Supplementary Information (SI) for Chemical Communications.

Tuning the spin state of FePc via selectively defected carbon for enhanced oxygen reduction reaction

Yanqiu Wang,[a] Jianye Liu,[a] Wenhao He,[a] Zhongliang Tian,[b] JiaJin Yang,*[c, d] and Jie Li *[a]

[a] *School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, Hunan, China*

[b] *School of Metallurgy and Environment, Central South University, Changsha, 410083, Hunan, China*

[c] *Department of Hepatobiliary Surgery, The First Affiliated Hospital of Hunan Normal University, Changsha, 410005, China*

[d] *Hunan Engineering Research Center of Digital Hepatobiliary Medicine, Changsha, 410005, China*

*Corresponding author.

E-mail addresses: lijieliu@csu.edu.cn (J. Li).

E-mail addresses: yjudging@163.com (J. Yang).

Experiments

Synthesis of NC-acid material. The synthesis of NC sample was based on our previously published paper[1]. Firstly, 2-methylimidazole (9.288 g) and zinc nitrate hexahydrate (8.552 g) were separately dissolved in 160 mL and 240 mL of mixed solvent (anhydrous methanol/N,N-dimethylformamide = 1:1, v/v). Both solutions were subjected to sonication and stirring to achieve complete dissolution. Subsequently, the 2-methylimidazole solution was introduced into the zinc nitrate hexahydrate solution by dropwise addition. The the mixture was allowed to react for 24 hours at room temperature. After the reaction, the milky suspension was centrifuged, and the resulting solid was washed three times with methanol. Finally, the washed solid was dried in a vacuum oven at 80 °C for 12 hours to obtain the zeolite imidazole framework (ZIF-8) precursor. The obtained ZIF-8 precursor was subjected to thermal treatment in a tube furnace under N_2 atmosphere. In detail, the heating rate was 3 °C min^{-1}, with 350 °C for 30 min, followed by to 1000 °C for 2 hours. After the thermal treatment, the sample was allowed to cool to room temperature, yielding the final product (NC). 600 mg of NC sample was immersed in 240 mL of 3 mol L^{-1} hydrochloric acid and stirred at room temperature for 10 hours. The mixture was filtered, and thoroughly washed until neutralization was achieved. Finally, the samples was vacuum-dried at 100 °C for 24 hours to gain the NC-acid sample.

Synthesis of defect-engineered carbon material via CO_2 selective etching (NC-CO_2-900). The NC-acid sample was pyrolysed at 900 °C for 2 h under a sealed CO_2

atmosphere, with a heating rate was 5 °C min^{-1}. The resulting sample was designated as NC-CO_2-900.

Synthesis of FePc/NC-CO_2-900 and FePc/NC-acid samples. 60 mg of NC-CO_2-900 and 10 mg of FePc were separately added into 60 mL and 10 mL of N,N-dimethylformamid (DMF) solvent by ultrasonication for 1 hour. Subsequently, 10 mL of DMF solution containing FePc was dropwised into 60 mL of DMF solution containing NC-CO_2-900, followed by continued ultrasonication for 1 hour to achieve a uniform suspension. The mixture was then stirred at room temperature for 20 hours. The FePc/NC-CO_2-900 sample was collected by centrifugation, washed with DMF and ethanol, and dried under vacuum at 60 °C for 12 hours. In addition, the FePc/NC-acid sample was prepared using the same procedure of FePc/NC-CO_2-900 sample, with NC-acid serving as the carbon support.

Synthesis of INC and NC (Ar) material. The ZIF-8 precursor was mixed with potassium iodide (KI) in a mass ratio of 4:1 and they were thoroughly grounded to form a homogeneous powder. The mixture was then subjected to pyrolysis at 950 °C for 2 hours in a tube furnace under an argon atmosphere, with a heating rate of 5 °C per minute. After the pyrolysis process, the sample was cooled to room temperature. The above sample (200 mg) was added into 400 mL of deionized water, and which was stirred at room temperature for 12 hours. The mixture was filtered, and thoroughly washed with deionized water. The samples was vacuum-dried at 100 °C for 24 hours to gain the INC sample for further use. In addition, the ZIF-8 precursor was then subjected to pyrolysis at 950 °C for 2 hours with a heating rate of 5 °C min^{-1} in a tube furnace under an argon atmosphere. After the pyrolysis process, the sample was allowed to cool to room temperature, which was labled as NC (Ar).

Synthesis of FePc/INC and FePc/NC (Ar) samples. The FePc/INC and FePc/NC (Ar) samples were prepared using the same procedure of FePc/NC-CO_2-900 sample, with INC and NC (Ar) serving as the carbon support, respectively.

Physical characterization. The microstructure of samples was characterized using scanning electron microscopy (SEM, JSM-7610F, JEOL) and transmission electron microscopy (TEM, JEOL/JEM-F200). To investigate the chemical states of the samples, X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi) was employed. Additionally, the magnetic properties of the FePc and FePc/NC-CO_2-900 samples were measured using a superconducting quantum interference device (SQUID, Quantum Design MPMS3, USA) at a magnetic field of 2000 Oe. Electron paramagnetic resonance (EPR) spectra of FePc and FePc/NC-CO_2-900 were gain on the Bruker A300 spectrometer at 100 K.

Electrochemical measurement

Electrochemical experiments were performed using a three-electrode system on a CHI760e electrochemical workstation, which was equipped with a rotating disk electrode (RDE, 5 mm in diameter) and a rotating ring-disk electrode (RRDE, disk diameter, 5.61 mm). An Ag/AgCl electrode in a saturated KCl solution was used as the reference electrode. A graphite rod served as the counter electrode. To prepare the homogeneous catalyst ink, 5 mg of catalyst power was dispersed in a 980 μL mixture of ethanol and deionized water (v:v = 4:1), followed by the addition of 20 μL 5% Nafion solution, and the mixture was sonicated to ensure uniformity. The catalyst loading on RDE was maintained at 0.8 mg cm^{-2}. In addition, Pt/C loading on RDE was 0.3 mg cm^{-2}. Linear sweep voltammetry (LSV) measurements were carried out at a scan rate of 5 mV s^{-1} at 1600 rpm in a 0.1 M KOH solution with saturated oxygen. The kinetic current density (j_k) was calculated by the Koutecky-Levich equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L}$$

Where j, j_k and j_L present the measured current density, kinetic current density and limiting current density, respectively.

Chronoamperometric measurement (i-t) was further employed to evaluate the stability of the catalyst. The potential was held at 0.60 V (vs. RHE) in an O_2-saturated 0.1 M KOH solution, with the electrode rotating at a constant rate of 900 rpm.

In addition, for RRDE test, the catalyst loading was 0.2 mg cm^{-2} and the ring potential was set at 1.2 V vs RHE during the LSV measurements.

$$H_2O_2 = 200 \times \frac{I_r/N}{I_d + I_r/N}$$

$$n = 4 \times \frac{I_d}{I_d + I_r/N}$$

Where I_d and I_r present the disk current and ring current, individually. N (0.37) is the ring current collection efficiency for Pt ring.

Computation methods

Spin-polarized density functional theory (DFT) simulations were performed using the Vienna ab initio simulation package (VASP)[2]. The interaction of the electron-ion was described by the projector augmented wave (PAW) potentials[3]. In addition, the electron-electron exchange and correlation functional were described by Perdew-Burke-Ernzerhof (PBE) of the generalized gradient approximation (GGA)[4]. A cutoff energy of 500 eV was employed, and the vacuum space in the z-direction was set to 23.4 Å (FePc-NC) and 20 Å (FePc) to eliminate periodic boundary effects. The convergence criteria were set to 0.02 eV $Å^{-1}$ for the force and 1×10^{-5} eV for the energy. Geometry optimizations were conducted using a Monkhorst-Pack k-point grid of 2×2×1. van der Waals (VDW) forces were corrected with DFT-D3 method of Grimme with zero-damping function. The DFT+U method was employed, and the *U-J* value was 3 eV for Fe 3*d* orbitals.

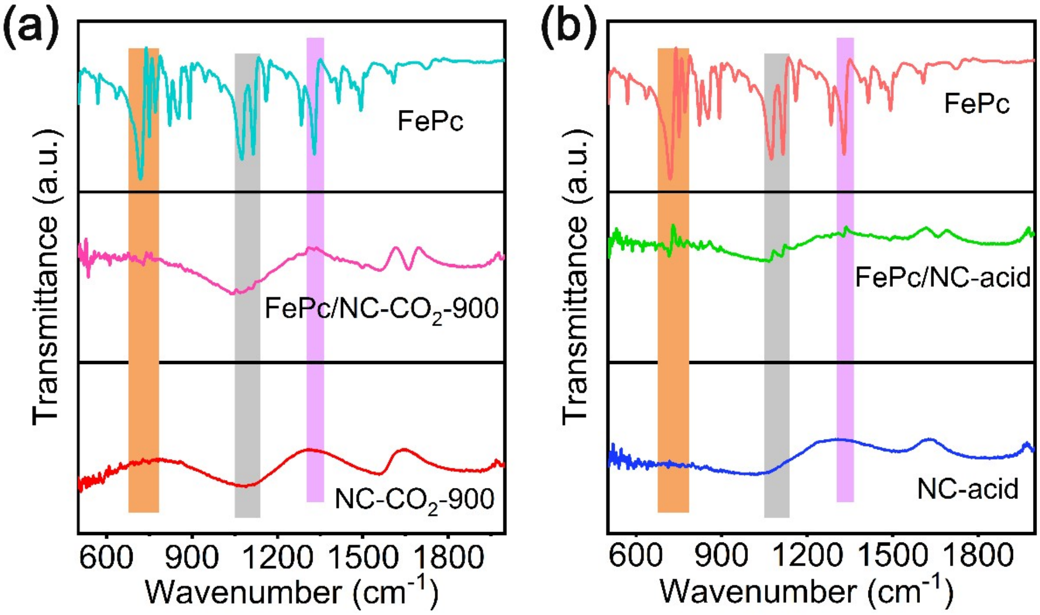

Fig. S1 The Fourier-transform infrared (FT-IR) spectra of various samples.

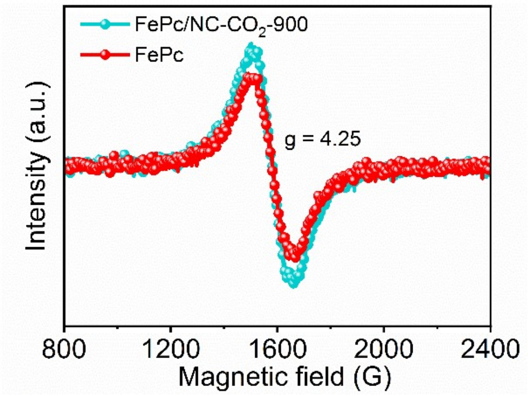

Fig. S2 The EPR spectra of samples.

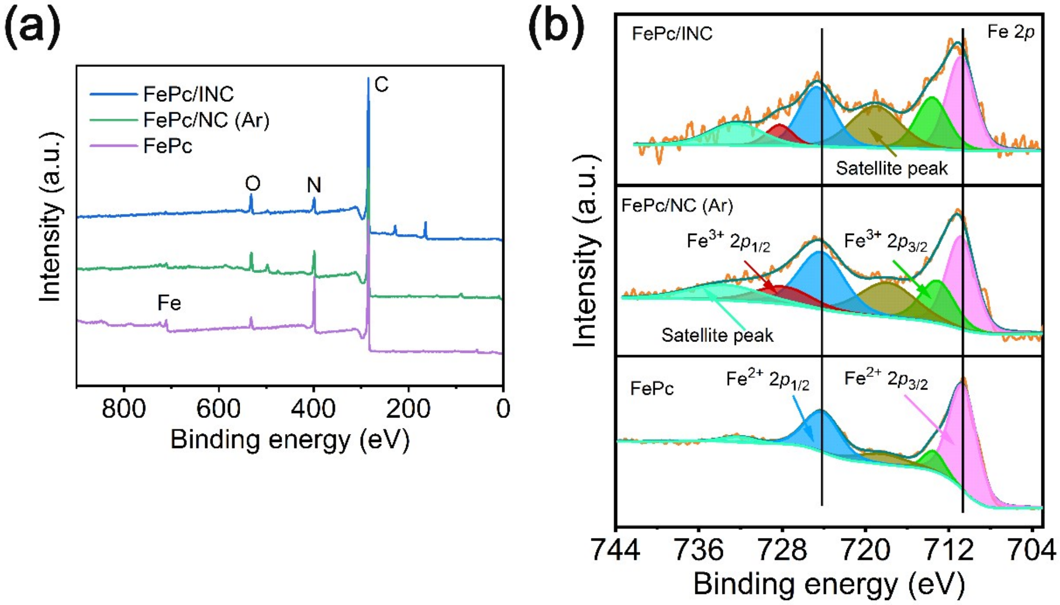

Fig. S3 (a) The XPS full spectra and (b) high-resolution XPS spectra of Fe 2*p* for samples.

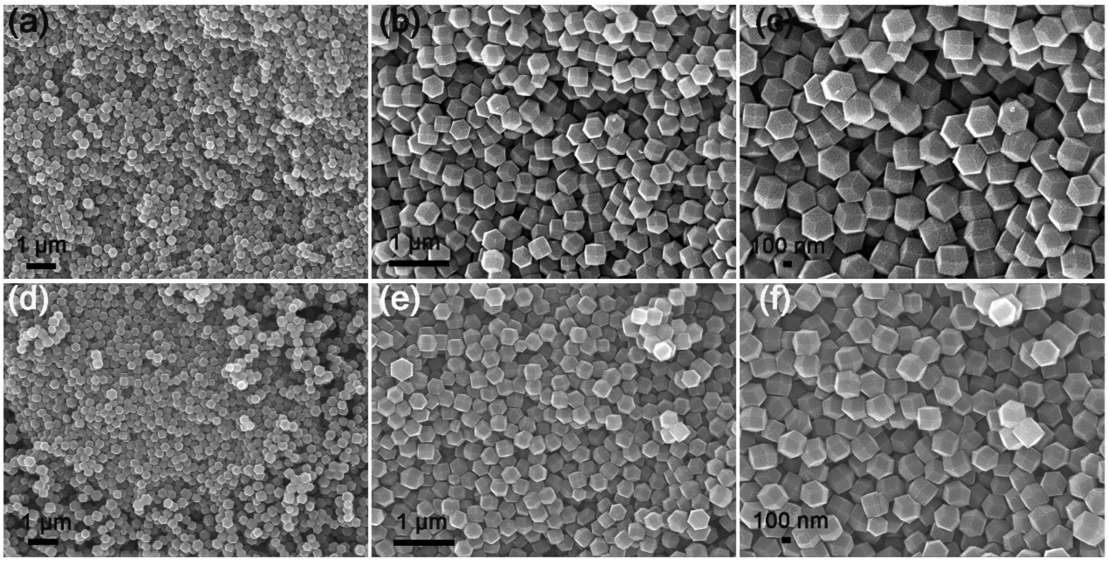

Fig. S4 SEM images of (a-c) NC-CO_2-900 and (d-f) FePc/NC-CO_2-900.

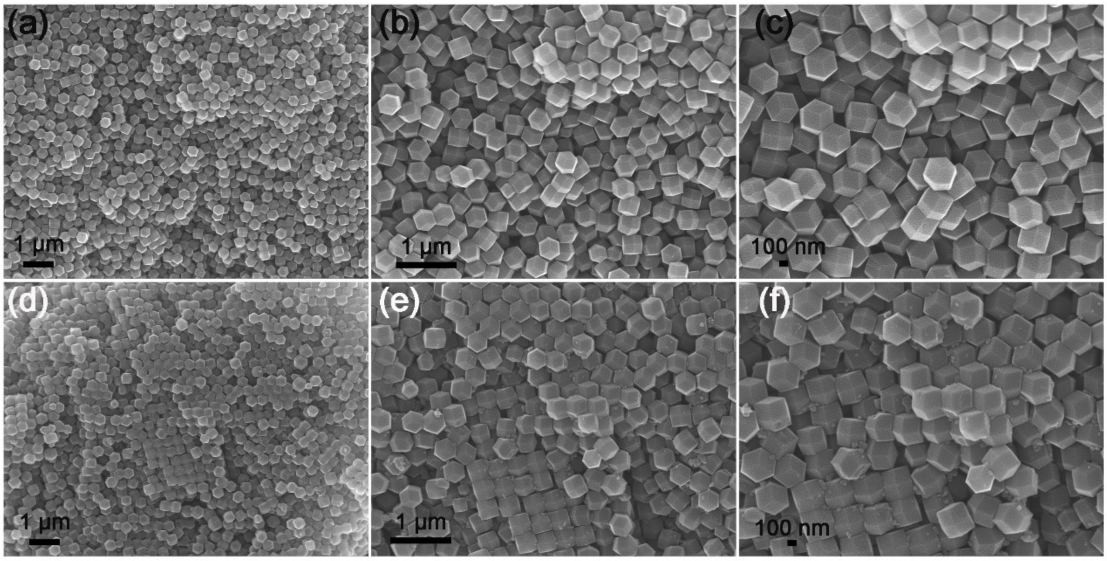

Fig. S5 SEM images of (a-c) NC-acid and (d-f) FePc/NC-acid.

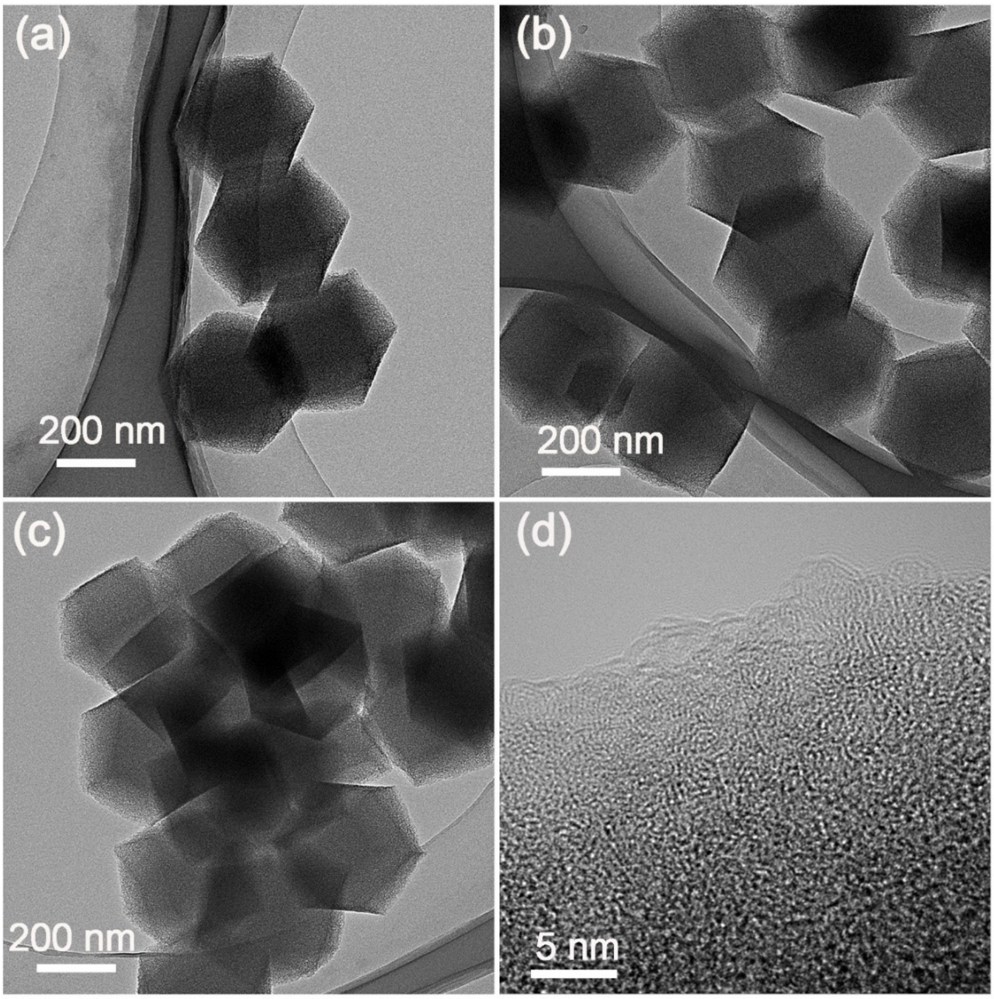

Fig. S6 (a-c) TEM and (d) HRTEM images of NC-CO_2-900 samples.

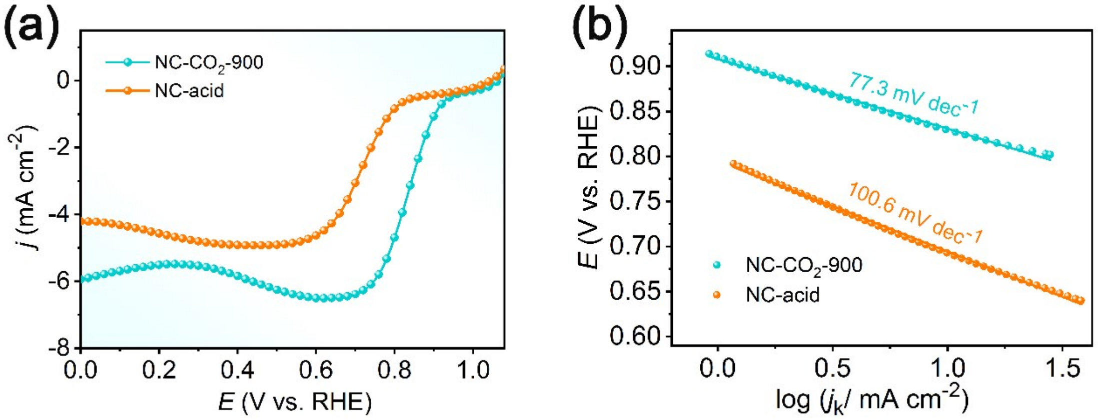

Fig. S7 (a) LSVs and (b) Tafel slopes of samples.

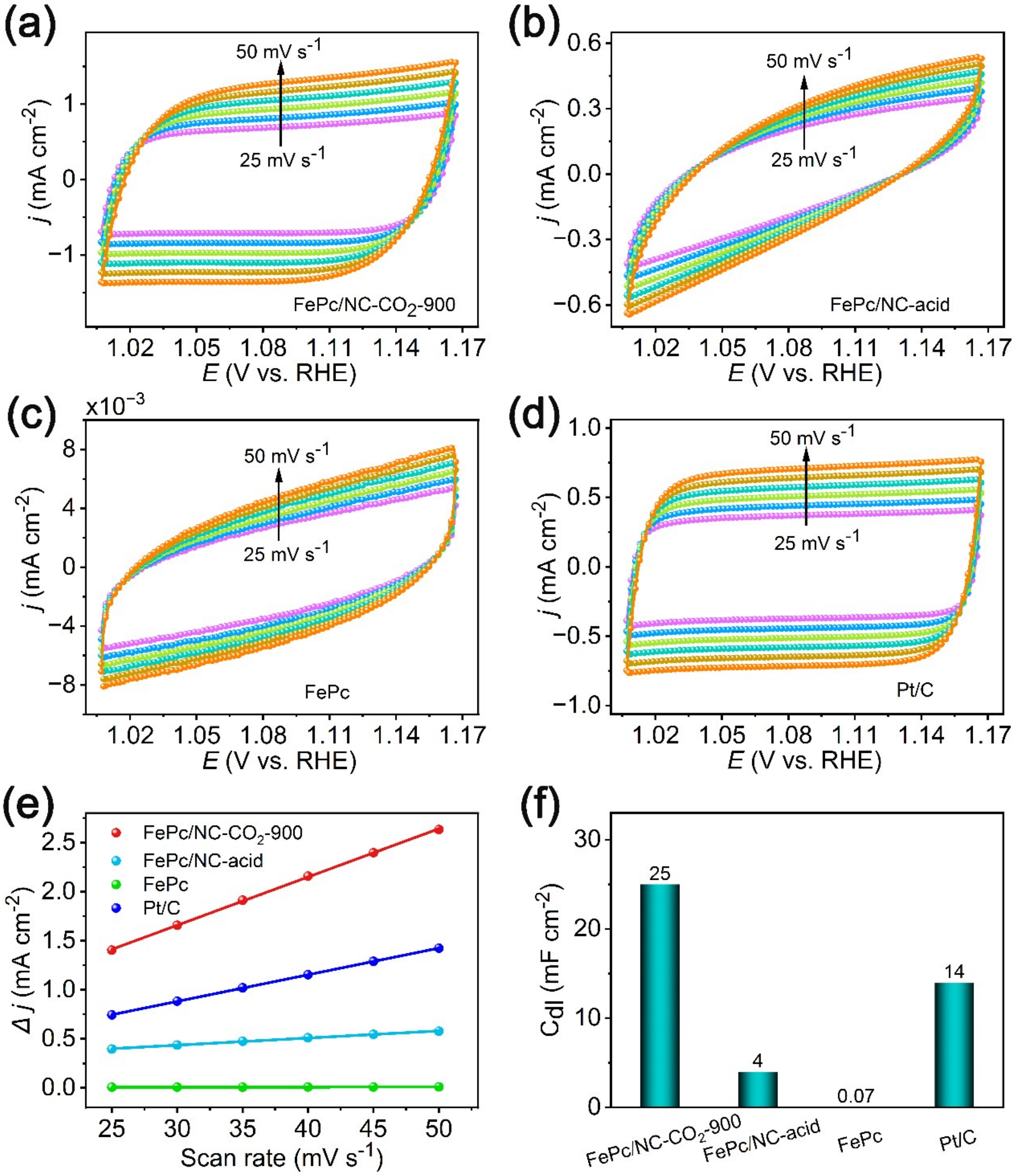

Fig. S8 (a-d) The CV curves at various scan rates under 1.007 V-1.167 V vs RHE, (e) the capacitive current density (Δ *j*) as a function of the scan rate and (f) C_{dl} values for catalysts.

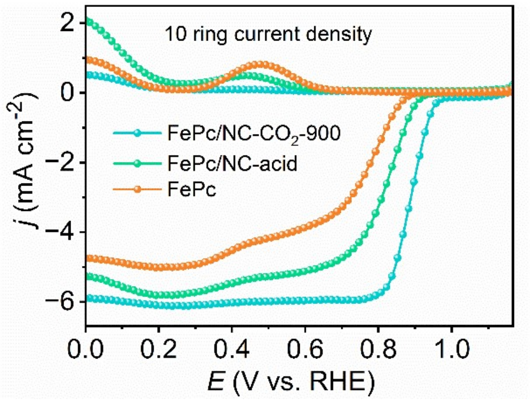

Fig. S9 LSVs of samples on RRDE.

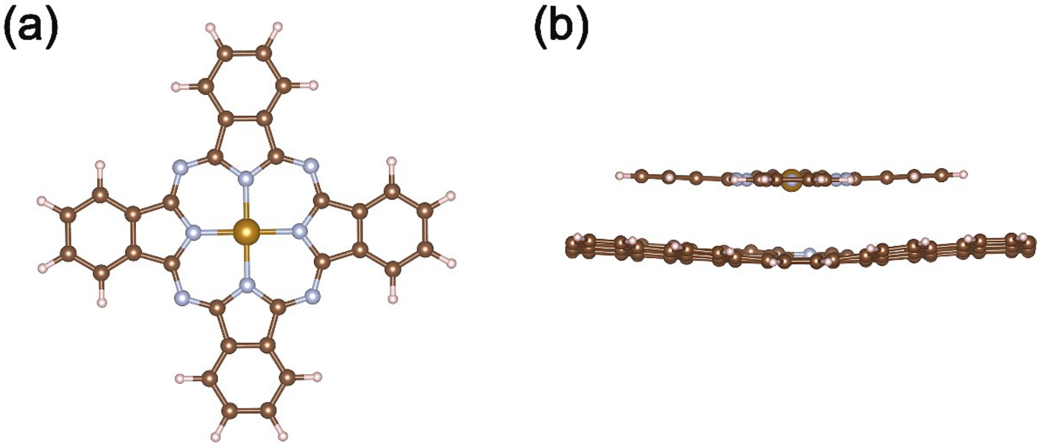

Fig. S10 Optimized structures of (a) FePc and (b) FePc-NC.

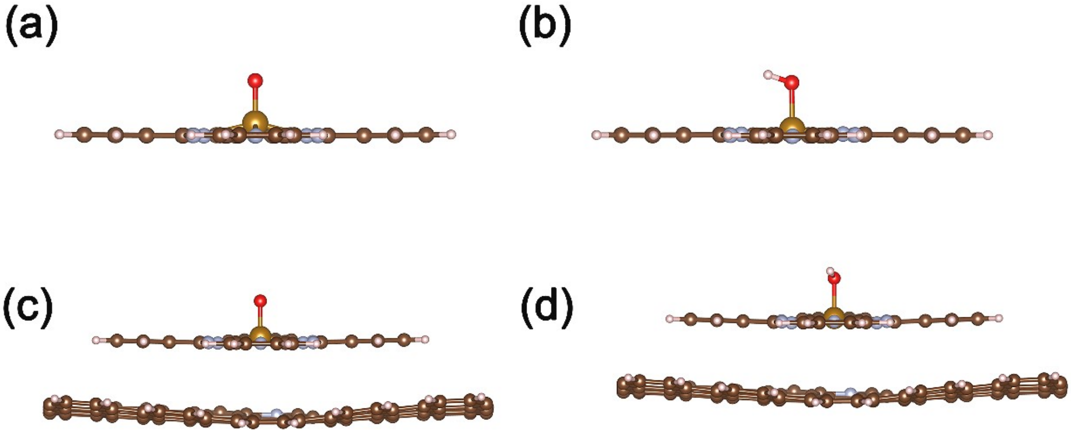

Fig. S11 Optimized structures of the intermediates (O*, OH*) on (a and b) FePc and (c and d) FePc-NC.

References

1. Y. Wang, X. Huang, Y. Liu, W. He, Z. Tian, Y. Li and W. Li, *J. Energy Chem.*, 2024, **99**, 417-425.
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