

## Supporting information

### **MXene-supported NH<sub>2</sub>CNT and BiOCl composite as sulfur reservoir for Li-S batteries with high energy density**

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## Experiment 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  $0.4 \text{ mg mL}^{-1}$ , 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 NH<sub>2</sub>CNT. The MXene-NH<sub>2</sub>CNT 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 (Na<sub>2</sub>SO<sub>3</sub>) and 6.4 mmol of sodium sulfide nonahydrate (Na<sub>2</sub>S·9H<sub>2</sub>O) 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 $\alpha$  radiation ranging from 3° to 80°. The morphologies and structures of few-layer MXene, BiOCl, NH<sub>2</sub>CNT, MXene-BiOCl, MXene-NH<sub>2</sub>CNT 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 N<sub>2</sub> 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%.

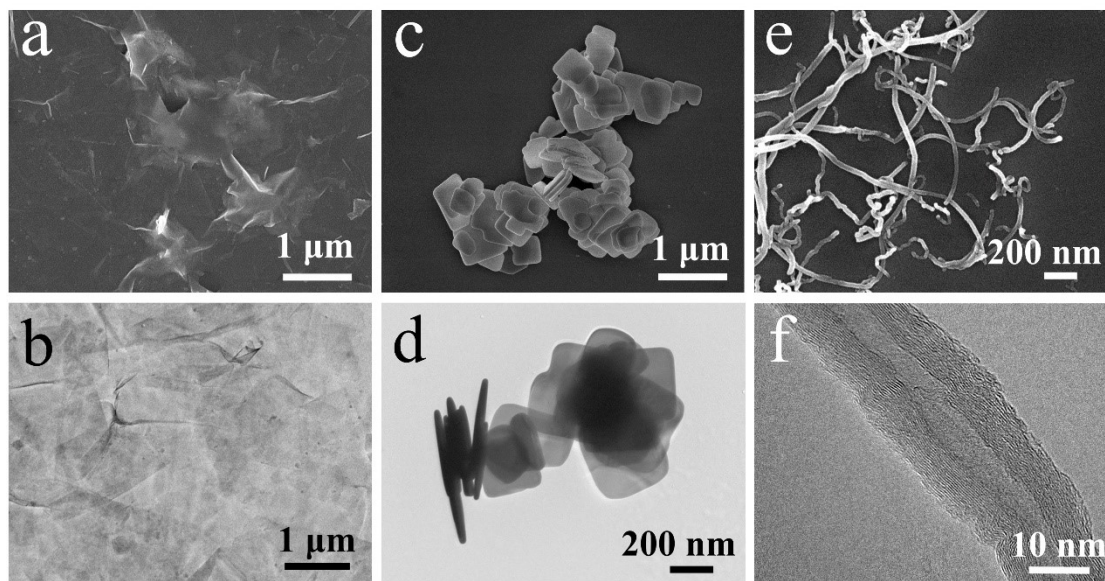
**Lithium Polysulfide Adsorption Measurements:** 1,3-dioxolane (DOL) and ethylene glycol dimethyl ether (DME) with a volume ratio of 1:1 were prepared for 30 mL, and then Li<sub>2</sub>S (6.6 mg) and S<sub>8</sub> (24 mg) were added. The mixture was stirred in an argon-filled glove box for 24 h, until a yellow liquid was obtained. The concentration of Li<sub>2</sub>S<sub>6</sub> solution obtained is 0.005 M.

**Electrochemical Measurements:** MXene-S, MXene-BiOCl-S, MXene-NH<sub>2</sub>CNT-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<sup>-2</sup> (1.1-1.6 mg on each Al-foil) with E/S ratio of about 8.9 μL mg<sup>-1</sup> 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% LiNO<sub>3</sub> (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<sup>+</sup>/Li in an incubator with a constant temperature of 25 °C.

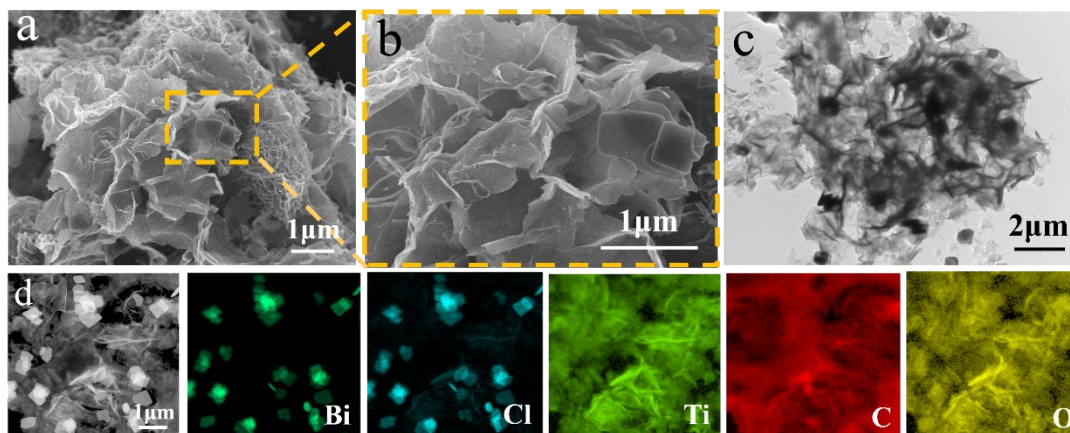
**Symmetric cells of Li<sub>2</sub>S<sub>6</sub>:** Symmetric cells were assembled with two electrodes, which consisted of a mixture of active material and PVDF with a mass ratio of 9:1. 40 μL Li<sub>2</sub>S<sub>6</sub> based electrolyte was added in each identical electrode. The CV test was performed between -0.8 and 0.8 V at the scan rate of 50 mV s<sup>-1</sup>. The areal active material mass loading was controlled by about 1.5 mg cm<sup>-2</sup>.

**Nucleation of Li<sub>2</sub>S:** Li<sub>2</sub>S<sub>8</sub> catholyte was prepared by mixing S and Li<sub>2</sub>S 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 μL Li<sub>2</sub>S<sub>8</sub>-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 Li<sub>2</sub>S nucleation and growth until the current was below 10<sup>-5</sup> A.

**The Li<sub>2</sub>S oxidization behaviors** were investigated by LSV at a scanning rate of 10 mV s<sup>-1</sup>. A three-electrode configuration was employed with platinum sheet as counter electrode, Ag/AgCl electrode as reference, and 0.1 M Li<sub>2</sub>S/methanol solution as electrolyte.



**Figure S1** SEM and TEM images of (a, b) few-layer MXene, (c, d) BiOCl nanosheets, (e, f) NH<sub>2</sub>CNT.



**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.

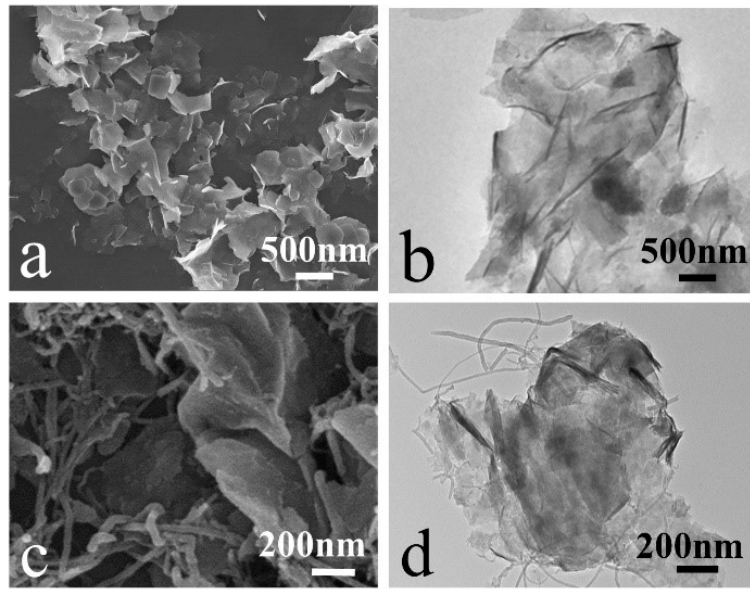
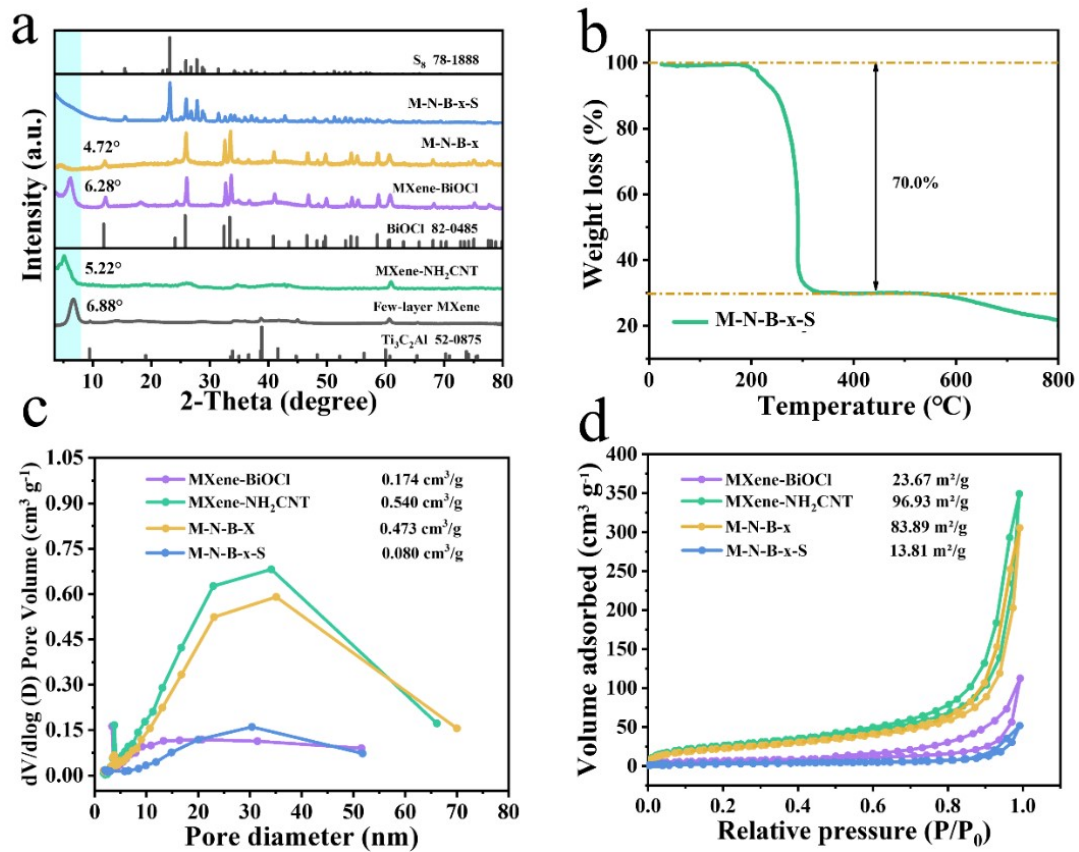
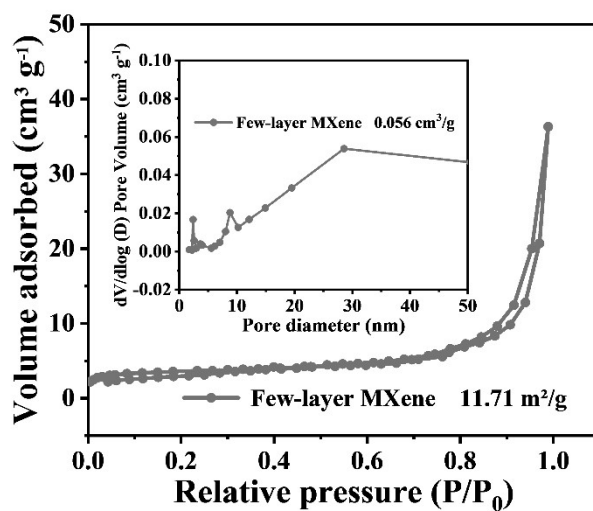


Figure S3 SEM and TEM images of (a, b) MXene-BiOCl, (c, d) MXene-NH<sub>2</sub>CNT.

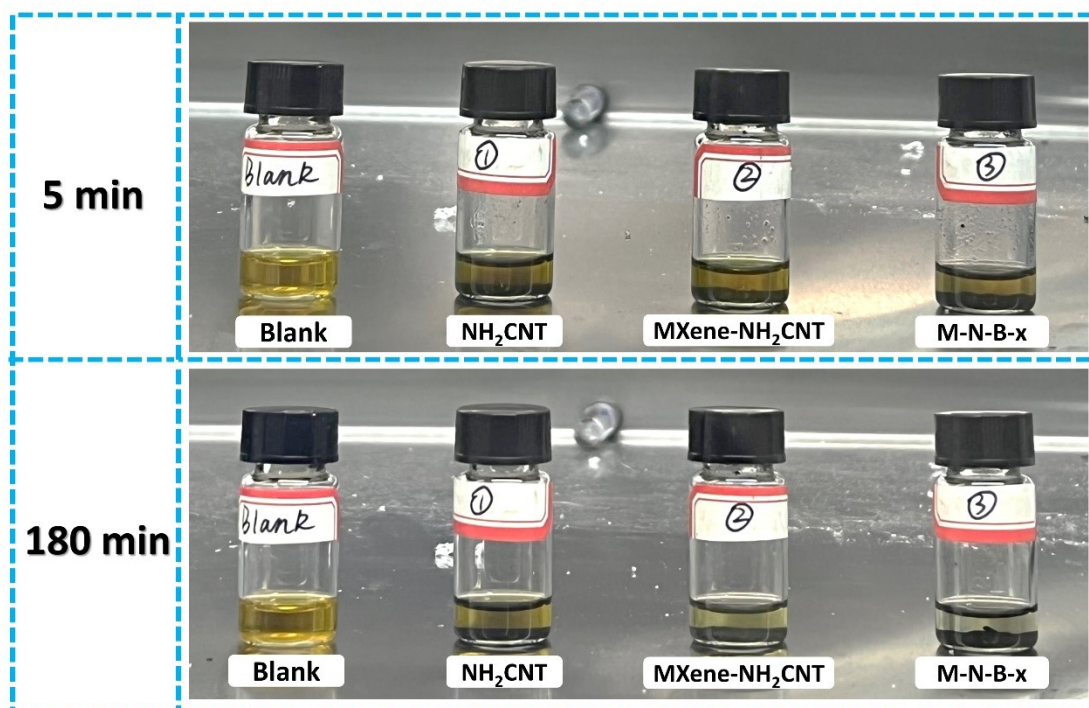


**Figure S4.** The characterization of few-layer MXene-BiOCl, MXene-NH<sub>2</sub>CNT, M-N-B-x and M-N-B-x-S (x=10%). (a) XRD patterns, (b) TGA image, (c) N<sub>2</sub> adsorption–desorption isotherm curves and (d) the pore size distribution.



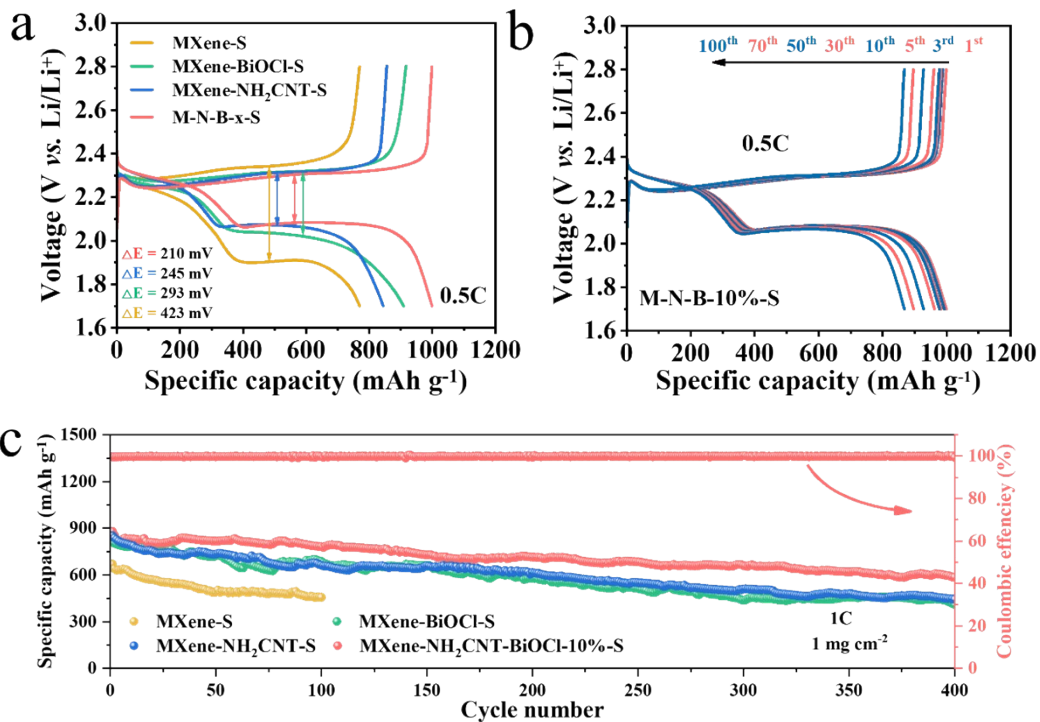
**Figure S5** (a) N<sub>2</sub> adsorption–desorption isotherm curves of few-layer MXene (inset is the pore size distribution).



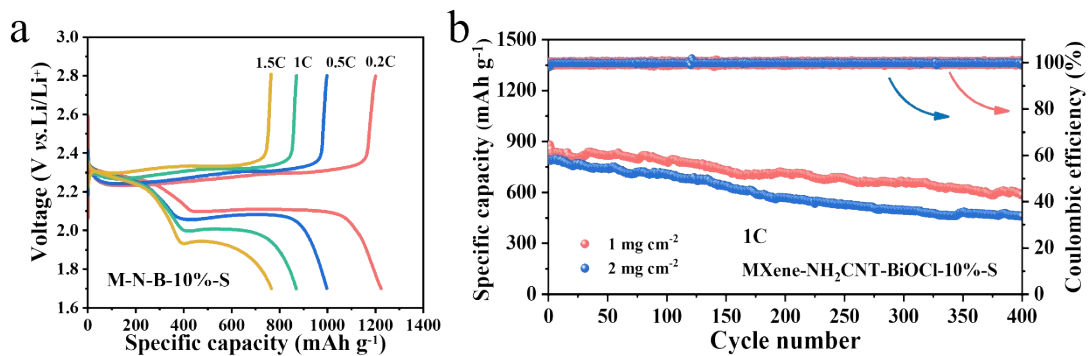


**Figure S6** The comparison of adsorption capabilities of NH<sub>2</sub>CNT, MXene-NH<sub>2</sub>CNT and M-N-B-x (x=10%) to Li<sub>2</sub>S<sub>6</sub> solution (5 mM) at different absorbing time sections.

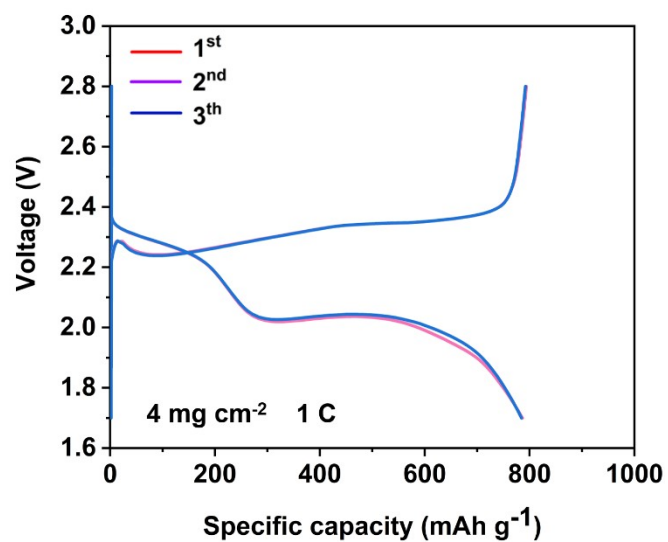




**Figure S6** The electrochemical performances of MXene-S, MXene-NH<sub>2</sub>CNT-S, MXene-BiOCl-S and M-N-B-x-S (x=5%, 10%, and 15%) electrodes: (a) the first charge-discharge profiles at 0.5C, (b) charge-discharge profiles of M-N-B-10%-S at 0.5C from 1<sup>st</sup> to 100<sup>th</sup> cycles, (c) cycling performances at 1 C with a mass loading of 1 mg cm<sup>-2</sup>.



**Figure S7** (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 S8** Charge/discharge profiles of M-N-B-10%-S at 1 C with sulfur loadings of 4 mg cm<sup>-2</sup> and with E/S ratio of about 5.5  $\mu$ L mg<sup>-1</sup>.