

Supporting information

MXene-supported NH₂CNT and BiOCl composite as sulfur reservoir for Li-S batteries with high energy density

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Experimental Section

Synthesis of few-layer MXene ($Ti_3C_2T_x$): Typically, LiF (2 g) was dissolved with 9 M hydrochloric acid (20 mL) in a Teflon beaker, and Ti_3AlC_2 (one kind of MXene, 2 g) was then slowly added into it, strongly stirring for 24 h at 35 °C in a water bath. Then, the suspension was washed by centrifugation with deionized water until the pH was around 7, and the obtained precipitate was multi-layer MXene ($Ti_3C_2T_x$). The multi-layer MXene was then intercalated with absolute ethanol to obtain few-layer MXene colloid with a concentration of $\sim 2 \text{ mg mL}^{-1}$.

Synthesis of BiOCl nanosheets: Specifically, 4 mmol bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) was dissolved in 10 mL of ethylene glycol, marked as solution A. And 4 mmol NH_4Cl was dissolved in 30 mL of deionized water, marked as solution B. Then, the two solutions were finally mixed and stirred for 30 min. The mixture was then transferred to a 100 mL Teflon-lined autoclave and reacted at 160 °C for 12 h. After cooling to room temperature, the suspension was then washed with ethanol and deionized water for several times by centrifugation, and dried in an oven at 80 °C for 12 h. Finally, the white powder of BiOCl nanosheets was obtained.

Modification of BiOCl and NH_2CNT : CTAB aqueous solution with a mass fraction of 0.1% (50 mL) was prepared, and 0.05 g of BiOCl powder was dispersed in the prepared CTAB solution and sonicated for 30 min to obtain CTAB-modified BiOCl. NH_2CNT s were treated by the similar method. NH_2CNT powders (0.05 g) were dispersed in CTAB solution (50 mL) with a mass fraction of 0.1%, and sonicated for 30 min to obtain CTAB-modified NH_2CNT s.

Synthesis of M-N-B-x, MXene-BiOCl and MXene- NH_2CNT : 0.05 g of MXene colloid was diluted to 0.4 mg mL^{-1} , and then the colloid was dispersed evenly by ultrasonic for 30 min in an 800 W ultrasonic machine. A certain amount of CTAB modified BiOCl and NH_2CNT were slowly added in the colloid with strong stirring and ultrasonic treatment for 30 min. Then the products were obtained after washing with deionized water and freeze-drying. According to the mass fraction of the added BiOCl, the

products were denoted as M-N-B-5%, M-N-B-10% and M-N-B-15%, respectively. Then, MXene-BiOCl was prepared by ultrasonic assisted method without adding NH₂CNT. The MXene-NH₂CNT was obtained in the same method without adding BiOCl.

Synthesis of M-N-B-x-S: A series of M-N-B-x-S samples were prepared *via* wet sulfur fixation. 3.2 mmol of sodium sulfite (Na₂SO₃) and 6.4 mmol of sodium sulfide nonahydrate (Na₂S·9H₂O) were dissolved in a mixed solution of deionized water (50 mL) and ethanol (10 mL). Then, M-N-B-x powder (0.05 g) was added, and stirred for 30 min. Hydrochloric acid solution (20 mL, 1 mol/L) was dropwise added with rapid stirring, and then continue stirring for 30 min. Polyvinylpyrrolidone (PVP, 0.01 g) was further added in it and continuously stirred for 3 h, and ultrasonic in ice bath for 30 min. The final products were centrifuged and washed with deionized water, and then freeze-dried to get the final products of M-N-B-x-S (x=5 wt.%, 10 wt.%, and 15 wt.%).

Materials Characterization: The phase structure of the samples was identified by X-ray diffractometer (XRD, Bruker D8 Advance) with Cu K α radiation ranging from 3° to 80°. The morphologies and structures of few-layer MXene, BiOCl, NH₂CNT, MXene-BiOCl, MXene-NH₂CNT and M-N-B-x were analyzed by field emission scanning electron microscope (FE-SEM, JSM-7500F) and transmission electron microscope (TEM, JEM-2010F). The thermogravimetric analyzer (TGA, TGA-2050) was used to obtain and determine the mass content of each component in the composites. The specific surface area and pore size distribution of materials were determined by the BET N₂ adsorption-desorption method (BET, MICROMERITICS-ASAP 2020M+C). If the value of x in M-N-B-x is not clearly indicated, x refers to 10%.

Lithium Polysulfide Adsorption Measurements: 1,3-dioxolane (DOL) and ethylene glycol dimethyl ether (DME) with a volume ratio of 1:1 were prepared for 30 mL, and then Li₂S (6.6 mg) and S₈ (24 mg) were added. The mixture was stirred in an argon-filled glove box for 24 h, until a yellow liquid was obtained. The concentration of Li₂S₆ solution obtained is 0.005 M.

Electrochemical Measurements: MXene-S, MXene-BiOCl-S, MXene-NH₂CNT-S, M-N-B-x-S were used as cathode materials for Li-S battery. The cathode was fabricated by a homogeneous slurry which mixed 80 wt.% of active material, 10 wt.% of acetylene black, and 10 wt.% of polyvinylidene difluoride in NMP coated onto Al foil with a diameter of 12 mm. The sulfur loading was controlled at 1-1.5 mg cm⁻² (1.1-1.6 mg on each Al-foil) with E/S ratio of about 8.9 μ L mg⁻¹ for the electrochemical measurements. The mass ratio of active sulfur in the cathode electrode is about 56%. The cell was assembled by using Celgard 2400 (Celgard, USA) as the separator, Li foil as the anode, and LS-009 (DME/DOL mixture containing 1.0 M LiTFSI and 2.0% LiNO₃ (volume ratio of 1:1)) as the electrolyte. Galvanostatic charge/discharge (GCD) tests were performed on a Neware battery tester with a voltage window of 1.7–2.8 V vs. Li⁺/Li in an incubator with a constant temperature of 25 °C.

Symmetric cells of Li₂S₆: Symmetric cells were assembled with two electrodes, which consisted of a mixture of active material and PVDF with a mass ratio of 9:1. 40 μ L Li₂S₆ based electrolyte was added in each identical electrode. The CV test was performed between -0.8 and 0.8 V at the scan rate of 50 mV s⁻¹. The areal active material mass loading was controlled by about 1.5 mg cm⁻².

Nucleation of Li₂S: Li₂S₈ catholyte was prepared by mixing S and Li₂S in DOL and DME solution with a molar ratio of 7:1 and stirred for 24 h. The working electrode was prepared by mixing the active material and PVDF with a mass ratio of 3:1. 20 μ L Li₂S₈-containing catholyte was added. The assembled cells were first discharged galvanostatically at 0.1 mA to until the voltage reached to 2.06 V and then discharged potentiostatically at 2.05 V for Li₂S nucleation and growth until the current was below 10⁻⁵ A.

The Li₂S oxidization behaviors were investigated by LSV at a scanning rate of 10 mV s⁻¹. A three-electrode configuration was employed with platinum sheet as counter electrode, Ag/AgCl electrode as reference, and 0.1 M Li₂S/methanol solution as electrolyte.

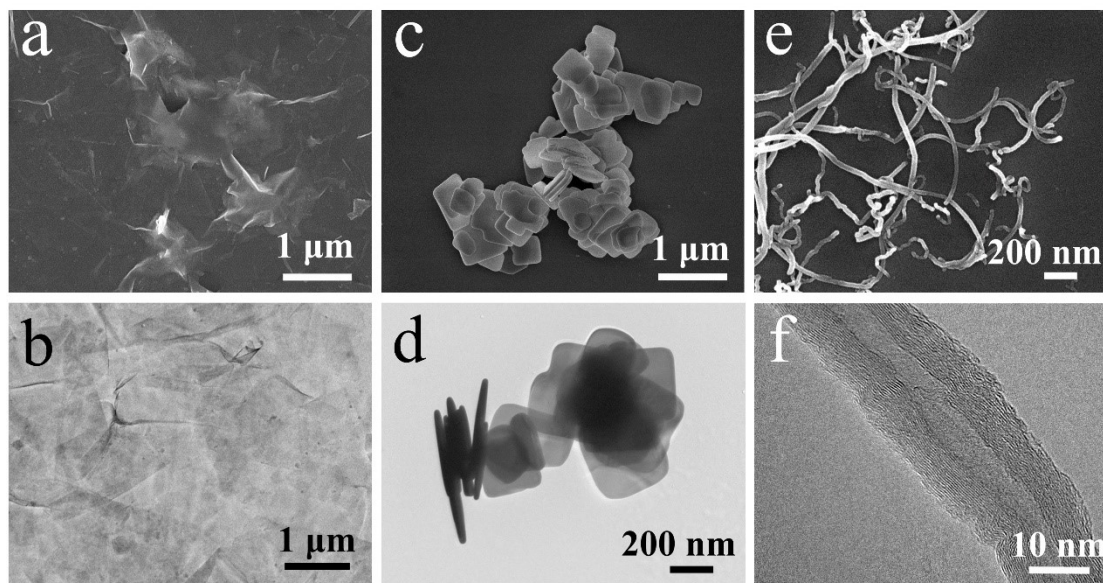


Figure S1 SEM and TEM images of (a, b) few-layer MXene, (c, d) BiOCl nanosheets, (e, f) NH₂CNT.

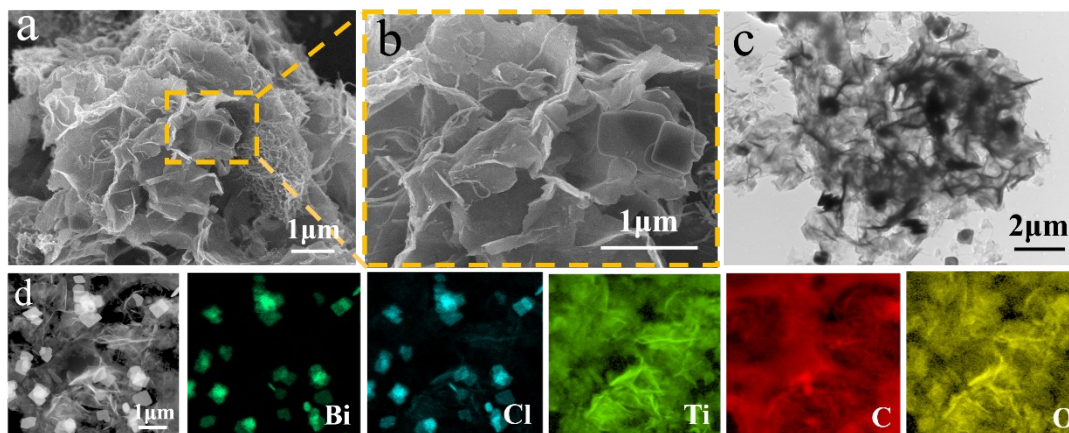


Figure S2. The morphology characterization of M-N-B-x: (a-b) the low and high magnification of SEM images, (c) TEM image, and (d) corresponding elemental mapping images of bismuth, chlorine, titanium, carbon and oxygen of M-N-B-x.

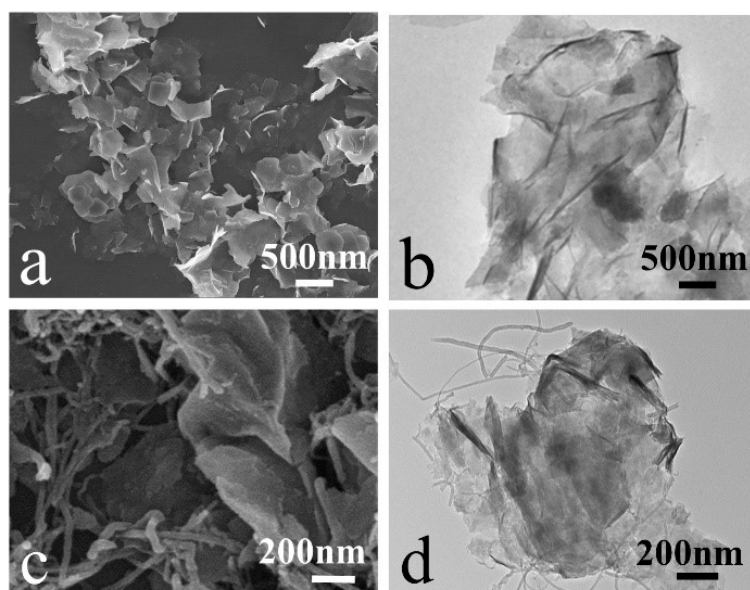


Figure S3 SEM and TEM images of (a, b) MXene-BiOCl, (c, d) MXene-NH₂CNT.

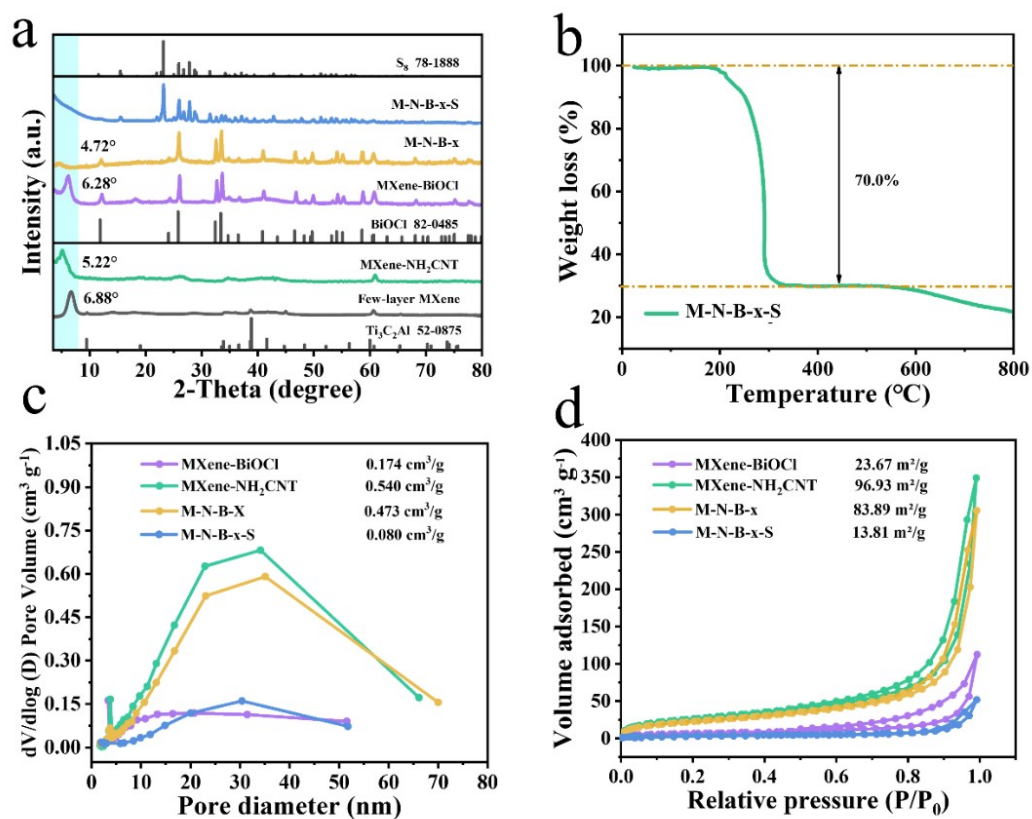


Figure S4. The characterization of few-layer MXene-BiOCl, MXene-NH₂CNT, M-N-B-x and M-N-B-x-S (x=10%). (a) XRD patterns, (b) TGA image, (c) N₂ adsorption–desorption isotherm curves and (d) the pore size distribution.

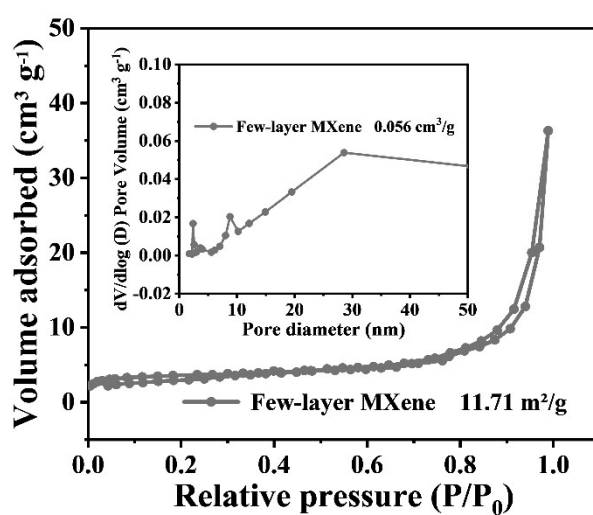


Figure S5 (a) N₂ adsorption–desorption isotherm curves of few-layer MXene (inset is the pore size distribution).

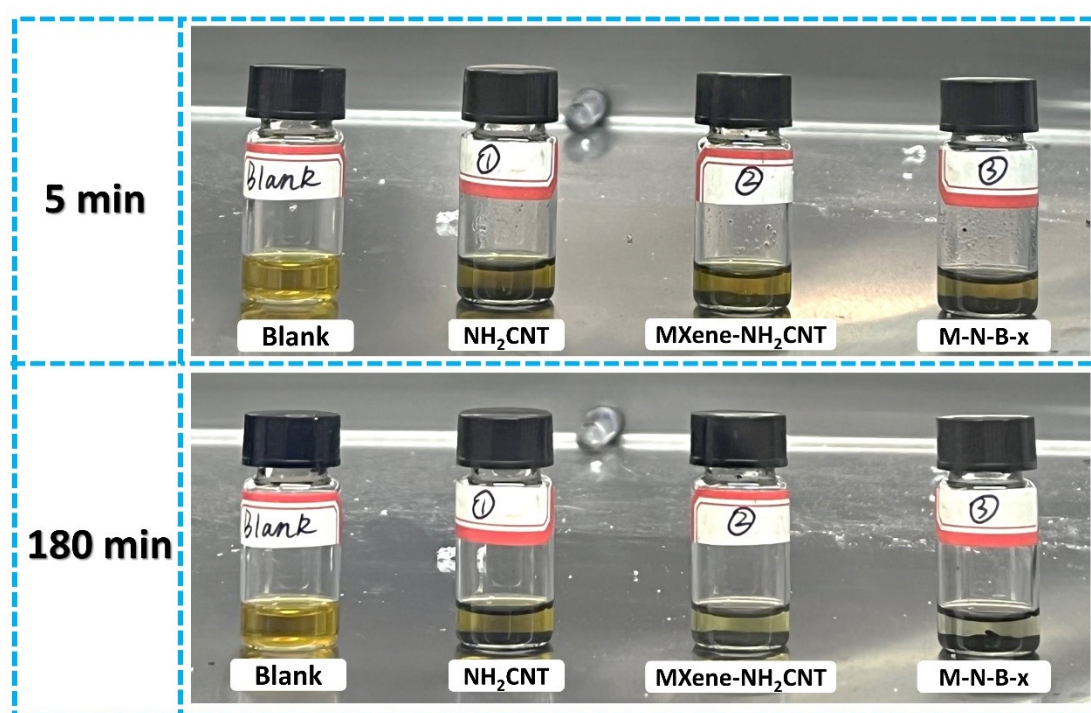


Figure S6 The comparison of adsorption capabilities of NH_2CNT , $\text{MXene-NH}_2\text{CNT}$ and M-N-B-x ($x=10\%$) to Li_2S_6 solution (5 mM) at different absorbing time sections.

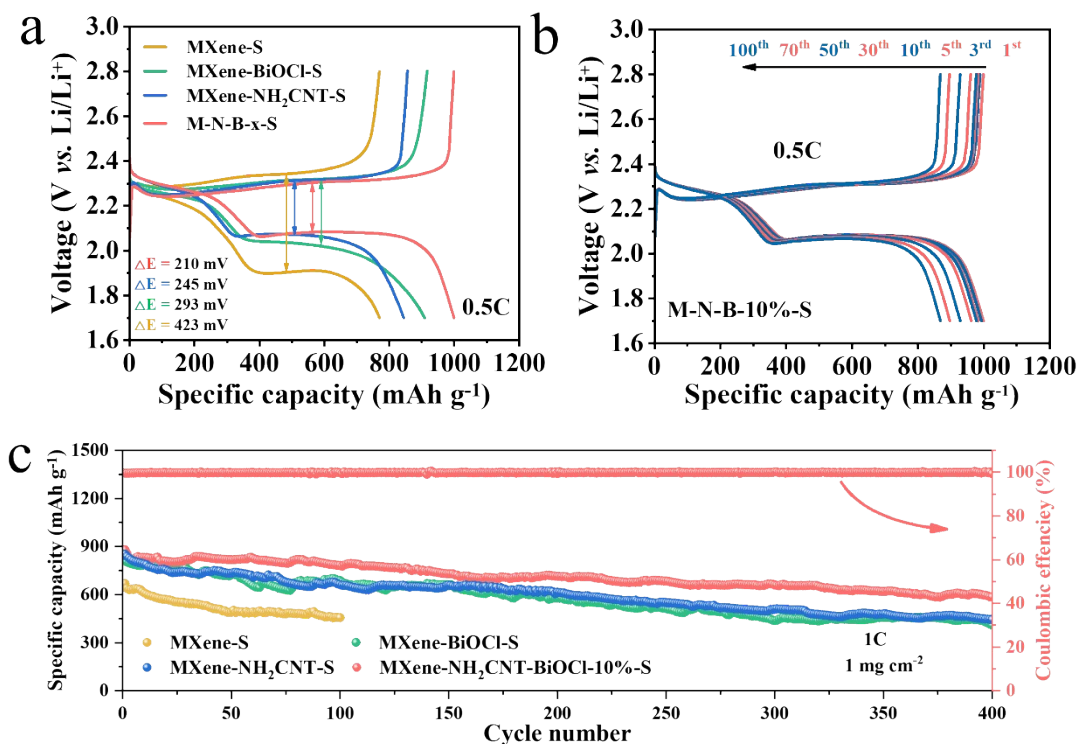


Figure S7 The electrochemical performances of MXene-S, MXene-NH₂CNT-S, MXene-BiOCl-S and M-N-B-x-S (x=5%, 10%, and 15%) electrodes: (a) the first charge-discharge profiles at 0.5C, (b) charge-discharge profiles of M-N-B-10%-S at 0.5C from 1st to 100th cycles, (c) cycling performances at 1 C with a mass loading of 1 mg cm⁻².

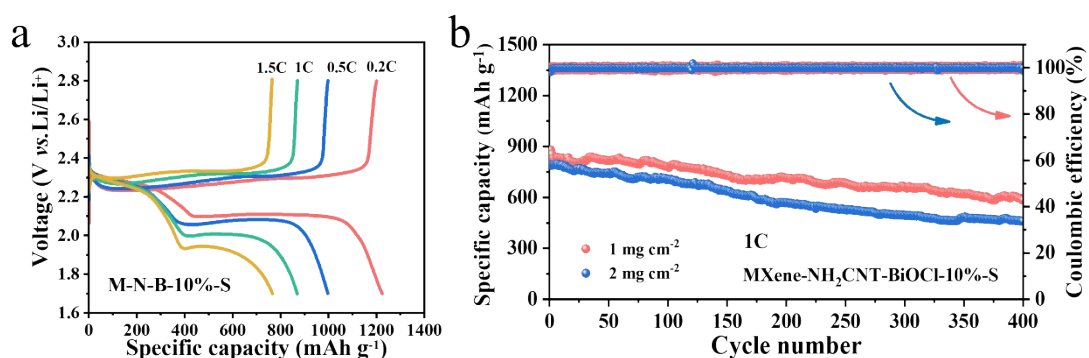


Figure S8 (a) Charge/discharge profiles of M-N-B-10%-S at different current densities; (b) Cycling performances of M-N-B-10%-S at 1C with different mass loadings.

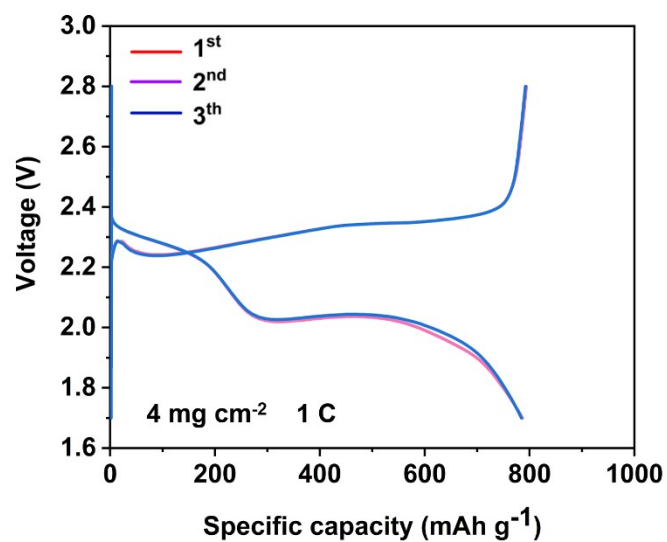


Figure S9 Charge/discharge profiles of M-N-B-10%-S at 1 C with sulfur loadings of 4 mg cm⁻² and with E/S ratio of about 5.5 μ L mg⁻¹.

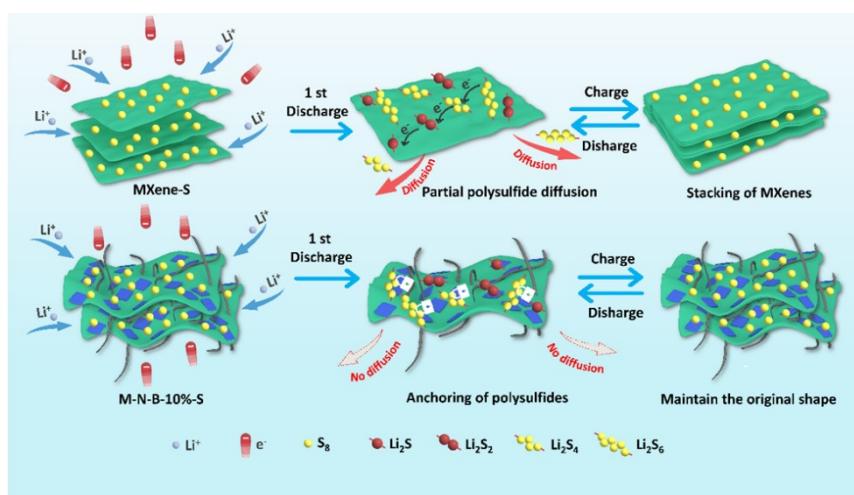


Figure S10 Schematic diagram of mechanism between MXene-S and M-N-B-10%-S electrodes in charge-discharge cycle.