Edge Engineering in 2D Molybdenum Disulfide: Simultaneous Regulation of Lithium and Polysulfides for Stable Lithium–Sulfur Batteries

Xiaoliang Yu, Ting Liao, Jie Tang,* Kun Zhang, Shuai Tang, Run-Sheng Gao, Shiqi Lin, and Lu-Chang Qin

Polysulfides shuttling and lithium dendrite growth are two challenges confronting lithium–sulfur batteries (LSBs). Herein, edge engineering of 2D transition metal dichalcogenides (TMDs) is proposed to simultaneously address these two issues. First, utilizing MoS$_2$ as a model material, theoretical calculations demonstrate the strong binding affinity of polysulfides to molybdenum edges and the robust electrovalent bonds between Li$^+$ and sulfur edges, thus predicting the multifunctional regulation capability of edge-rich MoS$_2$. Holey atomically thin MoS$_2$-constructed nanobrushes (HATM-NBs) are then prepared by a polar functionality-assisted anchoring strategy. The functionality anchoring effectively inhibits longitudinal growth of 2D MoS$_2$ and more impressively facilitates formation of plentiful in-plane nanopores due to the fast nucleation and growth. Spectroscopy and electrochemical techniques verify the superior adsorption/catalytic conversion of polysulfides by Mo edges and therefore accelerated redox reactions. The sulfur edge-rich nanobrush structure promotes good contact with the lithium metal anode, homogenized Li$^+$ flux, and thus uniform lithium plating/stripping. A fabricated laminate cell with ultrathin HATM-NBs-coated separator demonstrates superior electrochemical performances even under harsh test conditions (high sulfur loading of 7.43 mg cm$^{-2}$ and low E/S ratio of 5 mL g$^{-1}$). The rational design of multifunctional edge-rich 2D TMDs provides fresh insights for developing stable LSBs.

1. Introduction

Lithium-sulfur batteries (LSBs), normally consisting of a sulfur cathode and a lithium metal anode, provide a fascinating solution to the ever-growing high energy demand for portable electronics and electric vehicles.$^{[1]}$ Sulfur is low cost, eco-friendly, and delivers a high theoretical lithium storage capacity of 1675 mAh g$^{-1}$ through the multielectron redox reaction.$^{[2]}$ Lithium metal anodes possess an ultrahigh specific capacity of 3860 mAh g$^{-1}$ as well as the most negative redox potential ($-$3.04 V vs standard hydrogen electrode).$^{[3]}$ Therefore, LSBs own an overwhelming advantage in theoretical energy density (2500 Wh kg$^{-1}$, 2800 Wh L$^{-1}$)$^{[4]}$. However, both electrode chemistries face severe challenges to achieve high energy storage capacity and long lifespan for commercialization.

For the sulfur cathode, its widespread applications are impeded by the well-known shuttling effect. Lithium polysulfides (LiPSs) as the intermediate products can be dissolved into the electrolyte, diffuse across the separator, and deposit on the surface of lithium anode.$^{[5]}$ The loss of active sulfur material would result in low Coulombic efficiency (CE), undesirable self-discharge, and sluggish redox reaction kinetics.$^{[6,7]}$ Various carbonaceous$^{[8–11]}$ and noncarbonaceous materials$^{[12–16]}$ have been explored as sulfur hosts to provide adsorption affinity for LiPSs. Electrolyte engineering has also been performed to control the solubility of LiPSs.$^{[17–19]}$ For the lithium metal anode, uneven lithium deposition may lead to the formation of dendrite and thus critical safety problems. The infinite volume fluctuation results in easy breakage of the...
formed solid electrolyte interface (SEI) and massive consumption of electrolyte.\textsuperscript{[28]} To respond to these concerns, several approaches have been proposed to construct robust SEI and to suppress lithium dendrite formation, including developing 3D lithium host,\textsuperscript{[21]} modification on the electrode/electrolyte interface,\textsuperscript{[23]} building artificial SEI,\textsuperscript{[23]} and creative electrolyte design.\textsuperscript{[24]}

However, the aforementioned strategies focused only on cathode or anode side but rarely take the whole picture into considerations. Very recently, increasing research attentions has been paid on exploiting multifunctional materials for simultaneously suppressing polysulfides shuttling and lithium dendrite formation.\textsuperscript{[25–39]} Conductive polymer,\textsuperscript{[27]} electrocatalytic birnessite nanosheet,\textsuperscript{[28] and single atom array mimic} have been reported to possess strong Li\textsuperscript{+} adsorption affinity and meanwhile enable chemical immobilization of polysulfides. Metal organic framework particles with uniform pore sizes facilitate homogenous Li\textsuperscript{+} flux and synchronously serve as an effective barrier for trapping polysulfides.\textsuperscript{[133]} However, the catalytic conversion of polysulfides needs to be further improved in these works. Transition metal compounds including ZnS\textsuperscript{[14]} and V\textsubscript{2}S\textsubscript{3}\textsuperscript{[17]} have been shown to display robust catalytic activity and concurrently work as Li\textsuperscript{+} regulators. Nevertheless, their abilities for homogenizing Li\textsuperscript{+} distribution are still far from being satisfactory due to the lack of polar adsorption sites.

We can see from the aforementioned discussion that a clear understanding of how to design efficient multifunctional materials has not yet been established. The trial-and-error strategy in previous reports is of low efficiency, which inherently limits the material variety. Moreover, the material design principles for suppressing polysulfides shuttling and for homogenizing lithium deposition are distinctive. The former generally requires metal-based clusters with a high electrocatalytic activity for robust catalytic conversion of polysulfides,\textsuperscript{[30,41]} while the latter necessitates abundant electrocatalyst groups with strong Li\textsuperscript{+} adsorption affinity.\textsuperscript{[42]} It is still quite challenging to fulfill all the requirements in one functional material.

Edge sites in 2D transition metal dichalcogenides (TMDs) can alter their intrinsic physicochemical properties and have been reported to be able to enormously improve their performance as adsorbents\textsuperscript{[43]} and catalysts.\textsuperscript{[44]} Herein, utilizing MoS\textsubscript{2} as a model material, we first study theoretically the adsorption affinity of edge sites for polysulfides and Li\textsuperscript{+}. We discover that Mo edges could provide robust binding affinity of polar polysulfides and S edges can offer strong adsorption of Li\textsuperscript{+}. These calculation results suggest that edge-rich holey ultrathin MoS\textsubscript{2} can be very promising for multifunctional regulation in LSBs. However, it is very difficult to synthesize ultrathin 2D materials since they tend to restack\textsuperscript{[45]} and the porosity formation within 2D nanosheets could further deteriorate their structural stability. Current researches usually prepare the 2D layers by chemical vapor deposition first and then generate nanopores by plasma etching.\textsuperscript{[46,47]} The process is of high cost and unfavorable for massive production. In this research, we propose a polar functionality-assisted anchoring strategy to obtain holey atomically thin MoS\textsubscript{2}-constructed nanobrushes (HATM-NBs). The functionality anchoring restraints longitudinal growth of 2D MoS\textsubscript{2}, generating stable atomically thin layers. More impressively, it promotes the generation of abundant in-plane nanopores owing to the rapid nucleation and growth kinetics. Massive edge sites are thus exposed. The structural and electrochemical tests demonstrate a dramatic enhancement of immobilization/conversion of polysulfides and homogenization of Li\textsuperscript{+} flux comparing with the nonporous and thick counterpart, which is consistent with the simulation results. This work paves a new avenue to improve the multifunctional regulation capability of 2D materials for stabilizing LSBs.

2. Results and Discussion

Density functional theory (DFT) calculations were first conducted to investigate the nanoscale interactions between MoS\textsubscript{2} edge sites and LiPSs or Li\textsuperscript{+}. The corresponding interaction strengths for MoS\textsubscript{2} basal plane were also simulated for reference. Figure 1a–c shows the adsorption configuration and binding energy comparison between Li\textsubscript{2}S\textsubscript{4} on MoS\textsubscript{2} base and Li\textsubscript{2}S\textsubscript{4} on Mo edge. From Figure 1a,b, it can be seen that the interaction of Li\textsubscript{2}S\textsubscript{4} to the Mo edge site was attained through strong Mo–S covalent bonds, while Li–S bonds are formed when Li\textsubscript{2}S\textsubscript{4} was adsorbed on the basal plane of MoS\textsubscript{2}. The undersaturated Mo atoms on the Mo edge sites act as an electron source to facilitate the attraction of anionic polysulfide Li\textsubscript{2}S\textsubscript{4}. The binding energies were calculated, as shown in Figure 1c. It demonstrates a much stronger bonding strength of Li\textsubscript{2}S\textsubscript{4} to Mo edge sites (\(\Delta E_{\text{bind}} = -3.08\) eV) than that for MoS\textsubscript{2} basal plane (\(\Delta E_{\text{bind}} = -0.72\) eV). The big difference on the Li\textsubscript{2}S\textsubscript{4} binding energies on selective MoS\textsubscript{2} adsorbed sites interprets the diverse entrapment capabilities of LiPSs to MoS\textsubscript{2} basal planes and Mo edge sites.

DFT simulations also provide the optimized structures of MoS\textsubscript{2} monolayer with Li atoms adsorbed on the basal plane and the S edge sites (Figure S1, Supporting Information and Figure 1d,e), which is helpful to understand the nature of their bonding strength with Li atoms. For example, from Figure 1d,e, we can see that sulfur atoms are fully saturated on the MoS\textsubscript{2} basal plane surface, so their reactivities to adsorb Li atoms are reduced with relatively weak S–Li bonds formed in the end. In contrast, sulfur atoms on the S edge sites are undersaturated wherein the unpaired electrons are inclined to form strong electrovalent bonds with cations, such as Li atoms. It could provide a considerable driving force for Li\textsuperscript{+} to be efficiently adhered by S edge sites. Figure 1f shows the calculated binding energies of a number of Li\textsubscript{1} atom(s) (n = 1–4) adsorbed on the MoS\textsubscript{2} basal plane and S edge sites separately. It is clear that the basal plane and S edge sites of MoS\textsubscript{2} exhibit different reactivity to adsorb and release Li atoms; in other words, the affiliation of Li to the basal plane and S edge is diverse. As shown in Figure 1f, the binding energies of Li to the S edge sites are higher than the counterparts on the MoS\textsubscript{2} basal plane by 0.61–0.98 eV. The strong Li\textsuperscript{+} affinity renders the S edge-rich MoS\textsubscript{2} material as a promising ion redistributor to homogenize the Li\textsuperscript{+} flux and promote a uniform lithium deposition.

The DFT calculations revealed the multifunction of edge sites in MoS\textsubscript{2} for regulating the Li–S chemistry: the robust adsorption affinity of polysulfides to the Mo edges as well as the strong electrovalent bonds between the S edges and lithium ions. To obtain an edge-rich MoS\textsubscript{2} material for maximizing the electrochemical activity, HATM-NB product was prepared by a polar functionality-assisted anchoring strategy (schematically shown...
in Figure 2a). To be specific, multiwall carbon nanotubes with surface nitrogen functionalities were used as the growth substrate, ammonium molybdate served as molybdenum source, and thioacetamide (TAA) acted as sulfur source. During the solvothermal reaction, ammonium molybdate released MoO$_4^{2-}$/C$^0$ and NH$_4^+$, and TAA generated S$_2$/C$^0$. Being in a layered structure, MoO$_4^{2-}$/C$^0$ reacted with S$_2$/C$^0$ to form 2D MoS$_2$ and the intercalation of residual ammonia prevented the restacking of MoS$_2$ layers. For HATM-NBs, the positively charged amino groups could interact strongly with negatively charged MoO$_4^{2-}$/C$^0$ via electrostatic forces. Therefore, during the initial nucleation process, a strong interface bonding was created to anchor the MoS$_2$ nucleus. This further inhibits the longitudinal growth of 2D MoS$_2$, leading to an atomically thin 2D structure. By contrast, using carbon nanotubes as the substrate without functionality anchoring, much thicker MoS$_2$ nanosheets constructed a flower-like structure designated as FLM/CNT. The released gas-derived defects would be repaired during crystallization process and finally a nonporous structure is obtained. This mechanism is confirmed by the time-dependent solvothermal experiment. Intermediate products after solvothermal reaction for 3 h with and without anchoring were examined. Plentiful nanoflake-like products were generated in the presence of surface functionalities (Figure S3a, Supporting Information). In contrast, there is almost no Mo-based solid product collected after 3 h reaction for FLM/CNT (Figure S3b, Supporting Information). Such comparison verifies the much faster nucleation and growth kinetics of HATM-NBs.

To observe the morphology of as-prepared products, transmission electron microscopy (TEM) images at different magnifications were collected and demonstrated in Figure 2b–e and Figure S4, S5, Supporting Information. HATM-NBs show a typical morphology of fibrous network with the diameter of nanobrushes in the range of 50–100 nm (Figure 2b). Carbon nanotubes are located in the core section of nanobrushes and MoS$_2$ nanoflakes are vertically aligned on the surface of carbon nanotubes (Figure 2c). The magnified image of MoS$_2$ nanoflakes shows a plenty of in-plane nanopores with pore size of about 3 nm (Figure 2d). It can also be found that these nanoflakes display a thickness of 1–2 nm, corresponding to one to three layers of MoS$_2$ (Figure S4, Supporting Information).
A high-resolution TEM image demonstrated that the majority of the plane region owns a well-crystallized structure (Figure 2e). A lattice fringe of \( d = 0.27 \) nm is revealed, in accordance with the (100) plane of 2 H-phase MoS\(_2\). In contrast, a defect-induced distorted lattice can be seen in the edge region. Different from HATM-NBs, FLM/CNT shows a mixed morphology of flower-like aggregates composed of nonporous nano flakes (Figure S5a, Supporting Information) and individual carbon nanotube (Figure S5c, Supporting Information). The nanoflakes here exhibit a thickness of 5–8 nm, corresponding to 7–11 layers of MoS\(_2\) (Figure S5b, Supporting Information).

X-ray photoelectron spectroscopy (XPS) tests were used to investigate the chemical composition and valence states of the samples (Figure S6, S7, Supporting Information and Figure 2a) Schematic illustration of solvothermal synthesis of HATM-NBs with polar functionality anchoring. b–e) TEM images of HATM-NBs at different magnifications. f) High-resolution Mo 3d and S 2p XPS spectrum of HATM-NBs. g) XRD patterns and h) Raman spectra of carbon nanotube, FLM/CNT and HATM-NBs samples. i) Nitrogen adsorption–desorption isotherm and corresponding pore size distribution curve of HATM-NBs.

**Figure 2.** a) Schematic illustration of solvothermal synthesis of HATM-NBs with polar functionality anchoring. b–e) TEM images of HATM-NBs at different magnifications. f) High-resolution Mo 3d and S 2p XPS spectrum of HATM-NBs. g) XRD patterns and h) Raman spectra of carbon nanotube, FLM/CNT and HATM-NBs samples. i) Nitrogen adsorption–desorption isotherm and corresponding pore size distribution curve of HATM-NBs.
The XPS wide scan spectra reveal the existence of C, N, O, S, and Mo elements in HATM-NBs (Figure S6a, Supporting Information), while FLM/CNT contains only C, S, and Mo elements (Figure S6c, Supporting Information). Figure S6b, Supporting Information shows a high-resolution spectrum in the binding energy range of 390–405 eV, which manifests the detailed information of nitrogen bonding configurations in HATM-NBs. In general, the peak at 396.2 eV corresponds to Mo 3p 3/2. The crossover peak in the middle of the spectrum (at 392.9 eV) can be ascribed to the Mo–N bond (N 1s).

The broadened diffraction peaks can be ascribed to the functional coating layer and nitrogen atoms in amino groups can provide a strong affinity for polysulfide adsorption. The high-resolution Mo and S spectra in Figure 2f demonstrate Mo 3d 3/2, Mo 3d 5/2 peaks located at 232.3, 229.1 eV, and S 2p 1/2 and S 2p 3/2 peaks located at 163.1, 162.0 eV, respectively. They are in good agreement with Mo 4f and S 2p oxidation state of 2H-MoS2. The XPS spectra of FLM/CNT sample present quite similar results (Figure S7, Supporting Information). The crystalline features of as-prepared samples were clarified by X-ray diffraction (XRD) measurement (Figure 2g). The XRD pattern of multiwall carbon nanotubes exhibits the characteristic peak at 26°, corresponding to the (002) plane of graphitic carbon. The diffraction peaks of FLM/CNT can be well assigned to (002), (101), (103), and (110) planes of 2H-MoS2 (JCPDS No. 37-1492). The broadened diffraction peaks can be ascribed to the small crystal size of MoS2 nanoflakes. As for HATM-NBs, weaker and broader diffraction peaks of 2H-MoS2 can be observed, agreeing well with the atomically thin structure.

Figure 2h shows Raman spectra collected from three samples. All three samples demonstrate characteristic G band at about 1580 cm\(^{-1}\) for sp\(^{2}\) carbons and D band at about 1350 cm\(^{-1}\) corresponding to the disorder in the graphitic structure. Two distinctive modes of E\(_{2g}\) and A\(_{1g}\) correspond to the in-plane vibration of Mo, S atoms and the out-of-plane vibration of S atoms. A certain frequency difference between two modes is determined by the number of MoS2 layers. In the Raman spectrum of HATM-NBs, E\(_{2g}\) and A\(_{1g}\) mode are located, respectively, at 384 and 406 cm\(^{-1}\). The frequency difference of 22 cm\(^{-1}\) indicates the bilayer or trilayer characteristics of 2H MoS2 in HATM-NBs. By contrast, the frequency difference for FLM/CNT can be calculated to be about 25 cm\(^{-1}\), indicating a thick film of over six layers.

The broadening of E\(_{2g}\) and A\(_{1g}\) bands as well as the enormously weakened 2LAM mode suggest the reduction of MoS2 crystal symmetry and increase in disorder in the lattice due to the creation of defect sites. Moreover, previous research found that E\(_{2g}\) mode is preferentially excited for terraced-terminated sites, while A\(_{1g}\) mode is preferentially excited for edge-terminated sites due to the polarization dependence. The relative integrated intensities between the two Raman modes (A\(_{1g}\)/E\(_{2g}\)) could thus shed some light on the intensity of edge sites. It can be seen that the intensity ratio of A\(_{1g}\)/E\(_{2g}\) in HATM-NBs is obviously higher than FLM/CNT, indicating its more exposed edge sites.

To clarify the porosity property of as-prepared samples, nitrogen adsorption-desorption isotherms were tested and corresponding pore size distribution (PSD) curves were plotted, as shown in Figure 2i and Figure S8, Supporting Information. For HATM-NBs, an intensive mesopore peak can be observed with a pore size of about 3.8 nm. However, the mesopore distribution is much weakened in FLM/CNT. This is in good accordance with the above TEM observation. A high specific surface area of 85 m\(^2\) g\(^{-1}\) can also be evaluated by the isotherms.

HATM-NBs were coated on two sides of the commercial PP separator through vacuum filtration and the resulting functional separator is designated as HATM-NBs@PP. Figure S9, Supporting Information shows the scanning electron microscopy (SEM) images of the separators before and after coating. It can be seen that pristine PP owns abundant macropores with pore sizes of up to hundreds of nanometers through which Li\(^+\) and soluble LiPSs can pass freely (Figure S9a, Supporting Information). The top-view SEM image of HATM-NBs@PP reveals a fibrous network fully covering on the PP separator (Figure S9b, Supporting Information). The plentiful macropores within the network assure the smooth mass transfer through HATM-NBs@PP. The cross-sectional SEM image reveals that the coating layer adhered closely onto the surface of PP separator and the thickness can be evaluated to be about 1.5 μm (Figure S10, Supporting Information).

Physicochemical properties of HATM-NBs@PP separator were further evaluated, and the results are shown in Figure 3. The folding/recovery test demonstrates high and robust adhesion between the HATM-NBs coating layer and the PP substrate (Figure 3a). Good thermal stability is critical for the practical application of lithium batteries. Modified separator with reduced thermal shrinkage could keep the battery cell from internal short circuiting and thus be quite favorable. Herein, thermal stability tests of PP and HATM-NBs@PP separators at different temperatures from 90 to 150 °C are shown in Figure 3b. The pristine PP separator undergoes gradually enhanced deterioration with increased temperature. On the contrary, HATM-NBs@PP exhibits negligible deformation, indicating its superior thermal stability. It is noteworthy that a phase transition from 2H MoS2 to 1T MoS2 may occur during discharge, which makes the coating layer facing the anode side own a certain electronic conductivity. The composite separator as a whole would still be insulating.

The HATM-NBs@PP separator owns great affinity with the electrolyte. As shown in Figure 3c, the contact angle of electrolyte on the HATM-NBs@PP separator is only 6°, much lower than that on the PP separator (31°). This enhanced electrolyte wettability facilitates smooth Li\(^+\) transportation from electrolyte to electrode. The holdup of electrolyte in the functional separator can also reduce the Li\(^+\) concentration gradient at the interface, which would benefit even lithium deposition under low potentials. The ionic conductivities of two separators were evaluated by electrochemical impedance spectroscopy (EIS) tests (Figure 3d). The electrolyte impregnated separator was placed between two stainless-steel (SS) plates. The ionic conductivities of PP separator and HATM-NBs@PP separator are calculated to be 0.24 and 0.23 mS cm\(^{-1}\), respectively, according to the formula: \(\sigma = \frac{d}{R_0S}\), where \(d\) and \(S\) represent the thickness and area of the separator, respectively; \(R_0\) is the bulk ohmic resistance of the electrolyte.

For a practical LSB cell unit, ultrathin and lightweight functional coating is of crucial importance for maintaining the high...
overall volumetric energy density. Here, we compared the areal mass loading and thickness of the HATM-NBs film with previously reported multifunctional coating layers, as shown in Figure 3e. The loading mass of two-side HATM-NBs coating is evaluated to be 0.09 mg cm\(^{-2}\) and the thickness is determined to be about 3 μm as discussed earlier, which is one of the lowest loading masses reported so far [23, 26, 29, 30, 33, 35, 36, 37]. Considering the areal mass of the commercial PP separator (1.4 mg cm\(^{-2}\)), the mass ratio of HATM-NBs coating layer in the HATM-NBs@PP is as low as 6%.

To verify the multifunction regulation capability of edge-rich 2D MoS\(_2\), we first conducted the LiPSs adsorption experiment. The HATM-NBs sample with abundant edge sites exhibits a robust adsorption affinity for LiPSs (Figure 4a). In sharp contrast, the FLM/CNT product with few edge sites adsorbs little LiPSs. Subsequently, we fabricated symmetric cells consisting of two identical CNT, FLM/CNT, or HATM-NBs electrodes to study the LiPSs conversion at the electrode/electrolyte interface. Li\(_2\)S\(_6\) (0.4 M) dissolved in 1,3-dioxolane/dimethoxymethane (DOL/DME, 1:1 v/v) was used as the electrolyte. Under the same conditions...
test conditions, it can be obviously seen that the HATM-NBs cell reveals the highest current in the cyclic voltammogram (CV) curve, indicating the fastest redox conversion of LiPSs at the electrode surface (Figure 4b). The much faster reaction kinetics in edge-rich HATM-NBs than in edge-deficient FLM/CNT (Figure 4d) can be ascribed to the efficient physicochemical adsorption of polysulfides at the electrode surface and the rapid interfacial charge transfer. The former is evidenced by the LiPSs adsorption experiments, and the latter is verified by the small diameter of the semicircle in the EIS curve (Figure 4c).

To evaluate the electrochemical properties of HATM-NBs@PP functional separator in LSBs, coin cells were assembled. A carbon–sulfur composite serves as cathode (the synthesis and microstructure detail of the composite shown in Figure S11, S12, Supporting Information) with areal sulfur loading of 1.5 mg cm$^{-2}$ and lithium metal foil serves as anode. FLM/CNT@PP was also fabricated and tested for reference. Figure 5a shows the galvanostatic charge/discharge profiles of LSB cells with pristine PP, FLM/CNT@PP, and HATM-NBs@PP separators at 0.2 C. One charge plateau and two distinctive discharge plateaus can be observed. The discharge plateaus at 2.25 V can be ascribed to the reduction of S8 molecules to long-chain LiPSs.[60] The low discharge plateau at 2.1 V originates from further reduction of long-chain LiPSs into Li2S2/Li2S. Conversely, the charge plateau at 2.35 V is due to the oxidation process from Li2S2/Li2S to high-order LiPSs. The aforementioned process occurs repeatedly during cycling, creating the so-called “shuttling effect” in Li–S batteries. It decreases the active mass utilization from three aspects: 1) the Li2S2/Li2S covers the positive electrode and hinders the lithium ion diffusion into the bulk electrode; 2) the corrosion reaction between Li2S and lithium metal intensifies the uneven lithium deposition; and 3) the insulating Li2S2/Li2S is coated on the lithium electrode, hindering the effective utilization of lithium metal.

The sulfur cathode with HATM-NBs@PP separator demonstrates high initial discharge capacities of 1412 mAh g$^{-1}$ at 0.2 C, which corresponds to 84.3% of the theoretical capacity. This high capacity value is superior to those with FLM/CNT@PP (1250 mAh g$^{-1}$) and PP (949 mAh g$^{-1}$) separators. Figure 5b manifests the specific discharge capacities at various discharge rates from 0.2 to 5 C. The sulfur cathode with PP separator shows a sudden capacity drop in the initial three cycles at 0.2 C, indicating the severe shuttling effect. As current rates increase, the discharge capacities undergo a drastic decline. It only retains a specific capacity of 109 mAh g$^{-1}$ at 5 C, revealing the large electrochemical resistance during redox reaction. The sulfur cathode with FLM/CNT@PP separator displays a slower capacity decay at high rates with a discharge capacity of 258 mAh g$^{-1}$ maintained at 5 C. In contrast, the HATM-NBs@PP counterpart shows a much enhanced rate performance with discharge capacity of 639 mAh g$^{-1}$ maintained at 5 C, which is more than twice that of FLM/CNT@PP.

CV curves at a scan rate of 0.1 mV s$^{-1}$ were collected to further investigate the electrochemical behaviors with different...
As shown in Figure 5c, the positions of the redox peaks are well consistent with the above charge/discharge plateaus. For instance, LSB cell with PP separator shows two reduction peaks at 1.94 and 2.19 V as well as an oxidation peak at 2.48 V. The potential gap between the redox peaks is calculated to be as high as 0.54 V, indicating the severe electrode polarization. After functional coating, the potential gaps are reduced to 0.46 V for FLM/CNT@PP separator and further to 0.35 V for HATM-NBs@PP separator. Such comparison clearly demonstrates the accelerated conversion reaction kinetics of LiPSs by HATM-NBs coating.

EIS tests were further performed to clarify the internal resistances in LSB cells with various separators. Nyquist plots with typical semicircles in the high-frequency region and sloping lines in the low-frequency region are shown in Figure 5d. The semicircle corresponds to the charge transfer resistance ($R_{ct}$) and the slope line originates from the Li$^+$ diffusion resistance. The sulfur cathode with HATM-NBs@PP separator shows the lowest $R_{ct}$ value, confirming the fastest kinetics of conversion reaction.

The cyclic stability of LSB cells with different separators was investigated at a current rate of 1 C and the results are shown in Figure 5e. The sulfur cathode with HATM-NBs@PP separator delivers a high specific capacity of 848 mAh g$^{-1}$ over 500 cycles, corresponding to an ultralow capacity decay of 0.025%. Moreover, the average CE is evaluated to be 99.6%, indicating its great potential for practical application. It can also be found that this cycling performance is much superior to those with pristine PP and FLM/CNT@PP separators, revealing the significantly enhanced entrapment of LiPSs by HATM-NBs coating.

Here, we also compared the electrochemical performance of the sulfur cathodes after functional modification by our HATM-NBs layer and other reported multifunctional coating layers [23, 26, 29, 30, 33, 35, 36, 37]. The mass loading of coating layer, initial discharge
capacity at a low current rate, and the capacity decay after prolonged cycling at a high rate are shown in Table S1, Supporting Information. It can be clearly seen that despite the lowest mass loading, HATM-NBs coating in this work enable the best electrochemical performance in terms of lithium storage capacity, kinetics, and stability. This verifies the superior shuttle suppression capability of the edge-rich 2D structure in this study. It is noteworthy that this shuttle suppression ability is not only of crucial importance for stabilizing sulfur cathode but also essential for protecting lithium metal from deterioration by the shuttle LiPSs. The effect of coating thickness on the electrochemical performance has also been explored. Coating layers with gradually increased thickness were fabricated (see the details in Figure S13, Supporting Information). It can be seen that Li|S cell with separator of thickness 2\# shows much enhanced specific capacities upon prolonged cycling than thickness 1\#. When the thickness is further increased to thickness 3\#, the specific capacity is increased, but at a very limited level. Considering the increased thickness would cause increased mass/volume content of the inactive component and reduce the mechanical strength of the composite separator, the authors think that the thickness of functional coating here (0.09 mg cm\(^{-2}\)) could be a proper value.

In addition to the shuttle suppression function, the regulation ability of HATM-NBs@PP on lithium metal anode was also investigated. Li|Cu half cells with pristine PP and other two functional separators were first fabricated to evaluate the CE, which is calculated by the ratio of capacity between plating and stripping in each cycle.\(^{[61]}\) At a current density of 0.5 mA cm\(^{-2}\) and areal capacity of 1 mAh cm\(^{-2}\), the CE values of the cell with pristine PP separator drop fast to 69\% after 45 cycles (Figure S14, Supporting Information). The irreversible capacity loss has been reported to mainly originate from the “dead” lithium, which consists of both electrochemically formed lithium compounds in SEI and electrically isolated unreacted metallic Li\(^0\).\(^{[62]}\) The corresponding voltage profiles exhibit the typical lithium plating/striping plateaus and rapidly decreased lithium stripping capacity with cycling (Figure S15, Supporting Information). The cell with FLM/CNT@PP separator shows a quite similar electrochemical behavior. A sudden decay in CE value after 50 charge/discharge cycles can be observed (Figure 6a). It reveals that the FLM/CNT coating does not endow the separator with the ability to regulate Li\(^+\) flux. Impressively, the HATM-NBs@PP counterpart demonstrates a much enhanced cycle life. A steady Coulombic efficiency of 97\% is kept even after 150 charge/discharge cycles. Quite stable plating/striping voltage profiles with prolonged cycling can be collected (Figure 6b), indicating the even lithium metal deposition and effectively suppressed dendritic growth.

To verify the Li deposition behavior, the morphologies of Li-deposited Cu electrodes with lithium plating capacity of 5 mAh cm\(^{-2}\) were observed by the ex situ SEM technique. The electrode from cells with PP separator exhibits a rough surface with massive cracks and holes (Figure S16, Supporting Information). The electrode from cells with FLM/CNT@PP separator shows a similar rough texture with mossy and rugged hilary sites (Figure 6a). The contrary, a much more smooth electrode surface is manifested in the cell with HATM-NBs@PP separator after plating the same amount of Li (Figure 6d). This comparison reveals that the HATM-NBs coating on PP separator could continuously guide the uniform lithium deposition. As pristine PP and FLM/CNT@PP separators make little difference in determining the electrochemical behavior, in the following discussion we mainly compare the functions of two coating separators to clarify the unique contribution of HATM-NBs.

To evaluate long-term cycling stability promoted by HATM-NBs, Li|Li symmetric cells with FLM/CNT@PP and HATM-NBs@PP separators were assembled. Figure 6e,f and Figure S17, Supporting Information present the voltage profiles of Li|Li cells measured at various current densities and a constant lithium plating/striping capacity of 1 mAh cm\(^{-2}\). At a current density of 1 mAh cm\(^{-2}\), the symmetric cell with HATM-NBs@PP separator displays a low-voltage hysteresis of about 76 mV in the initial cycle, and an excellent cycling stability with stable voltage plateaus for over 500 h (Figure 6e). In sharp contrast, the cell with FLM/CNT@PP separator exhibits a large voltage hysteresis of 107 mV in the first cycle. And an abrupt increase in the voltage hysteresis can be observed after cycling for only 150 h. Such voltage deterioration corresponds to the enormously increased electrode polarization. With continuous formation of SEI as well as repeated growth of Li dendrites, electrical disconnection of active Li becomes more and more severe, leading to the internal resistance enhancement. At an increased current density of 2 mA cm\(^{-2}\), the cells with HATM-NBs@PP separator still exhibit quite stable long-term cycling, which greatly outperforms the cells with FLM/CNT@PP separator (Figure S17, Supporting Information). Even at a high current density of 5 mA cm\(^{-2}\), the cells with HATM-NBs@PP separator maintain stable voltage profiles during prolonged cycling with very small voltage hysteresis increase over 250 cycles. On the contrary, the cells with FLM/CNT@PP and PP separators show a gradual rise in voltage hysteresis and then dendrite-induced short-circuit (Figure 6f, Figure S18, Supporting Information).

The surface morphologies of Li metal electrodes in symmetric cells after 100 cycles at 1 mA cm\(^{-2}\) were further observed by ex situ SEM. As shown in Figure S19, Supporting Information, a porous and dendritic structure can be seen when a FLM/CNT@PP separator is used, revealing the uneven Li deposition during cycling. By contrast, densely packed, flat, coarse lithium grains emerge on the surface of Li electrode from cells with HATM-NBs@PP separator. This observation confirms the capability of HATM-NBs in regulating Li\(^+\) flux and guiding even lithium plating/striping.

The aforementioned spectroscopy and electrochemical tests clearly reveal the multifunction of HATM-NBs: physicochemical adsorption and catalytic conversion of polysulfides as well as homogenization of Li\(^+\) flux (Figure 7a,b). To investigate the potential of HATM-NBs@PP for practical application, a laminate cell with ultrathin separator coating of 0.09 mg cm\(^{-2}\), a high areal sulfur loading of 7.43 mg cm\(^{-2}\), and a lean electrolyte usage of 5 \(\mu\)L mg\(^{-1}\) S was fabricated. A lithium foil with thickness of 100 \(\mu\)m (areal capacity of about 20 mAh cm\(^{-2}\)) was used as the counter electrode. The cell with FLM/CNT@PP separator was also tested for reference (with similar areal sulfur loading of 7.55 mg cm\(^{-2}\)). Figure 7c shows the scheme and optical photo of the laminate cell, which owns an electrode size of 50 mm \times 50 mm. The charge–discharge curves of cells with different separators at 1 mA cm\(^{-2}\) are shown in Figure 7d. The cell with HATM-NBs@PP separator shows an areal capacity of
7.83 mAh cm\(^{-2}\). It corresponds to a gravimetric capacity of 1052 mAh g\(^{-1}\), suggesting a high sulfur utilization. In contrast, the FLM/CNT@PP counterpart delivers an areal capacity of 6.64 mAh cm\(^{-2}\) with a much lower gravimetric capacity of 879 mAh g\(^{-1}\). Moreover, a clear difference in the charge/discharge profiles of the cells with two separators can be seen. In comparison with HATM-NBs@PP, the FLM/CNT@PP counterpart demonstrates an obvious depression in the low discharge plateaus and a voltage increase in the charge plateaus, implying the severe electrode polarization under such practical test condition of high sulfur loading and lean electrolyte. The capacity retention with prolonged cycling was tested, as shown in Figure 7e. The cells were first tested at a small current density of 1 mA cm\(^{-2}\) for five cycles to activate the cell and then charged/discharged at 5 mA cm\(^{-2}\) for 200 cycles. The cell with PP separator only delivers an areal capacity of 1.77 mAh cm\(^{-2}\) after cycling. On the contrary, the laminate cell with HATM-NBs@PP separator maintains a much higher areal capacity of 4.70 mAh cm\(^{-2}\) with 76% capacity retention over 200 cycles. The aforementioned laminate cell test further reveals the great potential of HATM-NBs in regulating Li–S chemistries toward practically viable LSBs.

3. Conclusion

In summary, we have reported theory-assisted rational design of edge-rich 2D TMDs for stable LSBs. DFT calculations reveal the multifunction of edge sites in MoS\(_2\) for regulating Li–S chemistry. Holey atomically thin MoS\(_2\)-constructed nanobrushes with massive exposed edge sites are then prepared through polar functionality-assisted anchoring. The anchoring effect helps inhibit the longitudinal growth, facilitate the nanopore formation, and stabilize the ultrathin holey structure in 2D MoS\(_2\).
On the sulfur cathode side, spectroscopy and electrochemical tests reveal not only superior physicochemical immobilization but also catalytic conversion of polysulfides by HATM-NBs, therefore enormously enhanced lithium storage capacity, kinetics, and stability. On the lithium anode side, the nanobrush architecture promotes good contact with lithium electrode and thus homogenization of Li$^+$ flux and uniform lithium plating/stripping. The open porous network of HATM-NBs helps improve the electrolyte wettability and promote smooth mass transfer. A practical laminate cell with ultrathin separator coating of 0.09 mg cm$^{-2}$, a high areal sulfur loading of 7.43 mg cm$^{-2}$, and lean electrolyte usage of 5 $\mu$L mg$^{-1}$ S has been fabricated. It delivers a high areal capacity of 7.82 mAh cm$^{-2}$ and maintains 4.70 mAh cm$^{-2}$ after prolonged 200 cycles at 5 mA cm$^{-2}$. This work will open an avenue for the rational design of efficient multifunctional materials toward stable LSBs by edge engineering.

4. Experimental Section

Material Synthesis: CNTs were refluxed in H$_2$SO$_4$/HNO$_3$ (1:1 v/v). Then amino groups were introduced according to the reported amide formation process.$^{[63]}$ Afterward, the HATM-NBs sample was prepared through a solvothermal process. Typically, 60 mg of ammonium molybdate (NH$_4$)$_6$Mo$_7$O$_{24}$ and 180 mg of TAA were added into a mixed solvent.
of 20 mL of water and 20 mL of ethanol. Modified carbon nanotubes (20 mg) were then added, mixed, and transferred into an autoclave of 100 mL. After reaction at 210 °C for 24 h, the solid HATM-NBs product was collected, washed, and dried. The reference FLM/CNT sample was prepared by the same procedure except that pristine carbon nanotubes were used.

**Material Characterization:** The morphology was examined by a SEM (LEO-1530). The microstructure was measured with TEM (Tecnai G20, 200 kV). N₂ adsorption isotherms were measured by using a volume adsorption apparatus (autosorb-1) at 77 K. PHI Quantera Imaging XPS was used to investigate the surface chemistry. Raman spectra were collected using a Renishaw InVia Reflex 322 with an incident wavelength of 532 nm. XRD patterns were obtained from a D8 Advance Diffractometer with a Cu Kα source.

**Electrochemical Measurements:** The sulfur cathode was prepared by mixing the carbon–sulfur composite, carbon black (super P), and polyvinylidene difluoride (PVDF) binder at a weight ratio of 88:6:6. N-methyl-2-pyrrolidone (NMP) was used as the solvent. The obtained slurry was blade-casted on a carbon-coated Al foil. The electrode film was dried at 60 °C for 24 h and then punched into a disk with a diameter of 15 mm for electrochemical tests. 2032 coin cells were assembled using as-prepared sulfur cathode and lithium foil as an anode. The electrolyte was 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LITFSI) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) at 1:1 volume ratio with 1 wt% LiNO₃ added as an additive. A LAND battery tester (Jinnuo Electronics Co., Wuhan, China) was used to perform the galvanostatic charge–discharge tests. CV and EIS tests were performed in VSP-300 electrochemical interface. The CV tests were conducted at a scan rate of 0.1 mV s⁻¹ in the potential range of 1.7–2.8 V. EIS tests were performed in frequency range of 0.1 Hz to 100 kHz with an amplitude of 5 mV. The electrodes for symmetrical cells were fabricated without the presence of elemental sulfur. HATM-NBs or FLM/CNT was mixed with PVDF at a weight ratio of 3:1 and fabricated into round disks by the same blade-casting and punching process. These disks were used as identical working and counter electrodes with 0.4 M Li₂S₆ as the electrolyte. CE in lithium batteries, long cycle life, multifunctional regulation

**Conduct of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

atomically thin materials, edge engineering, holey MoS₂, lithium–sulfur batteries, long cycle life, multifunctional regulation

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