

Supporting Information

Fe₃C cluster-promoted single-atom Fe, N doped carbon for oxygen-reduction reaction

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Electrochemical details

The catalyst inks were prepared by dispersing the catalyst in 1 mL mixture of water and isopropanol with a volume ratio of 1:4 with another 0.5 μL Nafion (5 wt%). The prepared catalysts were characterized as thin films drop-casted on a GC collector electrode. The 10 μL as-prepared ink with catalysts concentration of 10 mg/mL was dropped on the glassy carbon (GC) electrode to lead the catalyst loading of 0.5 mg cm^{-2} . All the linear sweep voltammetry (LSV) tests were conducted in 0.5 M H_2SO_4 or 0.1 M KOH electrolytes with a rotation speed of 1600 rpm at a scan rate of 10 mV s^{-1} . The RDE polarization curves were recorded at different speeds and the background current measured in the N_2 saturated electrolyte. Tafel analysis was performed by plotting $\log j_k$ versus potential in the kinetically controlled region. In order to evaluate the durability of the as-prepared catalysts, the cycle voltammetry was carried out at the potential ranging from 0.6 to 1.0 V (vs. RHE)^{1, 2}. After 8000 cycles, the LSV at 1600 rpm was measured for comparison. The measurement was performed in both N_2 and O_2 saturated electrolyte solution.

The electron transfer number for the ORR is determined from the fitting of the Koutecky-Levich (K-L) equation:

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

where J and J_K are the measured current density and kinetic current density and ω is the rotation speed. And the B can be expressed as

$$B = 0.62nFC_0D^{2/3}\nu^{-1/6}$$

where n is the electron transfer number, F (96,485 C mol^{-1}) is the Faraday constant, ν (0.01 $\text{cm}^2 \text{S}^{-1}$) is the viscosity of the electrolyte solution, C_0 ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$) is concentration of oxygen and D ($1.9 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$) is the diffusion coefficient.

In the Test of rotating Ring-disk electrode, the disk electrode was scanned cathodically at a rate of 10 mV s^{-1} and the ring potential was constant at 1.14 V versus RHE. The yield of HO-2 and the electron transfer number (n) from RRDE measurements were calculated with the following equations:

$$H_2O_2(\%) = 200 \times \frac{|J_R/N|}{|J_D| + |J_R/N|}$$

$$n = 4 \times \frac{|J_D|}{|J_D| + |J_R/N|}$$

where J_R is the ring current density, J_D is the disk current density, N is the current collection efficiency of the Pt ring ($N=37\%$).

The TOF for each catalyst was calculated by following equation:

$$TOF = \frac{J_K \times N_A}{nF \times ECSA}$$

where J_K is the current during linear sweep measurement, F is the Faraday constant (96485 C mol^{-1}) and n is 4 of electron transfer number for oxygen reduction. N_A is Avogadro's constant, and $ECSA$ is electrochemically active surface area.

Reversible nitrite poisoning experiment

To determine the active sites, it is necessary to perform a series of experiments with the catalyst. In the range of 0.4~0.3V (vs. RHE), charge stripping will occur in the buffer solution of the sample, and the nitrite ligand may be converted to the nitroso ligand during the cycle. After the reaction, charge stripping was carried out again in the buffer solution, and the sample was reduced to Fe-N₄ structure.

A 0.5 M acetate buffer at pH 5.2 was used as an electrolyte to improve reproducibility because the reduction of nitrite was sufficiently easy at this pH, while the nitrite anion was sufficiently stable. The reversible nitrite poisoning process was carried out according to Kucernak et al³.

Supplementary Figures and Tables

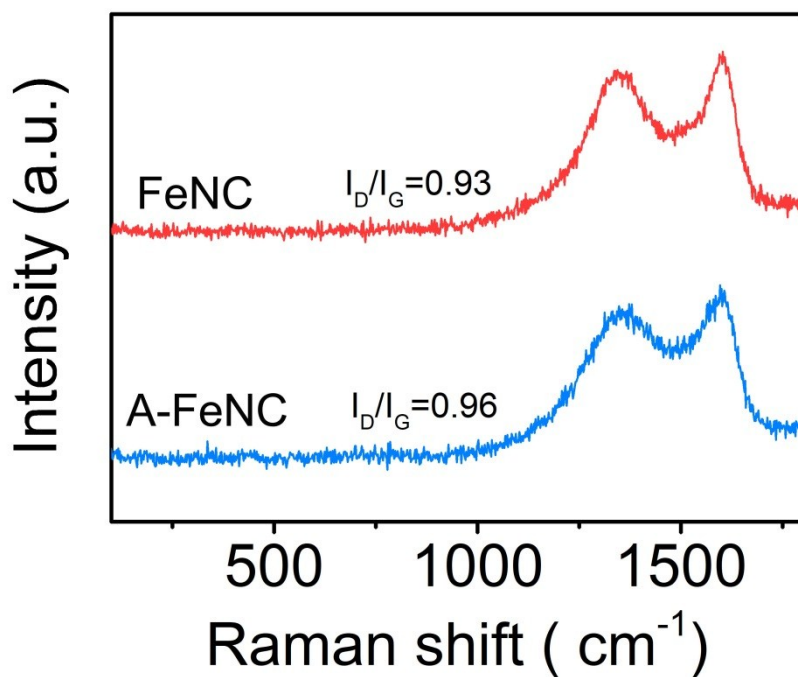


Figure S1 Raman spectra of FeNC and A-FeNC.

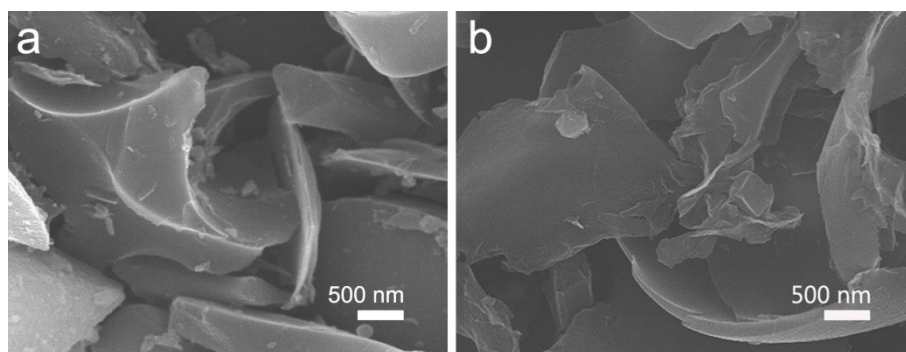


Figure S2 SEM of A-FeNC (a) and FeNC (b).

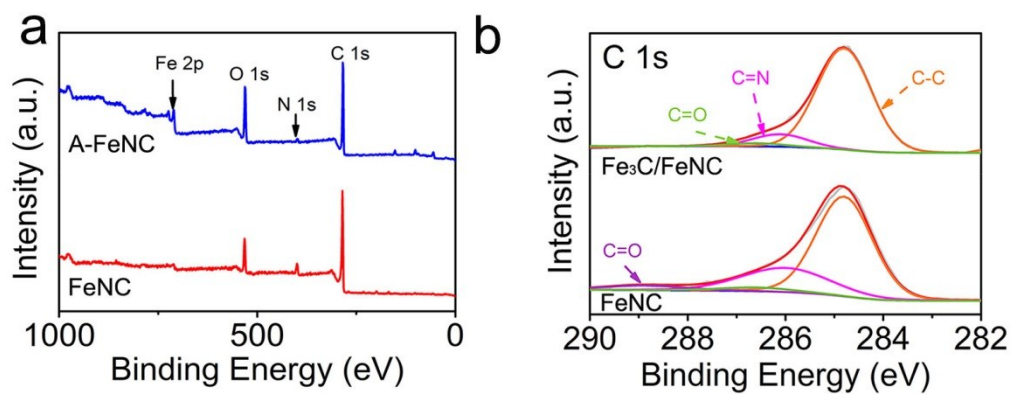


Figure S3. (a). Wide band XPS survey of FeNC and Fe₃C/FeNC. (b) High resolution C1s of A-FeNC

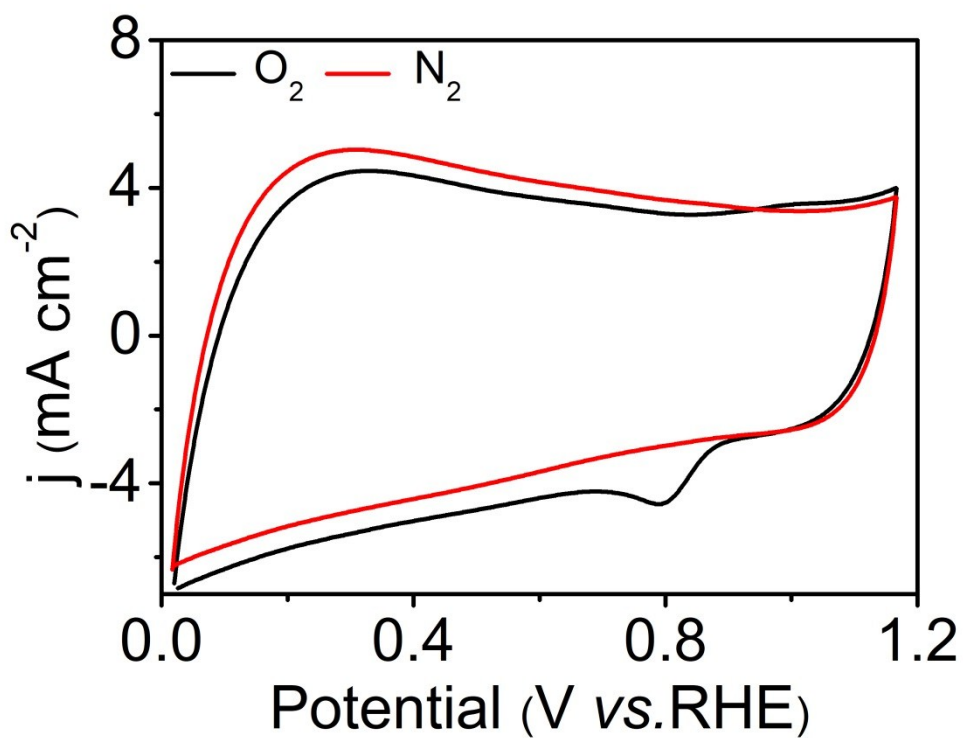


Figure S4. CV curves of A-FeNC in O₂ (black line) or N₂ (red line) saturated 0.1 M KOH electrolyte

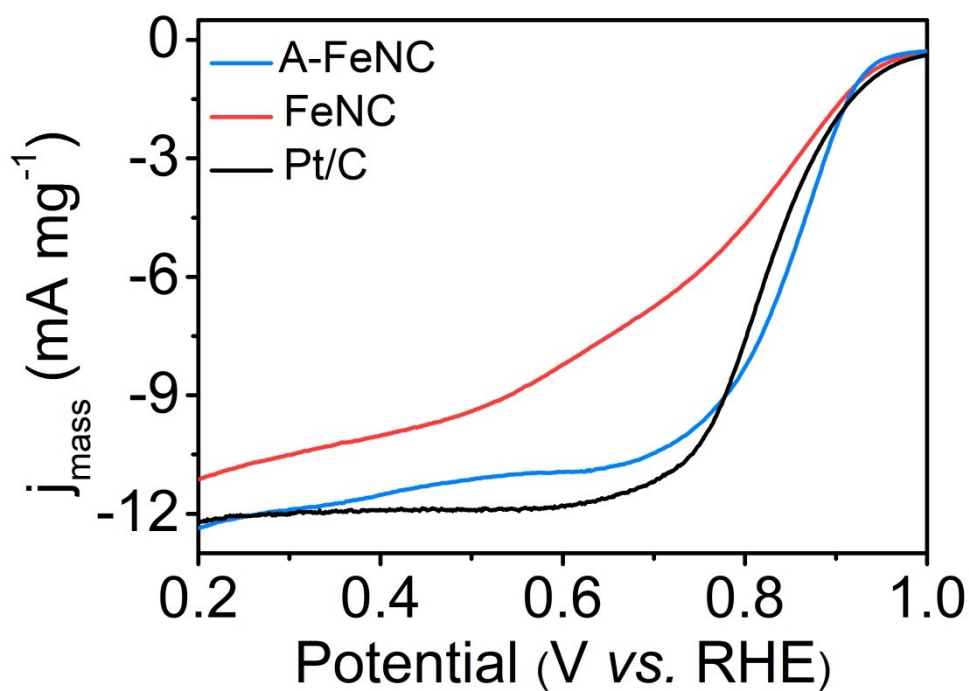


Figure S5. The mass activity of A-FeNC, FeNC and Pt/C.

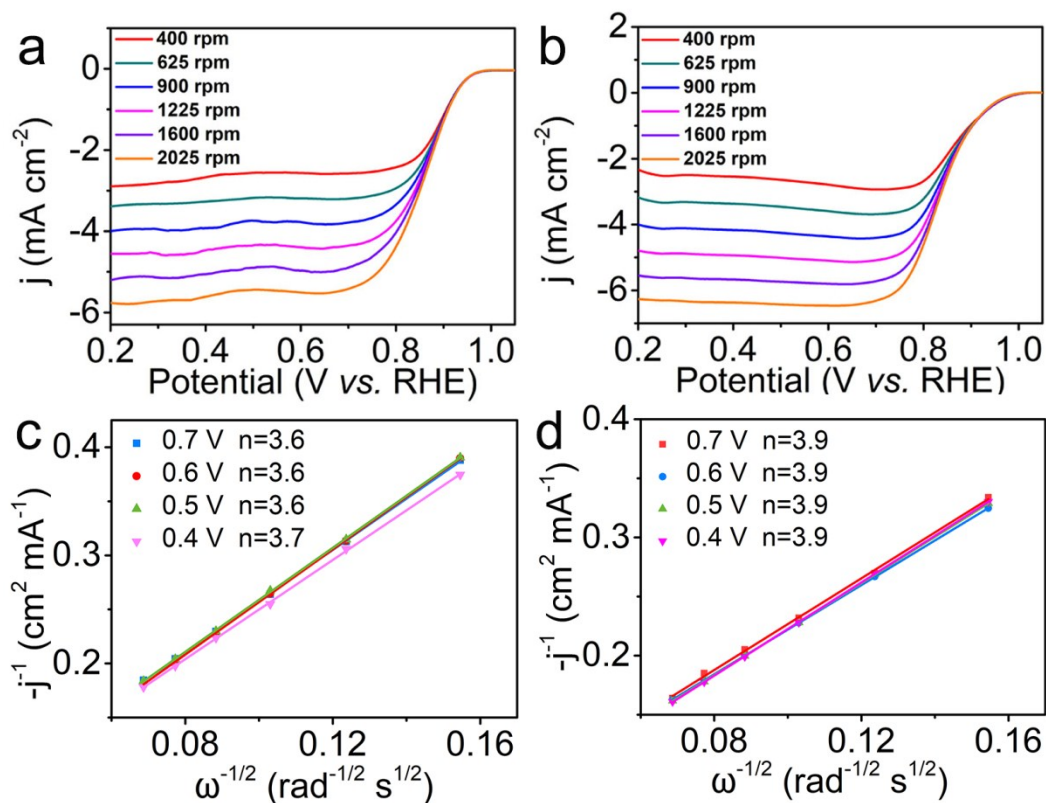


Figure S6. RDE polarization curves of (a) A-FeNC and (b) Pt/C with different rotation rates in O₂-saturated 0.1 M KOH solution at a scan rate of 10 mV s⁻¹. Koutecky-Levich plots of (c) A-FeNC and (d) Pt/C at different potentials

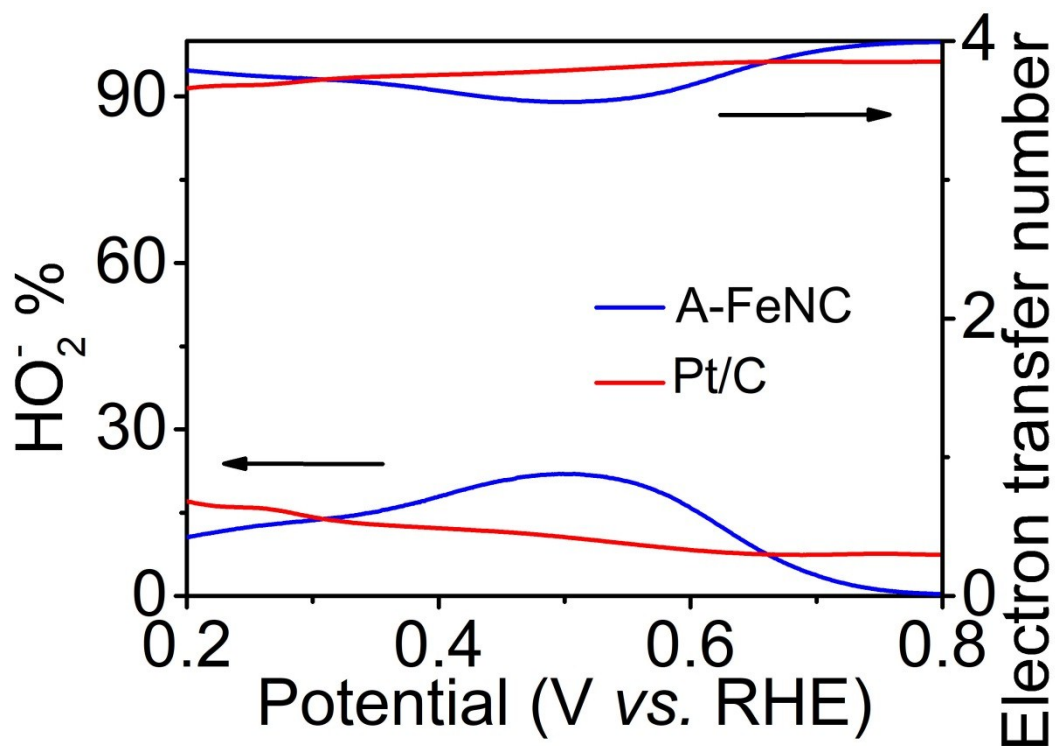


Figure S7. HO₂⁻ yield (left) and Electron transfer number (n) (right) vs. potential of A-FeNC with the RRDE test at 1600 rpm

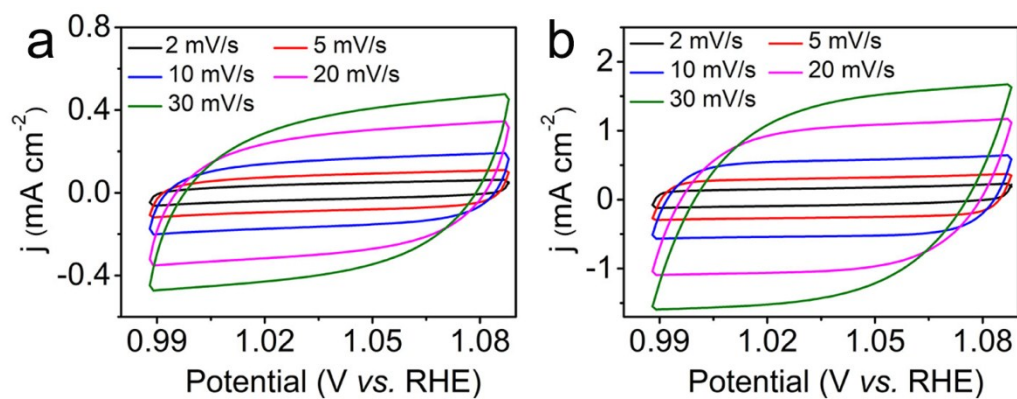


Figure S8. (a) The cycle voltammetry with different scan rate of FeNC and (b) A-FeNC

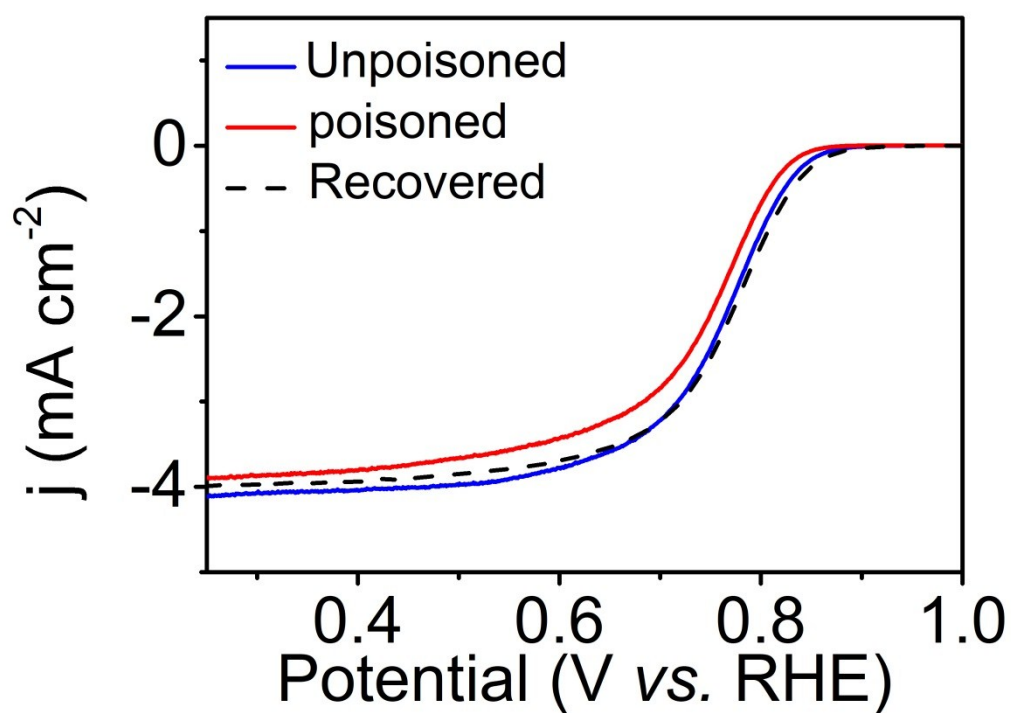


Figure S9. ORR performance of catalyst layer before, during and after nitrite adsorption

Table S1. Mössbauer parameters of A-FeNC. Isomer shift (IS), quadrupole splitting (QS), hyperfine field (HF) and relative spectral area % of each component

Component	IS (mm s ⁻¹)	QS (mm s ⁻¹)	HF (T)	Area(%)
Doublet	0.20	0.73	-	41.6
sextet	0.21	-0.03	20.70	58.4

Supplementary references

1. Q. Cheng, S. Han, K. Mao, C. Chen, L. Yang, Z. Zou, M. Gu, Z. Hu and H. Yang, *Nano Energy*, 2018, **52**, 485-493.
2. S. J. Kim, J. Mahmood, C. Kim, G. F. Han, S. W. Kim, S. M. Jung, G. Zhu, J. J. De Yoreo, G. Kim and J. B. Baek, *Journal of the American Chemical Society*, 2018, **140**, 1737-1742.
3. D. Malko, A. Kucernak and T. Lopes, *Nature Communications*, 2016, **7**, 13285.