Supporting Information

Bidirectional Catalyst Design for Lithium-Sulfur Batteries: Phase Regulation Cooperates with N-Doping

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Experimental Section

1. Synthesis of MoS_2@CNTs: Before the preparation of MoS_2@CNTs, purchased CNTs were first activated by hydrothermal treatment with concentrated nitric acid at 90 ℃ to obtain better hydrophilicity. And the ultrathin MoS_2 nanoflakes anchored CNTs was synthetic by a hydrothermal method. In a typical preparation, 40 mg of CNTs were dispersed into 40 mL of deionized water, and 0.4 g of glucose was added to the above solution stirred for 30 minutes until dissolved. 0.4 g of sodium molybdatate dihydrate ($Na_2MoO_4{\cdot}2H_2O$) and 0.8 g of thiourea were added to the homogeneous solution and stirred for 30 min, respectively. Finally, the reaction liquid was transferred to a 100 mL reactor, sealed, and kept at 200 ℃ for 2 h. Afterwards, the precipitate was collected by centrifugation and cleaned several times with deionized water and ethanol.

2. Preparation of N-MoS_2@CNTs: Firstly, the as-prepared MoS_2@CNTs powder is evenly dispersed on the surface of the quartz plate in a thin layer. Then, the quartz plate loaded with the sample was transferred to the plasma reaction chamber. We chose NH_3 as the nitrogen source and fed it into the system at a fed rate of 25 sccm. The pressure in the reaction chamber was maintained at 10 Pa during the glow discharge process. The power of RF plasma was at 250 W for 30-120 s to control N doping content.

3. Preparation of S/CNTs, S/MoS_2@CNTs and S/N-MoS_2@CNTs: The preparation methods of the S/CNTs, S/MoS_2@CNTs, S/N-MoS_2@CNTs are similar, so we take the

preparation of S/N-MoS_2@CNTs composite as an example. CNT, N-MoS_2@CNTs and S were mixed and ground at a mass ratio of 2:2:6, then encapsulated in a Pasteures-tube, sealed and heated at 155 ℃ for 12 h. The preparation method of S/CNTs and S/MoS_2@CNTs composite positive electrodes is the same as above, except that N-MoS_2 is replaced by responding samples.

4. Materials Characterization: SEM (Hitachi SU8020) was used to the morphology of the samples. TEM (JEOL JEM-2100) equipped with an energy dispersive spectrometer was used to further characterize the morphology and microstructure of the samples. XRD of all samples were performed on the EMPYREAN X-ray diffractometer using Cu Kα radiation from 5° to 80°. XPS spectra were obtained using a PHI 5000Versa Probe system. TGA was conducted on a Perkin-Elmer TGA 7 thermogravimetric analysis. The EPR measurement of vacancies was conducted with an Endor spectrometer (Bruker A300) at 77 K.

5. Electrochemical Measurements:

The prepared sulfur composite cathode (S/CNTs, S/MoS_2@CNTs, S/N-MoS_2@CNTs) was mixed with Super P and PVDF at a mass ratio of 8:1:1 and dispersed in NMP. The homogeneous slurry formed was blade coating onto an aluminum foil and dried at 60 °C for 24 h in a vacuum oven to ensure the complete removal of solvent. The S load on the single electrode is about 1.1-1.35 mg cm^{-2} and the electrolyte was a combination of 1 M lithium bis (trifluoromethane sulfonyl)imide and 2 wt% $LiNO_3$ dissolved in 1,3-dioxolane and 1,2-dimethoxyethane (DOL: DME=1:1, v/v). The E/S is 20 μL/mg. All cyclic performance tests were carried out under this condition except for the performance test of high sulfur load. The E/S under the condition of high sulfur load is 12 μL/mg. The electrochemical tests were performed with coin-type cells (CR2032) constructed with lithium metal foil as the anode. A microporous polypropylene film membrane (Celgard 2325) was used to separate the electrodes. All cells were prepared in an Ar-filled dry box (MBRAUN). The cells were typically cycled at 25 °C at constant currents equivalent to 0.2 C and 1 C rates within the voltage range of 1.8-2.6 V. The rate values in this paper are based on the theoretical capacity of sulfur (1675 mA g^{-1}). The specific capacities were calculated based on the sulfur mass loadings.

6. Preparation of Li_2S_6 Electrolyte: Li_2S and sulfur were mixed at a molar ratio of 1:5 in conventional electrolyte in a glass bottle. The mixture was magnetic stirred for 24 h at 50 °C in an Ar-filled glove box to obtain a Li_2S_6 electrolyte (0.2 M) for the symmetric cell characterizations. In addition, Li_2S_6 electrolyte (5×10^{-3} M) was prepared through the same method for the adsorption test.

7. Preparation of Li_2S_8 Electrolyte: Li_2S and sulfur were mixed at a molar ratio of 1:7 in

tetraglyme solution. The mixture was magnetically stirred for 24 h at 50 °C in an Ar-filled glove box to obtain a Li_2S_8 electrolyte (0.25 M) for the symmetric cell characterizations.

8. Symmetric Cells Assembly and Performance Measurement: The electrodes for symmetric cells were prepared by mixing actively materials and PVDF binder at a weight ratio of 9:1 in NMP to obtained slurry, which was then coated on carbon cloth with a mass loading of 1.2 mg cm^{-2}. The punched electrode disks (12 mm) were used as identical working and counter electrodes to assemble symmetric cells with Li_2S_6 electrolyte (40 μL). The CV curves were measured on electrochemical workstation (Chenhua CHI-660e) at a scanning rate of 0.5 mV s^{-1} from -1.5 to 1.5 V.

9. Theoretical Calculation:

All the calculations were carried out via the plane projector augmented wave based density functional theory (DFT) method on CASTEP code in Material Studio package of Accelrys Inc. The Perdew-Burke-Ernzerhof (PBE) of generalized gradient approximation (GGA) were adopted for the electron exchange and correlation energy with the ultrasoft pseudo-potentials (US) for the core electrons. The MoS_2 and N-MoS_2 (002) surface were set with periodic 1.3 layer slab and a vacuum width of 15 Å between the slabs along the Z axis. A cutoff energy of 350 eV for plane-wave basis set was adopted f electron wave description. The Brillouin zone was sampled by $3 \times 3 \times 1$ k-points grid with Monkhorst-Pack mesh method for surface calculation and the self-consistent field (SCF) tolerance was 1×10^{-5} eV/atom for energy convergence criterion and 0.03 eV/Å for force convergence criterion. The polysulfide adsorption energy E_{ad} is calculated by $E_{ad} = E_{Li_2S_x/surf} - E_{Li_2S_x} - E_{surf}$, where $E_{Li_2S_x/surf}$ and E_{surf} are the total energies of the surface with and without the polysulfide adsorbate and $E_{Li_2S_x}$ is the total energy of a free polysulfide molecule.

Figure Captions

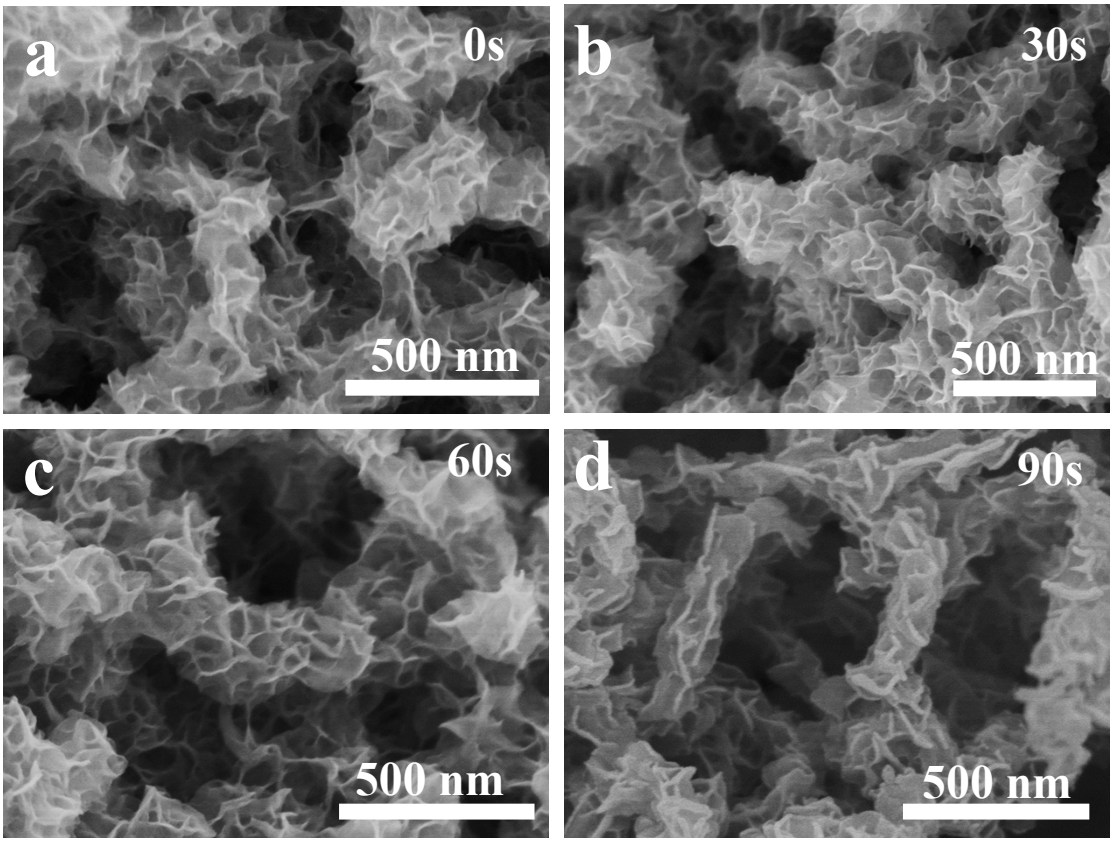

Figure S1. SEM images of a) N-MoS_2@CNTs-0s; b) N-MoS_2@CNTs-30s; c) N-MoS_2@CNTs-60s; d) N-MoS_2@CNTs-90s.

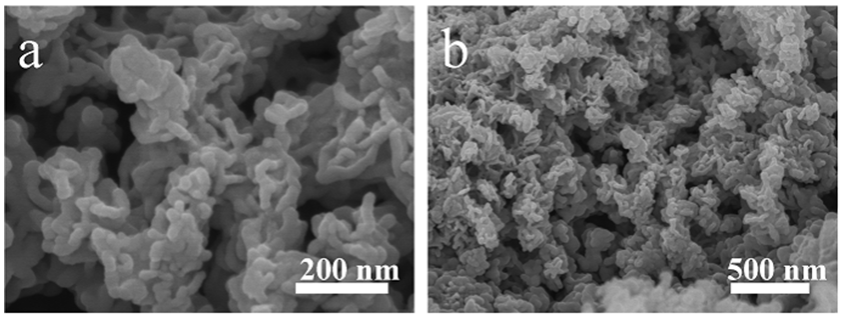

Figure S2. SEM images of S/N-MoS_2@CNTs-60s.

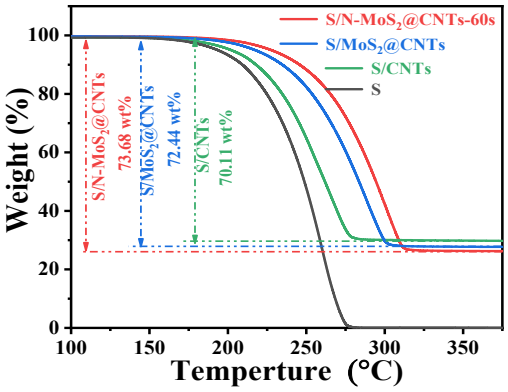

Figure S3. TGA curves of different samples.

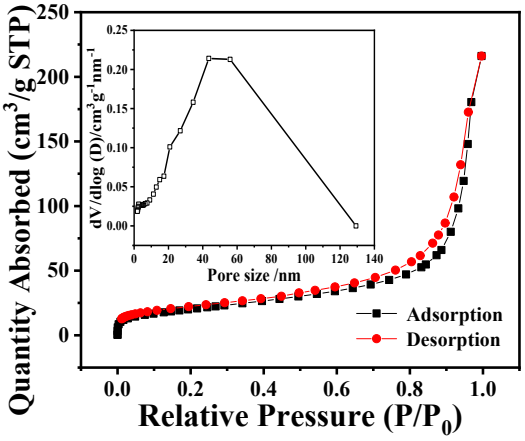

Figure S4. Nitrogen adsorption–desorption isotherm curves of N-MoS_2@CNTs, the inset shows their pore-size distribution curves.

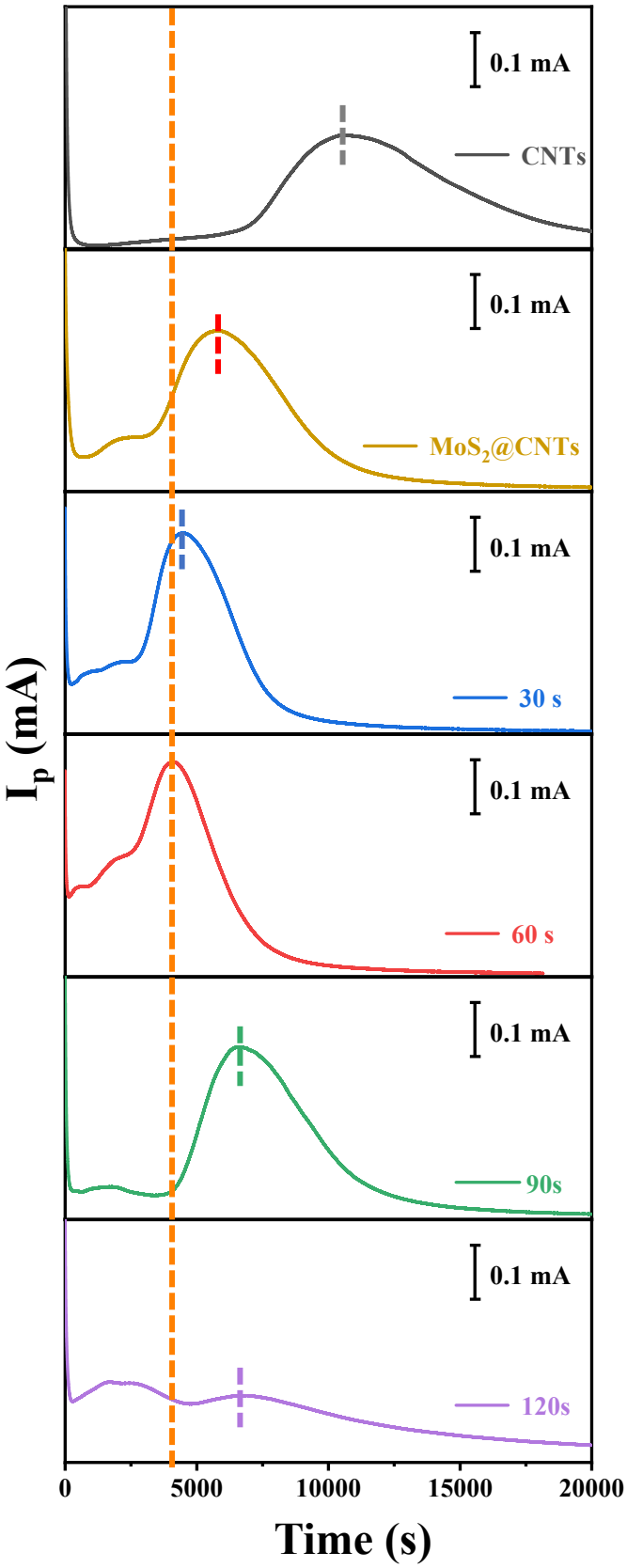

Figure S5. Potentiostatic discharge profiles of a Li_2S_8/tetraglyme solution on various surfaces at 2.05 V.

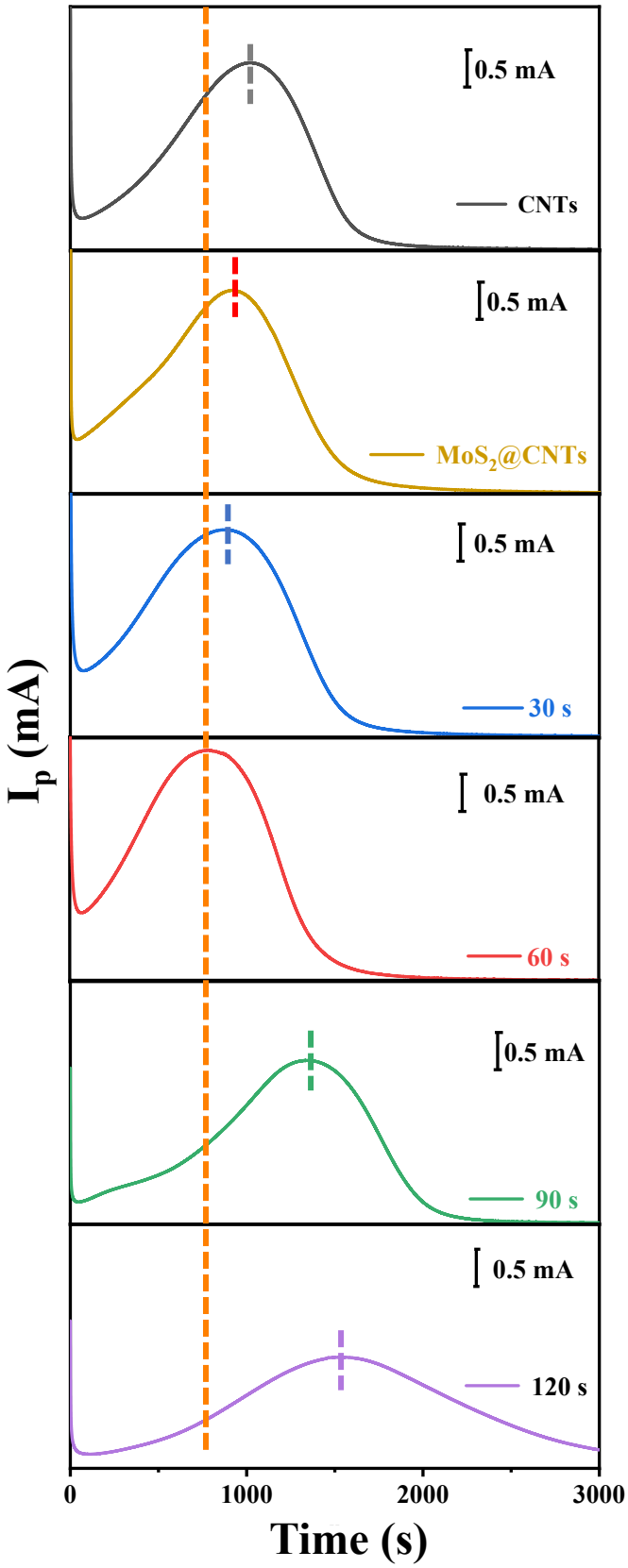

Figure S6. Potentiostatic charge profiles of a Li_2S_8/tetraglyme solution on various surfaces at 2.4 V.

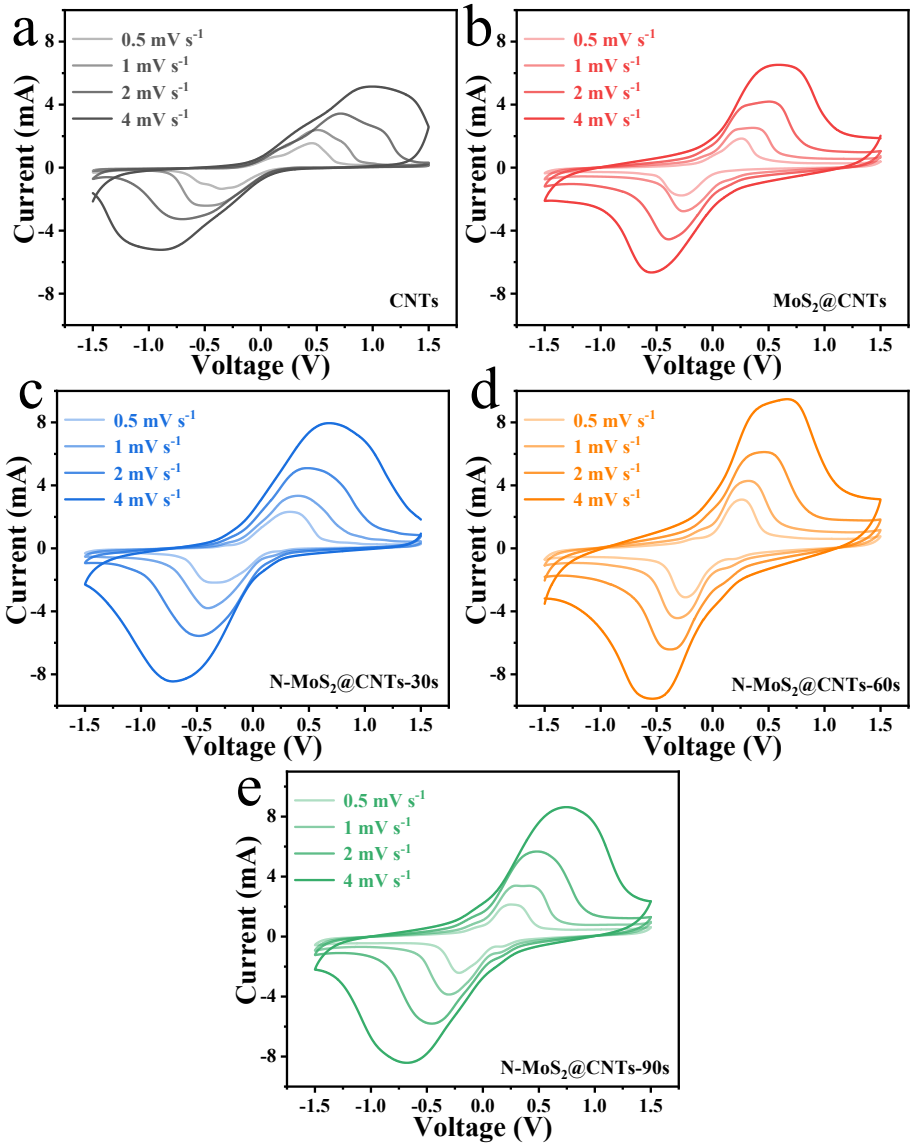

Figure S7. CV curves at different scan rates of different samples.

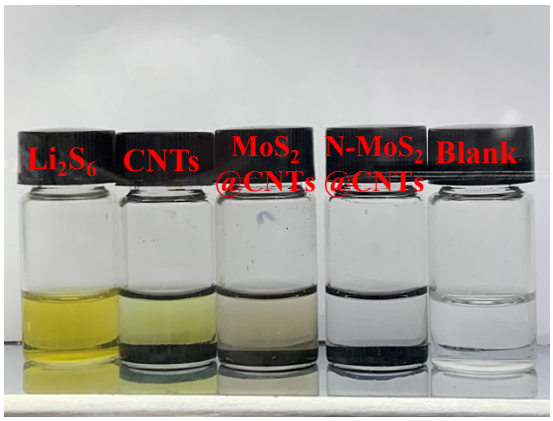

Figure S8. Digital photo of Li_2S_6 adsorption test.

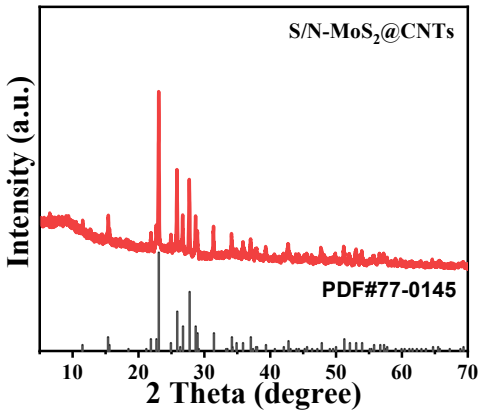

Figure S9. XRD curve of S/N-MoS_2@CNTs.

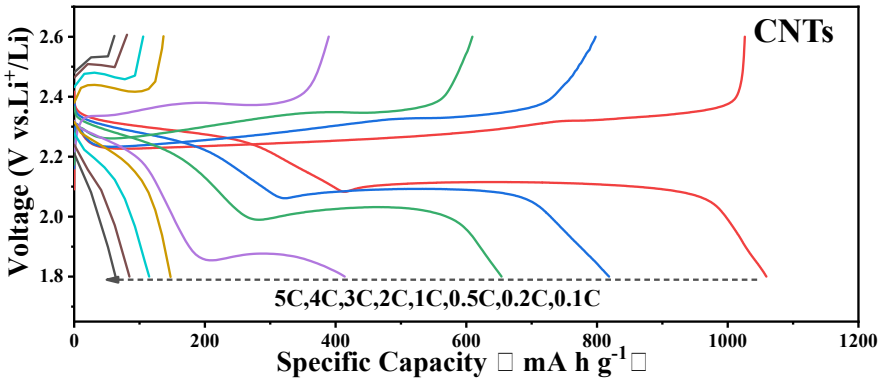

Figure S10. Charge/discharge curves of S/CNTs at various C-rates (0.1 C to 5 C).

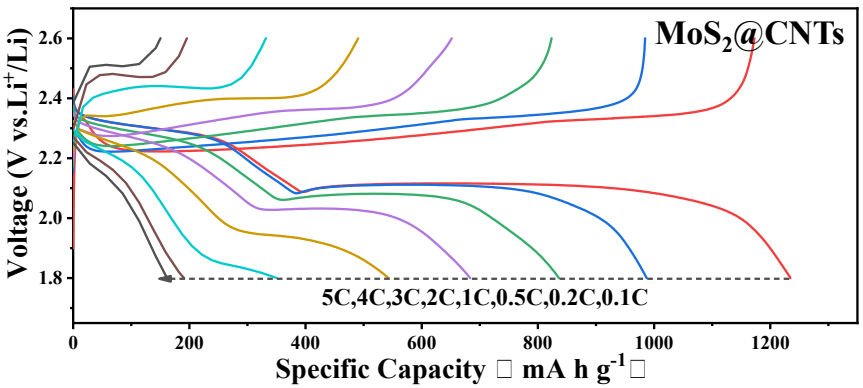

Figure S11. Charge/discharge curves of MoS_2@CNTs at 0.1 C to 5 C.

Table S1. Performance comparison of N-MoS_2/CNTs composite with other MoS_2 based materials in literatures.

Sample	S loading (mg cm^{-2})	S content (wt.%)	Current density	Initial discharge capacity (mAh/g) Cycle Number Capacity decay rate			[ref.]
MoS_2 coated separator	——	65	0.5C	808	600	0.083%	[1]

Thin layered MoS_2 coated on separator	4	70	0.5C	983	150	0.34%	[2]
MoS_2/g-C_3N_4 as sulfur host	1.5	59.1	1C	780	400	0.067%	[3]
rGO/MoS_2 coated separator	1.8-2	70	0.2C	1121	200	0.2%	[4]
rGO/MoS_2 as sulfur host	0.85	80	1C	873	300	0.15%	[5]
CC@MoS_2 as sulfur host	2	——	0.5C	898	300	0.074%	[6]
P-$Mo_{0.9}Co_{0.1}S_2$ as sulfur host	2	80	0.5C	1332	150	0.072%	[7]
MoS_2/Graphene as interlayer	0.8–1.2	60	0.5 A g^{-1}	850	200	0.094%	[8]
MoS_2@G-PCNFs as sulfur host	1	——	0.1	1385	100	0.38%	[9]
N-MoS_2@CNTs as sulfur host	**1.1 1.1 5.1**	**73.68**	**0.1C 1C 0.1C**	**1313.6 804 970.4**	**200 1000 100**	**0.13% 0.047% 1.01%**	**This work**

References

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