# **Supporting information**

# Co, Fe codoped holey carbon nanosheets as bifunctional oxygen electrocatalysts for rechargeable Zn-Air batteries

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# **Experimental section**

### Synthesis of M@HNSs

All chemicals were used without further purification. *N*, *N*-dimethylformamide (DMF) was purchased from Aladdin. Nitrilotriacetic acid (NTA), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were purchased from Alfa Aesar. Concentrated HNO<sub>3</sub> (70 %) was purchased from Xiya.

Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (570 mg, 1.92 mmol) in combination with either Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (15 mg, 0.048 mmol) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (20 mg, 0.048 mmol)) was dissolved in 30 mL DMF and stirred with a magnetic stirrer for 30 min. When Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O or Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was added separately, the molar amount of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O or Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was doubled. NTA (490 mg, 2.56 mmol) and 240  $\mu$ L HNO<sub>3</sub> were separately stirred in 30 mL DMF for 30 min. Finally, both solutions were then completely mixed and placed in a 100 mL Teflon reactor at 120 °C for 24 h. The precipitates of different colors were collected by centrifugation, repeatedly washed with DMF, and then dried under vacuum at 85 °C for 12 h. For the conversion of M@HNSs, M-Zn-MOF was annealed under N<sub>2</sub> at 900 °C for 2 h after heating at a rate of 5 °C min<sup>-1</sup>.

## Physical characterization

Phase analysis of M@HNSs was performed using an X-ray diffraction (XRD; RINT2000, Japan) with Cu Ka radiation ( $\lambda = 0.154$  nm) at a scanning rate of 5° min<sup>-1</sup>. Raman spectroscopy (Renishaw Invia Reflex, America) was used to analyze the D and G peaks of carbon materials. The specific surface area and pore diameter of the material were estimated by measuring the extent of N<sub>2</sub> adsorption and desorption (ASAP 2020). The micromorphology and microstructure of the materials were observed using scanning electron microscopy (SEM; MDTC-EQ-M18-01) and transmission electron microscopy (TEM; JEOL JEM 2100), respectively. The X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific K-Alpha) was used to analyze the electronic state of the material surface.

#### Electrochemical measurements

The ORR catalytic performance of the material was evaluated using a three-electrode system (CHI 760E). A carbon rod (3 mm diameter) was used as the counter electrode, a saturated calomel electrode (SCE) was treated as the reference electrode, and the working electrode was based on a glassy carbon (GC) with 5 mm diameter. When the ORR performance was tested in 0.1 M KOH electrolyte solution, the potential relative to the reversible hydrogen electrode (RHE) was obtained by using the equation:  $E_{(vs RHE)} = E_{(vs SCE)} + 0.0591pH + 0.2415V$ . A well-dispersed ink, prepared from 1 mg M@HNSs, 470 µL ethanol, and 30 µL 5 wt% Nafion, was added dropwise on the GC surface and dried naturally to prepare a working electrode with a catalyst loading of 0.24 mg·cm<sup>-2</sup>. Before testing, O<sub>2</sub> was

bubbled through the electrolyte for at least 30 min to assure oxygen saturation, and then the ORR catalytic performance was measured under a continuous supply of oxygen. First, 20 cyclic voltammetry (CV) cycles were performed to activate the catalyst, and then the linear sweep voltammetry (LSV) curves at 5 mV·s<sup>-1</sup> were obtained to evaluate the catalyst performance. The methanol tolerance of targeted catalysts was judged by observing the current change during the chronoamperometric (i-t) process after adding a certain amount of methanol. The electron transfer number was calculated from the Koutecky-Levich (K-L) analysis as follows:

$$J^{-1} = J_K^{-1} + (B\omega^{1/2})^1$$
$$B = 0.62nF(D_0)^{2/3}v^{-1/6}C_0$$
$$J_k = nFkC_0$$

where *J* is the measured current density,  $J_k$  is kinetic current density, and  $\omega$  is the angular velocity of electrode conversion. *B* is the slope of the *K*-*L* curve, *n* is the electron transfer number, *F* is the Faraday constant,  $D_0$  is the diffusion coefficient of oxygen in 0.1 M KOH solution, *v* is the mass transfer rate, and  $C_0$  is the oxygen concentration.

The  $H_2O_2$  conversion rate and the electron transfer number *n* were mainly calculated from the following formulas:

$$n = \frac{4I_{D}}{I_{D} + \frac{I_{R}}{N}}$$
  
%  $H_{2}O^{-} = 200 * \frac{\frac{I_{R}}{N}}{I_{D} + \frac{I_{R}}{N}}$ 

where  $I_D$  is the disc current,  $I_R$  is the ring current, and N is the ring current collection coefficient. For this study, N is 0.37, as measured in a K<sub>3</sub>[Fe(CN)<sub>6</sub>]<sup>+</sup> solution. The signal on electrode 2 is collected at 0.5 V (vs. SCE).

The OER performance test process was similar with ORR, except that the working electrode was 3 mm diameter GC, the reference electrode was Hg/HgO electrode, and the test environment was 1 M KOH solution.

### Fabrication and testing of Zn-Air batteries

The Zn-air battery consists of a hydrophobic carbon cloth pre-coated with electrocatalyst (0.5 mg cm<sup>-1</sup>), a polished zinc sheet, and an aqueous electrolyte mixed with 0.2 M Zn(CH<sub>3</sub>COO)<sub>2</sub> and 6 M KOH. The constant current charge/discharge curve of the battery was measured at room temperature on the LAND battery system, and one cycle includes a 5 min charge and 5 min discharge process at a current density of 2 mA cm<sup>-2</sup>. The charge and discharge polarization curves of the battery were measured on the electrochemical workstation (CHI 760E).



Figure S1. The SEM image of the CoFe-Zn-MOF



Figure S2. a) SEM image, b) TEM images, d-g) the mapping of elements of Fe@HNSs.



Figure S3. EDS of Fe@HNSs



Figure S4. a) SEM image, b) TEM images and d-g) the mapping of elements of Co@HNSs.



Figure S5. The EDS of Co@HNSs



Figure S6. The SEM images of HNSs



**Figure S7**. a), b) distribution of Co and Fe elements of CoFe@HNSs, c) High-resolution TEM image of CoFe@HNSs and its corresponding FFT.



Figure S8. The N<sub>2</sub> sorption isotherms of NS



Figure S9. Spectra obtained from X-ray photoelectron spectroscopy.



Figure S10. a, b) LSVs and k-l fitting lines of Co@HNSs, c, d) LSVs and K-L fitting lines of Fe@HNSs material.



Figure S11. The electron transfer number and  $H_2O_2$  yield at the potential range from 0.4~0.8 V for CoFe@HNSs and Pt/C.



**Figure S12**. a) The long-term stability test of CoFe@HNSs, Fe@HNSs and Co@HNSs in O<sub>2</sub> saturated 0.1 M KOH solution at a potential of 0.4 V (vs. RHE) at the speed of 1600 rpm, b) LSV curves before and after 3000 potential cycles at a sweep speed of 50 mV·s<sup>-1</sup> from 0.1 V to -0.4 V (vs. SCE). c) Methanol tolerance of CoFe@HNSs, Fe@HNSs, Co@HNSs, and Pt/C.



Figure S13. TEM images of CoFe@HNSs after 36 h i-t test.



**Figure S14**. LSV curves of CoFe@HNSs before and after the addition of potassium thiocyanide (KSCN) to the electrolyte solution.



Figure S15. a) i-t, b) LSV curves before and after 3000 potential cycles of Fe@HNSs, Co@HNSs, and CoFe@HNSs.



Figure S16. The ORR and OER performance of materials with different Co and Fe metals added amounts.

	C (at. %)	N (at. %)	O (at. %)	Fe (at. %)	Co (at. %)
Fe@HNSs	79.02	5.63	11.60	3.75	-
Co@HNSs	78.00	7.58	10.86	-	3.56
CoFe@HNSs	82.09	7.02	7.72	1.93	1.23

 Table S1. SEM analysis result of elements content of catalysts.

Table S2. Catalytic indicators of ORR for HNSs, Pt/C, IrO2, Fe@HNSs, Co@HNSs and CoFe@HNSs

Indicators	HNSs	Pt/C	IrO <sub>2</sub>	Fe@HNSs	Co@HNSs	CoFe@HNSs
E <sub>j10</sub> (V)	1.754	1.697	1.653	1.612	1.652	1.601
$E_{j1}(V)$	1.659	1.511	1.575	1.554	1.591	1.540
$\Delta E(V)$	0.982	0.811	-	0.745	0.791	0.704
Tafel (mV dec <sup>-1</sup> )	91.1	147.3	90.3	69.6	88.5	69.5

Table S3. Catalytic indicators of OER for HNSs, Pt/C, Fe@HNSs, Co@HNSs and CoFe@HNSs

Indicators	HNSs	Pt/C	Fe@HNSs	Co@HNSs	CoFe@HNSs
E <sub>j10</sub> (V)	1.754	1.697	1.612	1.652	1.601
$E_{j1}(V)$	1.659	1.511	1.554	1.591	1.540
ΔE (V)	0.982	0.811	0.745	0.791	0.704
Tafel (mV dec <sup>-1</sup> )	91.1	147.3	69.6	88.5	69.5

Catalysts	Electrolyte	E <sub>1/2</sub> (V)	E <sub>0</sub> (V)	J(mA/cm <sup>2</sup> )	Reference
CoFe@HNSs	0.1M KOH	0.897	0.998	4.784	This work
FexN/N-CNT-GR	0.1M KOH	0.89	-	5.5	1
Fe1-HNC-500-850	0.1M KOH	0.842	0.93	5.80	2
Co <sub>1</sub> -HNC-500-850	0.1M KOH	0.84	0.90	4.98	2
NPMC/CoFe	0.1M KOH	0.847	0.896	5.7	3
CoFe/NC-0.2-900	0.1M KOH	0.82	0.94	6.4	4
CoFe/SNC-25	0.1M KOH	0.843	-	6.96	5
CoFe@NC-NCNT-H	0.1M KOH	0.69	0.83	5.53	6
CoFe@NCNTs	0.1M KOH	0.84	0.95	5.5	7

 Table S4. Comparison of ORR performance of our catalyst with recently reported catalysts

Catalysts	ORR (E <sub>1/2</sub> , V)	OER (E <sub>j=10</sub> , V)	Activity (E=E <sub>j=10</sub> -E <sub>1/2</sub> )	Reference
CoFe@HNSs	0.897	1.601	0.704	This work
FeCo@NC	0.81	1.53	0.72	8
FeCo@MNC-S	0.83	1.56	0.73	8
FeCo/NC-800	0.80	1.63	0.83	9
FeCo@NC-750	0.80	1.49	0.69	10
FeCo-NCNFs-800	0.817	1.686	0.869	11
meso/micro-FeCo-N <sub>x</sub> -CN-30	0.88	1.66	0.78	12
FeCo-NC-850	0.873	1.675	0.802	13
CoFe/SN-C-25	0.843	1.504	0.661	14
Co-Fe-P-Se/NC	0.760	1.500	0.74	15
CMP-CoFe/C	0.83	1.53	0.70	16
CoFe/N-HCSs	0.791	1.522	0.731	17
CNTs@(Fe, Co)PP-700	0.86	1.64	0.78	18
CoFe-Co@PNC	0.887	1.550	0.673	19
(Fe, Co)-SA/CS	0.86	1.59	0.73	20

Table S5. Recently reported performance of CoFe based bifunctional oxygen electrocatalyst

## **Reference:**

1. W. Y. Noh, J. H. Lee and J. S. Lee, Appl. Catal., B, 2020, 268.

2. X. Zhang, S. Zhang, Y. Yang, L. Wang, Z. Mu, H. Zhu, X. Zhu, H. Xing, H. Xia, B. Huang, J. Li, S. Guo and E. Wang, *Adv. Mater.*, 2020, **32**, e1906905.

3. Y. Ma, L. Gan, D. Li, Y. Gao, X. Yang, K. Wang, S. Lu, H. Wu, S. Ding and C. Xiao, J. Power Sources, 2019, 441.

4. Z. Du, P. Yu, L. Wang, C. Tian, X. Liu, G. Zhang and H. Fu, Sci. China-Mater., 2019, 63, 327-338.

5. C. Li, E. Zhou, Z. Yu, H. Liu and M. Xiong, *Appl. Catal.*, *B*, 2020, 269.

6. Z. Shang, Z. Chen, Z. Zhang, J. Yu, S. Tan, F. Ciucci, Z. Shao, H. Lei and D. Chen, *J. Alloy. Compd.*, 2018, 740, 743-753.

- 7. P. Cai, Y. Hong, S. Ci and Z. Wen, Nanoscale, 2016, 8, 20048-20055.
- 8. C. Li, M. Wu and R. Liu, Appl. Catal., B, 2019, 244, 150-158.
- 9. N. Wu, Y. Lei, Q. Wang, B. Wang, C. Han and Y. Wang, Nano Res., 2017, 10, 2332-2343.
- 10. P. Cai, S. Ci, E. Zhang, P. Shao, C. Cao and Z. Wen, *Electrochim. Acta*, 2016, 220, 354-362.
- 11. L. Yang, S. Feng, G. Xu, B. Wei and L. Zhang, ACS Sustain. Chem. Eng. 2019, 7, 5462-5475.
- 12. S. Li, C. Cheng, X. Zhao, J. Schmidt and A. Thomas, Angew. Chem. Int. Ed., 2018, 57, 1856-1862.
- 13. G. Li, K. Zheng and C. Xu, Appl. Surf. Sci., 2019, 487, 496-502.
- 14. C. Li, E. Zhou, Z. Yu, H. Liu and M. Xiong, Appl. Catal., B, 2020, 269, 118771.
- 15. H. Wu, J. Wang, J. Yan, Z. Wu and W. Jin, Nanoscale, 2019, 11, 20144-20150.
- 16. H. Li and Z. Sui, New J. Chem., 2019, 43, 17963-17973.
- 17. J. Li, Y. Kang, W. Wei, X. Li, Z. Lei and P. Liu, Chem. Eng. J., 2021, 407, 127961.
- 18. Y. Qi, S. Yuan, L. Cui, Z. Wang, X. He, W. Zhang and T. Asefa, ChemCatChem, 2020, n/a.
- 19. Z. Lei, Y. Tan, Z. Zhang, W. Wu, N. Cheng, R. Chen, S. Mu and X. Sun, *Nano Res.*, 2020, DOI: 10.1007/s12274-020-3127-8.
- 20. V. Jose, H. Hu, E. Edison, W. Manalastas Jr, H. Ren, P. Kidkhunthod, S. Sreejith, A. Jayakumar, J. M. V. Nsanzimana,
- M. Srinivasan, J. Choi and J.-M. Lee, Small Methods, 2020, n/a, 2000751.