Electronic Supplementary Information (ESI)

Honeycomb-Like Carbon with Doping of Transition-Metal and Nitrogen for Highly Efficient Zinc-Air Battery and Zinc-Ion Battery

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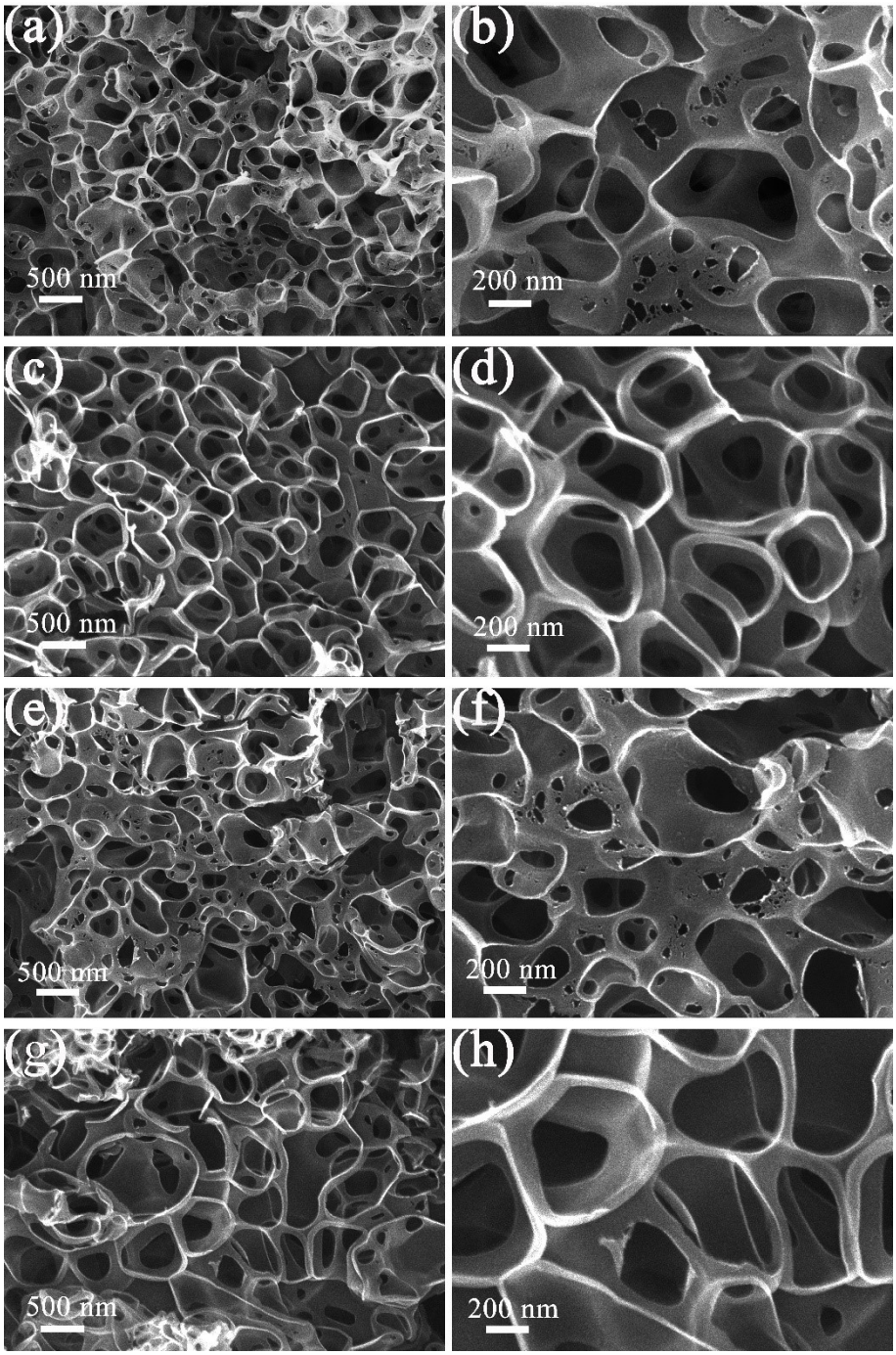

Fig. S1 SEM images of (**a, b**) FeZnN-C; (**c, d**) FeN-C; (**e, f**) ZnN-C; (**g, h**) N-C catalysts.

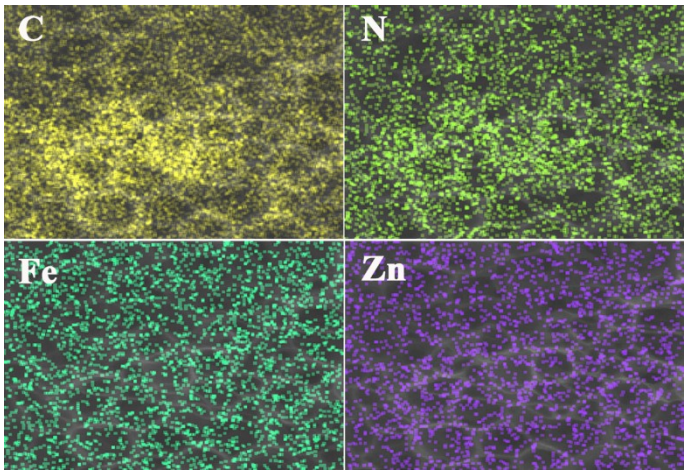

Fig. S2 The EDX mapping images of FeZnN-C for C, N, Fe and Zn elements.

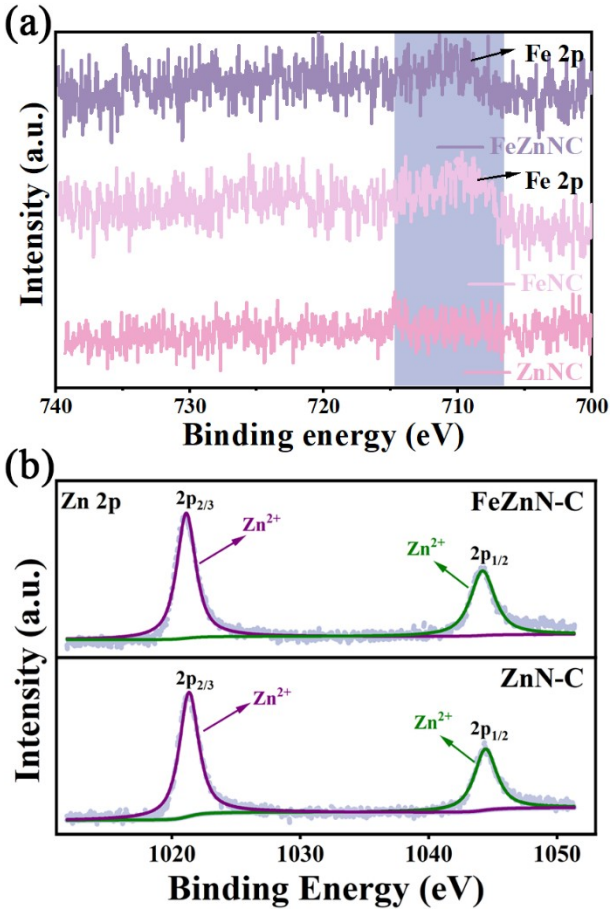

Fig. S3 (**a**) Fe 2p spectrum of FeN-C, ZnN-C, FeZnN-C catalysts; (**b**) Zn 2p spectrum of FeZnN-C and ZnN-C catalysts.

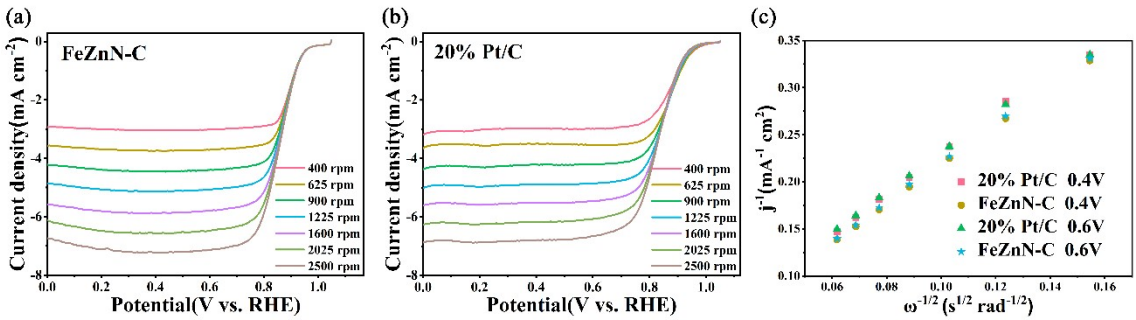

Fig. S4 The LSV curves of (**a**) FeZnN-C and (**b**) 20% Pt/C at different rotation rates; (**c**) the corresponding Koutecky-Levich curves at 0.4 V and 0.6 V.

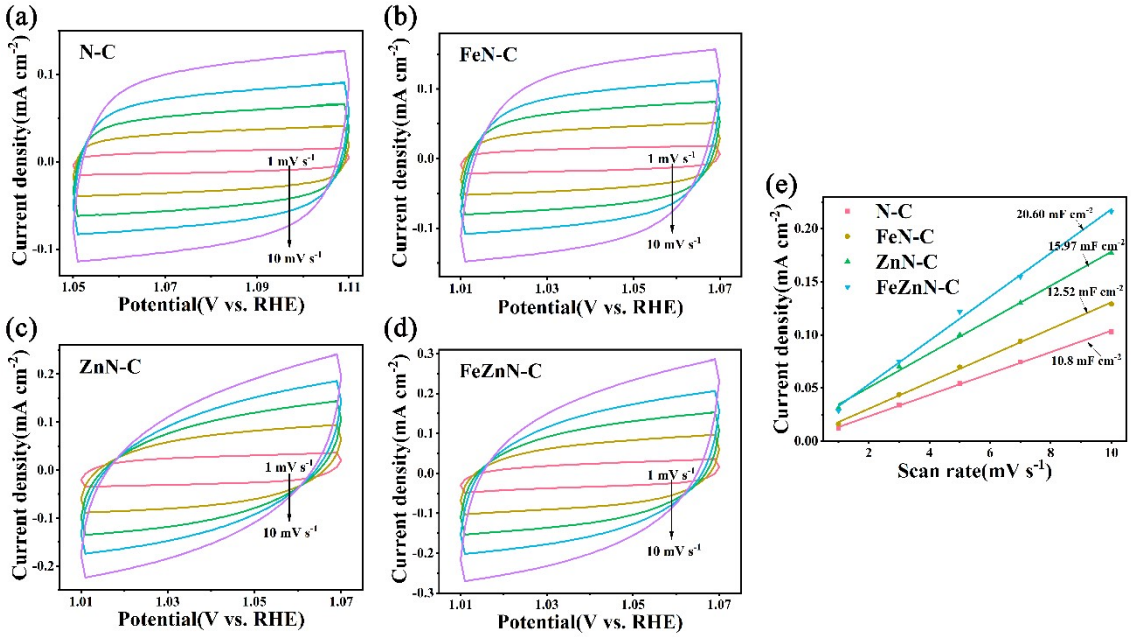

Fig. S5 CV curves of (**a**) N-C, (**b**) FeN-C, (**c**) ZnN-C, (**d**) FeZnN-C at different scan rates in Ar-saturated 1 M KOH; (**e**) the corresponding C_{dl} values.

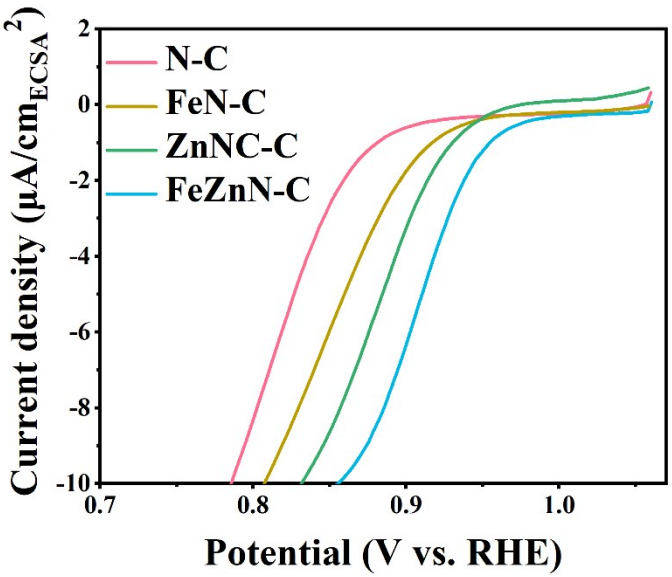

Fig. S6 The ECSA normalized LSV curves of N-C, FeN-C, ZnN-C and FeZnN-C.

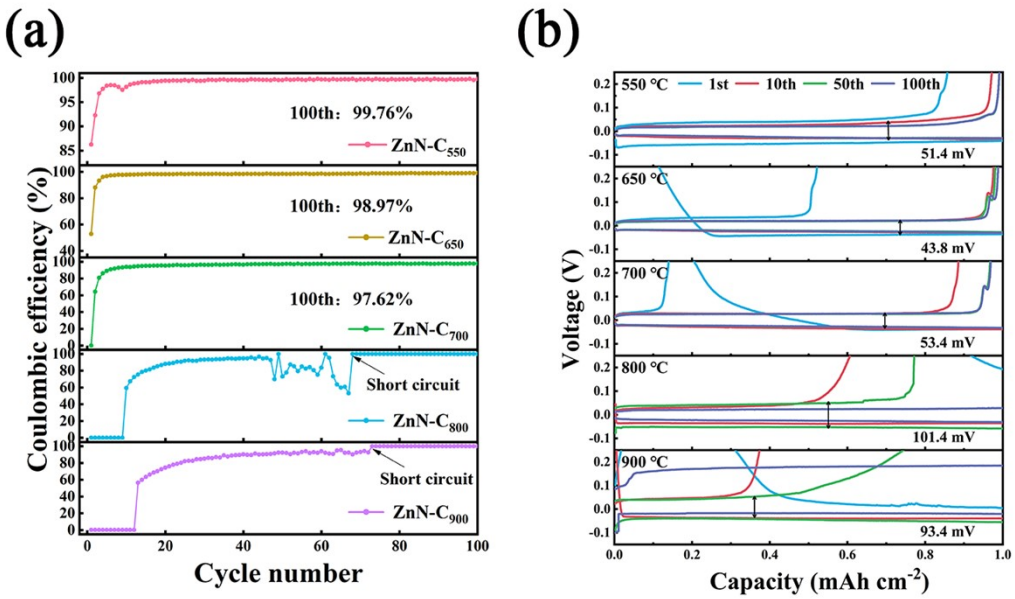

Fig. S7 (a) Coulombic efficiency of coin cell of ZnN-C_x ‖ Zn plate, (b) Polarization curves of the plating/stripping of ZnN-C_x at 1 mA cm^{-2} - 1 mAh cm^{-2}.

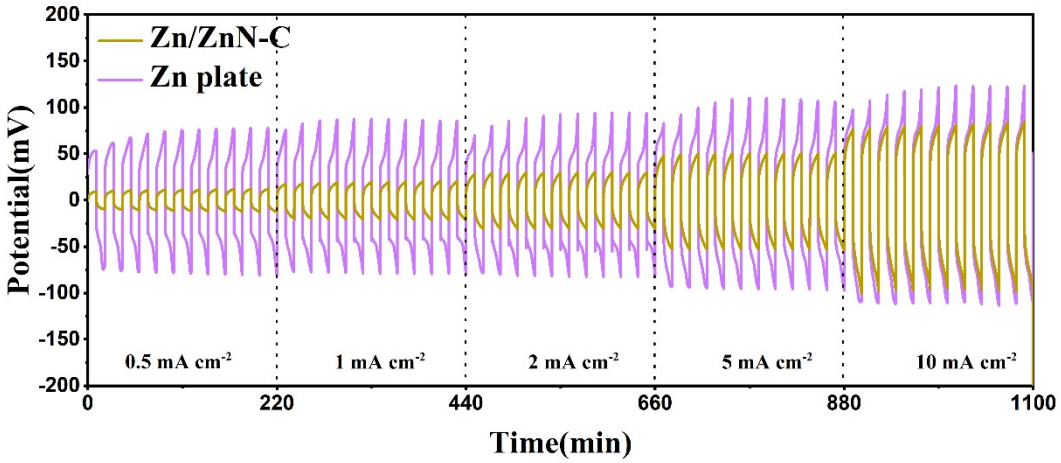

Fig. S8 Rate performance of symmetric coin cells of Zn/ZnN-C ‖ Zn/ZnN-C and Zn plate ‖ Zn plate.

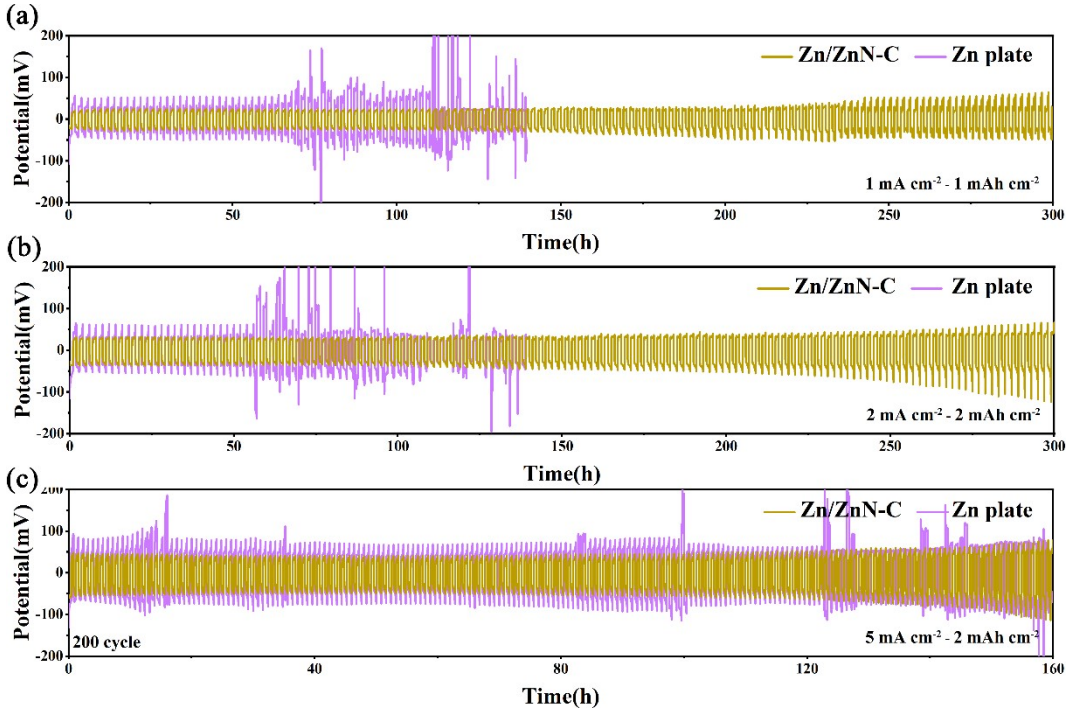

Fig. S9 Electrochemical stability (Zn plating/stripping) tests of symmetric coin cells of Zn/ZnN-C ‖ Zn/ZnN-C and Zn plate ‖ Zn plate at different current densities - area capacities: (**a**) 1 mA cm^{-2} - 1 mAh cm^{-2}; (**b**) 2 mA cm^{-2} - 2 mAh cm^{-2}; (**c**) 5 mA cm^{-2} - 2 mAh cm^{-2}.

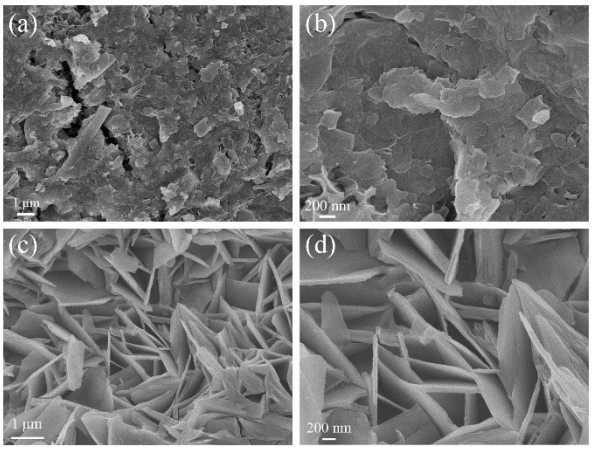

Fig. S10 The SEM images of (**a-b**) Zn/ZnN-C and (**c-d**) commercial Zn plate after plating/striping tests.

Table S1. Atomic percentage of different elements and various N species for N-C, FeN-C, ZnN-C, FeZnN-C catalysts.

Atomic %		N-C		FeN-C		ZnN-C		FeZnN-C	
C		86.82		85.40		85.05		84.17	
N	Pyridinic N	8.95	3.019	9.58	3.459	8.10	2.544	9.85	3.158
	Graphitic N		3.036		3.303		2.701		3.367
	Metal N		0		1.146		1.418		1.915
	Pyrrolic N		2.227		1.259		0.890		0.924
	Oxidized N		0.668		0.413		0.547		0.486
Effective N		67.70		82.50		82.30		85.70	
O		4.22		4.74		6.12		5.17	
Fe		0		0.28		0		0.21	
Zn		0		0		0.73		0.60	

Table S2. The comparison of ORR activity of different catalysts in 0.1 M KOH.

Catalysts	E_{onset} (V vs.RHE)	$E_{1/2}$ (V vs.RHE)	j_L (mA cm^{-2})	References
FeZnN-C	**1.052**	**0.901**	**-6.04**	**This work**
ZnN-C	**1.039**	**0.856**	**-5.72**	**This work**
FeN-C	**0.959**	**0.810**	**-5.16**	**This work**
N-C	**0.925**	**0.789**	**-4.51**	**This work**
FeNi@NCNT-CP	1.0	0.85	-6.0	1
CoNi@N-DCNT	0.92	0.83	-6.0	2
Fe/Co-N/P-9	0.96	0.85	-4.5	3
SA-Fe-HPC	/	0.89	-5.4	4
NC-Co SA	1.00	0.87	/	5
$FeN\text{-}HPC_{GD2}$	0.98	0.888	-5.42	6
FeNC-1	/	0.90	-6.0	7
Fe-Zn-SA/NC	0.94	0.85	/	8
Fe/N-PCNs	0.96	0.86	/	9
(Zn,Co)/NSC	1.07	0.893	-5.4	10

Table S3. The performance of Zn-air batteries of nonprecious catalysts in 6 M KOH.

Catalysts	Peak power density ($mW\ cm^{-2}$)	References
FeZnN-C	**257**	**This work**
$FeN\text{-}HPC_{GD2}$	241	6
$Ni_3Fe/N\text{-}S\text{-}CNTs$	180	11
Fe,Mn/N-C	160.8	12
BTC-Co-O-Cu-BTA MOF	200	13
GNCNTs	207	14
CoN_4/NG	115	15
Zn/CoN-C	230	16
$Mo–N/C@MoS_2$	196.4	17

Table S4. Discharge voltages at different current densities of Zinc-air batteries using FeZnN-C and 20% Pt/C as cathodic electrocatalysts.

Current density ($mA\ cm^{-2}$)	Cell Voltage (V)	
	FeZnN-C	**20% Pt/C**
1	1.44	1.37
10	1.36	1.30
50	1.24	1.18
100	1.15	1.09

Table S5. The comparison of the battery performance based on different catalysts.

Electrode	Electrolyte	Current density ($mA\ cm^{-2}$)	Lifetime (h)	Voltage hysteresis (mV)	References
Zn/ZnN-C	**2 M $ZnSO_4$**	**0.5**	**600**	**21**	**This work**
CNT-Zn	2 M $ZnSO_4$	2	200	27	18
3D Zn Anode	2 M $ZnSO_4$	0.5	350	40	19
$CC@MnO_2$-UTF@Zn	2 M $ZnSO_4$	1	150	150	20
ZnSe@Zn	2 M $ZnSO_4$	1	1530	128	21
Cu foil@Zn	2M $ZnSO_4$ + 0.1 M $MnSO_4$	2	140	40	22
$S/MX@ZnS@Zn\text{-}_{300}$	2M $ZnSO_4$	1	1100	75	23
Zn micromesh	3.0 M $Zn(CF_3SO_3)_2$	1	500	50	24

Reference

1. X. Zheng, X. Cao, K. Zeng, J. Yan, Z. Sun, M. H. Rümmeli and R. Yang, *Small*, 2021, **17**, 2006183.
2. C. Zhu, W. Yang, J. Di, S. Zeng, J. Qiao, X. Wang, B. Lv and Q. Li, *J Energy Chem*, 2021, **54**, 63-71.
3. J. Di, J. Guo, N. Wang and G. Ma, *ACS Sustain Chem Eng*, 2019, **7**, 7716-7727.
4. Z. Zhang, J. Sun, F. Wang and L. Dai, *Angew Chem Int Edit*, 2018, **57**, 9038-9043.
5. W. Zang, A. Sumboja, Y. Ma, H. Zhang, Y. Wu, S. Wu, H. Wu, Z. Liu, C. Guan, J. Wang and S. J. Pennycook, *ACS Catal*, 2018, **8**, 8961-8969.
6. Y. Chen, I. Kone, Y. Gong, A. Xie, H. Hu, D. Kong, J. Liu, Y. Tang, X. Yang, R. Pang and P. Wan, *Carbon*, 2019, **152**, 325-334.
7. W. Wang, M. Tang, Z. Zheng and S. Chen, *Adv Energy Mater*, 2019, **9**, 1803628.
8. J. Xu, S. Lai, D. Qi, M. Hu, X. Peng, Y. Liu, W. Liu, G. Hu, H. Xu, F. Li, C. Li, J. He, L. Zhuo, J. Sun, Y. Qiu, S. Zhang, J. Luo and X. Liu, *Nano Res*, 2021, **14**, 1374-1381.
9. L. Zheng, S. Yu, X. Lu, W. Fan, B. Chi, Y. Ye, X. Shi, J. Zeng, X. Li and S. Liao, *ACS Appl Energ Mater*, 2020, **12**, 13878-13887.
10. D. Liu, B. Wang, H. Li, S. Huang, M. Liu, J. Wang, Q. Wang, J. Zhang and Y. Zhao, *Nano Energy*, 2019, **58**, 277-283.
11. C. Lai, J. Wang, W. Lei, C. Xuan, W. Xiao, T. Zhao, T. Huang, L. Chen, Y. Zhu and D. Wang, *ACS Appl Energ Mater* 2018, **10**, 38093-38100.
12. G. Yang, J. Zhu, P. Yuan, Y. Hu, G. Qu, B.-A. Lu, X. Xue, H. Yin, W. Cheng, J. Cheng, W. Xu, J. Li, J. Hu, S. Mu and J.-N. Zhang, *Nat Comm*, 2021, **12**, 1734.
13. M. F. Sanad, A. R. Puente Santiago, S. A. Tolba, M. A. Ahsan, O. Fernandez-Delgado, M. Shawky Adly, E. M. Hashem, M. Mahrous Abodouh, M. S. El-Shall, S. T. Sreenivasan, N. K. Allam and L. Echegoyen, *J Am Chem Soc*, 2021, **143**, 4064-4073.
14. Y. Xu, P. Deng, G. Chen, J. Chen, Y. Yan, K. Qi, H. Liu and B. Y. Xia, *Adv Funct Mater*, 2020, **30**, 1906081.
15. L. Yang, L. Shi, D. Wang, Y. Lv and D. Cao, *Nano Energy*, 2018, **50**, 691-698.
16. Z. Lu, B. Wang, Y. Hu, W. Liu, Y. Zhao, R. Yang, Z. Li, J. Luo, B. Chi, Z. Jiang, M. Li, S. Mu, S. Liao, J. Zhang and X. Sun, *Angew Chem Int Edit*, 2019, **58**, 2622-2626.
17. I. S. Amiinu, Z. Pu, X. Liu, K. A. Owusu, H. G. R. Monestel, F. O. Boakye, H. Zhang and S. Mu, *Adv Funct Mater*, 2017, **27**, 1702300.
18. Y. Zeng, X. Zhang, R. Qin, X. Liu, P. Fang, D. Zheng, Y. Tong and X. Lu, *Adv Mater*, 2019, **31**, e1903675.
19. Z. Kang, C. Wu, L. Dong, W. Liu, J. Mou, J. Zhang, Z. Chang, B. Jiang, G. Wang, F. Kang and C. Xu, *ACS Sustain Chem Engin*, 2019, **7**, 3364-3371.
20. Y. Chen, J. Li, S. Zhang, J. Cui and M. Shao, *Adv Mater Inters*, 2020, **7**, e2000510.
21. X. Yang, C. Li, Z. Sun, S. Yang, Z. Shi, R. Huang, B. Liu, S. Li, Y. Wu, M. Wang, Y. Su, S. Dou and J. Sun, *Adv Mater*, 2021, e2105951.
22. C. Li, X. Shi, S. Liang, X. Ma, M. Han, X. Wu and J. Zhou, *Chem Engin J*, 2020, **379**, 379.
23. Y. An, Y. Tian, C. Liu, S. Xiong, J. Feng and Y. Qian, *ACS Nano*, 2021, **15**, 15259-15273.
24. H. Liu, J. Li, X. Zhang, X. Liu, Y. Yan, F. Chen, G. Zhang and H. Duan, *Adv Funct Mater*, 2021.