Supporting Information

High-performance zinc-air batteries enabled by hybridizing atomically dispersed FeN_2 with Co_3O_4 nanoparticles

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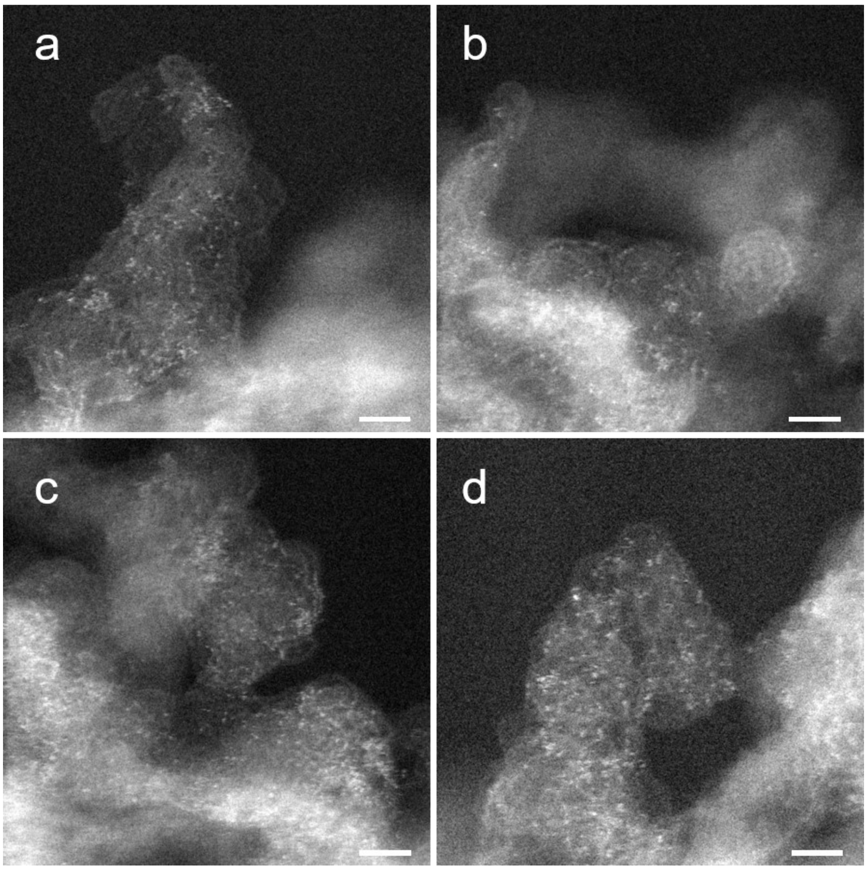


Fig. S1 (a-d) Aberration-corrected HAADF-STEM images of Fe-HPNC. Scale bar: 2 nm.

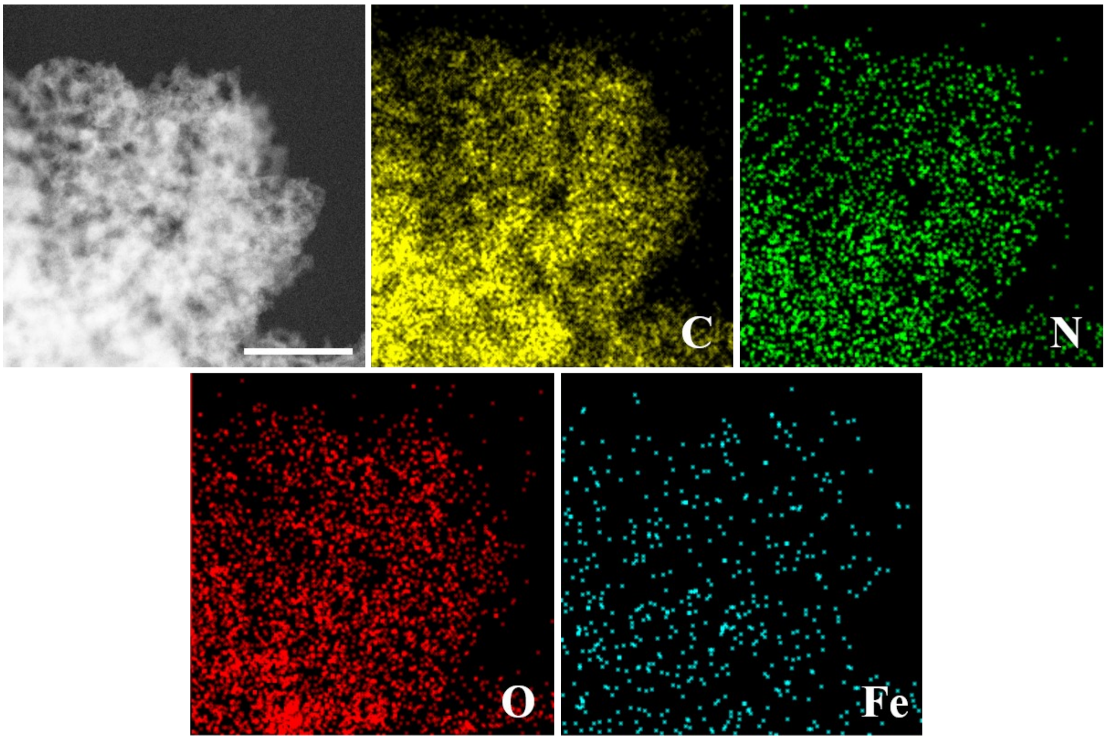


Fig. S2 STEM image and corresponding elemental mapping images of Fe-HPNC. Scale bar, 50 nm.

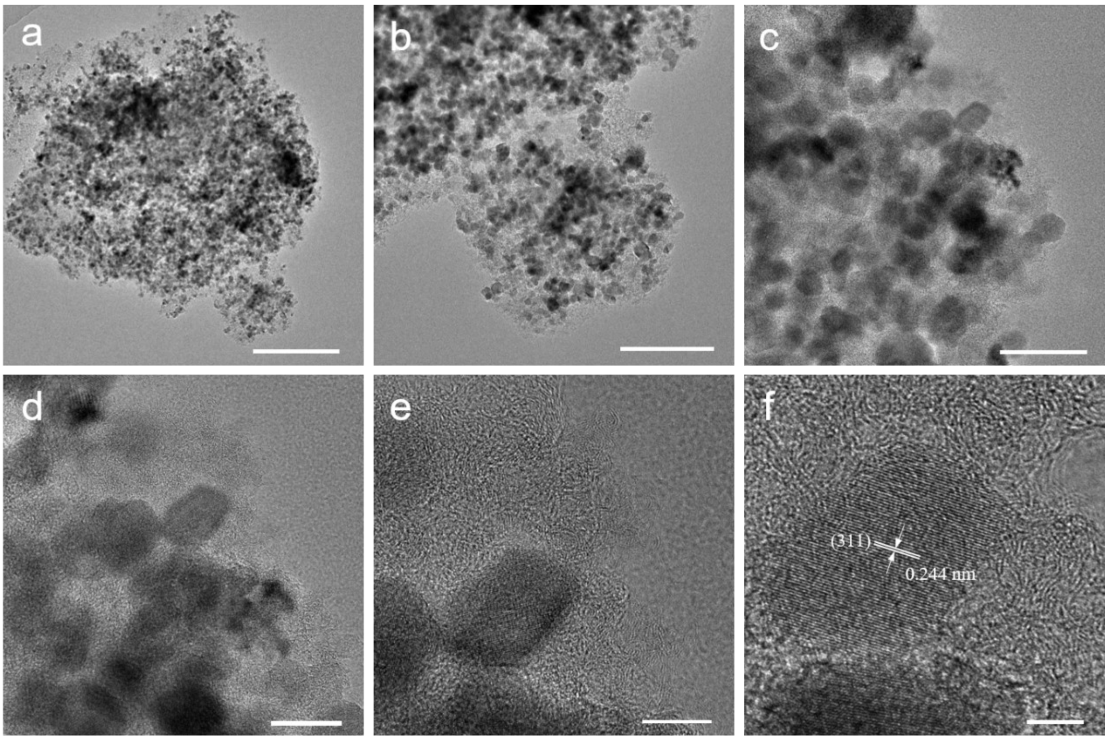


Fig. S3 (a-f) TEM and HR-TEM images of Fe-HPNC/Co_3O_4. Scale bar: (a) 500 nm, (b) 200 nm, (c) 50 nm, (d) 20 nm, (e) 10 nm, (f) 5 nm.

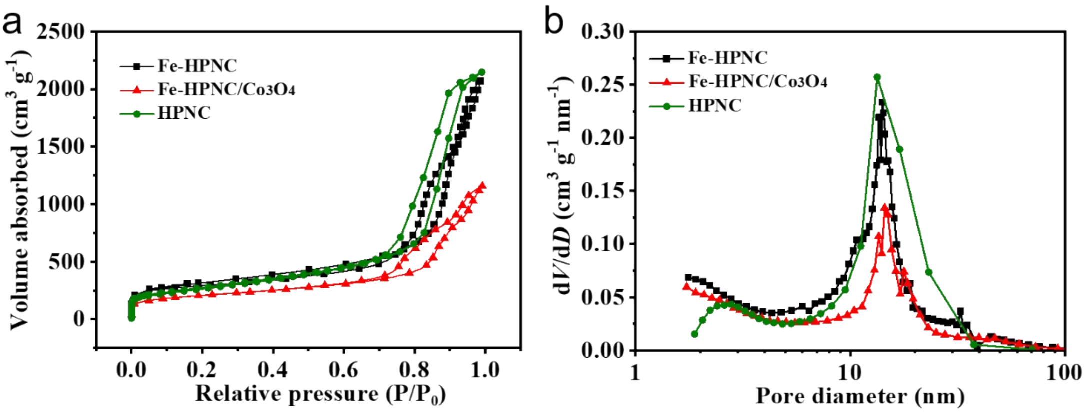


Fig. S4 (a) Nitrogen absorption-desorption isotherms and **(b)** corresponding pore size distribution curves of Fe-HPNC, Fe-HPNC/Co_3O_4 and HPNC.

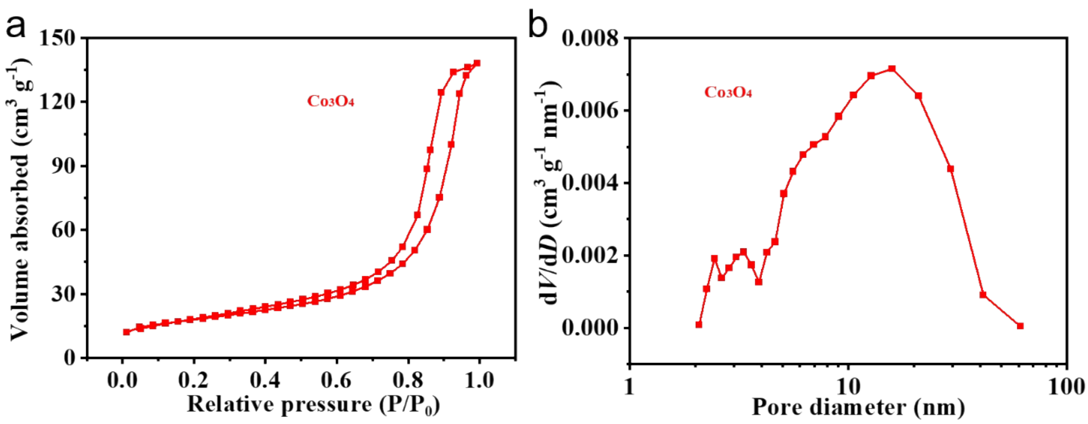


Fig. S5 (a) Nitrogen absorption-desorption isotherms and **(b)** corresponding pore size distribution curves of Co_3O_4 nanoparticles.

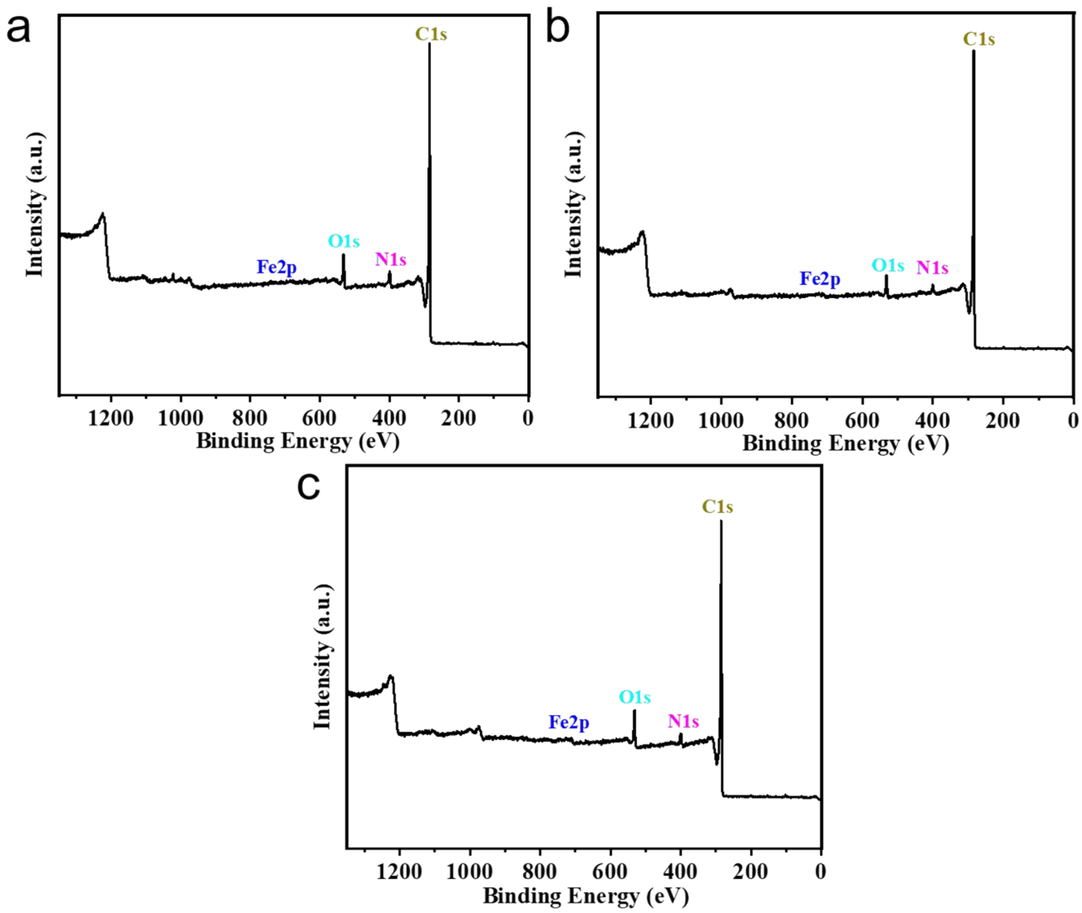


Fig. S6 XPS survey spectra of **(a)** Fe-HPNC-700, **(b)** Fe-HPNC-800 and **(c)** Fe-HPNC-900.

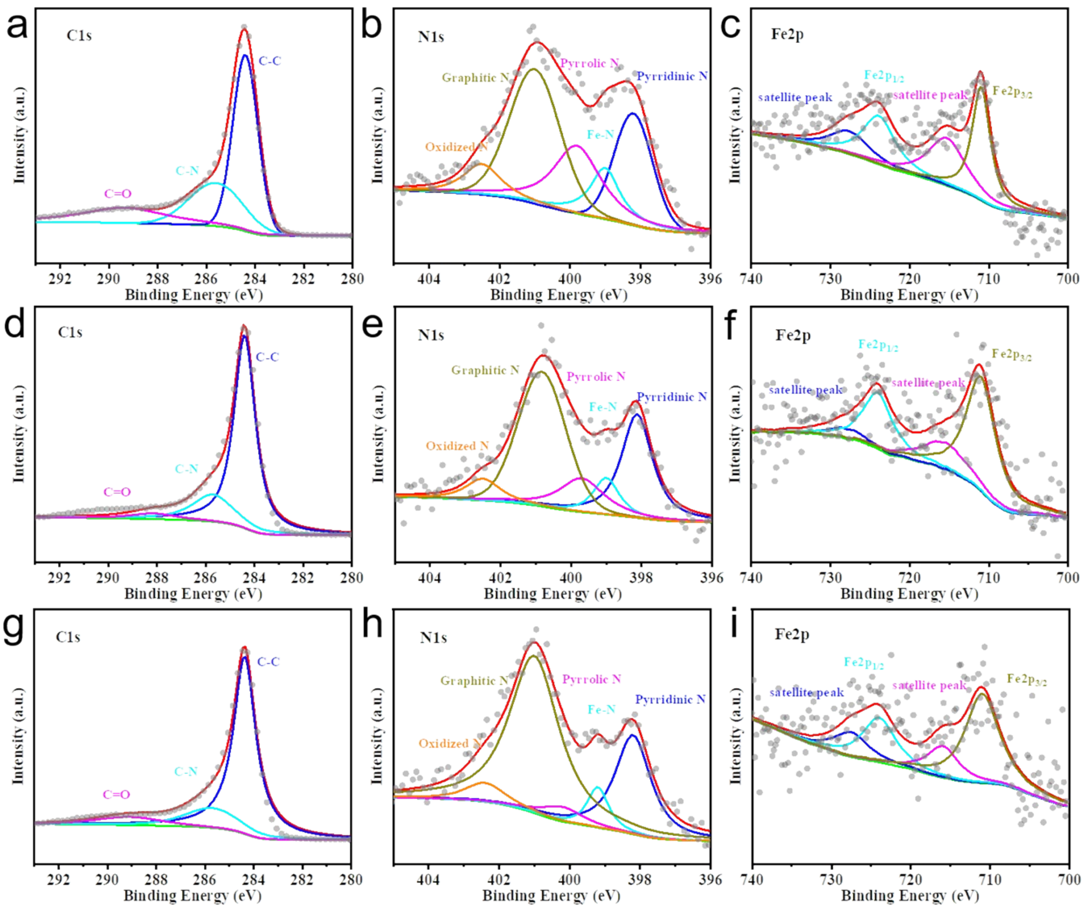


Fig. S7 High-resolution C1s, N1s and Fe 2p spectra of **(a,b,c)** Fe-HPNC-700, **(d,e,f)** Fe-HPNC-800 and **(g,h,i)** Fe-HPNC-900.

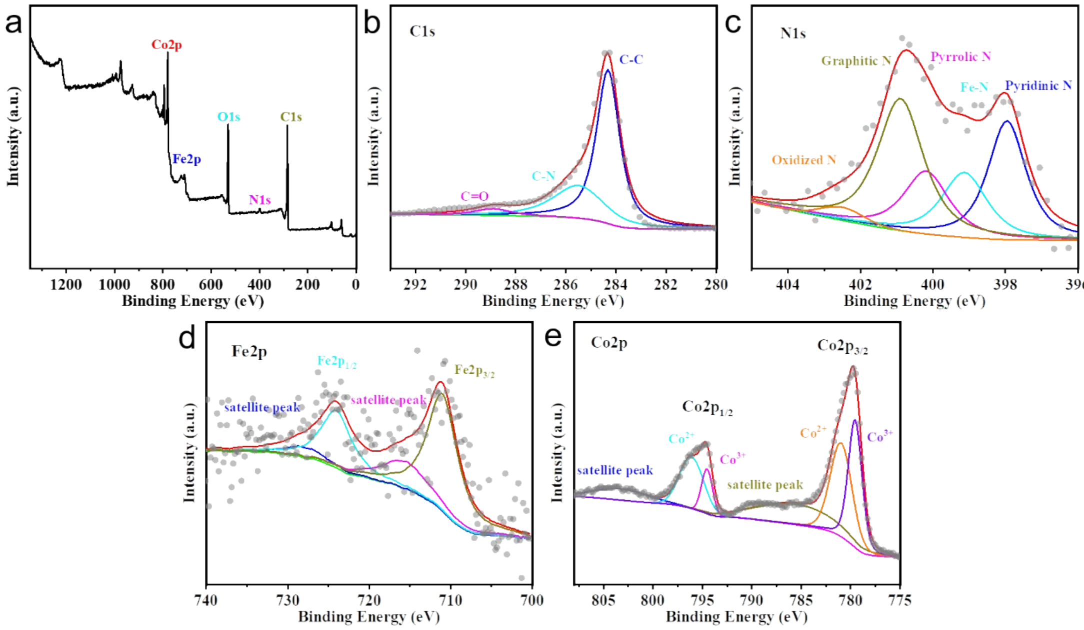


Fig. S8 (a) XPS survey spectra and high-resolution **(b)** C 1s, **(c)** N 1s, **(d)** Fe 2p and **(e)** Co 2p spectra of Fe-HPNC/Co_3O_4.

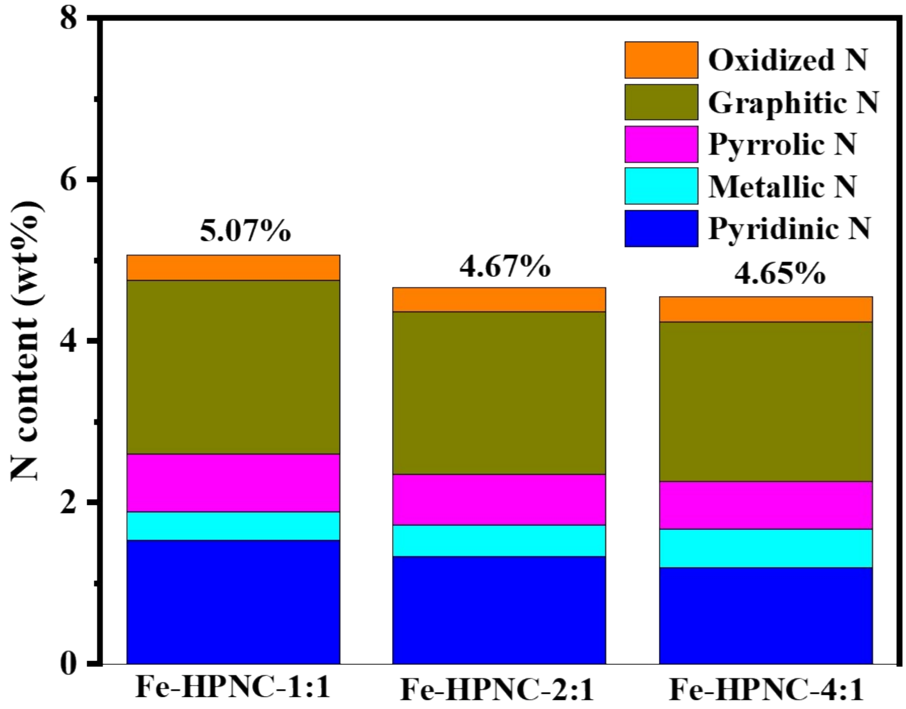


Fig. S9 Configurations of nitrogen dopants of Fe-HPNC-1:1, Fe-HPNC-2:1 and Fe-HPNC-4:1.

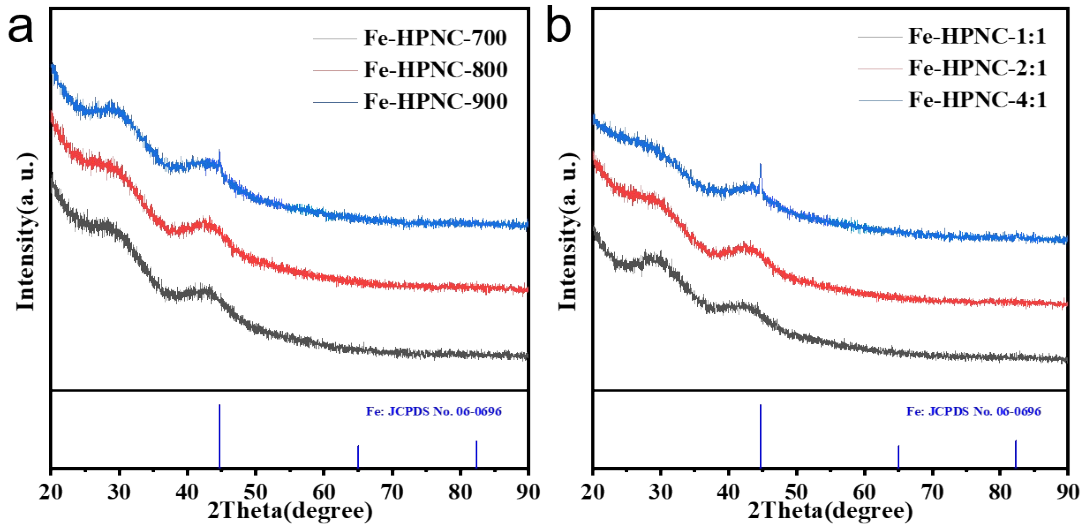


Fig. S10 XRD patterns of **(a)** Fe-HPNC-700, Fe-HPNC-800, Fe-HPNC-900 and **(b)** Fe-HPNC-1:1, Fe-HPNC-2:1 and Fe-HPNC-4:1.

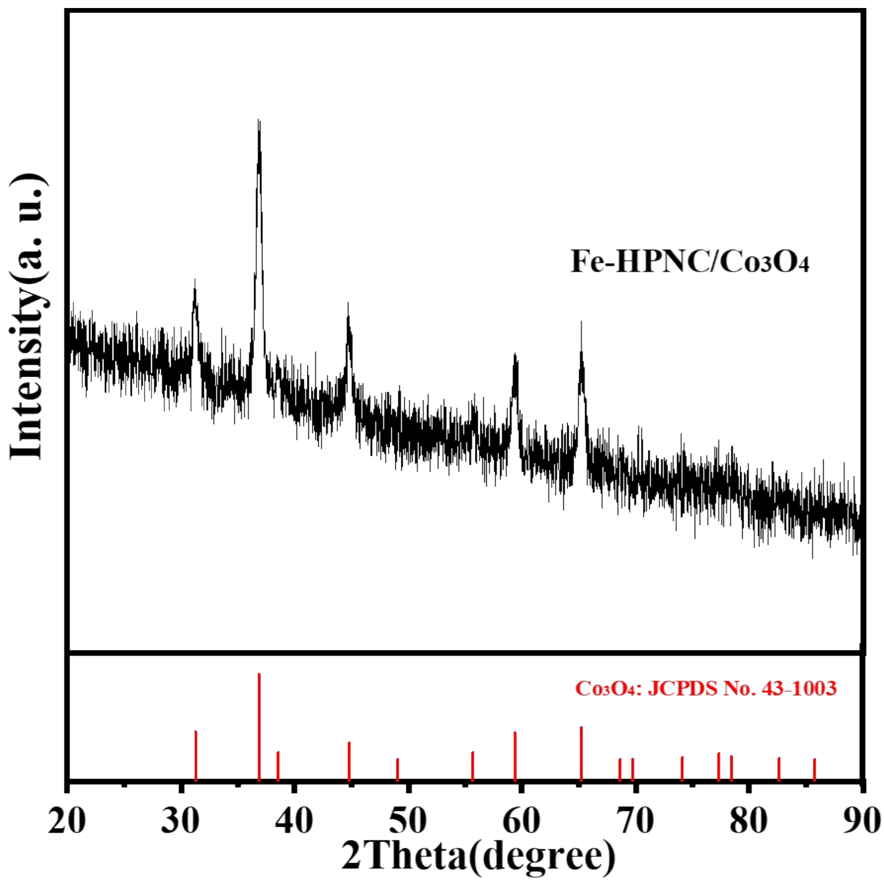


Fig. S11 XRD pattern of Fe-HPNC/Co_3O_4.

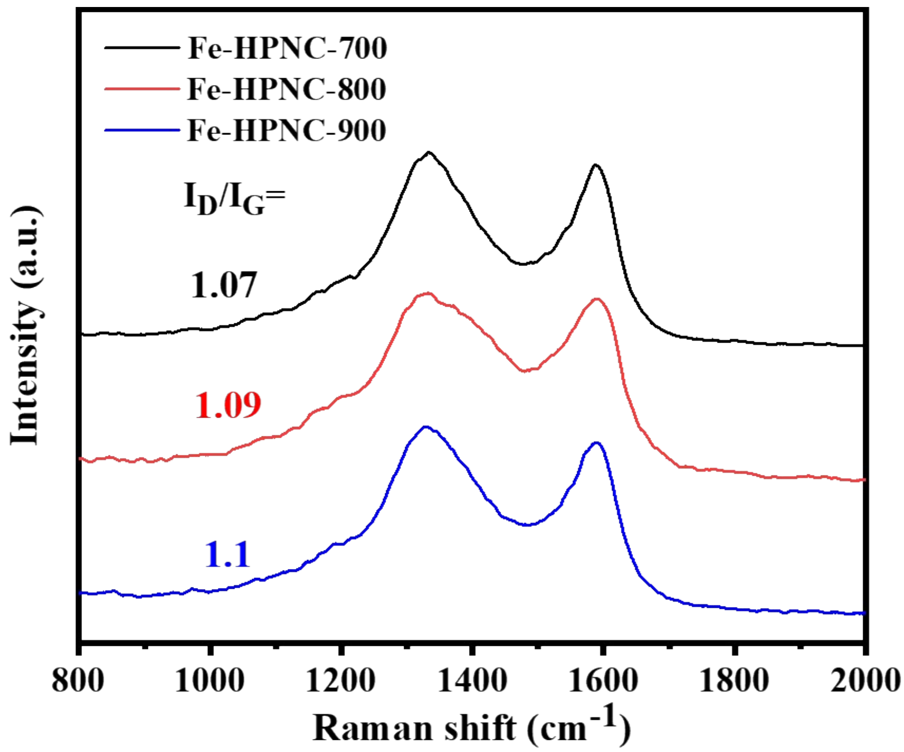


Fig. S12 Raman spectra of Fe-HPNC-700, Fe-HPNC-800 and Fe-HPNC-900.

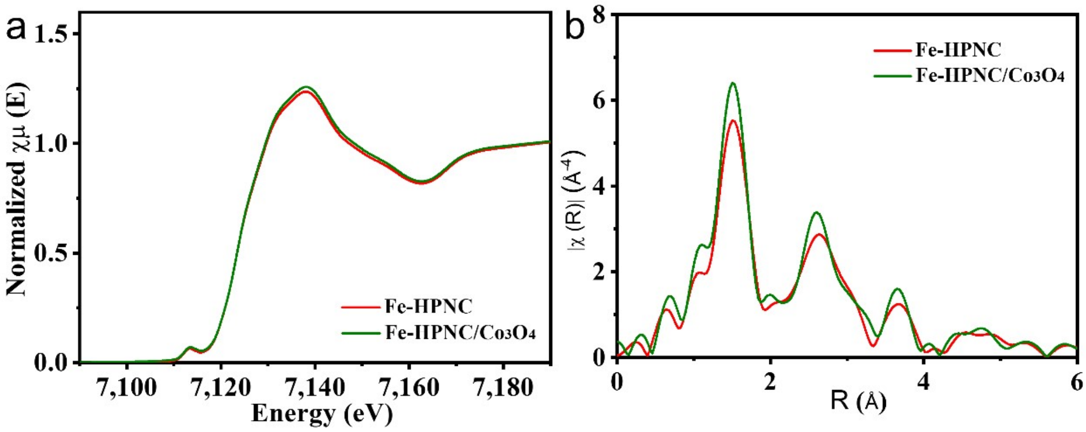


Fig. S13 Fe k-edge **(a)** XANES spectra and **(b)** Fourier-transfer EXAFS spectra of Fe-HPNC and Fe-HPNC/Co_3O_4.

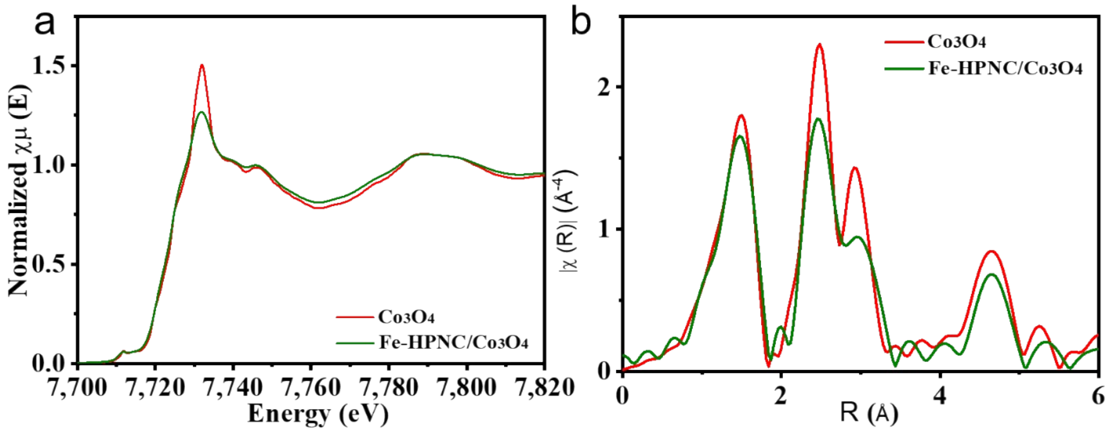


Fig. S14 Co k-edge **(a)** XANES spectra and **(b)** Fourier-transfer EXAFS spectra of Fe-HPNC/Co_3O_4 and commercial Co_3O_4.

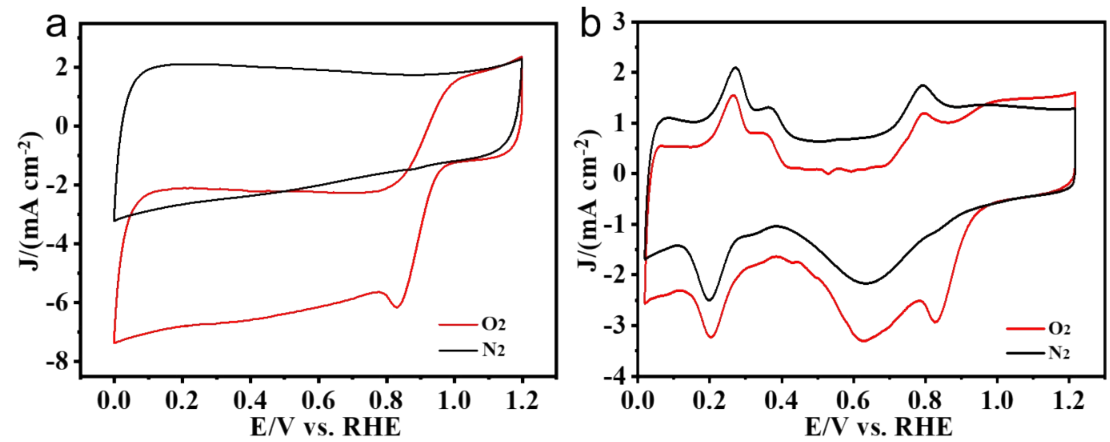


Fig. S15 Cycle voltammetry (CV) curves of **(a)** Fe-HPNC/Co_3O_4 and **(b)** Pt/C in 0.1 M KOH solution saturated with oxygen (red lines) and nitrogen (black lines). Scan rate: 50 mV s^{-1}.

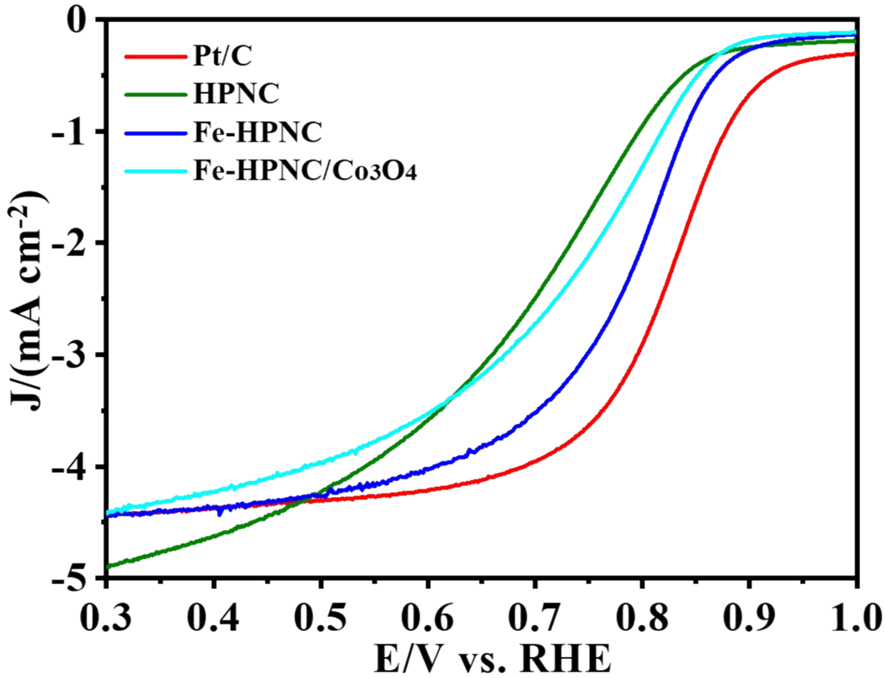


Fig. S16 ORR polarization curves of various catalysts in O_2-saturated 0.5 M H_2SO_4 solution with a rotating speed of 1600 rpm and a scan rate of 10 mV s^{-1}.

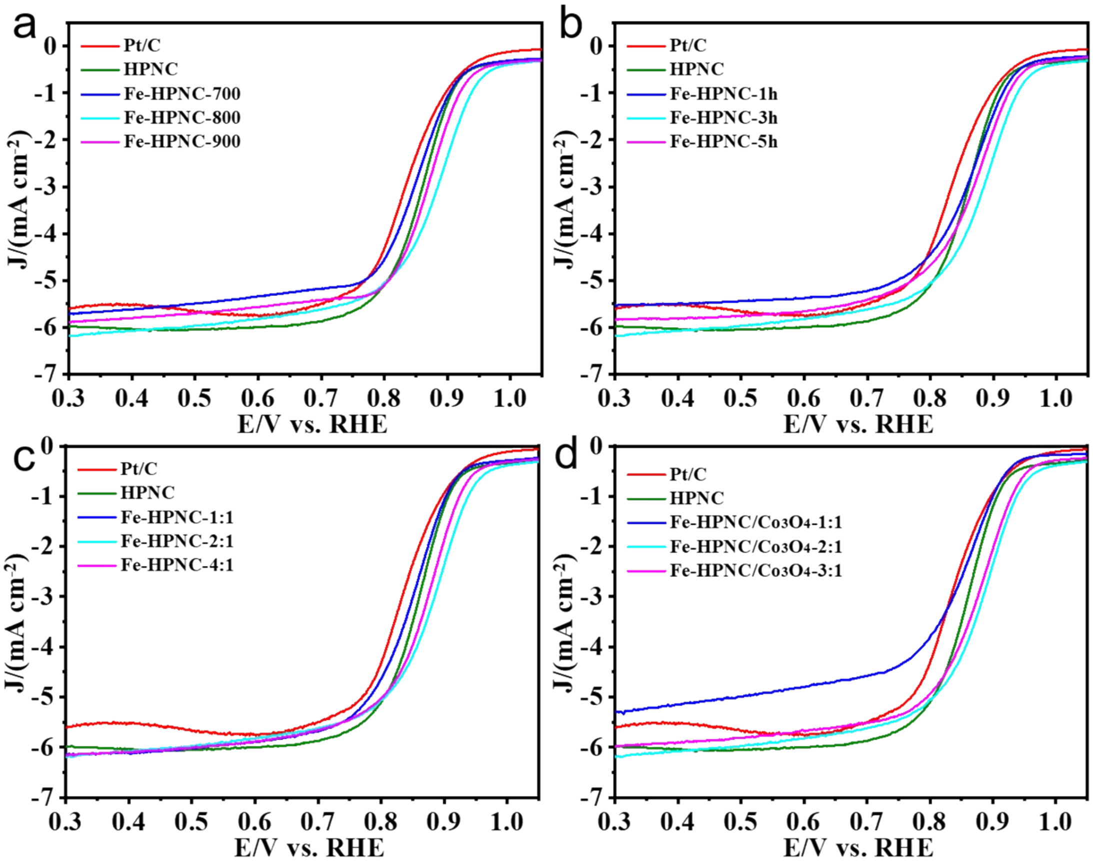


Fig. S17 ORR polarization curves of various catalysts synthesized with different **(a)** annealing temperature, **(b)** annealing time, **(c)** mass ratios of $FeCl_3$ to HPNC and **(d)** mass ratios of Fe-HPNC to Co_3O_4 in O_2-saturated 0.1 M KOH solution with a rotating speed of 1600 rpm and a scan rate of 10 mV s^{-1}.

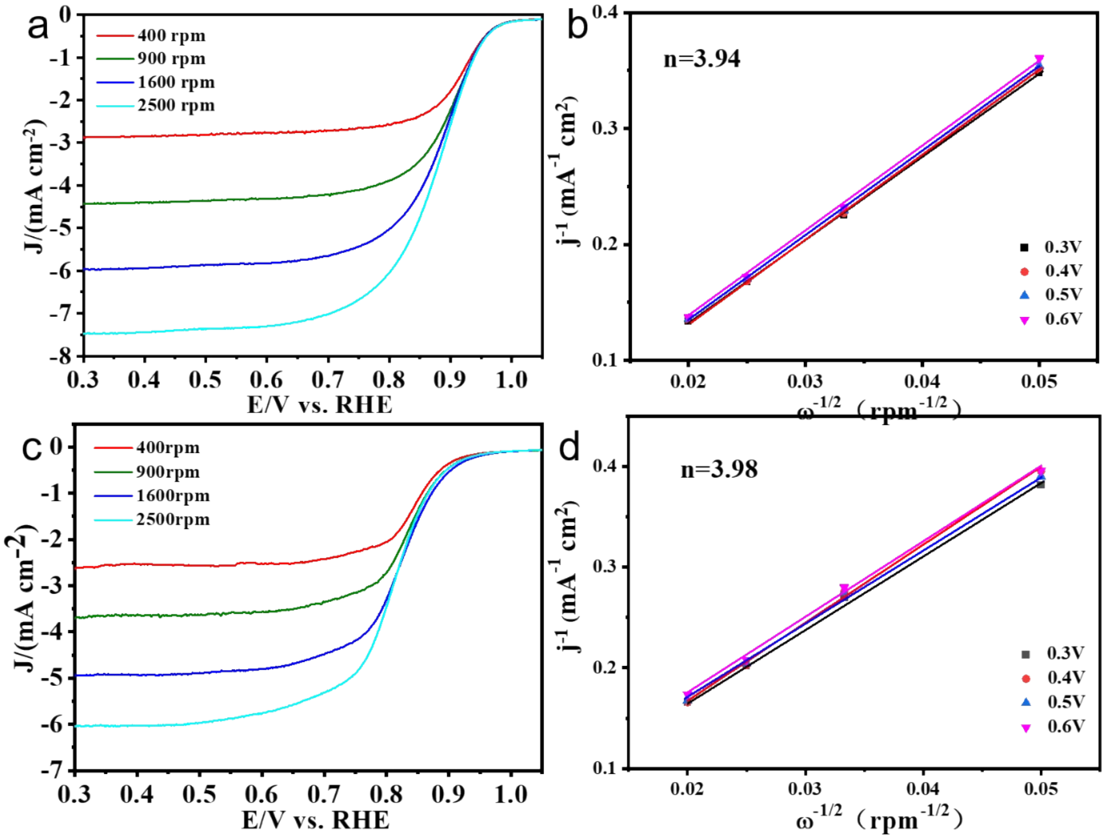


Fig. S18 ORR polarization curves at various rotating speeds and corresponding K-L plots at various potentials of **(a,b)** Fe-HPNC/Co3O4 and **(c,d)** Pt/C in O_2-saturated 0.1 M KOH solution.

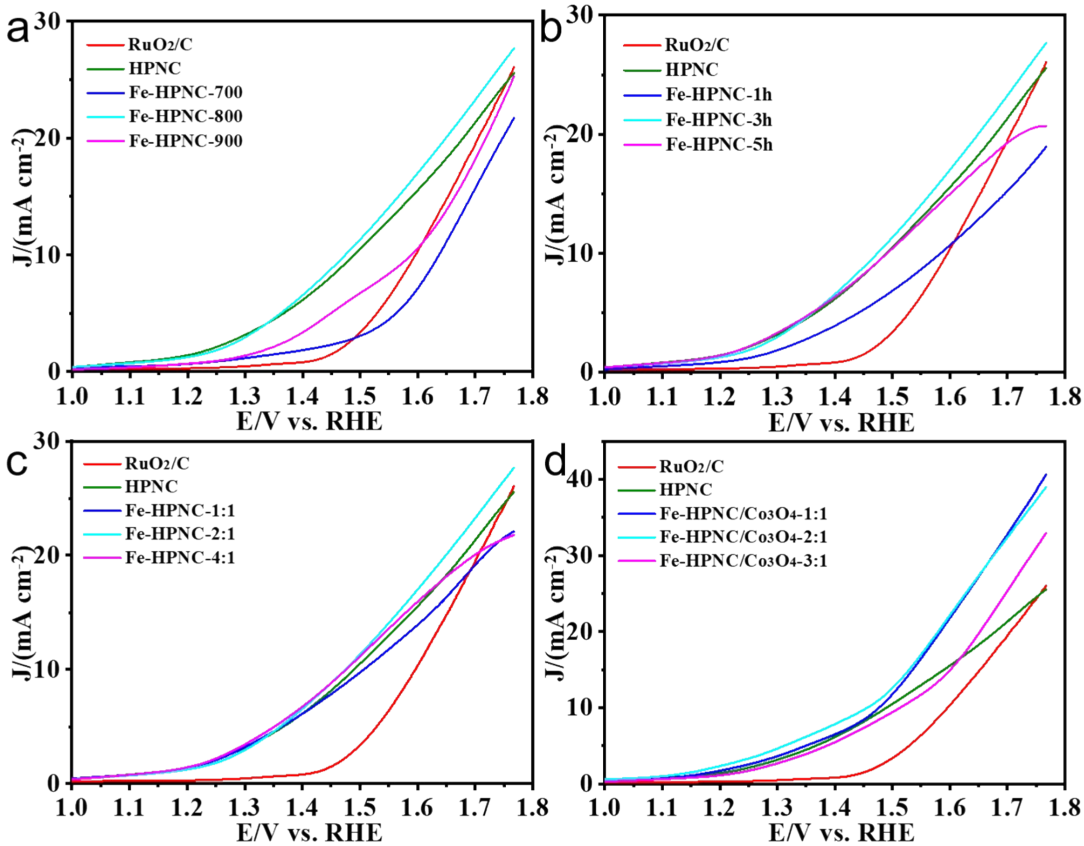


Fig. S19 OER polarization curves of various catalysts synthesized with different **(a)** annealing temperature, **(b)** annealing time, **(c)** mass ratios of $FeCl_3$ to HPNC and **(d)** mass ratios of Fe-HPNC to Co_3O_4 in O_2-saturated 0.1 M KOH solution with a rotating speed of 1600 rpm and a scan rate of 10 mV s^{-1}.

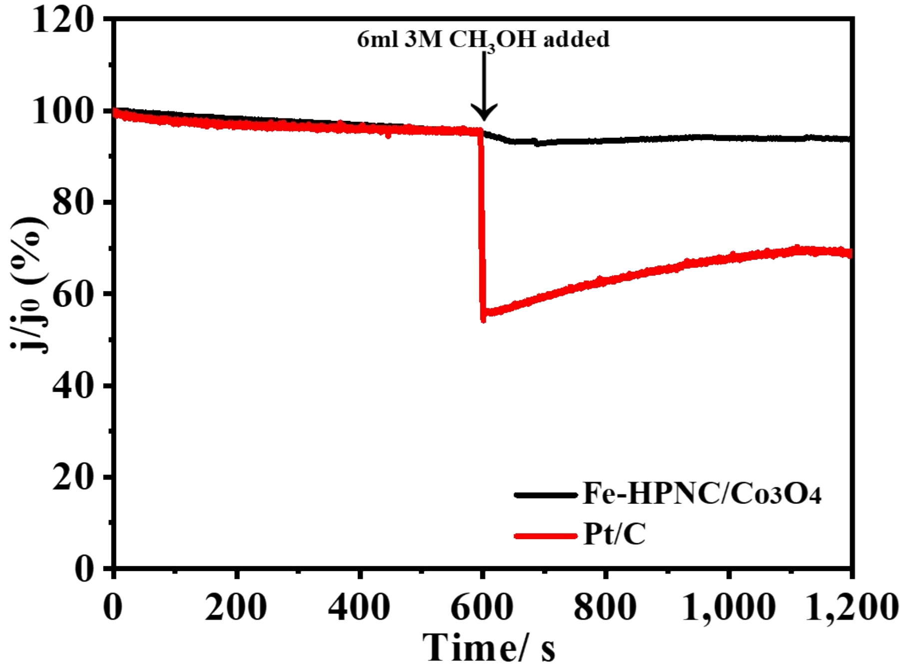


Fig. S20 ORR chronoamperometric responses of Fe-HPNC/Co_3O_4 and Pt/C at 0.65 V (vs. RHE) and 1600 rpm in O_2-saturated 0.1 M KOH solution with the addition of 6 ml 3 M methanol.

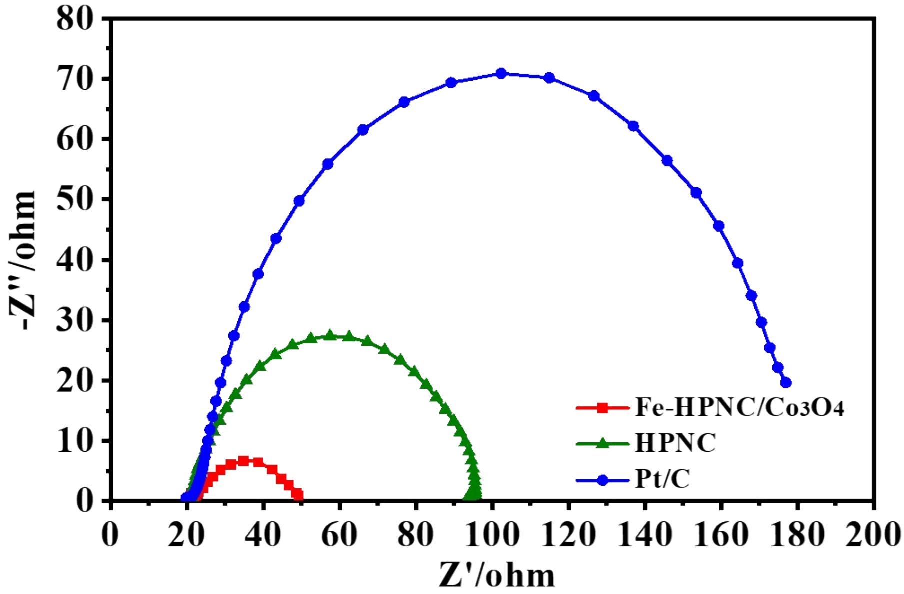


Fig. S21 Electrochemical impedance spectrum (EIS) of Fe-HPNC /Co_3O_4, HPNC and Pt/C at 0.85 V (vs. RHE) with the frequency ranging 10 kHz to 0.01 Hz and an amplitude of 5 mV in O_2-saturated 0.1 M KOH solution.

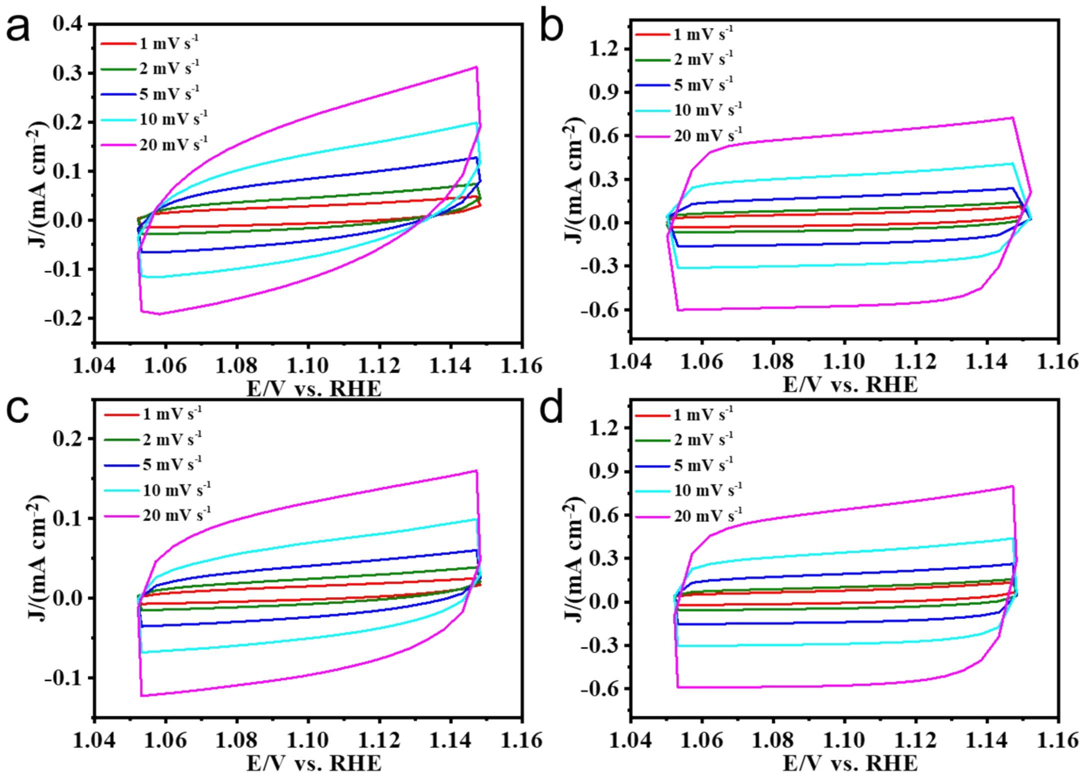


Fig. S22 CV curves of **(a)** Fe-HPNC-700, **(b)** Fe-HPNC-800, **(c)** Fe-HPNC-900 and **(d)** Fe-HPNC/Co_3O_4 with different scan rates in 0.1 M KOH solution.

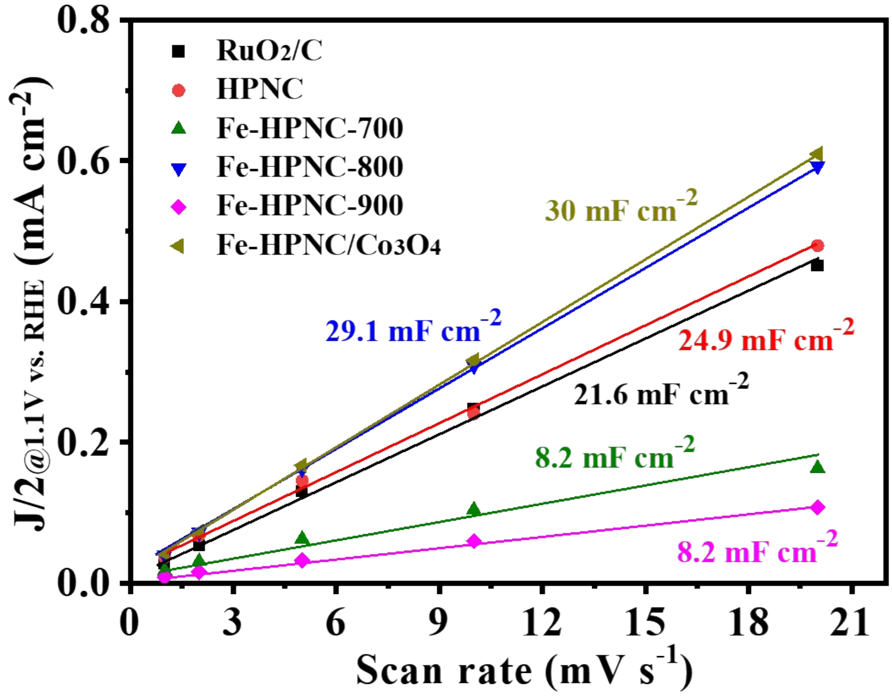
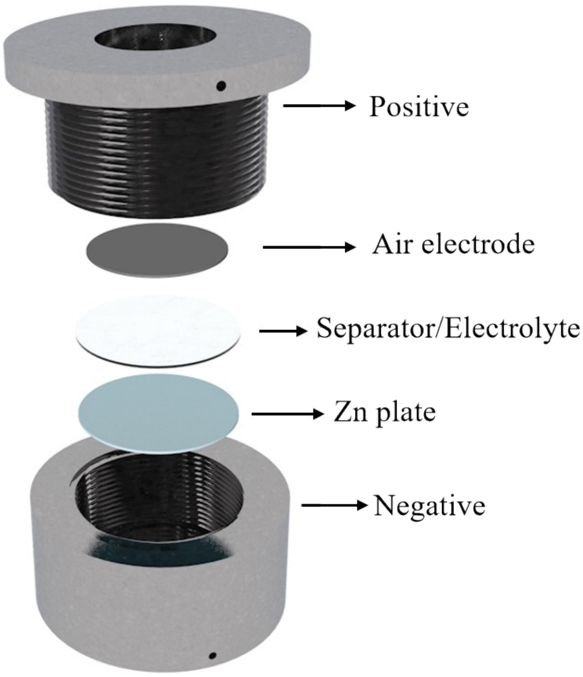


Fig. S23 Comparison of the electrochemical surface areas of various catalysts.

Fig. S24 Schematic illustration of the fabricated Zn-air battery.



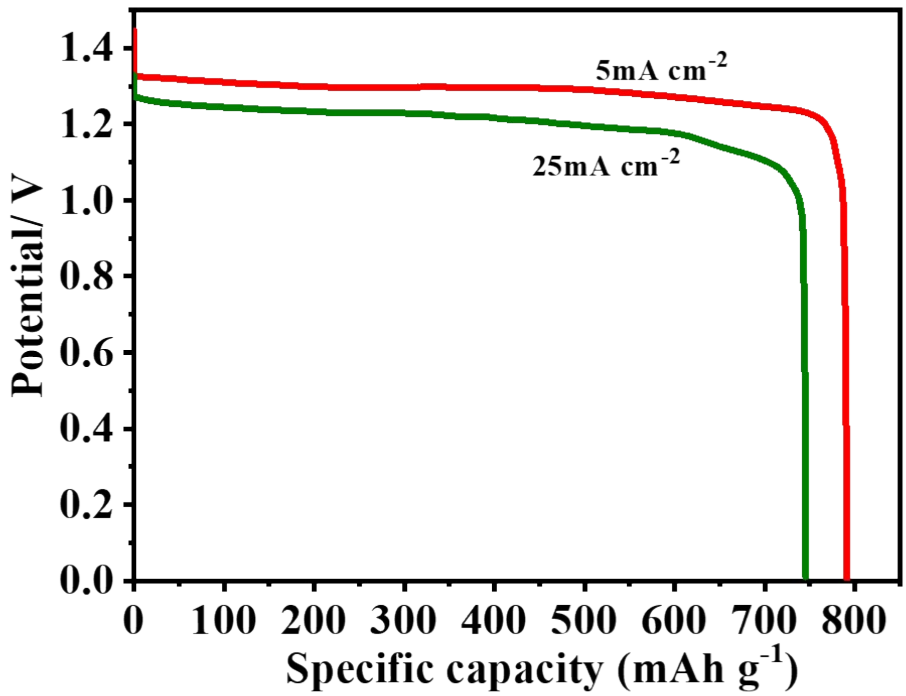


Fig. S25 Galvanostatic discharge curves of Zn-air battery employing Fe-HPNC/Co_3O_4 as cathodic catalysts at 5 mA cm^{-2} and 25 mA cm^{-2}.

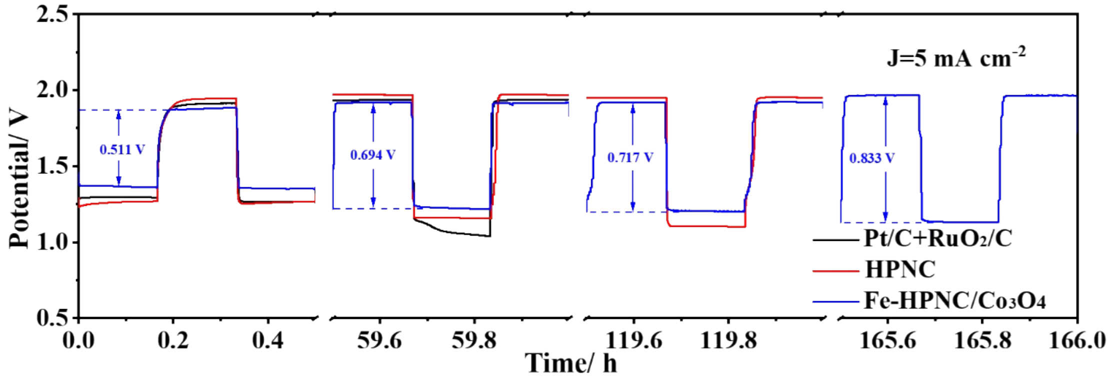


Fig. S26 Galvanostatic discharge-charge cycling curves of Zn-air batteries employing Pt/C+RuO_2/C, HPNC and Fe-HPNC/Co_3O_4 as cathodic catalysts at 5 mA cm^{-2} showing the changes of the voltage windows.

Table S1 Comparison of the porosity of various catalysts.

Sample	**S_{BET} (m^2 g^{-1})**	**S_{micro} (m^2 g^{-1})**	**S_{meso} (m^2 g^{-1})**	**Total pore volume (cm^3 g^{-1})**
Fe-HPNC	1083.831	224.441	859.39	2.661
Fe-HPNC/Co_3O_4	708.268	156.775	551.492	1.447
HPNC	1458.991	369.012	1089.98	2.617
Co_3O_4	61.493	49.511	11.912	0.197

Table S2 Elemental contents of various catalysts based on XPS results.

sample	C wt%	N wt%	O wt%	Fe wt%	Co wt%
Fe-HPNC-1:1	86.97	5.07	5.72	2.24	/
Fe-HPNC-2:1	86.23	4.67	5.67	3.45	/
Fe-HPNC-4:1	85.95	4.55	5.25	4.25	/
Fe-HPNC-700	83.73	4.8	6.56	4.31	/
Fe-HPNC-800	86.23	4.67	5.67	3.45	/
Fe-HPNC-900	87.79	4.54	5.48	2.19	/
Fe-HPNC/Co_3O_4	63.01	2.96	22.58	2.71	7.89

Table S3 Fe and Co contents of various catalysts based on ICP-OES results.

sample	Fe wt%	Co wt%
Fe-HPNC-1:1	0.34	/
Fe-HPNC-2:1	2.04	/
Fe-HPNC-4:1	2.84	/
Fe-HPNC-700	2.46	/
Fe-HPNC-800	2.04	/
Fe-HPNC-900	1.12	/
Fe-HPNC/Co_3O_4	1.56	7.29

Table S4 Fe K-edge EXAFS curve fitting parameters.

Samples	Path	C_N	R(Å)	R factor
Fe-HPNC	Fe-N	1.8(9)	1.99	0.03
	Fe-O	0.3(1)	2.33	
	Fe-C	1.2(5)	2.98	
	Fe-C	1.4(8)	3.55	

C_N is coordination number; R is the distance between absorber and backscatter atoms; R factor indicates the goodness of the fit; ΔE_0 is inner potential correction which is 4.09±3.6; S_0^2 is the amplitude reduction factor which is fixed to be 0.75.

Table S5 Comparisons of Fe content, active sites and ORR performance for Fe-HPNC and other Fe-based single-atom catalysts.

Catalysts	**Fe content (ICP-OES)**	**Active sites**	**$E_{1/2}$ (V vs. RHE)**	**Electrolyte**	**Ref.**
Fe-HPNC	2.04 wt%)	FeN_2	0.886	0.1 M KOH	*This work*
Fe_{SA}-N-C	1.76 wt%	FeN_4	0.891	0.1 M KOH	1
Fe-Z8-C	3 wt%	FeN_4	0.871	0.1 M KOH	2
FeNCNs-800	0.44 at%	FeN_4 and [illegible]	0.89	0.1 M KOH	3
SA-Fe-NHPC	1.25 wt%	FeN_x	0.93	0.1 M KOH	4
HSAC/Fe-3	2.78 wt%	FeN_4	0.814	0.5 M H_2SO_4	5
FeNC-CVD-750	2.0 wt%	FeN_4	0.85	0.5 M H_2SO_4	6
Fe, Mn/N-C	2.3 wt%	Fe, Mn-N_6	0.928	0.1 M KOH	7
KB-tpy-Fe-700	-	FeN_3	0.81	0.1 M KOH	8
Fe-N-C-900	0.66 at%	FeN_2	0.927	0.1 M KOH	9
Fe-SNC	0.34 at%	FeN_2	0.77	0.5 M H_2SO_4	10
FeCo/FeN_2/NHOPC	0.73 at%	Fe-N_2	0.86	0.1 M KOH	11
FeN_2-NOMC	0.5 at%	Fe-N_2	0.863	0.1 M KOH	12

Table S6 Comparisons of bifunctional electrocatalytic activities and the performance of the fabricated Zn-air batteries based on Fe-HPNC/Co_3O_4 and other recently reported non-noble metal catalysts.

Catalysts	**$E_{1/2}$ (V vs. RHE)**	**$E_{j=10}$ (V vs. RHE)**	**ΔE (V)**	**Peak Power Density (mW cm^{-2})**	**Durability**	**Ref.**
Fe-HPNC /Co_3O_4	0.886	1.457	0.571	236	165 h at 5 mA cm^{-2}	*This work*
HPNC	0.854	1.474	0.62	201	120 h at 5 mA cm^{-2}	13
Co_3O_4C-NA	0.78	1.52	0.74	-	-	14
Co@Co_3O_4/NC	0.80	1.65	0.85	-	-	15
Co_3O_4/NPGC	0.842	1.725	0.883	84	80 h at 5 mA cm^{-2}	16
Co_3O_4/CC	0.79	1.72	0.93	35	25 h at 3 mA cm^{-2}	17
Co_3O_4-NP/N-rGO	0.76	1.61	0.85	118	1000 min at 5 mA cm^{-2}	18
NC-Co_3O_4-90	0.87	1.588	0.718	82	210 h at 10 mA cm^{-2}	19
ZIF-L-D-Co_3O_4/CC	0.9	1.54	0.64	74	384 h at 5 mA cm^{-2}	20
CoO_x/N-RGO	0.896	1.6	0.704	120	10 h at 6 mA cm^{-2}	21
NP-Co_3O_4/CC	0.9	1.56	0.66	200	400 h at 5 mA cm^{-2}	22
Co/Co_3O_4@CoS-SNC	0.86	1.59	0.73	101	1000 min at 5 mA cm^{-2}	23

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