

Supporting Information for

MOF-Derived Co and Fe Species Loaded on N-Doped Carbon Networks as Efficient Oxygen Electrocatalysts for Zn-Air Batteries

Yuanyuan Xue¹, Yibo Guo¹, Qinming Zhang¹, Zhaojun Xie^{1,*}, Jinping Wei¹, and Zhen Zhou^{2,*}

¹ School of Materials Science and Engineering, Institute of New Energy Material Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Renewable Energy Conversion and Storage Center (ReCast), Nankai University, Tianjin 300350, People's Republic of China

² School of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, People's Republic of China

*Corresponding authors. E-mail: zjxie@nankai.edu.cn (Zhaojun Xie), zhengzhou@zzu.edu.cn (Zhen Zhou)

Supplementary Figures and Tables

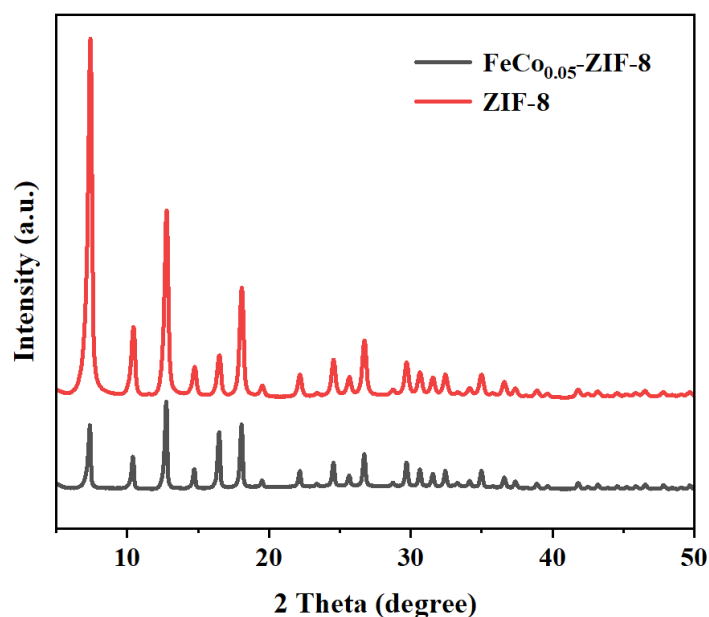


Fig. S1 XRD patterns of FeCo_{0.05}-ZIF-8 and ZIF-8

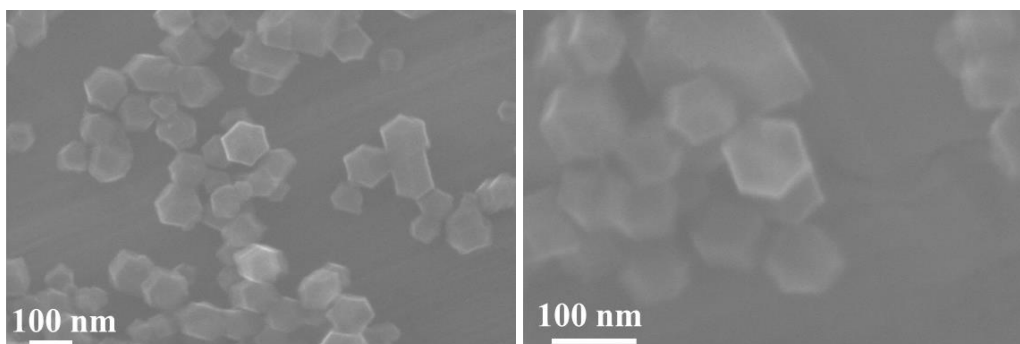


Fig. S2 SEM images of FeNC

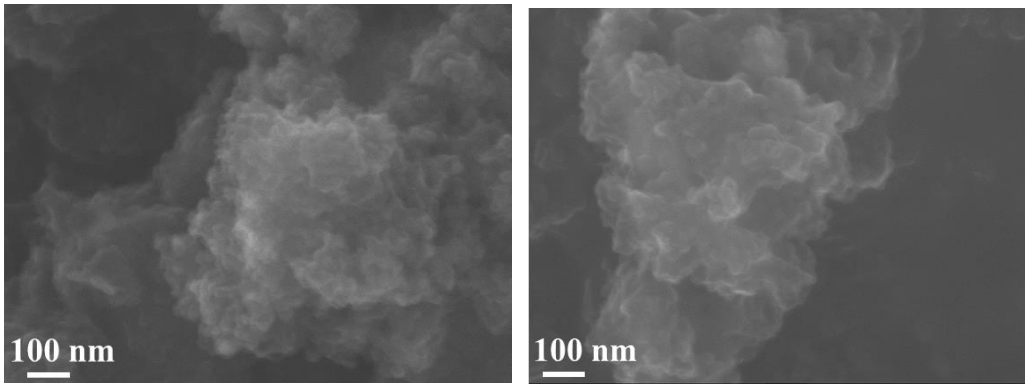


Fig. S3 SEM images of CoNP@NC

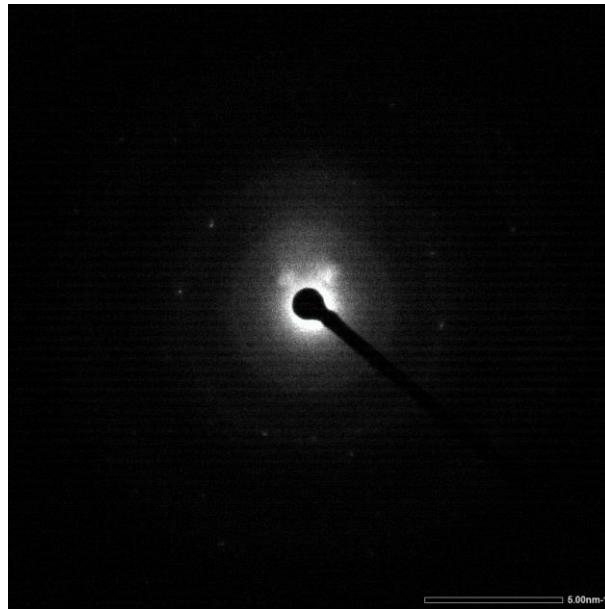


Fig. S4 SAED image of CoNP@FeNC-0.05

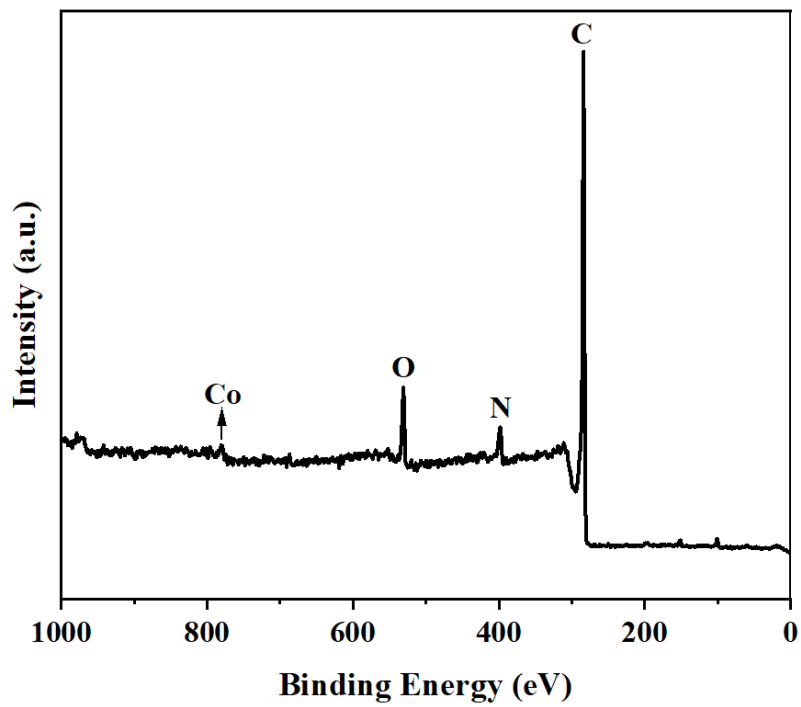


Fig. S5 XPS survey spectrum of CoNP@FeNC-0.05

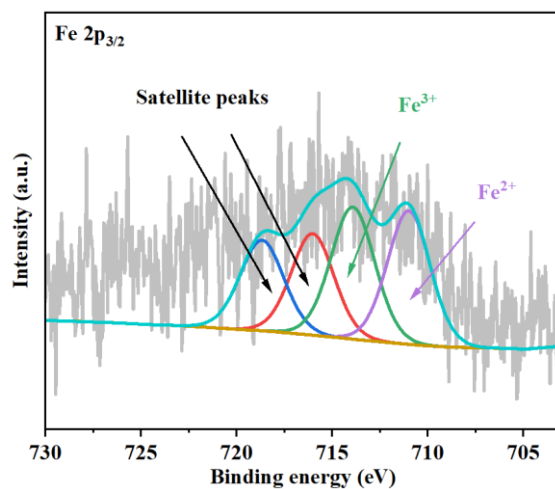


Fig. S6 High-resolution Fe 2p XPS of CoNP@FeNC-0.05

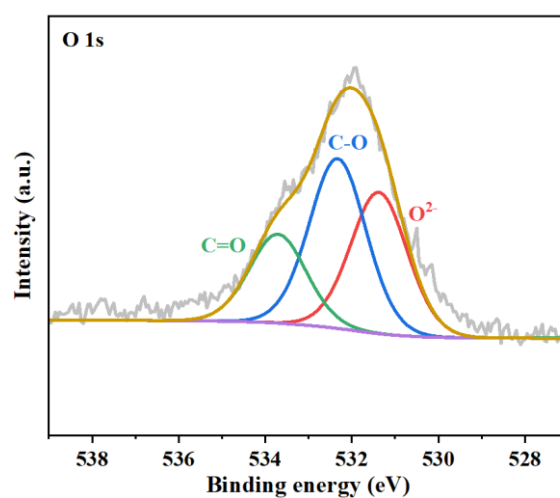


Fig. S7 High-resolution O 1s XPS of CoNP@FeNC-0.05

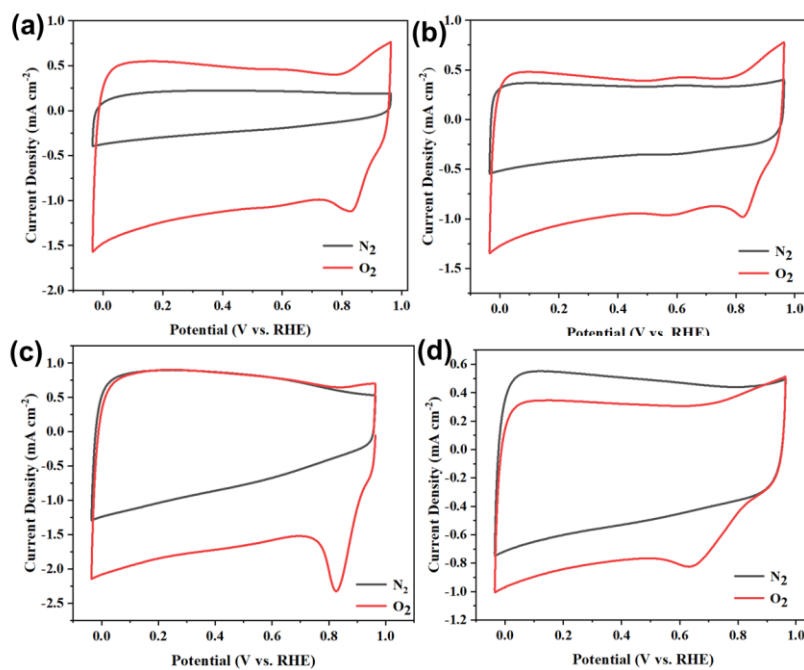


Fig. S8 CV curves of (a) CoNP@FeNC-0.05, (b) CoNP@NC, (c) FeNC, (d) NC under N₂ or O₂ saturated 0.1 M KOH for ORR

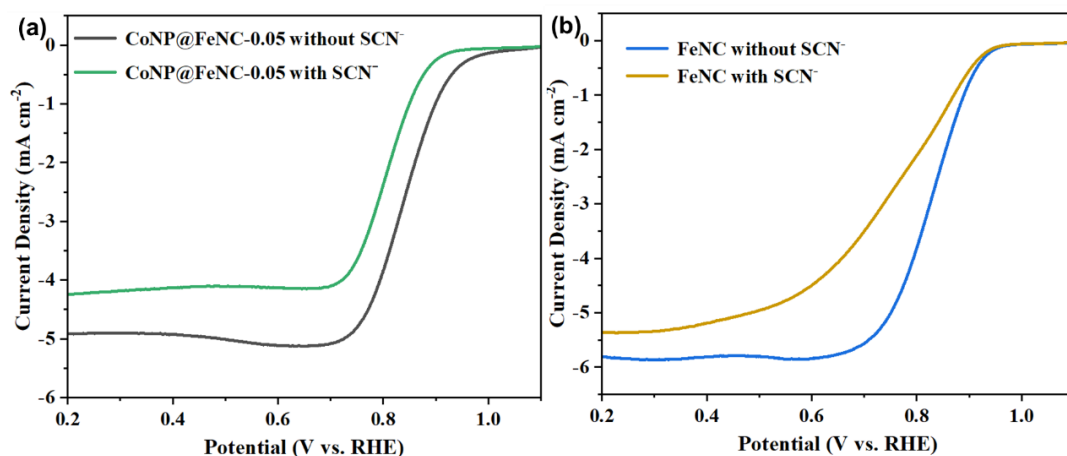


Fig. S9 LSV curves of catalysts for OER under 0.1 M KOH, measured before and after adding SCN^- (0.1 M)

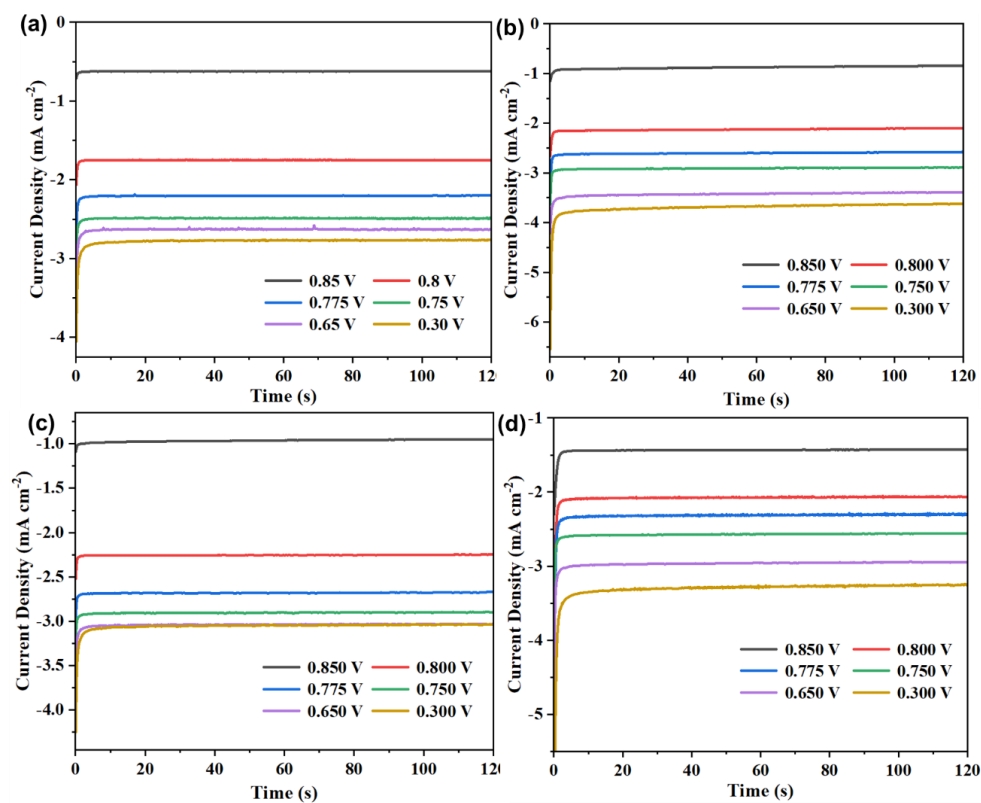


Fig. S10 The *i-t* curves of (a) CoNP@FeNC-0.05, (b) Pt/C, (c) CoNP@NC, and (d) FeNC, under 0.1 M KOH, with a rotation speed of 800 rpm

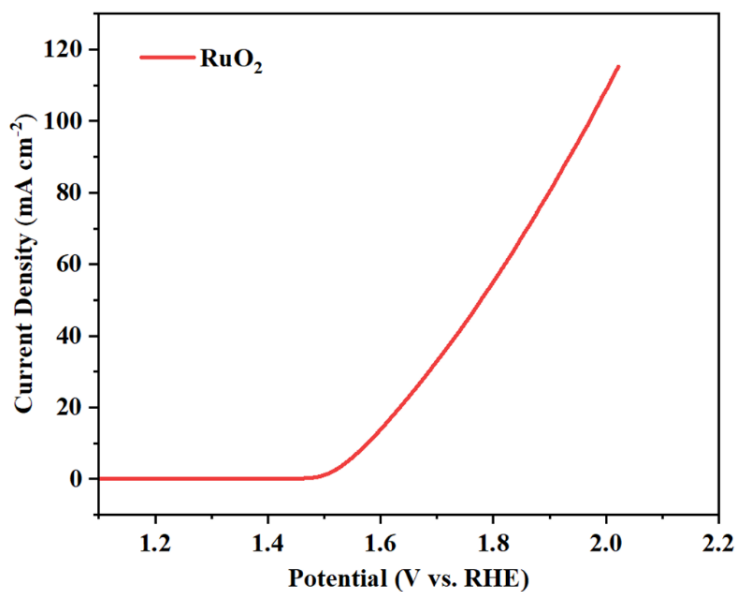


Fig. S11 LSV curve of RuO₂ catalyst for OER with a scan rate of 5 mV s⁻¹ under 1 M KOH, at 1600 rpm

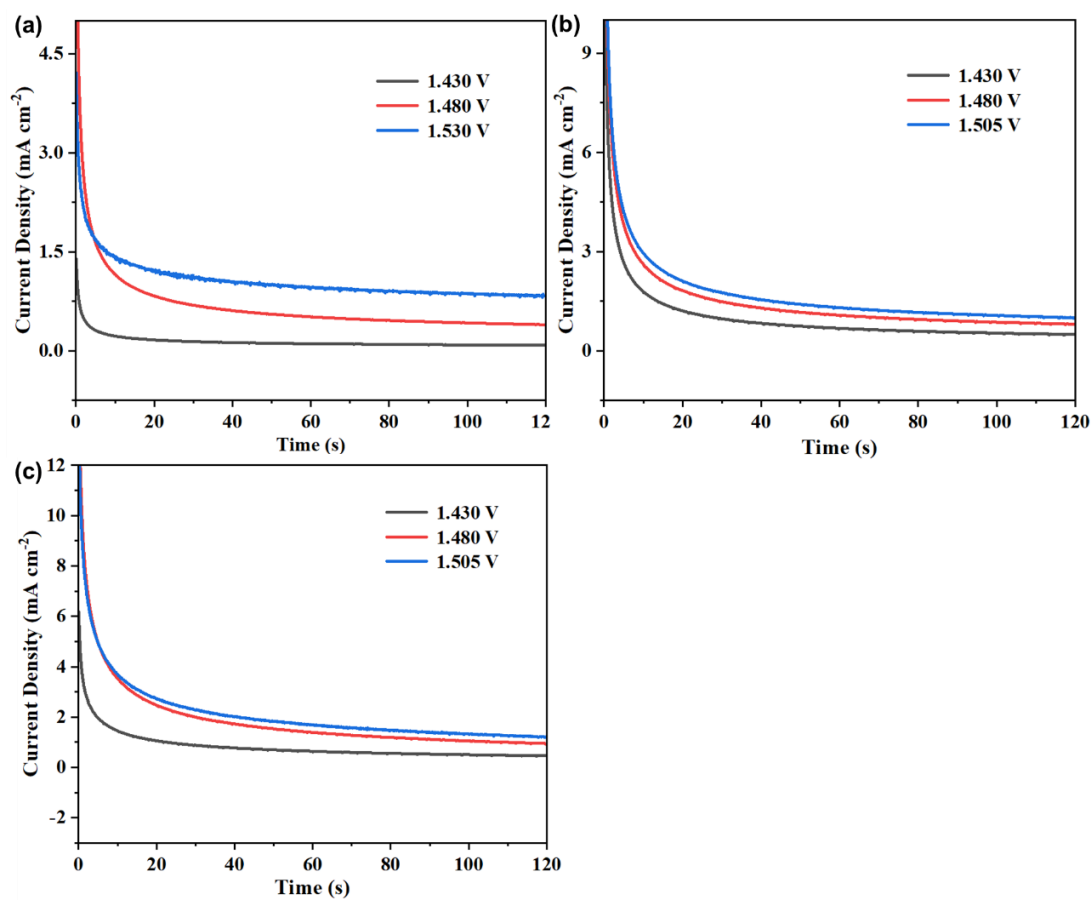


Fig. S12 The i-t curves of (a) CoNP@FeNC-0.05, (b) CoNP@NC, and (c) FeNC, under 1 M KOH, with a rotation speed of 800 rpm

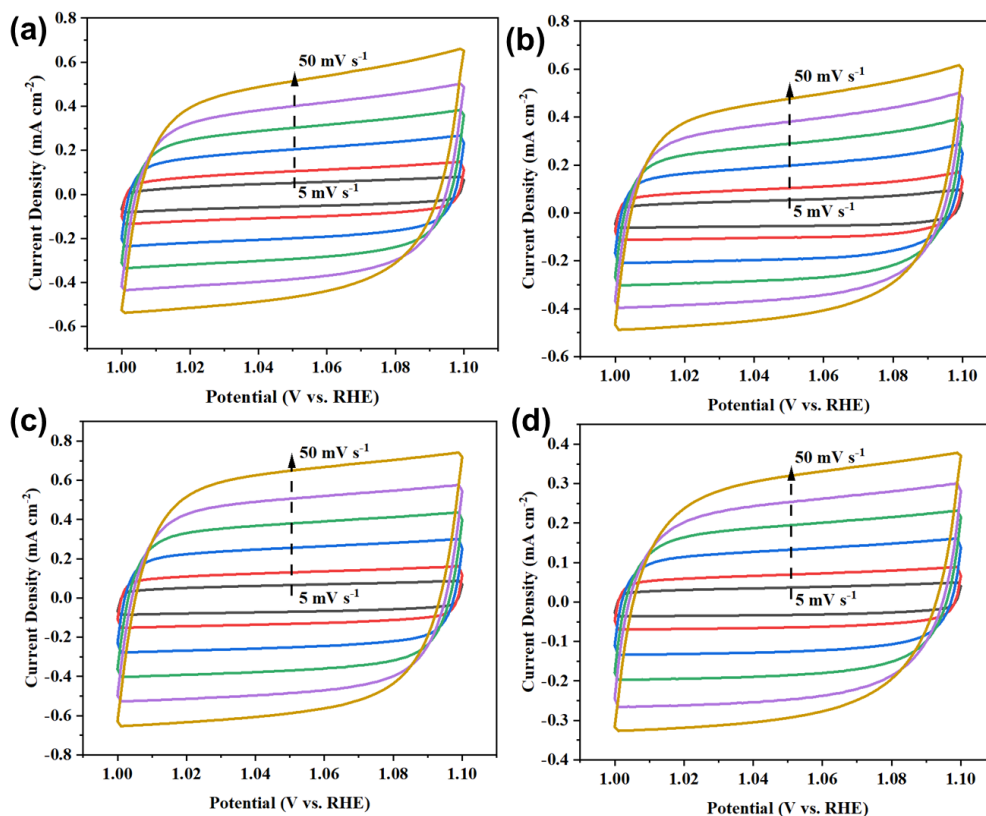


Fig. S13 CV curves at various scan rates within a potential window from 1.0 to 1.1 V vs. RHE without Faradaic processes: (a) CoNP@FeNC-0.05, (b) CoNP@NC, (c) FeNC, and (d) NC

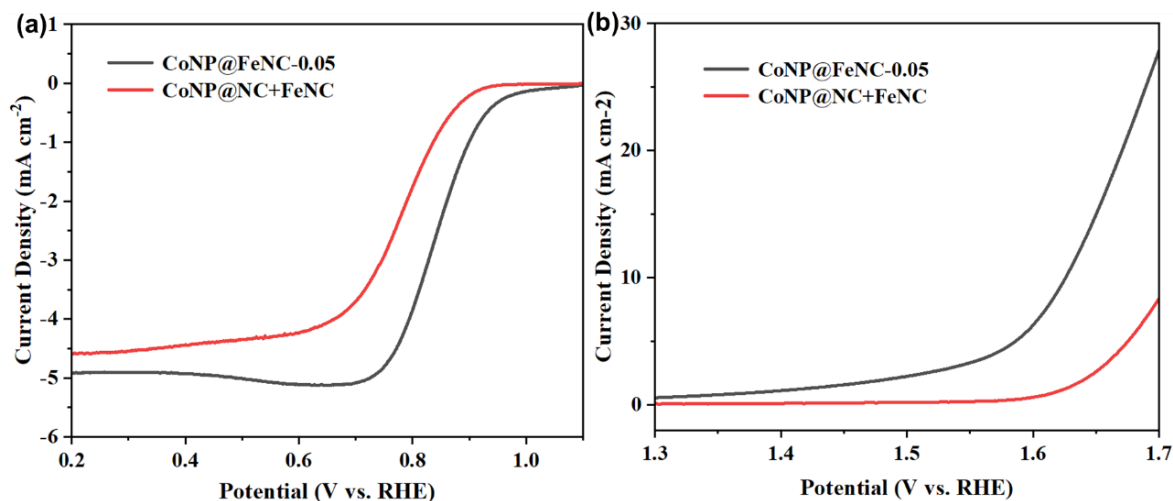


Fig. S14 (a) LSV curves of CoNP@FeNC-0.05 and CoNP@NC+FeNC for ORR under 0.1 M KOH. (b) LSV curves of CoNP@FeNC-0.05 and CoNP@NC+FeNC for OER under 1 M KOH

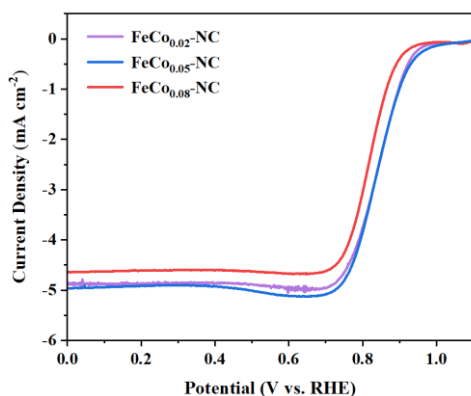


Fig. S15 LSV curves of CoNP@FeNC catalysts for ORR with a scan rate of 5 mV s⁻¹ under 0.1 M KOH, at 1600 rpm

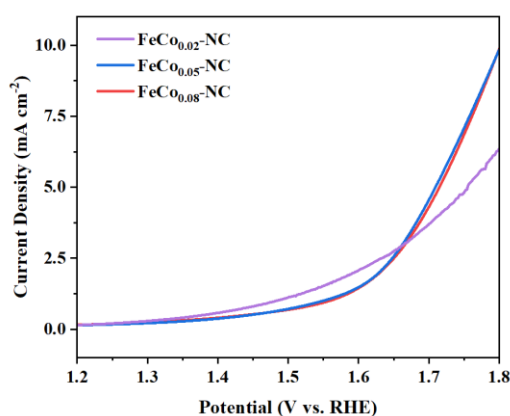


Fig. S16 LSV curves of CoNP@FeNC catalysts for OER with a scan rate of 5 mV s⁻¹ under 1 M KOH, at 1600 rpm

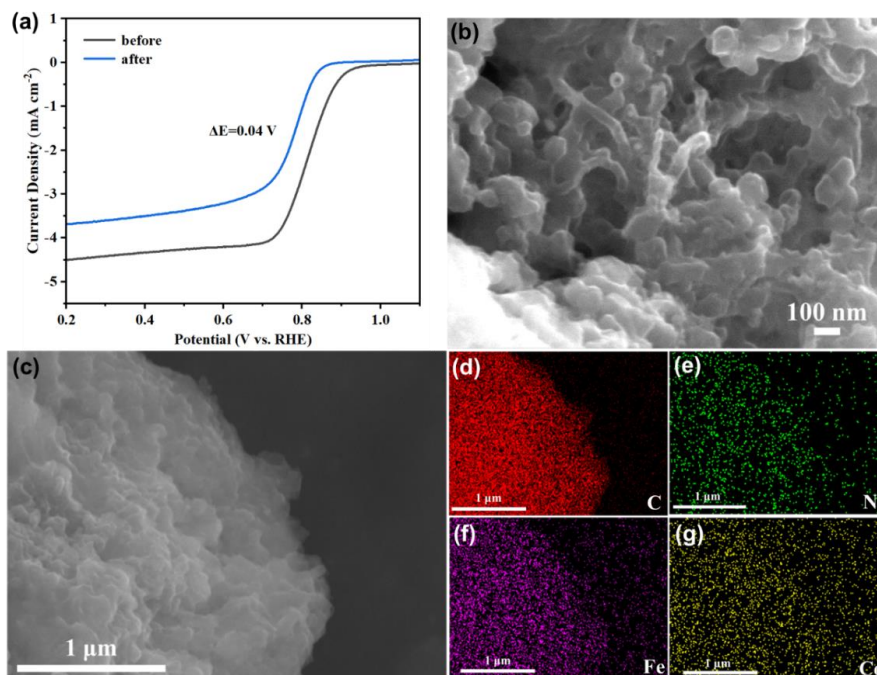


Fig. S17 (a) LSV curves of CoNP@FeNC-0.05 for ORR, before and after CV tests of 5000 cycles under 0.1 M KOH. (b) SEM image of CoNP@FeNC-0.05 after CV tests of 5000 cycles. (c-g) SEM image and corresponding EDS mapping of CoNP@FeNC-0.05 after CV tests of 5000 cycles

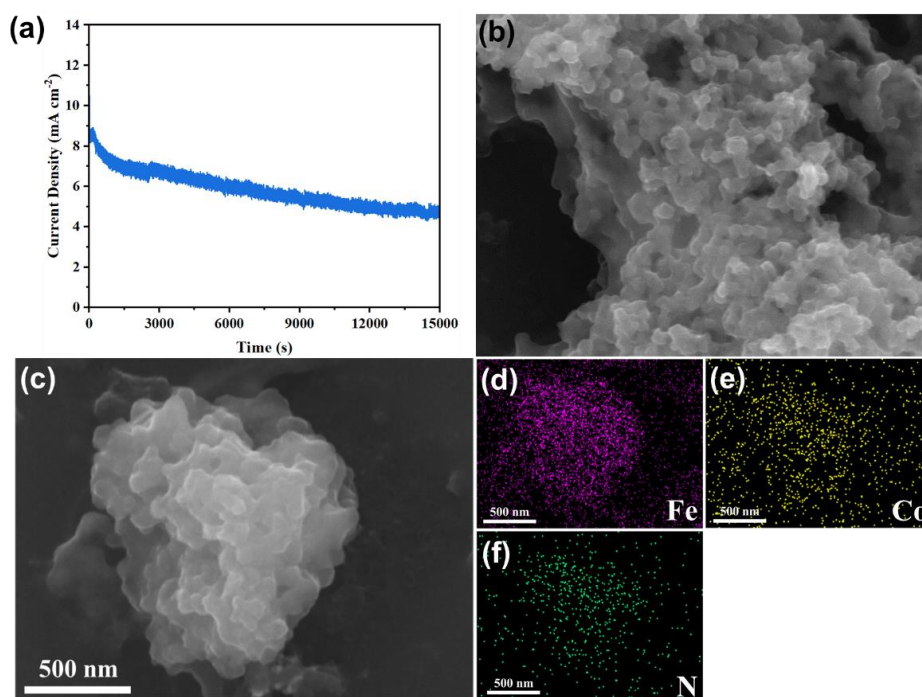


Fig. S18 (a) The i-t curve of CoNP@FeNC-0.05 for OER at 1.67 V under 1 M KOH. (b) SEM image of CoNP@FeNC-0.05 after 15000-s reaction. (c-f) SEM image and corresponding EDS mapping of CoNP@FeNC-0.05 after 15000-s reaction. The distribution of carbon is not offered since CoNP@FeNC-0.05 was loaded on carbon paper under durability tests

Table S1 The element contents of prepared catalysts from ICP-OES tests

	FeNC	CoNP@NC	CoNP@FeNC-0.05
Fe (wt%)	1.05	-	1.04
Co (wt%)	-	1.82	4.02

Table S2 The element contents of prepared catalysts from XPS tests

	FeNC	CoNP@NC	CoNP@FeNC-0.05
Fe (wt%)	1.46	-	1.41
Co (wt%)	-	2.45	1.87
C (wt%)	83.33	85.11	82.00
O (wt%)	8.08	6.82	8.38
N (wt%)	7.13	5.62	6.33

Table S3 Comparisons of ORR performance (vs. RHE) of CoNP@FeNC-0.05 with control catalysts in 0.1 M KOH

	NC	CoNP@NC	FeNC	CoNP@FeNC-0.05	Pt/C
Half-wave potential (V)	0.68	0.82	0.83	0.85	0.82
Onset potential (at -0.1 mA cm⁻²) (V)	0.85	0.95	0.96	1.02	0.98

Table S4 Comparison of ORR performance (vs. RHE) of CoNP@FeNC-0.05 with reported related catalysts in 0.1 M KO

Catalysts	Half-wave potential (V)	Onset potential (V)	Scan rate (mV s ⁻¹)	Rotation rate (rpm)	Refs.
CoNP@FeNC-0.05	0.85	1.02	5	1600	This work
FeCo-N-HCN	0.86	0.98	-	1600	Adv. Funct. Mater. 2021, 31, 2011289.
Co-NHC-900	0.85	-	10	1600	ACS Appl. Mater. Interfaces 2017, 9, 38499-38506.
PPy/FeTCPP/Co	0.86	1.01	10	1600	Adv. Funct. Mater. 2017, 27, 1606497.
Fe ₃ Co ₂ N-CNP(0.3)	0.875	0.979	-	1600	ACS Appl. Mater. Interfaces 2018, 10, 12651-12658.
Fe ₃ C-Co/NC	0.885	-	10	1600	Adv. Funct. Mater. 2019, 29, 1901949.
COF@ZIF ₈₀₀	0.85	0.99	-	1600	J. Mater. Chem. A 2022, 10, 228-233.
Co@NPC/C-MWCNTs	0.79	0.87	10	1600	Chem. Eng. J. 2022, 432, 134192.
CoNC-CNF-1000	0.8	-	10	1600	Small 2018, 14, 1800423.
Fe/Meso-NC-1000	0.885	0.97	5	1600	Adv. Mater. 2022, 34, 2107291.
Fe/N/S-PCNT	0.84	0.96	10	1600	J. Mater. Chem. A 2019, 7, 1607-1615.
Co-SAs@NC	0.82	0.96	5	1600	Angew. Chem. Int. Ed. 2019, 58, 5359-5364.
Co-N ₃ C ₁ @GC	0.846	0.904	10	1600	ACS Catal. 2020, 10, 5862-5870.
Fe ₁ -HNC-500-850	0.842	0.93	5	-	Adv. Mater. 2020, 32, 1906905.

Table S5 Comparison of OER performance of CoNP@FeNC-0.05 with reported related catalysts (vs. RHE)

Catalysts	Potential at $j=10$ mA cm^{-2} (V)	Electrolyte	Scan rate (mV s^{-1})	Rotation rate (rpm)	Refs.
CoNP@FeNC-0.05	1.63	1 M KOH	5	1600	This work
Fe ₃ C-Co/NC	1.57	1 M KOH	5	-	Adv. Funct. Mater. 2019, 29, 1901949.
CF-NG-Co	1.63	1 M KOH	5	1600	J. Mater. Chem. A 2018, 6, 489-497.
PPy/FeTCPP/Co	1.61	0.1 M KOH	10	1600	Adv. Funct. Mater. 2017, 27, 1606497.
CoO@Co/N-rGO	1.65	0.1 M KOH	5	1600	J. Mater. Chem. A 2017, 5, 5865-5872.
Co/N-C-800	1.504	1 M KOH	10	-	ACS Appl. Mater. Interfaces 2022, 14, 8549-8556.
CoN-HPCNF-900	1.63	0.1 M KOH	5	-	Chem. Eng. J. 2021, 407, 127157.
Co/NGC-3	1.626	0.1 M KOH	5	1600	ACS Appl. Mater. Interfaces 2020, 12, 5717-5729.
CoNC-CNF-1000	1.68	0.1 M KOH	10	1600	Small 2018, 14, 1800423.
CoFe/Co@NCNT/NG	1.611	0.1 M KOH	10	1600	J. Power Sources 2020, 449, 227512.
Co@NHCC-800	1.512	1 M KOH	10	-	Appl. Catal. B 2019, 254, 55-65.
Co/N-CNTs (1500 sccm)	1.54	1 M KOH	5	1600	Small 2020, 16, 2002427.
Co@CNT-NC	1.633	0.1 M KOH	10	-	J. Power Sources 2022, 527, 231205.

Table S6 Comparison of performance of Zn-air batteries of CoNP@FeNC-0.05 with reported related results.

Catalysts	Open-circuit potential (V)	Maximum Power density (mW cm^{-2})	Cycling stability	Refs.
CoNP@FeNC-0.05	1.51	104.4	500 cycles (60 min/cycle) @ 5 mA cm^{-2}	This work
CoNi-SAs/NC	1.45	101.4	95 cycles (20 min/cycle) @ 5 mA cm^{-2}	Adv. Mater. 2019, 31, 1905622.
FeCo-DACs/NC	1.50	175	480 cycles (30 min/cycle) @ 10 mA cm^{-2}	Adv. Mater. 2022, 34, 2107421.
(Fe,Co)-SA/CS	1.43	86.65	300 cycles (20 min/cycle) @ 5 mA cm^{-2}	Small Methods 2021, 5, 2000751.
Fe/Co-N/S-Cs	1.395	102.63	80 cycles (20 min/cycle) @ 5 mA cm^{-2}	Appl. Catal. B 2019, 241, 95-103.
Fe-N4 SAs/NPC	-	232	108 cycles (20 min/cycle) @ 2 mA cm^{-2}	Angew. Chem. Int. Ed. 2018, 57, 8614-8618.
FeNx/C-700-20	1.6	36	-	Adv. Energy Mater. 2018, 8, 1800955.
SAFe-SWCNT film	1.47	210	-	Appl. Catal. B 2021, 294, 120239.

Nano-Micro Letters

Fe/N-G-SAC	-	120	240 cycles (60 min/cycle) @ 10 mA cm ⁻²	Adv. Mater. 2020, 32, 2004900.
CoNC-NB2	1.50	246	420 cycles (20 min/cycle) @ 2 mA cm ⁻²	Small 2020, 16, 2001171.
CNT@SAC- Co/NCP	1.45	172	100 cycles (20 min/cycle) @ 5 mA cm ⁻²	Adv. Funct. Mater. 2021, 31, 2103360.
H- Co@FeCo/N/C	1.45	125.2	400 cycles (30 min/cycle) @ 10 mA cm ⁻²	Appl. Catal. B 2020, 278, 119259.
Co@hNCTs- 800	1.45	149	3000 cycles (10 min/cycle) @ 5 mA cm ⁻²	Nano Energy 2020, 71, 104592.
Co@Co ₃ O ₄ @N C-900	0.842	64	100 cycles (120 min/cycle) @ 5 mA cm ⁻²	J. Mater. Chem. A 2018, 6, 1443- 1453.
