Supplementary materials

In-situ Space-Confined Growth of Co_3O_4 Nanoparticles Inside N-Doped Hollow Porous Carbon Nanospheres as Bifunctional Oxygen Electrocatalysts for High-performance Rechargeable Zinc-Air Batteries

Jingbiao Kuang[a], Nengfei Yu[a,*], Zhongtang Yang[a], Yi Zhang[a], Lifei Ji[b], Jilei Ye[a,*], Wen Huang[b], Qinghong Huang[a], Na Tian[b], Yuping Wu[a] and Shigang Sun[b]

[a] School of Energy Science and Engineering, Nanjing Tech University, Nanjing, 211816, China
[b] State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
E-mail: yunf@njtech.edu.cn; yejilei@njtech.edu.cn

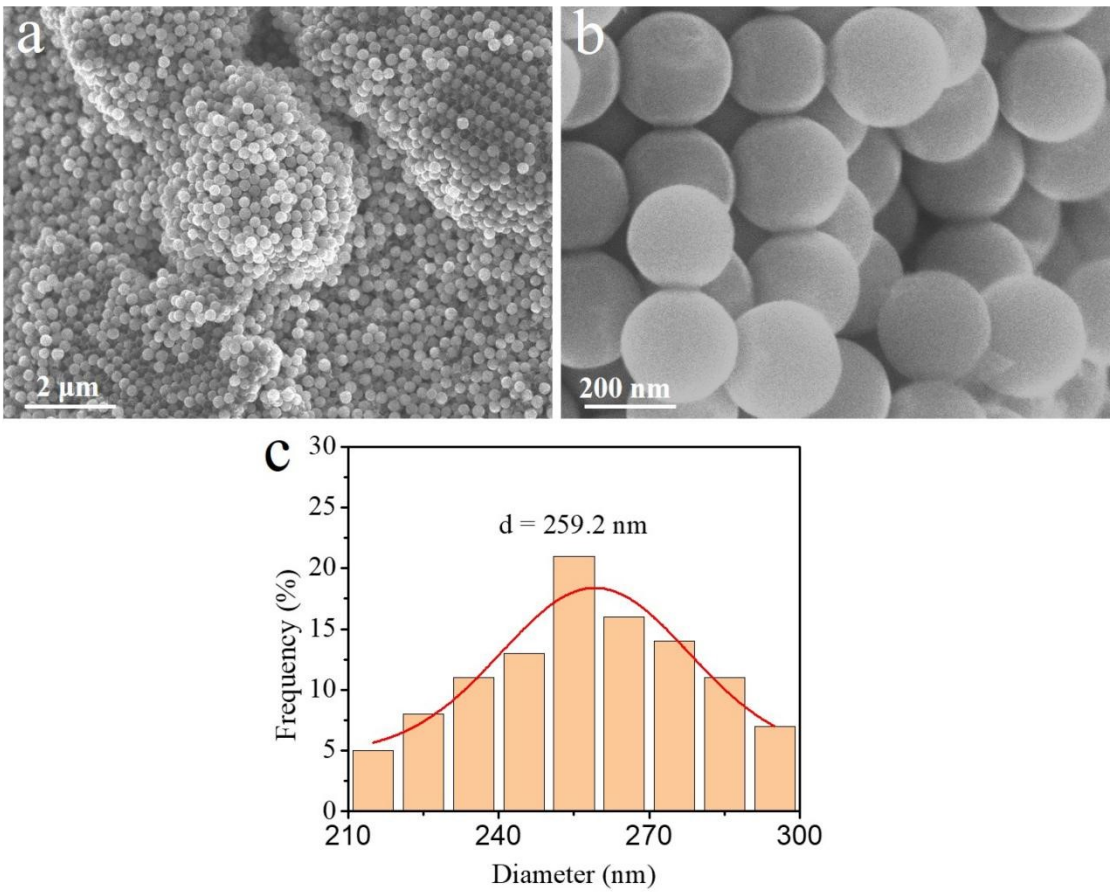

Figure S1. a) FESEM and b) enlarged FESEM images of SiO_2 nanospheres. c) size distribution of SiO_2 nanospheres

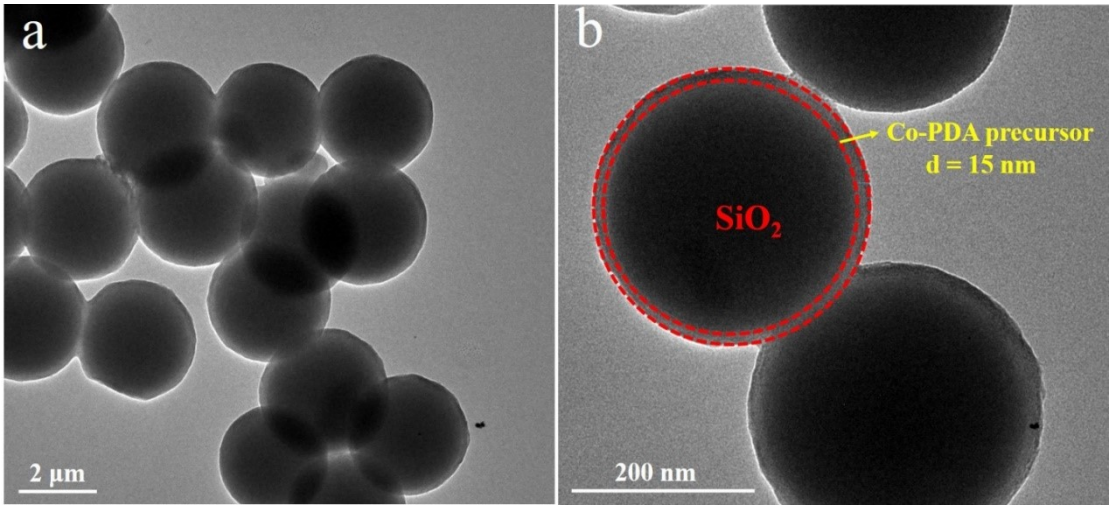

Figure S2. TEM images of SiO_2@Co-PDA nanospheres.

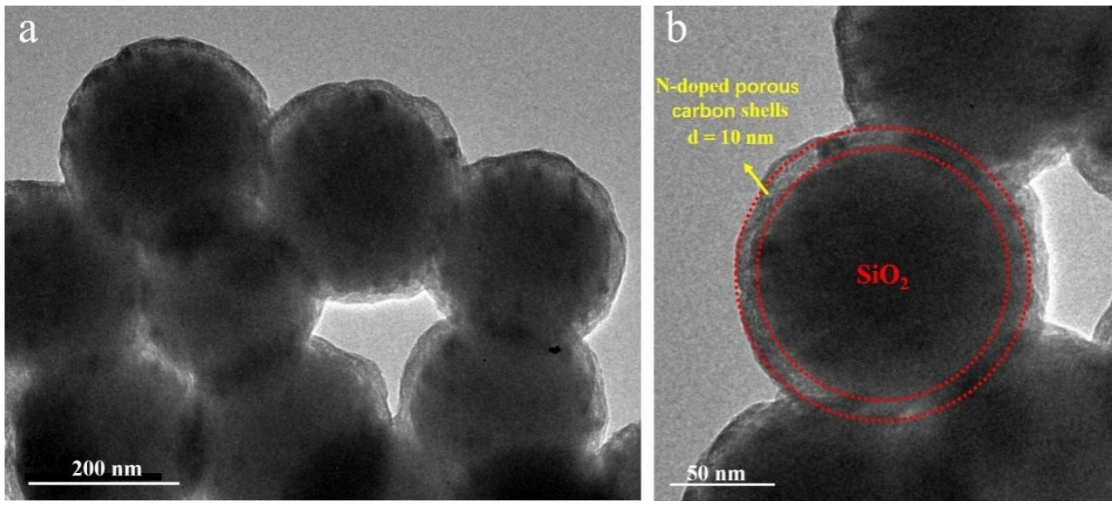

Figure S3. TEM images of SiO_2@Co_3O_4@N-PCSs nanospheres.

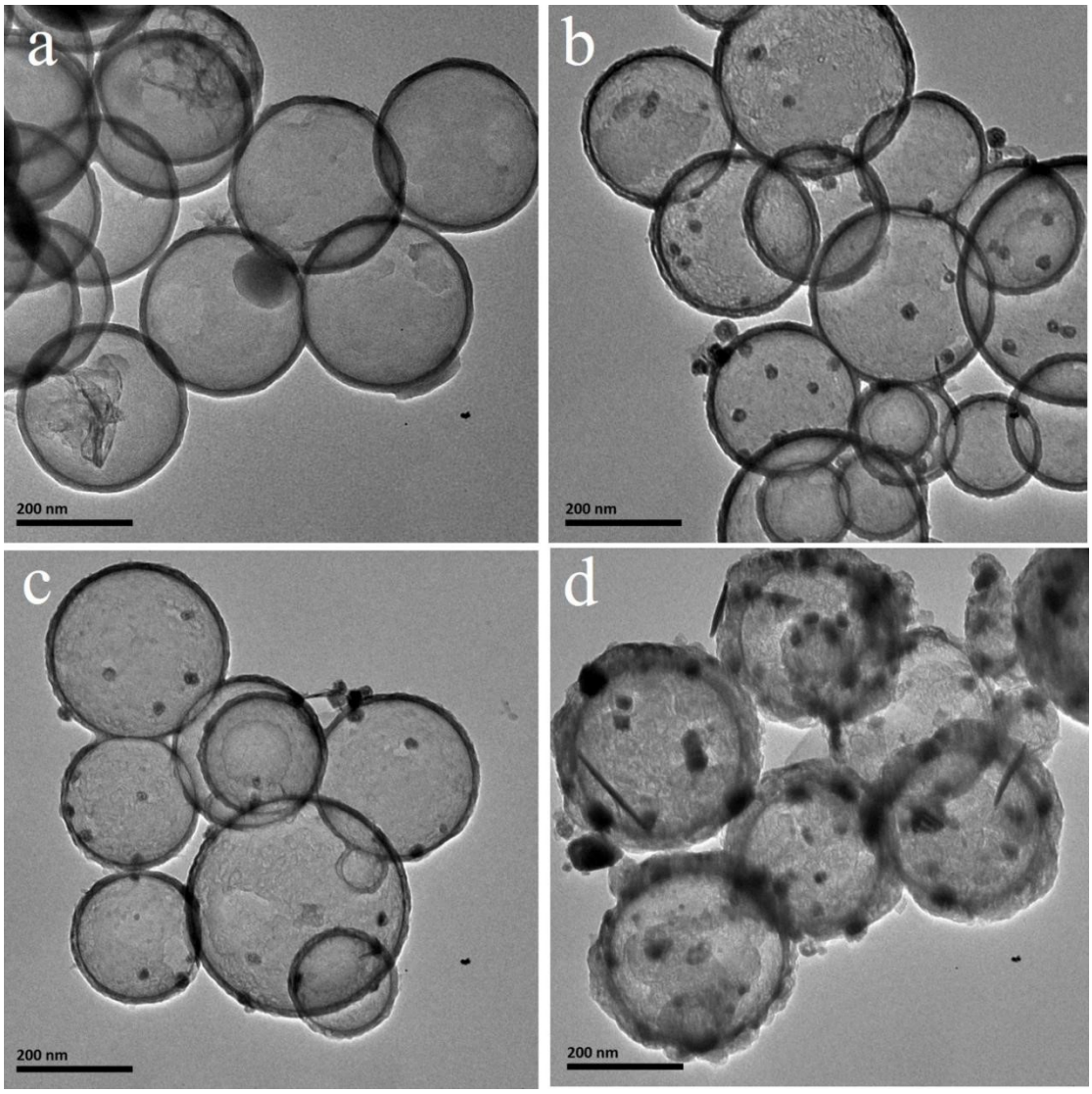

Figure S4. TEM images of a) N-HPCNSs, b) Co_3O_4-5%@N-HPCNs, c) Co_3O_4-10%@N-HPCNs and d) Co_3O_4-15%@N-HPCNs.

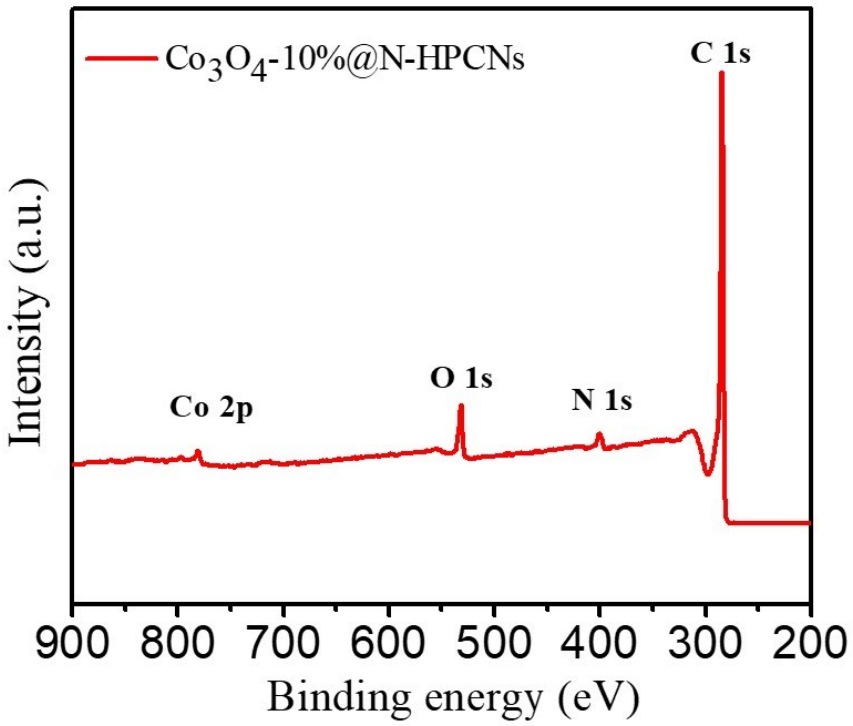

Figure S5. XPS survey spectrums of Co_3O_4-10%@N-HPCNs

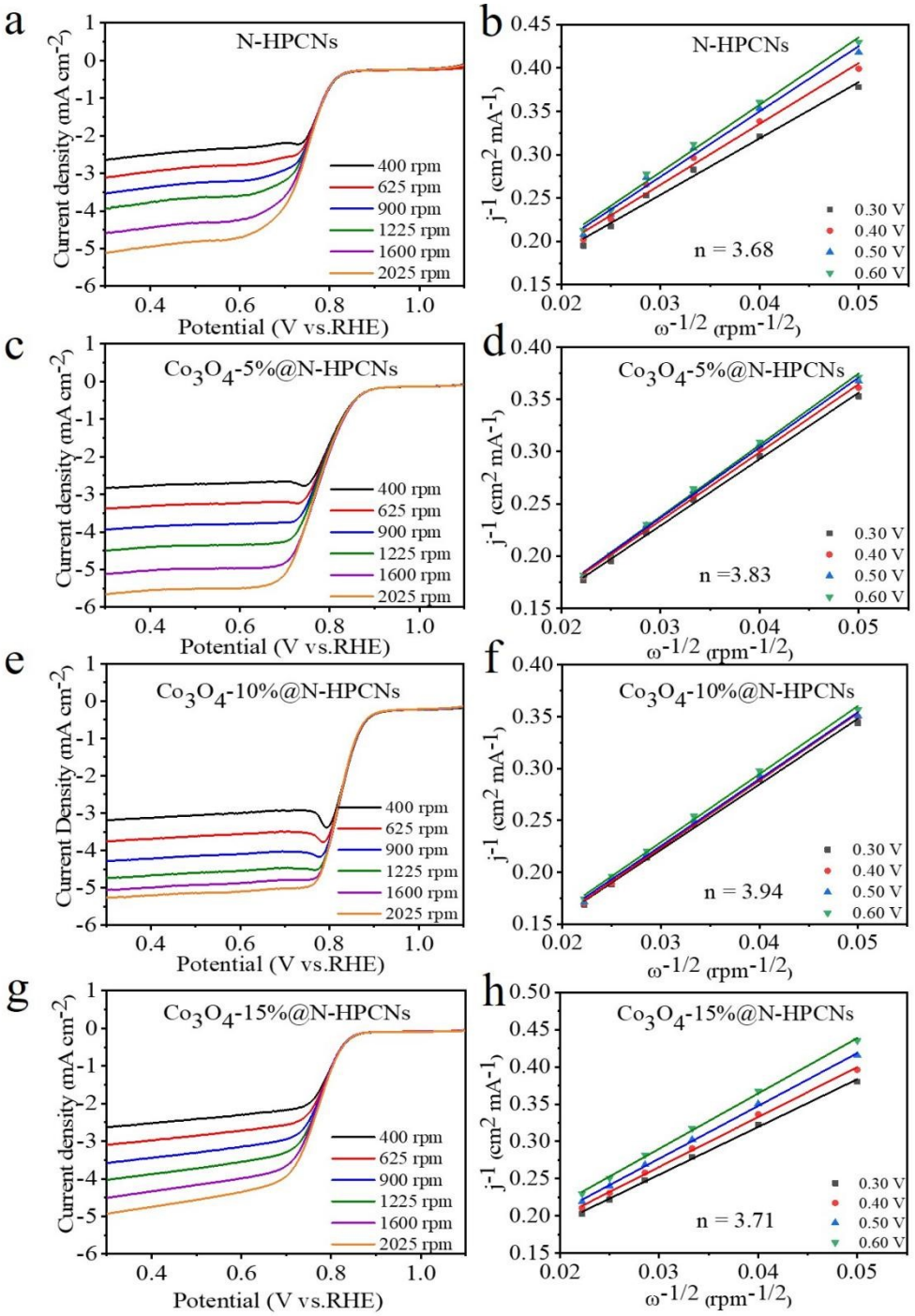

Figure S6. The RDE measurements of a) N-HPCNs, c) Co_3O_4-5%@N-HPCNs, e) Co_3O_4-10%@N-HPCNs and g) Co_3O_4-15%@N-HPCNs at a scan rate of 10 mV s-1, The Koutecky-Levich (K-L) plots of b) N-HPCNs, d) Co_3O_4-5%@N-HPCNs, f) Co_3O_4-10%@N-HPCNs and h) Co_3O_4-15%@N-HPCNs.

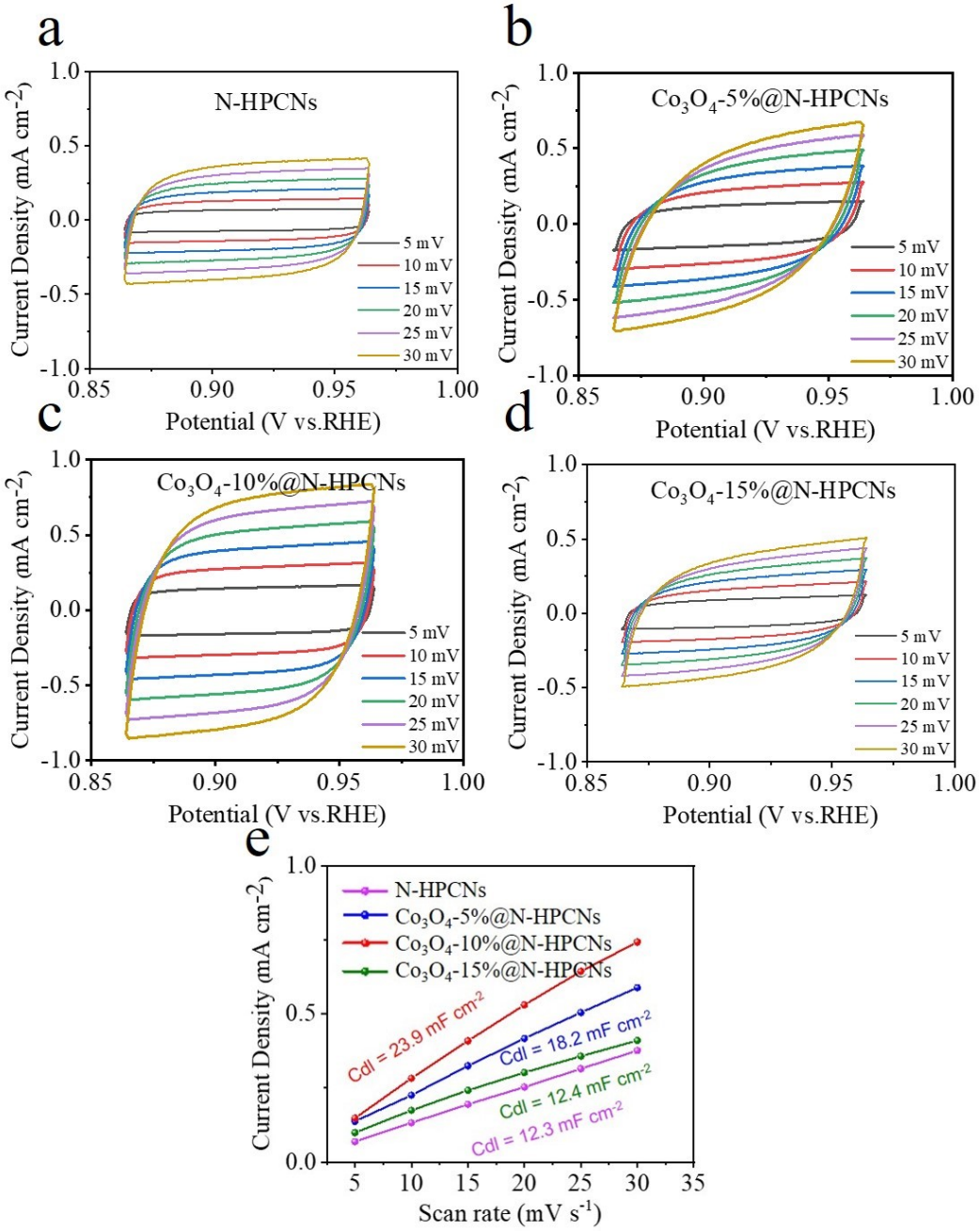

Figure S7. Scan rate dependence of current densities in CV curves for different electrocatalysts for ORR. a) N-HPCNs, b) Co_3O_4-5%@N-HPCNs, c) Co_3O_4-10%@N-HPCNs, d) Co_3O_4-15%@N-HPCNs, e) Calculated Cdl values for all samples.

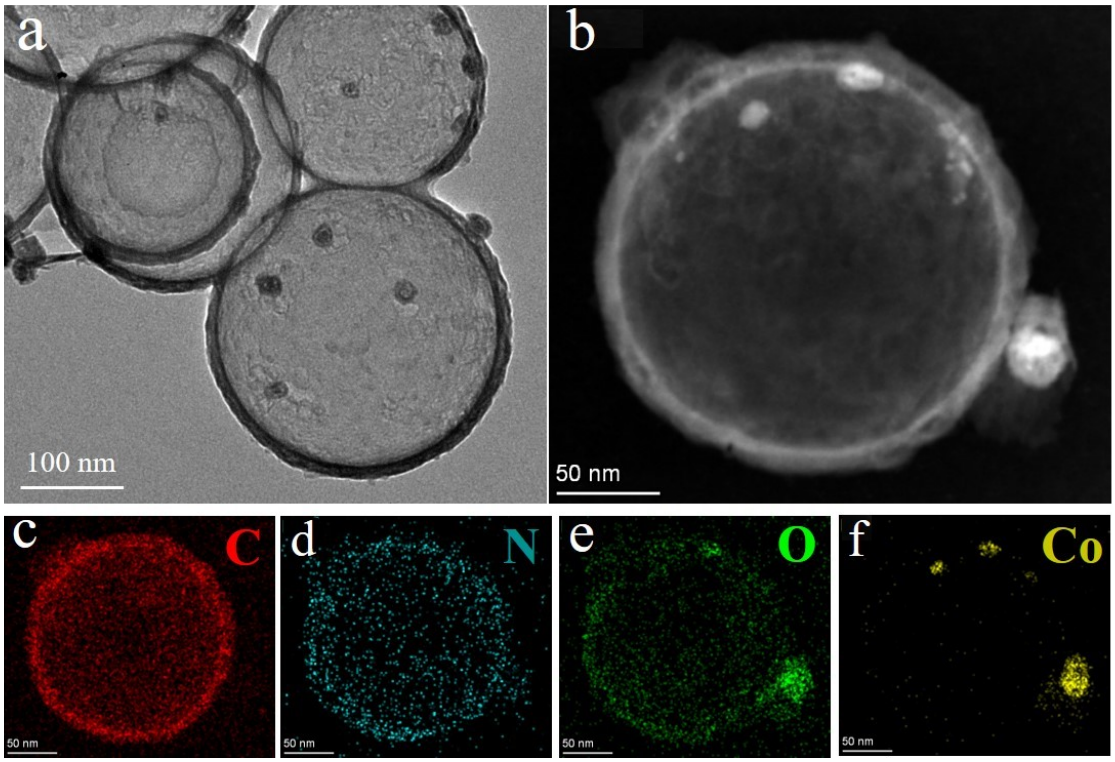

Figure S8. a) TEM and (b-f) EDS mapping images of HAADF-STEM elemental mapping images of Co_3O_4-10%@N-HPCNs after long-term ORR and OER stability tests.

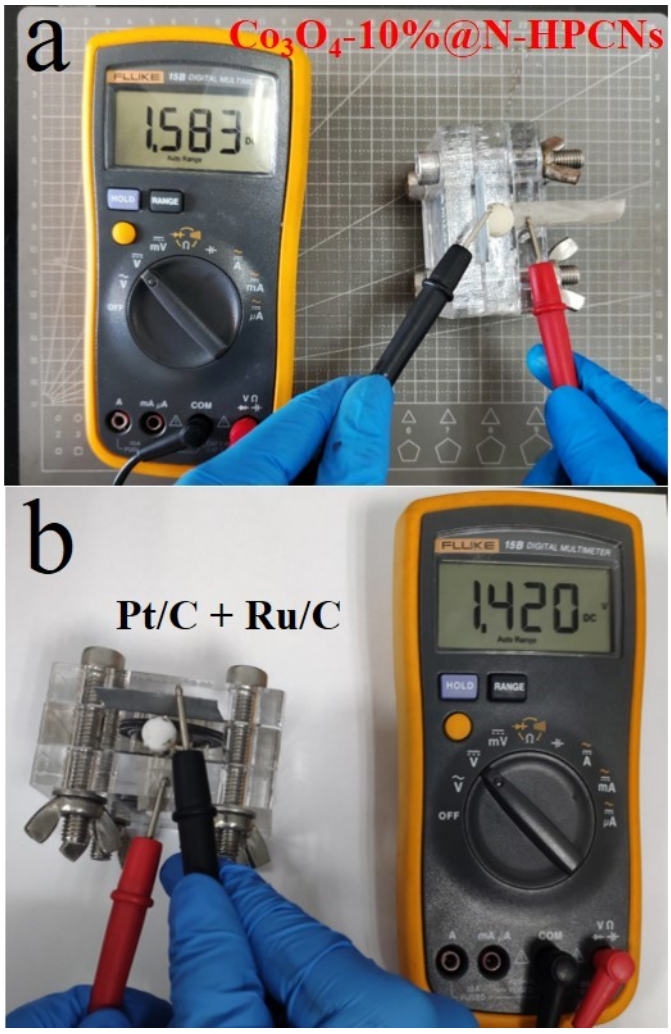

Figure S9. Photographs of open-circuit voltage of RZABs based on a) Co_3O_4-10%@N-HPCNs and b) Pt/C + Ru/C.

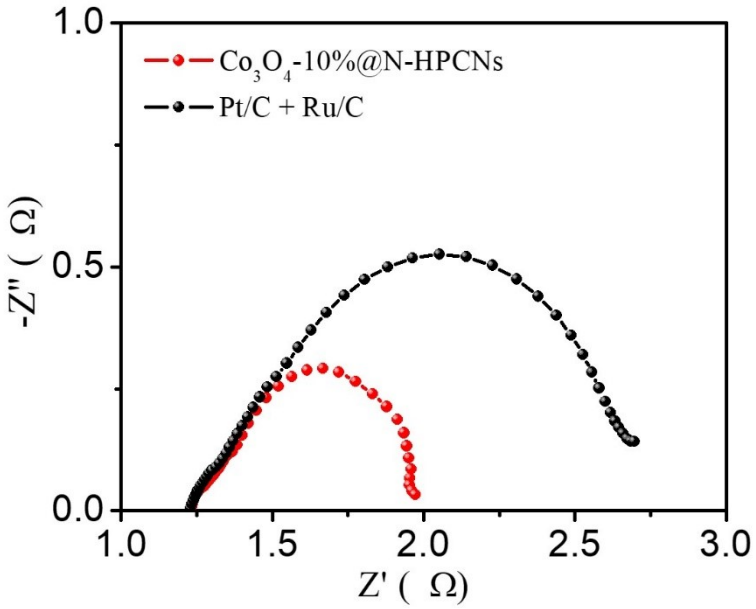

Figure S10. Nyquist plots of the RZABs based on Co_3O_4-10%@N-HPCNs and Pt/C + Ru/C.

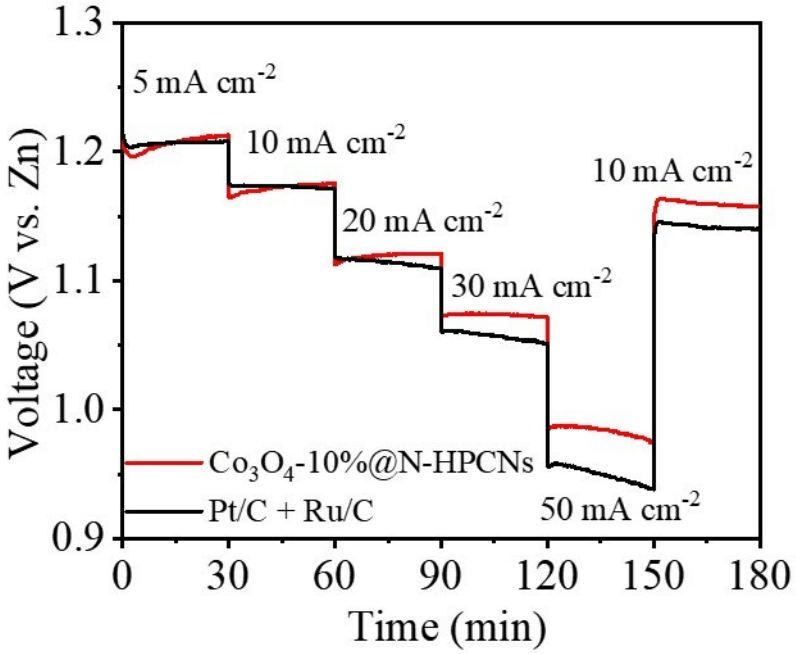

Figure S11. Discharge curves of the RZABs based on Co_3O_4-10%@N-HPCNs and Pt/C + Ru/C at various discharge current densities.

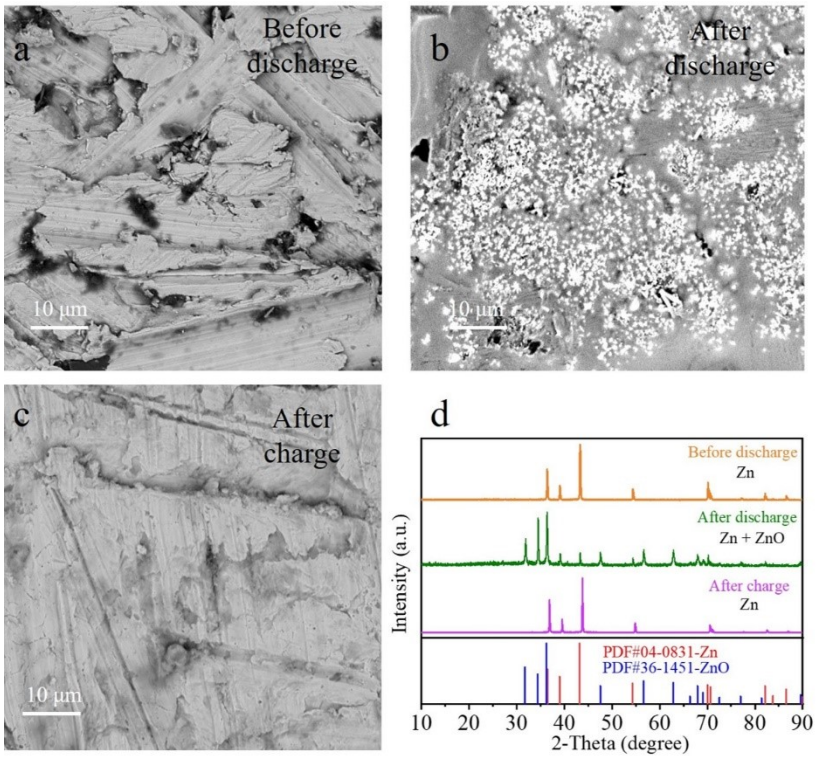

Figure. S12 The SEM images of Zn anode a) before, b) after discharge and c) after charge, d) the XRD patterns of Zn anode before and after discharge and after charge.

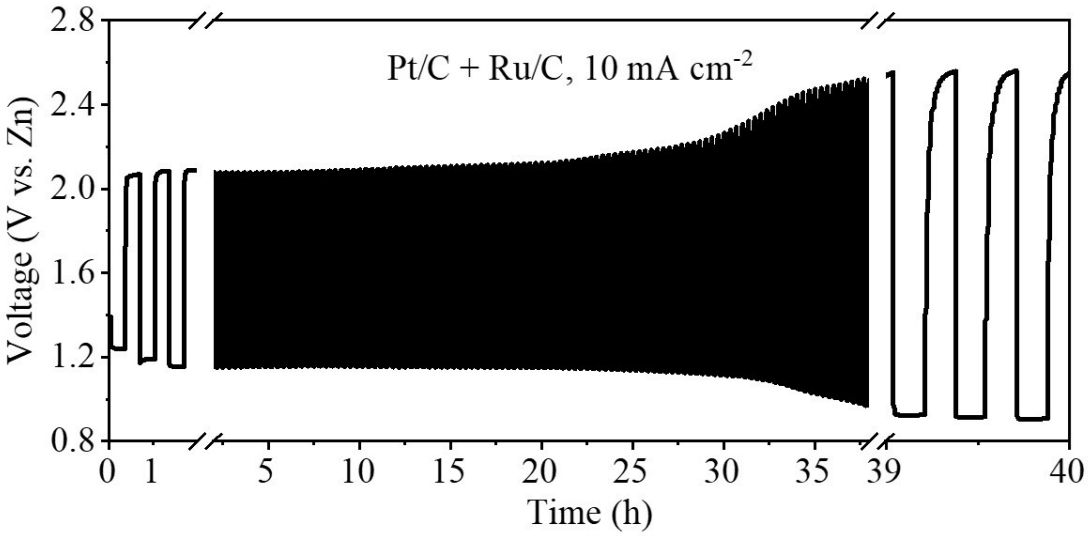

Figure S13. Galvanostatic cycling stability of RZABs with Pt/C + Ru/C cathode at a current density of 10 mA cm^{-2}.

Table S1. Thorough comparison of performances of recently reported bifunctional oxygen electrocatalysts.

Catalyst	ORR ($E_{1/2}$, V)	OER （$E_{j=10}$, V）	Activity ($\Delta E=E_{j=10}-E_{1/2}$, V)	Reference
Co_3O_4-10%@N-HPNCs	**0.83**	**1.61**	**0.78**	**This work**
Co-Co3O4@NAC	0.79	1.61	0.81	S1
Co3O4-Co/CoFe@C	0.81	1.59	0.78	S2
Co@Co3O4/NC	0.80	1.65	0.85	S3
Co9S8-NSHPCNF	0.82	1.58	0.76	S4
CoFe2O4@CNTs	0.78	1.74	0.96	S5
N–CNSP	0.85	1.62	0.77	S6
NiO/CoN PINWs	0.68	1.53	0.85	S7
Co7Fe3/CFNC	0.83	1.63	0.80	S8
Fe3C/Fe2O3@NGNs	0.76	1.69	0.93	S9
CNTs@(Fe,Co)PP-700	0.86	1.80	0.94	S10
Co2P/CoN-in-NCNTs	0.85	1.65	0.80	S11
p-CoNi@NSCs	0.81	1.65	0.84	S12
NiFe-LDH/Co,N-CNF	0.79	1.54	0.75	S13

Co@N-CNT	0.83	1.61	0.78	S14
Zn−Co−S NN/CFP	0.81	1.55	0.74	S15
FeCo-NCNFs-800	0.79	1.68	0.89	S16
ZnCoNC-0.1	0.84	1.75	0.91	S17
Co-NC@LDH	0.80	1.60	0.80	S18
CoFe/NGCT	0.79	1.67	0.88	S19
CoNi/BCF	0.80	1.60	0.80	S20
Ni3Fe/N-C	0.76	1.60	0.84	S21
NCO/N-rGO	0.78	1.63	0.85	S22
Co@NPCFs	0.66	1.63	0.97	S23
CoNC-MOG-9	0.79	1.63	0.84	S24

Catalyst	Open circuit voltage (V)	power density (mW cm^{-2})	Stability of RZABs[a]	Reference
Co_3O_4-10%@N-HPNCs	**1.583**	**145**	**1000 h 10 mA cm^{-2}**	**This work**
Co-Co3O4@NAC	1.449	164	35 h 10 mA cm^{-2}	S1
NiO/CoN PINWs	1.460	79.6	8 h 3 mA cm^{-2}	S7
Co_7Fe_3/CFNC	1.446	100.6	260 h 10 mA cm^{-2}	S8
CNTs@(Fe,Co)PP-700	1.537	74	116 h 2 mA cm^{-2}	S10
Co_2P/CoN-in-NCNTs	1.362	194.6	95 h 10 mA cm^{-2}	S11
p-CoNi@NSCs	1.460	87.9	430 h 10 mA cm^{-2}	S12
Co@N-CNT	1.450	168	9.5 h 20 mA cm^{-2}	S14
FeCo-NCNFs-800	1.480	74	40 h 10 mA cm^{-2}	S15
CoNi/BCF	1.438	155.1	30 h 10 mA cm^{-2}	S20
Co@NPCFs	1.450	91.9	80 h 2 mA cm^{-2}	S24
Co@NCNT-300	1.521	162.5	0.6 h 10 mA cm^{-2}	S25
Co-SAs@NC	1.460	105.3	85 h 10 mA cm^{-2}	S26
FeCo@MNC	1.410	143	48 h 20 mA cm^{-2}	S27
Fe/Co-N/S-C	1.395	102.6	26.7 h 5 mA cm^{-2}	S28

FeCoMoS@NG	1.440	118	70 h 2 mA cm^{-2}	S29
CoFe@NC-SE	1.581	102	30 h 5 mA cm^{-2}	S30
Co@NGC-NSs	1.360	52.3	16 h 5 mA cm^{-2}	S31
N-HCNT-70	1.492	189.3	84 h 10 mA cm^{-2}	S32
CoO/NG	1.490	169.6	40 h 10 mA cm^{-2}	S33

[a]The cycling conditions and period of rechargeable Zn-air batteries.

References

S1. X. Zhong, W. Yi, Y. Qu, L. Zhang, H. Bai, Y. Zhu, J. Wan, S. Chen, M. Yang, L. Huang, M. Gu, H. Pan and B. Xu, *Appl. Catal. B*, 2020, **260**, 118188.

S2. T. Li, Y. Lu, S. Zhao, Z. Gao and Y. Song, *J. Mater. Chem. A*, 2018, **6**, 3730-3737.

S3. A. Aijaz, J. Masa, C. Rosler, W. Xia, P. Weide, A. J. Botz, R. A. Fischer, W. Schuhmann and M. Muhler, *Angew. Chem. Int. Ed.*, 2016, **55**, 4087-4091.

S4. W. Peng, Y. Wang, X. Yang, L. Mao, J. Jin, S. Yang, K. Fu and G. Li, *Appl. Catal. B*, 2020, **268**, 118437.

S5. N. Xu, J. Qiao, Q. Nie, M. Wang, H. Xu, Y. Wang and X.-D. Zhou, *Catal. Today*, 2018, **318**, 144-149.

S6. L. Zong, W. Wu, S. Liu, H. Yin, Y. Chen, C. Liu, K. Fan, X. Zhao, X. Chen, F. Wang, Y. Yang, L. Wang and S. Feng, *Energy Stor. Mater.*, 2020, **27**, 514-521.

S7. J. Yin, Y. Li, F. Lv, Q. Fan, Y. Q. Zhao, Q. Zhang, W. Wang, F. Cheng, P. Xi and S. Guo, *ACS Nano*, 2017, **11**, 2275-2283.

S8. T. Tu, X. Zhou, P. Zhang, L. Tan, Z. Xu, M. Liu, W. Li, X. Kang, Y. Wu and J. Zheng, *ACS Sustainable Chem. Eng.*, 2022, **10**, 8694-8703.

S9. Y. Tian, L. Xu, J. Qian, J. Bao, C. Yan, H. Li, H. Li and S. Zhang, *Carbon*, 2019, **146**, 763-771.

S10. Y. Qi, S. Yuan, L. Cui, Z. Wang, X. He, W. Zhang and T. Asefa, *ChemCatChem*, 2020, **13**, 1023-1033.

S11. Y. Guo, P. Yuan, J. Zhang, H. Xia, F. Cheng, M. Zhou, J. Li, Y. Qiao, S. Mu and Q. Xu, *Adv. Funct. Mater.*, 2018, **28**, 1805641.

S12. X. He, J. Fu, M. Niu, P. Liu, Q. Zhang, Z. Bai and L. Yang, *Electrochim. Acta*, 2022, **413**, 140183.

S13. Q. Wang, L. Shang, R. Shi, X. Zhang, Y. Zhao, G. I. N. Waterhouse, L. Wu, C. Tung and T. Zhang, *Adv. Energy Mater.*, 2017, **7**, 1700467.

S14. Q. Dong, H. Wang, S. Ji, X. Wang, Z. Mo, V. Linkov and R. Wang, *Chem. Eur. J.*, 2020, **26**, 10752-10758.

S15. X. Wu, X. Han, X. Ma, W. Zhang, Y. Deng, C. Zhong and W. Hu, *ACS Appl. Mater. Interfaces*, 2017, **9**, 12574-12583.

S16. L. Yang, S. Feng, G. Xu, B. Wei and L. Zhang, *ACS Sustainable Chem. Eng.*, 2019, **7**, 5462-5475.

S17. X. Wu, G. Meng, W. Liu, T. Li, Q. Yang, X. Sun and J. Liu, *Nano Research*, 2017, **11**, 163-173.

S18. D. Chen, X. Chen, Z. Cui, G. Li, B. Han, Q. Zhang, J. Sui, H. Dong, J. Yu, L. Yu and L. Dong, *Chem. Eng. J.*, 2020, **399**, 125718.

S19. X. Liu, L. Wang, P. Yu, C. Tian, F. Sun, J. Ma, W. Li and H. Fu, *Angew. Chem. Int. Ed.*, 2018, **57**, 16166-16170.

S20. W. Wan, X. Liu, H. Li, X. Peng, D. Xi and J. Luo, *Appl. Catal. B*, 2019, **240**, 193-200.

S21. G. Fu, Z. Cui, Y. Chen, Y. Li, Y. Tang and J. B. Goodenough, *Adv. Energy Mater.*, 2017, **7**, 1601172.

S22. P. Moni, S. Hyun, A. Vignesh and S. Shanmugam, *Chem. Commun. (Cambridge, U. K.)*, 2017, **53**, 7836-7839.

S23. Y. Chen, W. Zhang, Z. Zhu, L. Zhang, J. Yang, H. Chen, B. Zheng, S. Li, W. Zhang, J. Wu and F. Huo, *J. Mater. Chem. A*, 2020, **8**, 7184-7191.
S24. N. Shang, S. Li, X. Zhou, S. Gao, Y. Gao, C. Wang, Q. Wu and Z. Wang, *Appl. Surf. Sci.*, 2021, **537**, 147818.
S25. P. Rao, P. Cui, L. Yang, M. Wang, S. Wang, H. Cai, Y. Wang, X. Zhao, D. P. Wilkinson and J. Zhang, *J. Power Sources*, 2020, **453**, 227858.
S26. X. Han, X. Ling, Y. Wang, T. Ma, C. Zhong, W. Hu and Y. Deng, *Angew. Chem. Int. Ed.*, 2019, **58**, 5359-5364.
S27. C. Li, M. Wu and R. Liu, *Appl. Catal. B*, 2019, **244**, 150-158.
S28. C. Li, H. Liu and Z. Yu, *Appl. Catal. B*, 2019, **241**, 95-103.
S29. S. Ramakrishnan, J. Balamurugan, M. Vinothkannan, A. R. Kim, S. Sengodan and D. J. Yoo, *Appl. Catal. B*, 2020, **279**, 119381.
S30. A. Samanta and C. R. Raj, *J. Power Sources*, 2020, **455**.
S31. P. Thakur, M. Yeddala, K. Alam, S. Pal, P. Sen and T. N. Narayanan, *ACS Appl. Energy Mater.*, 2020, **3**, 7813-7824.
S32. E. Y. Choi, D. E. Kim, S. Y. Lee and C. K. Kim, *Carbon*, 2020, **166**, 245-255.
S33. L. Xu, C. Wang, D. Deng, Y. Tian, X. He, G. Lu, J. Qian, S. Yuan and H. Li, *ACS Sustainable Chem. Eng.*, 2019, **8**, 343-350.