

Supplementary Information

γ -CD-MOF-Derived Heterostructure as Bifunctional Electrocatalyst for Rechargeable Zinc-Air Batteries

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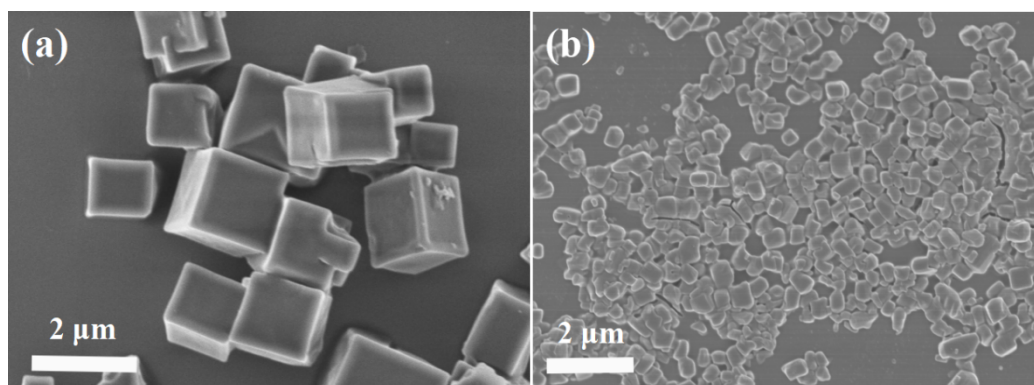


Fig. S1. SEM images of (a) γ -CD-MOF. (b) Co-CD-MOF.

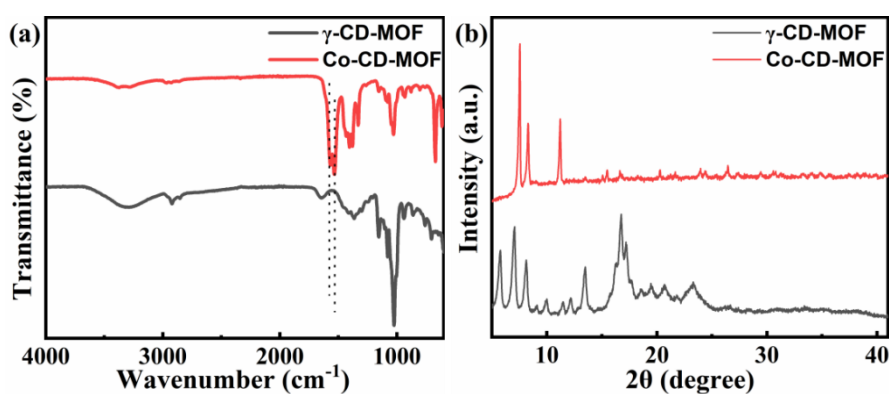


Fig. S2. (a) FT-IR spectra and (b) XRD patterns of γ -CD-MOF and Co-CD-MOF.

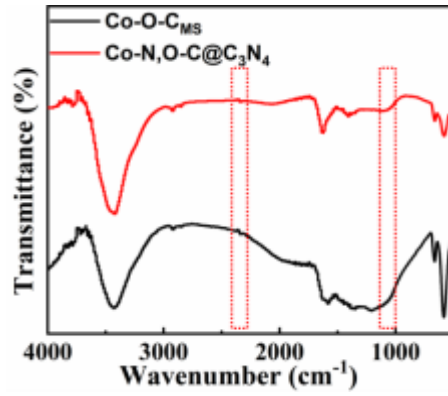


Fig. S3. FT-IR spectra of Co-O-C_{MS} and Co-N,O-C@C₃N₄.

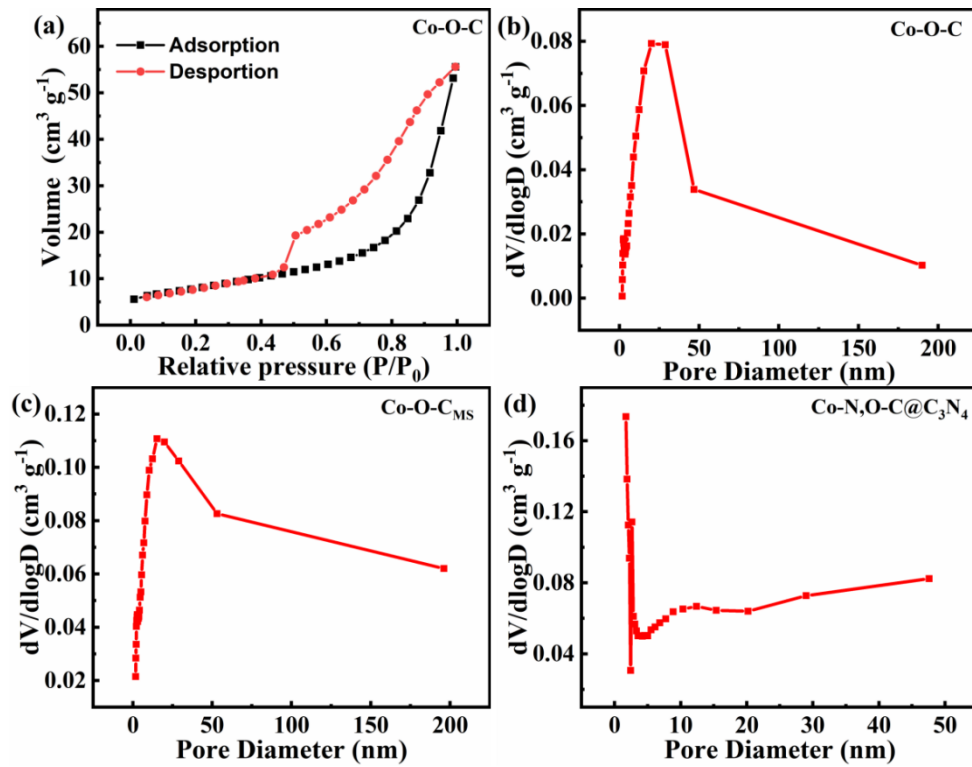


Fig. S4. (a) Nitrogen adsorption-desorption isotherms and (b) pore distribution curve of Co-O-C; Pore distribution curve of (c) Co-O-C_{MS} and (d) Co-N,O-C@C₃N₄.

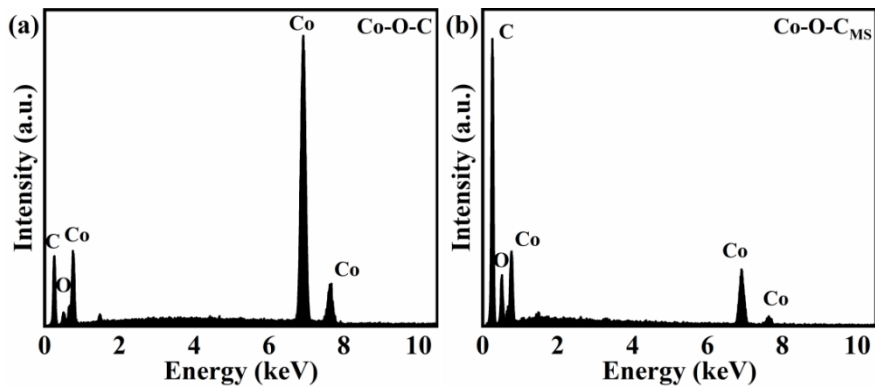


Fig. S5. EDS spectra of (a) Co-O-C and (b) Co-O-C_{MS}.

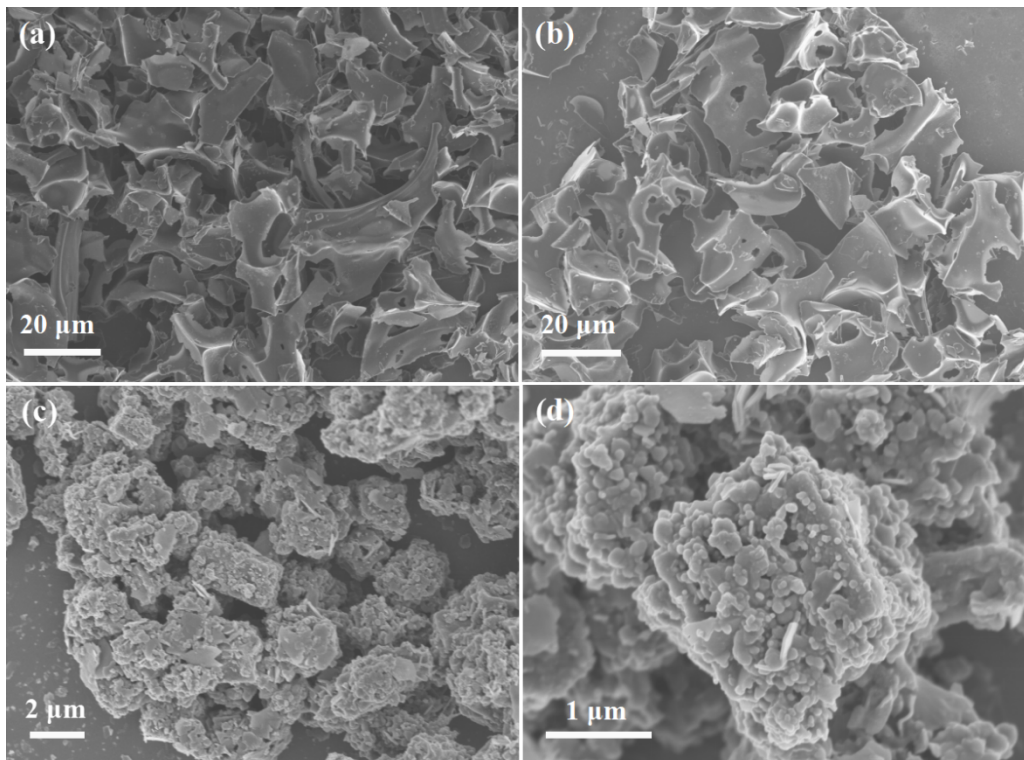


Fig. S6. SEM images of (a,b) Co-O-C and (c,d) Co-O-C_{MS}.

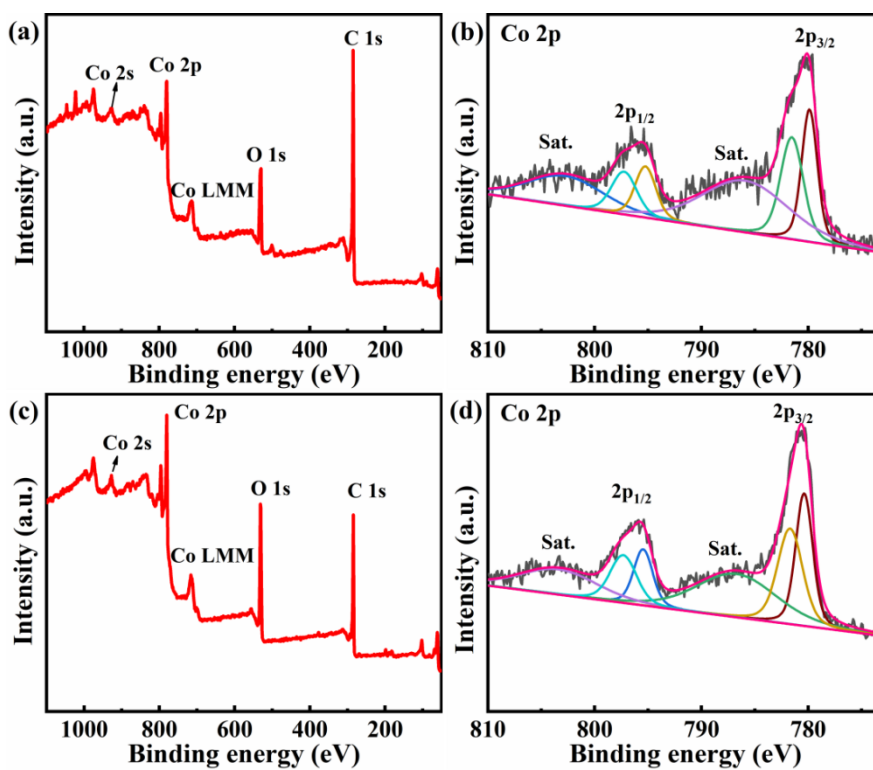


Fig. S7. (a,c) XPS survey spectra of Co-O-C and Co-O-C_{MS}, and (b,d) the corresponding high-resolution of Co 2p spectra.

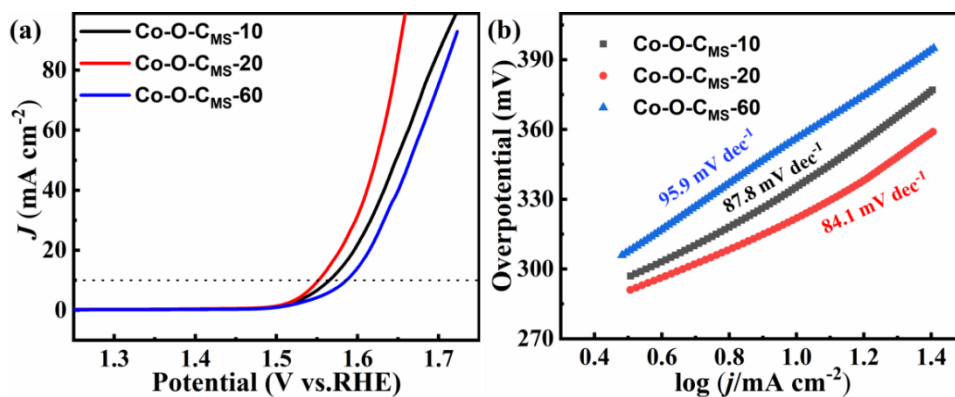


Fig. S8. (a) OER polarization curves and (b) Tafel slopes of Co-O-C_{MS} with different molten salt ratio.

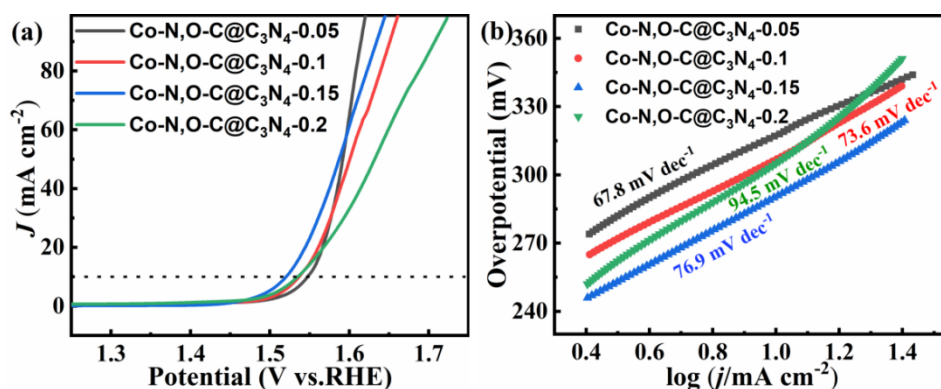


Fig. S9. (a) OER polarization curves and (b) Tafel slopes of Co-N,O-C@C₃N₄ with different melamine addition.

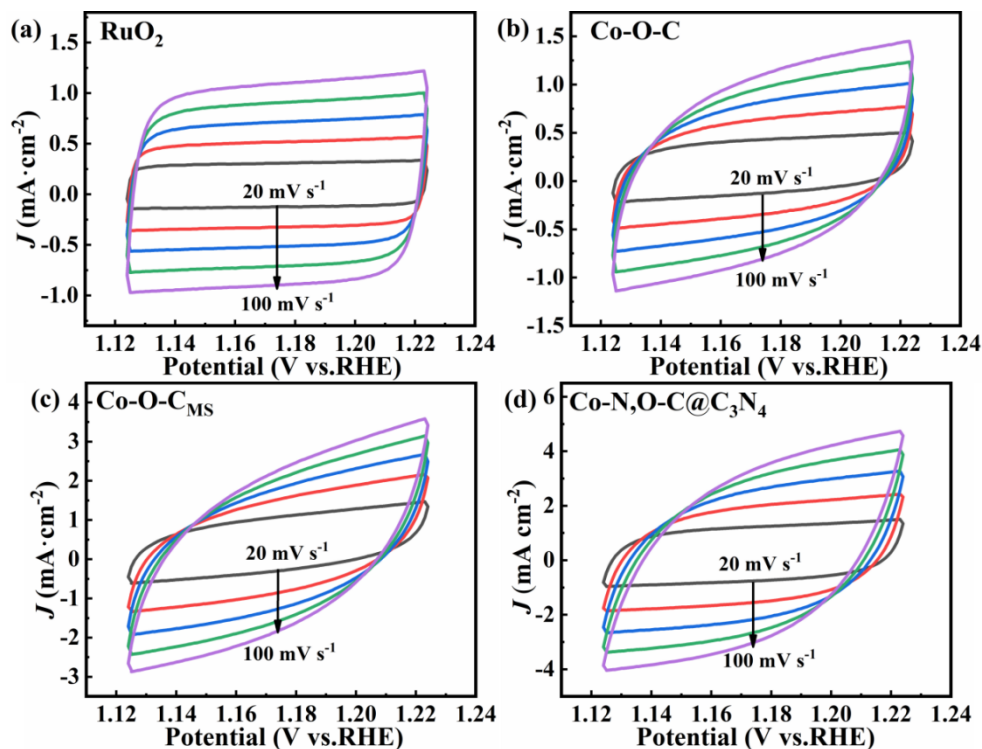


Fig. S10. CV curves of (a) RuO₂, (b) Co-O-C, (c) Co-O-C_{MS} and (d) Co-N,O-C@C₃N₄ at different sweeping rates from 20 mV s⁻¹ to 100 mV s⁻¹ in 1 M KOH.

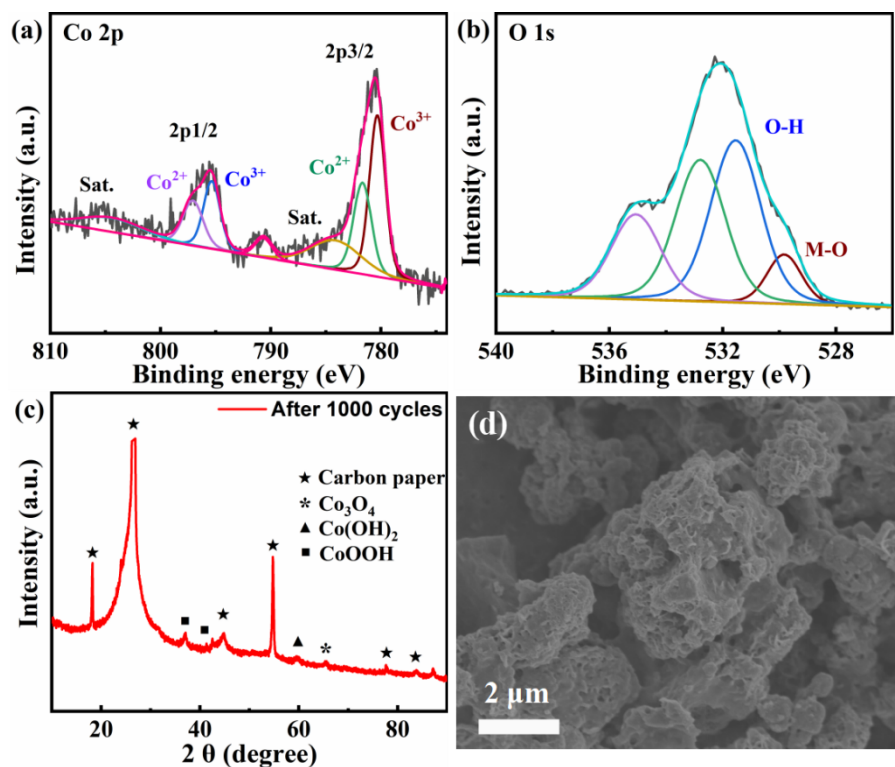


Fig. S11. (a) Co 2p and (b) O 1s spectra, (c) XRD and (d) SEM image of Co-N,O-C@C₃N₄ after 1000 CVs OER durability.

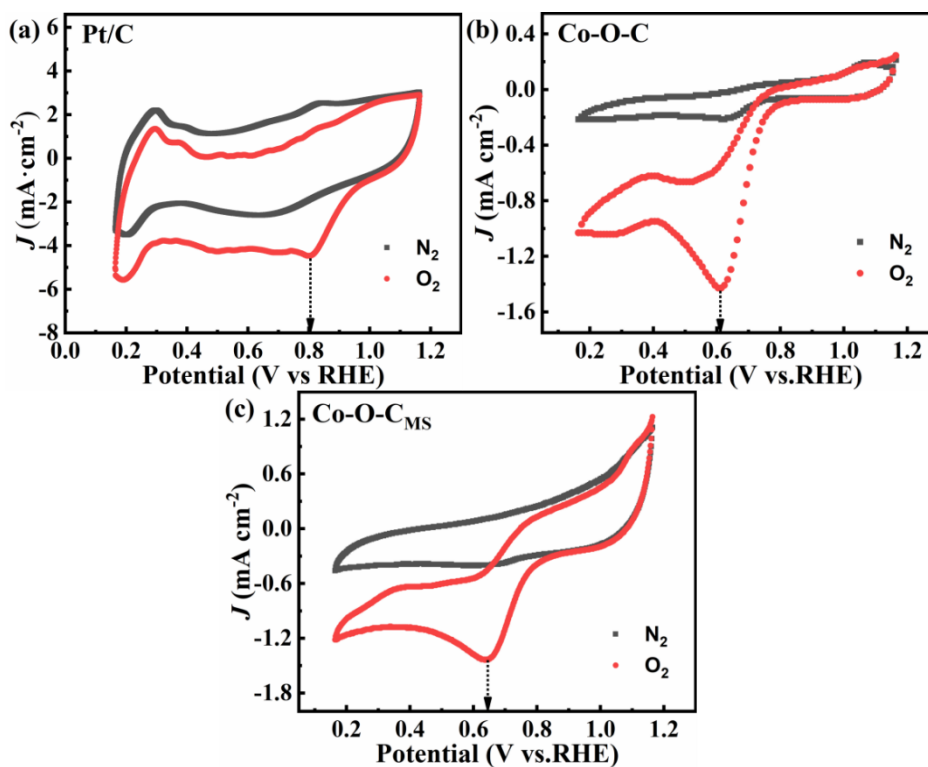


Fig. S12. CV curves of (a) Pt/C, (b) Co-O-C and (c) Co-O-C_{MS} in N₂ and O₂-saturated 0.1 M

KOH.

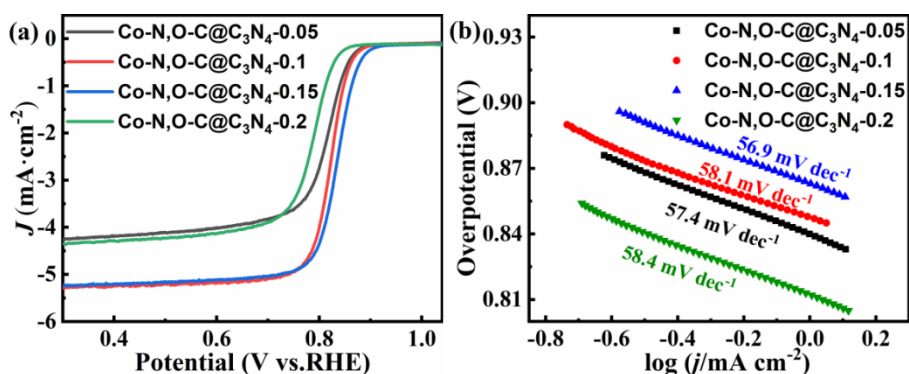


Fig. S13. (a) ORR polarization curves and (b) Tafel slopes of Co-N,O-C@C₃N₄ with different melamine addition.

Table S1 Sample composition based on XPS results

Sample	Co-O-C _{MS} (atomic%)	Co-N,O-C@C ₃ N ₄ (atomic%)
Co 2p	8.14	6.87
C 1s	68.84	70.95
N 1s	-	1.38
O 1s	23.02	20.80

Table S2 Comparison of the OER performances of Co-N,O-C@C₃N₄ with reported catalysts.

Catalyst	Overpotential/ mV (10 mA cm ⁻²)	Tafel slope (mV dec ⁻¹)	Mass loading (mg cm ⁻²)	Reference
Co-N,O-C@C ₃ N ₄	290	76.9	0.39	This work
Co ₃ N@AN-C NCs	280	69.6	2.6	1
Co/HNCP	383	81	0.204	2
Co/CNFs (1000)	320	79	0.3	3
Co ₂ P/Co-Foil	319	79	-	4

Co@N-CNTF	350	61.4	0.28	5
Co/CoO@NC@CC	284	76	0.19	6
S-CoO/Co ₃ O ₄	275	92	0.38	7
CoO _x -ZIF/C	318	70.3	0.194	8
Co ₃ O ₄ @C-TMA	320	85.18	0.15	9
Co@HOPC	320	31.2	0.2	10

Table S3 Comparison of the ORR performances of Co-N,O-C@C₃N₄ with reported catalysts.

Catalyst	$E_{1/2}$ (V)	Mass loading	Reference
		(mg cm ⁻²)	
Co-N,O-C@C ₃ N ₄	0.84	0.39	This work
ZIFCNDA	0.84	0.5	11
Co-SAs@NC	0.82	0.612	12
Co-NC@CoP-NC	0.78	0.28	13
Co-N _x -C	0.8	0.25	14
ACTP5@Co ₃ N-800	0.891	0.3	15
Co ₃ O ₄ -C ₃ N ₄ /rGO	0.81	0.13	16
f-CoNC/GO	0.86	0.31	17
Co@Co ₃ O ₄ /NC-2	0.74	0.21	18
Co-CoO/N-rGO	0.78	0.21	19
C-MOF-C2-900	0.817	0.2	20

Table S4 Comparison of the rechargeable Zn-air Battery performance of Co-N,O-C@C₃N₄ with reported catalysts.

Catalyst	Electrolyte	Power density (mW cm ⁻²)	Open-circuit voltage (V)	Reference
Co-N,O-C@C ₃ N ₄	6.0 M KOH + 0.2 M Zn(Ac) ₂	112	1.43	This work
Pt/C+RuO ₂	6.0 M KOH + 0.2 M Zn(Ac) ₂	92	1.39	This work
ZIFCNDA	6.0 M KOH + 0.1 M ZnCl ₂	57	1.14	11
Co-SAs@NC	6.0 M KOH + 0.2 M ZnCl ₂	105.3	1.46	12
f-CoNC/GO	6.0 M KOH + 1 M Zn(OAc) ₂	152	1.38	17
C-MOF-C2-900	6.0 M KOH + 0.2 M Zn(Ac) ₂	105	1.28	20
Co-N-CNTs	6.0 M KOH + 0.2 M Zn(Ac) ₂	101	1.365	21
Co ₃ O _{4-x} @N-C-2	6.0 M KOH + 0.2 M Zn(Ac) ₂	105.2	1.524	22
Co@CNT/MS	6.0 M KOH + 0.2 M Zn(Ac) ₂	128.6	1.46	23
HMT-Co@SiO ₂ -900	6.0 M KOH + 0.2 M Zn(Ac) ₂	80.17	1.417	24

References

1. B. K. Kang, S. Y. Im, J. Lee, S. H. Kwag, S. B. Kwon, S. Tiruneh, M.-J. Kim, J. H. Kim, W. S. Yang, B. Lim and D. H. Yoon, *Nano Research*, 2019, **12**, 1605-1611.
2. D. Ding, K. Shen, X. Chen, H. Chen, J. Chen, T. Fan, R. Wu and Y. Li, *ACS Catal.*, 2018, **8**, 7879-7888.
3. Z. Yang, C. Zhao, Y. Qu, H. Zhou, F. Zhou, J. Wang, Y. Wu and Y. Li, *Adv. Mater.*, 2019, **31**, 1808043.
4. C.-Z. Yuan, S.-L. Zhong, Y.-F. Jiang, Z. K. Yang, Z.-W. Zhao, S.-J. Zhao, N. Jiang and A.-W. Xu, *J. Mater. Chem. A*, 2017, **5**, 10561-10566.
5. H. Guo, Q. Feng, J. Zhu, J. Xu, Q. Li, S. Liu, K. Xu, C. Zhang and T. Liu, *J. Mater. Chem. A*, 2019, **7**, 3664-3672.
6. K. Dai, N. Zhang, L. Zhang, L. Yin, Y. Zhao and B. Zhang, *Chem. Eng. J.*, 2021, **414**, 128804.
7. T. Sun, P. Liu, Y. Zhang, Z. Chen, C. Zhang, X. Guo, C. Ma, Y. Gao and S. Zhang, *Chem. Eng. J.*, 2020, **390**, 124591.

8. S. Dou, C.-L. Dong, Z. Hu, Y.-C. Huang, J.-l. Chen, L. Tao, D. Yan, D. Chen, S. Shen, S. Chou and S. Wang, *Adv. Funct. Mater.*, 2017, **27**, 1702546.
9. K. Karuppasamy, R. Bose, D. Vikraman, S. Ramesh, H. S. Kim, E. Alhseinat, A. Alfantazi and H.-S. Kim, *J. Alloys Compd.*, 2023, **934**, 167909.
10. C. Tang, M. Ramírez-Hernández, B. Thomas, Y.-W. Yeh, P. E. Batson and T. Asefa, *Small Methods*, 2022, **6**, 2200519.
11. B. J. Ferraz, J. Kong, B. Li, N. Neng Tham, C. Blackman and Z. Liu, *J. Electroanal. Chem.*, 2022, **921**, 116702.
12. X. Han, X. Ling, Y. Wang, T. Ma, C. Zhong, W. Hu and Y. Deng, *Angew. Chem. Int. Ed.*, 2019, **58**, 5359-5364.
13. X. Li, Q. Jiang, S. Dou, L. Deng, J. Huo and S. Wang, *J. Mater. Chem. A*, 2016, **4**, 15836-15840.
14. C. Tang, B. Wang, H.-F. Wang and Q. Zhang, *Adv. Mater.*, 2017, **29**, 1703185.
15. J. Zhang, T. Zhang, J. Ma, Z. Wang, J. Liu and X. Gong, *Carbon*, 2021, **172**, 556-568.
16. L. Gong, X. Li, Q. Zhang, B. Huang, Q. Yang, G. Yang and Y. Liu, *Appl. Surf. Sci.*, 2020, **525**, 146624.
17. Y. Jia, Y. Wang, G. Zhang, C. Zhang, K. Sun, X. Xiong, J. Liu and X. Sun, *J. Energy Chem.*, 2020, **49**, 283-290.
18. A. Aijaz, J. Masa, C. Rösler, W. Xia, P. Weide, A. J. R. Botz, R. A. Fischer, W. Schuhmann and M. Muhler, *Angew. Chem. Int. Ed.*, 2016, **55**, 4087-4091.
19. X. Liu, W. Liu, M. Ko, M. Park, M. G. Kim, P. Oh, S. Chae, S. Park, A. Casimir, G. Wu and J. Cho, *Adv. Funct. Mater.*, 2015, **25**, 5799-5808.
20. M. Zhang, Q. Dai, H. Zheng, M. Chen and L. Dai, *Adv. Mater.*, 2018, **30**, 1705431.
21. T. Wang, Z. Kou, S. Mu, J. Liu, D. He, I. S. Amiin, W. Meng, K. Zhou, Z. Luo, S. Chaemchuen and F. Verpoort, *Adv. Funct. Mater.*, 2018, **28**, 1705048.
22. Y. Wang, R. Gan, Z. Ai, H. Liu, C. Wei, Y. Song, M. Dirican, X. Zhang, C. Ma and J. Shi, *Carbon*, 2021, **181**, 87-98.
23. C. Xiao, J. Luo, M. Tan, Y. Xiao, B. Gao, Y. Zheng and B. Lin, *J. Power Sources*, 2020, **453**, 227900.
24. X. Zhang, J. Xu and L. Wu, *Mater. Today Sustain.*, 2022, **19**, 100180.