# Supporting Information

# MoO<sub>3</sub>/MoO<sub>2</sub>-CP Self-Supporting Heterostructure for Modification of Lithium-Sulfur Batteries

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# Experimental

## Synthesis of the MoO<sub>3</sub>-CP Composite

The MoO<sub>3</sub>-CP composite was obtained by a one-step hydrothermal reaction. Firstly, 0.125 g of molybdenum powder (Aladdin, 99.9 %) was added to 30 mL of deionized (DI) water, and then 6.25 mL  $H_2O_2$  (Aladdin, AR, 30 %) was dripped to the solution slowly. When the color of the solution completely turns yellow, one piece of carbon paper (CP) was added into the solution. Finally, the solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 12 h. When the temperature of the autoclave is cooled to room temperature, the MoO<sub>3</sub>-CP composite was washed with DI water and ethanol for three times, respectively. The prepared samples were dried at 40 °C for 60 min.

## Synthesis of the MoO<sub>3</sub>/MoO<sub>2</sub>-CP and MoO<sub>2</sub>-CP composite

The NH<sub>3</sub> atmosphere treatment was applied to deal with the MoO<sub>3</sub>-CP to obtain the desired composite. The MoO<sub>3</sub>/MoO<sub>2</sub>-CP composite was achieved by thermal reduction of MoO<sub>3</sub>-CP at 400  $^{\circ}$ C for 1 h in an NH<sub>3</sub> atmosphere with a flow of 20 sccm. MoO<sub>2</sub>-CP can be obtained in the same way while the sintering temperature is changed to 500  $^{\circ}$ C.

# Preparation of Li<sub>2</sub>S<sub>8</sub>

0.0688 g Li<sub>2</sub>S and 0.3366 g S were mixed with 5 mL electrolyte composed of 1 M LiTFSI in a mixture of 1,3-dioxolane (DOL) and dimethoxymethane (DME) (v/v = 1:1) with 1 % LiNO<sub>3</sub>. The mixture was stirred at 60 °C for 24 h to obtain a homogeneous dispersion of Li<sub>2</sub>S<sub>8</sub>. The synthesized Li<sub>2</sub>S<sub>8</sub> was added dropwise to the surface of MoO<sub>3</sub>-

CP,  $MoO_3/MoO_2$ -CP and  $MoO_2$ -CP as a positive electrode, respectively, and labeled as  $MoO_3$ -CP-Li<sub>2</sub>S<sub>8</sub>,  $MoO_3/MoO_2$ -CP-Li<sub>2</sub>S<sub>8</sub> and  $MoO_2$ -CP-Li<sub>2</sub>S<sub>8</sub>. The whole process was performed in an Ar-filed glove box while the moisture and oxygen levels were both less than 0.1 ppm.

#### Material characterization

XRD measurements were performed on X-ray diffractometer (Rigaku D/max2500PC) equipped with Cu K $\alpha$  radiation ( $\lambda$ =0.15405 nm). SEM images were observed by Hitachi SU8020 field emission scanning electron microscop. TEM, HRTEM and EDX were performed under the JEOL JEM-2100F. Raman spectroscopies (Renishaw inVia) of samples were tested at Horiba Jobin-Yvon LabRAM Aramis Raman microscopy. UV optical absorption spectra was characterized by Lambda 35 (Perkin Elmer, USA) UV– vis spectrophotometer. XPS measurements were conducted on a ESCALAB 250Xi instrument.

#### **Electrochemical measurements**

The electrochemical performances were investigated by a standard CR2025 coin cell using lithium foil as the anode, a microporous polypropylene separator (Celgard 2400) as the separator, and the electrolyte was composed of 1 M LiTFSI in a mixture of 1,3-dioxolane (DOL) and dimethoxymethane (DME) (v/v = 1:1) with 1% LiNO<sub>3</sub>. The amount of electrolyte is about 40  $\mu$ L for each cell. The synthesized Li<sub>2</sub>S<sub>8</sub> (1 mg) was added dropwise to the surface of MoO<sub>3</sub>-CP (MoO<sub>3</sub> ~0.5 mg), MoO<sub>3</sub>/MoO<sub>2</sub>-CP (MoO<sub>3</sub> ~0.5 mg) and MoO<sub>2</sub>-CP (MoO<sub>2</sub> ~ 0.5 mg) as the cathode, respectively, and labeled as MoO<sub>3</sub>-CP-Li<sub>2</sub>S<sub>8</sub>, MoO<sub>3</sub>/MoO<sub>2</sub>-CP-Li<sub>2</sub>S<sub>8</sub> and MoO<sub>2</sub>-CP-Li<sub>2</sub>S<sub>8</sub>. The areal

density of MoO<sub>3</sub>/MoO<sub>2</sub> on the CP is 0.32 mg cm<sup>-2</sup> ( $\Phi_{CP}$ =1.4 cm). Galvanostatic charge/discharge behavior were measured by Land CT2001A cell test system at different current densities from 0.05 to 5 C (1 C = 1675 mA g<sup>-1</sup>) between 2.8 and 1.8 V versus Li<sup>+</sup>/Li at 25 °C. CV was investigated by using CHI760E electrochemical workstation at a scanning rate of 0.05 mV·s<sup>-1</sup> within the range of 1.8 to 2.8 V at 25 °C. Electrochemical impedance spectroscopy (EIS) was performed at various overpotentials with frequency from 0.01 to 10<sup>5</sup> Hz with an AC voltage of 5 mV.

### **Density functional theory calculations**

All the spin-polarized DFT-D2 calculations<sup>1</sup> were conducted using the "Vienna *ab initio* simulation package" (VASP 5.4.1),<sup>2,3</sup> applying the generalized gradient correlation functional.<sup>4</sup> A plane-wave basis set with cut-off energy 400 eV within the framework of the projector-augmented wave method was employed.<sup>5</sup> The Gaussian smearing width was set to 0.2 eV. The Brillouin zone was sampled with a  $3 \times 3 \times 1$  Monkhorst pack. All atoms were converged to 0.03 eV Å<sup>-3</sup>.



Fig. S1 SEM images of the prepared samples. (a)  $MoO_3$ -CP. (b)  $MoO_3$ -CP sintered at 400 ° C for 1 h under NH<sub>3</sub> conditions. (c) SEM image of  $MoO_3$  without CP.



Fig. S2 The X-ray diffraction (XRD) pattern of  $MoO_3$  treated by  $H_2$  at 400 °C for 1 h.



Fig. S3 SEM images of  $MoO_3$ -CP treated by  $H_2$  at 500 °C for 1 h. (a) SEM images of  $MoO_3$ -CP. (b) Enlarged image of  $MoO_3$ -CP.



Fig. S4 Corresponding TEM imag and elemental mapping of O , Mo and N of  $MoO_3/MoO_2$ , respectively.



Fig. S5 XRD spectra of MoO<sub>3</sub> sintered at 400 °C for 0.5-1.5 h.



Fig. S6 (a) Mo 3d spectra of MoO\_3. (b) Mo  $3p_{3/2}$  spectra of MoO\_3/MoO\_2.

cps/eV	- 8- - - 6-					Spectrum 1	
		Element	Line Type	k Factor	Absorption Correction	wt %	wt % Sigma
	-	N	K series	1.914	1.00	0.00	0.00
	4-0	0	K series	1.100	1.00	22.41	0.35
	- T	Мо	L series	0.986	1.00	77.59	0.35
	-	Total				100.00	
	2- - - 0-	Mo Mo					
				.5 20	25		35

Fig. S7 Energy dispersive X-ray spectroscopy (EDX) of  $MoO_2/MoO_3$ 

The process of static adsorption is used to further analysis the adsorptivity of  $MoO_3/MoO_2$  heterostructure, pure  $MoO_2$  and pure  $MoO_3$  (Fig. S8). The static adsorption tests<sup>6</sup> were carried out in 10 mL Li<sub>2</sub>S<sub>4</sub> (10 mM) solutions by using different materials with similar surface area. The whole process of adsorption lasts for 6 h. Owing to the use of CP as the self-supporting electrode material, the area of electrode is standard to ensure the quality of adsorbent in each Li<sub>2</sub>S<sub>4</sub> solution. The experimental phenomena indicated that the distinct bulk adsorptivity with a sequence of  $MoO_3/MoO_2$ -CP>  $MoO_3$ -CP >  $MoO_2$ -CP > CP, which is obviously correlated to the number of available surface polar sites. This illustrates that the  $MoO_3/MoO_2$  composite has stronger adsorption capacity for Li<sub>2</sub>S<sub>4</sub> compared with pure  $MoO_3$  and  $MoO_2$ , respectively. Although the surface area of  $MoO_3$  is reduced after sintering, the appearance of interfaces between  $MoO_3$  and  $MoO_2$  with high activity will not sacrifice its overall adsorption ability to LiPS.



Fig. S8 Lithium polysulfide (Li<sub>2</sub>S<sub>4</sub>) adsorption in DOL/DME solution for 6 h. (a) original Li<sub>2</sub>S<sub>4</sub> solution. (b) with carbon paper (CP). (c) with MoO<sub>3</sub>-CP. (d) with MoO<sub>3</sub>/MoO<sub>2</sub>-CP. (e) with MoO<sub>2</sub>-CP. (P.



Fig. S9 Charge/discharge curves of  $MoO_3$ -CP-Li<sub>2</sub>S<sub>8</sub> at 0.05, 0.1, 0.25, 0.5 and 1 C.



Fig. S10 Rate performance of  $MoO_3/MoO_2$ -CP host at 0.05, 0.1, 0.25, 0.5, 1, 2.5 and 5 C.



Fig. S11 Rate capabilities of  $CP-Li_2S_8$  cathodes at 0.05, 0.1, 0.25, 0.5, 1, 2.5 and 5 C.



Fig. S12 Long cycling performance of CP-Li $_2S_8$  cathode at 0.5 C.

# References

- 1 S.J. Grimme, J. Comput. Chem. 2006, 27, 1787-1799.
- 2 G. Kresse, J.J. Furthmuller, Phys. Rev. B 1996, 54, 11169-11186.
- 3 G. Kresse, J. Furthmuller, Comput. Mater. Sci. 1996, 6, 15-50.
- 4 J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865-3868.
- 5 P.E. Blochl, Phys. Rev. B 1994, 50, 17953-17979.
- 6 L. Ma, R. Chen, G. Zhu, Y. Hu, Y. Wang, T. Chen, J. Liu, Z. Jin, ACS Nano 2017, 11, 7274-7283.