

Supporting Information

Nanorods Assembled Urchin-like Molybdenum-Manganese Oxide Heterostructure with Enhanced Oxygen Vacancies as Cathode for Quasi Solid State Zinc-ion Batteries

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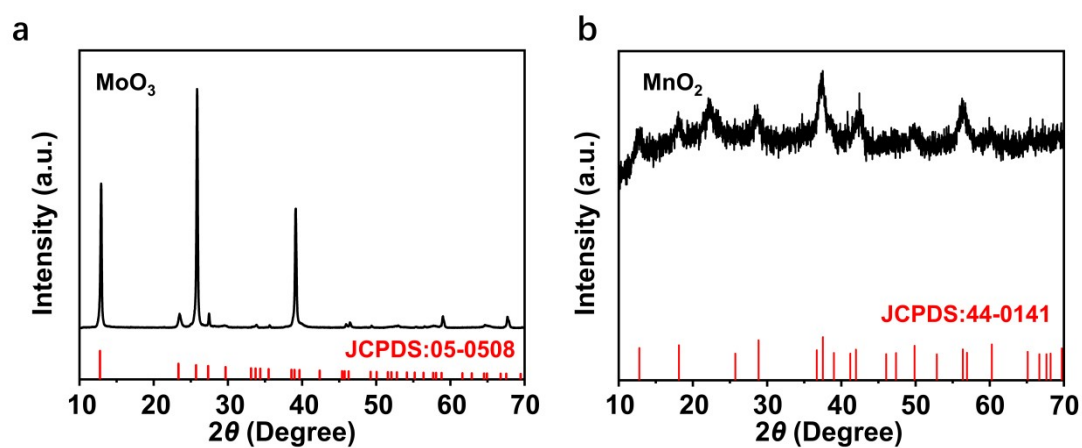


Figure S1. The XRD patterns of a) MoO_3 and b) MnO_2

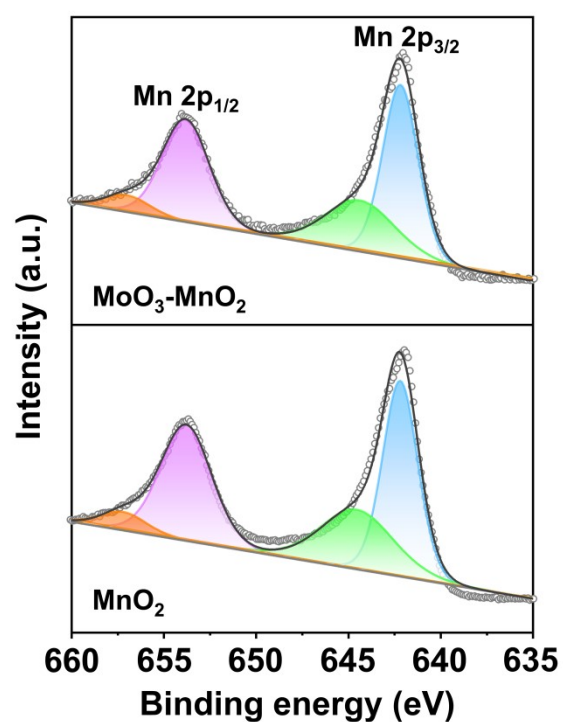


Figure S2. Mn 2p XPS spectra of MnO_2 and $\text{MoO}_3\text{-MnO}_2$

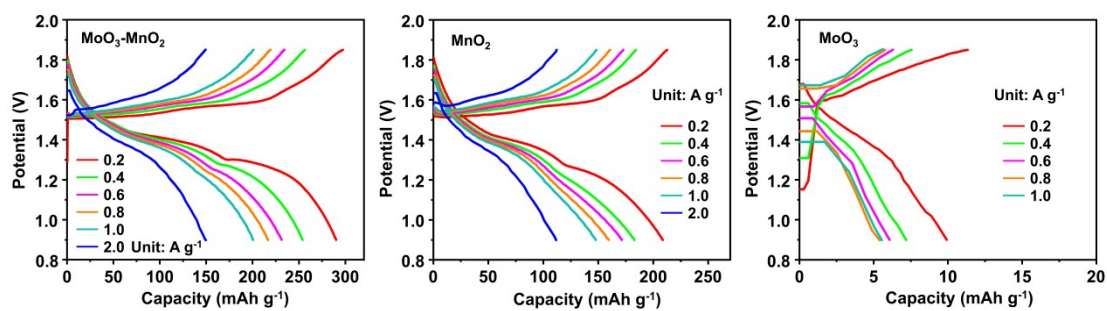


Figure S3. The charging and discharging curves at various current densities for a) $\text{MoO}_3\text{-MnO}_2$, b) MnO_2 and c) MoO_3

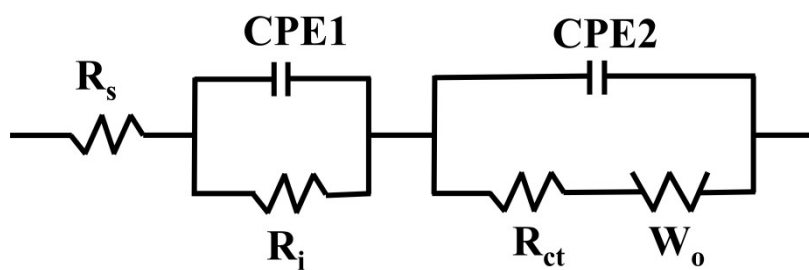


Figure S4. The equivalent circuit diagram of samples

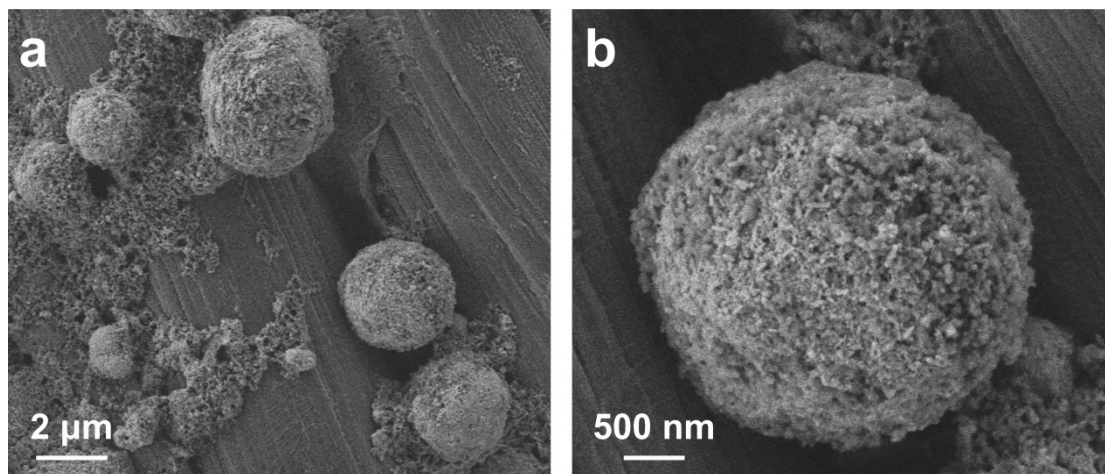


Figure S5. SEM images of $\text{MoO}_3\text{-MnO}_2$ electrode after 1000 cycles

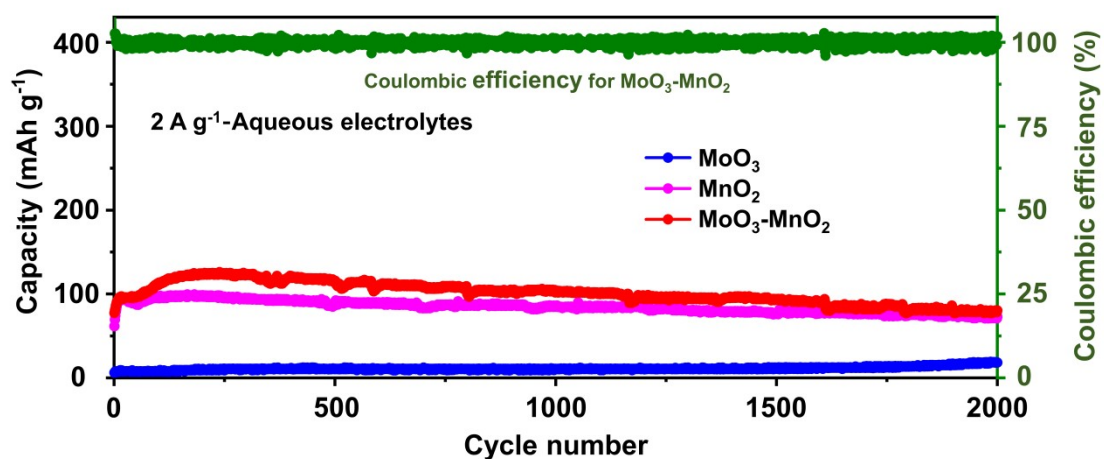


Figure S6. The cycling performance of MoO_3 , MnO_2 , and $\text{MoO}_3\text{-MnO}_2$ at 2 A g^{-1} in aqueous electrolytes

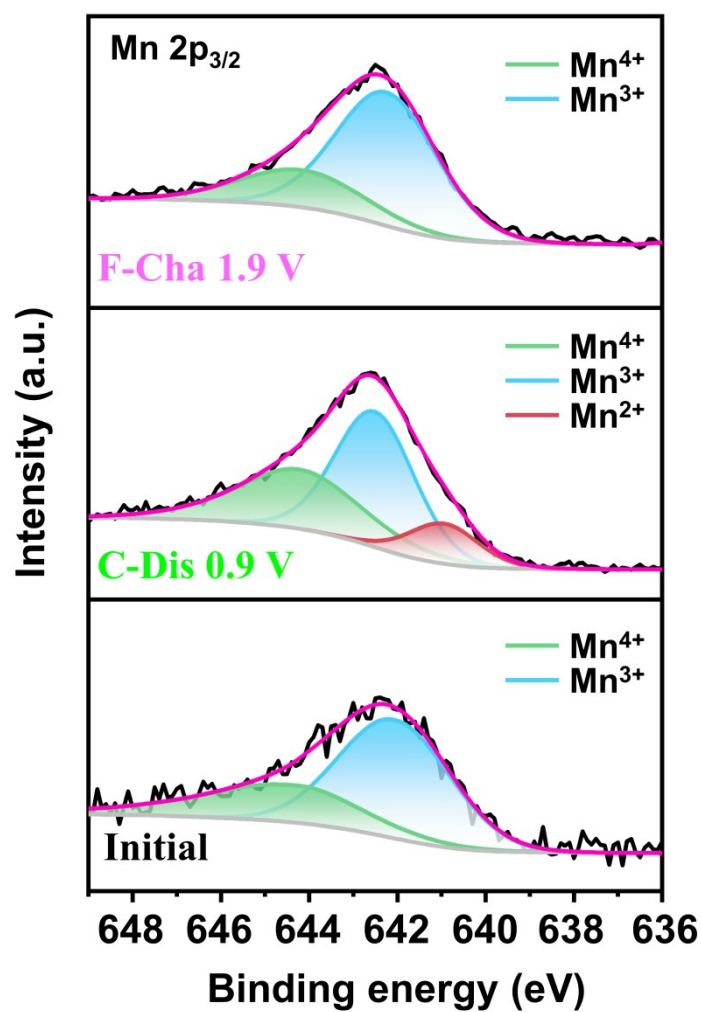


Figure S7. Mn $2p_{3/2}$ ex-situ high-discern XPS spectra of $\text{MoO}_3\text{-MnO}_2$

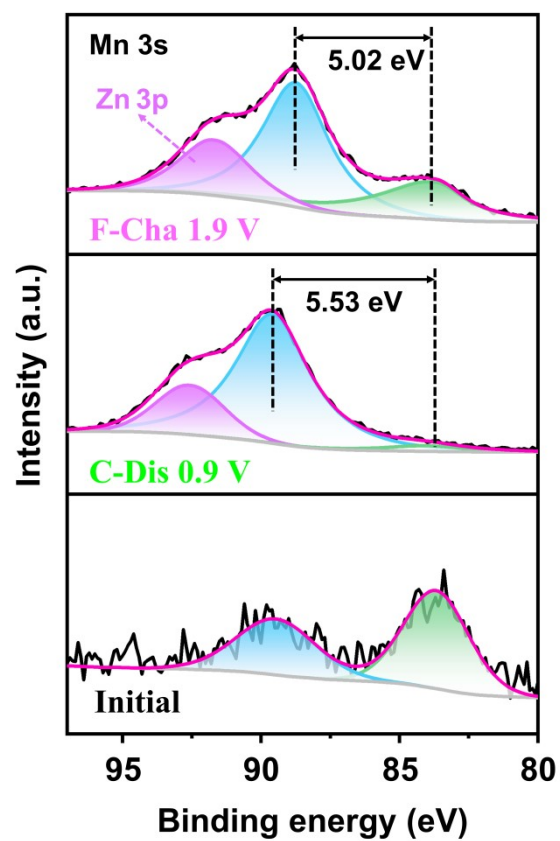


Figure S8. Mn 3s ex-situ high-discern XPS spectra of MoO₃-MnO₂

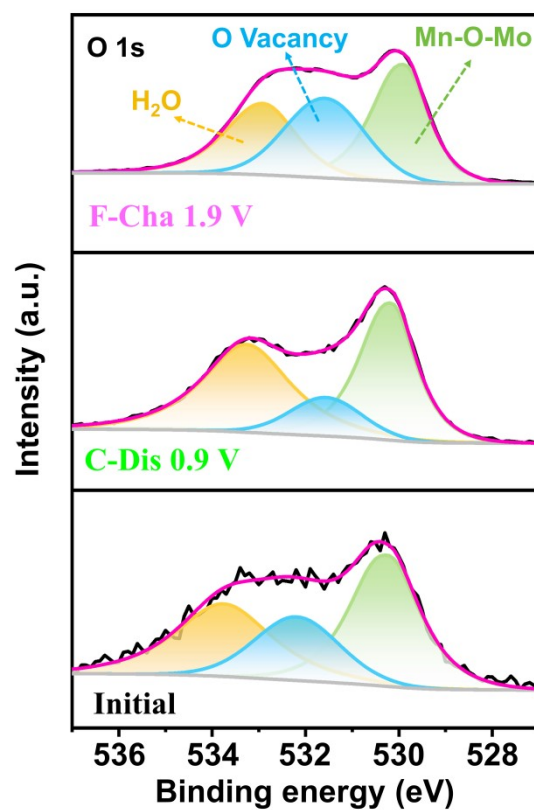


Figure S9. O 1s ex-situ high-discern XPS spectra of MoO₃-MnO₂

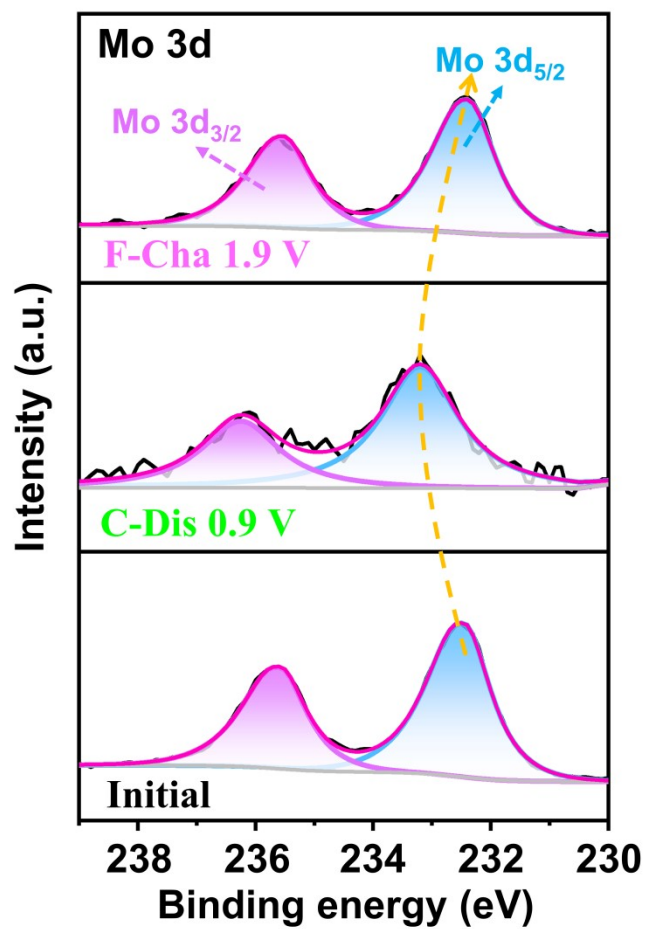


Figure S10. Mo 3d ex-situ high-discern XPS spectra of MoO₃-MnO₂

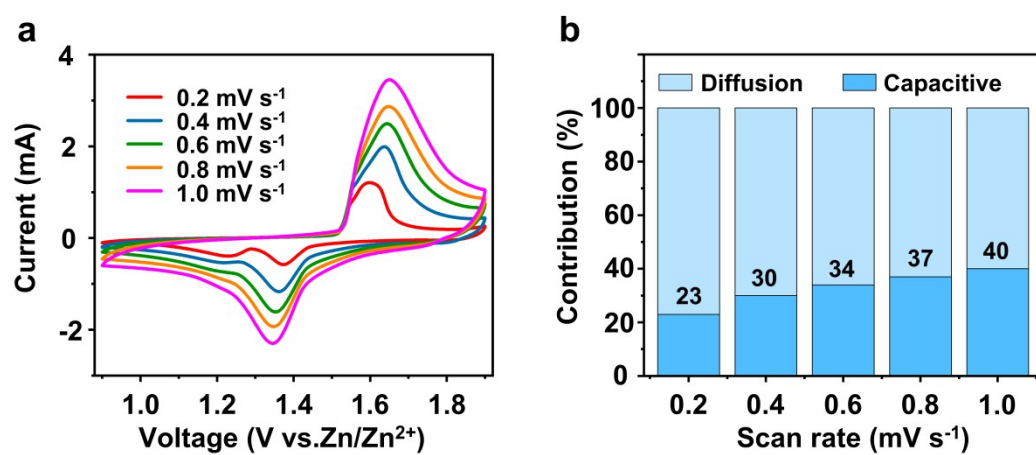


Figure S11. a) CV curves of the pure MnO₂ electrode at different scan rates, b) Contribution ratios of the capacitive and diffusion-controlled capacities at different scan rates

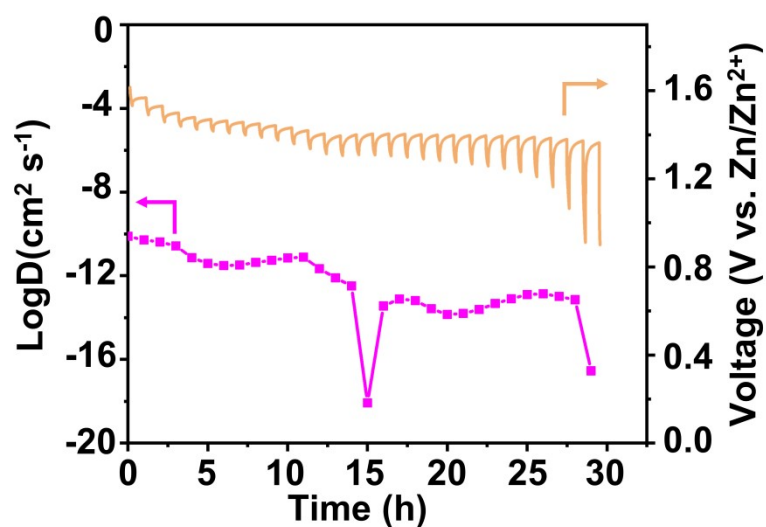


Figure S12. GITT of the MnO₂ electrode

The calculation of Diffusion coefficient

The Zn//MnO₂ and Zn//MoO₃-MnO₂ batteries were discharged at 0.1 A g⁻¹ for 10 min and then relaxed for 1 h, which repeated the above operation from 0.9 V to 1.9 V. The specific calculation is as follows:

$$D = \frac{4}{\pi \Delta \tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2$$

Where τ is the pulse duration; m_B , V_M , and M_B are the mass, molar volume, and molar mass of active materials; S is the area in contact with electrolytes; ΔE_s and ΔE_τ represent the voltage change caused by the pulse and the voltage change of constant current charge-discharge, respectively.

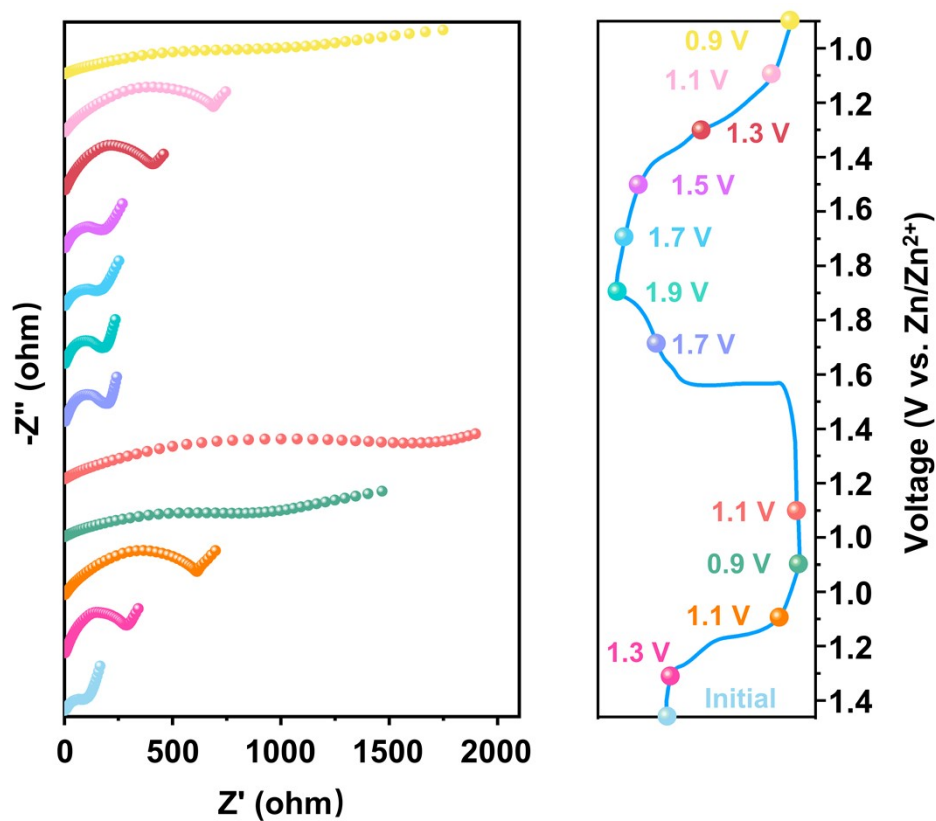


Figure S13. Nyquist plots for MoO₃-MnO₂ cathode during the discharge and charge process

Table S1. Fitting results of R_s and R_{ct} of the EIS based on the equivalent circuit. The ion diffusion coefficient was calculated based on EIS

	$R_s(\Omega)$	$R_{ct}(\Omega)$	Diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
MoO ₃	4.452	101.9	2.98×10^{-12}
MnO ₂	2.048	55.75	1.25×10^{-11}
MoO ₃ -MnO ₂	2.123	39.6	2.71×10^{-11}

Table S2. Comparison of cathode performance in AZIBs between this work and previously reported

Cathode Materials	Specific capacity mAh g ⁻¹ @A g ⁻¹	Capacity after cycling (mAh g ⁻¹ @ A g ⁻¹) (Cycle number)	Rate performance (mAh g ⁻¹)		Ref.
			1 A g ⁻¹	2 A g ⁻¹	
MoO₃-MnO₂	319@0.2	155@1 (1000) 116@2 (2000)	201	150	This work
β -MnO ₂ (O _d)	307@0.1	169@1 (800)	195	154	¹
SbMO-6	276@0.1	113@2 (2000)	192	171	²

NiCo ₂ O ₄ -MnO ₂	313@0.1	192@1 (1000)	202	—	3
α -MnO ₂ / γ -MnO ₂	278@0.1	65@3 (2800)	134	—	4
CaMnO	260@0.3	140@1.5 (750)	193	104	5
1.05 KCl-MnO ₂	275@0.1	96@1 (1000)	109	—	6
a-H-MnFeO	247@0.2	~135@1 (1000)	109	50	7
Ti-Na _{0.44} MnO ₂	252@0.0 5	~90@1 (2400)	110	—	8
Pr ₆ O ₁₁ -Mn ₂ O ₃	347@0.1	140.8@1 (2000)	197	186	9

Reference

1. J. Zheng, C. Qin, C. Chen, C. Zhang, P. Shi, X. Chen, Y. Gan, J. Li, J. Yao, X. Liu, J. Cheng, D. Sun, H. Wan and H. Wang, *Journal of Materials Chemistry A*, 2023, **11**, 24311-24320.
2. H. Huang, H. Feng, Z. He, Y. Huang, J. Xu, C. Hu, Z. Chen, Z. Yang and W. Zhang, *ACS Nano*, 2024, **18**, 25601-25613.
3. X. Lu, L. Chen, R. Orenstein, W. Li, W. Chi, M. Peng, C. Wang, Y. Liu and X. Zhang, *Small*, 2024, 2406680.
4. K. Wang, D. Wu, X. Sun, W. Zhang, Z. Zhang, Y. Zhen, Y. Yang and J. Wang, *ACS Sustainable Chemistry & Engineering*, 2023, **11**, 15818-15825.
5. D. Xie, Y. Wang, L. Tian, H. Huang, J. Sun, D.-W. Kim, J. Zhao and J. Mao, *Adv Funct Mater*, 2024, 2413993.
6. Y. Gao, J. Zhou, L. Qin, Z. Xu, Z. Liu, L. Wang, X. Cao, G. Fang and S. Liang, *Green Energy & Environment*, 2023, **8**, 1429-1436.
7. F. Jing, C. Lv, L. Xu, Y. Shang, J. Pei, P. Song, Y. Wang, G. Chen and C. Yan, *Journal of Energy Chemistry*, 2023, DOI: 10.1016/j.jechem.2023.08.036.
8. K. Wang, G. Guo, X. Tan, L. Zheng and H. Zhang, *Chemical Engineering Journal*, 2023, **451**.
9. Q. Liu, G. Fan, Y. Zeng, X. Zhang, D. Luan, Y. Guo, X. Gu and X. W. Lou, *Adv Energy Mater*, 2024, **14**, 2402743.