

Supporting Information

Urea with Trifunctional Effects: An Assistant for Highly Exposing Single-Atom Active Sites on 2D Nanosheets via Structural Transformation

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Experimental Section

Materials and reagents. Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99%, Aladdin), Zinc Gluconate (98%, Aladdin), Urea (99.5%, Solarbio), a-D-Glucose (96%, Aladdin), Ammonium chloride (NH_4Cl , 99.5%, Aladdin), Melamine (99%, Aladdin), Platinum on carbon catalyst (Pt/C, 20 wt.%, Sigma), methanol (CH_3OH , >99.5%, Greagent), ethanol ($\text{C}_2\text{H}_5\text{OH}$, >99.5%, Greagent), Nafion solution (5 wt.%, Sigma) were all used as received without further purification. The water used in all experiments was ultrapure ($R = 18.2 \text{ M}\Omega$).

Synthesis of ZnFe-co-doped carbon spheres (ZnFe-CS) precursor. ZnFe-CS was prepared by supramolecular coordination assembly strategy. Typically, 50 mg $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 3 g Zinc Gluconate were simultaneously dissolved in 30 ml deionized water and stirred for 1 h. After stirring, put the clear mixture in a 100ml Teflon autoclave, heated at 180 °C for 3h. The product was collected by centrifugation and washed with deionized water and ethanol, finally dried in an oven at 60 °C overnight.

Synthesis of single-atoms Fe dispersed nitrogen-doped multilayered porous carbon nanosheet (SAFe-NMPC). Urea was mixed with the obtained ZnFe-CS at a mass ratio of 13:1 (0.6 g urea + 0.046 g ZnFe-CS) and ground by pestle milling for 15 min. Then the mixture was pyrolyzed at 900 °C for 2 h at a heating rate of 5 °C min^{-1} under a continuously flowing Ar atmosphere to form the SAFe-NMPC sample. The as-prepared products were directly used without any post-treatment.

Synthesis of other control samples. The control samples were prepared with similar strategies. Replacing the zinc gluconate with same molar mass sucrose (2.25 g), the SAFe-NMC was obtained. While, placing the urea on the front side instead of mixing and milling, the SAFe-NPC was obtained. Moreover, SAFe-H/LNMPC was prepared by changing the ratio of the mixed urea (increase to 1:20 / decrease to 1:7).

Characterization. Scanning electron microscopy (SEM) was carried out on a PHILIPS XL-30 ESEM with an accelerating voltage of 20 kV. X-ray diffraction (XRD) spectra were recorded on a Bruker D8 Advance diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) X-ray radiation. X-ray photoelectron spectroscopy (XPS) experiments were carried out on an ESCALAB-MKII photoelectron spectrometer using $\text{Al K}\alpha$ radiation. High-resolution TEM (HRTEM) and the corresponding energy disperse spectroscopy for elemental mapping were performed on a Tecani-G2 T20 working at 200 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was carried out on Thermo Fisher themis Z. Fe K-edge XAFS analyses were performed with Si (111) crystal monochromators at the BL14W beam line at the Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China). Thermogravimetric

analysis (TGA) was conducted under N₂ conditions using a PerkinElmer Thermal Analysis system. The content of Fe and N was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) and elemental analysis respectively. The BET (Brunauer-Emmett-Teller) tests were performed on an ASAP 2020 Physisorption Analyzer.

Electrochemical measurement. All electrochemical tests were performed on an electrochemical workstation of CHI 832C (Shanghai, China) based on a classical three-electrode setup. A graphite rod and a Hg/HgO electrode as counter and reference electrodes, respectively. 5 mg of catalysts were dispersed in 1 mL ethanol mixed with 20 μL nafion solution (5 wt. %) and then sonicated for 30 min to obtain a homogeneous catalyst ink. Catalyst ink (10 μL) was dispersed on a glassy carbon electrode and dried naturally to serve as the working electrode. Cyclic voltammetry (CV) tests were performed at a scan rate of 10 mV s⁻¹ in 0.1 M KOH solution with saturated N₂ or O₂. Linear sweep voltammetry (LSV) curves were obtained using a rotating disk electrode (RDE) by varying speed rates from 400 to 1600 rpm with a scan rate of 5 mV s⁻¹. Rotating ring-disk electrode (RRDE) voltammetry was carried out with a Pt ring electrode, and the ring potential was set at 1.3 V vs. RHE. The durability test of the electrocatalysts was conducted by cycling from 0.6 to 1.0 V vs. RHE at 50 mV s⁻¹ for 5000 cycles, the chronoamperometry curves was tested at 0.7 V. All control samples were drop-cast onto the electrode with the same loading. All potentials reported were calibrated to the RHE based on the equation $E(\text{RHE}) = E(\text{Hg}/\text{HgO}) + 0.865 \text{ V}$.

The kinetic current of electrocatalyst and transferred electron number (n) were calculated by Koutecky–Levich equation as shown below:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

$$B = 0.62nFC_{O_2}D_{O_2}^{2/3}\nu^{-1/6}$$

Where J is the measured current density, J_K is the kinetic current density, J_L is the diffusion-limiting, ω is the rotation rate of RDE (rpm), B is determined by the slope of Koutechy-Levich (K-L) graph according to Levich equation, n is the transferred electron number, F is the Faraday constant (96485 C mol⁻¹), C is the O₂ concentration in the electrolyte (1.26 × 10⁻⁶ mol cm⁻³), D is the diffusion coefficient of O₂ (1.93 × 10⁻⁵ cm² s⁻¹), and ν is the kinetic viscosity (0.01009 cm² s⁻¹).

H₂O₂ yield and corresponding electron transfer number (n) are calculated by the following equation with RRDE test:

$$H_2O_2(\%) = 200 \times \frac{I_R/N}{I_D + I_R/N}$$

$$n = 4 \times \frac{I_D}{I_D + I_R/N}$$

Where I_R is the ring current, I_D is the disk current, N is the ring current collection efficiency (0.37).

The electrochemically active specific surface area (S_{ECSA}) of catalyst is calculated according to the following equation:

$$C_{dl} = \frac{j}{v}$$

$$ECSA = \frac{C_{dl}}{C_{dlRef}}$$

$$S_{ECSA} = \frac{A_{Geom} \times ECSA}{m_{Electrode}}$$

Where j is current density, v is scan rate, $A_{Geom}=0.19625 \text{ cm}^2$, $C_{dlRef}=0.02 \text{ mF cm}^{-2}$, $m_{Electrode}$ is mass of catalyst loaded on the electrode.

Zn-Air battery test. A stack-type Zn-air battery was assembled and tested under the following procedure. The ink was dropped onto carbon paper with a loading of 1 mg cm^{-2} , then dried naturally as. A polished Zn plate was used as anode, and $6 \text{ M KOH} + 0.2 \text{ M Zn(OAc)}_2$ aqueous solution was used as electrolyte. All tests were on the CHI 660E. The discharge curves were tested at a scanning rate of 5 mV s^{-1} . The specific capacity was tested at 10 mA cm^{-2} . The rate capability was tested from 2 mA cm^{-2} to 50 mA cm^{-2} . The charge-discharge curves were tested at 5 mA cm^{-2} and the catalyst loading was replaced with $0.5 \text{ mg cm}^{-2} \text{ SAFe-NMPC} + 0.5 \text{ mg cm}^{-2} \text{ RuO}_2$.

The specific capacity is calculated according to the following equation:

$$\text{specific capacity} = \frac{\text{current} * \text{service hours}}{\text{weight of consumed zinc}}$$

Supplementary Figures

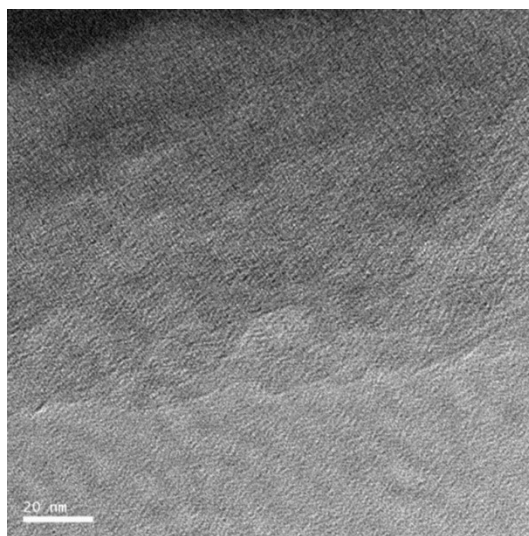


Figure S1. HRTEM image of SAFe-NMPC.

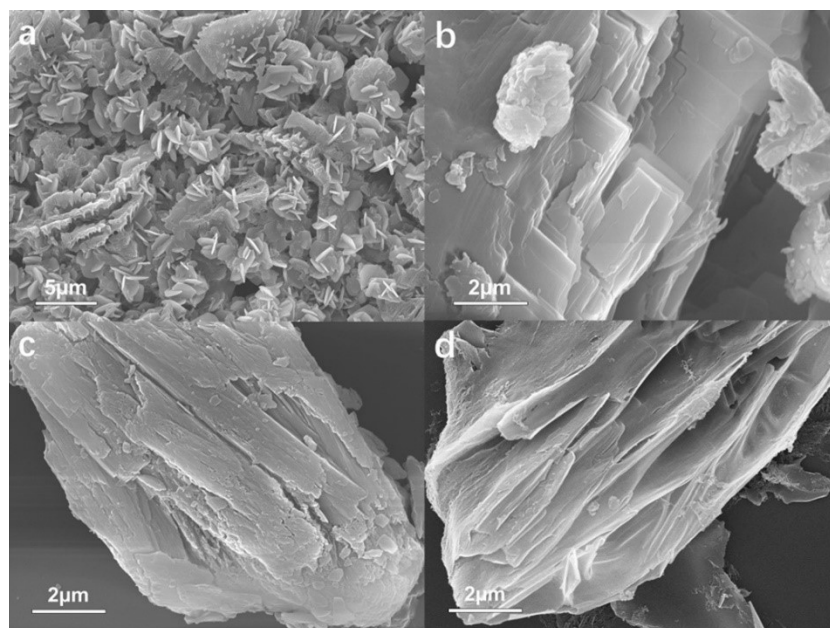


Figure S2. SEM images of samples pyrolyzed in (a) 150 °C, (b) 210 °C, (c) 300 °C, and (d) 400 °C.

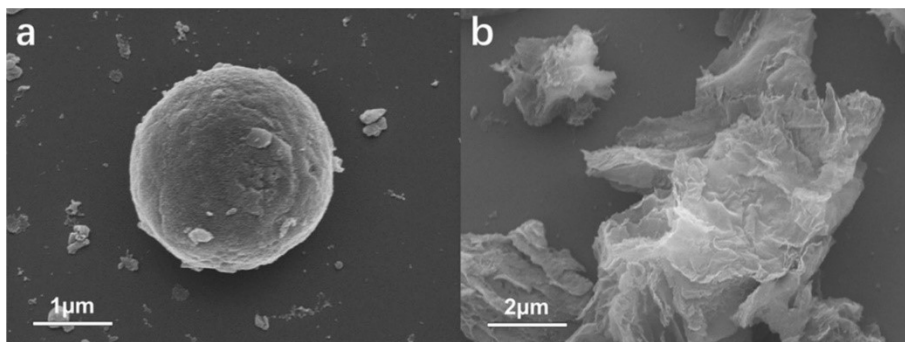


Figure S3. SEM images of samples obtained by changing urea with (a) NH_4Cl or (b) melamine.

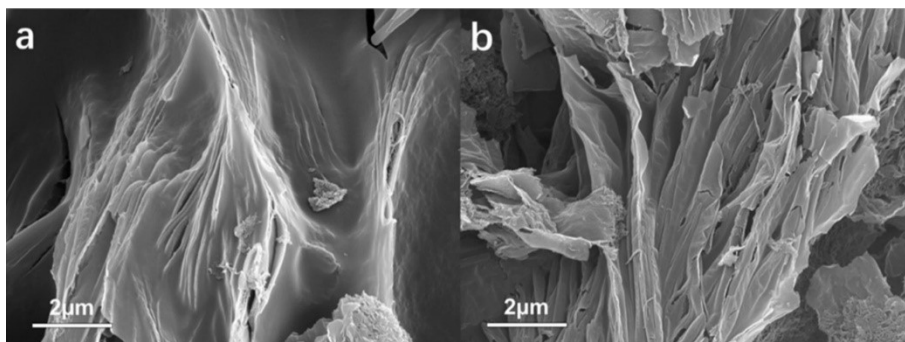


Figure S4. SEM images of (a) SAFe-LNMPC and (b) SAFe-HNMPC.

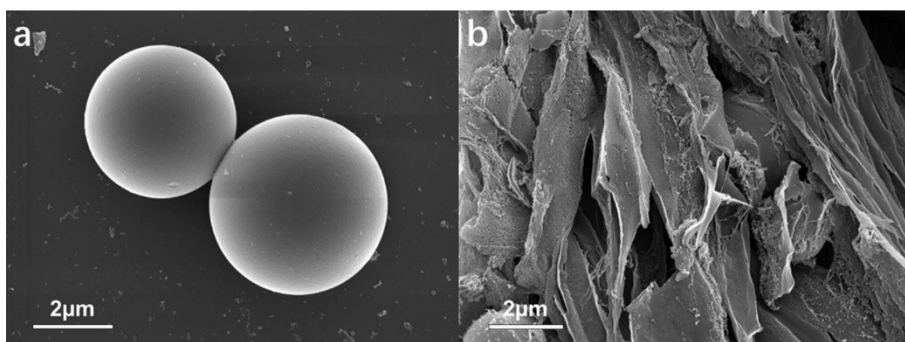


Figure S5. SEM images of (a) SAFe-NPC and (b) SAFe-NMC.

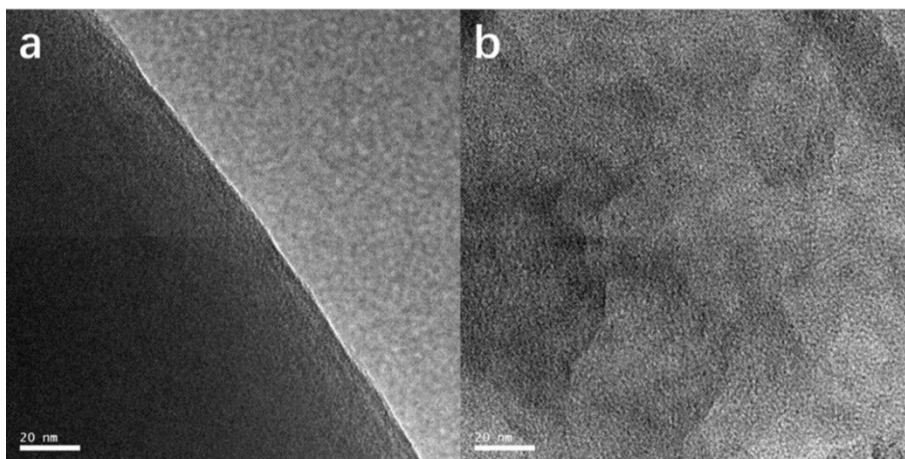


Figure S6. HRTEM images of (a) SAFe-NPC and (b) SAFe-NMC.

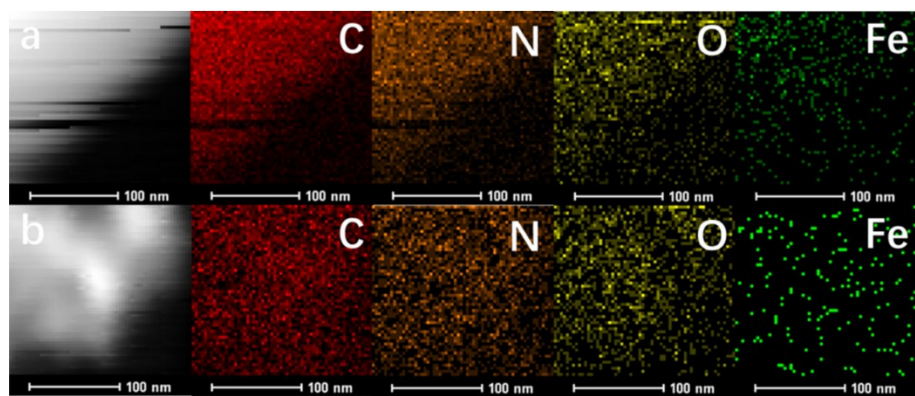


Figure S7. Elements mapping of (a) SAFe-NPC and (b) SAFe-NMC.

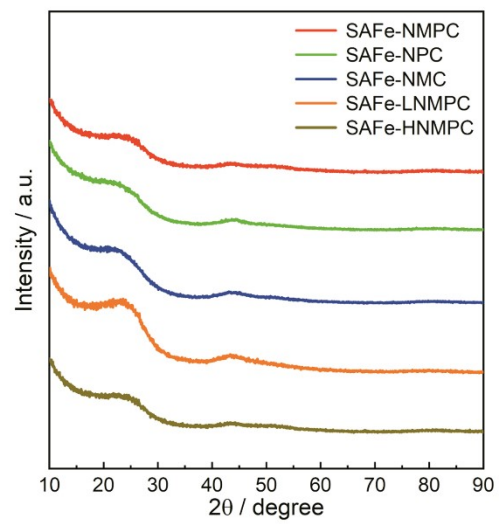


Figure S8. XRD pattern of all samples.

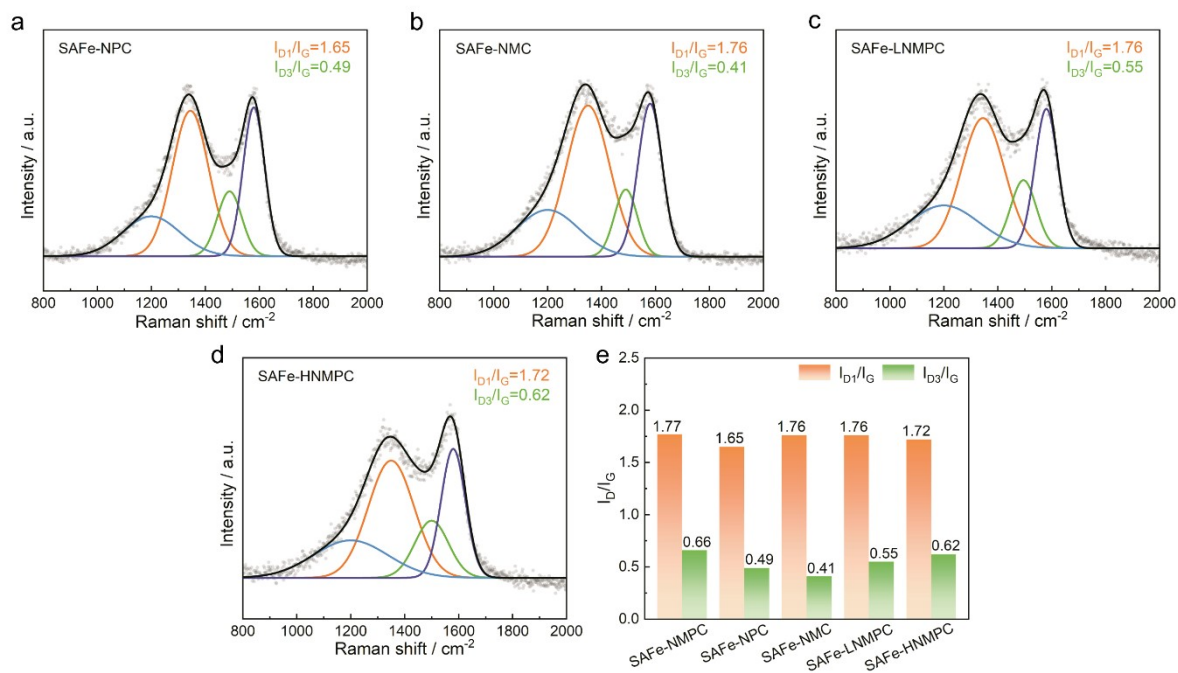


Figure S9. Raman spectra of (a) SAFe-NPC, (b) SAFe-NMC, (c) SAFe-LNMPC, (d) SAFe-HNMPC. (e) I_{D1}/I_G and I_{D3}/I_G of all samples

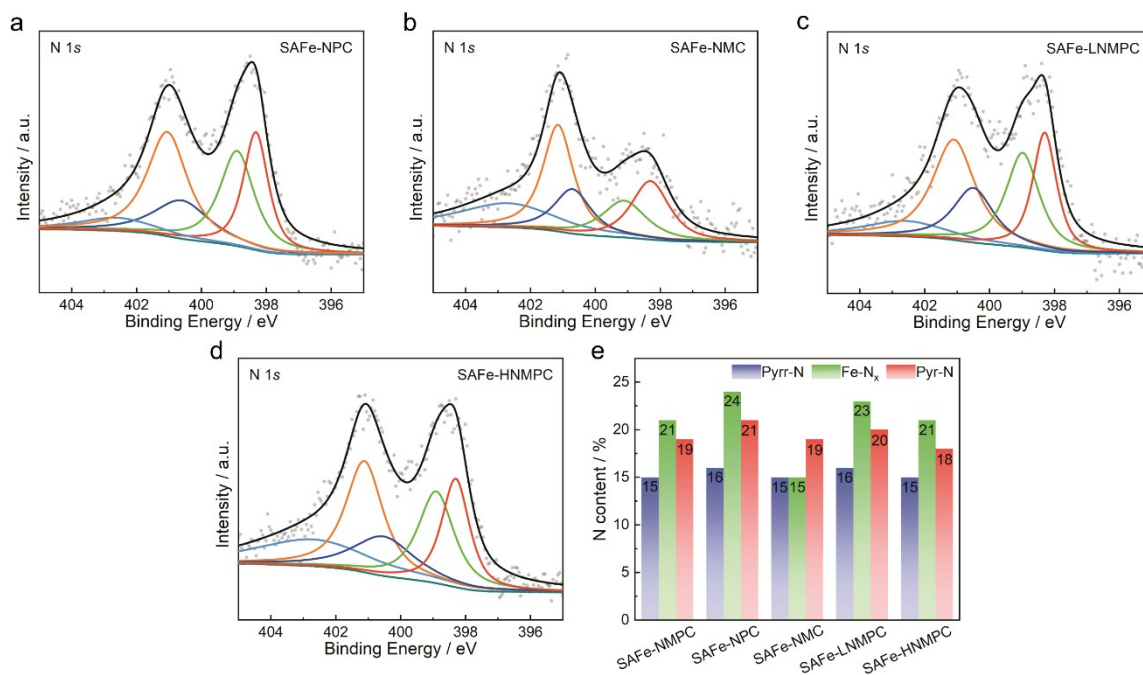


Figure S10. XPS N 1s spectra of (a) SAFE-NPC, (b) SAFE-NMC, (c) SAFE-LNMPC, (d) SAFE-HNMPC. (e) different N content ratios of all samples.

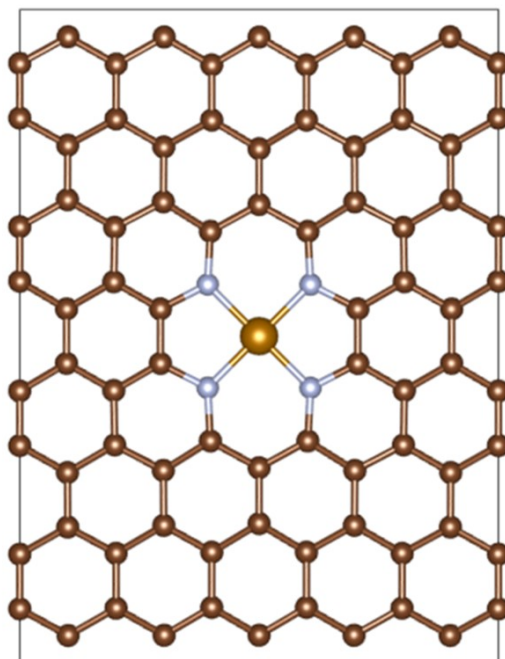


Figure S11. DFT optimized molecular model for Fe-N-C structure.

All the DFT calculations were conducted based on the Vienna Ab-initio Simulation Package (VASP). The exchange-correlation effects were described by the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) method. The core-valence interactions were accounted by the projected augmented wave (PAW) method. The energy cutoff for plane wave expansions was set to 500 eV. The structural optimization was completed for energy and force convergence set at 1.0×10^{-5} eV and 0.02 eV \AA^{-1} , respectively. The Brillouin zone was sampled with the $3 \times 3 \times 1$ K-point. Grimme's DFT-D3 methodology was used to describe the dispersion interactions.

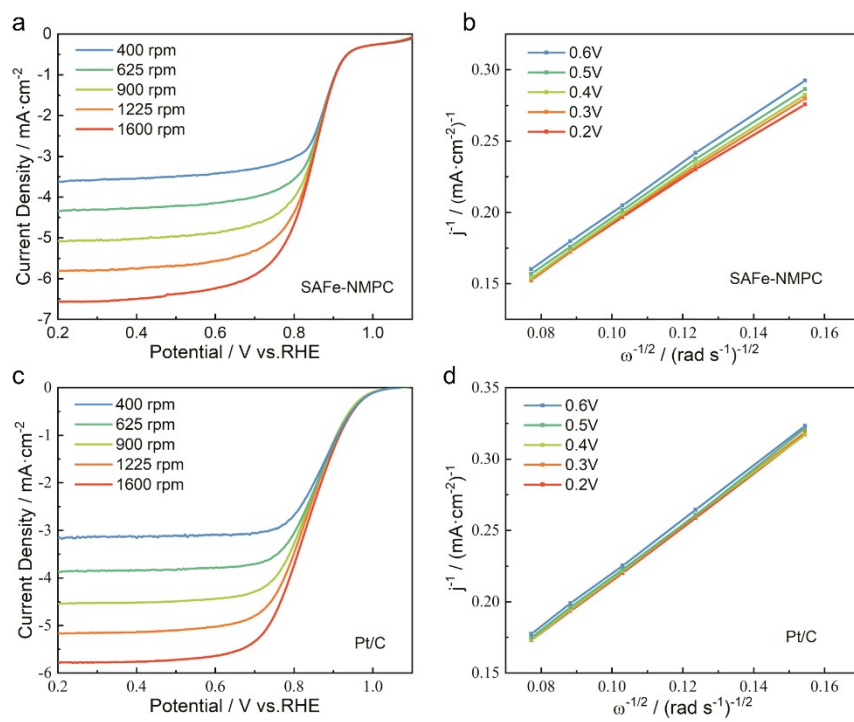


Figure S12. ORR polarization curves at different rotating speeds in O₂-saturated 0.1 M KOH and corresponding K-L equation curves for (a, b) SAFe-NMPC and (c, d) Pt/C.

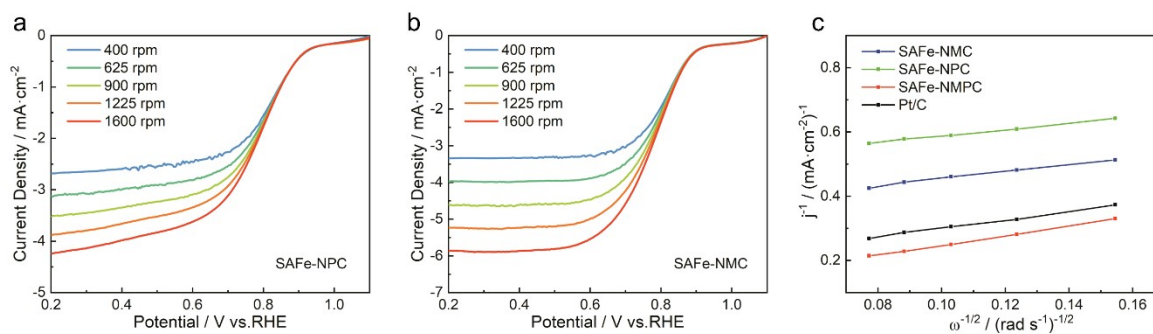


Figure S13. ORR polarization curves at different rotating speeds in O₂-saturated 0.1 M KOH for (a) SAFe-NPC and (b) SAFe-NMC, and (c) corresponding K-L equation curves for all samples at 0.8V vs. RHE.

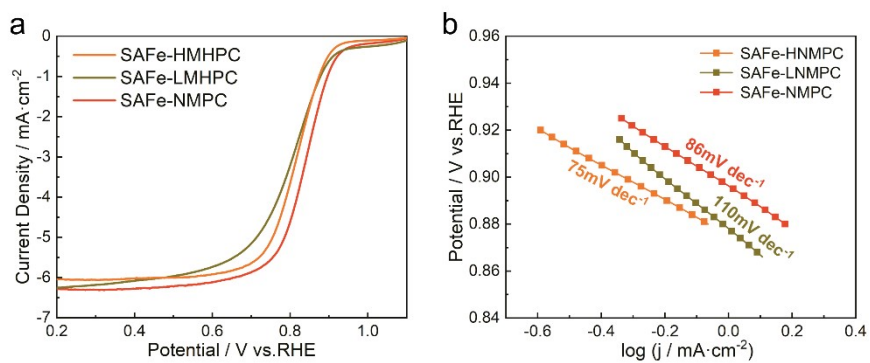


Figure S14. (a) ORR polarization curves at a rotating rate of 1600 rpm in O₂-saturated 0.1 M KOH and corresponding (b) Tafel slope for SAFe-NMPC, SAFe-LNMPC, and SAFe-HNMPC.

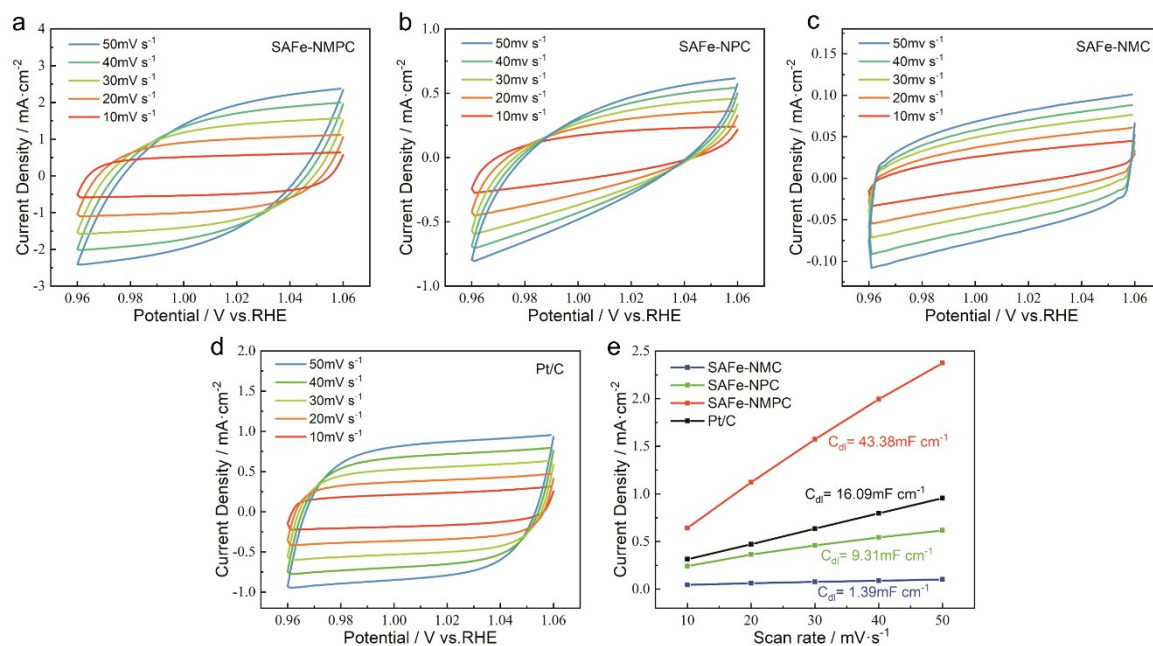


Figure S15. The CV curves at different sweep speeds of (a) SAFe-NMPC, (b)SAFe-NPC, (c)SAFe-NMC, and (b) Pt/C in N₂-saturated 0.1 M KOH, and (e) corresponding double layer capacitance (C_{dl}).

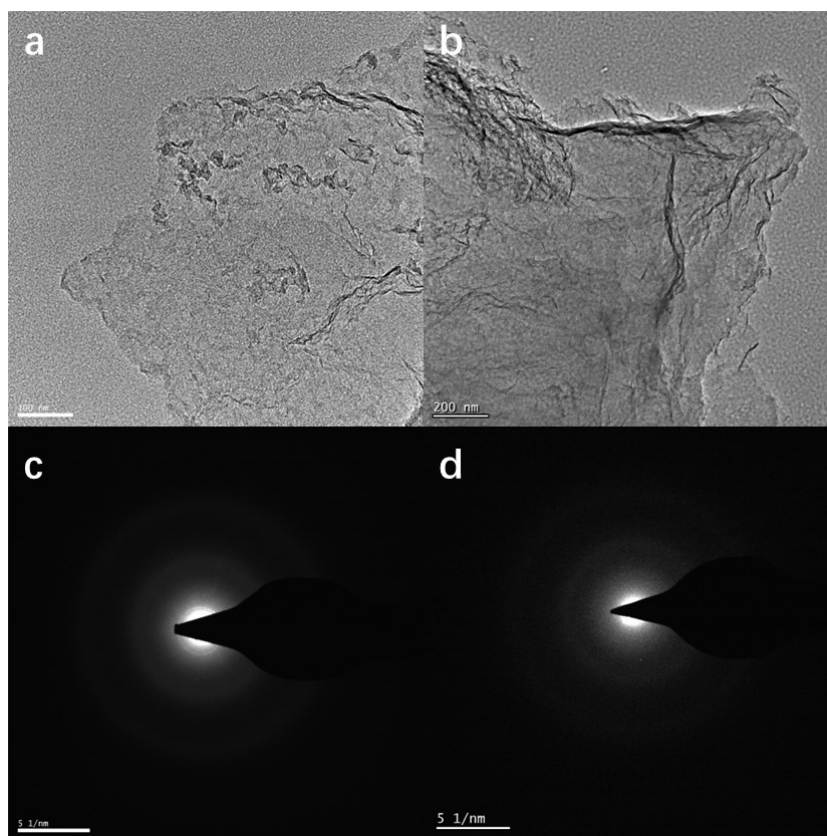


Figure S16. HRTEM images and SAED patterns of SFe-NMPC before (a, c) and after (b, d) 5000 CV cycles.

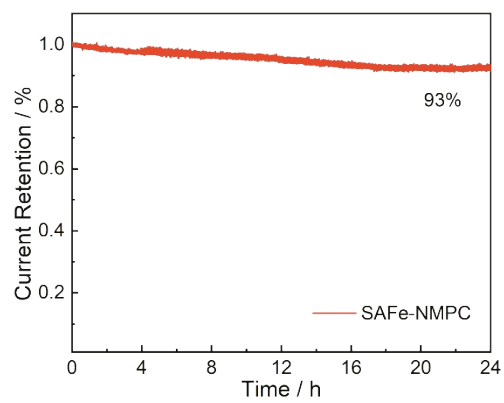


Figure S17. Normalized chronoamperometry curve of SAFe-NMPC at the constant potential of 0.7 V.

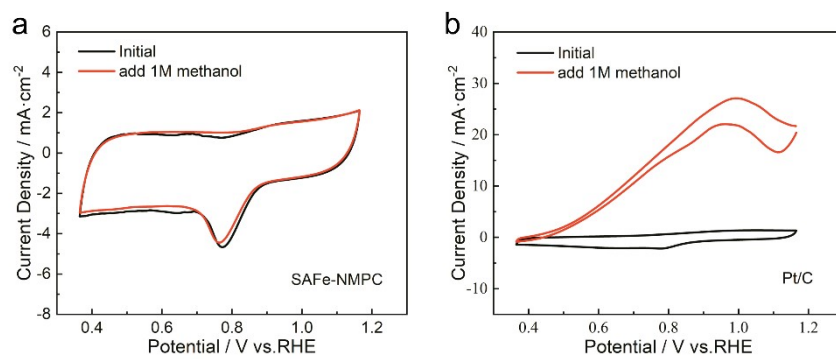


Figure S18. The CV curves of (a) SAFe-NMPC, and (b) Pt/C before and after the addition of 1M methanol in O₂-saturated 0.1 M KOH.

Table S1. Porosity comparison of the samples

Sample	SAFe-NMPC	SAFe-NPC	SAFe-NMC
S_{BET} ($\text{m}^2 \text{g}^{-1}$)	1207	733.4	720.7
microporous surface area ($\text{m}^2 \text{g}^{-1}$)	143.6	455.5	343.1
mesoporous surface area ($\text{m}^2 \text{g}^{-1}$)	580.8	144.4	148.2

Table S2. Fe and N contents of all samples.

Sample	SAFe-NMPC	SAFe-NPC	SAFe-NMC	SAFe-LNMPC	SAFe-HNMPC
Fe content (w t.%)	2.1	1.9	0.2	1.6	1.8
N content (w t.%)	6.20	4.99	5.86	5.40	6.71

Fe is determined by ICP-MS, N is determined by elemental analysis.

Table S3. Structural parameters extracted from EXAFS fitting at Fe K-edge

Sample	path	CN	R(Å)	S0²	ΔE₀(eV)	σ²(Å²)	R factor
SAFe-NMPC	Fe-N	4.08	2.01	0.51	5.67	0.013	0.010

CN is the coordination number; R is interatomic distance; S0² is the amplitude reduction factor; ΔE₀ is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model); σ² is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); R factor is used to value the goodness of the fitting. Error bounds that characterize the structural parameters obtained by EXAFS spectra were estimated as CN ± 20%; R ± 1%; ΔE₀ ± 20%; σ² ± 20%.

Table S4. C_{dl} and corresponding S_{ECSA} of the samples

Sample	SAFe-NMPC	SAFe-NPC	SAFe-NMC	Pt/C
C_{dl} (mF cm ⁻²)	43.38	9.31	1.39	16.09
S_{ECSA} (m ² g ⁻¹)	851.3	182.7	27.3	315.8

Table S5. Open-circuit voltage and power density of SAFe-NMPC and other catalysts

Catalysts	Open-circuit voltage (V)	Power density (mW cm⁻²)	Reference
SAFe-NMPC	1.49	169	This work
FeMn-DSAC	1.45	184	1
3D SAFe	1.47	156	2
(Fe,Co)-SA/CS	1.43	86.65	3
CoSAs-NGST	1.49	148	4
Fe/PVP-M	1.50	99.85	5
Co@hNCTs-800	1.45	149	6
NC@Co-NGC DSNC	1.45	109	7
CoO/CoxP	1.40	122.7	8
Co-NCS@CNT	1.42	90.6	9
FeCo-N-C-700	1.39	150	10
FeNiCo@NC-P	1.36	112	11
Fe-NPC-1000	1.50	55.1	12
CoFe@NCNT/NCS-800	1.51	196.1	13
Fe/N/C-DT	1.48	220	14

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