

Supporting Information

Boosting activity toward oxygen reduction reaction of a hyper-crosslinked FeCu bimetal nanocatalyst *via* mimicking Cytochrome c oxidase

Kunpeng Song, Wenwen Yang, Jinfeng Wei, Fang Liao,*

College of Chemistry and Chemical Engineering, Chemical Synthesis and Pollution Control

Key Laboratory of Sichuan Province, China West Normal University, Shida Road, Nanchong

637009, China

**Corresponding author.*

E-mail address: song19880405@cwnu.edu.cn

Chemicals and materials

The synthesis of porphyrin and iron porphyrin:

According to literature, tetraphenyl porphyrin (TPP) was synthesized as follows: 36 mL of propionic acid and benzaldehyde (0.90 g) were added to a flask, heated to 125 °C, and then 0.50 g of pyrrole was added and refluxed for 5 hours. The mixture was cooled to room temperature, and 20 mL of anhydrous ethanol was added and left to stand for 12 hours. The resulting product was washed three times with deionized water and anhydrous ethanol, and dried at 60 °C. The obtained sample was named TPP.

0.30 g of TPP was dissolved in 10 mL of N, N-dimethylformamide by ultrasonication, and then 0.80 g of FeCl₃ was added and refluxed at 135 °C for 2 hours. After cooling to room temperature, 10 mL of ethanol was added and left to stand for 12 hours. The resulting purple powder was filtered, washed, and dried under vacuum for 12 hours, and was labeled as FeTPP.

The synthesis of iron porphyrin polymer:

The synthesis of hyper-crosslinked Fe polymers (HCP-Fe)

A mixed solution containing a certain amount FeTPP, 0.3 g 1, 3, 5-triphenyl benzene, 0.60 g FDA and 9 mL DCE was prepared, then anhydrous FeCl₃ (1.95 g) was added under various stirring. The resulting mixture was heated at 45 °C for 5 hours and then raised to 80 °C and for 19 h. The solid material obtained after the reaction was extracted with methanol and dried under a vacuum for 12 hours. The resulting product was named HCP-Fe.

The synthesis of Fe@NC nanocatalyst

A certain amount HCP-Fe was placed in a quartz tube and heated to 1000 °C at a rate of 5 °C·min⁻¹ under an N₂ atmosphere. The catalyst obtained after 2 h and cooling to room temperature, the sample was labeled as (1000-Fe@NC) Fe@NC.

The synthesis of copper phthalocyanine polymer:

The synthesis of hyper-crosslinked Cu polymers (HCP-Cu)

A mixed solution containing a certain amount CuPc, 0.3 g 1, 3, 5-triphenyl

benzene, 0.60 g FDA and 9 mL 1, 2-dichloroethan was prepared, then anhydrous FeCl₃ (1.95 g) was added under various stirring. The resulting mixture was heated at 45 °C for 5 hours and then raised to 80 °C and for 19 h. The solid material obtained after the reaction was extracted with methanol and dried under a vacuum for 12 hours. The resulting product was named HCP-Cu.

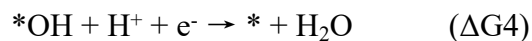
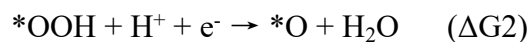
The synthesis of Cu@NC nanocatalyst

A certain amount HCP-Cu was placed in a quartz tube and heated to 1000 °C at a rate of 5 °C·min⁻¹ under an N₂ atmosphere. The catalyst obtained after 2 h and cooling to room temperature, the sample was labeled as Cu@NC (1000-Cu@NC).

Computational methods

In the framework of the Vienna ab initio Simulation Package (VASP), all the calculations are carried out using the projected enhanced wave method and based on density functional theory (DFT)^[1]. The electron exchange-correlation interaction is parameterized by the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)^[2, 3]. In this study, spin polarization effect was considered. The Brillouin region is sampled by a Γ centered K-grid with a resolution of $2\pi \times 0.04 \text{ \AA}^{-1}$ for geometric optimization. The plane wave energy cutoff is set to 450 eV, and the residual force and energy tolerance of each atom during structural relaxation are set to 0.02 eV·Å⁻¹ and 10⁻⁵ eV, respectively. To avoid interaction between adjacent configurations, A vacuum space of 20 Å is applied. In addition, the van der Waals interaction (DFT-D3 method with Becke-Jonson damping) is incorporated^[4]. In order to correct the artificial electron self-interaction, the DFT + U method is applied to the 3d orbits of Fe (U = 5 eV) and Cu (U = 6 eV)^[5, 6]. The results are pre-processed and post-processed using VASPKIT code^[7]. Structural visualization is performed by VESTA software^[8]. The ORR process was evaluated using the computational hydrogen electrode (CHE) model developed by Norskov and co-workers^[9]. The detailed pathway for the 4 e⁻ mechanism in ORR was adopted in this work as the following four steps:





where the * stands for the catalytic active site on the surface and the $\Delta\text{G}_1 \sim \Delta\text{G}_4$ represent the Gibbs free energies of the four reaction steps. The ΔG can be calculated by using the following equation:

$$\Delta\text{G} = \Delta\text{E} + \Delta\text{ZPE} - \text{T}\Delta\text{S}$$

where the ΔE was obtained from the DFT energy of structural relaxation. ΔZPE and ΔS were the change of zero-point energies (ZPE) and entropy. The temperature (T) and applied potential was set to 298.15 K. The DFT energy of H_2O and H_2 were calculated in a boxes of $15 \text{ \AA} \times 15 \text{ \AA} \times 15 \text{ \AA}$ with the gamma point only. The thermodynamic correction was carried out by using the VASPKIT code.

$$\text{G}(\text{H}^+) + (\text{e}^-) = 1/2 \text{G}(\text{H}_2)(\text{g})$$

The theoretical overpotential (η) of catalysts are defined in :

$$\eta = \max(\Delta\text{G}_1, \Delta\text{G}_2, \Delta\text{G}_3, \Delta\text{G}_4)/\text{e} - 1.23 \text{ eV}$$

The DFT energy (E), zero-point energy (ZPE) and entropy contribution (-TS) correction of gas phase are as Table S1:

Table S1. The DFT energy (E), zero-point energy (ZPE), entropy contribution (-TS) and free energy (G) of H_2O , H_2 and O_2 .

Species	E_{DFT}	ZPE	-TS	G
$\text{O}_2 (\text{g})$	-	-	-	-9.91924
$\text{H}_2 (\text{g})$	-6.76908	0.267244	-0.403068	-6.9049
$\text{H}_2\text{O} (\text{l})$	-14.2191	0.566972	-0.669862	-14.322

The DFT energy (E), zero-point energy (ZPE) and entropy contribution (-TS) correction of adsorbed species were listed in Table S2-S3.

Table S2. The DFT energy (E), zero-point energy (ZPE) and entropy contribution (-TS) correction of adsorbed species for FeCu@NC.

FeCu@NC	E _{DFT}	ZPE	-TS
Slab	-522.146	-	-
*OH	-536.372	0.422992	0.241577
*O	-527.257	0.047127	0.06511
*OOH	-532.183	0.320182	0.083003

Table S3. The DFT energy (E), zero-point energy (ZPE) and entropy contribution (-TS) correction of adsorbed species for FeN₄.

FeN ₄	E _{DFT}	ZPE	-TS
Slab	-336.085	-	-
*OH	-350.479	0.423297	-0.226605
*O	-340.947	0.060635	-0.079228
*OOH	-346.583	0.316232	-0.103196

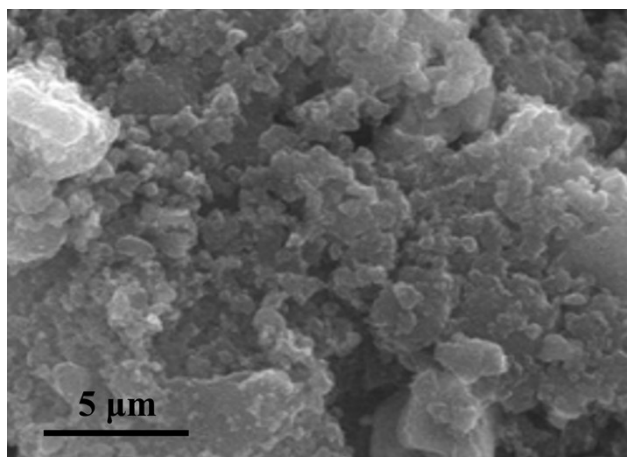


Figure S1. TEM image of Fe@NC.

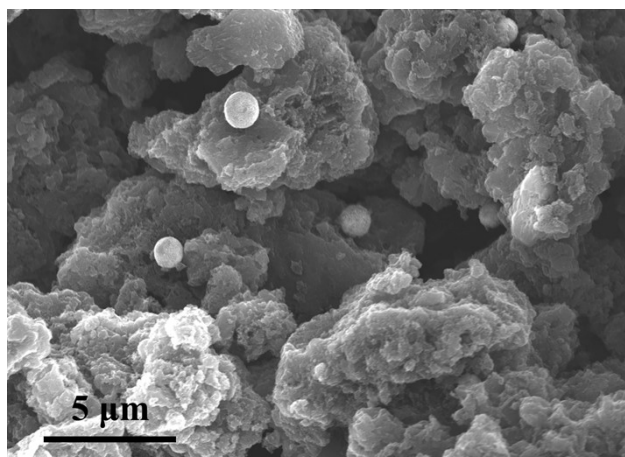


Figure S2. TEM image of Cu@NC.

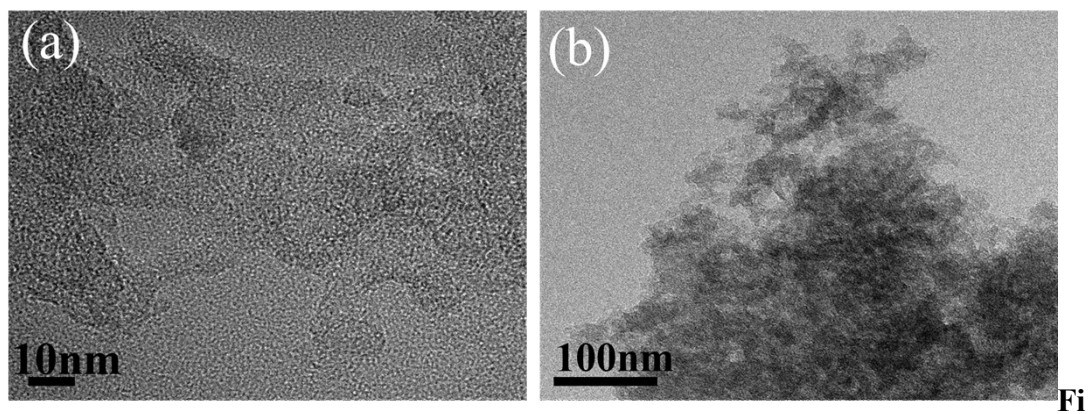


Figure S3. TEM images of FeCu@NC (a, b).

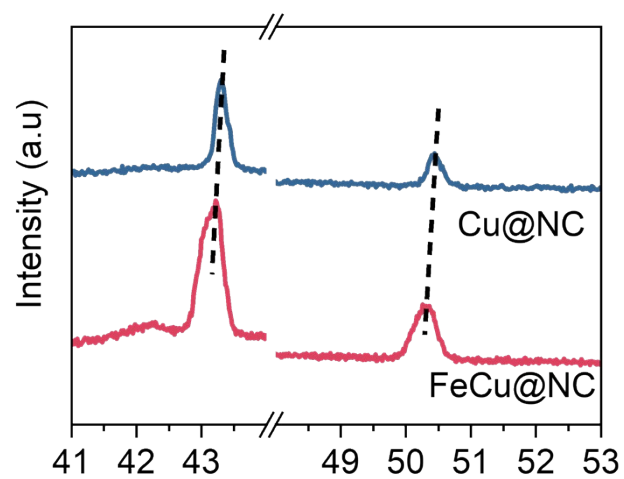


Figure S4. Partially enlarged XRD patterns of FeCu@NC and Cu@NC catalysts.

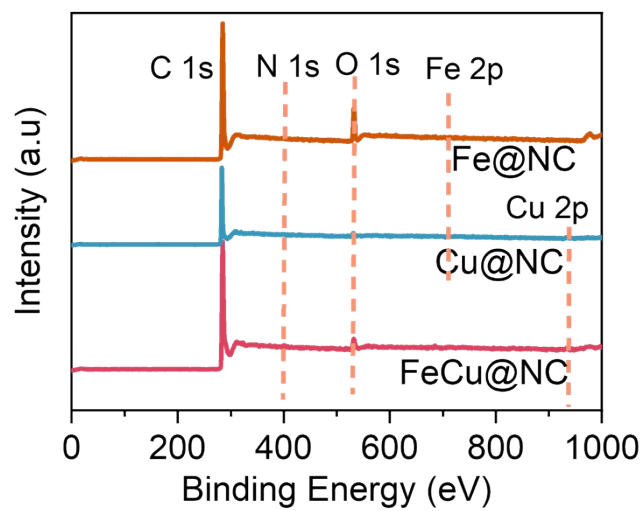


Figure S5. XPS survey scan of Fe@NC, Cu@NC and FeCu@NC.

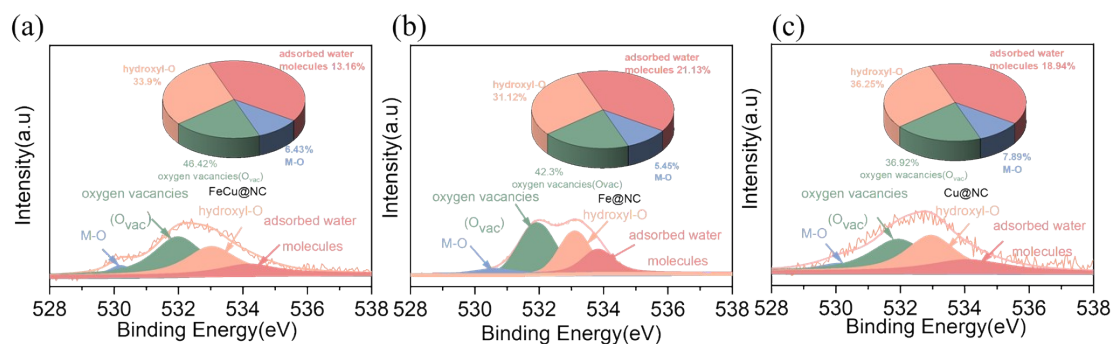


Figure S6. Percentage content (%) of O species in FeCu@NC (a), Fe@NC (b) and Cu@NC (c) electrocatalysts obtained from O 1s XPS spectral analysis.

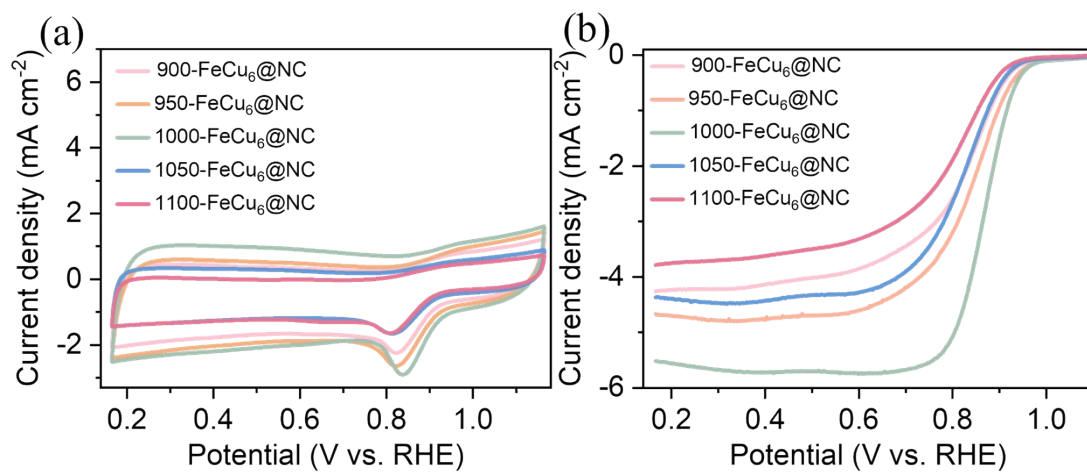


Figure S7. CV curves (a) and LSV curves (b) of 900-FeCu₆@NC, 950-FeCu₆@NC, 1000-FeCu₆@NC, 1050-FeCu₆@NC and 1100-FeCu₆@NC.

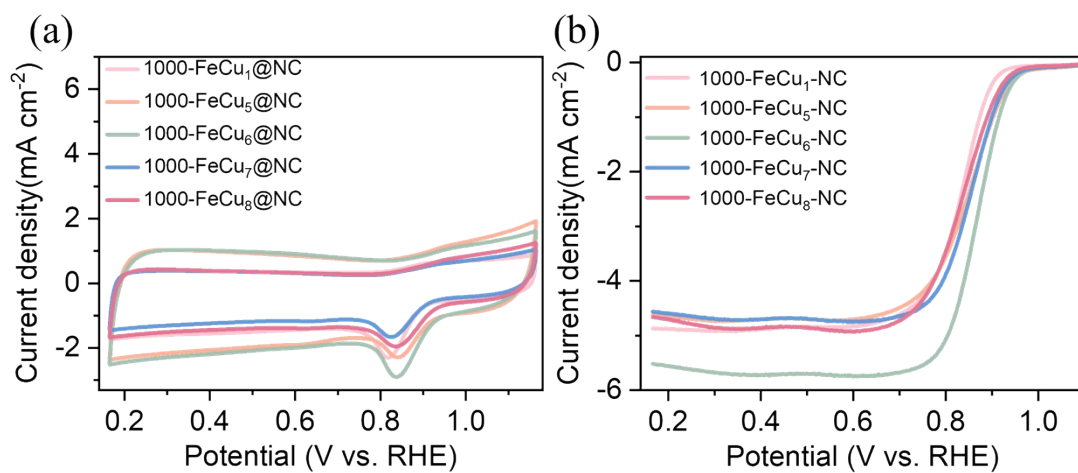


Figure S8. CV curves (a) and LSV curves (b) of 1000-FeCu₁@NC, 1000-FeCu₅@NC, 1000-FeCu₆@NC, 1000-FeCu₇@NC and 1000-FeCu₈@NC.

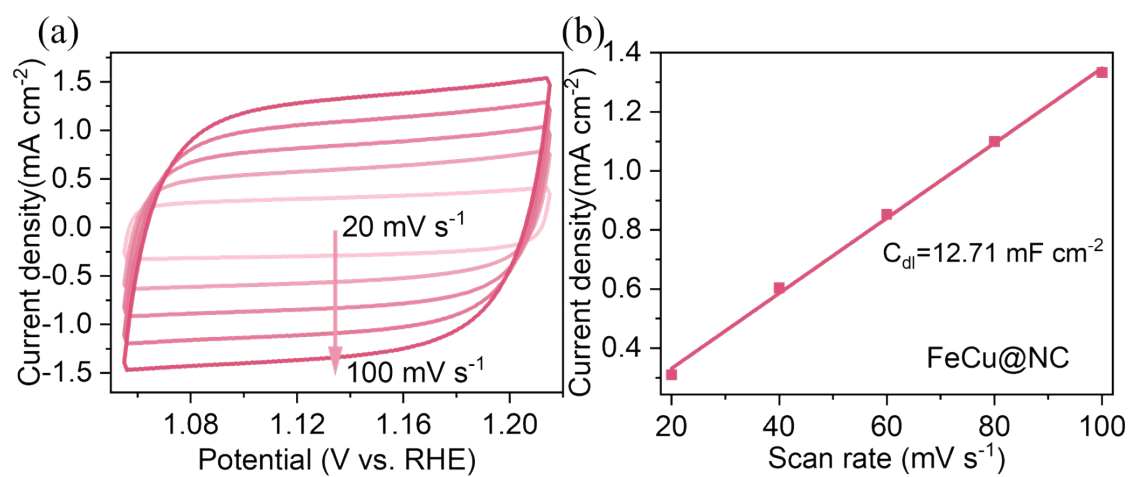


Figure S9. The cyclic voltammogram (a) and the double-layer capacitance value (b) of FeCu@NC at scan rates ranging from 20 mV·s⁻¹ to 100 mV·s⁻¹.

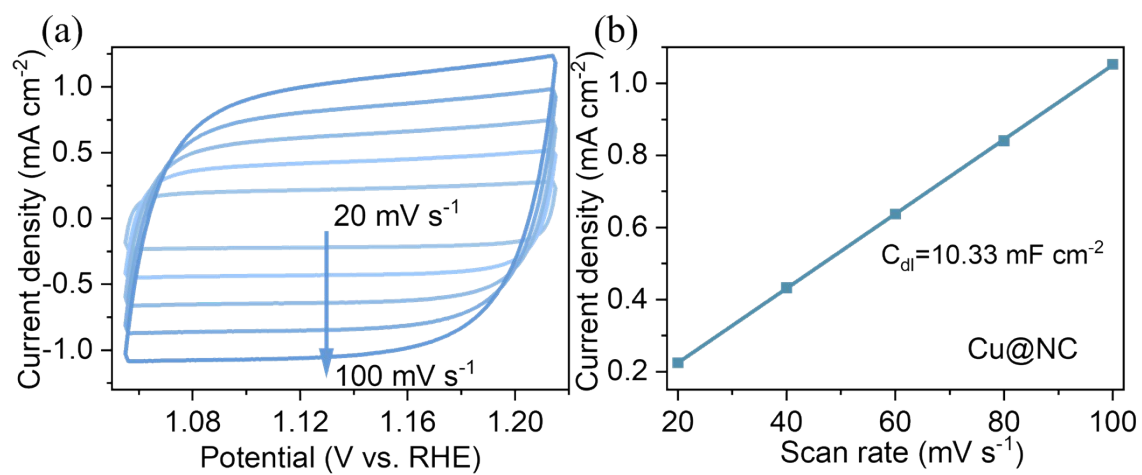


Figure S10. The cyclic voltammogram (a) and the double-layer capacitance value (b) of Cu@NC at scan rates ranging from 20 mV·s⁻¹ to 100 mV·s⁻¹.

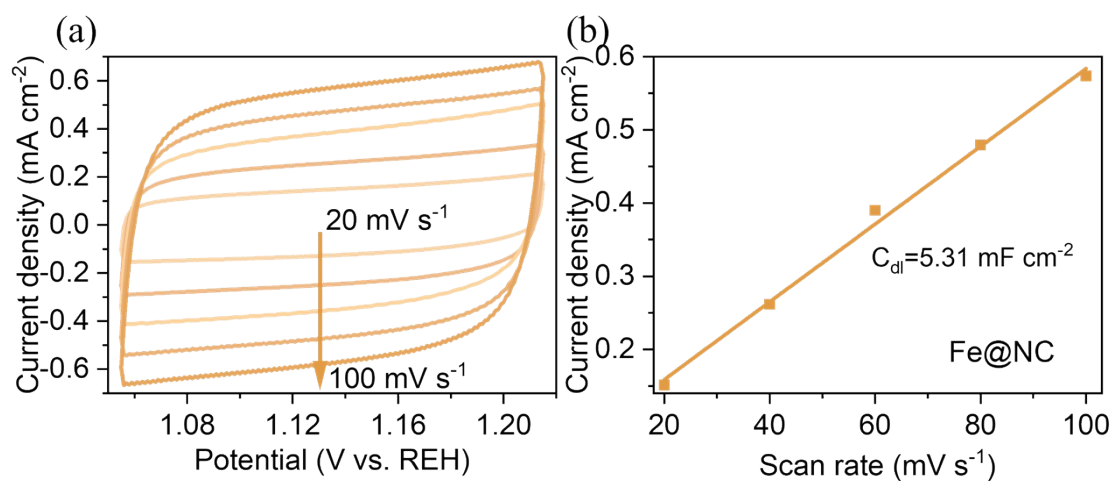


Figure S11. The cyclic voltammogram (a) and the double-layer capacitance value (b) of Fe@NC at scan rates ranging from 20 mV·s⁻¹ to 100 mV·s⁻¹.

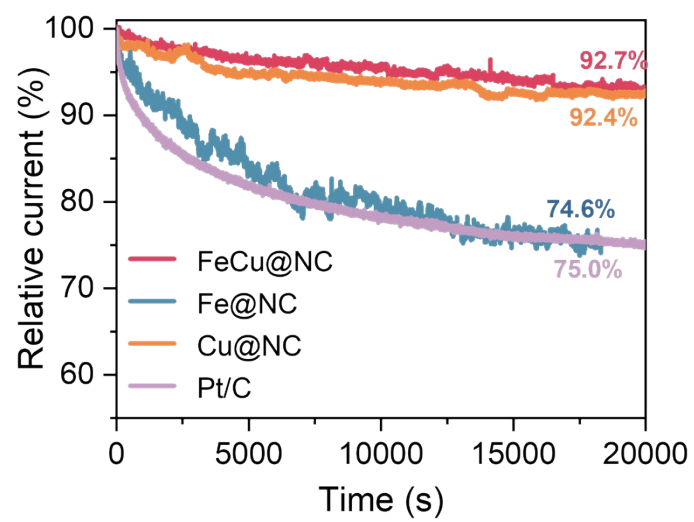


Figure S12. Current-Time stability test for FeCu@NC, Fe@NC, Cu@NC and Pt/C.

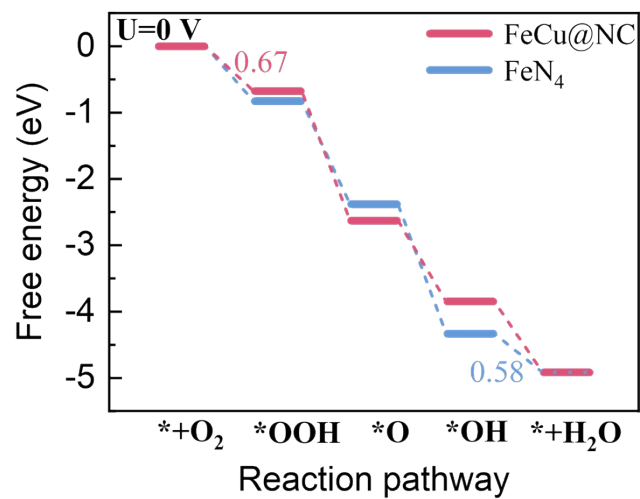


Figure S13. Free energy diagrams for the 4 e^- ORR over FeN₄ and FeCu@NC at different discharge voltages of $U = 0$ V.

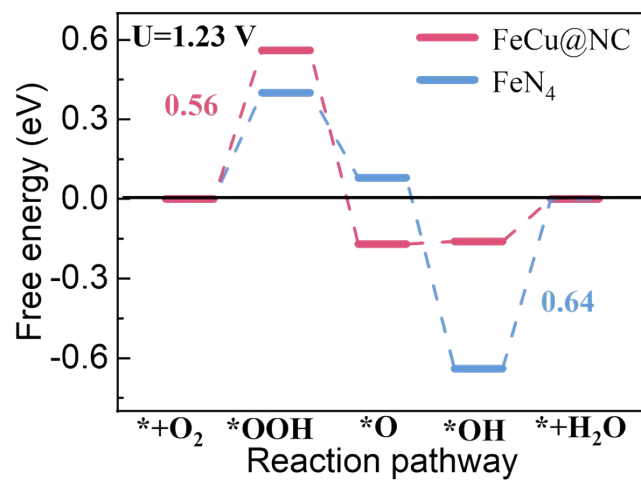


Figure S14. Free energy diagrams for the 4 e^- ORR over FeN₄ and FeCu@NC at different discharge voltages of $U = 1.23$ V.

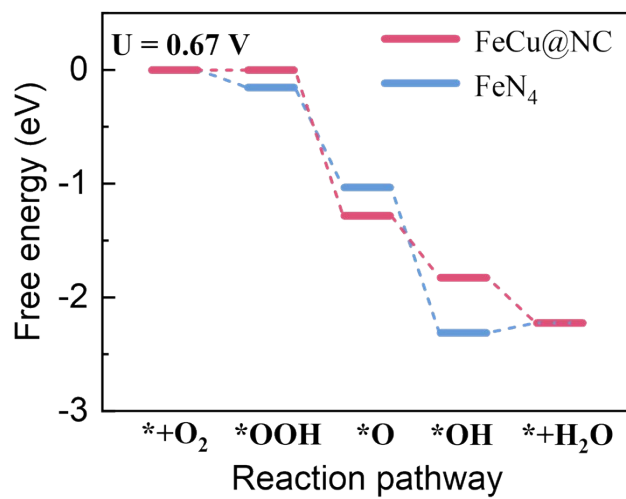


Figure S15. Free energy diagrams for the 4e⁻ ORR over FeN₄ and FeCu@NC at different discharge voltages of U = 0.67 V.

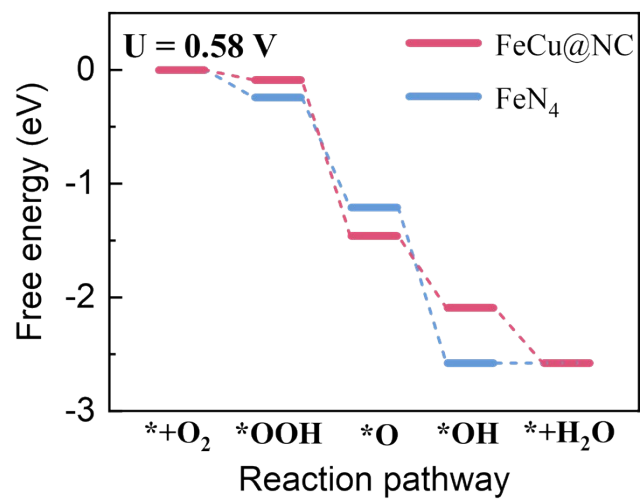


Figure S16. Free energy diagrams for the 4e⁻ ORR over FeN₄ and FeCu@NC at different discharge voltages of U = 0.58V.

Table S4. Specific surface area and pore structure information of FeCu@NC, Fe@NC and Cu@NC.

Catalysts	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	V_{pore} ($\text{cm}^3\cdot\text{g}^{-1}$)	W_{pore} (nm)
FeCu@NC	970.023	0.904	3.837
Fe@NC	425.642	0.651	3.821
Cu@NC	1312.77	1.154	7.304

Table S5. Relative ratios of the deconvoluted N species of N 1s spectra from catalysts.

Catalysts	Pyridinic-N	Pyrrole-N	Graphitic-N	Oxidized-N
Cu@NC	10.88%	20.26%	31.82%	37.04%
FeCu@NC	14.88%	17.29%	50.17%	18.06%
Fe@NC	21.16%	27.72%	31.42%	19.70%

Table S6. Relative ratios of the deconvoluted O species of O 1s spectra from catalysts.

Catalysts	M-O	Oxygen vacancies (O _{vac})	Hydroxyl-O	adsorbed water molecules
Cu@NC	7.89%	36.92%	36.25%	18.94%
FeCu@NC	6.43%	46.42%	33.90%	13.16%
Fe@NC	5.45%	42.30%	31.12%	21.13%

Table S7. Comparison of ORR performance between FeCu@NC and other reported nonprecious metal electrocatalysts in 0.1 M KOH.

Catalysts	E_0 (V vs RHE)	$E_{1/2}$ (V vs RHE)	J_L (mA·cm ⁻²)	$\Delta E_{1/2}$ (mV)	Reference
FeCu@NC	1.00	0.87	5.52	5	This work
Pt/C	0.97	0.83	5.38	34	
Cu-Fe@CNTs/NC	0.98	0.87	5.3	15	[10]
Fe ₃ O ₄ /CuNCs/ZnN _x -PHNC	0.866	0.832	5.69	2	[11]
Cu SA/g-C ₃ N ₄	0.93	0.85	5.0	12	[12]
FeCo-NSC	0.94	0.86	5.26	19	[13]
NiFe-DG	0.97	0.86	5.7	10	[14]
(Fe, Mo)-N/C	0.845	0.674	5.33	67	[15]
Fe-NMCNF	0.59	0.51	2.6	15	[16]
FePc-C	0.95	0.85	5.01	11	[17]
Fe-Fe-N _x /CNTs	0.93	0.87	5.31	6	[18]
GO-ZIF-8	0.88	0.75	5.06	18	[19]

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