Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Tunable phosphorization degree of Co_xP_y@N,P-doped carbon as a highly-active bifunctional electrocatalyst for rechargeable Zinc-air batteries

Yang Liu [a], *Chen Li* [a], *Min Yuan* [a], *Xinghao Zhang* [a], *Haikuo Lan* [a], *Yuting Chen* [a], *Minge Tian* [d], *Kang Liu** [a, c], *Lei Wang* * [a, b]

a Y. Liu, C. Li, M. Yuan, X. Zhang, Y. Chen, Prof. K. Liu, Prof. L. Wang
Key Laboratory of Eco-chemical Engineering, Taishan Scholar Advantage and Characteristic Discipline Team of Eco-Chemical Process and Technology, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China.
b Prof. L. Wang
College of Environment and Safety Engineering, Qingdao University of Science and Technology, Qingdao 266042, China.
c Prof. K. Liu
Chaofeng Steel Structure Group Co., Ltd., Hangzhou 311215, China.
d M. Tian
Scientific Green(shandong) Environmental Technology Co.Ltd, Jining Economic Development Zone, Shandong Province, 272499, China.
E-mail: liukang82@126.com;inorchemwl@126.com.

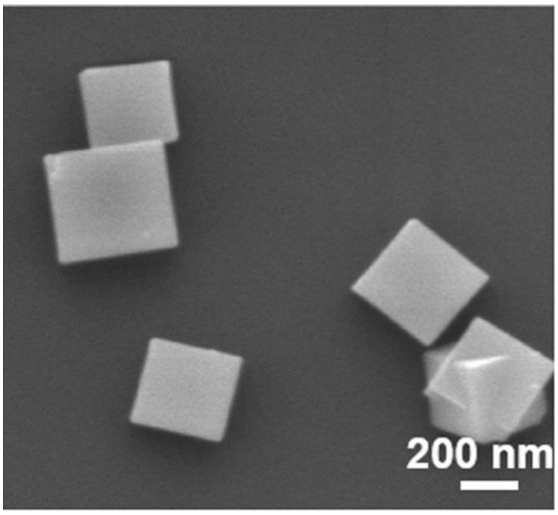

Figure S1. The SEM image of CoCo-PBA.

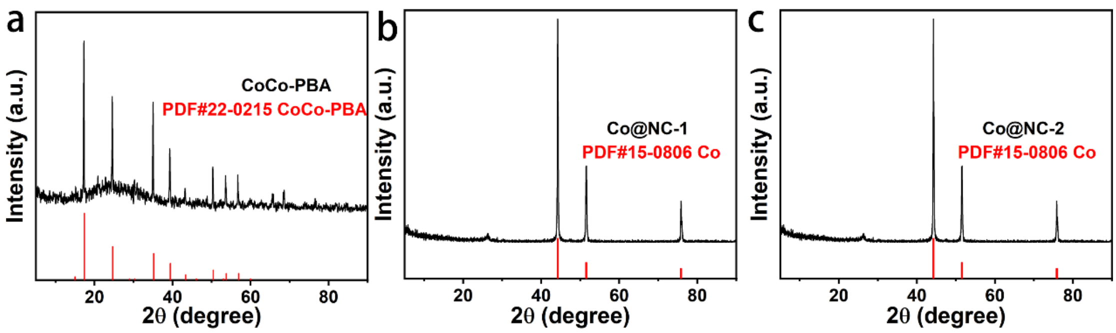

Figure S2. (a) XRD patterns of CoCo-PBA and CoCo-PBA simulated; (b) XRD patterns of Co@NC-1 and Co@NC-1 simulated; (c) XRD patterns of Co@NC-2 and Co@NC-2 simulated.

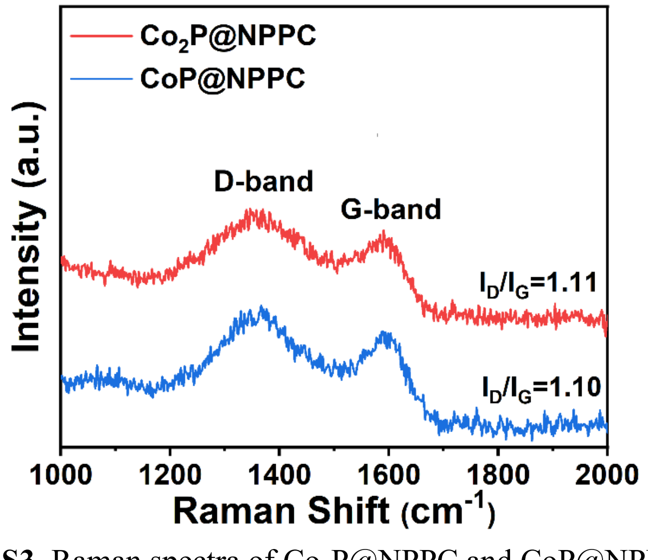

Figure S3. Raman spectra of Co_2P@NPPC and CoP@NPPC

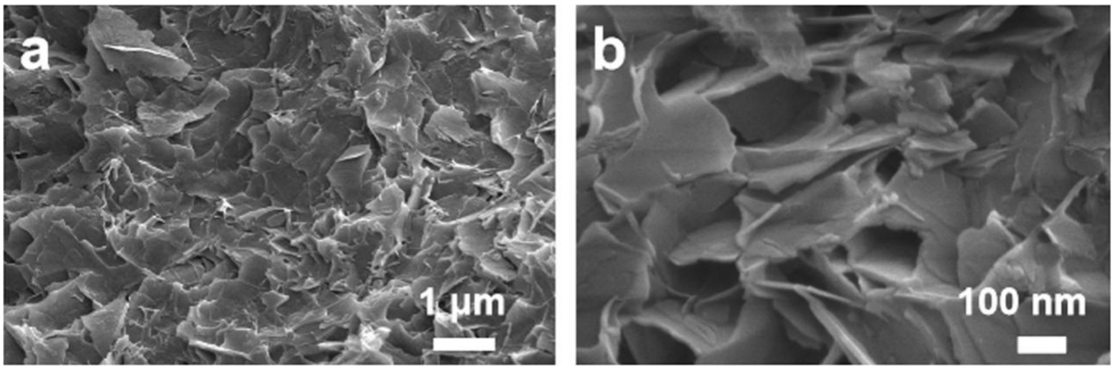

Figure S4. The SEM images of MPSA.

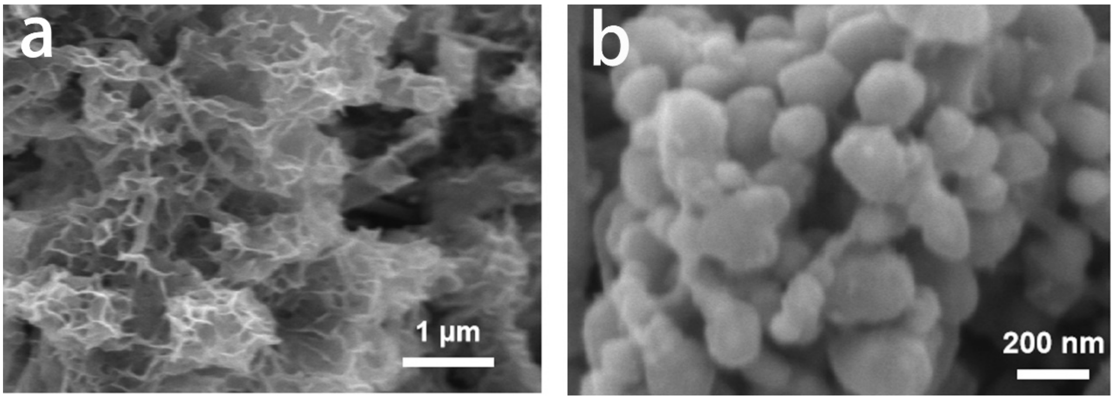

Figure S5. (a) The SEM images of Co@NC-1; (b) The SEM images of Co@NC-2.

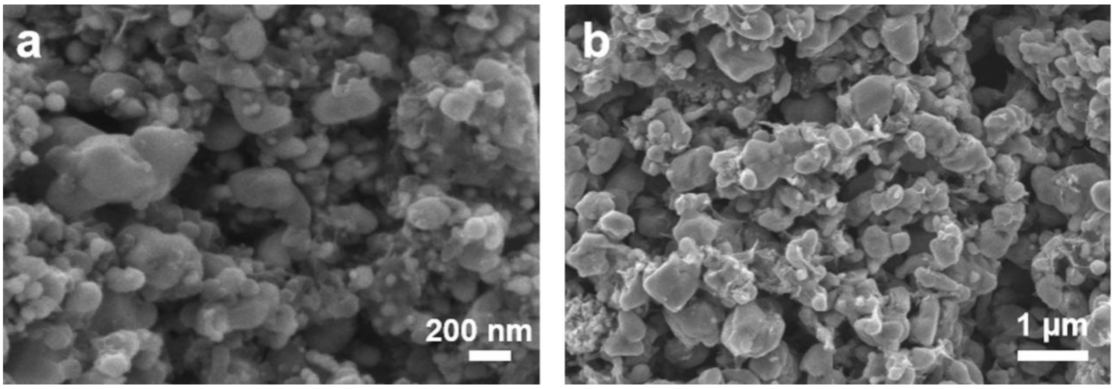

Figure S6. (a) The SEM images of CoP@NPPC; (b) The SEM images of Co_2P@NPPC.

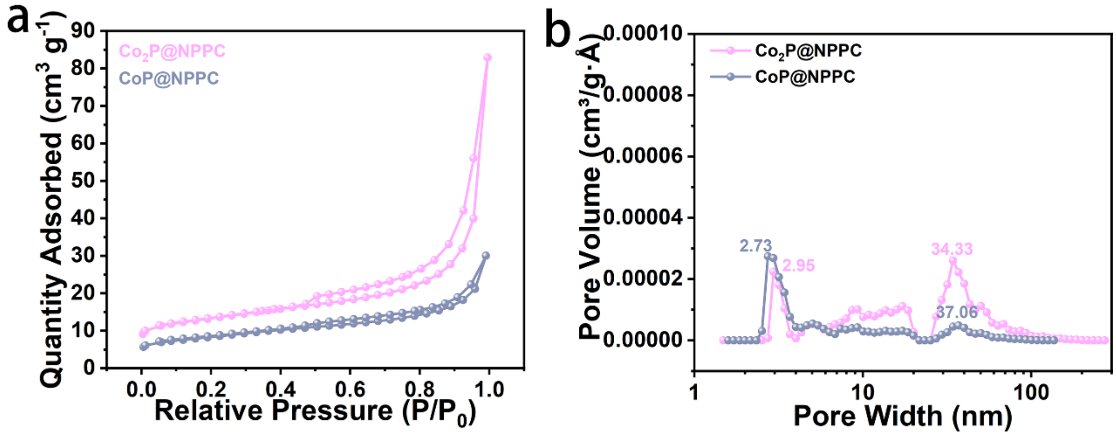

Figure S7. (a) N_2 adsorption-desorption curves of Co_2P@NPPC and CoP@NPPC; (b) Pore size distribution of Co_2P@NPPC and CoP@NPPC.

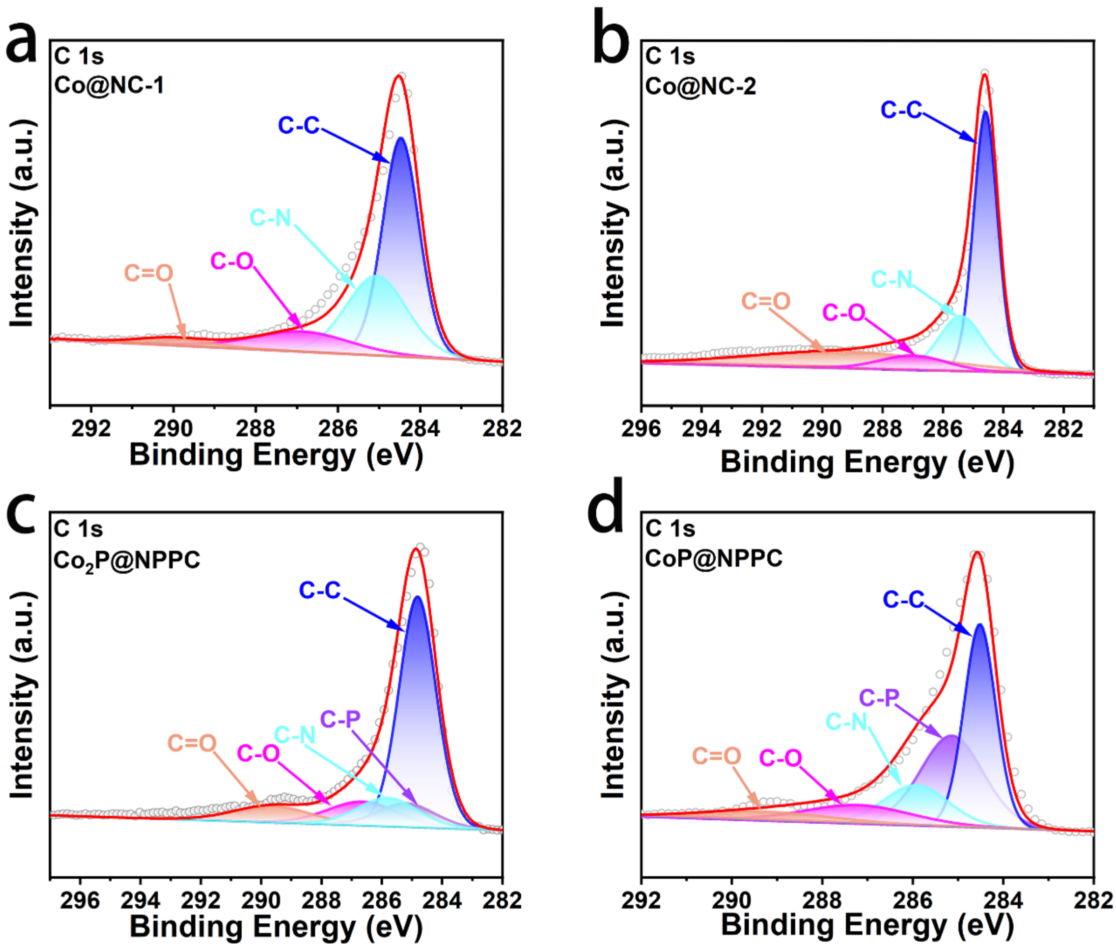

Figure S8. High-resolution C 1s XPS spectra of (a) Co@NC-1, (b) Co@NC-2, (c) Co_2P@NPPC, (d) CoP@NPPC.

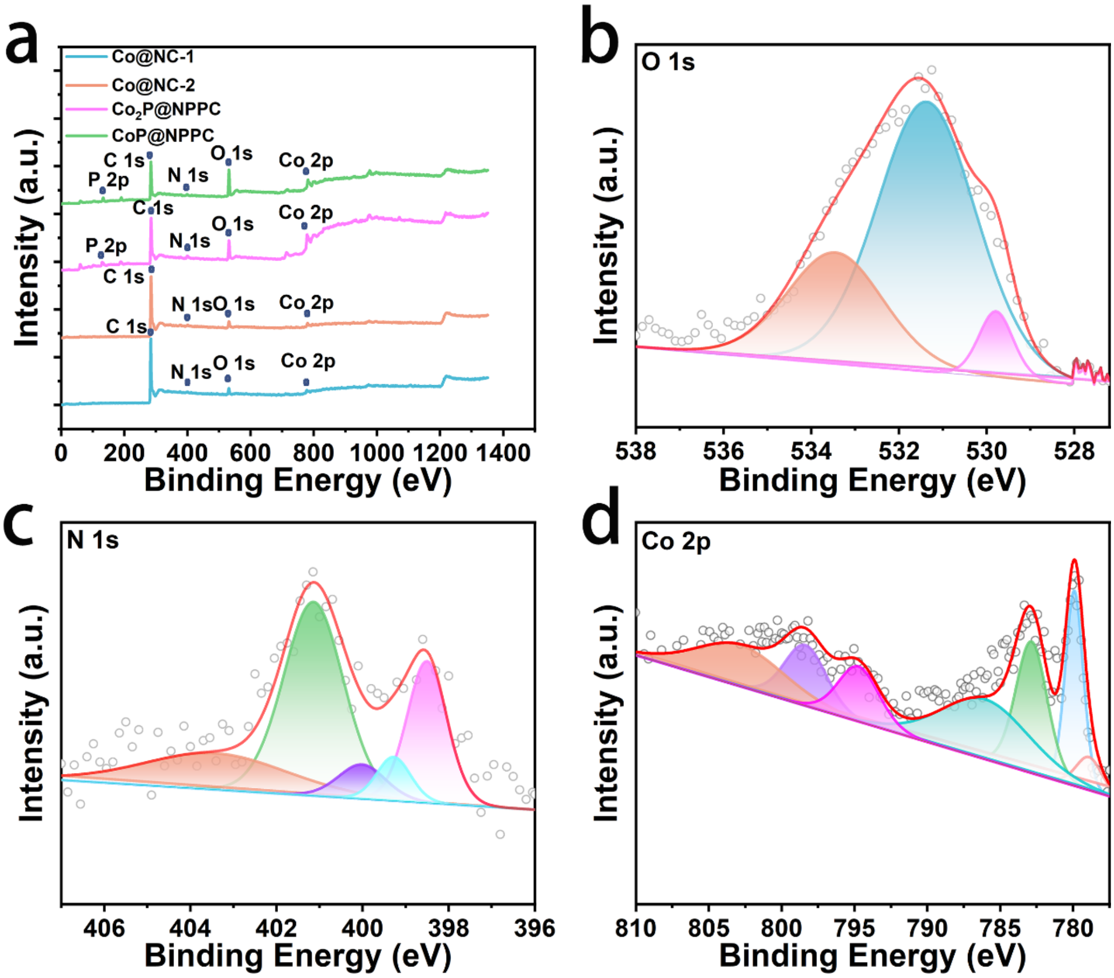

Figure S9. (a) XPS survey spectra of as-fabricated samples; XPS spectra of Co@NC-2. (b) O 1s, (c) N 1s, (d) Co 2p.

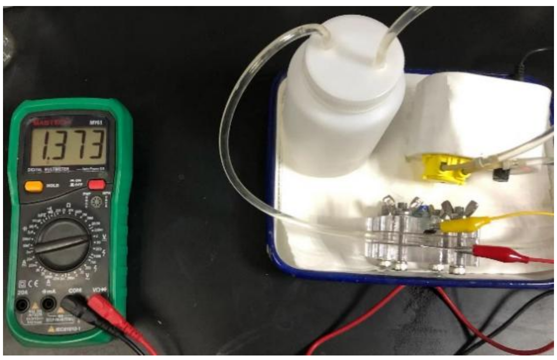

Figure S10. Open-circuit voltage of Pt/C+RuO_2-based primary ZABs;

Table S1. Comparison of ORR performance of Co_2P@NPPC with previously reported transition metal based electrocatalysts.

Materials	**E_{onset} (V vs. RHE)**	**$E_{1/2}$ (V vs. RHE)**	**Ref.**
Co_2P@NPPC	0.910	0.850	This work
Co_2P/NPG-900	0.890	0.810	1
Cu-Co_2P/CNFs	0.880	0.792	2
Mn(0.1)-Co_2P/NC	0.856	0.784	3
CoLIm-0@800	0.860	0.800	4
CoO/Co_xP	0.930	0.860	5
FeS/Fe_3C@NS-C-900	1.030	0.780	6
Co_2P/CoN-in-NCNT	0.960	0.850	7
Co@IC/MoC@PC	0.930	0.875	8
Co-MOF	0.780	0.700	9
$NiCo_2O_4$/MXene	0.880	0.700	10
$Mn_{0.9}Fe_{2.1}C$/NC	0.910	0.780	11

Table S2. Comparison of OER performance of Co_2P@NPPC with previously reported transition metal based electrocatalysts.

Materials	η_{10}**(V *vs.*RHE)**	**Tafel slope (mV dec^{-1})**	**Ref.**
Co_2P@NPPC	320	68	This work
CoP@NPCSs	355	103	12
CoO/CoS_2	320	77	13
NiCo-air	510	75	14
FeCo@NC-g	347	75	15
CoO_X	370	76	16
Ag-CeO_2-Co_3O_4	340	130.1	17
CoFe/S-N-C	358	259	18
$(SmSr)_{0.95}Co_{0.9}Pt_{0.1}O_3$	550	82	19
$CuCo_2O_4$@C	327	74	20
$ZnCo_2O_4$@NC-CNTs	370	64	21
H-NSC@Co/NSC	370	61.9	22
CoNi/BCF	370	166	23
CoFeP@C	336	82.5	24
Ni_3Fe/N-C	310	58	25

Table S3. Comparison of Zn-air batteries assembled using Co_2P@NPPC based electrocatalyst with other progressive electrode materials.

Materials	**Power density (mW cm^{-2})**	**Charge/discharge voltage gap (V)**	**Battery stability**	**Ref.**
Co_2P@NPPC	226	0.96	10 mA cm^{-2} for 160 h	This work
Fe-Nx-C	96.4	0.98	5 mA cm^{-2} for 300 h	26
SilkNC/KB	91.2	0.81	10 mA cm^{-2} for 100 h	27
NiFe@NC_x	82	0.78	50 mA cm^{-2} for 200 h	28
CoN/FeN@N,S-C-800	168.3	0.44	2 mA cm^{-2} for 100 h	29
r-$CoFe_2O_4$@DG	155.2	--	5 mA cm^{-2} for 60 h	30
FeCo/FeCoP@NMn-CNS-800	135	--	5 mA cm^{-2} for 200 h	31
Fe/Co-N/S-Cs	102.63	0.69	5 mA cm^{-2} for 27 h	32

References

1 Q. Shao, Y. Li, X. Cui, T. Li, H.-g. Wang, Y. Li, Q. Duan, Z. Si, Metallo phthalocyanine-based polymer-derived Co_2P nanoparticles anchoring on doped graphene as high-efficient trifunctional electrocatalyst for Zn-air batteries and water splitting, ACS Sustain. Chem, Eng., 2020, **8**, 6422-6432.

2 X. Sun, H. Liang, H. Yu, J. Bai, C. Li, Embedding Co_2P nanoparticles in Cu doping carbon fibers for Zn-air batteries and supercapacitors, Nanotechnology, 2022, **33**, 135202.

3 J. Tong, H. Wang, L. Bo, C. Li, X. Guan, D. Kong, Y. Zhang, W. Shi, Z. Lei, Mn-doped Co_2P/N-doped carbon composite materials as efficient bifunctional catalysts for rechargeable Zn-air batteries, Mater. Res. Bulletin, 2022, **147**, 111638.

4 A. Vilchez-Cozar, E. Armakola, M. Gjika, A. Visa, M. Bazaga-Garcia, P. Olivera-Pastor, D. Choquesillo-Lazarte, D. Marrero-Lopez, A. Cabeza, P.C. RM, K.D. Demadis, Exploiting the multifunctionality of M($^{2+}$)/imidazole-etidronates for proton conductivity (Zn($^{2+}$)) and electrocatalysis (Co($^{2+}$), Ni($^{2+}$)) toward the HER, OER, and ORR, ACS Appl. Mater. Interfaces, 2022, **14**, 11273-11287.

5 Y. Niu, M. Xiao, J. Zhu, T. Zeng, J. Li, W. Zhang, D. Su, A. Yu, Z. Chen, A "trimurti" heterostructured hybrid with an intimate CoO/Co_xP interface as a robust bifunctional air electrode for rechargeable Zn–air batteries, J. Mater. Chem. A, 2020, **8**, 9177-9184

6 Y.W. Li, W.J. Zhang, J. Li, H.Y. Ma, H.M. Du, D.C. Li, S.N. Wang, J.S. Zhao, J.M. Dou, L. Xu, Fe-MOF-derived efficient ORR/OER bifunctional electrocatalyst for rechargeable Zinc-air batteries, ACS Appl. Mater. Interfaces, 2020, **12**, 44710-44719.

7 Y. Guo, P. Yuan, J. Zhang, H. Xia, F. Cheng, M. Zhou, J. Li, Y. Qiao, S. Mu, Q. Xu, Co_2P-CoN double active centers confined in N-doped carbon nanotube: heterostructural engineering for trifunctional catalysis toward HER, ORR, OER, and Zn-air batteries driven water splitting, Adv. Funct. Mater., 2018, **28**, 1805641.

8 L. Zhang, Y. Zhu, Z. Nie, Z. Li, Y. Ye, L. Li, J. Hong, Z. Bi, Y. Zhou, G. Hu, Co/MoC

nanoparticles embedded in carbon nanoboxes as robust trifunctional electrocatalysts for a Zn-air battery and water electrocatalysis, ACS Nano, 2021, **15**, 13399-13414.

9 G. Chen, J. Zhang, F. Wang, L. Wang, Z. Liao, E. Zschech, K. Mullen, X. Feng, Cobalt-based metal-organic framework nanoarrays as bifunctional oxygen electrocatalysts for rechargeable Zn-air batteries, Chem., 2018, 24, 18413-18418.

10 H. Lei, S. Tan, L. Ma, Y. Liu, Y. Liang, M.S. Javed, Z. Wang, Z. Zhu, W. Mai, Strongly coupled $NiCo_2O_4$ nanocrystal/MXene hybrid through in situ Ni/Co-F bonds for efficient wearable Zn-air batteries, ACS Appl. Mater. Interfaces, 2020, **12**, 44639-44647.

11 C. Lin, X. Li, S.S. Shinde, D.-H. Kim, X. Song, H. Zhang, J.-H. Lee, Long-life rechargeable Zn air battery based on binary metal carbide armored by nitrogen-doped carbon, ACS Appl. Energy. Mater., 2019, **2**, 1747-1755.

12 K. Wu, Z. Chen, W.C. Cheong, S. Liu, W. Zhu, X. Cao, K. Sun, Y. Lin, L. Zheng, W. Yan, Y. Pan, D. Wang, Q. Peng, C. Chen, Y. Li, Toward bifunctional overall water splitting electrocatalyst: general preparation of transition metal phosphide nanoparticles decorated N-doped porous carbon spheres, ACS Appl. Mater. Interfaces, 2018, **10**, 44201-44208.

13 T. Qin, Y. Ding, R. Zhang, X. Gao, Z. Tang, Y. Liu, D. Gao, Bifunctional CoO/CoS_2 hierarchical nanospheres electrocatalyst for rechargeable Zn-air battery, FlatChem, 2022 **32**, 100343.

14 W. Liu, J. Bao, L. Xu, M. Guan, Z. Wang, J. Qiu, Y. Huang, J. Xia, Y. Lei, H. Li, $NiCo_2O_4$ ultrathin nanosheets with oxygen vacancies as bifunctional electrocatalysts for Zn-air battery, Appl. Sur. Sci., 2019, **478**, 552-559.

15 L.-B. Huang, L. Zhao, Y. Zhang, H. Luo, X. Zhang, J. Zhang, H. Pan, J.-S. Hu, Engineering carbon-shells of M@NC bifunctional oxygen electrocatalyst towards stable aqueous rechargeable Zn-air batteries, Chem. Eng. J., 2021, **418**, 129409.

16 T. Zhou, W. Xu, N. Zhang, Z. Du, C. Zhong, W. Yan, H. Ju, W. Chu, H. Jiang, C. Wu, Y. Xie, Ultrathin cobalt oxide layers as electrocatalysts for high-performance flexible Zn-air batteries, Adv. Mater., 2019, **31**, 1807468.

17 T. Li, Z. He, X. Liu, M. Jiang, Q. Liao, R. Ding, S. Liu, C. Zhao, W. Guo, S. Zhang,

H. He, Interface interaction of Ag-CeO_2-Co_3O_4 facilitate ORR/OER activity for Zn-air battery, Surfaces and Interfaces, 2022, **33**, 102270.
18 G. Li, Y. Tang, T. Fu, Y. Xiang, Z. Xiong, Y. Si, C. Guo, Z. Jiang, S, N co-doped carbon nanotubes coupled with CoFe nanoparticles as an efficient bifunctional ORR/OER electrocatalyst for rechargeable Zn-air batteries, Chem. Eng. J., 2022, **429**, 132174.
19 C. Wang, B. Hou, X. Wang, Z. Yu, D. Luo, M. Gholizadeh, X. Fan, High-performance a-site deficient perovskite electrocatalyst for rechargeable Zn–air battery, Catal., 2022, **12**, 703.
20 X. Wang, Y. Li, T. Jin, J. Meng, L. Jiao, M. Zhu, J. Chen, Electrospun thin-walled $CuCo_2O_4$@C nanotubes as bifunctional oxygen electrocatalysts for rechargeable Zn-air batteries, Nano. Lett., 2017, **17**, 7989-7994.
21 L. Yan, Z. Xu, W. Hu, J. Ning, Y. Zhong, Y. Hu, Formation of sandwiched leaf-like CNTs-Co/$ZnCo_2O_4$@NC-CNTs nanohybrids for high-power-density rechargeable Zn-air batteries, Nano. Energy, 2021, **82**, 105710.
22 W. Li, J. Wang, J. Chen, K. Chen, Z. Wen, A. Huang, Core-shell carbon-based bifunctional electrocatalysts derived from COF@MOF hybrid for advanced rechargeable Zn-air batteries, Small, 2022, **18**, 2202018.
23 W. Wan, X. Liu, H. Li, X. Peng, D. Xi, J. Luo, 3D carbon framework-supported CoNi nanoparticles as bifunctional oxygen electrocatalyst for rechargeable Zn-air batteries, Appl. Catal. B: Environ., 2019, **240**, 193-200.
24 L. Gao, S. Chang, Z. Zhang, High-quality CoFeP nanocrystal/N, P dual-doped carbon composite as a novel bifunctional electrocatalyst for rechargeable Zn-air battery, ACS Appl. Mater. Interfaces, 2021, **13**, 22282-22291.
25 P. Sun, Z. Zuo, M. He, L. Yang, D. Zhang, N. Huang, Z. Chen, Y. Sun, X. Sun, N-doped carbon sheets loaded with well-dispersed Ni_3Fe nanoparticles as bifunctional oxygen electrode for rechargeable Zn-air battery, Journal of Electroanalytical Chemistry, 2019, **851**, 113418.
26 C. Wang, N.-H. Xie, Y. Zhang, Z. Huang, K. Xia, H. Wang, S. Guo, B.-Q. Xu, Y. Zhang, Silk-derived highly active oxygen electrocatalysts for flexible and

rechargeable Zn–air batteries, Chemistry of Materials, 2019, **31**, 1023-1029.

27 J. Han, X. Meng, L. Lu, J. Bian, Z. Li, C. Sun, Single-atom Fe-Nx-C as an efficient electrocatalyst for Zinc–air batteries, Adv. Funct. Mater., 2019, **29**, 1808872.

28 J. Zhu, M. Xiao, Y. Zhang, Z. Jin, Z. Peng, C. Liu, S. Chen, J. Ge, W. Xing, Metal–organic framework-induced synthesis of ultrasmall encased NiFe nanoparticles coupling with graphene as an efficient oxygen electrode for a rechargeable Zn–air battery, ACS Catal., 2016, **6**, 6335-6342.

29 S. Ren, X. Duan, M. Lei, S. Liang, M. Zhang, H. Zheng, Energetic MOF-derived cobalt/iron nitrides embedded into N, S-codoped carbon nanotubes as superior bifunctional oxygen catalysts for Zn–air batteries, Appl. Sur. Sci., 2021, **569**, 151030.

30 X. Wang, L. Zhuang, Y. Jia, L. Zhang, Q. Yang, W. Xu, D. Yang, X. Yan, L. Zhang, Z. Zhu, C.L. Brown, P. Yuan, X. Yao, One-step in-situ synthesis of vacancy-rich $CoFe_2O_4$@defective graphene hybrids as bifunctional oxygen electrocatalysts for rechargeable Zn-air batteries, Chem. Res. Chin. Univer., 2020, **36**, 479-487.

31 Y.P. Chen, S.Y. Lin, R.M. Sun, A.J. Wang, L. Zhang, X. Ma, J.J. Feng, FeCo/FeCoP encapsulated in N, Mn-codoped three-dimensional fluffy porous carbon nanostructures as highly efficient bifunctional electrocatalyst with multi-components synergistic catalysis for ultra-stable rechargeable Zn-air batteries, J. Colloid Interface Sci., 2022, **605**, 451-462.

32 C. Li, H. Liu, Z. Yu, Novel and multifunctional inorganic mixing salt-templated 2D ultrathin Fe/Co-N/S-carbon nanosheets as effectively bifunctional electrocatalysts for Zn-air batteries, Appl. Catal. B: Environ., 2019, **241**, 95-103.