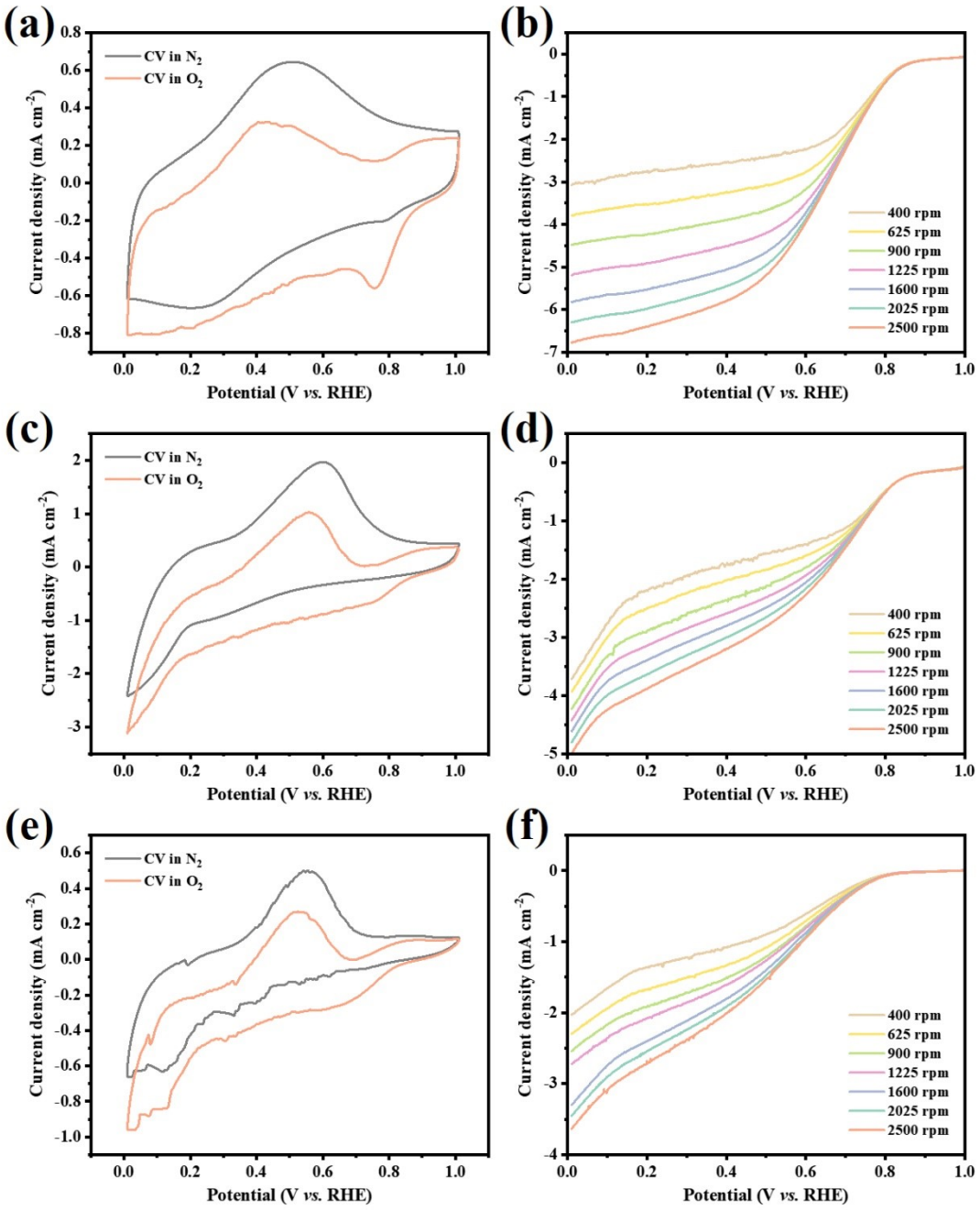

Fig. S10 Cyclic voltammograms in N_2- and O_2-saturated PBS with a scan rate of 5 mV s^{-1} and linear voltammograms in O_2-saturated PBS at various rotation speeds for (a, b) Nano-FeS/Fe_3C@NCNTs-700, (c,d) Nano-FeS/Fe_3C@NCNTs-800 and (e,f) Nano-FeS/Fe_3C@NCNTs-900.

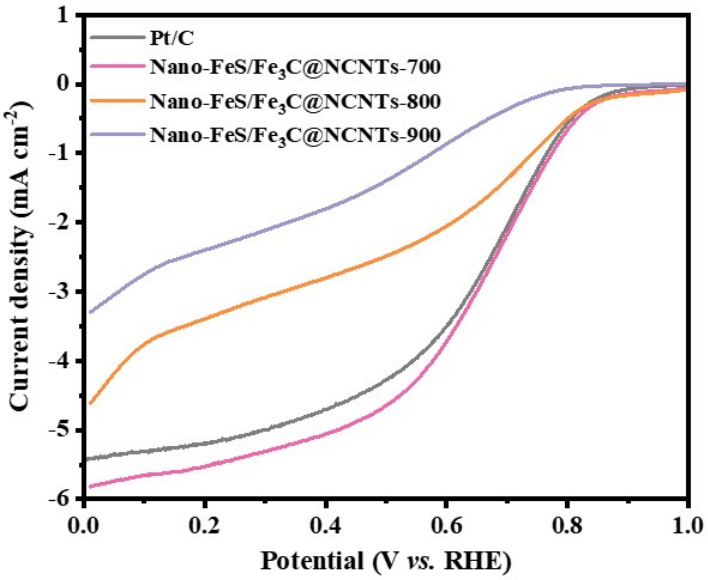

Fig. S11 Linear voltammograms of Nano-FeS/Fe_3C@NCNTs in O_2-saturated PBS at 1600 rpm.

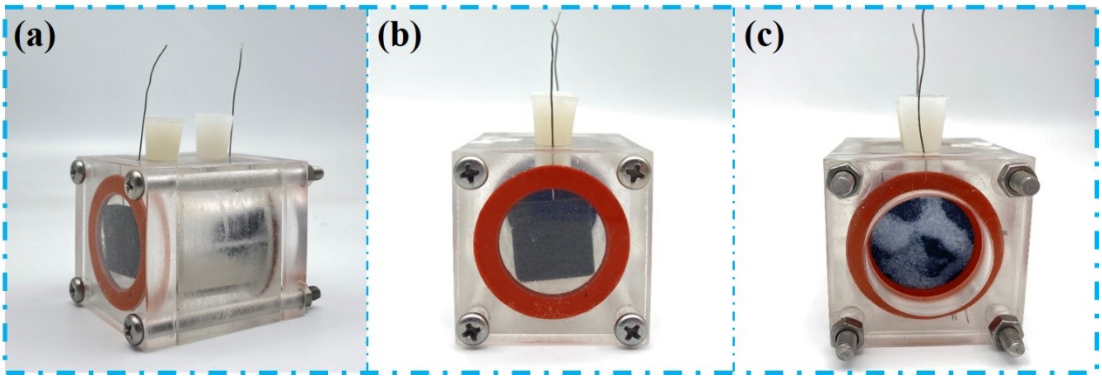

Fig. S12 Digital images of (a) the assembled MFCs with (b) carbon felt as anode and (c) carbon cloth coated with electrocatalysts as cathode.

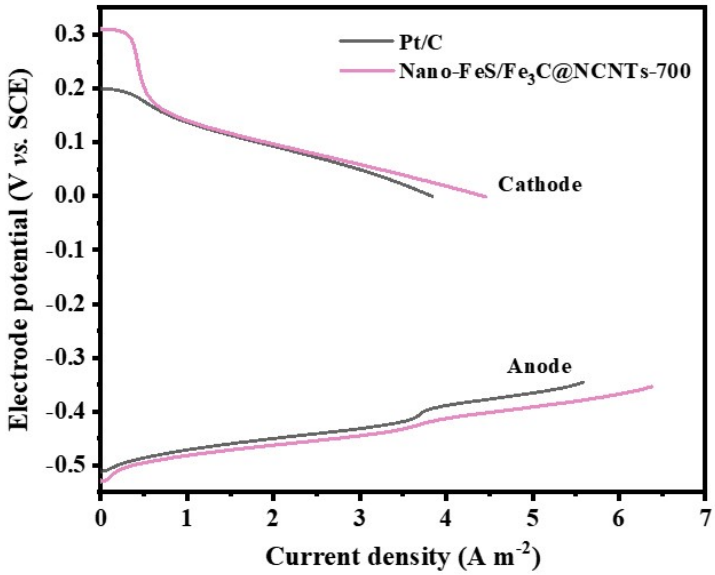

Fig. S13 Polarization curves of cathode and anode after two weeks' operation for the MFCs with different cathodes.

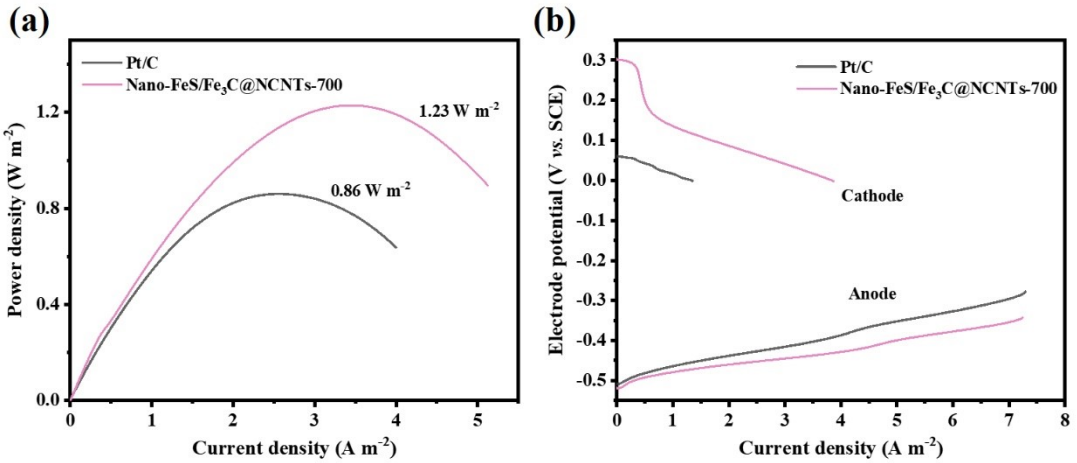

Fig. S14 (a) Power density curves and (b) polarization curves of cathode and anode after one month's operation for the MFCs with different cathodes.

References

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