

Supporting information

MOF derived MoP nanorods decorated N-doped thin carbon layer as robust lithiophilicity and sulfiphilicity nanoreactor for high-performance Li-S batteries

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Experimental

Fabrication of porous carbon nanofibers (PCNFs)

Polyvinylpyrrolidone K90 powder (PVP K90) with a degree of alcoholysis of about 88% and a molecular weight range of 60000-100000 was selected as the carbon precursor. The 2 g PVP powder was dissolved in 8 g distilled water at room temperature to form a solution with 20wt% concentration. The above solution was mixed with 25 g of a polytetrafluoroethylene emulsion (PTFE) with a solid content of 60wt%, and stirred for 1 hour to form the spinning solution.

First of all, the spinning solution was injected into an internal needle with a diameter of 1 cm and spun with 0.1 MPa gas pressure and 43 kV voltage of electrostatic field strength. The PVP/PTFE primary nanofiber membrane was collected by a bottom collector due to the dual function of high-speed airflow and electrostatic force. Secondly, the fiber membrane was annealed at 260 °C for 1h with a rate of 2 °C min⁻¹ under air atmosphere to keep the morphology during the carbonization process. After that, the PCNFs were obtained by heating at 1000 °C for an hour with a heating rate of 3 °C min⁻¹ under a continuous N₂ atmosphere. Finally, the chemical binding between PCNFs and sulfur due to the availability of more hydroxyl functional groups can be enhanced through immersing the PCNFs in HNO₃ solution and stirring 24 hours at 60 °C, thus inhibiting the “shuttle effect” of LiPS.

Fabrication of MoP@NC nanorods

The preparation of Mo-MOF is based on previous report¹. Briefly, 3.5 g of MoO₃ and 1.66 g of imidazole were mixed in 250 mL of deionized (DI) water until completely

being dissolved. Then, the mixture was transferred into a 100 mL Teflon-lined autoclave to be treated at 160 °C for 7 h. Finally, the sediment was obtained after washing with deionized water and absolute ethyl alcohol for several times and drying in vacuum oven at 60 °C for 24 h. Other different hydrothermal reactions are obtained for 1 h, 3 h, 5 h and 9 h at 160 °C.

A phosphorization process was conducted to convert Mo-MOF into MoP@NC nanorods². The as-synthesized Mo-MOF nanorods and NaH₂PO₂·H₂O were separately placed in two porcelain boats with a mass ratio of 1:10, and NaH₂PO₂·H₂O was placed upstream. The tube furnace was heated at 700 °C for 2 h under nitrogen flow, with a heating rate of 3°C min⁻¹. After cooling down to ambient temperature, MoP@NC nanorods were obtained.

Preparation of MoP@NC/PCNFs-Modified Separator.

The separators coated with MoP@NC nanorods were prepared by the same method. Briefly, the MoP@NC nanorods, PCNFs and poly(1,1-difluoroethylene) (PVDF) binder were mixed in N-methylpyrrolidinone (NMP) solution at the same ratio with continuously stir over 12 h to form a uniform slurry. Subsequently, the slurry was then coated on Celgard 2340 using a spreader method. Then, the slurry-coated separator was dried in an oven at 60 °C for 24 h under vacuum. Finally, the obtained separator was punched into circular disks with a diameter of 19 mm for battery assembly. The modified separator possesses a 19 mm diameter with the MoP@NC/PCNFs loadings of 0.65~0.70 mg cm⁻².

Structural characterization

The surface morphology and structures of the obtained materials were observed by high-resolution field emission scanning electron microscopy (FE-SEM, Gemini SEM500, Germany). Then, an energy dispersive spectrometer (EDS) affiliated with the Gemini SEM500 was used to provide the element mapping images. The internal morphology and structure of the sample were visualized by transmission electron microscope (TEM, Hitachi H7650, Japan) with 100 keV. A high-resolution transmission electron microscope (HRTEM, JEM-F200, JEOL, Japan) were employed to ascertain the morphologies and microstructures of the samples. The crystal structure was characterized by X-ray diffraction (XRD, BRUKER D8 ADVANCE, Germany). Meanwhile, the surface chemical composition of all samples was characterized by X-ray photoelectron spectroscopy (XPS, Kratos Analytical Ltd., UK). Thermal stability of samples was collected by thermogravimetric analyzer (TG, STA 409, Netzsch, Germany). The Brunauer Emmett-Teller (BET) surface areas of these samples were measured by Micromeritics ASAP-2020 N adsorption apparatus. The liquid electrolyte wettability of all samples was characterized via the Contact Angle Meter (JC2000D, Powereach Co., Ltd., Shanghai, China).

Assembly of the cell

The electrode samples of assembled Li-S batteries were obtained by coating slurry on carbon coated aluminum foil and then drying at 50 °C in a vacuum oven for 12 hours. The slurry consisted of a mixture of CMK-3, CNTs, polyvinylidene fluoride binder and MoS₂ with 8:1:1:1 mass ratio in NMP solvent. The introduction of moderate amount MoS₂ can not only present strong adsorption of LiPSs, but also facile Li⁺

penetration and charges transfer. Moreover, the strong interaction with polysulfide of MoS₂ can suppress the shuttle effect for an improved durability. The electrochemical performance was characterized with assembled CR2340-type coin cells in glove boxes filled with an argon atmosphere including the lithium metal anode, the completed cathode and MoP@NC/PCNFs separator or a Celgard 2340 separator. For each cell, the used electrolyte contained 1 M bis(trifluoromethane), sulfonamide lithium salt and 0.1 M LiNO₃ in a mixture of 1,3-dioxolane and 1,2-dimethoxyethane (volume ratio of 1:1), and the ratio of electrolyte/sulfur was 30 μL mg⁻¹. Symmetrical batteries were assembled in a similar manner for catalysis measure. The CMK-3-MoS₂ cathode as electrode without sulfur, the MoP@NC/PCNFs coated on Celgard 2340 was used as separator and the electrolyte was changed to 2 M Li₂S₈ in DOL / DME (1:1 vol).

Electrochemical measurements

The galvanostatic charge-discharge experiments were carried out using a LAND CT2001A battery-testing system in the voltage range from 1.5 V to 3.0 V. The electrochemical performance of the cathode was also measured by cyclic voltammetry (CV) at a scanning rate of 0.05 mV s⁻¹ and the impedance spectroscopy (EIS) in the frequency range from 100 kHz to 0.01 Hz using a CHI660E electrochemical measurement system. The long-term cycle performance was demonstrated at 0.5 C, 1 C, 2 C and 4 C, and the rate performance was demonstrated at 0.2 C, 0.5 C, 1 C, 2 C, 1 C, 0.5 C and 0.2 C. All experiments were performed at room temperature (25 °C) and at least ten cells were tested. In the same time, the CV tests were managed between -1.0 and 1.0 V versus Li⁺/Li at a scanning rate of 0.05 V s⁻¹ for symmetric batteries.

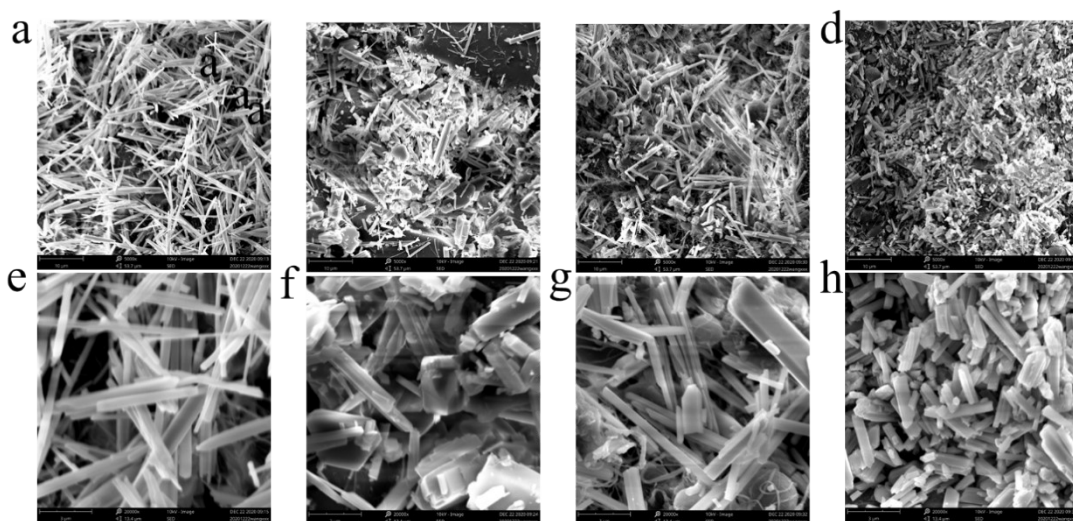


Fig S1 The morphology of MOF at 1h (a, e), 3h (b, f), 5h (c, g), and 9h (d, h) of 140°C.

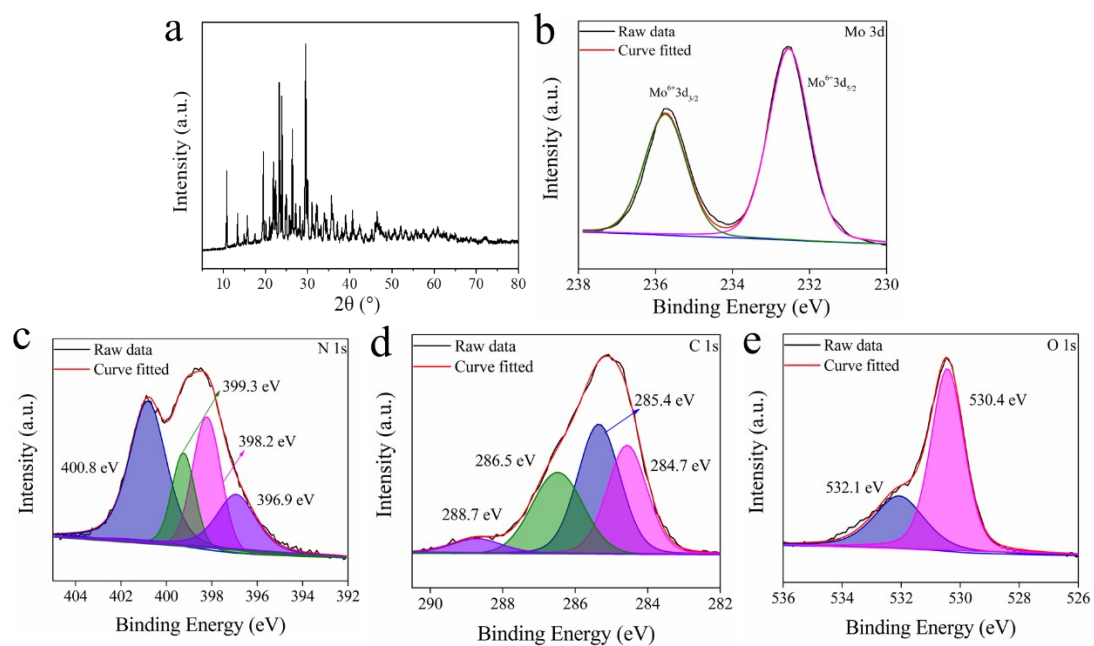


Fig S2 (a)XRD of Mo-MOF at 7h 140 $^\circ\text{C}$; High-resolution spectra of Mo 3d, N 1s, C 1s and O 1s of Mo-MOF at 7h 140 $^\circ\text{C}$.

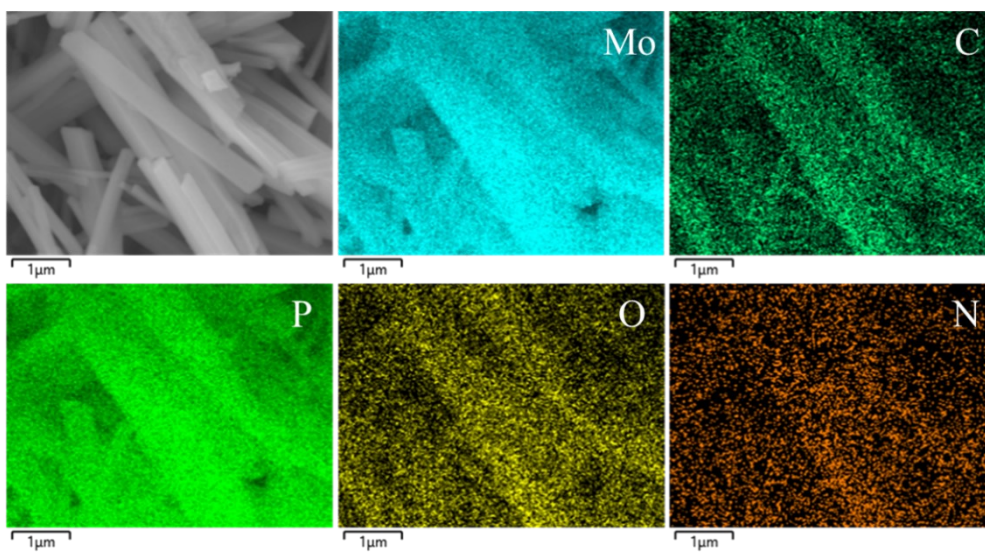


Fig. S3 Mapping of MoP@NC

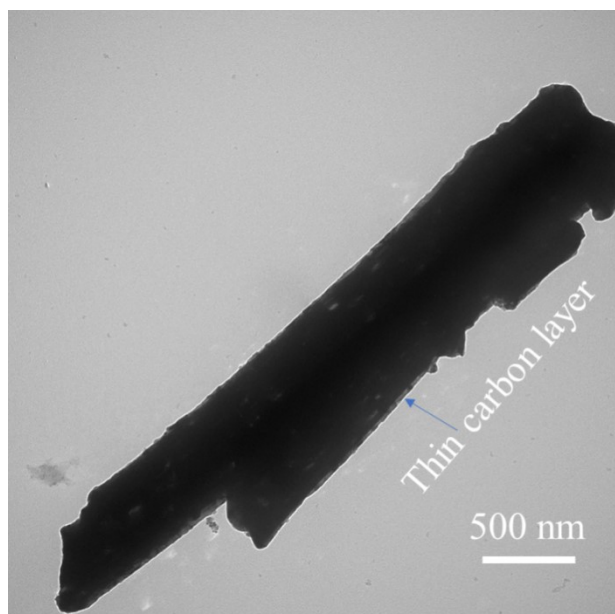


Fig. S4 TEM of MoP@NC

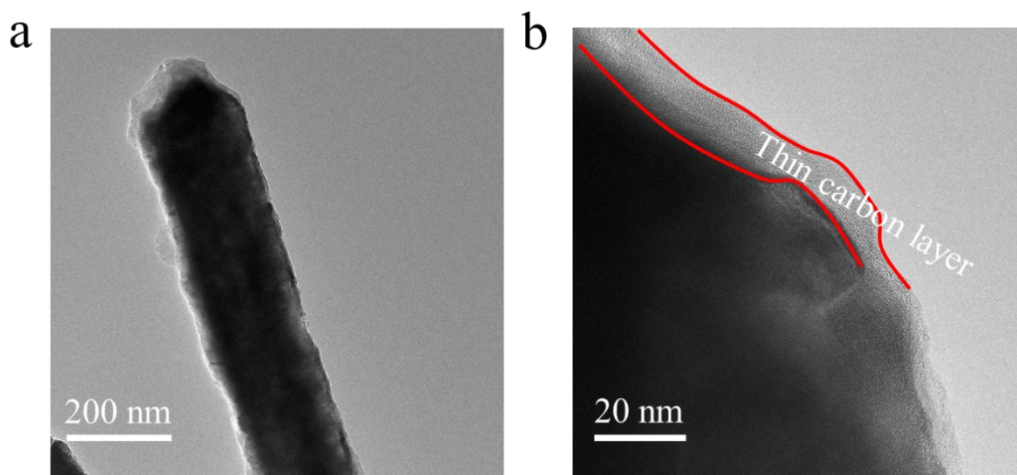


Fig. S5 HRTEM of MoP@NC

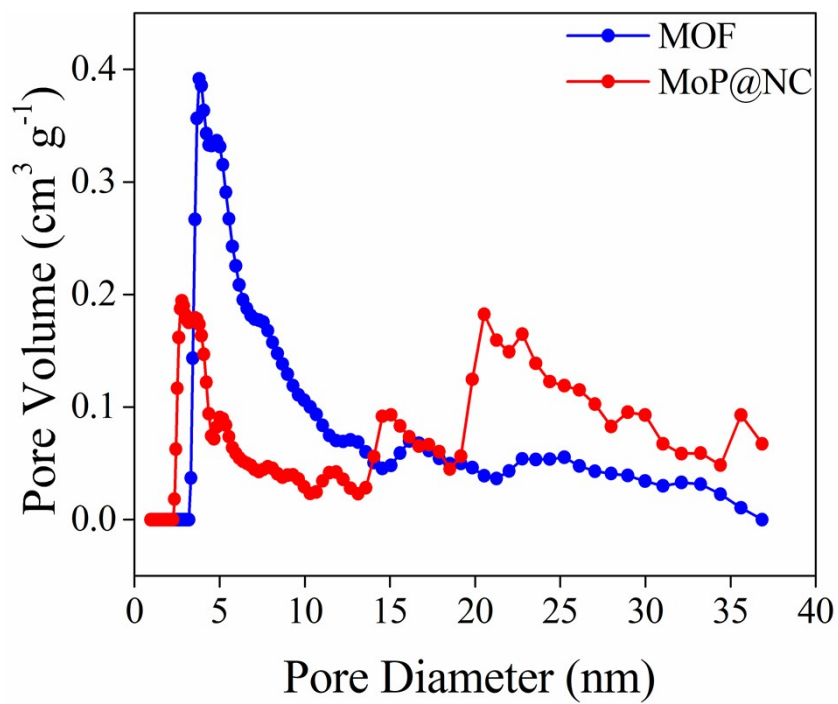


Fig. S6 Pore size distribution of MOF and MOF@NC

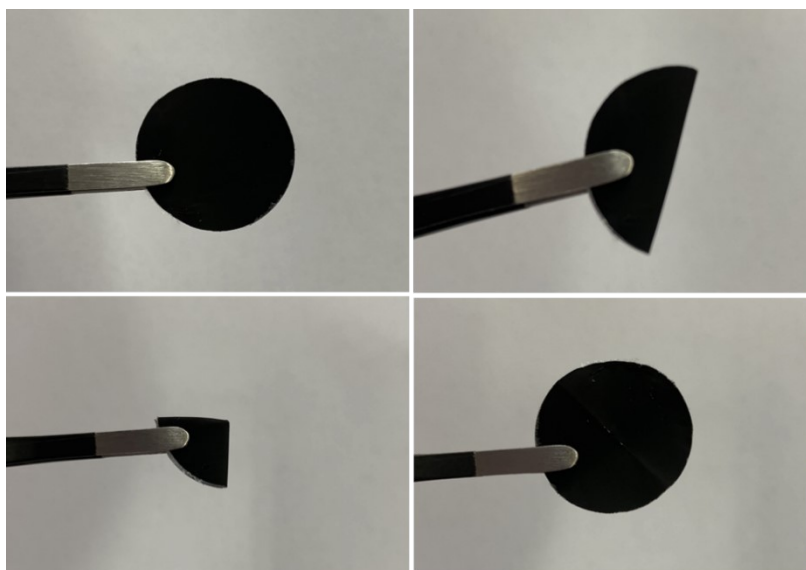


Fig. S7 Digital photograph of MoP@NC/PCNFs modified separator under mechanical stability tests.

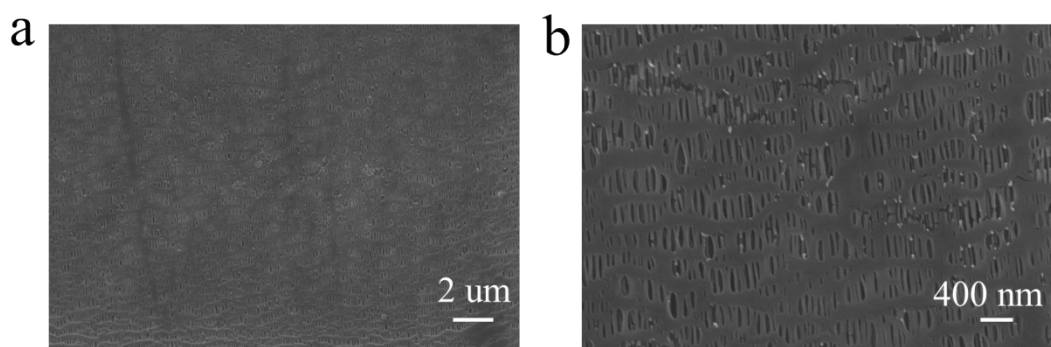


Fig. S8 (a) and (b) SEM of Celgard separator

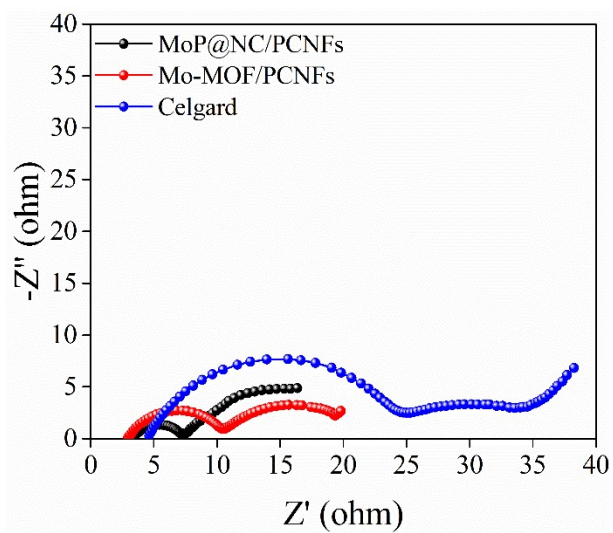


Fig. S9 The EIS curves of batteries with different separators before 400 cycles at 1 C

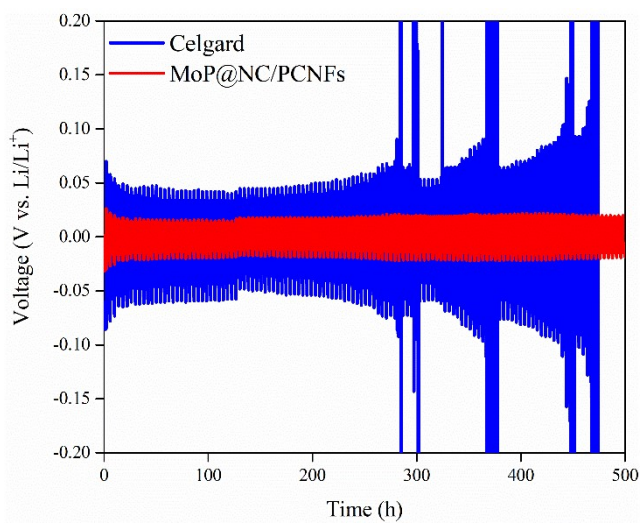


Fig. S10 Voltage versus time of symmetrical batteries assembled with various separators at 0.5 mA cm⁻².

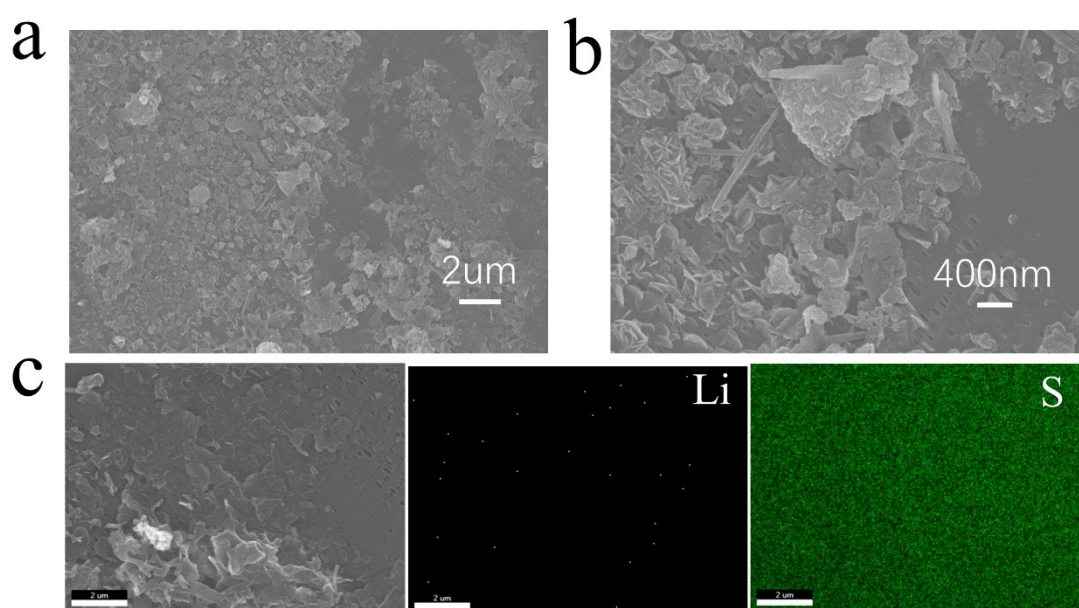


Fig. S11 (a) and (b), SEM and (c) Mapping of Celgard separator after 400 cycles at 1 C.



Fig. S12 Photograph of blank, MoP@NC and Mo-MOF immersed in Li_2S_6 solution after 2 h.

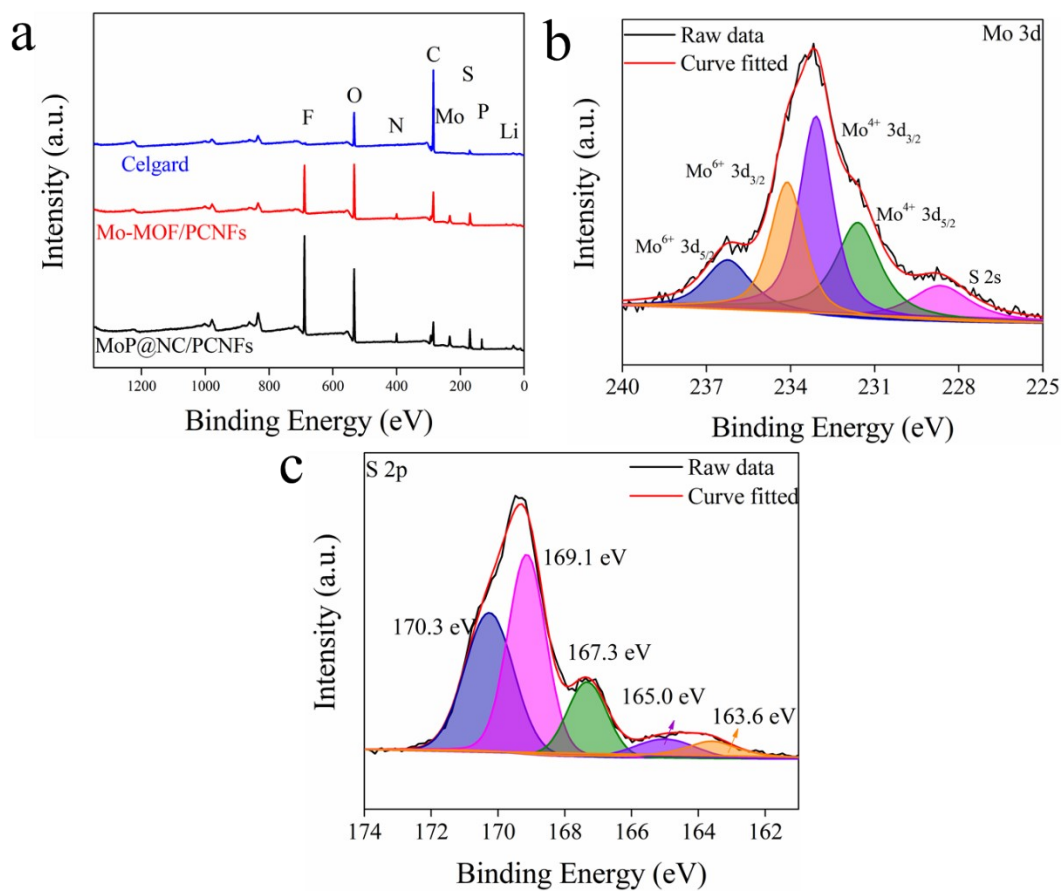


Fig. S13 (a) Full XPS spectra of MoP@NC /PCNFs, Mo-MOF/PCNFs and Celgard separators after 300 cycles at 1 C; (b) and (c), High-resolution spectra of Mo 3d and S 2p of MoP@NC/PCNFs separator after 300 cycles at 1 C

Table. S1 Element content of different separators after 400 cycles at 1C for EDS

	S(%)	Mo(%)	P(%)	C(%)	N(%)	O(%)
MoP@NC/PCNFs	0.17	15.81	15.34	63.51	2.08	2.55
Mo-MOF/PCNFs	30.17	13.63	0	41.74	1.13	11.47
Celgard	74.78	0	0	21.53	0	3.73

References

1. X. Cao, B. Zheng, W. Shi, J. Yang, Z. Fan, Z. Luo, X. Rui, B. Chen, Q. Yan and H. Zhang, *Adv. Mater.*, 2015, **27**, 4695-4701.
2. Y. Jiang, Y. Shen, J. Dong, S. Tan, Q. Wei, F. Xiong, Q. Li, X. Liao, Z. Liu, Q. An and L. Mai, *Adv. Energy Mater.*, 2019, **9**, 1900967.