

Supporting Information

Bimetallic Zeolitic Imidazolate Framework-Derived Iron-, Cobalt- and Nitrogen-Codoped Carbon Nano- Polyhedra Electrocatalyst for Efficient Oxygen Reduction

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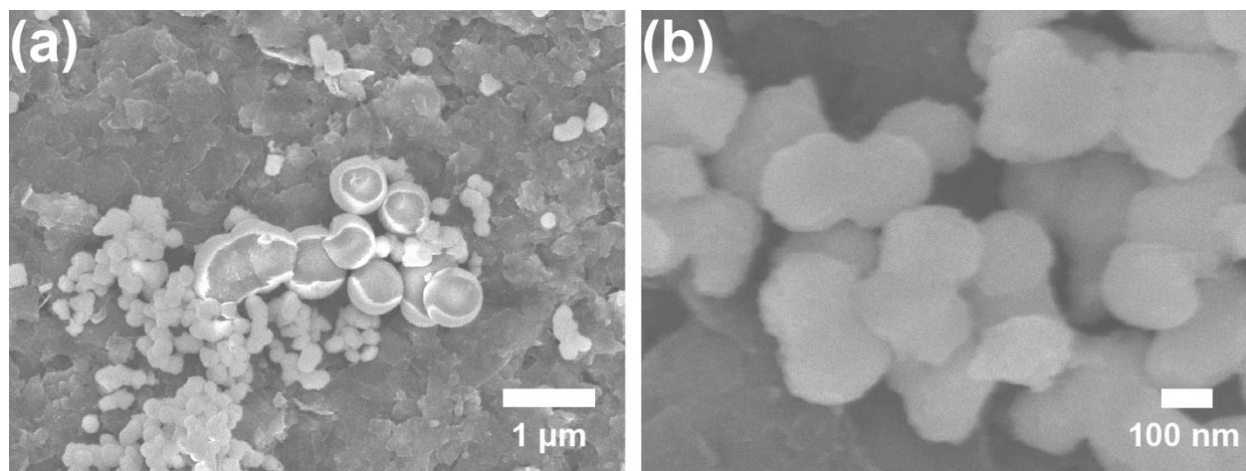


Fig. S1. Low (a) and high (b) magnification SEM images of Fe,Co-ZIF(0.2) synthesized under ambient condition

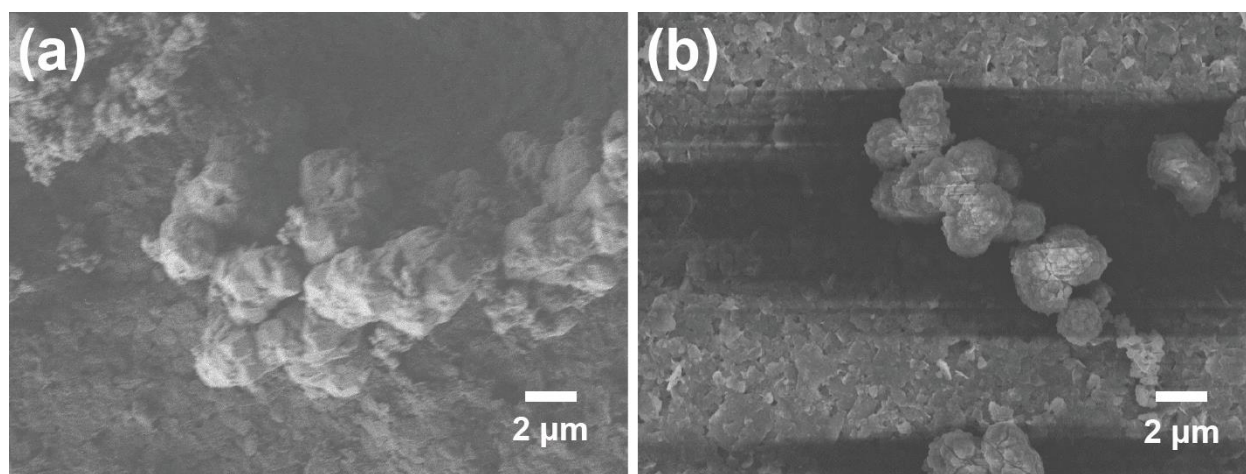


Fig. S2. SEM image of Fe,Co-ZIF with the Fe/Co ratio of 0.5 (a) and 1.0 (b)

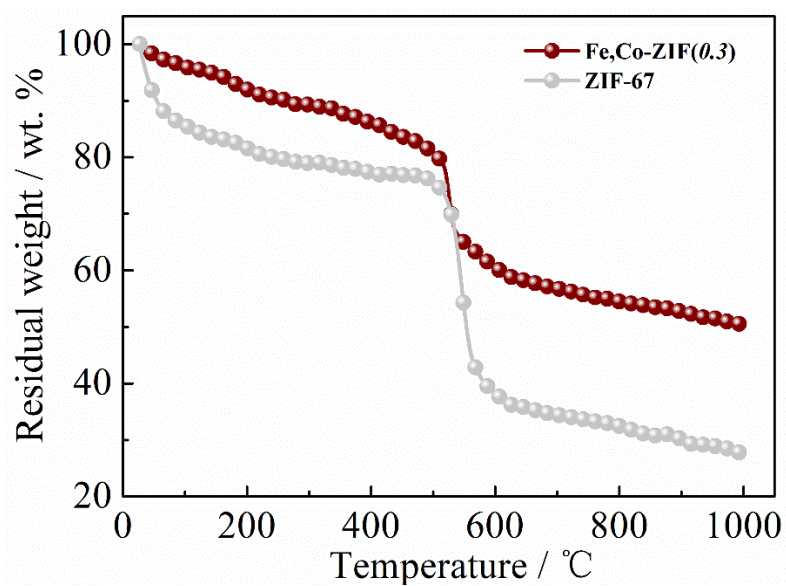


Fig. S3. TG analysis of Fe,Co-ZIF(0.3) in comparison with ZIF-67 under Argon atmosphere (temperature ramp rate: $10\text{ }^{\circ}\text{C min}^{-1}$).

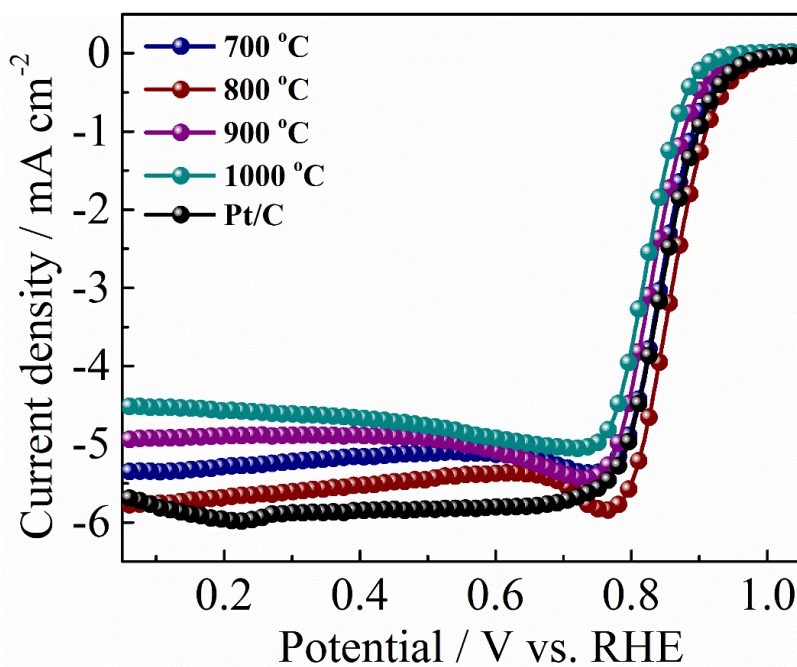


Fig. S4. LSV curves of Fe,Co,N-CNP prepared at various pyrolysis temperatures in O_2 -saturated 0.1 M KOH (scan rate: 5 mV s^{-1} , electrode rotation rate: 1600 rpm)

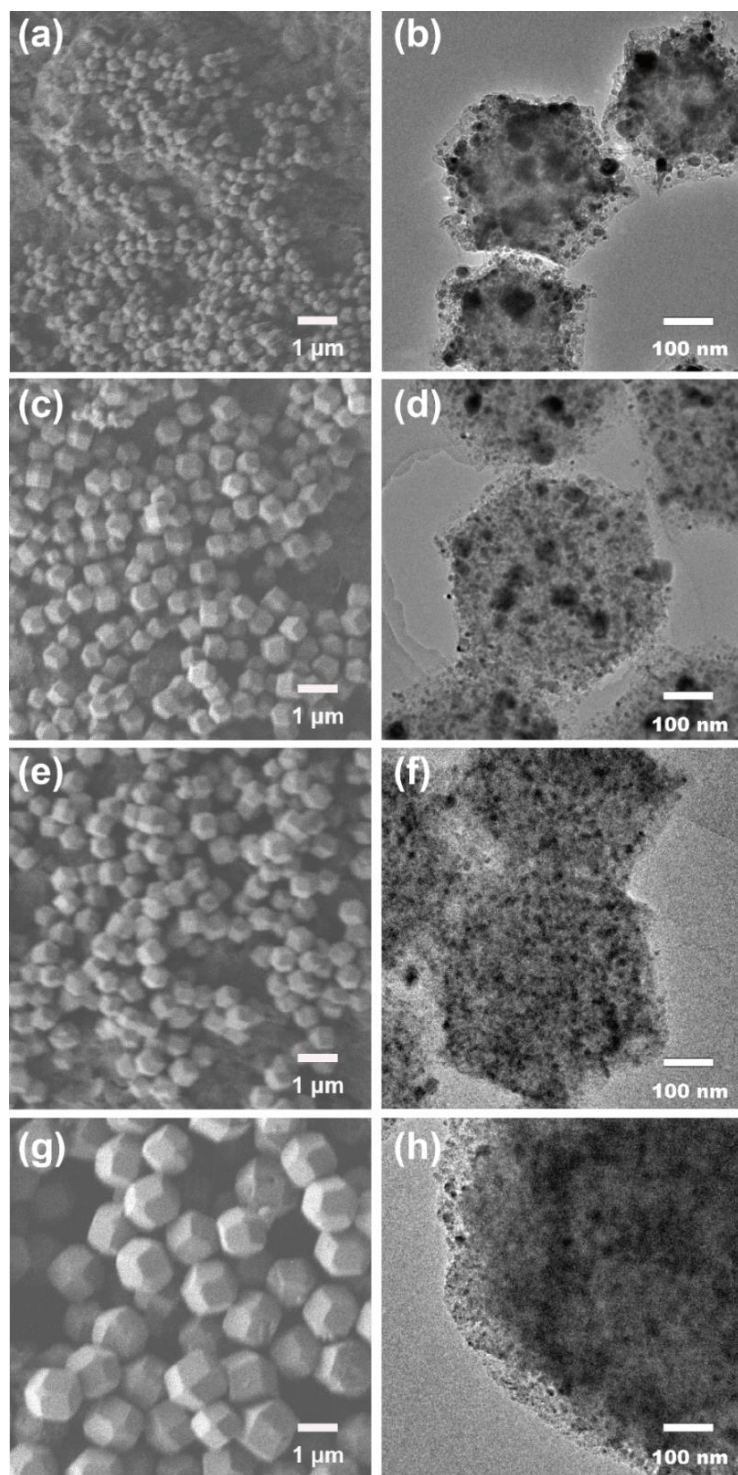


Fig. S5. Representative SEM images of (a) ZIF-67, (c) Fe,Co-ZIF(0.1), (e) Fe,Co-ZIF(0.2), and (g) Fe,Co-ZIF(0.3). HR-TEM images of (b) Co,N-CNP, (d) Fe,Co,N-CNP (0.1), (f) Fe,Co,N-CNP (0.2), and (h) Fe,Co,N-CNP (0.3)

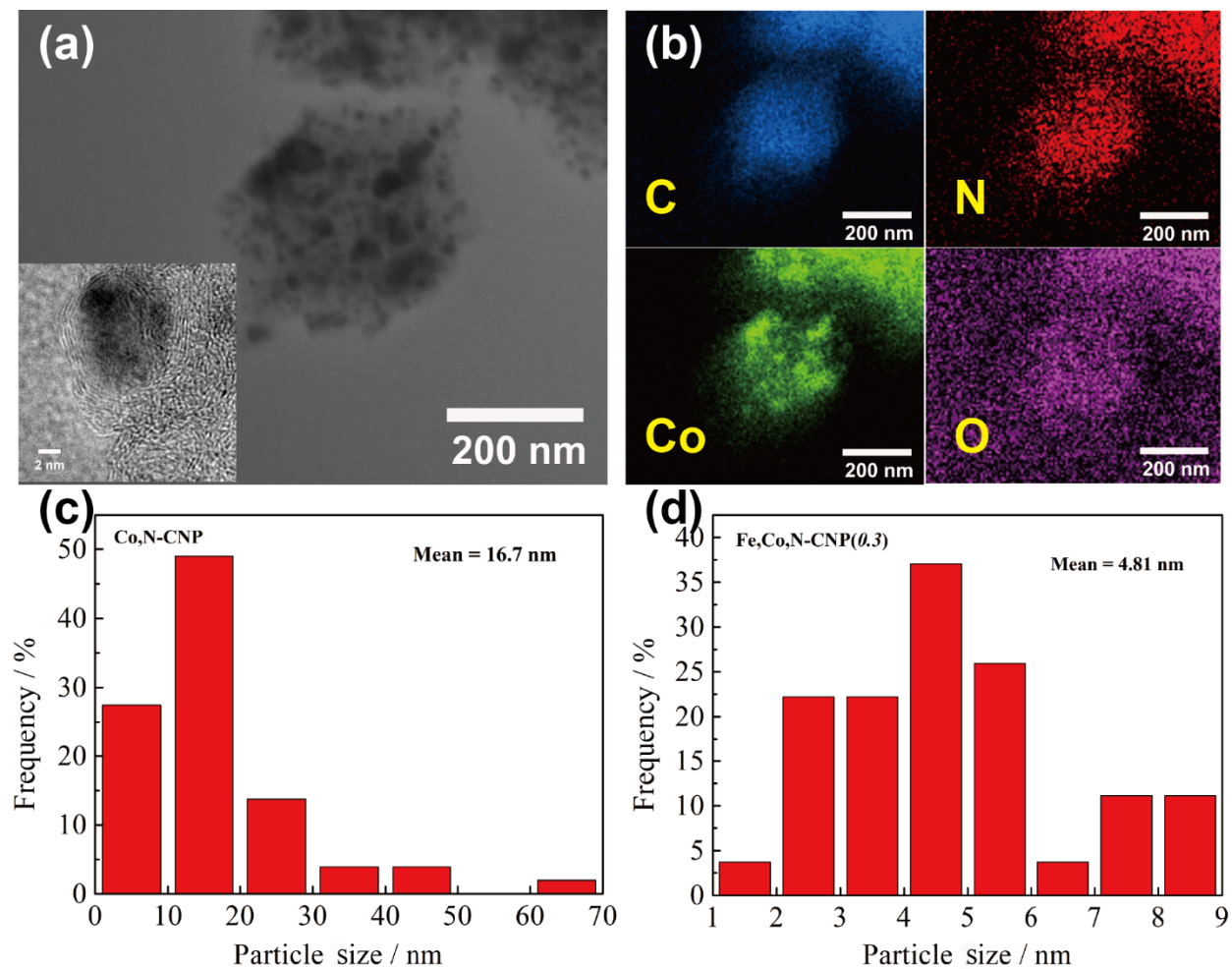


Fig. S6. HR-STEM (a) and the corresponding elemental mapping (b) of Co,N-CNP, and particle distribution of metal NPs in Co,N-CNP (c) and Fe,Co,N-CNP (0.3) (d).

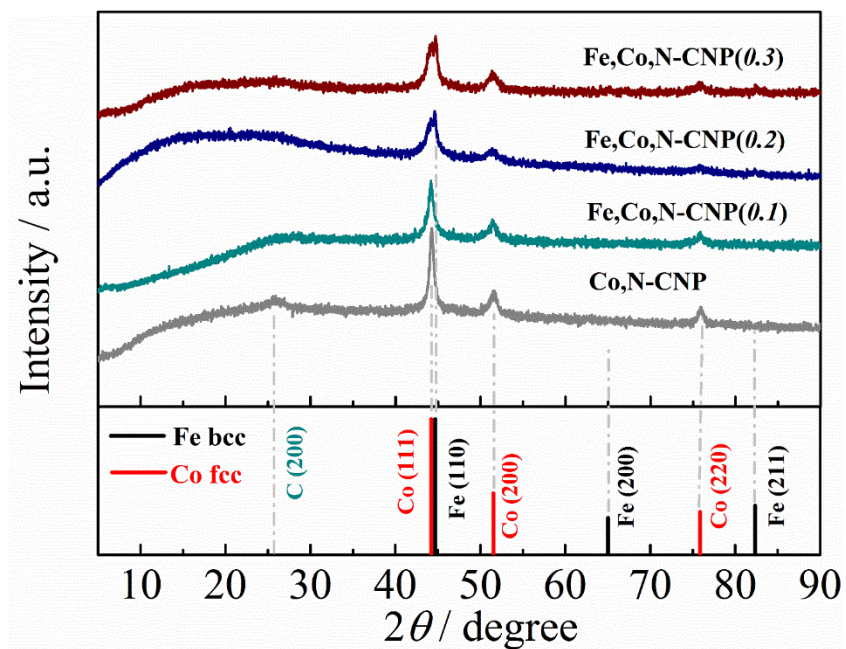


Fig. S7. XRD patterns of Co,N-CNP and Fe,Co,N-CNP(X)

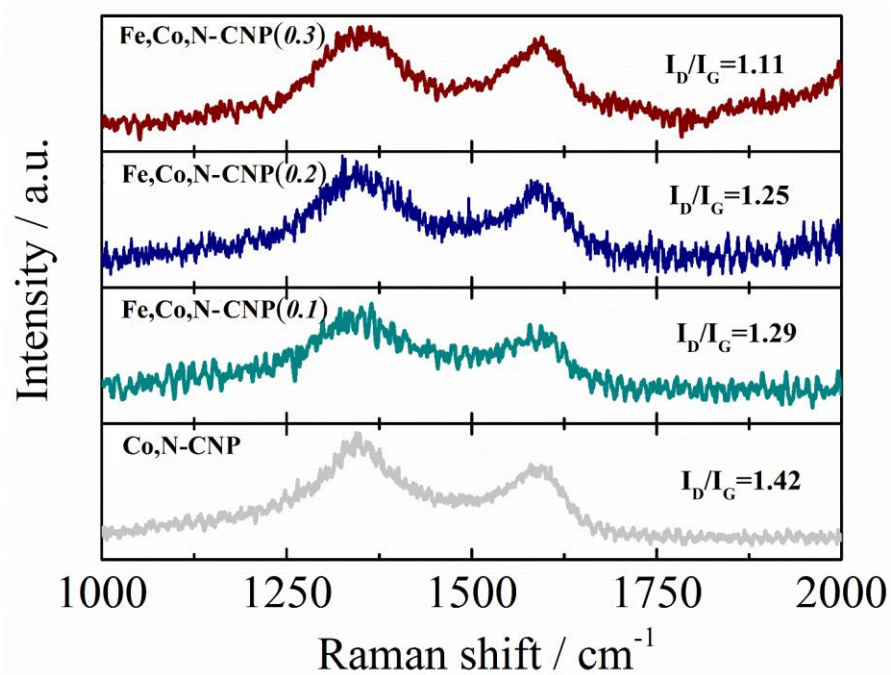


Fig. S8. Raman spectra of Co,N-CNP and Fe,Co,N-CNP(X)

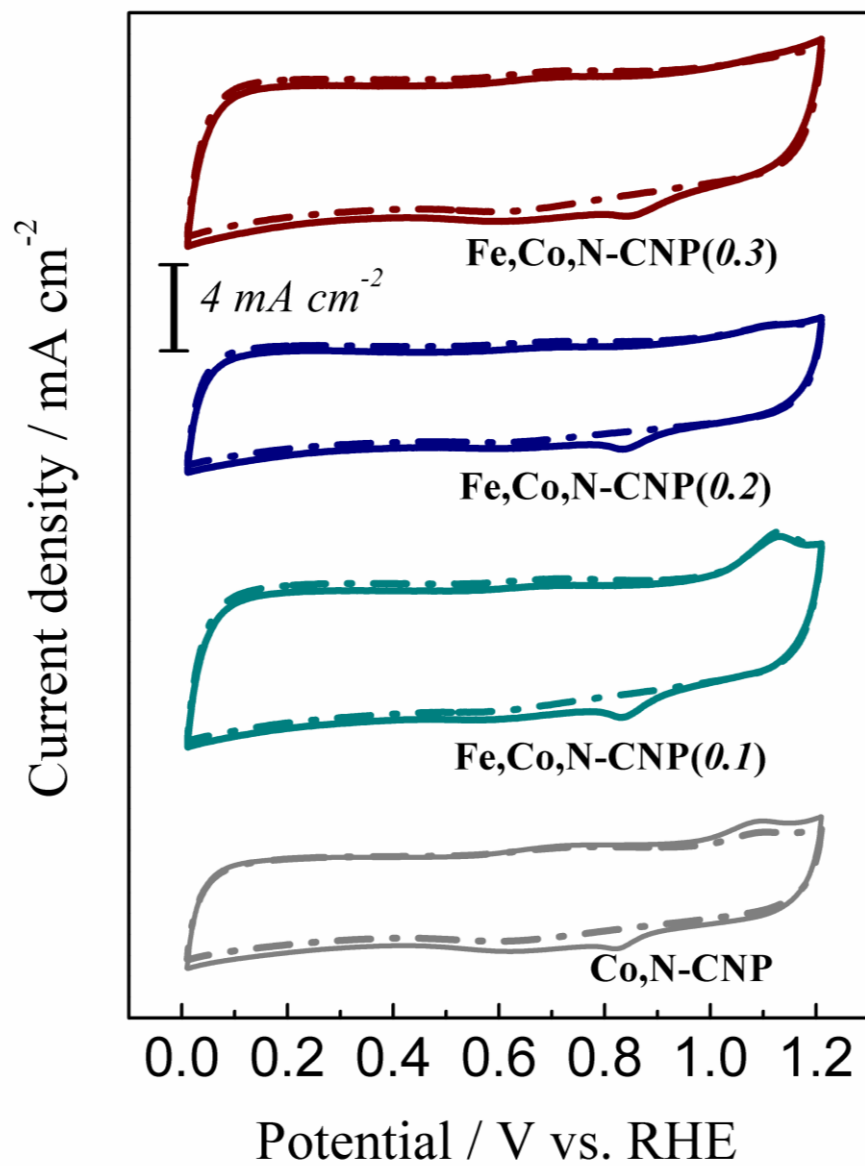


Fig. S9. Comparative CV curves of Co,N-CNP, and Fe,Co,N-CNP(*X*) in N₂- (dotted line) and O₂- (solid line) saturated 0.1 M KOH (scan rate: 50 mV s⁻¹).

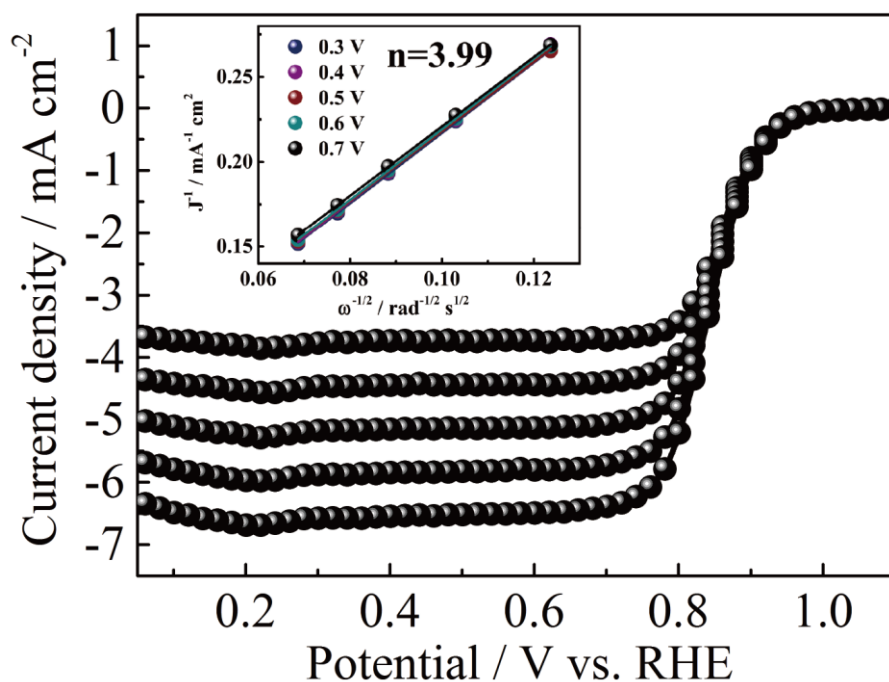


Fig. S10. LSV curves of the commercial Pt/C in O₂-saturated 0.1 M KOH (scan rate: 5 mV s⁻¹) under various rotation rates (Inset: the corresponding K-L plots).

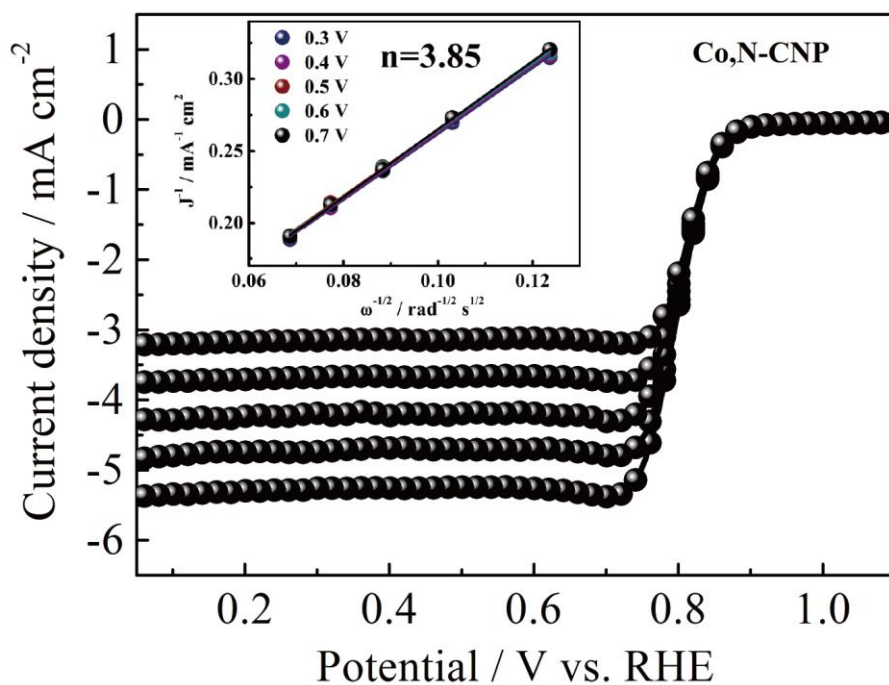


Fig. S11. LSV curves of Co,N-CNP in O₂-saturated 0.1 M KOH (scan rate: 5 mV s⁻¹) under different rotation rates (Inset: the corresponding K-L plots).

Table S1. Pore characteristics of ZIF-67 and Fe,Co-ZIF(*X*), and the corresponding electrocatalysts

Sample	S _{BET} (m ² g ⁻¹)	S _{micro} (m ² g ⁻¹)	S _{micro} / S _{BET} (%)	V _{pore} (cm ³ g ⁻¹)	Retention rate of S _{micro}
ZIF-67	1564.4	1515.3	96.7	0.717	-
Co,N-CNP	347.4	153.9	44.3	0.068	10.2
Fe,Co-ZIF(0.1)	1456.3	1363.1	93.6	0.758	-
Fe,Co,N-CNP(0.1)	413.5	136.3	32.9	0.336	10.0
Fe,Co-ZIF(0.2)	1447.4	1353.9	93.5	0.761	-
Fe,Co,N-CNP(0.2)	425.3	177.6	41.7	0.349	13.9
Fe,Co-ZIF(0.3)	1450.8	1299.5	89.5	0.670	-
Fe,Co,N-CNP(0.3)	422.0	204.9	48.6	0.312	15.8

Table S2. N content and configuration determined by XPS in Co,N-CNP and Fe,Co,N-CNP(*X*)

Sample	N (at. %)	Relative content of different N species			
		Pyridine N	Pyrrolic N	Graphic N	Oxidized N
Co,N-CNP	6.19	51.9	23.0	25.1	0
Fe,Co,N-CNP(0.1)	7.45	49.7	29.4	20.9	0
Fe,Co,N-CNP(0.2)	8.51	56.8	25.6	17.6	0
Fe,Co,N-CNP(0.3)	9.07	48.9	18.9	17.5	14.7

Table S3. The ORR activity of Co,N-CNP and Fe,Co,N-CNP(X) in 0.1 M KOH

Sample	$E_{1/2}$ (V)	E_{onset} (V)	$J_d / 0.3$ V (mA cm ⁻²)	$J_k / 0.85$ V (mA cm ⁻²)
Co,N-CNP	0.825	0.893	4.742	1.620
Fe,Co,N-CNP(0.1)	0.859	0.957	5.367	7.160
Fe,Co,N-CNP(0.2)	0.864	0.953	5.610	9.280
Fe,Co,N-CNP(0.3)	0.875	0.979	5.355	12.55
Pt/C	0.846	0.941	5.890	5.150

Table S4. Summary of ORR activity of the non-precious electrocatalysts in 0.1 M KOH electrolyte reported in literatures

Sample	E_{onset} (V vs. RHE)	$E_{1/2}$ (V vs. RHE)	Ref.
NGPC/NCNT	0.94	0.82	S1
hybrid FeNC-20-1000	1.040	0.880	S2
Co-N-C	~0.982	0.871	S3
C ₃ N ₄ @NH ₂ -MIL-101- 700	0.990	0.840	S4
Au@Zn-Fe-C	0.940	N/A	S5
MOFs-800	0.90	0.80	S6
CNPs	1.03	0.92	S7
FeNi@NC _x	1.03	0.86	S8
FePc/MWCNTs	0.916	N/A	S9
DCI-Fe-700	N/A	0.839	S10
CPM-99Fe/C	0.950	0.802	S11
Fe,Co,N-CNP(0.3)	0.979	0.875	This work

Table S5. The ORR activity of Co,N-CNP and Fe,Co,N-CNP(X) in 0.1 M HClO₄

Sample	$E_{1/2}$ (V)	E_{onset} (V)	J_d / 0.3 V (mA cm ⁻²)	J_k / 0.75 V (mA cm ⁻²)
Co,N-CNP	0.671	0.780	4.969	0.539
Fe,Co,N-CNP(0.1)	0.734	0.824	6.081	1.674
Fe,Co,N-CNP(0.2)	0.756	0.867	5.636	1.970
Fe,Co,N-CNP(0.3)	0.764	0.871	5.788	2.163
Pt/C	0.814	0.901	5.926	2.860

Table S6. Summary of ORR activity of the non-precious electrocatalysts in 0.1 M HClO₄ electrolyte reported in literatures

Sample	E_{onset} (V vs. RHE)	$E_{1/2}$ (V vs. RHE)	Ref.
C-Fe-Z8-Ar	0.95	0.82	S12
ZIF-67	0.86	0.71	S13
meso/micro-PoPD	0.84	~0.70	S14
hybrid FeNC-20-1000	0.9	0.770	S2
Co-N-C	N/A	0.761	S3
S-Fe/N/C	N/A	0.825	S15
Zn(Im) ₂	0.881	0.73	S16
CoIm	0.83	0.68	S17
C-Fe-ZIF-900-0.84	N/A	0.77	S18
Fe,Co,N-CNP(0.3)	0.871	0.764	This work

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