Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Ultra-Thin Amphiphilic Hydrogel Electrolyte for Flexible Zinc-ion Paper Batteries

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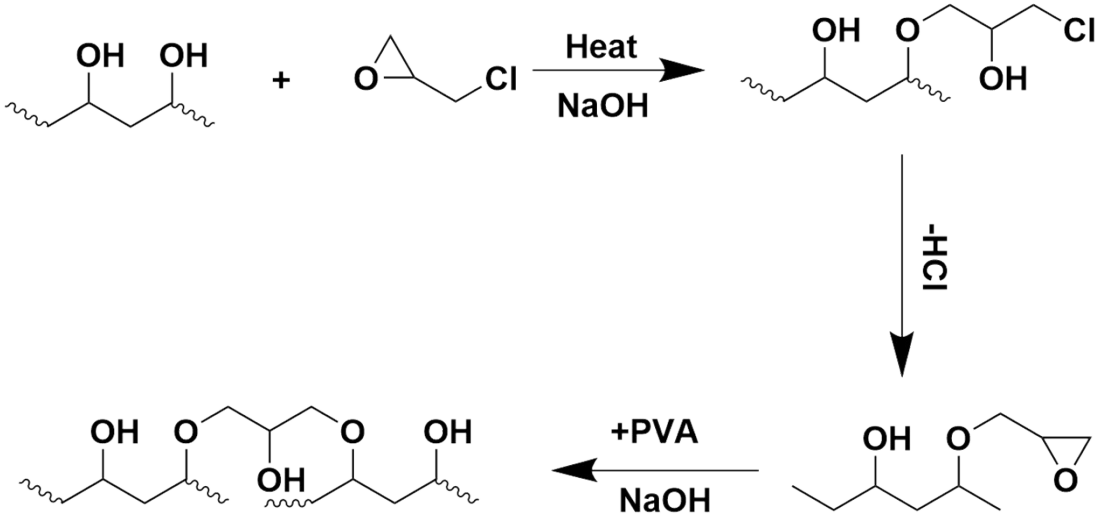

Figure S1. Synthetic diagram of chemically crosslinked PVA.

Figure S2. The thickness of an A4 sheet of paper measured by a spiral micrometer.

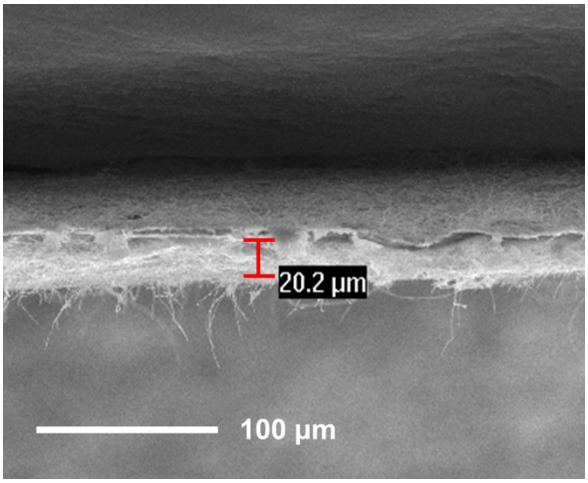

Figure S3. SEM image of the cross-section of the C-PVA/PAN hydrogel.

Figure S4. Optical photograph of the freeze-dried hydrogel.

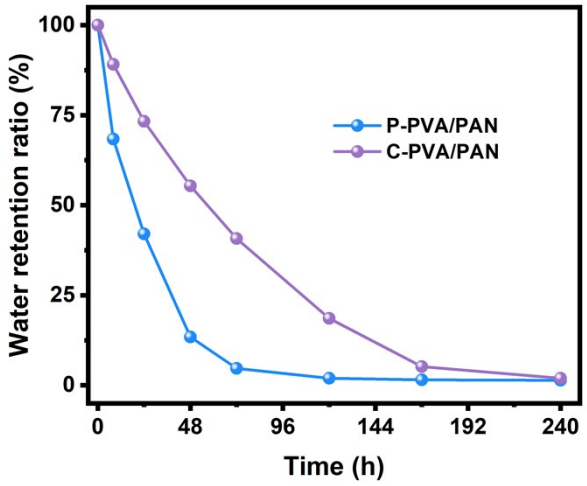

Figure S5. The water retentions of P-PVA/PAN and C-PVA/PAN stored under 25 °C.

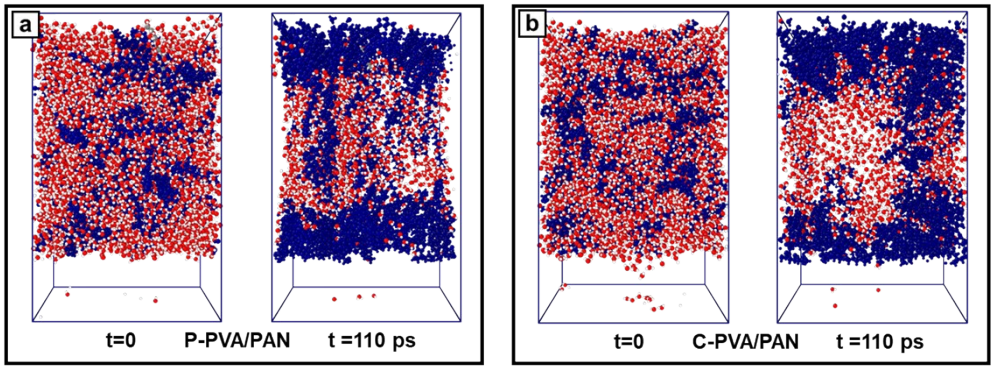

Figure S6. MD simulation diagram of water molecule binding at different time points in (a) P-PVA/PAN and (b) C-PVA/PAN systems.

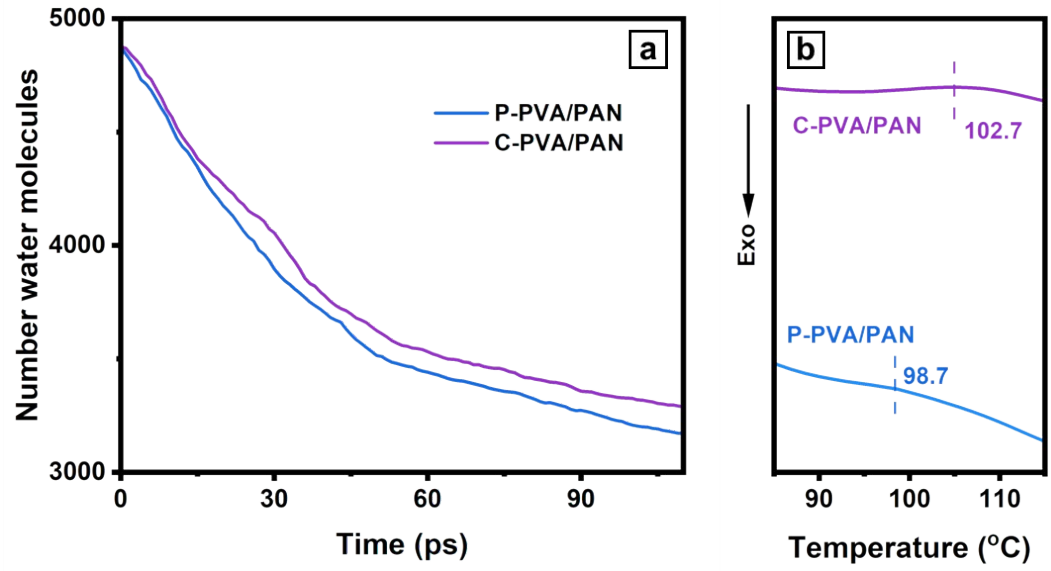

Figure S7. (a) The curve of the residual amount of water molecules with time. (b) DSC curve of P-PVA/PAN and C-PVA/PAN electrolyte.

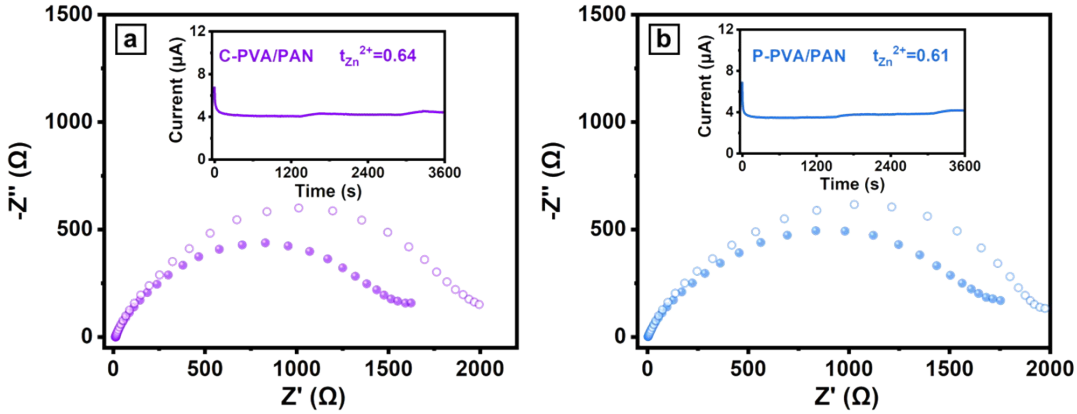

Figure S8. EIS spectra of the (a) Zn||C-PVA/PAN||Zn or (b) Zn||P-PVA/PAN||Zn symmetric cell before and after polarization, inset: variation of current with time during polarization at an applied voltage of 10 mV.

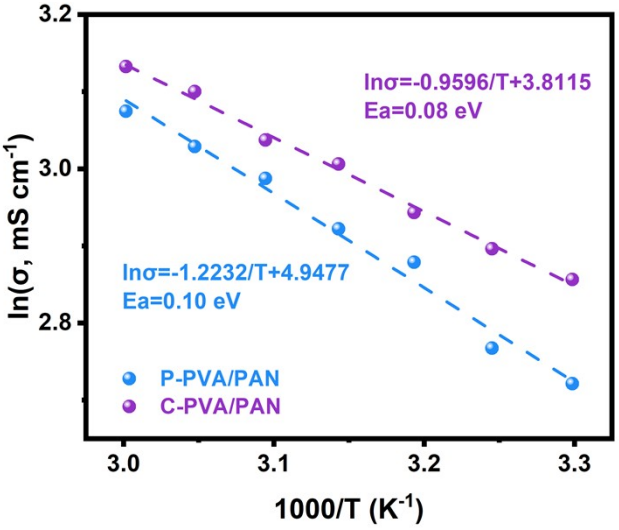

Figure S9. Corresponding Arrhenius curves and comparison of activation energies in P-PVA/PAN and C-PVA/PAN electrolytes.

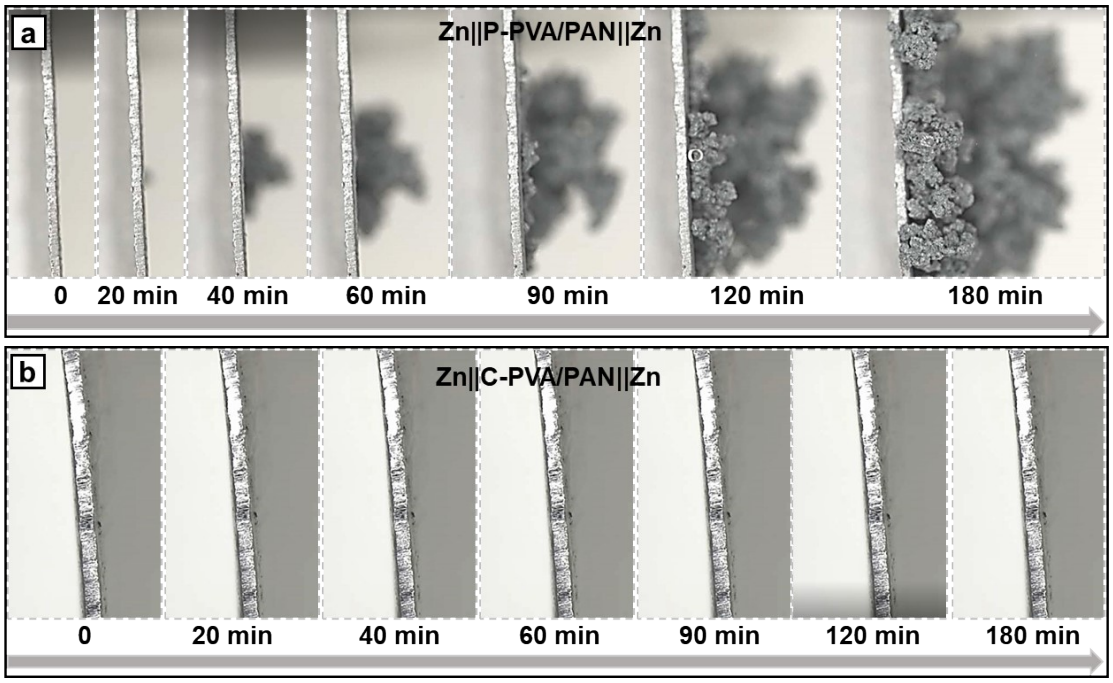

Figure S10. The in-situ optical images of the Zn plating behaviors with (a) P-PVA/PAN and (b) C-PVA/PAN electrolyte at 10 mA cm^{-2}.

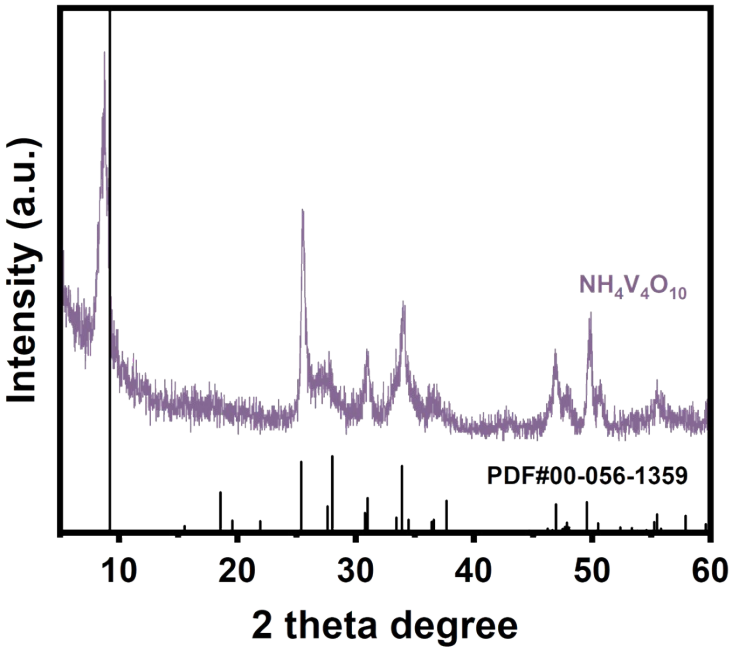

Figure S11. XRD pattern of the $NH_4V_4O_{10}$ synthesized by hydrothermal method.

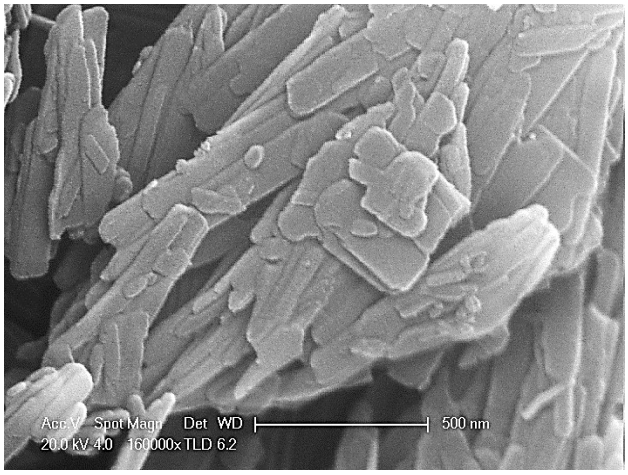

Figure S12. SEM image of the $NH_4V_4O_{10}$ synthesized by hydrothermal method.

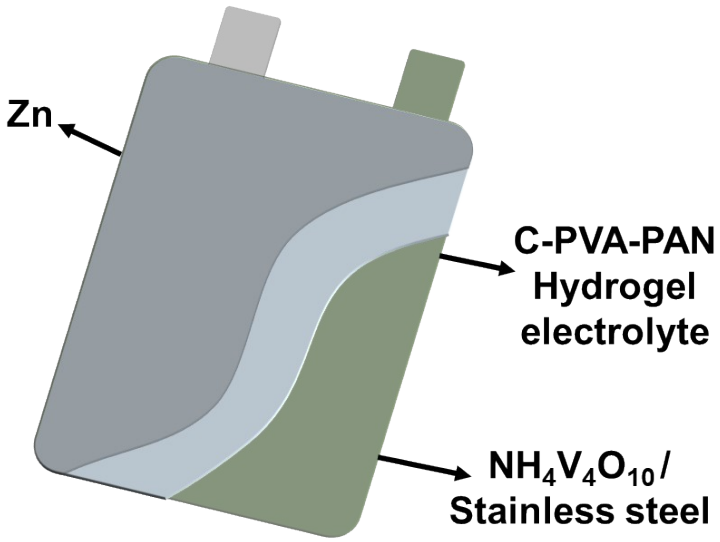

Figure S13. Schematic diagram of a flexible Zn||C-PVA/PAN|| $NH_4V_4O_{10}$ battery.

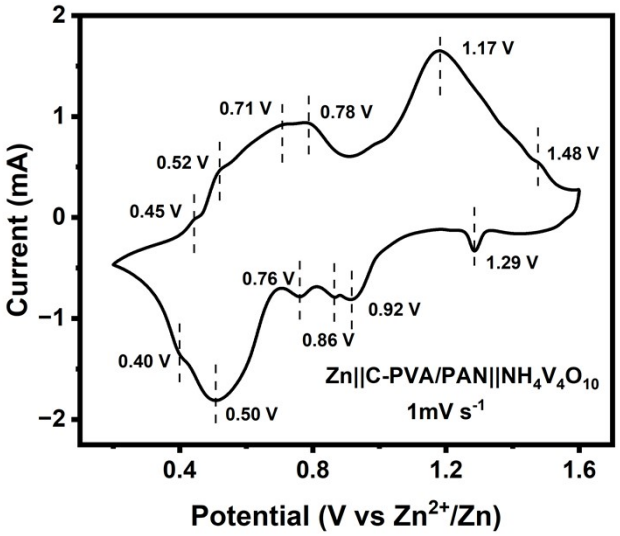

Figure S14. CV curves of Zn||C-PVA/PAN||$NH_4V_4O_{10}$ battery in the range of 0.2 to 1.6 V at 1mV s^{-1}.

Figure S15. Unencapsulated flexible Zn||C-PVA/PAN|| $NH_4V_4O_{10}$ with thickness of 82 μm.

Figure S16. Encapsulated flexible Zn||C-PVA/PAN|| $NH_4V_4O_{10}$ with thickness of 400 μm.

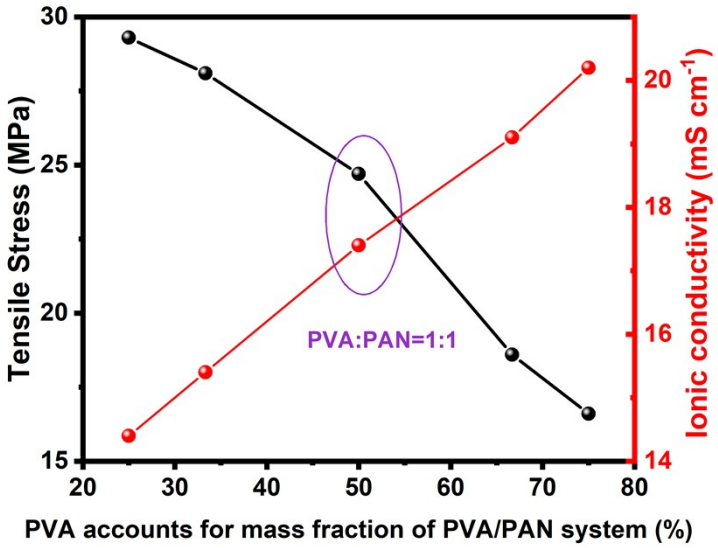

Figure S17. Graph of the relative content of PVA and PAN in the hydrogel electrolyte with mechanical properties and ionic conductivity.

Table S1. The specific capacity at a low current density and the thickness of hydrogel electrolytes with state-of-the-art flexible ZIBs.

Cathodes	**Hydrogel electrolytes**	**Current density (A g^{-1})**	**Specific capacity (mAh g^{-1})**	**Thickness (μm)**	**Reference**
MnO_2	ADC-gel	0.2	300	1200	[1]
$V_2O_5 \cdot V_3O_7$	PAM	0.1	445	1000	[2]
PANI	ZIS-PVA	0.1	151.2	1000	[3]
MnO_2	XG	0.1	211	300	[4]
MnO_2	Guar Gum	0.3	208.2	250	[5]
MnO_2	PZIB	0.308	341.5	198	[6]
V_2O_5	PAX-G	0.2	217	70	[7]
$NH_4V_4O_{10}$	C-PVA/PAN	0.1	501	20	This work
$NH_4V_4O_{10}$	C-PVA/PAN	0.2	480		
$NH_4V_4O_{10}$	C-PVA/PAN	0.5	356		

Table S2. The specific capacity at a low current density with state-of-the-art flexible ZIBs.

Cathodes	Hydrogel electrolytes	Current density (A g^{-1})	Specific capacity (mAh g^{-1})	Reference
VS_2	PVA	0.1	152	[8]
V_5O_{12}	Gelatin	0.1	300	[9]
MnO_2	Alginate/PAM	0.1	300.4	[10]
P-NVO	PAM-PVP	0.1	327.4	[11]
NVO	PCZ	0.1	329	[12]
MgVO	LPH	0.1	341.5	[13]
VO_2	PH/MXene	0.1	369.9	[14]
V_2O_5	PSX	0.1	380	[15]
V_2O_5	PMC	0.1	405.5	[16]
$NH_4V_4O_{10}$	TA-SA	0.1	409.6	[17]
MnO_2	PAM/PAANa	0.1	418	[18]
$Ni_{0.006}Ca_{0.0045}VO_2$	PVA	0.1	433.8	[19]
V_2O_5	PAMPSZn	0.1	438.9	[20]
LaV_2O_5	CD-PEO/PAM	0.1	439	[21]
$NH_4V_4O_{10}$	C-PVA/PAN	0.1	501	This work
VS_2	PZHE	0.2	150	[22]
$CoFe(CN)_6$	PAM	0.2	171.64	[23]
PANI	SFPAM-Zr	0.2	191	[24]
$Na_5V_{12}O_{32}$	Agr-PEG	0.2	198.3	[25]
$Zn_3V_2O_8$	PDZ-H	0.2	265.2	[26]
rGO/MnO_2	C-TEOS	0.2	277.3	[27]
P-NVO	PAM-PVP	0.2	278.1	[11]
MnO_2	GO-PVA	0.2	310	[28]
MgVO	LPH	0.2	310	[13]
NaV_3O_8	MMT-PAM	0.2	312	[29]
ZVO	CarraChi	0.2	349.6	[30]
MnO_2	PAM/PAANa	0.2	352	[18]
$NH_4V_4O_{10}$	SA	0.2	380	[17]
LaV_2O_5	CD-PEO/PAM	0.2	405	[21]
MnO_2	CPZ-H	0.2	480	[31]
$NH_4V_4O_{10}$	C-PVA/PAN	0.2	480	This work
VS_2	PZHE	0.5	120	[22]
$CoFe(CN)_6$	PAM	0.5	150	[23]
$Zn_3V_2O_8$	PDZ-H	0.5	251.1	[26]
rGO/MnO_2	cellulose-TEOS	0.5	257.3	[27]
VO_2	PH/MXene	0.5	306.3	[14]
V_2O_5	PAMPSZn	0.5	350	[20]
$NH_4V_4O_{10}$	C-PVA/PAN	0.5	356	This work

Reference

[1] Q. He, G. Fang, Z. Chang, Y. Zhang, S. Zhou, M. Zhou, S. Chai, Y. Zhong, G. Cao, S. Liang, A. Pan, *Nano-Micro Lett.* **2022**, *14*, 93.

[2] X. Li, L. Ma, Y. Zhao, Q. Yang, D. Wang, Z. Huang, G. Liang, F. Mo, Z. Liu, C. Zhi, *Mater. Today Energy* **2019**, *14*, 100361.

[3] L. Li, L. Zhang, W. Guo, C. Chang, J. Wang, Z. Cong, X. Pu, *J. Mater. Chem. A* **2021**, *9*, 24325.

[4] K. Ji, S. Li, Y. Lin, J. Zhang, M. Wang, C. Bai, D. Kong, *ACS Mater. Lett.* **2023**, *5*, 955.

[5] Y. Huang, J. Zhang, J. Liu, Z. Li, S. Jin, Z. Li, S. Zhang, H. Zhou, *Mater. Today Energy* **2019**, *14*, 100349.

[6] Y. Hao, D. Feng, L. Hou, T. Li, Y. Jiao, P. Wu, *Adv. Sci.* **2022**, *9*, 2104832.

[7] Y. Deng, Y. Wu, L. Wang, K. Zhang, Y. Wang, L. Yan, *J. Colloid Interface Sci.* **2023**, *633*, 142.

[8] J. Liu, J. Long, Z. Shen, X. Jin, T. Han, T. Si, H. Zhang, *Adv. Sci.* **2021**, *8*, 2004689.

[9] N. Zhang, M. Jia, Y. Dong, Y. Wang, J. Xu, Y. Liu, L. Jiao, F. Cheng, *Adv. Funct. Mater.* **2019**, *29*, 1807331.

[10] Z. Liu, D. Wang, Z. Tang, G. Liang, Q. Yang, H. Li, L. Ma, F. Mo, C. Zhi, *Energy Storage Mater.* **2019**, *23*, 636.

[11] Y. Lu, Z. Wang, M. Li, Z. Li, X. Hu, Q. Xu, Y. Wang, H. Liu, Y. Wang, *Adv. Funct. Mater.* **2024**, *34*, 2310966.

[12] H. Zhang, X. Gan, Z. Song, J. Zhou, *Angew. Chem. Int. Ed.* **2023**, *62*, e202217833.

[13] Z. Li, G. Zhou, L. Ye, J. He, W. Xu, S. Hong, W. Chen, M.-C. Li, C. Liu, C. Mei, *Chem. Eng. J.* **2023**, *472*, 144992.

[14] J. Feng, D. Ma, K. Ouyang, M. Yang, Y. Wang, J. Qiu, T. Chen, J. Zhao, B. Yong, Y. Xie, H. Mi, L. Sun, C. He, P. Zhang, *Adv. Funct. Mater.* **2022**, *32*, 2207909.

[15] C. Fu, Y. Wang, C. Lu, S. Zhou, Q. He, Y. Hu, M. Feng, Y. Wan, J. Lin, Y. Zhang, A. Pan, *Energy Storage Mater.* **2022**, *51*, 588.

[16] P. Lin, J. Cong, J. Li, M. Zhang, P. Lai, J. Zeng, Y. Yang, J. Zhao, *Energy Storage Mater.* **2022**, *49*, 172.

[17] B. Zhang, L. Qin, Y. Fang, Y. Chai, X. Xie, B. Lu, S. Liang, J. Zhou, *Sci. Bull.* **2022**, *67*, 955.

[18] Z. Shen, Z. Tang, C. Li, L. Luo, J. Pu, Z. Wen, Y. Liu, Y. Ji, J. Xie, L. Wang, Y. Yao, G. Hong, *Adv. Energy Mater.* **2021**, *11*, 2102055.

[19] X. Zhao, L. Mao, Q. Cheng, F. Liao, G. Yang, L. Chen, *Carbon* **2022**, *186*, 160.

[20] J. Cong, X. Shen, Z. Wen, X. Wang, L. Peng, J. Zeng, J. Zhao, *Energy Storage Mater.* **2021**, *35*, 586.

[21] H. Xia, G. Xu, X. Cao, C. Miao, H. Zhang, P. Chen, Y. Zhou, W. Zhang, Z. Sun, *Adv. Mater.* **2023**, *35*, 2301996.

[22] K. Leng, G. Li, J. Guo, X. Zhang, A. Wang, X. Liu, J. Luo, *Adv. Funct. Mater.* **2020**, *30*, 2001317.

[23] L. Ma, S. Chen, C. Long, X. Li, Y. Zhao, Z. Liu, Z. Huang, B. Dong, J. A. Zapien, C. Zhi, *Adv. Energy Mater.* **2019**, *9*, 1902446.

[24] Y. Cheng, Y. Jiao, P. Wu, *Energy Environ. Sci.* **2023**, *16*, 4561.

[25] Y. Meng, L. Zhang, M. Peng, D. Shen, C. Zhu, S. Qian, J. Liu, Y. Cao, C. Yan, J. Zhou, T. Qian, *Adv. Funct. Mater.* **2022**, *32*, 2206653.
[26] H. Lu, J. Hu, L. Wang, J. Li, X. Ma, Z. Zhu, H. Li, Y. Zhao, Y. Li, J. Zhao, B. Xu, *Adv. Funct. Mater.* **2022**, *32*, 2112540.
[27] M. Chen, J. Chen, W. Zhou, X. Han, Y. Yao, C.-P. Wong, *Adv. Mater.* **2021**, *33*, 2007559.
[28] X. Xiao, X. Xiao, Y. Zhou, X. Zhao, G. Chen, Z. Liu, Z. Wang, C. Lu, M. Hu, A. Nashalian, S. Shen, K. Xie, W. Yang, Y. Gong, W. Ding, P. Servati, C. Han, S. X. Dou, W. Li, J. Chen, *Sci. Adv.* **2021**, *7*, eabl3742.
[29] S. Ji, J. Qin, S. Yang, P. Shen, Y. Hu, K. Yang, H. Luo, J. Xu, *Energy Storage Mater.* **2023**, *55*, 236.
[30] F. Wang, J. Zhang, H. Lu, H. Zhu, Z. Chen, L. Wang, J. Yu, C. You, W. Li, J. Song, Z. Weng, C. Yang, Q.-H. Yang, *Nat. Commun.* **2023**, *14*, 4211.
[31] H. Lu, J. Hu, X. Wei, K. Zhang, X. Xiao, J. Zhao, Q. Hu, J. Yu, G. Zhou, B. Xu, *Nat. Commun.* **2023**, *14*, 4435.