Supporting Information

FeS-FeNC decorated N,S-codoped porous carbon for enhanced ORR activity in alkaline media

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Experimental Section

Materials: 5,10,15,20-Tetrakis(4-aminophenyl)porphyrin (TPAPP) was obtained from J&K Scientific Ltd.. Anhydrous $FeCl_3$, 2,5-Diformylthiophene (DFTh) were purchased from Aladdin Company. Nafion solution (5 wt%) and Commercial Pt/C(20% Pt) electrocatalyst was supplied by sigma-Aldrich company and Alfa Aesar Company respectively. 1,2-Dichloroethane, n-Butanol, alcohol, H_2SO_4, acetic acid, 1,4-Dioxane, tetrahydrofuran and acetone were acquired from Guangzhou Chemical Reagent Industry. All the solvents and regents were directly used without further purification.

Synthesis of PPF: Typically, 86 mg TPAPP were dispersed in 1.0 mL of 1,2-Dichloroethane, after sonicated for 10 min, the resulted solution was marked as solution A. 30 mg (10 mg, 60 mg) DFTh were dispersed in the mixture of 1.0 mL of n-Butanol and 1 mL of acetic acid, after sonicated for 10 min, the resulted solution was marked as solution B. Then, the solution A was added to solution B, and the mixture was sonicated for 30 min. The mixture was sealed in a glass tube under a N_2 atmosphere and reaction at 120 ^{o}C for 72 h. The resulted precipitate was filtered and purified by Soxhlet extraction using 1,4-Dioxane, tetrahydrofuran and acetone as solvent. The PPF was finally obtained after drying in the oven.

Synthesis of Fe-PPF: In the typical preparation of Fe-PPF, the anhydrous $FeCl_3$ was placed in the front of the tube furnace and the PPF was located in the bottom and then heated to 320 ^oC for 0.5 h under a N_2 flow (the flow rate of N_2 was 0.4 mL min^{-1}). The result product was washed with ethanol and water and then dried at 60 ^oC. The dried sample was denoted as Fe-PPF.

Synthesis of FeS-FeNC@NSC: The as-prepared Fe-PPF was heated to 900 ^oC for 2 h at a heating rate of 5 ^oC min^{-1} in nitrogen atmosphere to acquire FeS-FeNC@NSC.

Synthesis of other samples: The NSC was prepared following the above procedure without adding Fe. To obtain FeNC@NSC, the FeS-FeNC@NSC were leached with 2.0 M H_2SO_4 for 12 h and repeatedly washed with deionized water then dried at 60 ^oC.

Synthesis of the electrocatalysts: The electrocatalyst was synthesised by adding 5 mg of samples into the mixture of 50 μL Nafion solution, 475 μL ethanol and 475 μL water, then sonication for 1 h to form a homogeneous ink. 20 μL of ink was loaded on a glassy carbon rotating disk electrode and dried at room temperature, the loading mass was about 500 μg cm^{-2}. For Pt/C electrode, 250 μg cm^{-2} was loaded on the electrode.

Materials characterization: The microstructure and surface morphology of the samples were characterized by using field-emission scanning electron microscopy (SEM, Hitachi S-4800) operated at 10 kV. High-resolution TEM, HAADF-STEM, and corresponding EDS mapping analyses were using a JEOL ARM200F microscope (JEOL, Tokyo, Japan) with STEM aberration corrector. The crystal structures of the samples were analysed by Powder X-ray diffraction (XRD). X-ray photoelectron spectroscopy (XPS) was recorded on an Thermo Fisher Scientific K-Alpha with Al K alph source. FT-IR were measured on Bruker Equinox 55 Fourier transform infrared spectroscopy. Nitrogen adsorption and desorption isotherms were collected on a Micromeritics ASAP2020 analyser.

Electrochemical evaluation: The electrochemical properties were evaluated using a CHI660E electrochemical workstation (CHI760E) with a rotation control device. The ORR performance of the samples was performed using a standard three-electrode system with a glassy carbon electrode, Ag/AgCl, and a Pt plate as the working electrode, the reference electrode and the counter electrode, respectively. In all measurements, the potentials were converted to the reversible hydrogen electrode (RHE) potentials. All polarization curves were recorded in O_2-saturated 0.1 M KOH electrolyte after iR-corrected. CV curves were recorded at a scan rate of 20 mV s^{-1} in O_2-saturated and N_2-saturated 0.1 M KOH electrolyte.

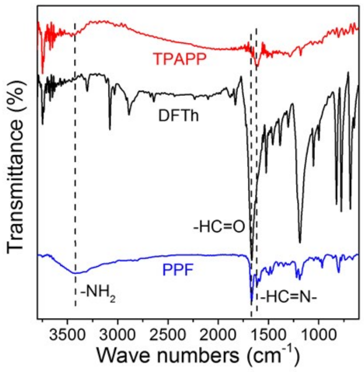

Figure S1. FT-IR spectrum of PPF.

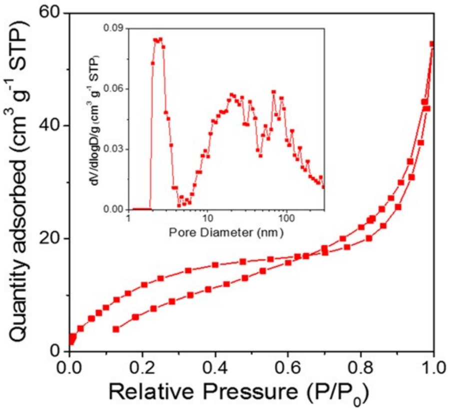

Figure S2. Nitrogen adsorption-desorption isotherms of PPF and the inset shows the corresponding pore size distributions.

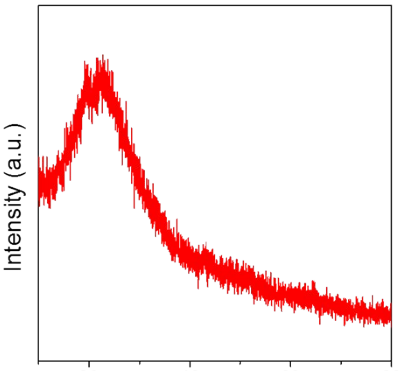

Figure S3. XRD pattern of PPF.

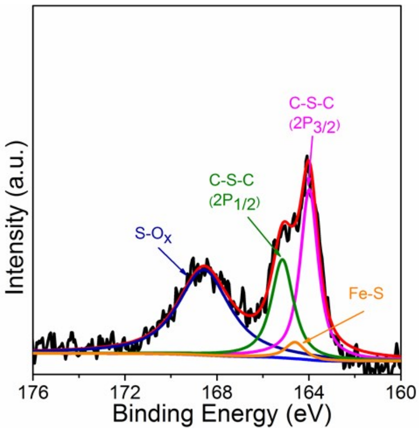

Figure S4. High resolution XPS spectra of S 1s for FeNC@NSC.

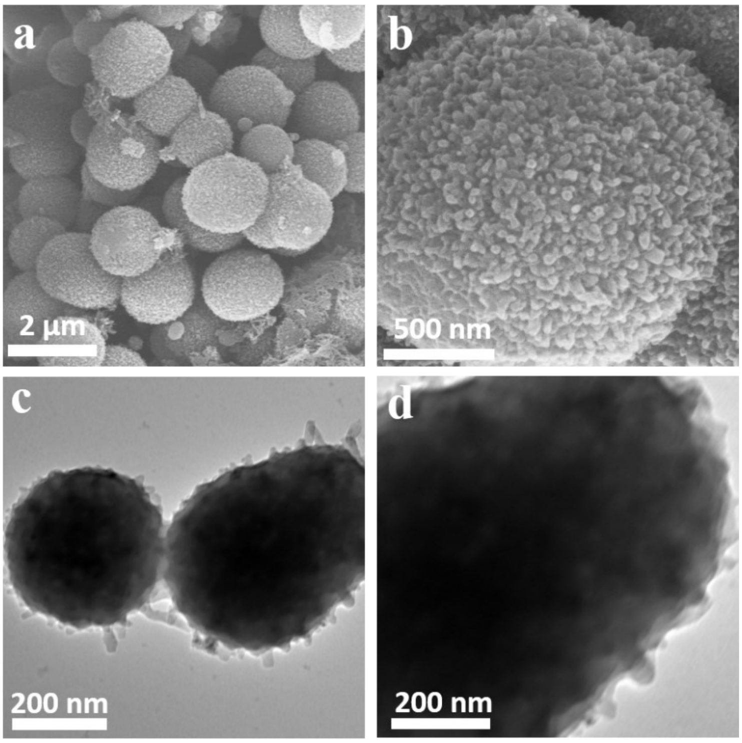

Figure S5. a, b) SEM and c,d) TEM images of PPF.

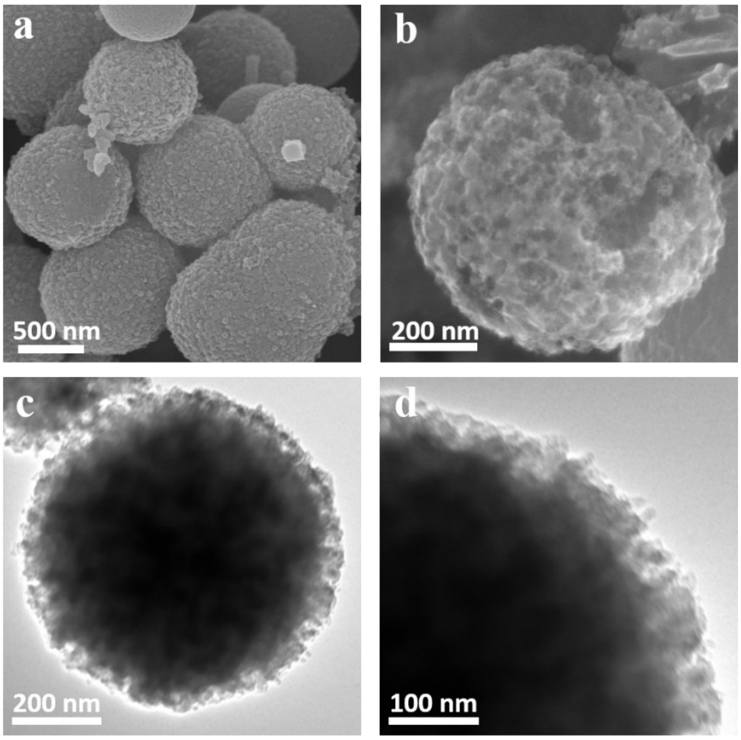

Figure S6. a, b) SEM images of NSC. c, d) TEM images of NSC.

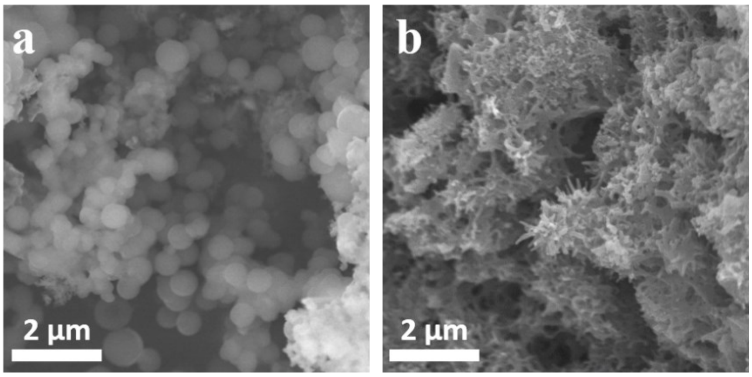

Figure S7. SEM images of PPF in different TPAPP:DFTh ratio of a) 86 mg : 10 mg and b) 86 mg : 60 mg.

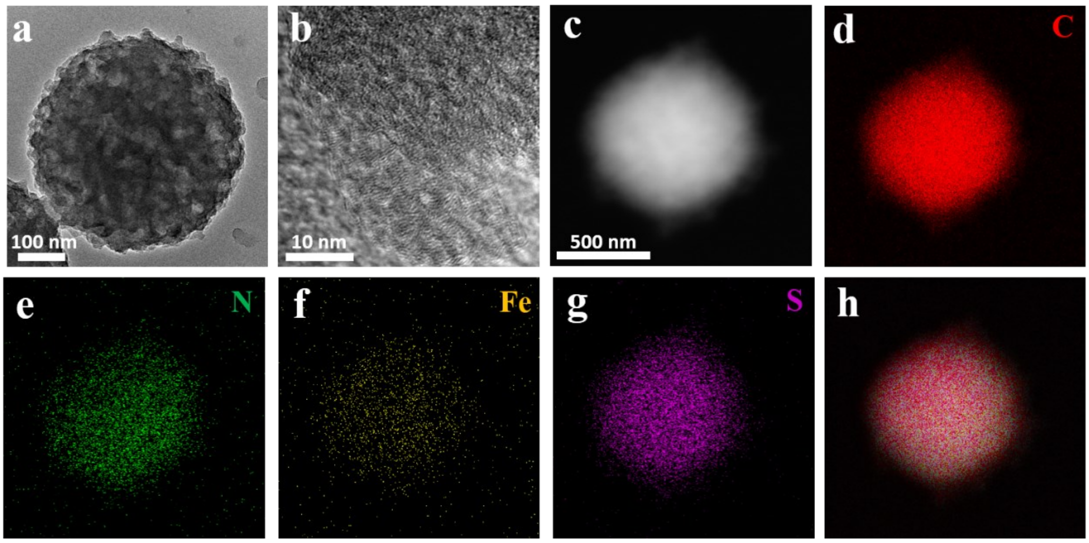

Figure S8. a, b) HRTEM images of FeNC@NSC and c-h) corresponding element mapping.

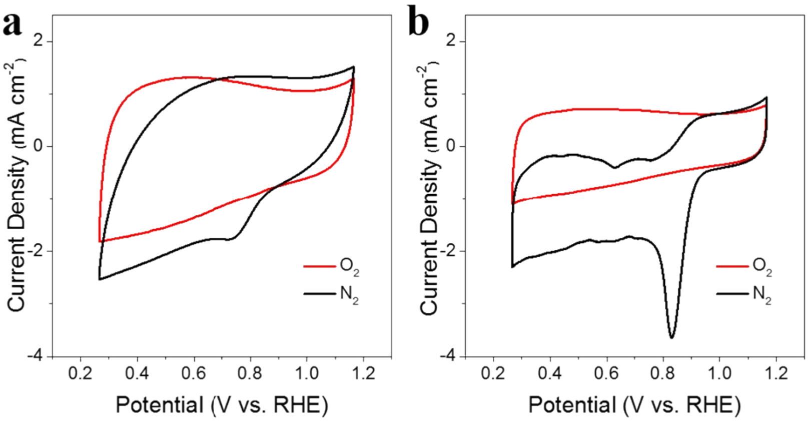

Figure S9. CV curves of a) NSC and b) FeNC@NSC.

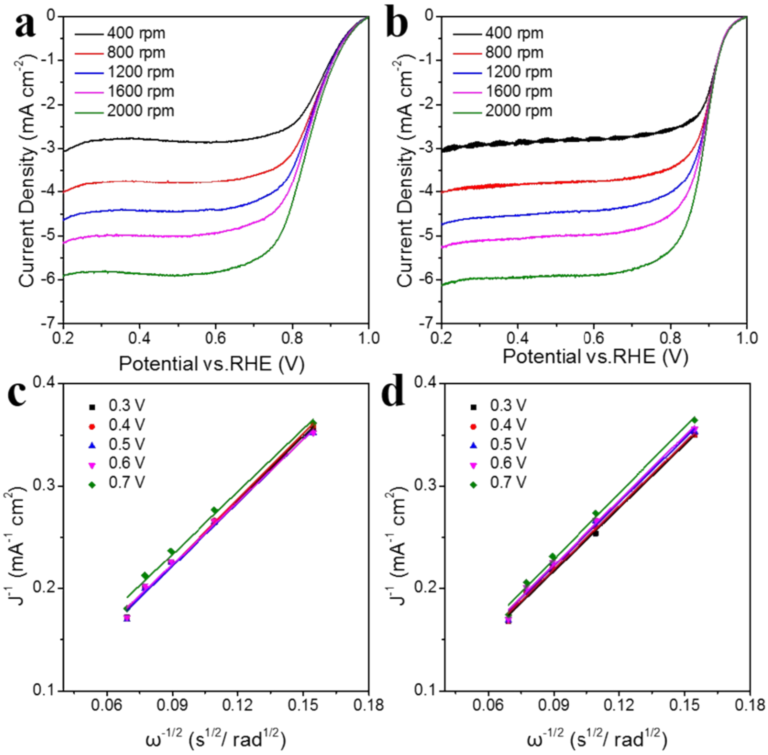

Figure S10. LSV curves of a) Pt/C and b) FeS-FeNC@NSC with the rotating speed range from 400 to 2000 rpm. The K-L plots of c) Pt/C and d) FeS-FeNC@NSC.

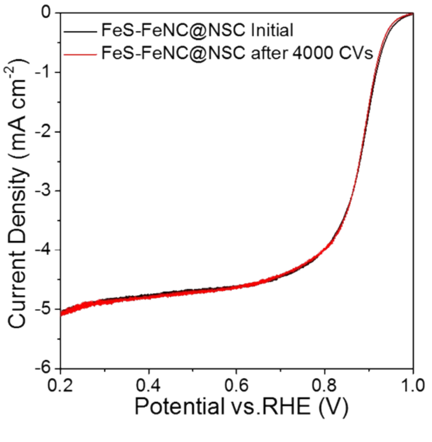

Figure S11. LSV curves of FeS-FeNC@NSC after 4000 CVs cycles.

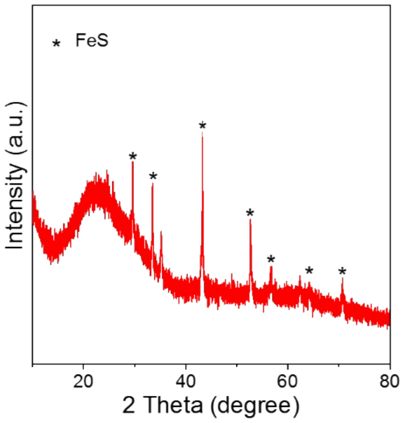

Figure S12. XRD pattern of FeS-FeNC@NSC after amperometric i-t measurement for 36000 s.

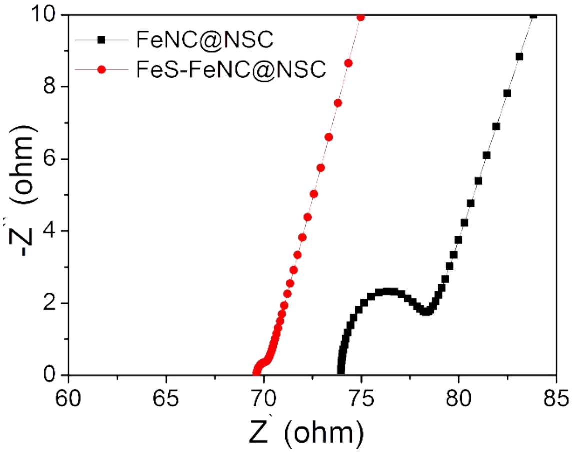

Figure S13. Nyquist plots of electrochemical impedance data.

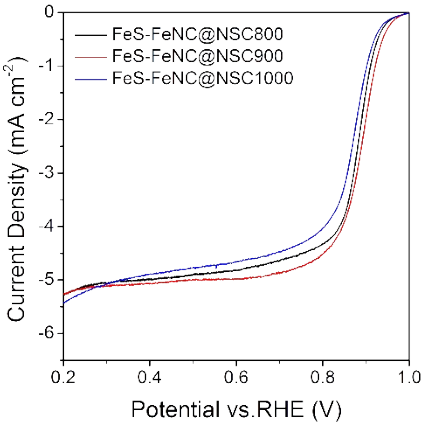

Figure S14. LSV polarization curve of FeS-FeNC@NSC in different carbonization temperature.

Table S1. Element content of samples.

Samples	C content (at.%)	N content (at.%)	Fe content (at.%)	S content (at.%)
FeNC@NSC	83.87	2.45	0.41	2.18
FeS-FeNC@NSC800	74.08	7.81	2.89	1.48
FeS-FeNC@NSC900	82.28	4.89	1.18	2.88
FeS-FeNC@NSC1000	84.5	2.8	0.79	0.99

Table S2. The ICP data of FeS-FeNC@NSC and FeNC@NSC.

Sample	Fe content (wt%)
FeS-FeNC@NSC	6.22
FeNC@NSC	0.77

Table S3. Comparison of ORR catalytic activity between Fe@NCA and other Fe-based carbonous electrocatalysts in 0.1 M KOH solution.

Samples	Half-wave Potential (V vs.RHE)	References
FeS-FeNC@NSC	0.886	This work
CAN-Pc(Fe/Co)	0.85	1
Fe1﹣HNC﹣500﹣850	0.84	2
Fe-N-C HNSs	0.87	3
FeNC-S-Fe_xC/Fe	0.887	4
Fe2-Z8-C	0.87	5

PFA-Fe10-900-ALP	0.86	6
S,N-Fe/N/C-CNT	0.85	7
Fe/SNC	0.86	8
CNT/PC	0.88	9
Fe/NS/C-g-C3N4/TPTZ-1000	0.868	10
Fe(1.5)/N/S-PAD	0.85	11
Fe-SNC@900 / ZnDTO 80Hb20	0.834	12
p-Fe-N-CNFs	0.82	13
FeS/Fe3C@N-S-C-800	0.87	14
OM-NCNF-FeNx	0.84	15

Notes and references

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