Electronic Supplementary Information for

## Atom-Dominated Relay Catalysis of High-Entropy MXene Promotes Cascade Polysulfide Conversion for Lithium-Sulfur Batteries

Mengyao Xu<sup>a</sup>, Qizhen Zhu<sup>\*a</sup>, Yanze Li<sup>a</sup>, Yuan Gao<sup>a</sup>, Ning Sun<sup>a</sup> and Bin Xu<sup>\*ab</sup>

 <sup>a</sup> State Key Laboratory of Organic-Inorganic Composites, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, China
 \*E-mail: zhuqz@mail.buct.edu.cn; xubin@mail.buct.edu.cn
 <sup>b</sup> Shaanxi Key Laboratory of Chemical Reaction Engineering, School of Chemistry and Chemical Engineering, Yan'an University, Yan'an 716000, China
 \*E-mail: xubin@yau.edu.cn

## **1** Experimental Section

**1.1 Materials.** Sublime sulfur (99.5 wt%) and lithium sulfide (Li<sub>2</sub>S, 99.98 wt%) were sourced from Sigma-Aldrich. Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI, 99.95 wt%), 1,3-dioxolane (DOL, 99.8 wt%), 1,2-dimethoxyethane (DME, 99.5 wt%), lithium nitrate (LiNO<sub>3</sub>, 99.99 wt%), and hydrofluoric acid (HF, 40 wt%) were obtained from Macklin reagent. Super-P carbon (99.5 wt%) was acquired from Canrd New Energy Technology Co., Ltd. Polyvinylidenefluoride (PVDF) was sourced from Alfa Aesar. N-methyl-2-pyrrolidone (NMP) was obtained from Sigma-Aldrich. TiVNbMoAlC<sub>3</sub> MAX phase was acquired from Jilin 11 Technology Co., Ltd. All materials were used as received without further modification.

**1.2 Preparation of TiVNbMoC<sub>3</sub> (HE-MXene) nanosheets.** The TiVNbMoAlC<sub>3</sub> MAX powder (1 g) was slowly immersed in 30 mL of 40% HF solution and magnetically stirred at 600 rpm at 55 °C for 96 h. Subsequently, the precipitate was retrieved by centrifugation at 8000 rpm for 6 min and the resulting powder was neutralized by repeated washing with deionized water. The multilayer HE-MXene nanosheets were then delaminated by 10wt % TMAOH solution with vigorous stirring at 55 °C for 8 h. Finally, the single-to-few-flake HE-MXene was washed repeatedly with deionized water by centrifugation at 10,000 rpm for 6 min until the pH value of the solution approached  $\approx$ 7. The collected material was freeze-dried for 48 h.

**1.3 Preparation of HE-MXene/S cathode.** The as-synthesized HE-MXene was ground with sublimed sulfur in a mortar. The resulting mixture was transferred to a corundum boat and placed in a quartz tube furnace, heated at 155 °C under argon atmosphere for 12 h with a heating rate of 5 °C min<sup>-1</sup>. After cooling to room temperature, the HE-MXene/S composite was obtained. For comparison, the Ti<sub>3</sub>C<sub>2</sub>/S and TiNbC/S composites were prepared using the same procedures, and the corresponding mass fraction of active sulfur in each composite was measured by thermogravimetric analysis (TGA). The HE-MXene/S composite, Super P and PVDF were mixed in a mass ratio of 8:1:1, with NMP as the dispersant. The homogenized slurry was coated onto Al foil and dried under vacuum at 60 °C for 12 h to produce the HE-MXene/S cathode with an areal loading of about 1.5 mg cm<sup>-2</sup>. Similarly, the Ti<sub>3</sub>C<sub>2</sub>/S and TiNbC/S cathodes were fabricated using the same preparation method as the HE-MXene/S. Additionally, a high sulfur loading cathode of HE-MXene/S was fabricated by increasing the mass ratio of sulfur and coating thickness of the slurry.

**1.4 Preparation of the modified separators.** The modified separators were prepared by a wet coating strategy. HE-MXene powders were mixed with PVDF in a mass ratio of 9:1 and thoroughly ground. The mixture was dispersed in NMP to form a homogeneous slurry, which was then coated onto one side of a commercial PP separator followed by a drying process under vacuum at 60 °C overnight. Subsequently, the HE-MXene slurry was coated on the reverse side of the PP separator using the same procedure. Finally, the double-sided separator, coated with the HE-MXene, was obtained through vacuum drying at 60 °C overnight. For control experiments,  $Ti_3C_2$  and TiNbC coated double-sided separators were fabricated using the same method. The modified separators were then cut into  $\Phi$ 16 mm circular discs. The mass loading of the MXenes on the PP separator was controlled at 0.2-0.3 mg cm<sup>-2</sup>.

**1.5 Adsorption test of Li\_2S\_6.** A 0.1M  $Li_2S_6$  solution was prepared by the chemical reaction between sublimed sulfur and  $Li_2S$  powder in a mixed DOL/DME solvent (v/v, 1/1) at a molar ratio of 5:1, followed by stirring at 60 °C for 24 h. Different MXene powders were immersed in 10 mL of the  $Li_2S_6$  solution. All

procedures were conducted in an argon-filled glove box. The adsorption capability of the MXenes was visually evaluated by monitoring the color change of the  $Li_2S_6$  solution over different time intervals. Ultraviolet-visible (UV-Vis) spectroscopy was also performed on the  $Li_2S_6$  solutions after 24 h of immersion using a UV-3600 spectrophotometer with the double beam measurement method in the wavelength range of 250-600 nm.

**1.6** Assembly and test of symmetric cells with MXene electrodes. The HE-MXene (or  $Ti_3C_2$ , TiNbC) powders and PVDF binder in a mass ratio of 5:1 were dispersed in NMP with stirring to obtain a uniform slurry. Subsequently, the slurry was coated onto aluminum foil and dried in a vacuum oven at 60 °C overnight. The coated aluminum foil was punched to produce electrode disks in diameter of 10 mm. A 0.4M  $Li_2S_6$  DOL/DME solution was used as the electrolyte, and two identical MXene electrodes without loading elemental sulfur served as both working and counter electrodes. The separators were PP membranes modified with different MXenes. The cyclic voltammetry (CV) measurement of the symmetric cell was conducted between -1 and 1 V at a scan rate of 1 mV s<sup>-1</sup>.

**1.7** Li<sub>2</sub>S nucleation test. The lithium sulfide and sublimed sulfur were mixed at a molar ratio of 1:7 in DOL/DME solvent (v/v, 1/1) and stirred at 60 °C for 24 h to synthesize the 0.2M Li<sub>2</sub>S<sub>8</sub> catholyte. The MXenemodified PP separator was placed between HE-MXene cathode (or Ti<sub>3</sub>C<sub>2</sub>, TiNbC cathodes) and lithium metal anode, and 25  $\mu$ L of the Li<sub>2</sub>S<sub>8</sub> solution was added as the electrolyte to assemble CR2025-type coin-like cells for Li<sub>2</sub>S nucleation test. Initially, the assembled cells were discharged galvanostatically at 0.112 mA until reaching 2.06 V, followed by discharging potentiostatically at 2.05 V until the current dropped to 10<sup>-5</sup> A. Then, the quantity Li<sub>2</sub>S precipitation was estimated from the current profiles according to Faraday's law.

**1.8 Assembly and electrochemical measurements of Li-S cells.** The Li-S cells were assembled using the as-prepared HE-MXene/S (or  $Ti_3C_2/S$ , TiNbC/S) cathode, along with lithium foil as the anode in an argon-filled glove box. The electrolyte consisted of 1 M LiTFSI in DOL/DME (1:1, v/v) containing 1% LiNO<sub>3</sub>, and PP membranes modified by different MXenes served as separators. The electrolyte-to-sulfur (E/S) ratio was approximately 9.2  $\mu$ L mg<sup>-1</sup> with a mass loading of 1.5 mg cm<sup>-2</sup>. In addition, cells with higher sulfur loading of 3.5, and 5.4 mg cm<sup>-2</sup> were studied with a lower E/S ratio of 8.3  $\mu$ L mg<sup>-1</sup>. CV and electrochemical impedance spectra (EIS) were measured on a Bio-Logic electrochemical workstation (VSP). CV curves were conducted from 1.5 to 2.8 V, while EIS was measured in the frequency range of 100 kHz-10 mHz with an amplitude of 10 mV. Galvanostatic intermittent titration technique (GITT) was performed at a constant current density of 0.05 C for 30 min, followed by 10 h to collect the potential response. Galvanostatic charge/discharge measurement were carried out using a LAND BT 2000 battery test system for investigating the cycling stability and rate performance. Furthermore, the Li-S pouch cell was assembled in an Ar-filled glove box, using the HE-MXene/S cathode and Li anode with dimensions of 3 cm × 4 cm, along with the HE-MXene-modified separator and the same electrolyte with the coin cells. The cell was encapsulated using an aluminum-plastic film, with an aluminum tab attached to the HE-MXene/S cathode and a nickel tab connected to the lithium anode.

**1.9 Electrochemical measurements of lithium anodes.** The Li||Li symmetrical cells were assembled using two identical Li foils with a diameter of 14 mm as the working electrode and counter electrode, separated by PP separators modified with different MXenes. The cycling stability of the Li||Li symmetrical cells were tested at different current densities. The Li||Cu asymmetric cells with Li foil as the counter electrode and bare

copper foil as the working electrode was used to test Coulombic efficiency (CE). The CEs of the Li||Cu cells were evaluated using a Li deposition capacity of 1 mA h cm<sup>-2</sup> and a cut-off voltage of 0.8 V at a current density of 1 mA cm<sup>-2</sup>. The CV curves of the Li||Cu cells were measured in the voltage range of -0.5 to 1.5 V at 1 mV s<sup>-1</sup>. The electrolyte used in the Li||Li and Li||Cu cells was 70  $\mu$ L of 1M LiTFSI in DOL/DME (1:1, v/v) with 1% LiNO<sub>3</sub>.

**2** Material characterizations. The morphologies of the samples were examined using scanning electron microscopy (SEM, HitachiS-4800). The microstructure and elemental mapping of the samples were characterized by transmission electron microscope (TEM, Tecnai G2 F30) with energy-dispersive X-ray spectroscopy (EDS). The atomic dispersion of single atoms in HE-MXene nanosheets were determined more accurately using aberration-corrected high-angle annular dark-field STEM (AC-HAADF-STEM, Thermo Fisher Scientific-Titan ETEM G2). X-ray diffraction (XRD) analysis was carried out using an XPert-Pro MPD diffractometer (PANalytical, the Netherlands) with Cu K $\alpha$  radiation ( $\lambda$  =0.154 nm). The nitrogen adsorptiondesorption isotherms were measured under N<sub>2</sub> atmosphere at 77 K on a Micromeritics ASAP2460 analyzer. The surface chemical compositions of the samples were determined using an ESCALab MKII X-ray photoelectron spectroscopy (XPS) system. Thermogravimetric analysis (TGA) was performed under N<sub>2</sub> atmosphere with a heating rate of 10 °C min<sup>-1</sup> using a Mettler Toledo TGA2 thermo gravimetric analyzer. Atomic force microscope (AFM, Bruker Dimension Icon) was used to observe the thickness of the MXene nanosheets and the roughness of lithium anodes after plating, in which a sharp probe with tip radius of 8 nm and spring constant of 26 N m<sup>-2</sup> was employed to ensure optimal lateral resolution for precise visualization of small features. The probe was calibrated on a clean sapphire sample before each AFM scan. A 5 µm × 5 µm scan area was mapped at 40 nN under the Bruker PeakForce Module for each electrode. The contact angles of PP, Ti<sub>3</sub>C<sub>2</sub>/PP TiNbC/PP, and HE-MXene/PP membranes with 1M LiTFSI in DOL/DME (1:1, v/v) containing 1% LiNO<sub>3</sub> electrolyte were measured using a contact angle tester (JGW-360B).

**3 COMSOL simulations.** The distributions of electric field intensity at the interface between the lithium anode and the MXene-modified separators were simulated using the finite element method in COMSOL Multiphysics as a function of the magnetic flux density. The simulation aimed to analyze lithium deposition and dendrite growth behaviors influenced by  $Ti_3C_2$ , TiNbC and HE-MXene and compare their effects. To ensure accuracy, a physical field-controlled grid with refined cell size was adopted as the sequence type during the simulation process.

**4 Density functional theoretical (DFT) calculations.** The first-principles calculations in this work were performed using the CASTEP module in Material Studio 2020 software package.<sup>[1]</sup> The Perdew-Burke-Ernzerhof (PBE) functional in the generalized gradient approximation (GGA) was employed for describing the exchange-correlation functional.<sup>[2]</sup> A supercell consisting of  $4 \times 4 \times 1$  primitive unit cells for a HE-MXene monolayer grafted with -O termination was selected. A Monkhorst-Pack *k*-point grid of  $3 \times 3 \times 1$  was employed, with a kinetic energy cutoff setting to 500 eV for geometry optimization and electronic property calculations. To minimize the interlayer interactions, a vacuum layer larger than 15 Å was applied. The convergence criteria of

10<sup>-6</sup> eV for the electronic self-consistent iteration and 0.03 eV Å<sup>-1</sup> for force were used. The adsorption energies  $(E_{ads})$  of Li<sub>2</sub>S<sub>n</sub> on different MXene substrates were defined as:

 $E_{ads} = E_{MXene - Li \ 2S \ n} - E_{MXene} - E_{Li \ 2S \ n}$ 

where  $E_{MXcme}$ . Lisse and  $E_{MXcme}$  are the total energies of MXene adsorbed with and without Li<sub>2</sub>S<sub>n</sub>, respectively, and  $E_{LisS_n}$  is the total energy of the Li<sub>2</sub>S<sub>n</sub>. With this definition, a more negative adsorption energy indicates a more energetically favorable interaction of MXene towards Li<sub>2</sub>S<sub>n</sub> species. The crystal orbital Hamilton population (COHP) was acquired with Dmol<sup>3</sup> code.<sup>[3]</sup> The climbing image nudged elastic band (CI-NEB) method was adopted to evaluate the activation energy of Li<sub>2</sub>S decomposition. Molecular dynamics (MD) simulations were conducted using the Forcite module to investigate the polysulfide aggregation dynamics within the DOL/DME electrolytes containing 0.2M of Li<sub>2</sub>S<sub>4</sub>, Li<sub>2</sub>S<sub>6</sub>, and Li<sub>2</sub>S<sub>8</sub>. The initial configurations for the dynamics simulations were obtained using the COMPASS force field in an NVT ensemble, with a time step of 1.0 fs and a simulation time of 3000 ps. The molecules were randomly packed within a box dimension of ~40 Å. The simulations were carried out at a constant temperature of 298 K using the Andersen thermostat.



Fig. S1 Density of states (DOS) of (a)  $Ti_3C_2$  and (b) TiNbC.



Fig. S2 Optimized adsorption geometries of S $_8$ , Li $_2$ S $_8$ , Li $_2$ S $_6$ , Li $_2$ S $_4$ , Li $_2$ S $_2$ , and Li $_2$ S on Ti $_3$ C $_2$ .



Fig. S3 Optimized adsorption geometries of  $S_8$ ,  $Li_2S_8$ ,  $Li_2S_6$ ,  $Li_2S_4$ ,  $Li_2S_2$ , and  $Li_2S$  on TiNbC.



Fig. S4 Optimized adsorption geometries of S $_8$ , Li $_2$ S $_8$ , Li $_2$ S $_6$ , Li $_2$ S $_4$ , Li $_2$ S $_2$ , and Li $_2$ S on HE-MXene.



**Fig. S5** Differential charge density between the adsorbed (a)  $Li_2S_8$ , (b)  $Li_2S_6$ , and (c)  $Li_2S_4$  and  $Ti_3C_2$ . The blue (yellow) color represents spatial regions of charge gain (loss). The isosurface value for the charge-difference figures is 0.0015 e Å<sup>-3</sup>.



**Fig. S6** Differential charge density between the adsorbed (a)  $Li_2S_8$ , (b)  $Li_2S_6$ , and (c)  $Li_2S_4$  and TiNbC. The blue (yellow) color represents spatial regions of charge gain (loss). The isosurface value for the charge-difference figures is 0.0015 e Å<sup>-3</sup>.



**Fig. S7** Differential charge density between the adsorbed (a)  $Li_2S_8$ , (b)  $Li_2S_6$ , and (c)  $Li_2S_4$  and HE-MXene. The blue (yellow) color represents spatial regions of charge gain (loss). The isosurface value for the charge-difference figures is 0.0015 e Å<sup>-3</sup>.



Fig. S8. Energetically preferable  $Li_2S$  dissociation pathways on (a)  $Ti_3C_2$ , (b) TiNbC and (c) HE-MXene surface.



Fig. S9 SEM images of HE-MAX phase.



**Fig. S10** High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the corresponding EDS element mappings of HE-MXene.



Fig. S11 XRD patterns of  $Ti_3C_2$  and TiNbC MXenes.



Fig. S12 High-resolution XPS spectra of (a) C 1s, (b) Ti 2p, (c) V 2p, (d) Nb 3d, and (e) Mo 3d of HE-MXene.



**Fig. S13** TGA curves of HE-MXene, pure sulfur, and HE-MXene/S composite for the electrode with an areal sulfur loading of 1 mg cm<sup>-2</sup>.



**Fig. S14** Photographs of  $Li_2S_6$  solutions (a) before and after adding  $Ti_3C_2$ , TiNbC, and HE-MXene powders for (b) 12 h and (c) 24 h.



**Fig. S15** UV-vis absorbance spectra of  $Li_2S_6$  solution and the  $Li_2S_6$  solution after interacting with  $Ti_3C_2$ , TiNbC, and HE-MXene.



Fig. S16 CV curves of symmetric cells using two identical MXene electrodes and the MXene-modified separator in  $Li_2S_6$  electrolyte.



Fig. S17 Contact angles of the electrolyte on bare PP separator and  $Ti_3C_2$ , TiNbC, and HE-MXene-modified separators.



**Fig. S18** Magnified GITT voltage profile of Li-S cell with the HE-MXene as sulfur host and modification layer on separator relative to normalized discharge-charge time.

The internal resistance ( $R_{internal}$ ) could be calculated with the voltage polarization during the discharge/charge process based on the following equation:

Rinternal  $(\Omega) = |\Delta V_{QOCV} - CCV| / I_{applied}$ 

where  $\Delta V$  (v) is the voltage difference between the points of quasi-open circuit voltage (QOCV) and closedcircuit voltage (CCV), and  $I_{applied}$  (A) is the current applied.



**Fig. S19** Nyquist plots of the cells with  $Ti_3C_2/S$ , TiNbC/S, and HE-MXene/S cathodes with the equivalent circuit in the inset.  $R_s$  refers to the internal resistance,  $R_{ct}$  refers to the charge transfer resistance at the electrode/electrolyte interface, CPE refers to the constant phase element, and  $W_o$  refers to the Warburg impedance.



**Fig. S20** CV curves of (a)  $Ti_3C_2/S$ , (b) TiNbC/S, and (c) HE-MXene/S electrodes at different scan rates from 0.1 to 0.5 mV s<sup>-1</sup>. Relationship between the corresponding CV peak currents and the square root of scan rates for (d)  $Ti_3C_2/S$ , (e) TiNbC/S, and (f) HE-MXene/S electrodes.

The Li<sup>+</sup> ion diffusion coefficient (*DLi*<sup>+</sup>) is obtained according to the Randles-Sevcik equation, as described below:  $I_p = 2.69 \times 10^5 \times n^{1.5} \times A \times (DLi^+)^{0.5} \times v^{0.5} \times CLi^+$ 

where  $I_p$  refers to the peak current (A), n is the number of electrons in the reaction, A is the electrode area (cm<sup>-2</sup>), v is the scan rate (V s<sup>-1</sup>), and  $CLi^+$  is the concentration of lithium ion in the electrolyte (mol cm<sup>-3</sup>). The  $DLi^+$  in the charge and discharge process can be obtained by extracting the linear relationship of  $I_p$ - $v^{1/2}$ , where  $I_p$  is the peak current of the oxidation and reduction peaks, respectively.



**Fig. S21** AFM images of lithium anodes with a plating capacity of 1 mAh cm<sup>-2</sup> in Li||Li cells using (a) PP and (b)  $Ti_3C_2$ , (c) TiNbC, and (d) HE-MXene-modified PP separators.



**Fig. S22** Height plots of measuring distance of (a) the first, (b) second, and (c) third white dotted lines from Figure 5e-h.



**Fig. S23** Digital photographs of the mechanical flexibility of the HE-MXene-modified separator under various deformations.



Fig. S24 Nyquist plots of Li||Li symmetric cells before cycling, after cycling at 2 mA cm<sup>-2</sup> for different times.



**Fig. S25** SEM images (with the photographs in the inset) of lithium anodes after cycling for 200 h at 5 mA cm<sup>-2</sup>, 5 mAh cm<sup>-2</sup> in Li||Li symmetrical cells using (a) bare PP separator and (b)  $Ti_3C_2$ , (c) TiNbC, and (d) HE-MXene-modified separators.



**Fig. S26** SEM images of the Li anodes on Cu foil after plating 50 cycles at 1 mA cm<sup>-2</sup> for Li||Cu symmetric batteries with a) PP separator b)  $Ti_3C_2$ , c) TiNbC separator, and HE-MXene separator.



**Fig. S27** Self-discharge curves of Li-S batteries based on different MXenes after 20 cycles for a rest period of 72 h.



**Fig. S28** Photographs of DOL/DME (1:1) solutions with the immersion of the cathode piece, Li anode, and separator disassembled from the Li-S cells after 200 cycles at 1 C.



**Fig. S29** Photographs of the cathode pieces, separators, and Li anodes disassembled from the Li-S cells based on the MXenes after 200 cycles at 1 C.



**Fig. S30** TGA curves of HE-MXene, pure sulfur, and HE-MXene/S composite for the electrodes with sulfur loadings of 3.5 and 5.4 mg cm<sup>-2</sup>.

-		
Element	Weight percentage	Atomic percentage
Ti	24.59%	24.98%
V	24.95%	25.01%
Nb	24.61%	24.99%

25.02%

Table S1. Element ratios of HE-MXene.

**Table S2.** Comparison of electrochemical performance in Li-S batteries based on the HE-MXene and othersulfur host or separator modification materials in recent studies.

25.85%

Мо

Host materials/separators	Sulfur loading (mg cm <sup>-2</sup> )	Current rate (C)	Cycle number (n)	Capacity retention (%)	Ref.
V <sub>4</sub> C <sub>3</sub> T <sub>x</sub> -PP	4	0.1	120	67.9	[4]
Co-CNT@MXene/S	6	0.2	170	85.8	[5]
VC-1	4.8	0.1	100	88.2	[6]
S/1T-VSe <sub>2</sub> -MXene	6.9	0.2	300	52.3	[7]
ZnS/MXene	5.2	0.2	60	73.6	[8]
NiS <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> //PP	5.25	0.2	50	75.7	[9]
Ti₃C₂T <sub>x</sub> (4 h)-GN	5.1	0.5	200	93	[10]
S/1T-VS <sub>2</sub> -MXene	5	0.1	50	81.5	[11]
S/V <sub>3</sub> S <sub>4</sub> @C-7	4.22	1	500	47	[12]
NbN-NbC	4.9	0.2	100	89.2	[13]

HE-MXene	5.4	0.2	50	98.5	This work
I-MXene/PP	6.5	0.2	20	80.4	[22]
S/Co-MoSe <sub>2</sub> /MXene	4.8	0.1	300	62.2	[21]
PA-MXene/CNT-50	7	0.5	800	80	[20]
MoS <sub>2</sub> /MXene	4	0.2	500	55	[19]
M-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> -S	4.3	0.5	150	78	[18]
S/CoZn-Se@N-MX	2.9	0.1	100	80	[17]
Fe <sub>3</sub> Se <sub>4</sub> /FeSe@MXene-PP	5.8	0.2	120	92.3	[16]
MXene-P(VIPS+AM)@S	8.15	0.1	50	87.5	[15]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> @CoSe <sub>2</sub> /PP	4	0.2	60	78.9	[14]

## References

[1] D. Zhao, Z. Li, X. Yu, W. Zhou, Q. Wu, Y. Luo, N. Wang, A. Liu, L. Li and S. Chen, *Chem. Eng. J.*, 2022, **450**, 138254.

[2] J. Perdew, K Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

[3] Y. Wen, Z. Shen, J. Hui, H. Zhang and Q. Zhu, Adv. Energy Mater., 2023, 13, 2204345.

[4] X. Yu, Y. Yang, L. Si, J. Cai, X. Lu and Z. Sun, J. Colloid Interface Sci., 2022, 627, 992-1002.

[5] C. Xiong, G. Zhu, H. Jiang, Q. Chen and T. Zhao, *Energy Storage Mater.*, 2020, **33**, 147-157.

[6] L. Chen, Y. Sun, X. Wei, L. Song, G. Tao, X. Cao, D. Wang, G. Zhou and Y. Song, *Adv. Mater.*, 2023, **35**, 2300771.

[7] W. Wang, X. Wang, L. Chen, D. Lu, W. Zhou and Y. Li, *Chem. Eng. J.*, 2023, **461**, 142100.

[8] C. Wei, B. Xi, P. Wang, Y. Liang, Z. Wang, K. Tian, J. Feng and S. Xiong, *Adv. Mater.*, 2023, **35**, 2303780.

[9] X. Wang, J. Guo, K. Xu, Z. Li, S. Liu, L. Sun, J. Zhao, H. Liu and W. Liu, *Appl. Surf. Sci.*, 2024, **645**, 158859.

[10] L. Jiao, C. Zhang, C. Geng, S. Wu, H. Li, W. Lv, Y. Tao, Z. Chen, G. Zhou, J. Li, G. Ling, Y. Wan and Q. Yang, *Adv. Energy Mater.*, 2019, **9**, 1900219.

[11] S. Wu, W. Wang, J. Shan, X. Wang, D. Lu, J. Zhu, Z. Liu, L. Yue and Y. Li, *Energy Storage Mater.*, 2022, **49**, 153-163.

[12] Z. Tan, S. Liu, X. Zhang, J. Wei, Y. Liu, L. Hou and C. Yuan, *J. Mater. Chem.*, A. 2022, **10**, 18679-18689.

[13] Z. Zhao, Y. Pan, S. Yi, Z. Su, H. Chen, Y. Huang, B. Niu, D. Long and Y. Zhang, *Adv. Mater.*, 2023, 36, 2310052.

[14] L. Cai, H. Ying, P. Huang, Z. Zhang, H. Tan, Q. Han and W. Han, *Chem. Eng. J.*, 2023, **474**, 145862.

[15] R. Mao, T. Zhang, W. Shao, S. Liu, Z. Song, C. Song, X. Li, X. Jin, W. Jiang, X. Jian and F. Hu, *Energy Storage Mater.*, 2023, **55**, 21-32.

[16] X. Zhou, Y. Cui, X. Huang, Q. Zhang, B. Wang and S. Tang, *Chem. Eng. J.*, 2023, **457**, 141139.

[17] Z. Ye, Y. Jiang, Li Li, F. Wu and R. Chen, *Adv. Mater.*, 2021, **33**, 2101204.

[18] T. Zhang, W. Shao, S. Liu, Z. Song, R. Mao, X. Jin, X. Jian and F. Hu, *J. Energy Chem.*, 2022, **74**, 349-358.

[19] J. Wang, X. Zou, W. Meng, L. Song, W. Xu, K. Zhang, Q. Liu, J. Chen, Y. Hou, J. Lu, X. Gao,
D. Cheng, Y. Ren, X. Zhan and Q. Zhang, *ACS Appl. Energy Mater.*, 2022, 5, 15392-15400.

[20] B. Zhang, C. Luo, G. Zhou, Z. Pan, J. Ma, H. Nishihara, Y. He, F. Kang, W. Lv and Q. Yang, *Adv. Funct. Mater.*, 2021, **31**, 2100793.

[21] W. Wang, L. Huai, S. Wu, J. Shan, J. Zhu, Z. Liu, L. Yue and Y. Li, *ACS Nano*, 2021, **15**, 11619-11633.

[22] W. Yu, S. Ma, M. He, R. Li, H. Yang, Y. Li, G. Yin and P. Zuo, *J. Phys. Chem. C.*, 2022, **126**, 10986-10994.