Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Rational Understanding of the Catalytic Mechanism of Molybdenum Carbide on Polysulfide Conversion in Lithium-Sulfur Battery

Mingzhu Sun, † a Zhao Wang, †a Xue Li,c Haibo Li,*a Hongsheng Jia,a Xiangxin Xue,b Ming Jin,a Jiaqi Li,a Yu Xie,*c and Ming Feng*a

a Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Changchun 130103, P.R. China
E-mail: mingfeng@jlnu.edu.cn and lihaibo@jlnu.edu.cn
bKey Laboratory of Preparation and Applications of Environmental Friendly Materials of the Ministry of Education, Jilin Normal University, Changchun, 130103, P.R. China
c Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education) and International Center of Computational Method and Software, College of Physics, Jilin University, Changchun 130012, China
E-mail: xieyu@jlu.edu.cn
† These authors contributed equally to this work.

Exerimental Section

***Preparation of Mo_2C@C**:* 4g C (TIMCAL 350G carbon, **Fig. S13** shows the SEM image of the TIMCAL 350G) was placed in a flask and put in an ultrasonic bath for 15 min to disperse the particles well. Subsequently, an aqueous solution of ammonium molybdate (1.56 g in 20 ml of distilled water) was added dropwise to the support, and the mixture was then homogenized for 30 min and dried at 110 °C overnight. Last, the sample was annealed in a tube furnace from ambient temperature to 850 °C at a rate of 5 °C min^{-1} under Ar flow for 4 h. The Ar atmosphere was retained throughout the cooling of the reactor to room temperature, and the the Mo_2C@C was thus obtained.

Preparation of Mo_2C@C-S: The Mo_2C@C-S cathode was synthesized by a melting diffusion strategy. 400 mg sulfur was well mixed with 100 mg Mo_2C@C. The mixture was sealed in a Teflon container and heated at 155 °C for 20 h to incorporate sulfur into the porous of Mo_2C@C. The S content of Mo_2C@C-S composite is 78.2 wt% **(Fig. S14)**.

Preparation of Clean Mo_2C@C-S: 1 g Mo_2C@C-S were added to the 50 ml CS_2 solvent. Then the mixture was kept for 2h at room temperature. The suspension was centrifuged and washed by CS_2, and then dried at 60 °C for 24 h to obtain Clean Mo_2C@C-S.

***Preparations of Mo_2C@C-S and C-S electrodes*:** Mo_2C@C-S or C-S: Super P: PVDF in the weight ratio 8:1:1 were dispersed in NMP to form a slurry, which was cast onto an Al foil. The electrode was dried overnight in an oven at 60 °C and then roll-pressed and punched a disc with a diameter of 12 mm. The sulfur loading of the electrode is about ～1.5 mg/cm^2.

Characterizations

XRD measurements were carried out on a Bruker D8-Advance powder X-ray diffractometer operating at 40 kV and 30 mA, using Cu-Kα radiation (λ = 1.5405 Å). The morphology, particle size and elements information were obtained *via* SEM (Hitachi S-5500) coupled with an EDS (Ametek). HRTEM (JEOL 2100F) was used to study the detailed particle and crystal information, operating at an accelerating voltage of 200 kV. Surface areas were determined from nitrogen adsorption and desorption isotherms performed on a Quantachrome Autosorb-1 instrument. Before measurement, the samples were degassed at 80 °C on a vacuumline. TGA analysis was used to determine the sulfur content of the material, on a TA Instruments SDT

Q600, employing a heating rate of 10 ^{o}C/min from room temperature to 800 ^{o}C under a N_2 atomosphere. The XPS analysis was collected by centrifugation and dried under vacuum overnight. The XPS samples were sealed in a vial before being quickly transferred to the chamber of an ultrahigh vacuum Imaging XPS Microprobe system for analysis (Thermo VGScientific ESCALab 250). All spectra were fitted with Gaussian-Lorentzian functions and a Shirley-type background using CasaXPS software. The binding energies were calibrated to the C 1s peak assigned to C-H at 284.6 eV.

Electrochemical measurements

Assembly of electrochemical cells: All Li-S cells were assembled in a glovebox filled with Ar by a coin-cell design with the components as following: using a Li metal foil as anode, a Celgard 2400 membrane as separator, and 1 M LiTFSI and 0.1 M $LiNO_3$ in 1:1 (v/v) dissolved in 1,3-dioxacyclopentane (DOL) and 1,2-dimethoxyethane (DME) as electrolyte, Mo_2C@C-S or C-S electrode as cathode. CV measurements were carried out by a Versa STAT 3 potenstiostat at a scan rate of 0.1 mV/s within a potential range of 1.6-2.8 V *vs.* Li^+/Li. Galvanostatic cycling testing for cells with different cathodes were conducted with a LAND CT2001A at variosu constant current densities of 0.1 C-2 C within a potential range of 1.6-2.8 V *vs.* Li^+/Li. EIS was performed with dc voltage kept at open-circuit voltage and an ac voltage of 5 mV in amplitude was applied in the frequency range 1000 kHz-0.1 mHz.

Li_2S nucleation tests

Li_2S nucleation was studied by loading host (Mo_2C@C or C) on carbon-fiber-paper (CP) current collectors, using Li_2S_8 as catholyte and lithium foil as the anodes. First, Li_2S_8 with a concentration of 0.20 mol/L was prepared by dissolving S and Li_2S (molar ratio 7:1) dissolved in tetraglyme, followed by vigorous stirring for 24 h. The CP was punched into circle disks with a diameter of 12 mm to load Mo_2C@C and C with the identical loading contents of 1.0 mg/cm^2, respectively. The cathodes and anodes were separated by Celgard 2400 separator. The 25 μL Li_2S_8 electrolyte was first distributed into the cathode and then 20 μL LiTFSI (1.0 mol/L) without Li_2S_8 was added onto the anode compartment. The batteries were galvanostatically discharged to 2.06 V at 0.112 mA and then maintained potentiostatically at 2.05 V until the current was below 0.01 mA. The entire process was recorded to evaluate the nucleation/growth rate of Li_2S based on Faraday's law.

Density functional theory calculations: First-principles calculations were performed within the framework of DFT, as implemented in the Vienna *ab initio* simulation package.[1] We adopted the all-electron projector-augmented wave potential (PAW) with Perdew-Burke-Ernzerhof generalized gradient approximation as the exchange-correlation function.[2,3] A energy cutoff of 500 eV for the plane-wave expansion and Monkhorst-Pack meshe of 4×4×1 were used to sample the Brillouin zone and ensure the total energy calculations converged with an error of less than 1 meV/atom.[4] Structural relaxations were performed with forces converged to less than 0.01 eV/Å. A vacuum distance of 15 Å was employed to avoid interactions of neighboring images. The van der Waals interactions were considering for all the simulations using the DFT-D3 method.[5] A (2 × 1) Mo_2C (101) slab model with a thickness of 5.94 Å was used to investigate the adsorption behavior of LiSPs. The climb-image nudged elastic band (CI-NEB) method with 5 images was applied for computing diffusion and decomposition barriers.[6] The force convergence criterion for optimization was set at 0.05 eV/Å.

Supplementary Result

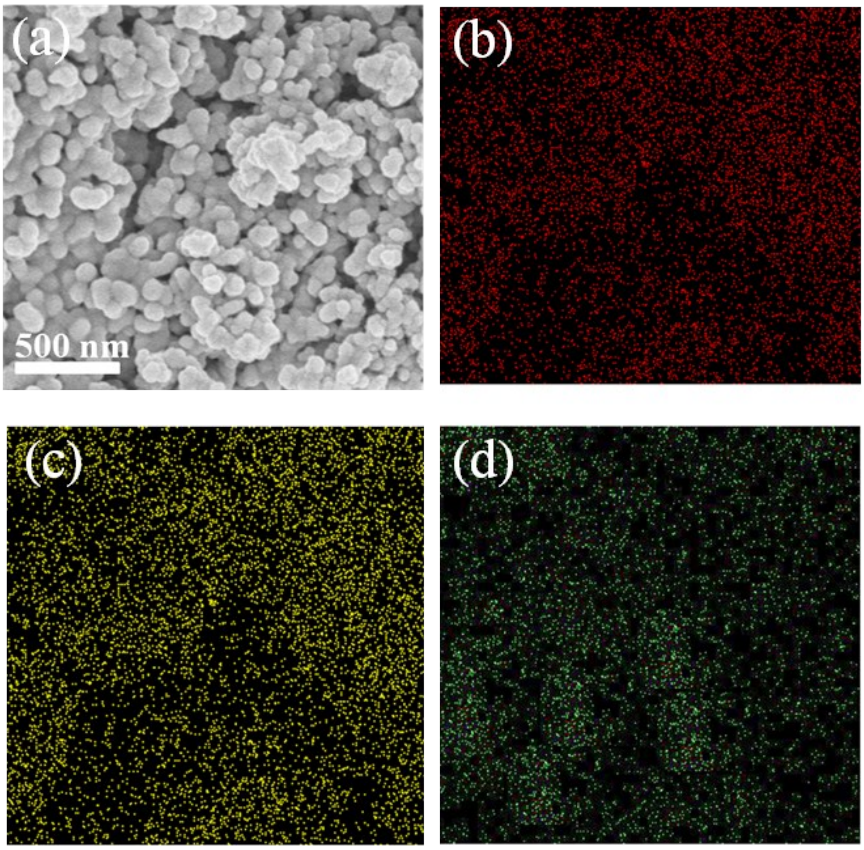


Fig. S1 (a) The Mo_2C@C-S; EDS mapping of (b) Mo, (c)S and (f) C in the SEM image.

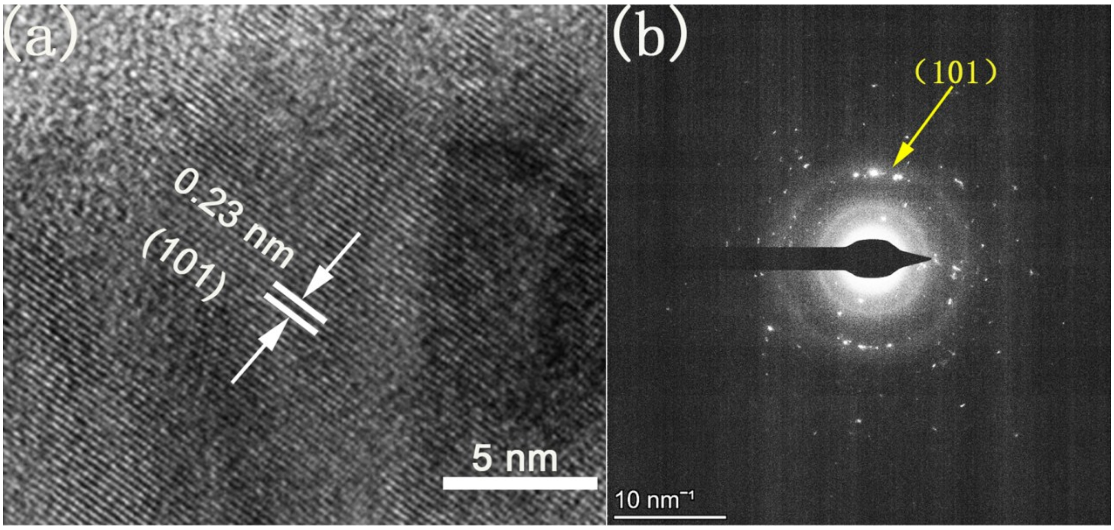


Fig. S2 The HRTEM and SAED patterns of the Mo_2C@C.

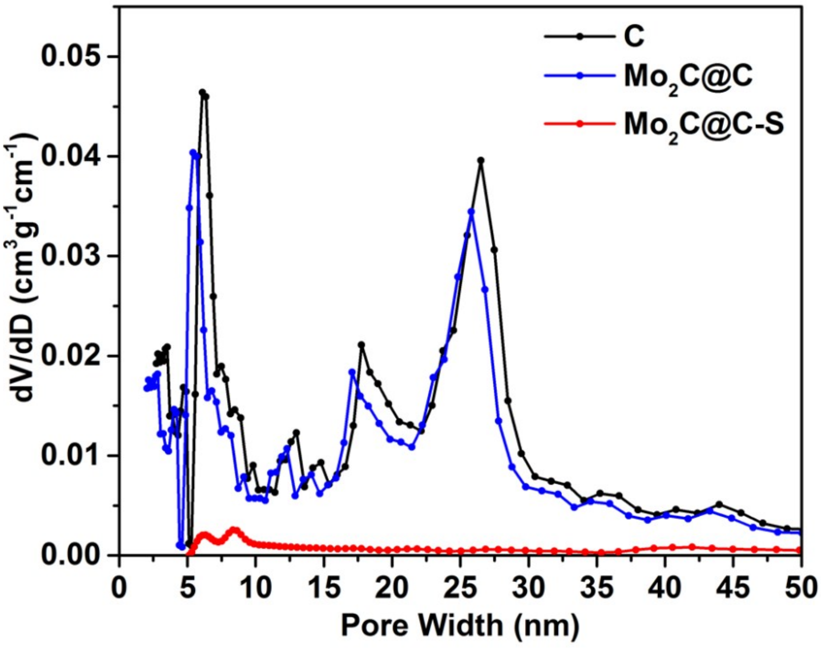
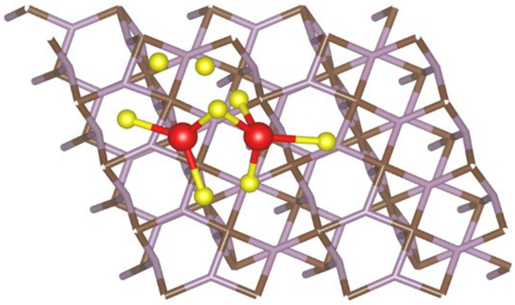
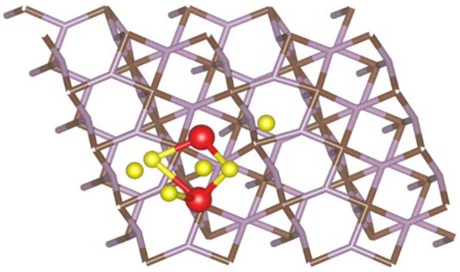


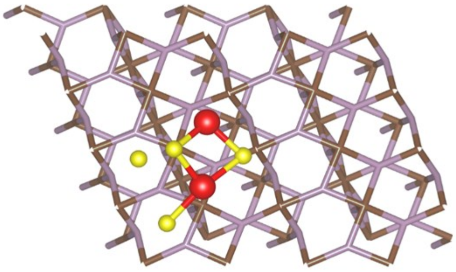
Fig. S3. The pore size distribution of the C, Mo_2C@C and Mo_2C@C-S.



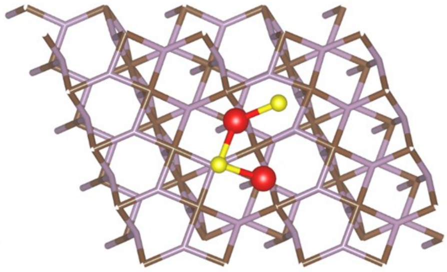
Li_2S_8 (-7.191 eV)



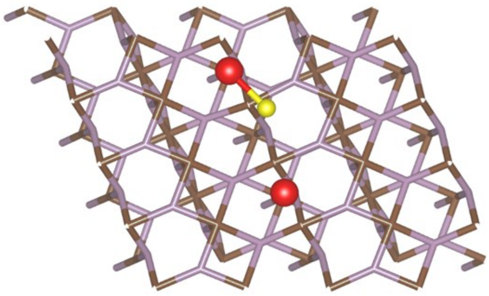
Li_2S_6 (-4.286 eV)



Li_2S_4 (-6.723 eV)



Li_2S_2 (-5.719 eV)



Li_2S (-4.814 eV)

Fig. S4. Optimized geometries of LiPSs on bare Mo_2C (101) surface. The black, light purple, and yellow balls represent C, Mo, and S, respectively.

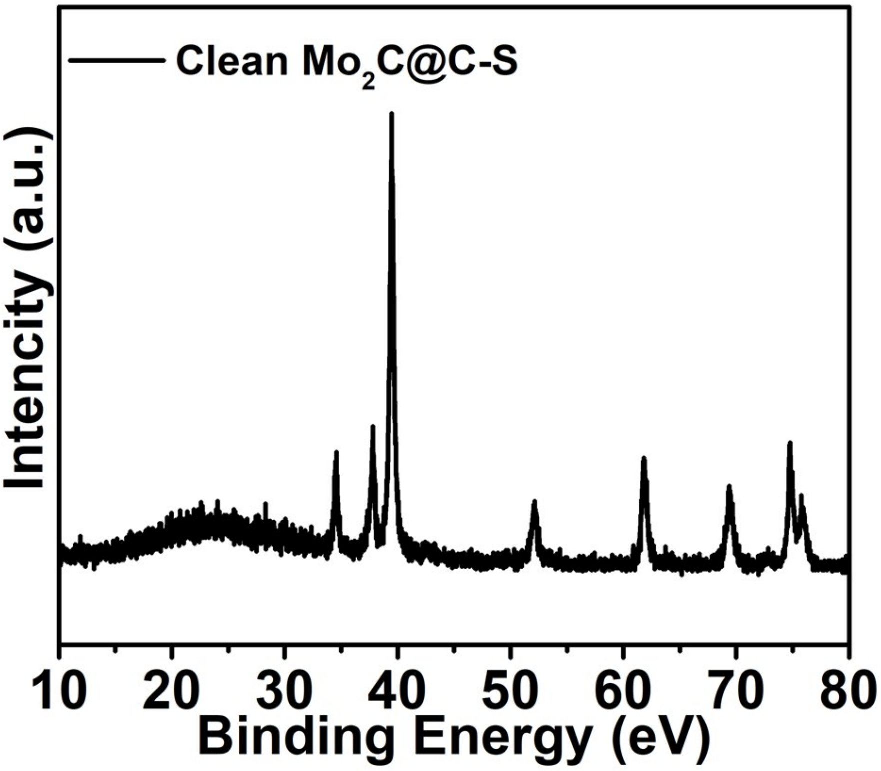


Fig. S5 The XRD of Clean Mo_2C@C@S.

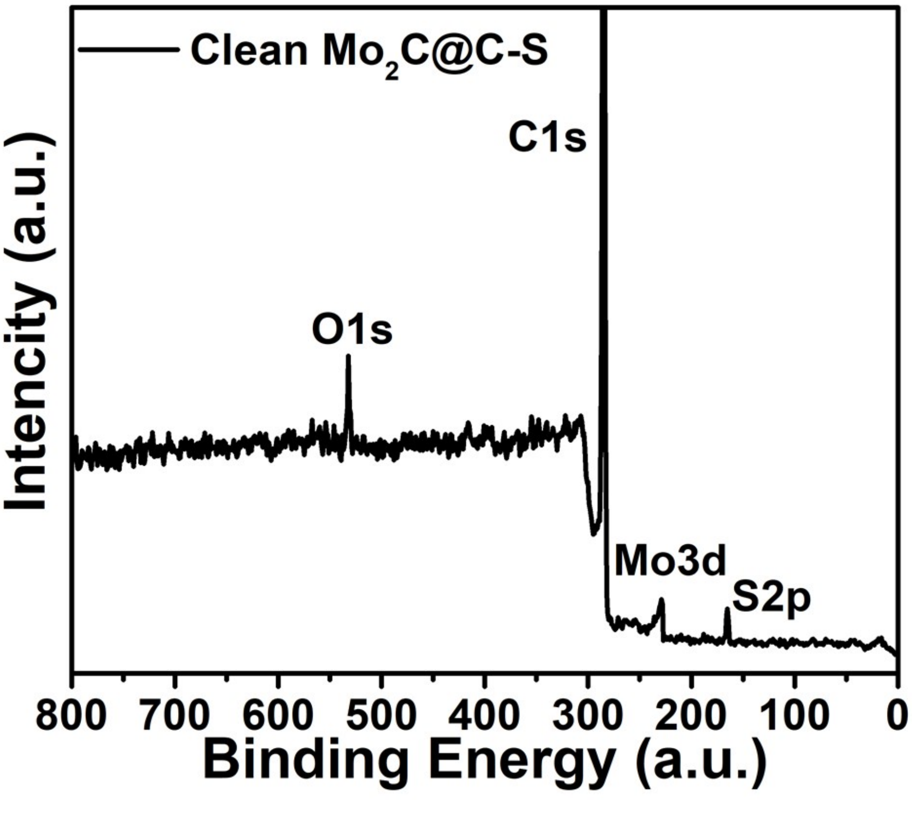


Fig. S6 XPS survey spectra of Clean Mo_2C@C-S.

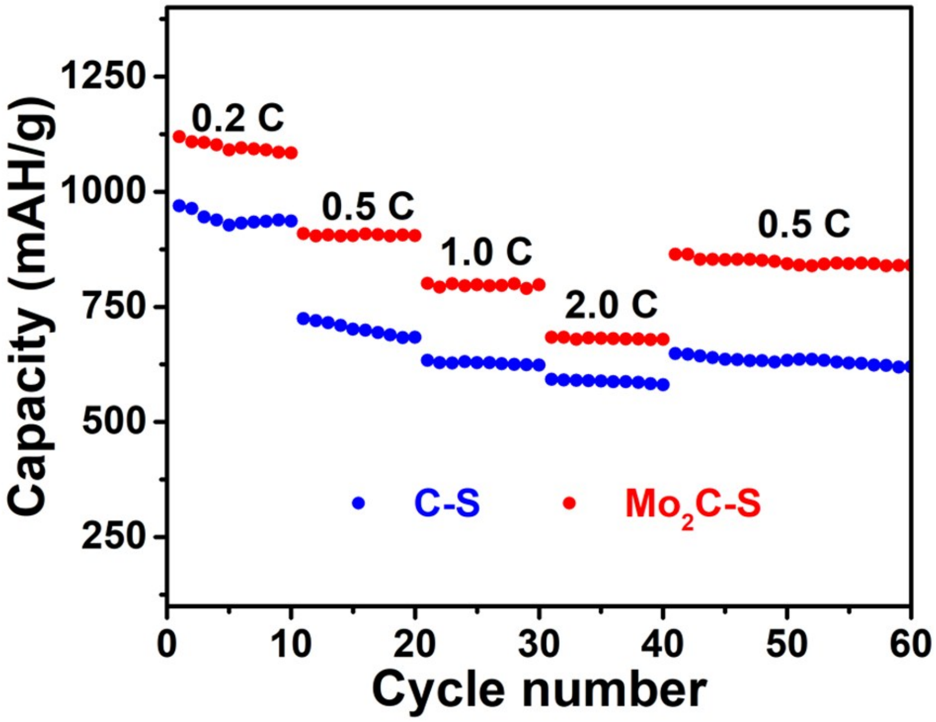


Fig. S7 The rate capabilities of the C-S and Mo_2C@C cathodes.

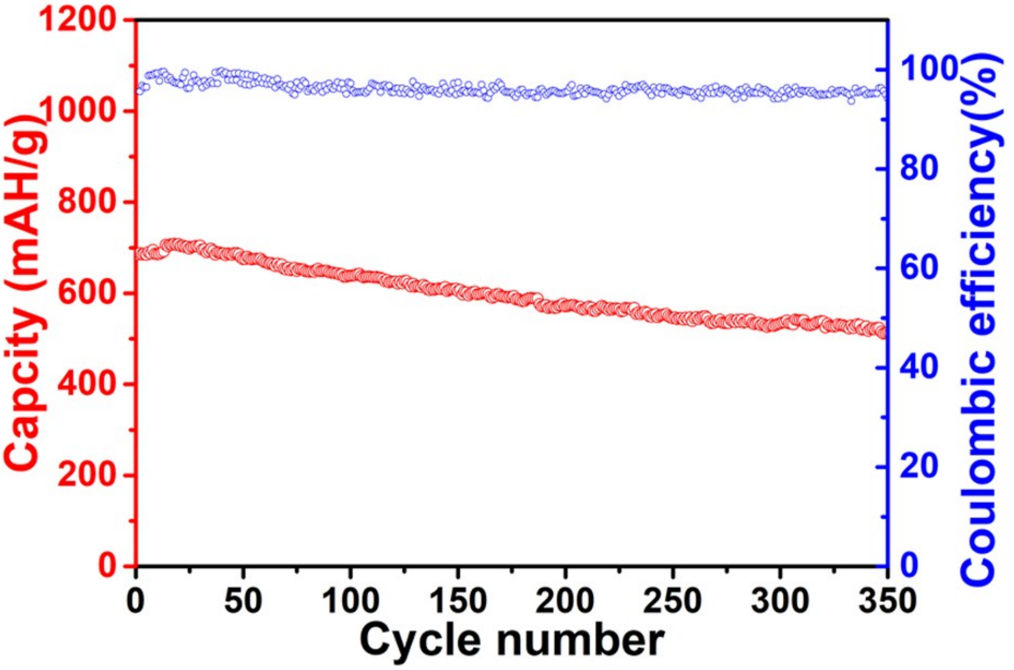


Fig. S8 The cycling performance of cells with Mo_2C@C-S over 350 cycles at a charge/discharge rate of 2 C.

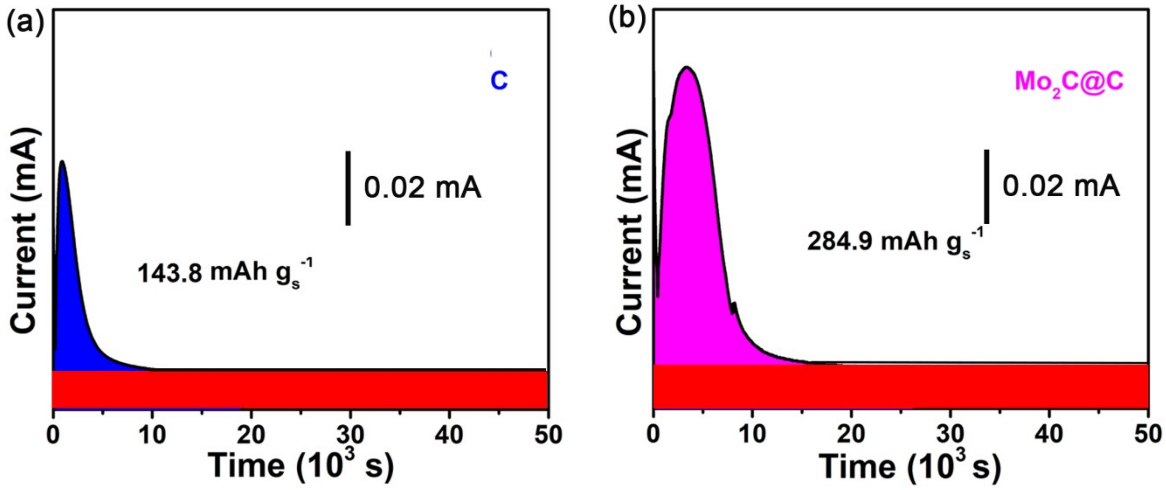


Fig. S9 (a, b) Potentiostatic discharge profiles of a Li_2S_8/tetraglyme solution on C (a) and $Mo_2C@C$ (b) surfaces at 2.05 V, respectively.

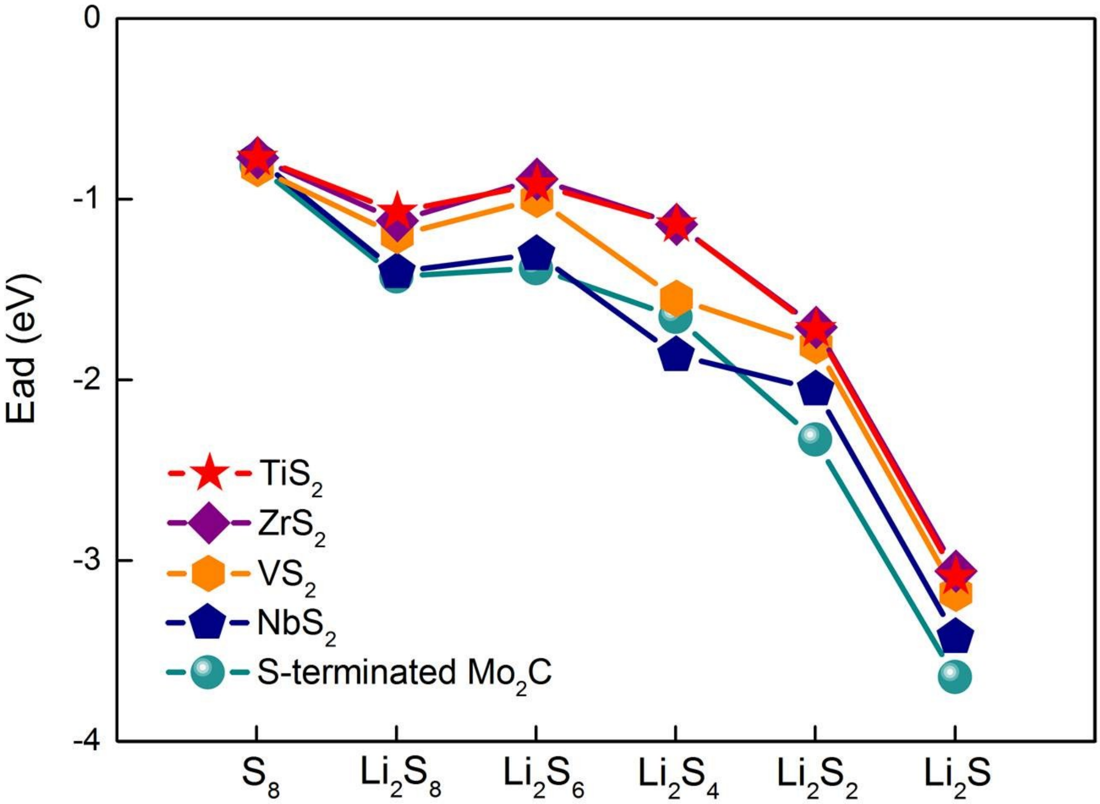


Fig. S10 Calculated adsorption energies of S_8 and LiPSs on S-Mo_2C (101).

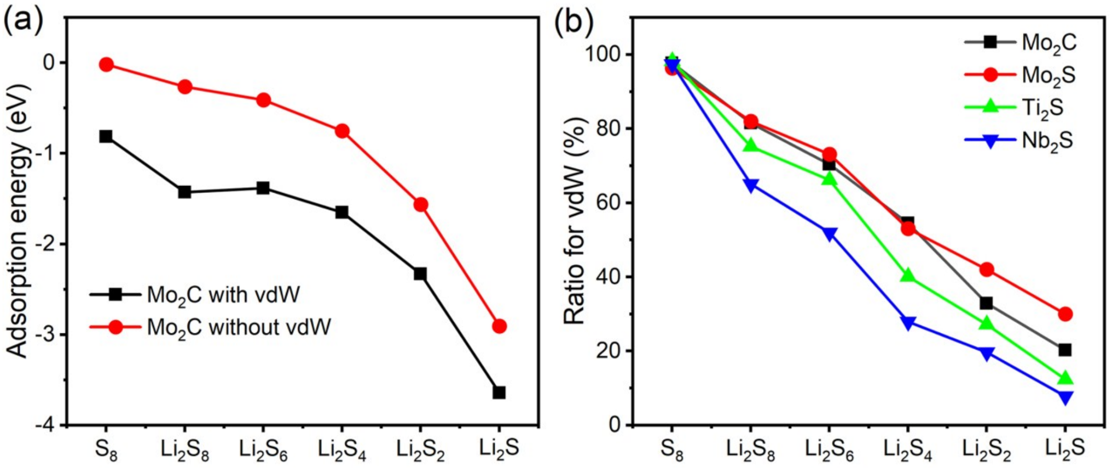


Fig. S11 (a) The adsorption energies of LiSPs on S-Mo$_2$C (101) surface with and without the vdW interactions. (b) The ratio for vdW of the total adsorption energy for LiSPs.

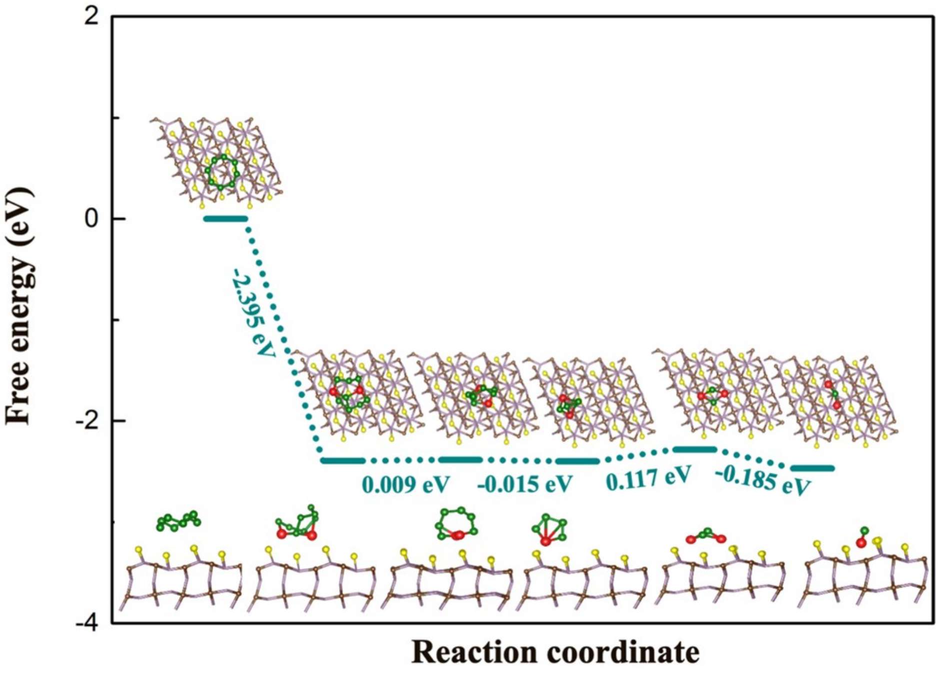


Fig. S12 Energy profiles for the reduction of LiPSs on S-Mo$_2$C (101). Inserts are the optimized adsorption conformations of intermediate species on S-Mo$_2$C (101). The black, light purple, yellow, green, and red balls represent C, Mo, S bonded with Mo, S of LiPSs, and Li, respectively.

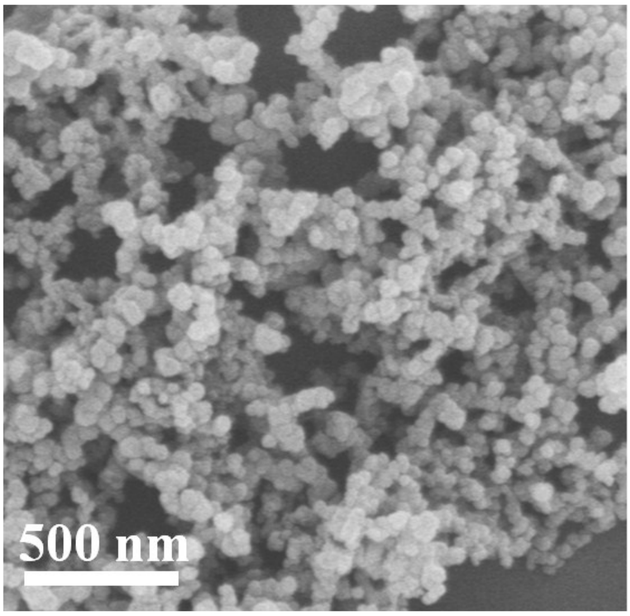


Fig. S13 SEM image of the C.

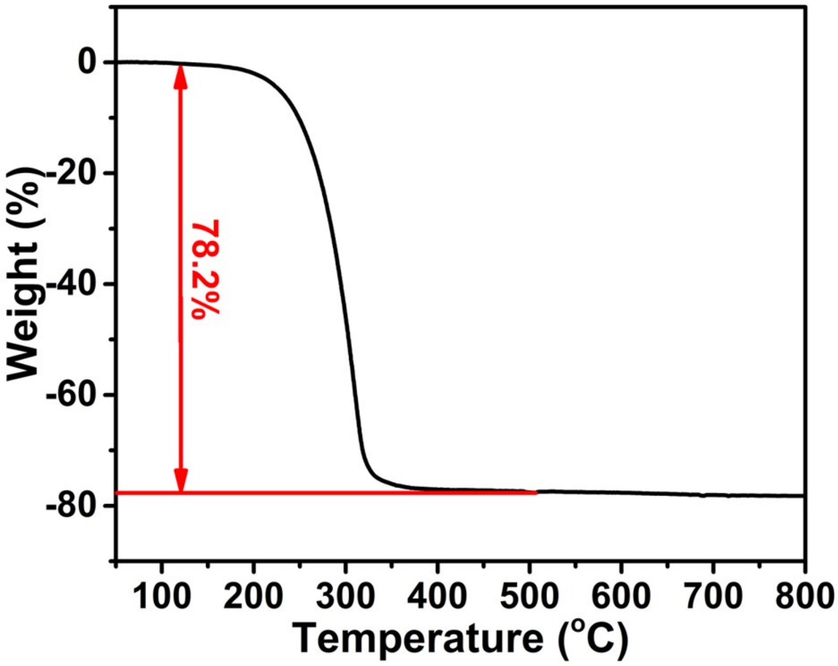


Fig. S14. The TGA curves of Mo_2C@C-S measured under a N_2 flow. The sulfur content is 78.6 wt. % for the Mo_2C@C-S composite.

Table S1. Summary of S 2*p3/2* binding energies (eV) of Mo_2C@C-S and Clean Mo_2C@C-S, measured by high-resolution XPS

Sulfur species	Mo-S bonding (***p3/2*** %Area)	S-S bonding (***p3/2*** %Area)
Mo_2C@C-S	**44.4% (162.8 eV)**	**22.2% (163.7 eV)**
Clean Mo_2C@C-S	**48.0% (162.7 eV)**	**18.0% (163.6 eV)**

Table S2. Energy difference between intact and destructed Li_2S_x on S-Mo_2C (101).

	E
Li_2S_6	0.47
Li_2S_4	0.62

References

1 G. Kresse, J. Furthmuller, Physical Review B: Condensed Matter, 1996, 54 (16), 11169-11186.

2 P. E. Blochl, Phys. Rev. B, 1994, 50**,** 17953.

3 J. P. Perdew, K. Burke, M. Ernzerhof, Physical Review Letters, 1996 , 77 (18), 3865-3868.

4 H. J. Monkhorst, J. D. Pack, Phys. Rev. B, 1976, 13, 5188–5192.

5 S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.

6 G. Henkelman, B. P. Uberuaga, H. Jonsson, J. Chem. Phys., **2000**, 113, 9901–9904.