

Electronic Supplementary Material

Dendrite-Free Zn Anode Enabled by PEDOT:PSS/MoS₂ Electrokinetical Channels for Aqueous Zn-ion Batteries

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Materials and methods

Materials. Monolayer Molybdenum disulfide (MoS_2), and N-methyl pyrrolidone (NMP, AR) were purchased from Aladdin Reagent (China) Co., Ltd. Ethanol was purchased from Sinopharm Chemical Reagent Co. and Polyvinylidene fluoride (PVDF, AR) was purchased from Sigma-Aldrich. PEDOT:PSS dispersion liquid (2%) was purchased from Shanghai Ouyi Organic Photoelectric Materials Co., LTD. Carbon black (Super P) was purchased from Alfa Aesar. Zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, AR) was bought from Sinopharm Chemical Reagent Co., Ltd., China. Zinc foil was purchased from Shenzhen AES Automation Technology Co., Ltd. Deionized water was prepared by laboratory ultrapure water machine. All the chemicals were used as received without further purification.

Assembly of PEPM. 0.5g monolayer MoS_2 and 5 g PEDOT:PSS were mixed in 80 mL water and the MoS_2 powder was dispersed in deionized water. The suspension is then treated ultrasonically with a low-power (100 W) water bath for 40 minutes. The obtained suspension was centrifuged at 1500 rpm for 10 minutes to remove the thick MoS_2 sheets, and finally the supernatant was collected by vacuum filtration and dried in a freeze dryer. The functionalized composite is labeled as PEDOT:PSS/ MoS_2 (PEPM).

Preparation of PEPM@Zn Anodes. The Zn foil was cleaned with ethanol and dried in a vacuum oven of 40 °C for further use. PEPM and PVDF binder, with a weight ratio of 9:1, were homogeneously mixed in NMP under continuous ultrasonic stirring, and then uniformly coated on the surface of Zn foil using a brush. The process parameters

were optimized to achieve expected thickness and best homogeneity for an ideal interfacial performance. The PEPM@Zn electrode was cut into ϕ 14 mm round pieces after dried at 40 °C in the oven.

Preparation of V₂O₅ Cathodes.

The V₂O₅ cathodes were prepared in NMP solution by combining the activated materials, carbon black and PVDF with a mass ratio of 70:20:10. The slurry is then spread on the carbon fibers with a thickness of about 50 μ m using the blade technique. After drying at 100 °C for 6 h, the electrodes was then calendered, cut into discs with a diameter of 12 mm and placed in a glove box. The active substance load is about 1.5~2 mg cm⁻².

Full Cell Assembly

The Zn//V₂O₅ full battery is assembled in a glove box filled with argon gas with V₂O₅ cathode, PEPM@Zn (or bare Zn) foil as the anode and 2 M ZnSO₄ as electrolyte. Glass fiber (Whatman GF/D) is embedded in the CR2032 coin-type battery. The assembled full cells were left standing for at least 10 h to ensure a proper wetting of the cell components before performing electrochemical tests.

Materials characterization

The structure and morphology of electrodes were characterized by scanning electron microscopy (SEM, JSM 7610 plus). The micro-structures of the electrode materials were characterized using transmission electron microscopy (TEM, JEOL JEM-2100FEG). The elemental content was obtained using X-ray Photoelectron

Spectroscopy (XPS, Thermo Scientific ESCALAB Xi+), X-ray Diffraction (XRD, Rigaku Ultima IV) and EDS (HORIBA EMAX).

Electrochemical characterization

Electrochemical measurements were conducted using CR2032-type coin cells at room temperature. For the Coulombic efficiency (CE) test, bare Zn and PEPM@Zn were punched into 12-mm diameter discs as the working electrodes, Ti foil was used as the counter electrode, and the glass fiber separator as the separator. The 2 M ZnSO₄ aqueous solution was used as the electrolyte. The current density is controlled at 1 mA cm⁻² as well as the surface capacity is 1 mAh cm⁻² to measure the Coulombic efficiency. Electrochemical impedance spectroscopy (EIS) was performed over the frequency range of 10 mHz to 100 kHz. Cyclic voltammetry (CV) data, Tafel plot, Chronoamperometry (CA) curves and EIS test were collected by using Shanghai Chenhua CHI660E electrochemical workstation. Galvanostatic charge-discharge and cyclic tests were carried out by using CT20001A cell test instrument (LAND Electronic Co.).

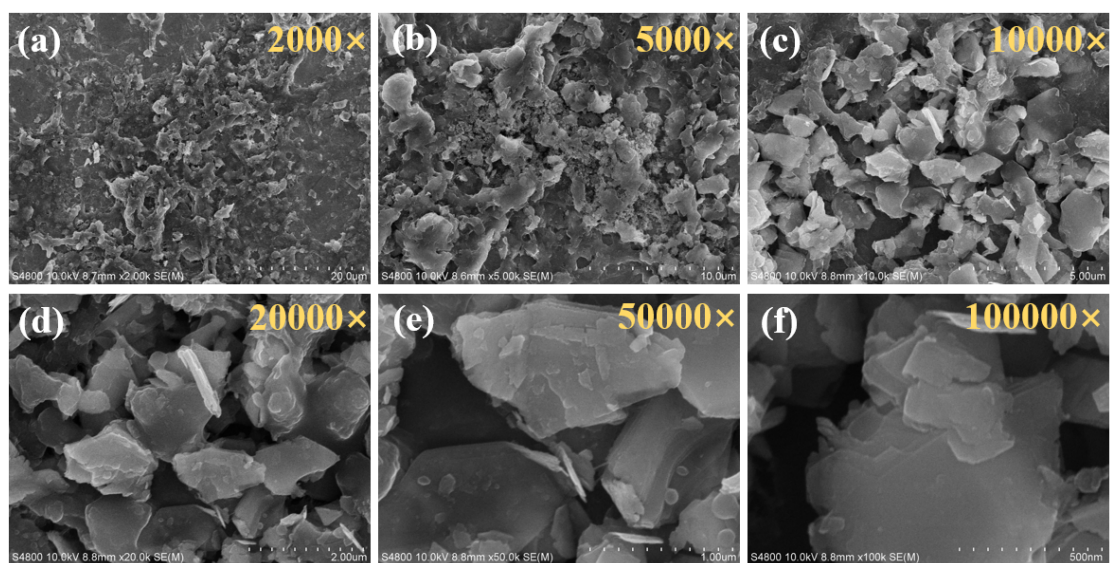


Figure S1 SEM images of PEPM@Zn anodes under different magnifications

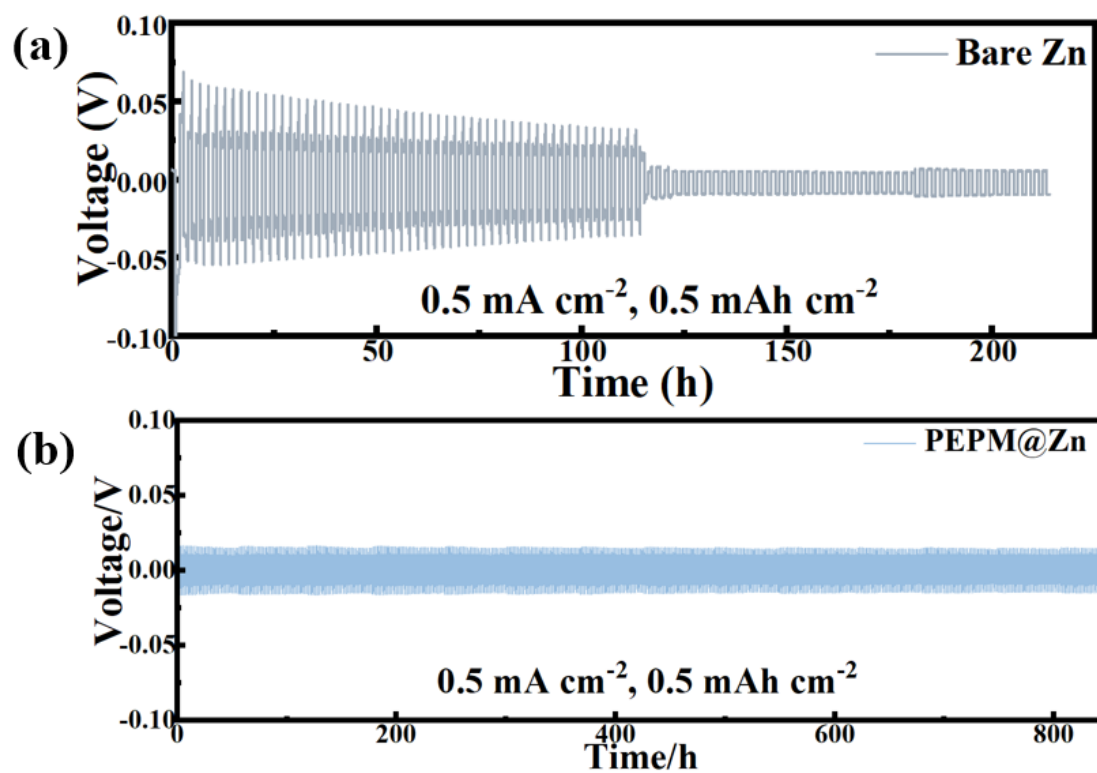


Figure S2 Galvanostatic performance of (a) bare Zn and (b) PEPM@Zn symmetric cells at the current density of 0.5 mA cm^{-2} and 0.5 mAh cm^{-2}

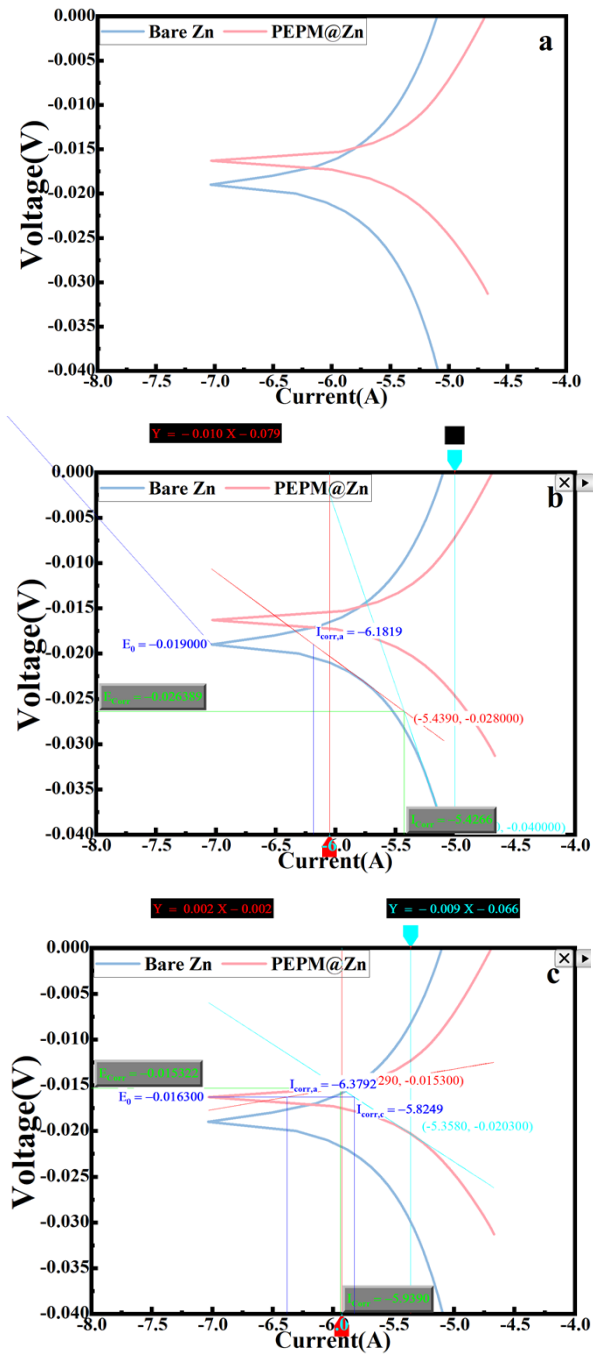


Figure S3 (a) Tafel polarization curves of symmetric cells in the same three-electrode cell, (b) fitted Tafel polarization curve of bare Zn anode, (c) fitted Tafel polarization curve of PEPM@Zn

anode

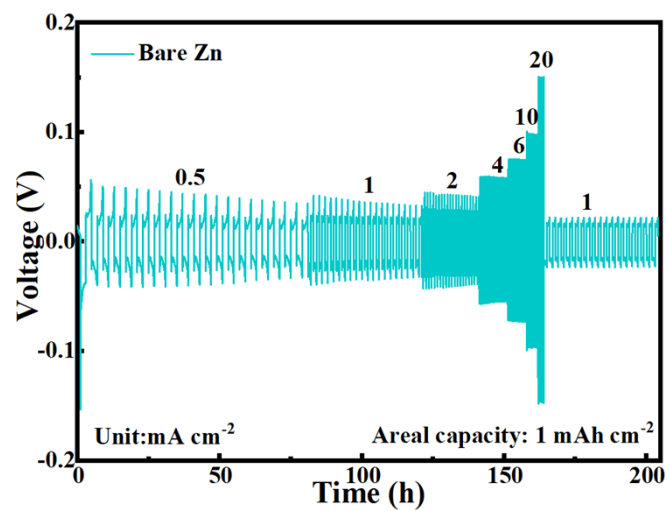


Figure S4 Rate performance of bare Zn anode

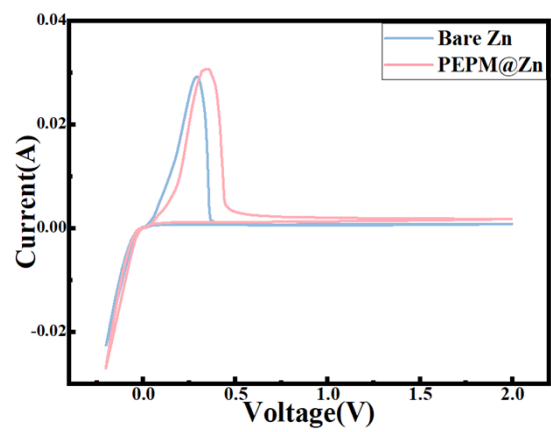


Figure S5 Cyclic voltammetry curves of symmetric cells of Bare Zn and PEPM@Zn

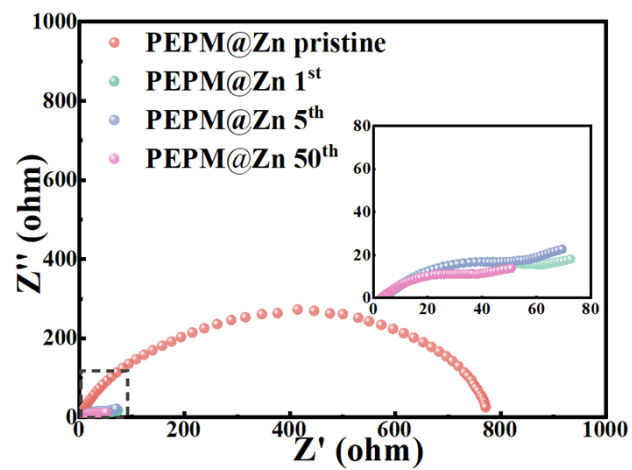


Figure S6 Nyquist plot of symmetric cell based on PEPM@Zn anode

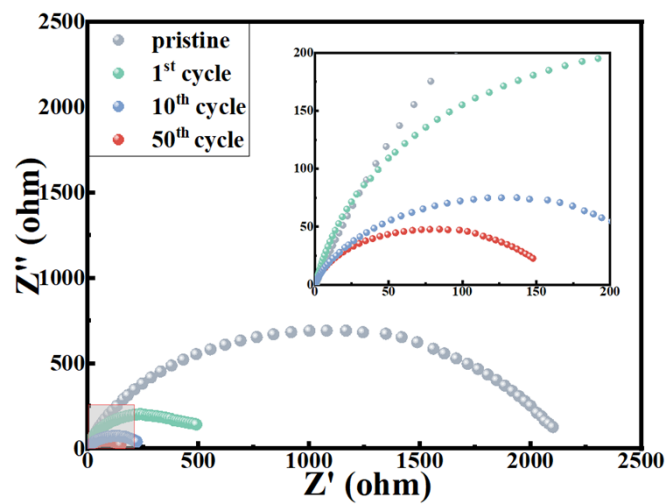


Figure S7 Nyquist plot of symmetric cell based on bare Zn anode

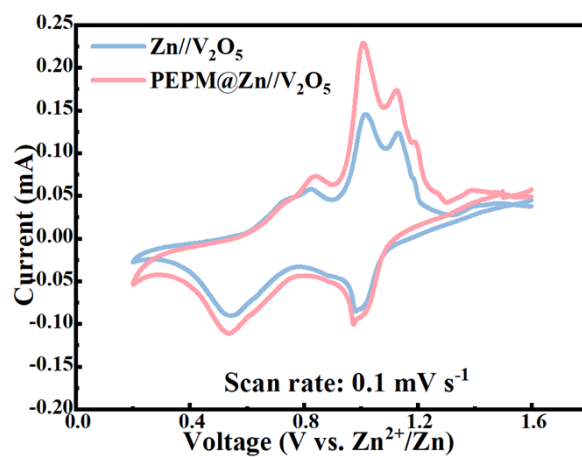


Figure S8 Comparison of CV curves of PEPM@Zn//V₂O₅ and Zn//V₂O₅ full cells

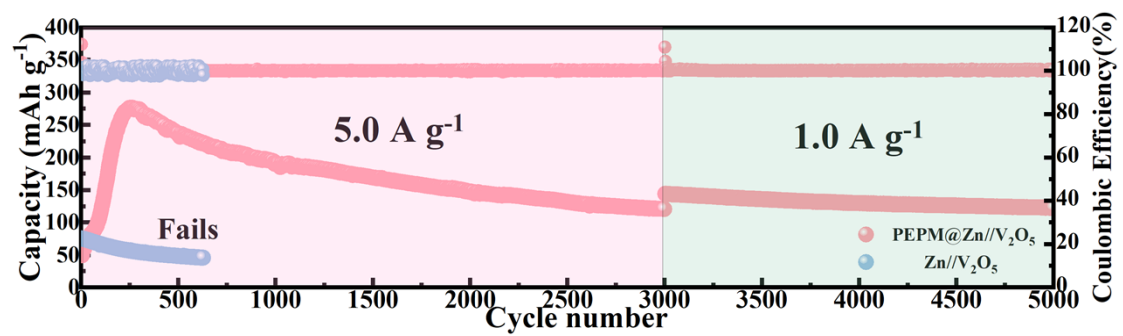


Figure S9 Long-term stability and performance of PEPM@Zn anode and bare Zn anode under various current densities

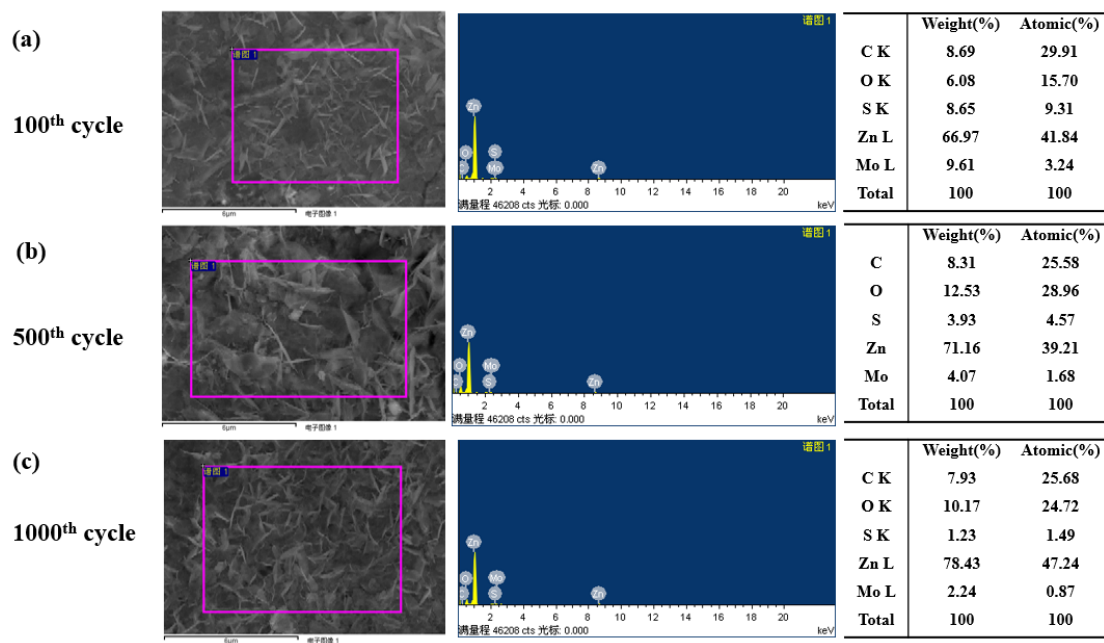


Figure S10 (a),(b) and (c) Ex-situ SEM images and EDS mapping of PEPM@Zn anode at different cycle stages

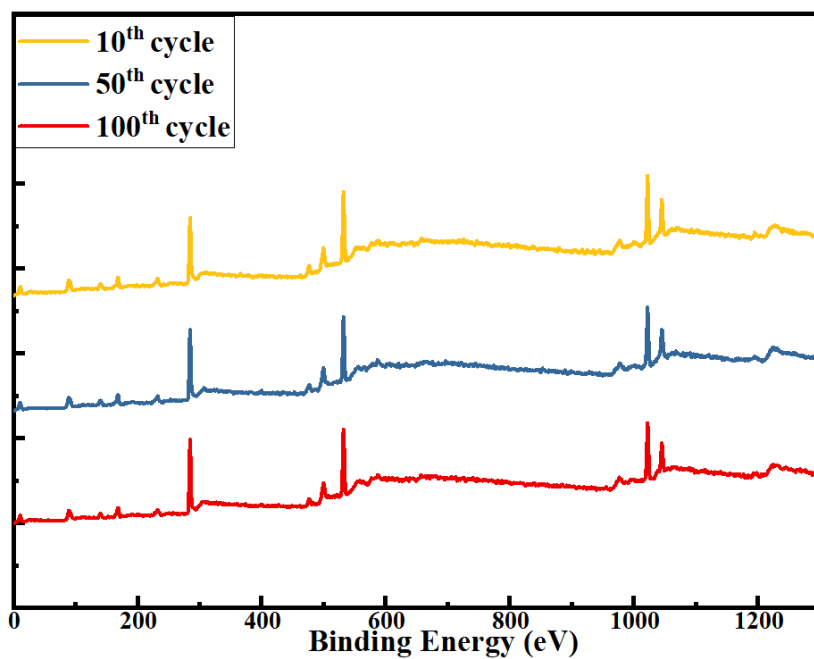


Figure S11 Overall XPS spectra of PEPM@Zn anode at different cycle stages

Table S1. Comparison of cycling performance for this work with reported devices

Anode	Electrolyte	Working condition (mA cm ⁻² -mAh cm ⁻²)	Lifespan(h)	Reference
GiZn	2 M ZnSO ₄	10-2	383	[33]
Zn@ZnO	1 M Zn(OTf) ₂	5-2.5	100	[34]
ZnS@Zn	1 M ZnSO ₄	2-2	1100	[35]
MZn-60	2 M ZnSO ₄	0.2-0.2	820	[36]
Zn@Sb	2 M ZnSO ₄ +0.1 M MnSO ₄	3-1	1000	[37]
MMT-Zn	2 M ZnSO ₄	1-0.25	1000	[38]
PEDOT:PSS/G S@Zn	2 M ZnSO ₄	0.1-5	500	[39]
PVB@Zn	1 M ZnSO ₄	0.5-0.5	2200	[40]
PTC@Zn	2 M ZnSO ₄	10-5	550	[41]
ILG-Zn	2 M ZnSO ₄	0.1-0.1	1000	[42]
MIL-125(Ti)- Zn	2 M ZnSO ₄	5-5	700	[43]
Zn/CNT	2 M ZnSO ₄	5-2.5	110	[44]
GFA-Zn	2 M ZnSO ₄	3-3	700	[45]
PEPM@Zn	2 M ZnSO ₄	5-5	390	This work

Theoretical calculations: The density function theory (DFT) calculations were implemented by using Vienna *ab-initio* simulation package (VASP).^{1,2} The Perdew-Burke-Ernzerhof (PBE) with generalized gradient approximation (GGA) was employed for the exchange-correlation functional.³ A plane wave basis with the cutoff energy of 400 eV was chosen in this work. A $1 \times 1 \times 1$ k-point mesh was used in these calculations.⁴⁻⁶ We consider the van der Waals (vdW) interaction using the DFT-D3 method. A vacuum layer along the out-plane direction of 15 Å was constructed to restrain the interactions between adjacent slabs. The residual force and energy convergence thresholds were set to 0.02 eV Å⁻¹ and 10⁻⁵ eV Å⁻¹, respectively. The MoS₂ model is a 3×5×1 supercell which includes 30 Mo atoms and 60 S atoms.

The charge density difference is calculated by the following equation:

$$\Delta\rho = \rho_{\text{total}} - \rho_{\text{base}} - \rho_{\text{Zn}}$$

Where ρ_{total} represents the optimized structural charge density of the interface, ρ_{base} represents the charge density of the base that forms the interface (PEDOT:PSS/MoS₂ or MoS₂), and ρ_{Zn} represents the charge density of Zn.

The adsorption energy for Zn atom is defined as:

$$E_{\text{ad}} = E_{\text{total}} - E_{\text{base}} - E_{\text{Zn}}$$

where E_{total} , E_{base} , and E_{Zn} represent the total energy of Zn adsorption on different surfaces, the energy of PEDOT:PSS/MoS₂ layer, and the energy of atomic Zn, respectively.

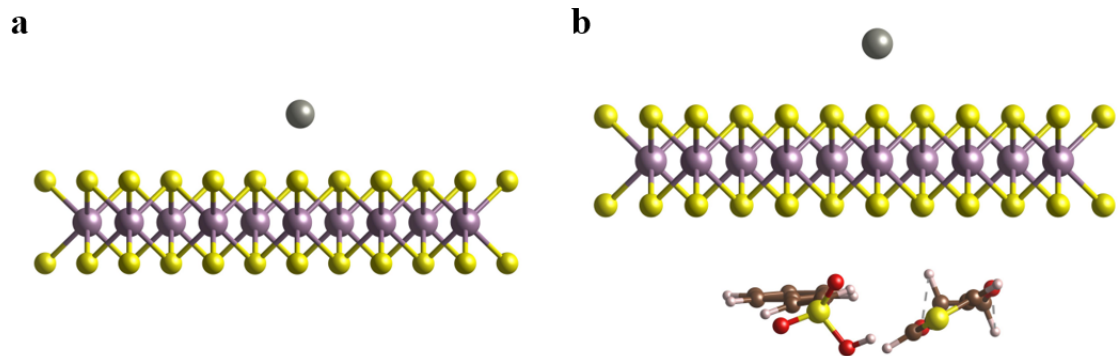


Figure S12 Interface model of (a) Zn-MoS₂ and (b) Zn-MgF₂/MoS₂, the gray, yellow, purple, brown, red and light brown balls represent Zn, S, Mo, C, O and H atoms respectively, the gray, yellow, red, brown, and light pink balls represent Zn, S, O, C, B, N and H atoms respectively.

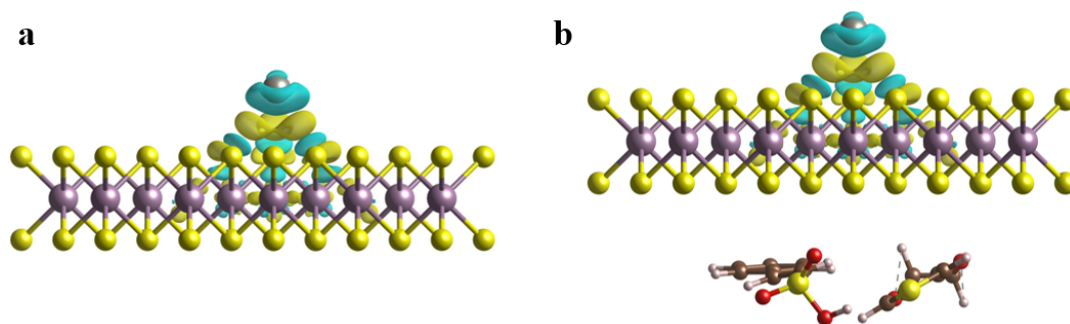


Figure S13 Comparison of charge density differences in (a) Zn-MoS₂ structure and (b) Zn-PEDOT:PSS/MoS₂ core-shell structure

Reference

- [1] Yi, Z.; Chen, G.; Hou, F.; Wang, L.; Liang, J. Strategies for the Stabilization of Zn Metal Anodes for Zn-Ion Batteries. *Adv. Energy Mater.* **2021**, *11*, 2003065.
- [2] Hao, J.; Li, B.; Li, X.; Zeng, X.; Zhang, S.; Yang, F.; Liu, S.; Li, D.; Wu, C.; Guo, Z. An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries. *Adv. Mater.* **2020**, *32*, 2003021.
- [3] Cao, Y.; Tang, X.; Li, L.; Tu, H.; Hu, Y.; Yu, Y.; Cheng, S.; Lin, H.; Zhang, L.; Di, J. Fast Zn²⁺ Mobility Enabled by Sucrose Modified Zn²⁺ Solvation Structure for Dendrite-Free Aqueous Zinc Battery. *Nano Res.* **2023**, *16*, 3839.
- [4] Li, H.; Liu, Z.; Liang, G.; Huang, Y.; Huang, Y.; Zhu, M.; Pei, Z.; Xue, Q.; Tang, Z.; Wang, Y.; Li, B.; Zhi, C. Waterproof and Tailorable Elastic Rechargeable Yarn Zinc Ion Batteries by a Cross-Linked Polyacrylamide Electrolyte. *ACS Nano* **2018**, *12*, 3140–3148.
- [5] Wang, L.; Cao, X.; Xu, L.; Chen, J.; Zheng, J. Transformed Akhtenskite MnO₂ from Mn₃O₄ as Cathode for a Rechargeable Aqueous Zinc Ion Battery. *ACS Sustainable Chem. Eng.* **2018**, *6*, 16055–16063.
- [6] Bhunia, A.; Boldog, I.; Möller, A.; Janiak, C. Highly Stable Nanoporous Covalent Triazine-Based Frameworks with an Adamantane Core for Carbon Dioxide Sorption and Separation. *J. Mater. Chem. A* **2013**, *1*, 14990–14999.