

Supporting Information

[Mo₃S₁₃]²⁻ as Bidirectional Cluster Catalysts for High-Performance Li-S Batteries

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Section SI. Experimental Methods

Synthesis of the MCHS. MHCS was prepared according to the previous publication.¹ Tetrapropyl orthosilicate (3.46 mL) was added in ethanol (70 mL) and deionized water (10 mL) with stirring while adding ammonia (3 mL, 25 wt%). Then resorcinol (0.4 g) and formaldehyde (0.56 mL, 37 wt%) were placed in the above solution with stirring for 24h. The achieved $\text{SiO}_2@\text{SiO}_2/\text{RF}$ was collected by deionized water and ethanol for three times. The synthesized $\text{SiO}_2@\text{SiO}_2/\text{RF}$ was calcined for 5h at 800 °C with an Ar atmosphere and finally etched SiO_2 with NaOH.

Preparation of $\text{S}@\text{MCHS}@\text{Mo}_3\text{S}_{13}$. The synthesized MHCS (30 mg) was added in ammonium polysulfide solution (6 ml, 25 wt%, Acros Organics) under an N_2 atmosphere. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (180 mg) was added into the water at room temperature, then the mixed solution was added to the above solution and heated to 90 °C for 24 hours. The products were collected by filtration, washed by water, carbon disulfide, diethyl ether and dried in a vacuum oven at 130 °C.² The synthesized $\text{MCHS}@\text{Mo}_3\text{S}_{13}$ were mixed with sublimed sulfur in the mass ratio of 3:7 and heated to 155 °C for 20 hours.¹

Lithium polysulfides adsorption study. Li_2S_4 solution was prepared by mixing Li_2S and S with a mole ratio of 1: 3 (184, 384 mg) adding in 100 mL of DME solution with continuous stirring.³ 0.5 mL of Li_2S_4 solution, 9.5 mL of DME and 50 mg of $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13}$ materials were added to a dilute Li_2S_4 solution with stirring for 30 min.³

Oxidation of Lithium Sulfide Test. Li_2S (5 mg) was added into DME (10 mL) solvent. Then 10 mg of $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13}$ was also added to the Li_2S reaction mixture with stirring for 20 min.⁴

Materials characterization. The structure of the sample was investigated by Powder X-ray diffraction (PXRD) (WAXD, D8 Advance, Bruker, $\text{Cu K}\alpha$, $\lambda = 1.54 \text{ \AA}$). Thermogravimetric Analysis (TGA, Netzsch TG209 F3) measurements were collected with a $10 \text{ }^\circ\text{C min}^{-1}$ from room temperature to 800 °C under N_2 flow. Scanning electron microscopy (SEM, Zeiss Supra-55VP) and transmission Electron

Microscopy (TEM, Philips TECNAI-12) was used to characterize the external morphology. An X-ray photoelectron spectrometer (XPS, Thermo Escalab 250 system) was used to analyze the elemental chemical status of the sample with Al $K\alpha$ radiation ($h\nu = 1486.6$ eV) and the chamber pressure was kept below 2×10^{-9} Torr. Ultraviolet-visible absorption spectra (UV/vis, Shimadzu UVmini-1280 spectrophotometer) was used to analyze the elemental chemical status of the sample.

Computational methods. All the computational studies of the $[\text{Mo}_3\text{S}_{13}]^{2-}$ clusters and Li_2S_x ($x=2, 4$ and 6) systems were performed using the Gaussian 09 package. All the $[\text{Mo}_3\text{S}_{13}]^{2-}$ clusters and Li_2S_x molecules were optimized by the density functional theory (DFT). Hybrid functional m06-2x was employed with the 6-31g(d) basis set for Li, O, and S elements, and SDD pseudopotential basis set for Mo element.^{5,6} The binding energy (E_b) was calculated as $E_b = E(\text{Mo}_3\text{S}_{13}\text{-Li}_2\text{S}_x) - E(\text{Li}_2\text{S}_x) - E(\text{Mo}_3\text{S}_{13})$, where $E(\text{Mo}_3\text{S}_{13}\text{-Li}_2\text{S}_x)$ is the energy of Li_2S_x and $[\text{Mo}_3\text{S}_{13}]^{2-}$ interaction system and $E(\text{Li}_2\text{S}_x)$ and $E(\text{Mo}_3\text{S}_{13})$ are the energies of the free Li_2S_x and $[\text{Mo}_3\text{S}_{13}]^{2-}$ cluster, respectively.

Li-S Cell Assembly and Electrochemical measurements. The working electrode was prepared by mixing 70 wt% of the designated sample, 20 wt% of Super P Li (TIMCAL), and 10 wt% of binder polyvinylidene fluoride (PVDF HSV900) in N-methylpyrrolidone (NMP) slurry onto a carbon paper (GDL 28 AA, SGL) current collector. Then electrode was dried in a vacuum drying oven at 60 °C for 12 h and cut into a disc with a diameter of 16 mm. The average sulfur loading on each electrode disk is about ~ 1.5 mg/cm² with an electrolyte-to-sulfur (E/S) ratio of ~ 16 mL g⁻¹ and ~ 8 mL g⁻¹. For comparison, a thick cathode with about ~ 3.6 mg cm⁻² sulfur loading was prepared with an electrolyte-to-sulfur (E/S) ratio of ~ 8 mL g⁻¹ in the same manner. The 2032-type coin-cells were assembled in an argon-filled glove box with a microporous membrane (Celgard 2300) as separator and Li metal as the counter electrode. The electrolyte was 1 M Lithium bis(trifluoromethylsulphonyl)imide (LiTFSI) in a mixture of 1,3-dioxolane (DOL) and dimethoxymethane (DME) (1:1 by volume) with 1 wt% LiNO₃ as an additive.

Pouch cell based on S@MCHS@Mo₃S₁₃/ cathode (S loading of 4.0 mg • cm⁻², S mass of 96 mg) with a size of 4.3 cm × 5.6 cm was assembled with two doublesided cathodes and a celgard 2300 separator. The cell was vacuum-sealed in an aluminum-plastic package after injecting electrolyte. The amount of the electrolyte was strictly controlled with an electrolyte-to-sulfur (E/S) ratio of ~12 mL g⁻¹. The discharge/charge cycles and galvanostatic intermittent titration technique (GITT) were tested galvanostatically on a battery measurement system (Neware) at room temperature in a voltage cut off protocol between 2.8 and 1.7 V. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and potentiostat intermittent titration technique (PITT) were measured on an electrochemical workstation (1010 E, Gamary, America). EIS was tested with an amplitude of 5 mV in a frequency range from 10 kHz to 10 mHz at open-circuit potential and CV was performed in the potential range of 2.8-1.7 V at a scan rate of 0.05 mV s⁻¹.

Section SII. Supplementary Figures and Table.

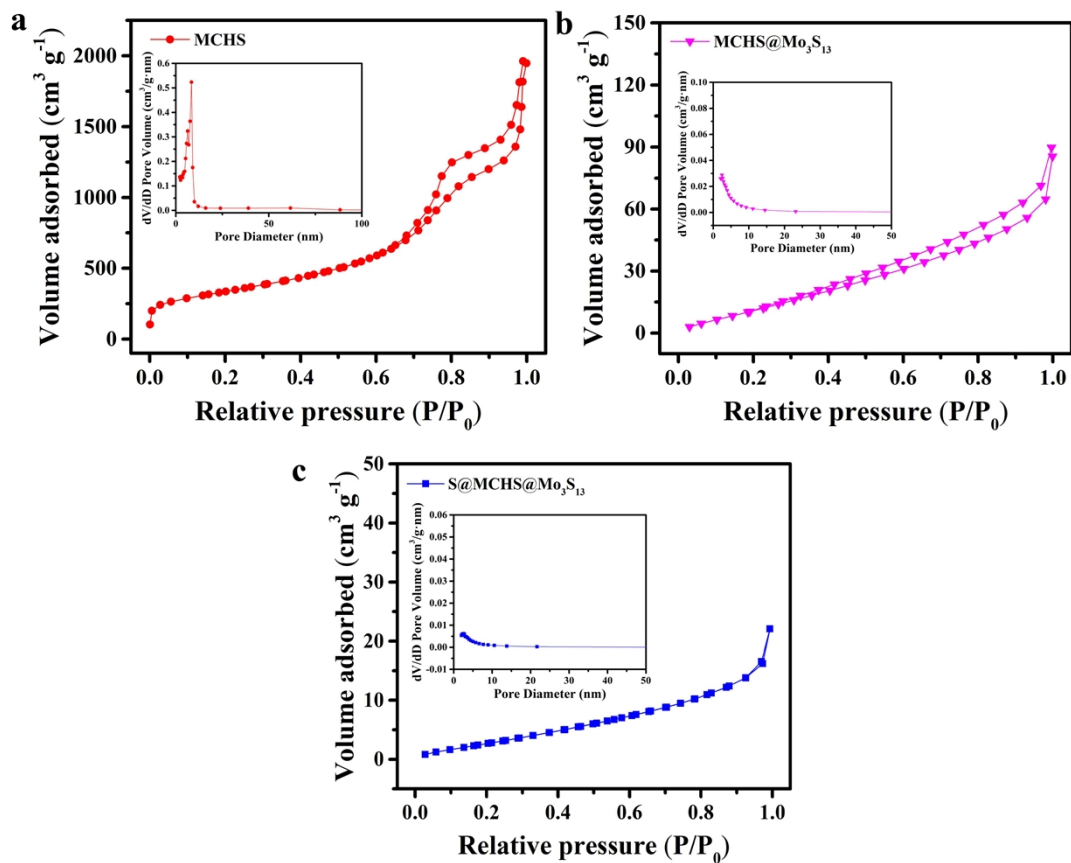


Figure S1. N_2 adsorption-desorption isotherms and corresponding pore size distribution curves for (a) MCHS, (b) MCHS@Mo₃S₁₃ and (c) S@MCHS@Mo₃S₁₃.

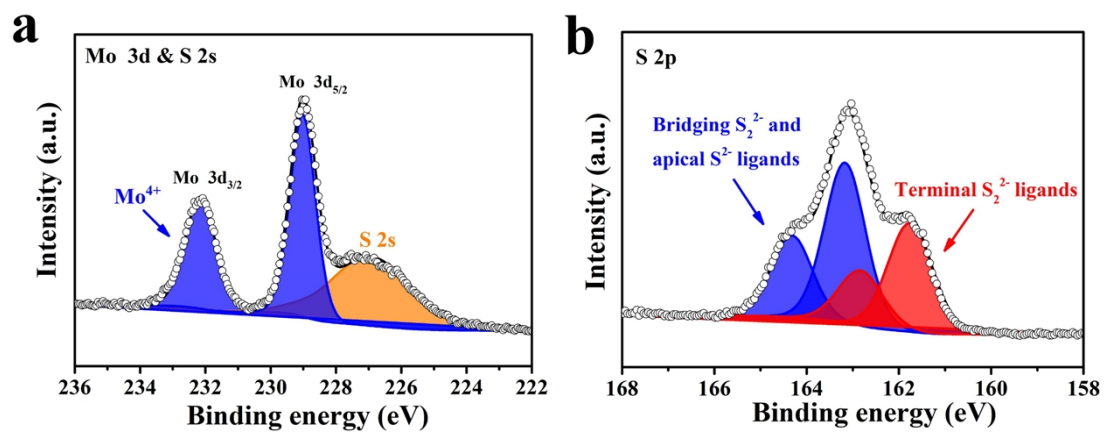


Figure S2. XPS survey spectrum of the as-prepared MCHS@Mo₃S₁₃ composite.

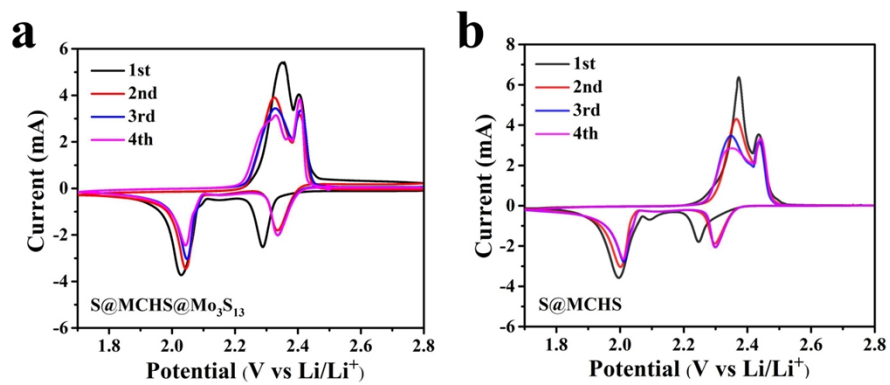


Figure S3. CV curves of (a) S@MCHS@Mo₃S₁₃ and (b) S@MCHS composite at a scanning rate of 0.05 mV·s⁻¹.

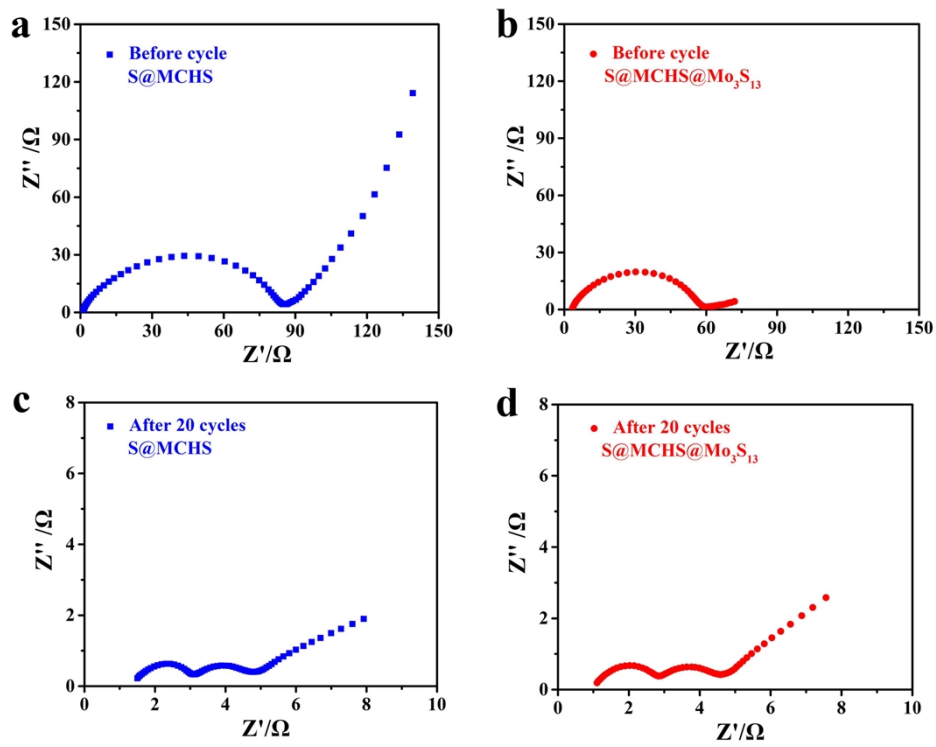


Figure S4. Nyquist plots of S@MCHS and S@MCHS@Mo₃S₁₃ composite before and after 20 cycles.

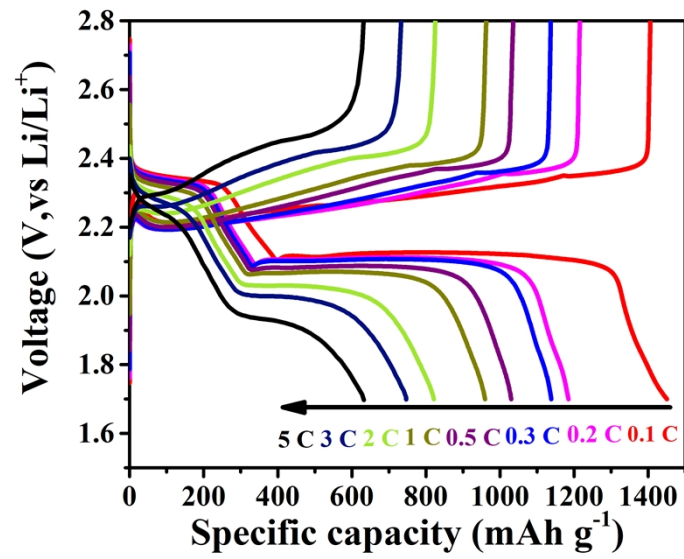


Figure S5. Galvanostatic charge/discharge curves of S@MCHS@Mo₃S₁₃ cathode at different current rates.

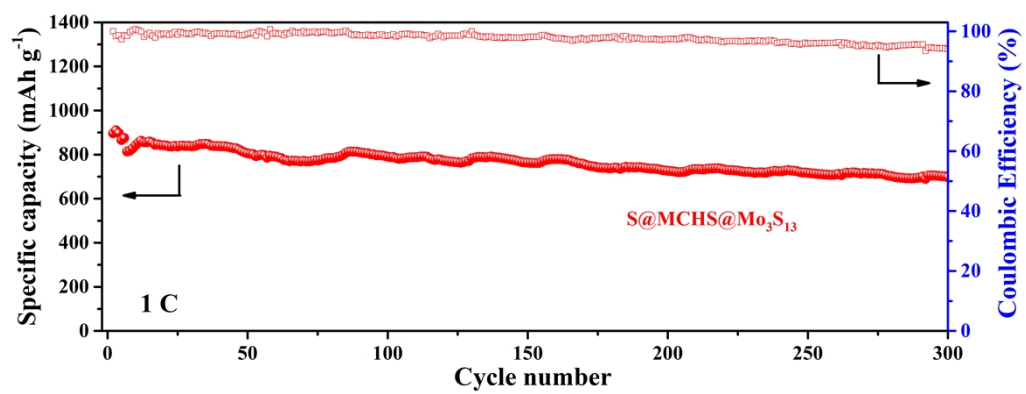


Figure S6. Cycling performance of S@MCHS@Mo₃S₁₃ cathodes and S cathodes at 1.0 C under low electrolyte to sulfur ratio of 8 mL g⁻¹.

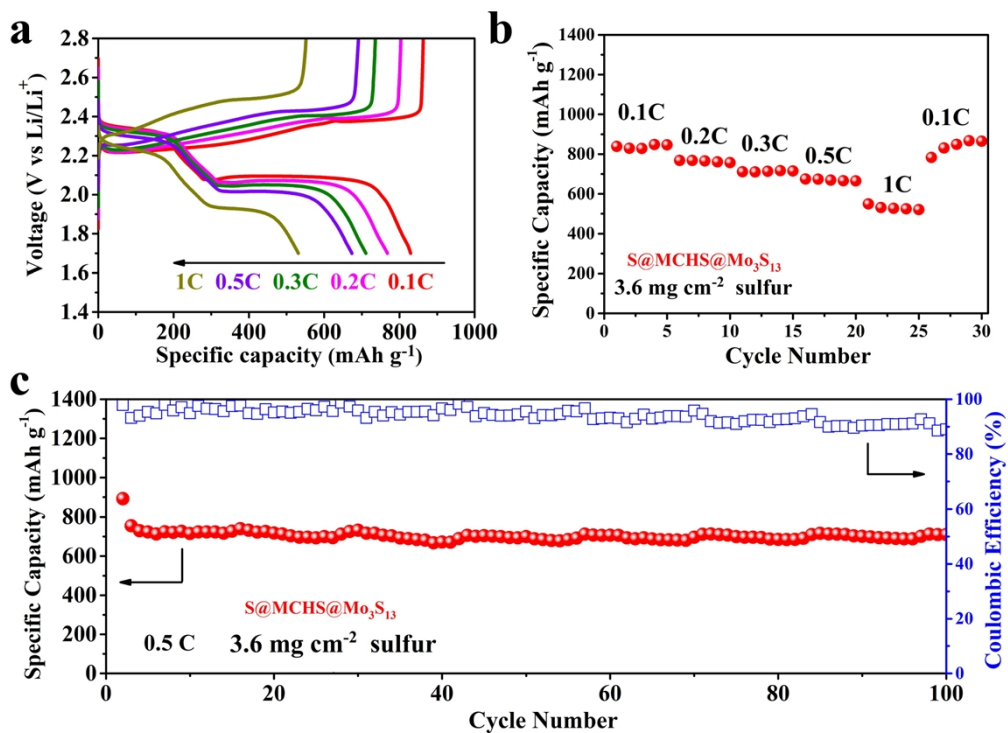


Figure S7. The electrochemical performance of S@MCHS@Mo₃S₁₃ cathodes with high S sulfur loading of 3.6 mg cm⁻² under low electrolyte to sulfur ratio of 8 mL g⁻¹. (a) GCD curves of S@MCHS@Mo₃S₁₃ cathode, (b) Rate performance of S@MCHS@Mo₃S₁₃ cathode, (c) Cycling performance of S@MCHS@Mo₃S₁₃ cathode at 0.5 C.

Table S1. A summary of representative MoS_x-based cathodes.

Cathode Material ^[a]	Maximum Initial Capacity (mAh g ⁻¹)	Highest Rate (C)	Cycle Number (cycles)	Capacity Retention at Highest Rate (mAh g ⁻¹)	Ref.
N-doped graphene/MoS ₂ /sulfur	1280	0.3	180	591	7
NMCS/MoS ₂ /sulfur	1250	1	500	480	8
MoS ₂ /Li ₂ S	1000	0.5	150	488	9
Graphene/MoS ₂ /S	1180	1	500	368	10
PEO/MoS ₂ /Graphene/sulfur	1250	1	200	524	11
Mo ₆ S ₈ /sulfur	1380	1	400	728	12
1T-MoS ₂ /Li ₂ S	1410	0.5	500	450	13
MoS ₃	1000	0.45 A/g	1000	600	14
S@MCHS@Mo₃S₁₃	1450	3	500	546	This work

^[a] NMCS = N-doped mesoporous carbon sphere, PEO = poly(ethylene oxide).

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