## **Electronic Supplementary Information**

## Self-assembly of MoO<sub>3</sub>-decorated carbon nanofiber interlayer for high-performance lithium–sulfur batteries

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Fig. S1 SEM images of PAN nanofibers at (a) low and (b) high magnifications.



Fig. S2 SEM images of (a, b) MoO<sub>3</sub>/CNF-1 and (c, d) MoO<sub>3</sub>/CNF-3 membranes.



Fig. S3 SEM images of pure MoO<sub>3</sub> nanorods at (a) low and (b) high magnifications.



**Fig. S4** Electrochemical properties of Li–S batteries with MoO<sub>3</sub>/CNF-1, MoO<sub>3</sub>/CNF-2, and MoO<sub>3</sub>/CNF-3 interlayer. (a) Typical galvanostatic discharge–charge profiles upon the 10th cycle at 0.2 C. (b) Cycling performance at 0.2 C. (c) Cycling performance at 0.5 C. (d) Rate performance. EIS spectra of the cells (e) before cycling and (f) after 500 cycles at 1 C.



Fig. S5 Cycling performance of cells without interlayer, with a CNF or  $MoO_3/CNF-2$  interlayer at 1 C.



**Fig. S6.** Cycling performance of the cell using the MoO<sub>3</sub>/CNF-2 membrane as the cathode and a Li-metal anode.

Fresh Li–S cells	pristine	CNF	MoO <sub>3</sub> /CNF-2
$R_{e}\left(\Omega ight)$	4.10	5.31	7.81
$CPE_{ct}$ (F cm <sup>-2</sup> s <sup>n-1</sup> )	2.51*10 <sup>-5</sup>	3.81*10 <sup>-5</sup>	1.86*10 <sup>-5</sup>
n	0.68	0.68	0.79
$R_{ct}\left(\Omega ight)$	47.38	35.86	35.20

**Table S1.** EIS fitted parameters of fresh Li-S cells without interlayer, with a CNF or  $M_0O_3/CNF-2$  interlayer.

 $R_e$  is the Ohmic resistance of the electrolyte.  $R_{ct}$  stands for the interfacial charge transfer resistance. CPE (constant phase element) denotes the capacitance of the component. n is the CPE exponent. When n = 1, the CPE becomes a pure capacitance. When n < 1, it represents a leaking (non ideal) capacitor.  $CPE_{ct}$  arises from the double-layer capacitance.

Cycled Li-S cells	pristine	CNF	MoO <sub>3</sub> /CNF-2
$R_{e}\left(\Omega ight)$	12.21	9.15	9.12
$CPE_{ct}$ (F cm <sup>-2</sup> s <sup>n-1</sup> )	3.78*10-5	1.25*10-4	1.89*10-4
n	0.76	0.64	0.66
$R_{ct}\left(\Omega ight)$	8.99	8.74	4.68
$CPE_{f} (F \text{ cm}^{-2} \text{ s}^{n-1})$	0.014	0.025	0.030
n	0.46	0.48	0.43
$R_{\mathrm{f}}\left(\Omega ight)$	17.26	5.97	4.17

**Table S2.** EIS fitted parameters of Li–S cells without interlayer, with a CNF or  $M_0O_3/CNF$ -2 interlayer after 500 cycles.

 $R_e$ ,  $R_{ct}$ , and  $R_f$  stand for the Ohmic resistance of the electrolyte, the interfacial charge transfer resistance, and the Li-diffusion resistance in the surface film, respectively.  $CPE_{ct}$  arises from the double-layer capacitance.  $CPE_f$  represents the capacitance on the surface film.



**Fig. S7.** EIS spectra of Li|Li symmetric cells with/without interlayer (a) before and (b) after cycling for 400 h at 0.5 mA cm<sup>-2</sup>, 1 mAh cm<sup>-2</sup>. (c) The equivalent circuit used to simulate EIS curves.

**Table S3.** EIS fitted parameters of fresh symmetric Li|Li cells without interlayer, witha CNF or  $MoO_3/CNF-2$  interlayer.

Fresh Li Li cells	pristine	CNF	MoO <sub>3</sub> /CNF-2
$R_{e}\left(\Omega ight)$	2.79	4.56	3.75
$CPE_{ct} (F \text{ cm}^{-2} \text{ s}^{n-1})$	1.23*10 <sup>-5</sup>	1.87*10 <sup>-5</sup>	1.02*10 <sup>-5</sup>
n	0.74	0.75	0.83
$R_{ct}(\Omega)$	60.96	34.65	35.01
$CPE_{f}(F \text{ cm}^{-2} \text{ s}^{n-1})$	3.19*10-3	4.42*10-3	1.05*10-2
n	0.59	0.54	0.44
$\mathrm{R_{f}}\left(\Omega ight)$	23.80	16.78	13.05

The meaning of each component is mentioned above.

Cycled Li Li cells	pristine	CNF	MoO <sub>3</sub> /CNF-2
$R_{e}\left(\Omega ight)$	4.25	3.89	3.52
$CPE_{ct}$ (F cm <sup>-2</sup> s <sup>n-1</sup> )	7.15*10 <sup>-5</sup>	1.71*10-4	1.18*10-4
n	0.83	0.78	0.85
$R_{ct}(\Omega)$	2.92	2.69	1.44
$CPE_{f}(F \text{ cm}^{-2} \text{ s}^{n-1})$	0.089	0.19	0.17
n	0.59	0.60	0.57
$ m R_{f}(\Omega)$	4.16	4.07	2.23

**Table S4.** EIS fitted parameters of cycled symmetric Li|Li cells without interlayer,with a CNF or  $MoO_3/CNF-2$  interlayer.

The meaning of each component is mentioned above.