Supporting Information

Bifunctional Interface Stabilizer of Promoting Preferential Crystal Face Adsorption and Inducing Planar Zn Growth

Experimental Section

Preparing various electrolytes*:* Firstly, 2 mol/L $ZnSO_4$ solution can be prepared by dissolving the specific amount of $ZnSO_4 \cdot 7H_2O$ (Sinopharm Chemical Reagent Co., Ltd) in deionized water. For the preparation of $ZnSO_4$-BIS electrolyte, weighed amount of 2-aminoethanesulfonic acid (Sinopharm Chemical Reagent Co., Ltd) was added into 2 mol/L $ZnSO_4$ solution and then stirred for 1 h. Specifically, the concentration of BIS should be controlled at 0.1 mol/L.

Synthesis of MnO_2: 0.25 g $KMnO_4$ and 0.4 g $MnSO_4 \cdot H_2O$ were added into 15 mL deionized water respectively and stirred for 15 min. The two solutions were mixed together under continuous stirring, and moved into a Teflon-lined autoclave and heated at 160 ℃ for 12 h. The products were centrifuged, washed with excess amount of deionized water and dried in an oven at 80 ℃ overnight.

***Material Characterization*:** Morphology observations of prepared samples and cycled electrodes could be obtained by Hitachi SU1510 (SEM). In/ex situ XRD patterns and structure component of samples have been determined by Bruker D8 ADVANCE. Nicolet iS50 FT-IR instrument was also used to obtain the ex/in situ FT-IR spectra. Dataphysics OCA20 has been applied for measuring the contact angles. To conduct the in situ optical microscopy test, Zeiss Smartzoom 5 has been applied to monitor the deposition behavior during continuous Zn plating process.

***Electrochemical measurements*:** Electrochemical performance of asymmetric and symmetric cells based on GF separators were assembled into CR 2032 coin cells at ambient atmosphere and tested on a Neware battery testing system. Aqueous solution of 2 mol/L $ZnSO_4$ was selected as the electrolyte, and the amount should be fixed at 60 μL per cell. For full cell test, cathodes were fabricated by dispersing MnO_2, acetylene

black and PVDF (7:2:1, m/m/m) in the solvent of NMP and casting on the stainless steel foil. After that, the foil was dried in a vacuum oven at 60 °C for 12 h, and then punched into disks with a diameter of 12 mm. All Zn-MnO_2 full cells were added with 2 M $ZnSO_4$ solution containing $MnSO_4$ (0.1 M) and tested between 0.8 V and 1.9 V. The CV profiles, CA and Tafel plots of assembled cells were conducted in an electrochemical workstation (CHI660E, Shanghai Chenhua Instrument).

Theoretical calculation: All calculations were performed by the first-principle method through the Cambridge serial total energy package (CASTEP) module in Materials Studio.

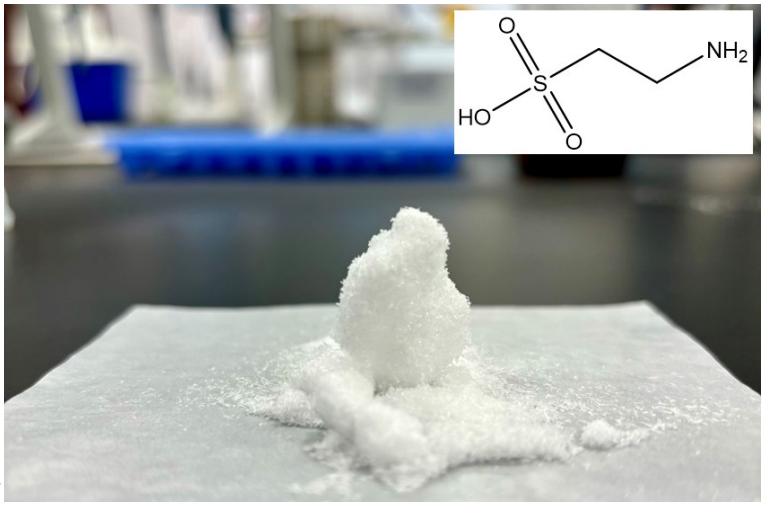


Fig. S1 Optical image of 2-aminoethanesulfonic acid and molecule structure.

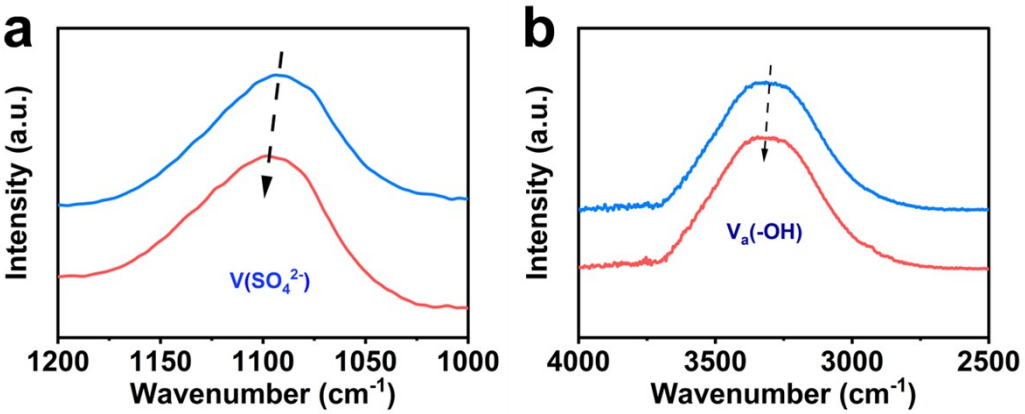


Fig. S2 Typical FTIR spectra for SO_4^{2-} and -OH group.

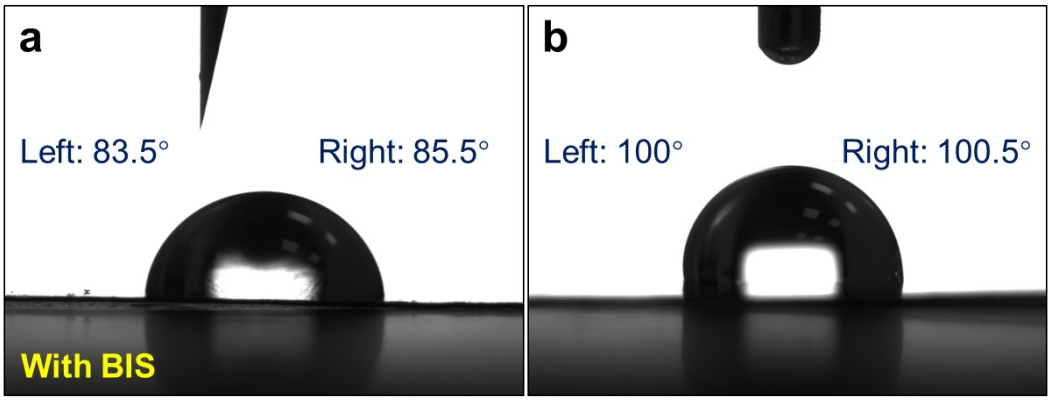


Fig. S3 Contact angle tests of $ZnSO_4$-BIS and pristine $ZnSO_4$ electrolytes on Zn foil.

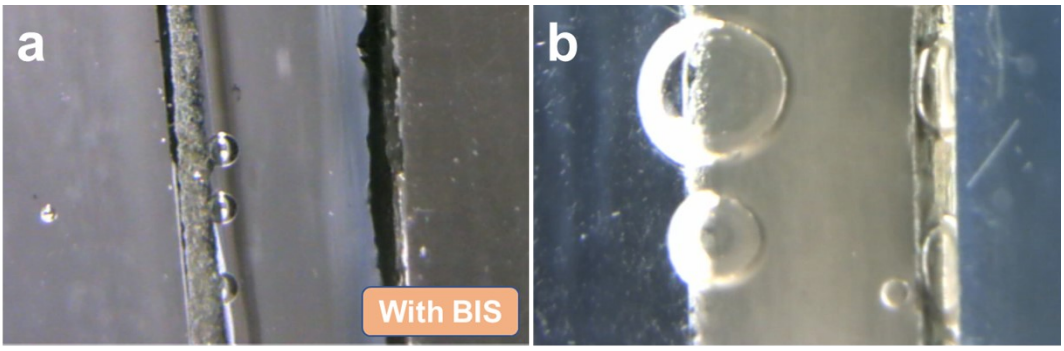


Fig. S4 Optical images of Zn deposition in (a) $ZnSO_4$-BIS and (b) $ZnSO_4$ electrolyte at 5 mA cm^{-2}.

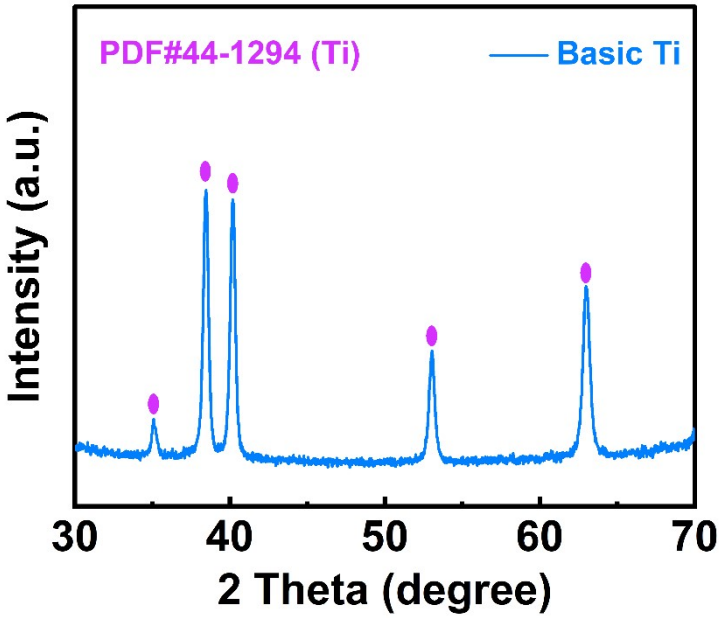


Fig. S5 XRD pattern of Ti substrate.

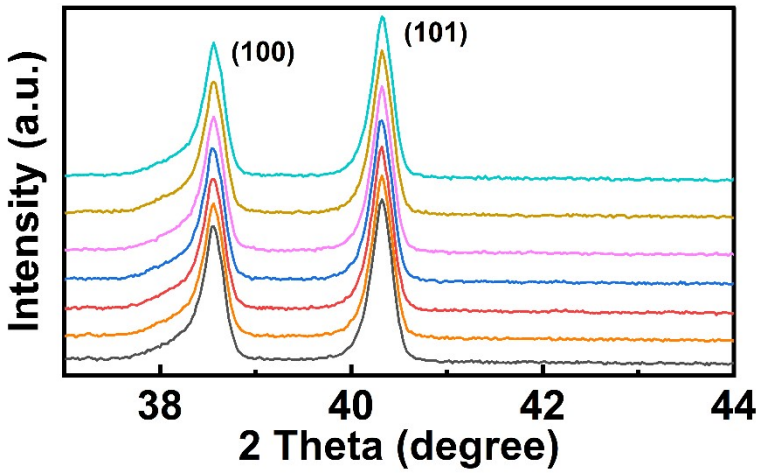


Fig. S6 *In situ* XRD patterns $ZnSO_4$-BIS electrolyte for observing (100) and (101) planes of Zn metal.

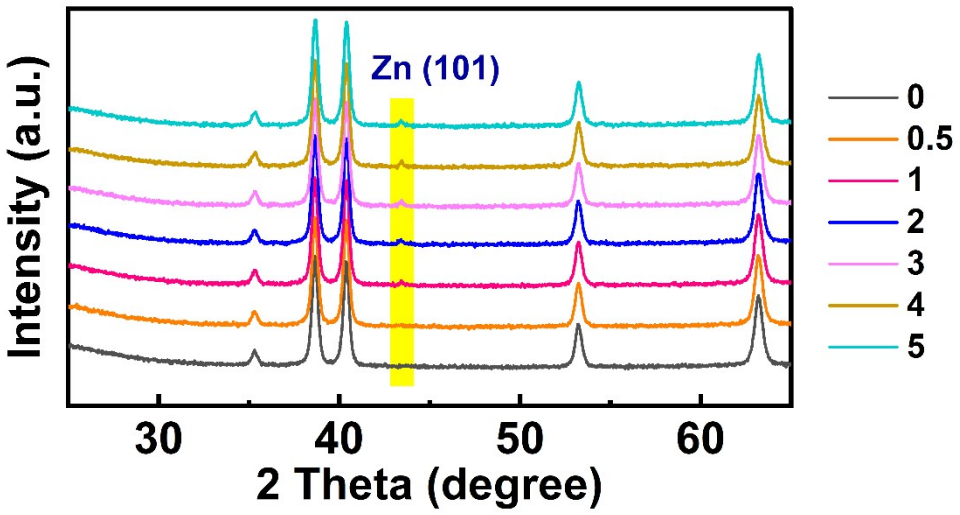


Fig. S7 In situ XRD patterns of electrodes at various capacities in pristine $ZnSO_4$ electrolyte.

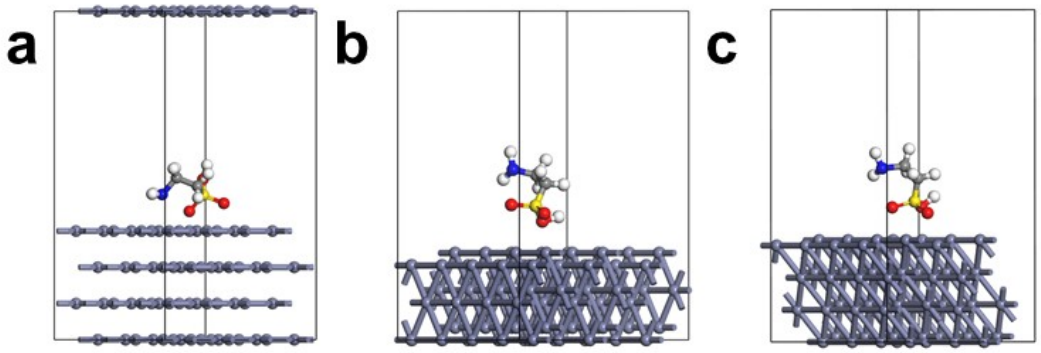


Fig. S8 Calculation model of sulfonic acid group with (a) (002), (100) and (101) plane of Zn metal.

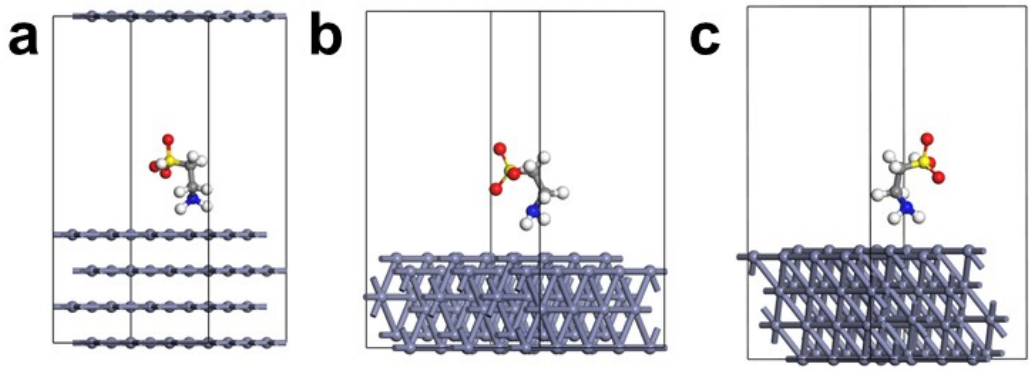
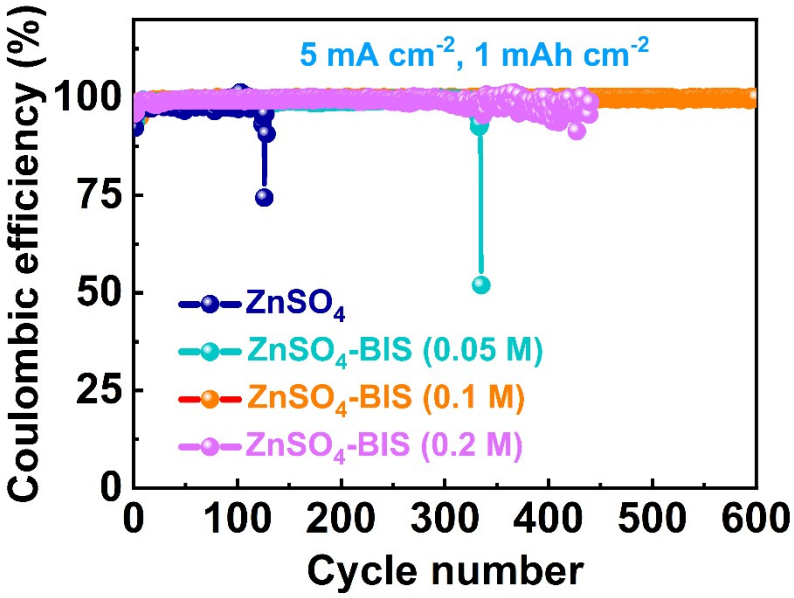


Fig. S9 Calculation model of amino group with (a) (002), (100) and (101) plane of Zn metal.



New Fig. S10 The CE plots in different electrolytes at 5 mA cm^{-2} and 1 mAh cm^{-2}.

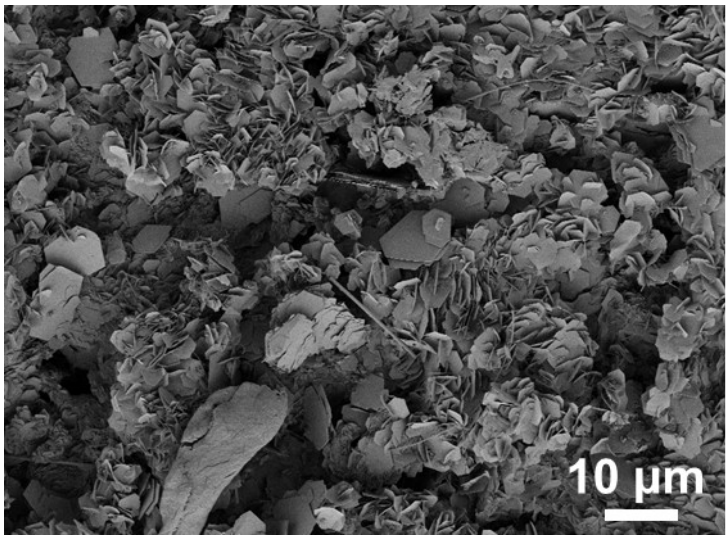


Fig. S11 SEM image of Zn electrode after 50 cycles in $ZnSO_4$.

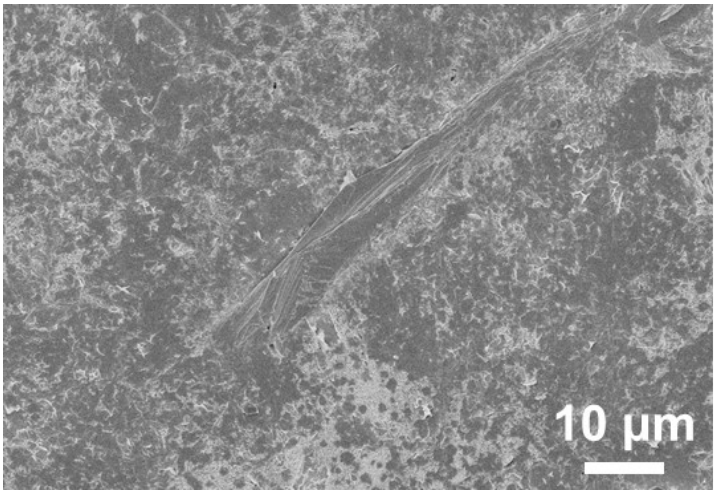


Fig. S12 SEM image of Zn electrode after 50 cycles in $ZnSO_4$-BIS.

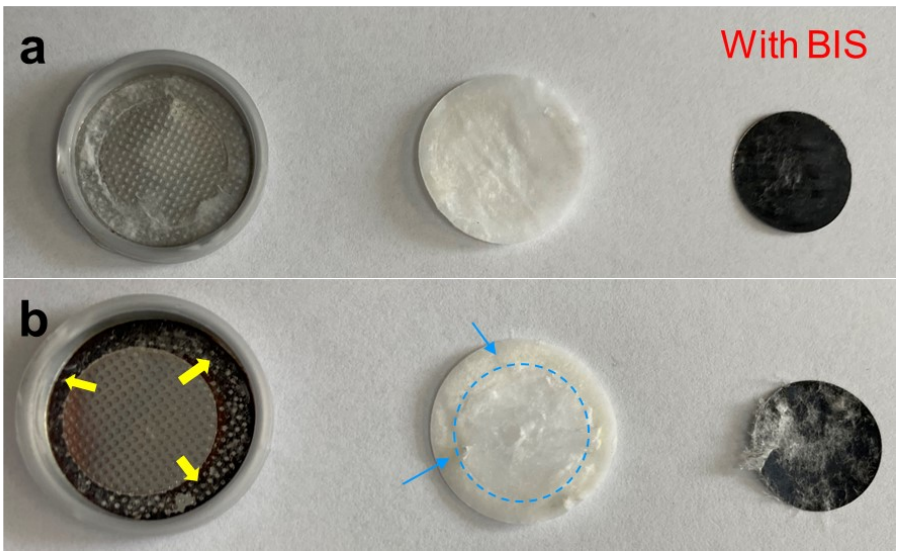


Fig. S13 Optical images of MnO_2 electrodes after 150 cycles in (a) $ZnSO_4$-BIS and pristine $ZnSO_4$.

Table S1 Electrochemical properties comparison of BIS and other electrolyte additives in AZBs.

Material	Working condition ($mA\ cm^{-2}$, $mAh\ cm^{-2}$)	Lifespan	Ref.
BIS	**1, 1** **5, 3**	**4000 h** **2000 cycles**	**This work**
Ala	0.5, 0.25	3750 h	1
DA	2, 1	1000 h	2
Thioacetamide	1, 1	1200 h	3
HPA	0.5, 0.5	3000 h	4
MPS	1, 1 1, 1	1000 h 850 cycles	5
$BMIM^+$	1, 0.5 2, 0.5	3500 h 3500 cycles	6
Adenosine	1, 1	1000 cycles	7
Nicotinic acid	1, 1	1300 cycles	8
Mlz	1, 1	1500 h	9
glycerol	1, 1	1500 h	10
PEO	1, 1	1500 cycles	11
PEO	1, 1	630 cycles	12
Taurine	1, 1	3000 h	13
EDA	1, 1	3000 h	14

Reference

1 G. Z. Guo, C. C. Ji, J. D. Lin, T. L. Wu, Y. L. Luo, C. R. Sun, M. J. Li, H. Y. Mi, L. X. Sun, H. J. Seifert, *Angew. Chem. Int. Edit.* **2024**, DOI: 10.1002/anie.202407417.

2 Y. Yang, Y. Z. Li, Q. Z. Zhu, B. Xu, *Adv. Funct. Mater.*, **2024**, DOI: 10.1002/adfm.202316371.

3 K. X. Ren, M. Li, Q. H. Wang, B. H. Liu, C. Sun, B. Y. Yuan, C. Lai, L. F. Jiao, C. Wang, *Nano-Micro Lett.*, **2024**, 16, 117.

4 Z. M. Yang, Y. L. Sun, S. T. Deng, H. Tong, M. Q. Wu, X. B. Nie, Y. F. Su, G. J. He, Y. H. Zhang, J. W. Li, G. L. Chai, *Energ. Environ. Sci.*, **2024**, 17, 3443-3453.

5 T. Q. Wu, C. Hu, Q. Zhang, Z. F. Yang, G. H. Jin, Y. X. Li, Y. G. Tang, H. H. Li, H. Y. Wang, *Adv. Funct. Mater.*, **2024**, DOI: 10.1002/adfm.202315716.

6 C. C. Fan, W. J. Meng, J. Han, T. H. Li, D. P. Zuo, S. X. Deng, D. S. Li, L. Jiang, *Energy Storage Mater.*, **2024**, 71, 103554.

7 O. Y. Li, K. C. Long, M. Fu, J. Zhou, C. L. Li, W. Y. Tang, B. Wang, L. L. Jiang, Y. J. Chen, L. B. Chen, *Energy Storage Mater.*, **2024**, 71, 103569.

8 S. N. Zheng, K. Zhang, B. Luo, L. L. Sun, Z. Bao, G. S. Duan, J. Y. Huang, Z. L. Gu, Z. Z. Ye, Y. Wang, *Energy Storage Mater.*, **2024**, 71, 103588.
9 J. Cao, M. Z. Sun, D. D. Zhang, Y. F. Zhang, C. W. Yang, D. Luo, X. L. Yang, X. Zhang, J. Q. Qin, B. L. Huang, Z. Y. Zeng, J. Lu, *ACS Nano*, **2024**, 18, 16610-16621.
10 Y. J. Zhang, M. Zhu, K. Wu, F. F. Yu, G. Y. Wang, G. Xu, M. H. Wu, H. K. Liu, S. X. Dou, C. Wu, *J. Mater. Chem. A*, **2021**, 9, 4253-4261.
11 Y. Jin, K. S. Han, Y. Y. Shao, M. L. Sushko, J. Xiao, H. L. Pan, J. Liu, *Adv. Funct. Mater.*, **2020**, 30, 202003932.
12 M. D. Yan, C. L. Xu, Y. Sun, H. L. Pan, H. Li, *Nano Energy*, **2021**, 82, 105739.
13 X. Xu, J. Y. Yin, R. M. Qin, H. L. Liu, X. Feng, M. H. Wang, M. Y. Li, W. Y. Sun, W. C. Shi, B. Xiao, Y. Q. Su, Y. H. Cheng, *J. Energy Chem.*, **2023**, 86, 343-350.
14 L. F. Deng, X. F. Xie, W. W. Song, A. Q. Pan, G. Z. Cao, S. Q. Liang, G. Z. Fang, *Chem. Eng. J.*, **2024**, 488, 151104.