Supporting Information

Ordered mesoporous carbon with binary CoFe atomic species for highly efficient oxygen reduction electrocatalysis

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Section S1. Experimental Section

1.1 Chemicals and Materials

All chemicals were used as received without further purification. Tetraethyl orthosilicate (TEOS) and P-123 (PEG-PPG-PEG) were obtained from Sigma-Aldrich Co., Ltd. hydrochloric acid (HCl) was purchased from Sinopharm Chemical Reagents Co., Ltd. Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), 2-Methylimidazole, sodium hydroxide (NaOH), potassium hydroxide (KOH) and Methyl alcohol (MeOH) were received from Shanghai Titan Chemical Co., Ltd.

1.2 Materials Preparations

Preparation of CoFe/NC-750. CoFe/NC-750 was obtained by using SBA-15 as hard template. Typically, SBA-15 (0.2000 g) was added to a clear solution formed by 2-methylimidazole (0.2497 g) and MeOH (30 mL), and the mixture was stirred at 80 °C until all the MeOH evaporated. Subsequently, $Co(NO_3)_2 \cdot 6H_2O$ (0.2166 g) and $Fe(NO_3)_3 \cdot 9H_2O$ (0.1009 g) were dissolved in 30 mL MeOH, added to the above solid solution, and stirred at 80°C until all the MeOH evaporated. Afterwards, the collected sample was pyrolyzed under Ar atmosphere at 750 °C for 2 h. Repeating the above steps three times to ensure that CoFe-MOF grows on the surface and pores of SBA-15 and is carbonized by subsequent pyrolysis. Then the SBA-15 template and exposed metal particles were removed by 2 M NaOH and 0.5 M H_2SO_4 hot solution, respectively. The final product was achieved after another annealing at the same conditions at 750 °C.

Preparation of Co/NC-750 and Fe/NC -750. Co/NC and Fe/NC catalysts were prepared by similar method to CoFe/NC without adding $Fe(NO_3)_3 \cdot 9H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$, respectively.

Preparation of CoFe/NC-T. CoFe/NC-T (T= 700 °C, 800 °C, 850 °C) catalysts were fabricated with similar procedure to CoFe/NC-750, but at different carbonization temperature.

1.3 Material Characterizations

Scanning electron microscope (SEM, JSM-7500F), transmission electron microscopy (TEM, JEM-2100F) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, JEM-ARM300F) were used to investigate morphologies, structures and compositions of samples. X-ray diffraction (XRD) patterns were taken on a D/MAX2200V PC (Cu Kα (λ= 0.15406 nm), 40 kV, 40 mA). Raman spectra was recorded on a Renishaw inVia Qontor. X-ray photoelectron spectroscopy (XPS) patterns were carried out on a Thermo Scientific K-Alpha. N_2 adsorption-desorption isotherms were obtained on an ASAP 2460 equipment. Inductively coupled plasma-mass spectrometry (ICP-MS) were collected on a Aglient 7800.

1.4 Electrochemical Measurements

The ORR performance evaluation of catalysts was conducted on a PINE electrochemical instrumentation (Pine AFCBP1) with a standard three-electrode setup. The catalysts were dropped on rotating disk electrode (RDE) (GC, 5 nm in diameter) acting as the working electrode, Hg/HgO electrode and carbon rod were used as the

reference electrode and the counter electrode, respectively. Catalysts (1 mg) and Nafion solution (5 μL, 5 wt.%) were added into ethanol (250 μL) and the obtained mixture was ultrasonically treated for 30 min to form a homogeneous ink. After that, 15 μL catalytic ink was loaded onto the RDE with a loading area of 300 μg cm^{-2}. The ORR performances were evaluated in O_2-saturated 1 M KOH solution at a scan rate of 10 mV s^{-1} by linear sweep voltammograms (LSV). All of potentials are referenced to the reverse hydrogen electrode (RHE) with the calibration equation: $E_{(RHE)} = E_{(Hg/HgO)} + 0.059 \times pH + 0.098$. The electron transfer numbers (n) and the yield of peroxide ($H_2O_2\%$) of the catalysts were investigated by the rotating ring-disk electrode (RRDE) experiment at a sweep rate of 10 mV s^{-1} with rotating speeds ranging from 400 to 2025 rpm.

The kinetic current (j_K) was calculated according to the Koutecky-Levich equation (1) and (2). For RRDE measurement, n and $H_2O_2\%$ were calculated as the following equation (3) and (4).

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{j_K} \quad (1)$$

$$B = 0.62nFC_{O_2}D_0^{2/3}\gamma^{1/6} \quad (2)$$

$$n = 4 \times \frac{I_d}{I_d + \dfrac{I_r}{N}} \quad (3)$$

$$H_2O_2\% = 200 \times \frac{\dfrac{I_r}{N}}{I_d + \dfrac{I_r}{N}} \quad (4)$$

In these equations, j is the measured current density, j_L and j_K represent the diffusion-limiting current density and kinetic-limiting current density, respectively. ω is the angular velocity of electrode. n is the transferred electron number. F is the Faraday constant (= 96485 C mol^{-1}). Co_2 is the bulk O_2 concentration in 0.1 M KOH solution (1.2×10^{-3} mol/L). D_0 is the diffusion coefficient of O_2 in electrolyte (1.9×10^{-5} cm^2/s) and Y is the kinematic viscosity of the electrolyte (0.01 cm^2/s). I_d and I_r represent the disk current and the ring current, respectively, and N is the current collection efficiency of the Pt ring ($N = 0.4$).

Section S2 Computational methods

Vienna Ab initio Simulation Package (VASP) was used to calculate the binding energy between catalysts and intermediates. The Perdew, Burke and Ernzerhof (PBE) parameterized generalized exchange-correlation interactions are implemented by the VASP package. The kinetic energy cutoff used in all calculations was 400 eV. A (2 × 2 × 1) Monkhorst-Pack k-point sampling was used for all surface calculations. H_2O and H_2 calculations were performed in boxes of 15 Å × 15 Å × 15 Å.
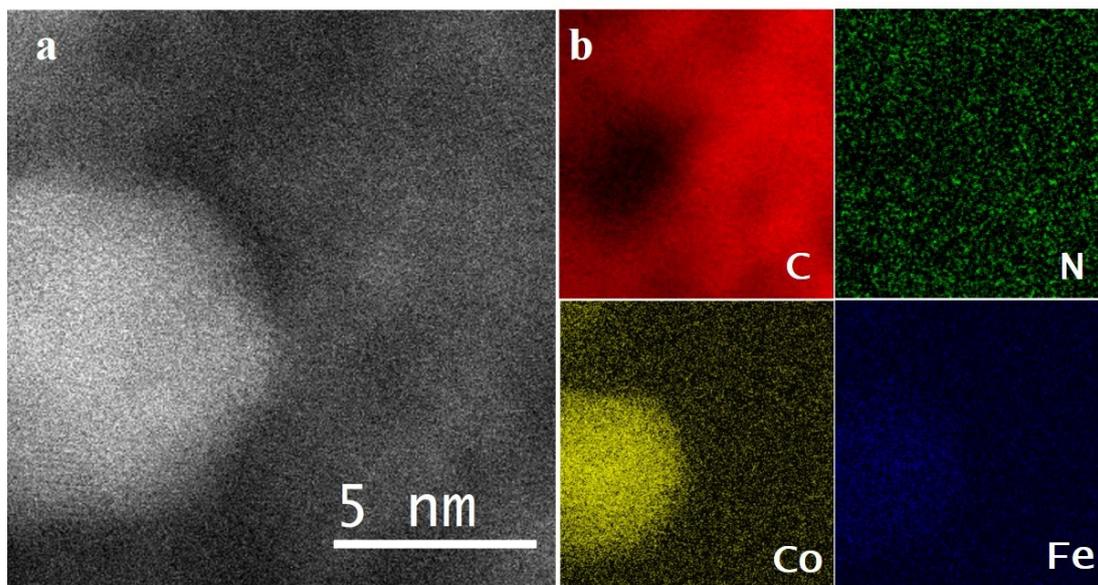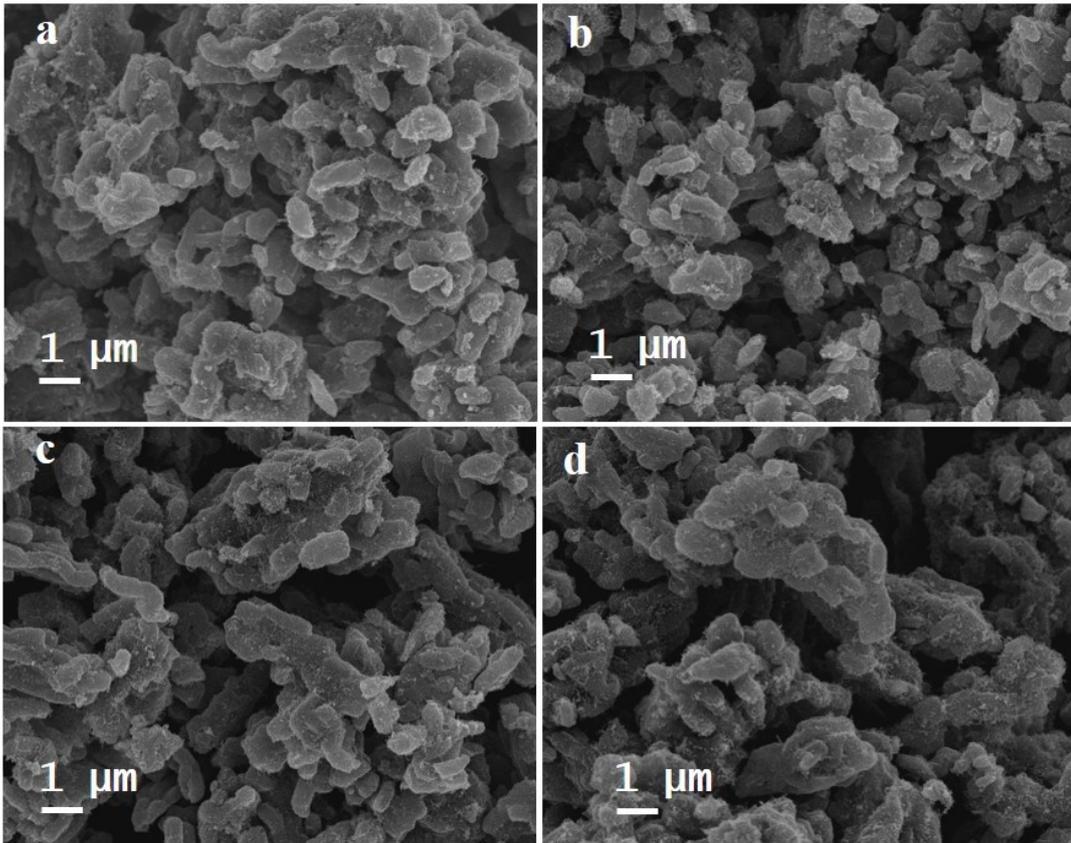
Section S3 Supplementary Figures
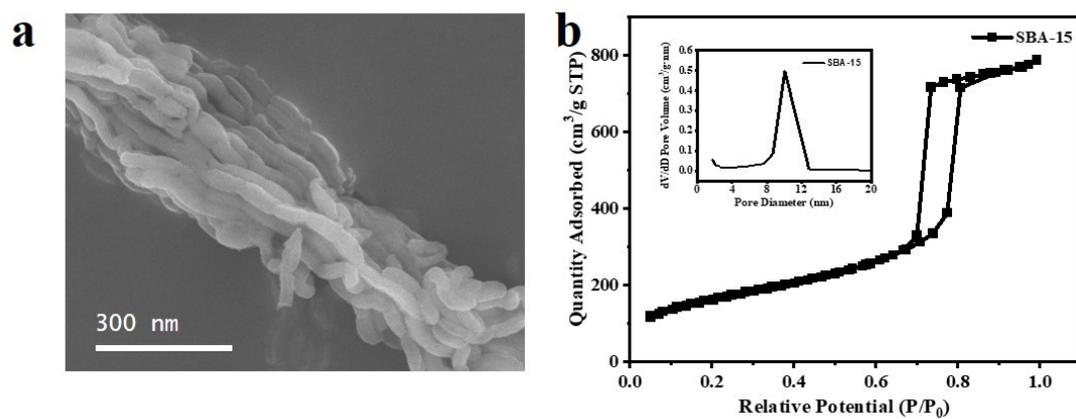
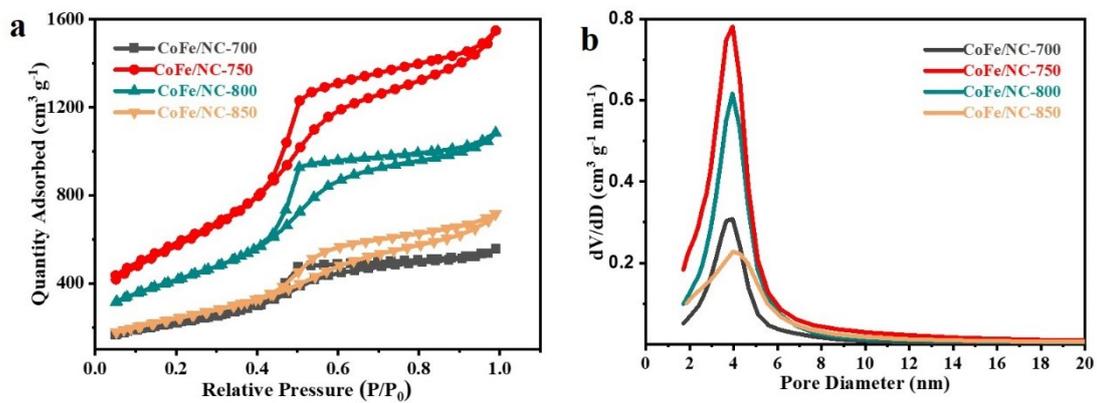**Figure S1.** (a) SEM image and (b) BET of SBA-15.
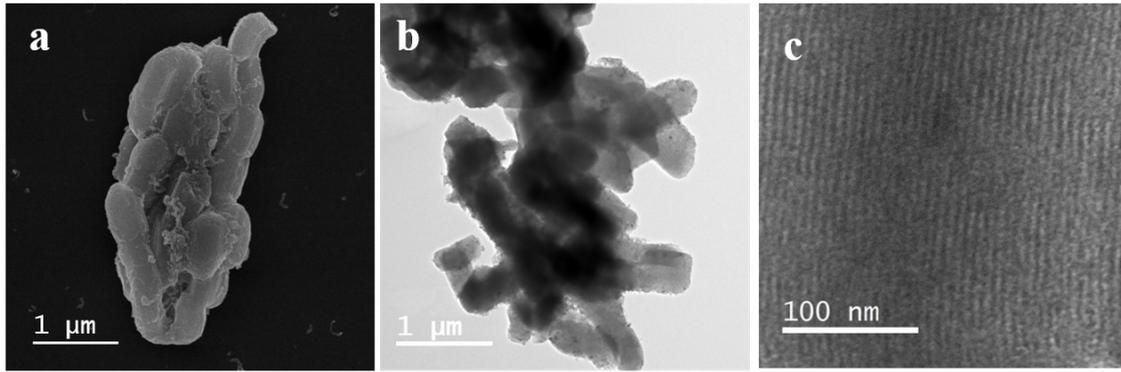
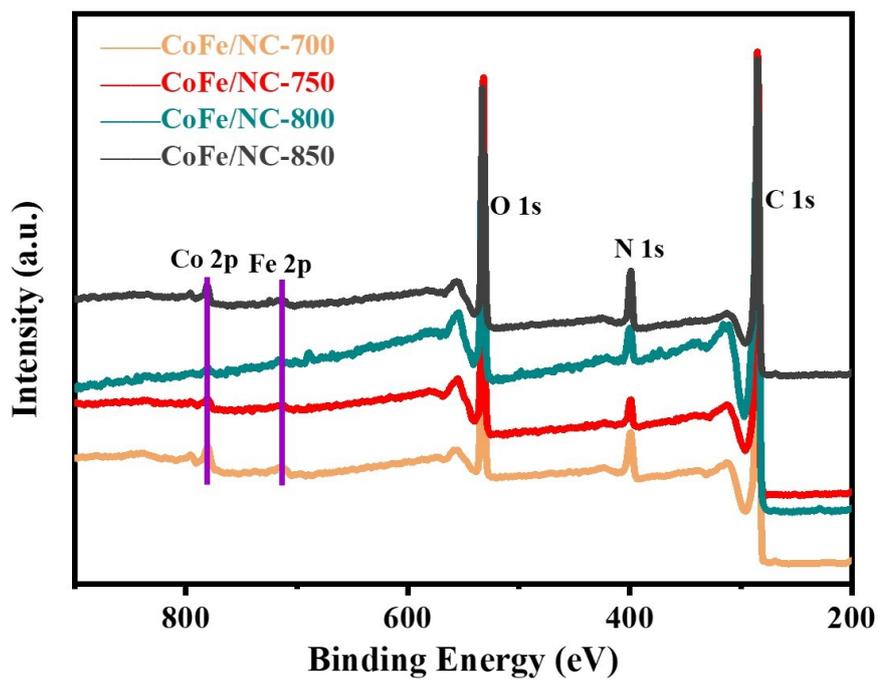**Figure S2.** (a) SEM, (b-c) TEM images of CoFe/NC-750.

Figure S3. (a) HAADF image, and (b) corresponding EELS mappings of CoFe/NC-750.
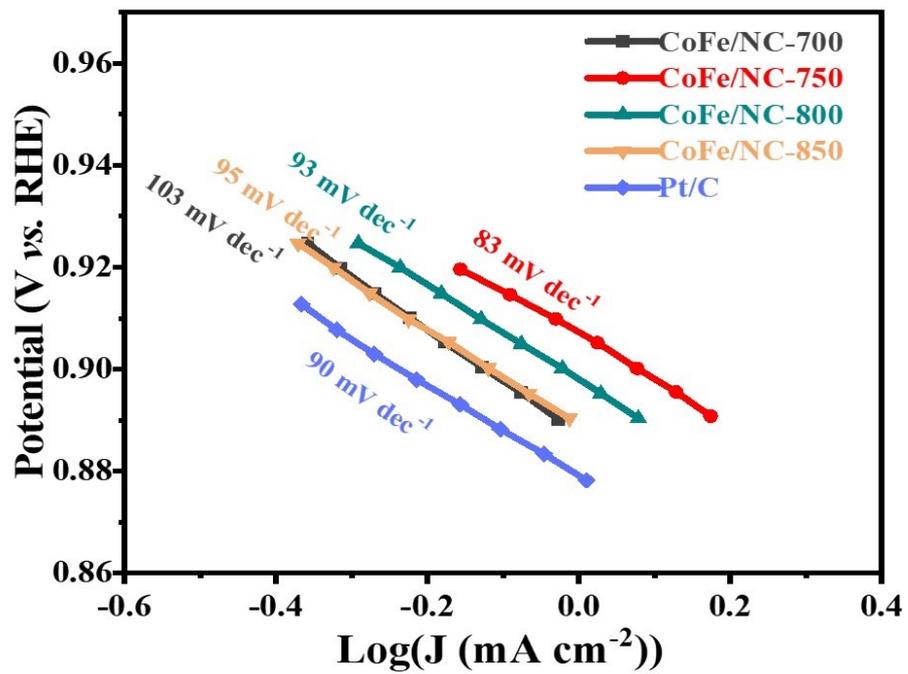
Figure S4. (a-d) SEM images CoFe/NC-700, CoFe/NC-750, CoFe/NC-800 and
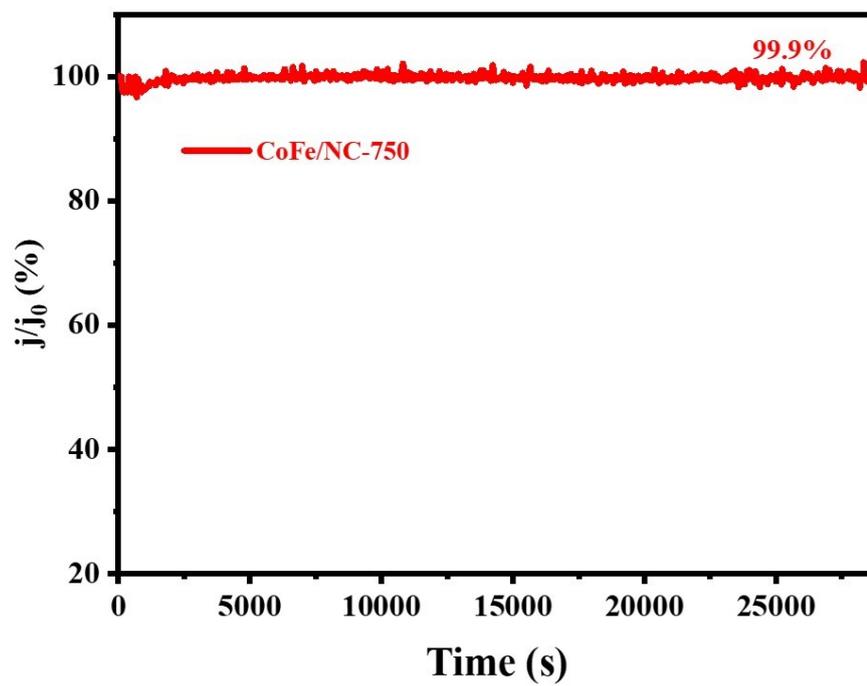
CoFe/NC-850.

Figure S5. (a-b) Nitrogen adsorption/desorption isotherm of CoFe/NC-700, CoFe/NC-750, CoFe/NC-800 and CoFe/NC-850.
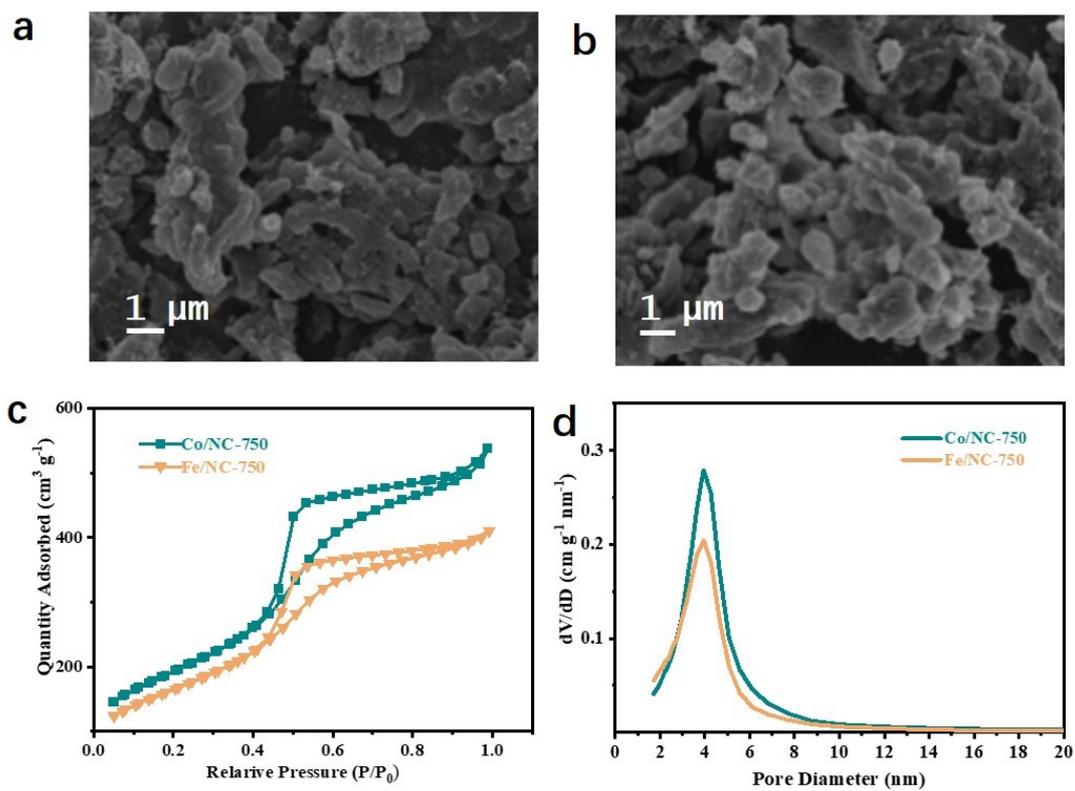
Figure S6. XRD patterns of CoFe/NC-700, CoFe/NC-750, CoFe/NC-800 and

CoFe/NC-850.

Figure S7. Tafel slope for CoFe/NC-700, CoFe/NC-750, CoFe/NC-800 and CoFe/NC-850.

Figure S8. Stability result for CoFe/NC-750.

Figure S9. (a-b) SEM imagines and (c-d) BET results of Co/NC-750 and Fe/NC-750.
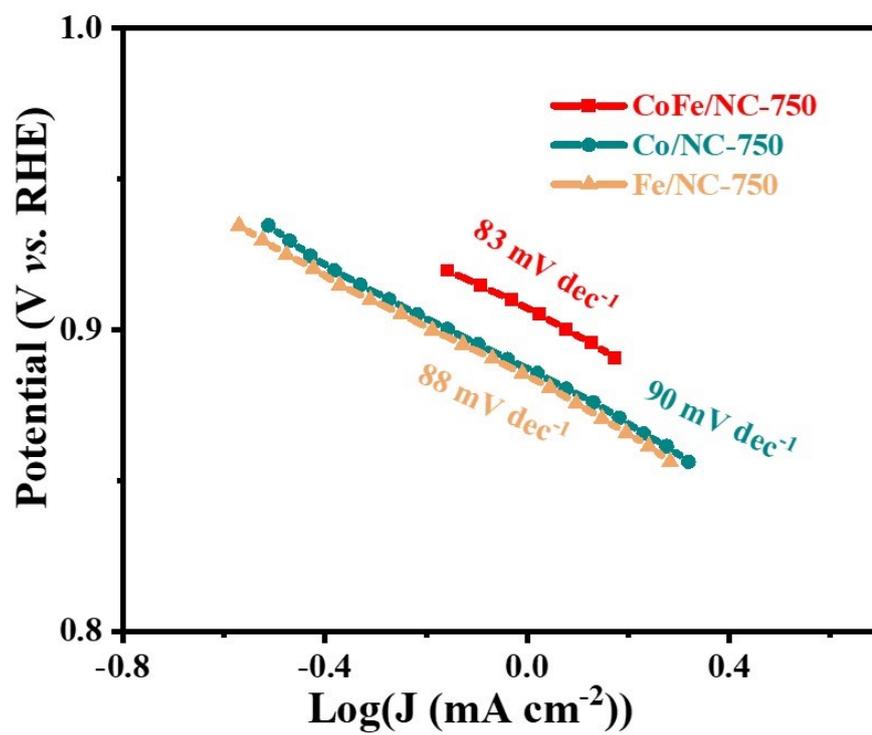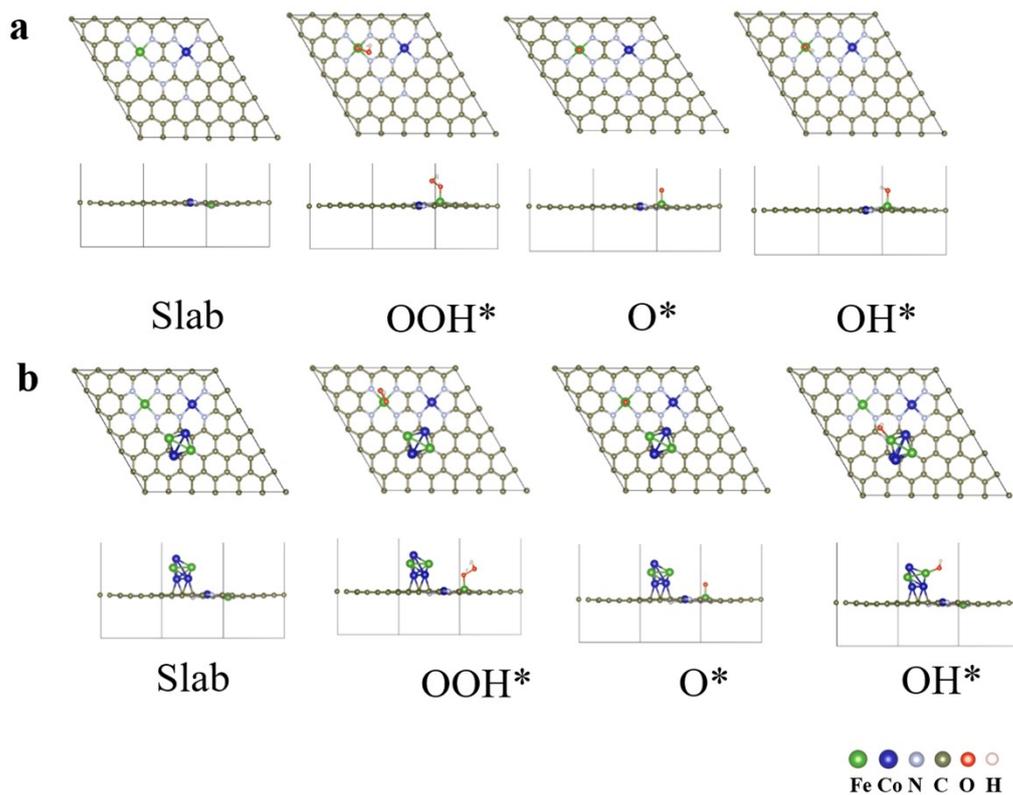
Figure S10. Tafel slope for CoFe/NC-750, Co/NC-750 and Fe/NC-750.

Figure S11. DFT calculation results (a) the reaction scheme with the intermediates in the ORR process on CoFe-dual atoms/NC, (b) the reaction scheme with the intermediates in the ORR process on CoFe/NC.

Section S4 supplementary Table

Table S1. Comparisons of the electrocatalytic activities of the reported materials in 0.1 M KOH.

Catalyst	E_{onset} (V)	$E_{1/2}$ (V)	Tafel (mV/dec)	$\lvert J_L \rvert$ (mA cm^{-2})	J_K at 0.85 V_{RHE} (mA cm^{-2})	Reference
CoFe/NC-750	1.02	0.87	83	5.69	8.76	This work
SA-CoCu@Cu/CoNP	0.98	0.88	59.9	N/A	N/A	Adv. Energy Mater., 2021, 11, 2100303
Co$_2$P/NP-C	~0.9	0.81	62.13	4.54	N/A	Composites, Part B, 2022,23 ,109589
Co-NP/MNCF	N/A	0.836	51.9	5.9	N/A	Chem. Eur. J., 2023,29, e202204034
Fe$_3$N/Fe$_{NP}$-N-C-3.3%	N/A	0.867	63.9	6.24	N/A	Carbon, 2023, 214, 118333
Fe$_3$C@NC/rGO 100NP	0.95	0.86	N/A	N/A	N/A	J. Mater. Res. Technol., 2022, 21, 1307-1315
Co-N-C/CNF	N/A	0.859	58	N/A	N/A	Nano Res, 2022, 16, 545-554
Fe–Nx–CNFs	N/A	0.875	88	6.08	24.5(at 0.8V)	Mater. Chem. Front, 2022, 6, 3213-3224
FeNb$_2$O$_6$/NICC	1.09	0.882	87.1	6.0	N/A	J Colloid Interf Sci, 2024, 661, 102-112
CNT@ZnCo/NSC	0.98	0.83	83.2	~5	N/A	Int. J. Hydrogen Energy, 2024, 51, 1229-1241
CV-FeP/NPCNT-30	1.142	0.92	100	5.89	N/A	Inorg. Chem. Front., 2024, DOI: 10.1039/D4QI00182F
FeNC-20	0.98	0.889	62.1	~6	4.5	Chem. Eng. J.,2023,474,145464
Fe/FexC@Fe-N-C-900	1.01	0.91	44.8	5.72	~20	Chem. Eng. J., 2023, 453, 139820