Supporting Information

Novel three-dimensional covalent organic frameworks hybrid catalysts with atomically dispersed FeN_4 site for highly efficient oxygen reduction reaction

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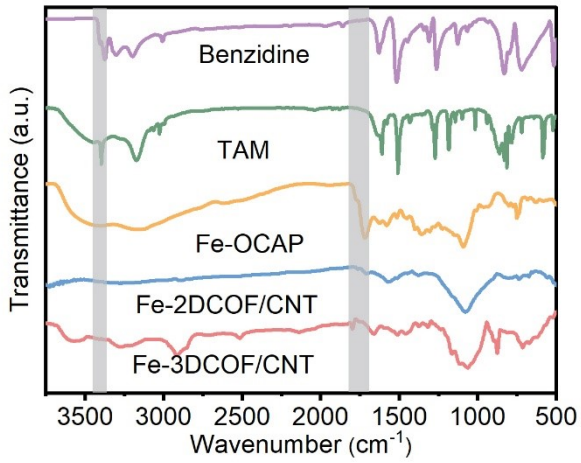

Fig. S1 FT-IR spectra of Benzidine (purple), and TAM (green), and Fe-OCAP (yellow), and Fe-2DCOF/CNT (blue) and Fe-3DCOF/CNT (red).

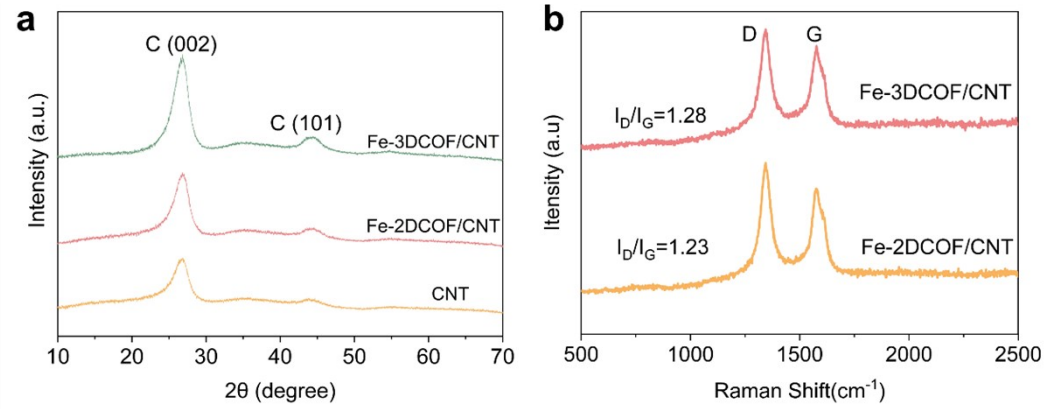

Fig. S2 (a) XRD pattern of Fe-3DCOF/CNT, Fe-2DCOF/CNT and CNT. (b) Raman spectra of Fe-3DCOF/CNT and Fe-2DCOF/CNT.

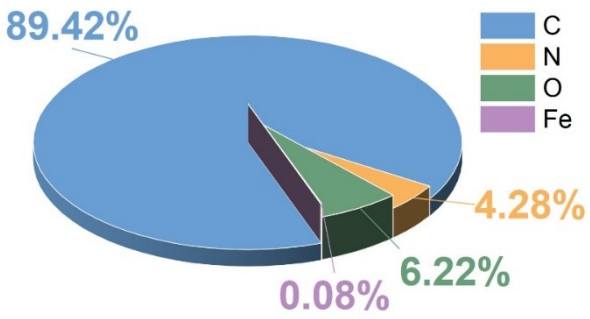

Fig. S3 XPS elemental content diagram of Fe-3DCOF/CNT.

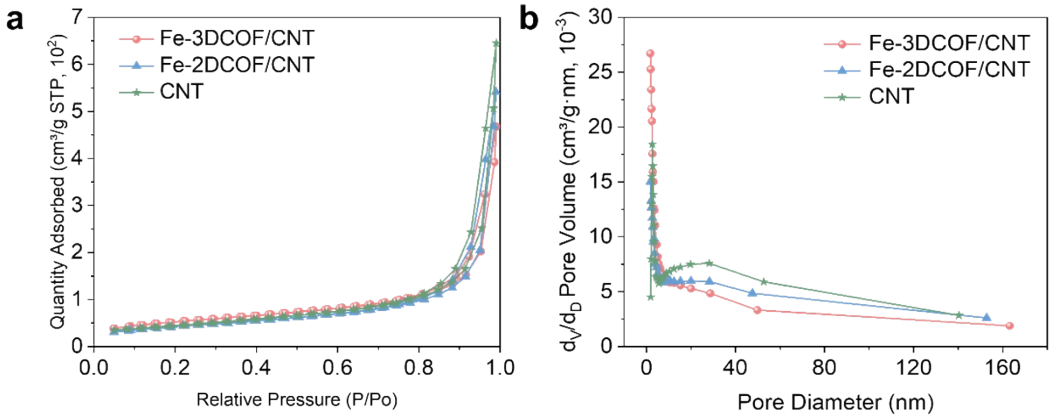

Fig. S4 (a) N_2 adsorption/desorption isotherms and (b) pore size distribution curves for Fe-3DCOF/CNT.

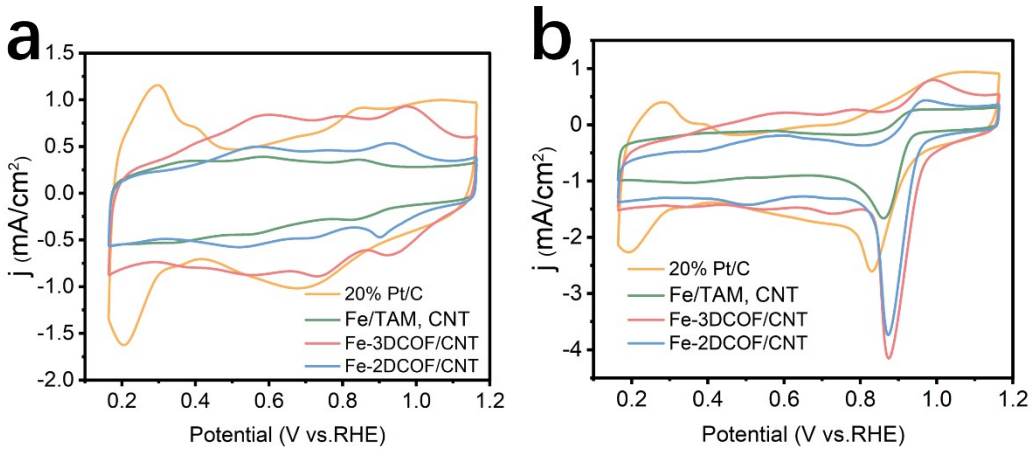

Fig. S5 (a) CV curves of Fe-3DCOF/CNT, Fe-2DCOF/CNT, 20% Pt/C and Fe/TAM, CNT in N_2-saturated 0.1 M KOH. (b) CV curves of Fe-3DCOF/CNT, Fe-2DCOF/CNT, 20% Pt/C and Fe/TAM, CNT in O_2-saturated 0.1 M KOH.

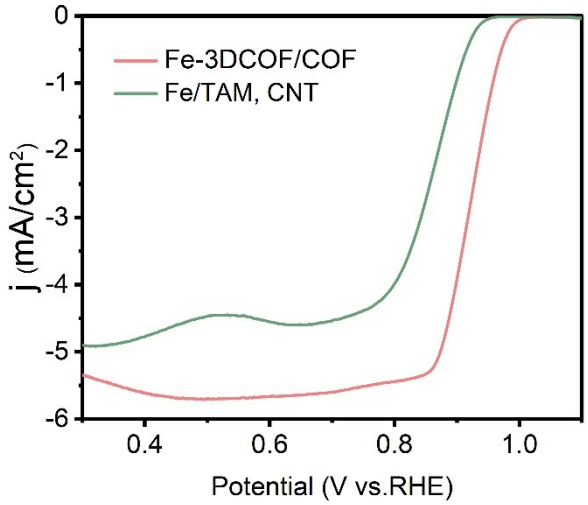

Fig. S6 LSV curves of Fe-3DCOF/CNT, Fe-2DCOF/CNT and Fe/TAM, CNT.

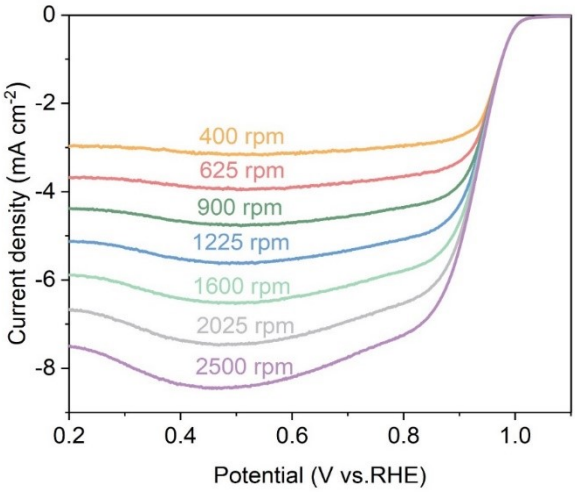

Fig. S7 LSV curves of Fe-3DCOF/CNT at different rotation speeds.

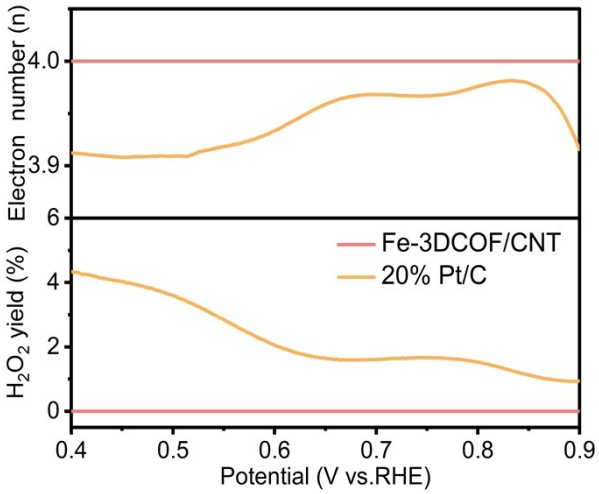

Fig. S8 Electron transfer number and H_2O_2 yield curves of Fe-3DCOF/CNT and 20% Pt/C.

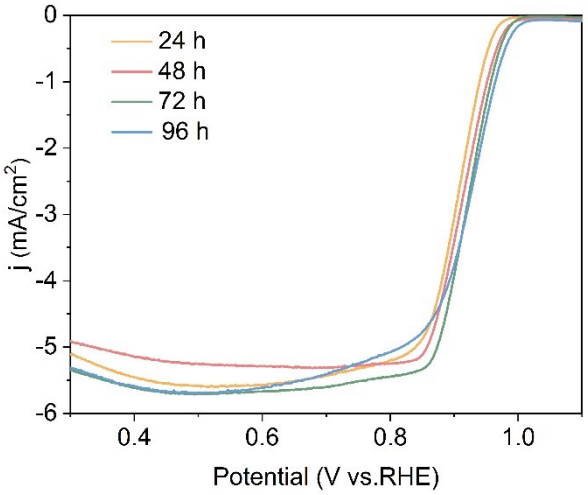

Fig. S9 LSV curves of Fe-3DCOF/CNT prepared with different reaction times.

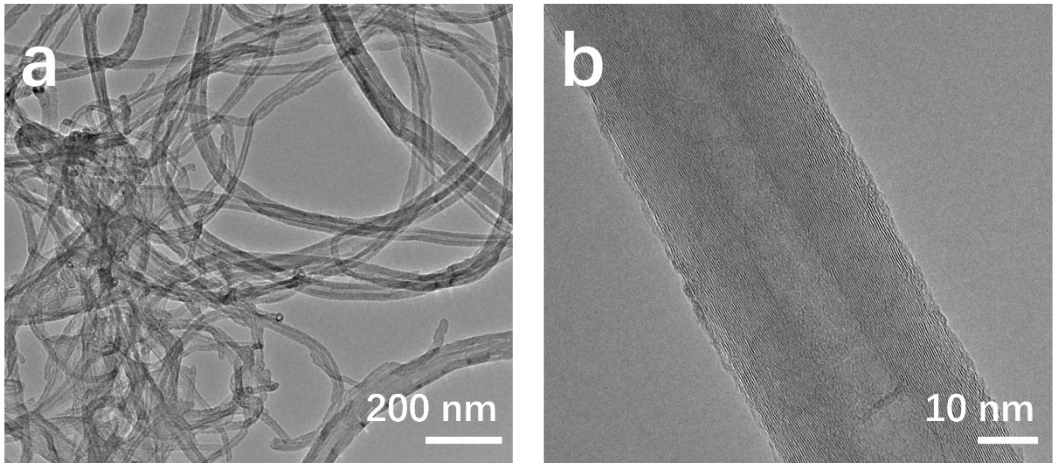

Fig. S10 TEM images of pure CNT.

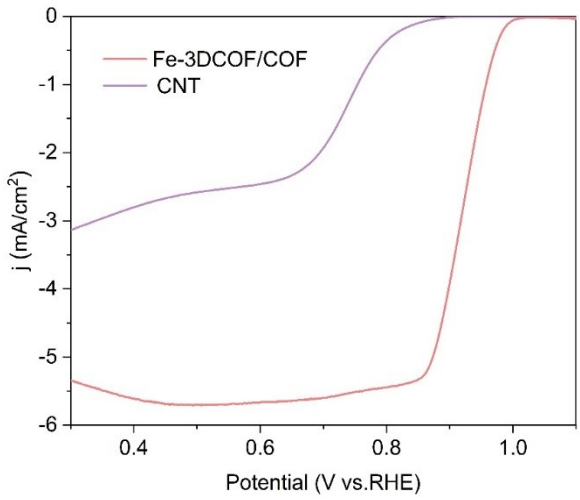

Fig. S11 LSV curves of Fe-3DCOF/CNT and pure CNT.

Table S1. BET test report of Fe-3DCOF/CNT.

	Fe-3DCOF/CNT	Fe-2DCOF/CNT	CNT
BET Surface Area（m^2/g)	190.72	155.82	158.39
cumulative volume of pores (cm^3/g）	0.71	0.83	0.99
average pore diameter (nm)	17.99	23.23	26.70

Table S2. Oxygen reduction potentials of Fe-3DCOF/COF, Fe2DCOF/COF, Pt/C and Fe/TAM, CNT.

Catalysts	Fe-3DCOF/COF	Fe-2DCOF/COF	Pt/C	Fe/TAM, CNT
E_{onset}/V	0.994	0.968	0.960	0.940
$J_{L/}$ (mA cm^{-2})	5.714	5.648	5.372	4.919
$E_{1/2}$/V	0.921	0.897	0.841	0.858

Table S3. ORR performance of Fe-3DCOF/CNT prepared with different reaction times

Times (Hours)	24	48	72	96
E_{onset}/V	0.976	0.994	0.995	1.012
$J_{L/}$ (mA cm^{-2})	5.602	5.316	5.714	5.694
$E_{1/2}$/V	0.905	0.916	0.921	0.923

Experiment section

Materials

Multi-walled carbon nanotube (99.5%), urea (AR), pyromellitic dianhydride (AR), N-N-Dimethylacetamide (AR), 1,2,4,5-benzenetetracarboxylic anhydride （AR）, ammonium molybdate (AR), 1-Methyl-2-pyrrolidinone (AR), sodium chloride (AR), isopropyl alcohol (AR), benzidine (AR), tetrakis (4-aminophenyl) methane (AR) were obtained from Shanghai Aladdin Bio-Chem Technology Co. Ltd. $FeCl_3 \cdot 6H_2O$ (AR), sodium hydroxide (AR) and potassium hydroxide (AR) were bought from Shanghai Macklin Biochemical Co. Ltd. Acetone (AR) and hydrochloric acid (AR) were purchased from Hangzhou Shuanglin Chemical Reagent Co. Ltd. Nafion (5wt.%) was obtained from DuPont. Platinum on carbon (Pt/C, 20wt% Pt) was purchased from Johnson Matthey Catalysts.

Synthesis of Octacarboxy iron phthalocyanine

Octacarboxy iron phthalocyanine (Fe-OACP) was synthesized according to previously reported methods.[1] 1,2,4,5-benzenetetracarboxylic anhydride (10.9 g, 0.02 mol), urea (45 g, 0.75 mol), $FeCl_3 \cdot 6H_2O$ (13.6 g,0.05 mol) and ammonium molybdate (as a catalyst 0.6 g, 0.5 mol) were mixed homogeneously and then added to NMP (100 ml) and reacted at 180 °C for 10 h. After cooling to room temperature, 200 ml of deionized water was added and filtered to obtain a solid. After boiling in saturated sodium chloride solution (containing 1M hydrochloric acid) for 1h, it was washed three times with methanol and deionized water, respectively. The dried solid powder (5 g, 5.4 mmol) was boiled in 2M sodium hydroxide solution (250 ml) at 100 °C for 24 h under nitrogen atmosphere. After cooling to room temperature, it was filtered to remove insoluble impurities, and the pH of the filtrate was adjusted to 2-3 with concentrated hydrochloric acid and left for 48 h to allow complete precipitation of the solid. The precipitate was washed repeatedly with deionized water until the filtrate was neutral. The solid was dried under vacuum to obtain dark blue Fe-OACP.

Material characterization

The micromorphology and configuration of the catalysts were investigated by emission scanning electron microscopy (FE-SEM) (Ultra 55) and high-resolution transmission electron microscopy (HR-TEM) (FEI Talos F200S). By Fourier transform infrared (FT-IR) spectroscopy, X-ray diffractometer (Bruker D8 Venture) and X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha), the composition and elemental presence of electrocatalytic materials were studied. The graphitization and defect degree of the material were detected with a laser Raman spectrometer (Renishaw in Via). Brunauer-Emmett-Teller (BET) underwent testing with Micromeritics ASAP 2460.

Electrochemical measurement conditions

All electrochemical tests were underwent using a CHI760E electrochemical workstation with a three-electrode system. A rotating disk electrode (RDE, S = 0.196 cm^2) and a rotating ring electrode (RRDE, S = 0.247 cm^2) were used as working electrodes, a graphite rob was used as a counter electrode, Ag/AgCl was used as a reference electrode, and the electrolyte was a 0.1 mol/L KOH solution. All potentials were converted to reversible hydrogen electrode (RHE) potentials by the following equation: $E_{RHE}=E_{Ag/AgCl}+0.197+0.059\times pH$.

[1] Z. Zhang, W. Wang, X. Wang, L. Zhang, C. Cheng, X. Liu, *Chem. Eng. J.* **2022**, *435*, 133872.