Electronic Supplementary Material (ESI) for Nanoscale Horizons.

# Electronic Supplementary Information

## Molybdenum Carbide Nanostructures for Electrocatalytic Polysulfide Conversion in Li-Polysulfide Batteries

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## Experimental Section

### 1. Preparation of $MoC_{1-x}/C$

In a typical synthesis, 2.960 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was first dissolved in 144 mL of $H_2O$ and 64 mL of ethanol to form a clear solution, and added with 3.2 mL of concentrated ammonia solution (25-28 wt%) to adjust pH ~8. 0.266 g of dopamine hydrochloride was dissolved in 10 ml of $H_2O$, and then added dropwise to the Mo solution, immediately leading to the precipitation of dark red solids. After 20 h of stirring at room temperature, the solid precipitates were collected by centrifugation, washed twice with ethanol and distilled water, and lyophilized (denoted as Mo/PDA). As-prepared Mo/PDA was subsequently annealed in a furnace tube under Ar protection at a temperature ramping rate of 10 °C $min^{-1}$ to 750 $^{o}C$, and maintained at this temperature for 3 h before cooled down naturally.

### 2. Structural characterizations

XRD was carried out on a PANalytical X-ray diffractometer using Cu Kα radiation (40 kV, 40 mA). SEM images were taken from a Zeiss scanning electron microscope. TEM images were collected on an FEI Tecnai F20 transmission electron microscope operating at an acceleration voltage of 200 kV. XPS spectra were obtained on an ESCALAB 250 XI XPS spectrometer.

### 3. Electrochemical Measurements

0.5 M $Li_2S_6$ catholyte was prepared by mixing 0.8 g of sulfur powder, 0.23 g of $Li_2S$ and 0.069 g of $LiNO_3$ in 10 mL of 1 M LiTFSI DOL/DME solution under heating at 60 °C and vigorous magnetic stirring for 24 h. To prepare the working electrode, $MoC_{1-x}/C$, Super P carbon black and polyvinylidene difluoride (PVDF) were dispersed at a weight ratio of 7:2:1 in N-methyl-2-pyrrolidone (NMP). The slurry was then uniformly loaded onto carbon cloth current collector to achieve an areal loading of 0.5-1 mg $cm^{-2}$. The working electrode was baked at 80 °C under vacuum overnight. Standard coin cells were assembled in an Ar-filled glove box.

The cathode was impregnated with a calculated amount of the $Li_2S_6$-containing catholyte, added with additional blank electrolyte if necessary for sufficient wetting, and assembled with a Celgard 2340 polypropylene membrane separator and a Li anode. As-assembled batteries were rested for 2 h before electrochemical tests. CV measurements were performed on a CHI 660E potentiostat between 1.7 V and 2.7 V. Galvanostatic charge and discharge experiments were carried out on Landian multichannel battery testers. All the specific capacities were normalized to the weight of the equivalent sulfur added to the catholyte at the beginning.

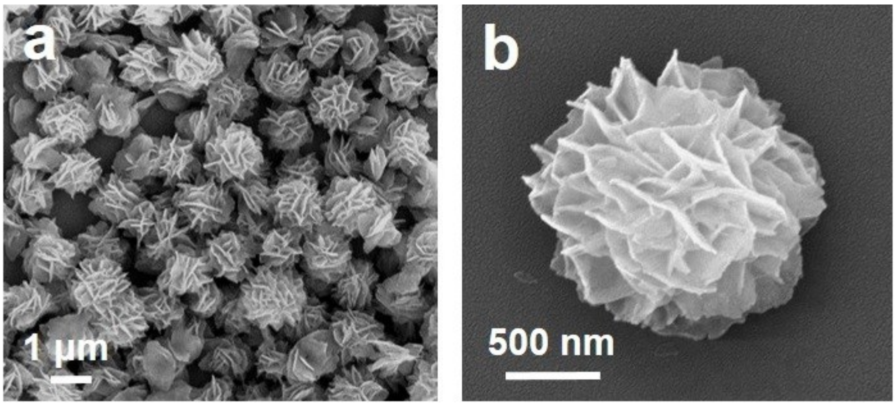

**Fig. S1.** SEM images of Mo/PDA.

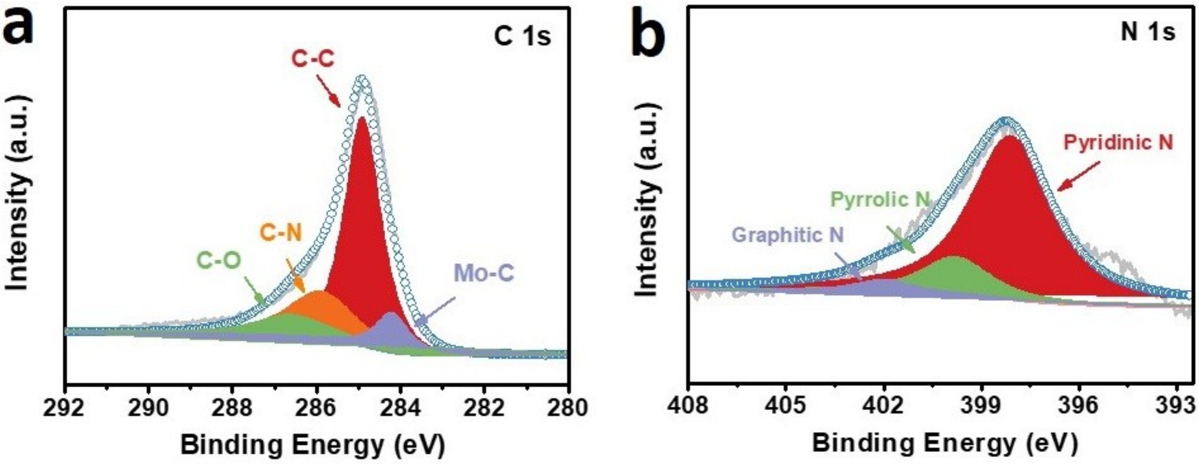

**Fig. S2.** C 1s and N 1s XPS spectra of $MoC_{1-x}/C$,

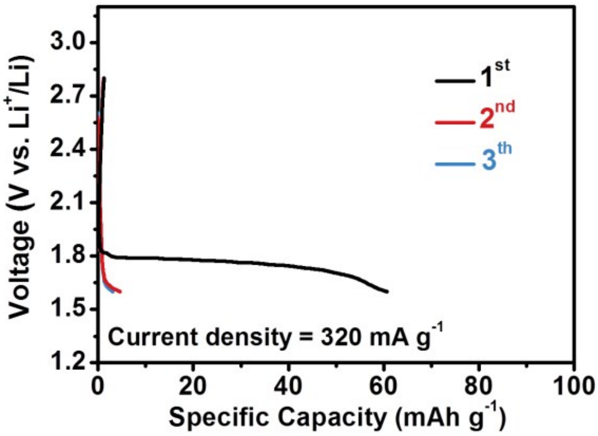

**Fig. S3**. Discharge-charge profiles of 0.5 mg cm$^{-2}$ MoC$_{1-x}$/C in polysulfide-free electrolyte between 1.6 V and 2.8 V. The capacity is normalized to the weight of MoC$_{1-x}$/C.

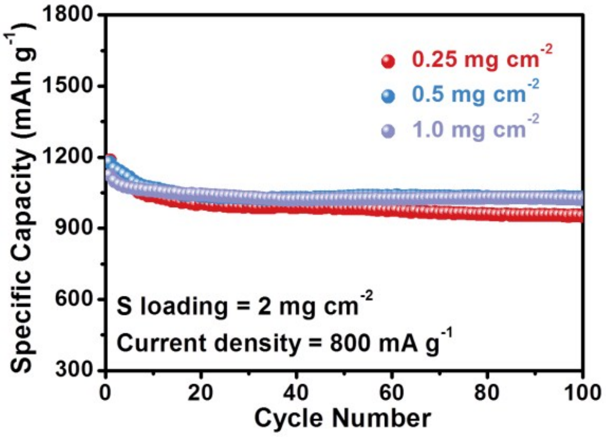

**Fig. S4.** Cycling stability of Li-polysulfide batteries using 0.25-1.0 mg cm$^{-2}$ MoC$_{1-x}$/C as the cathode electrocatalysts.

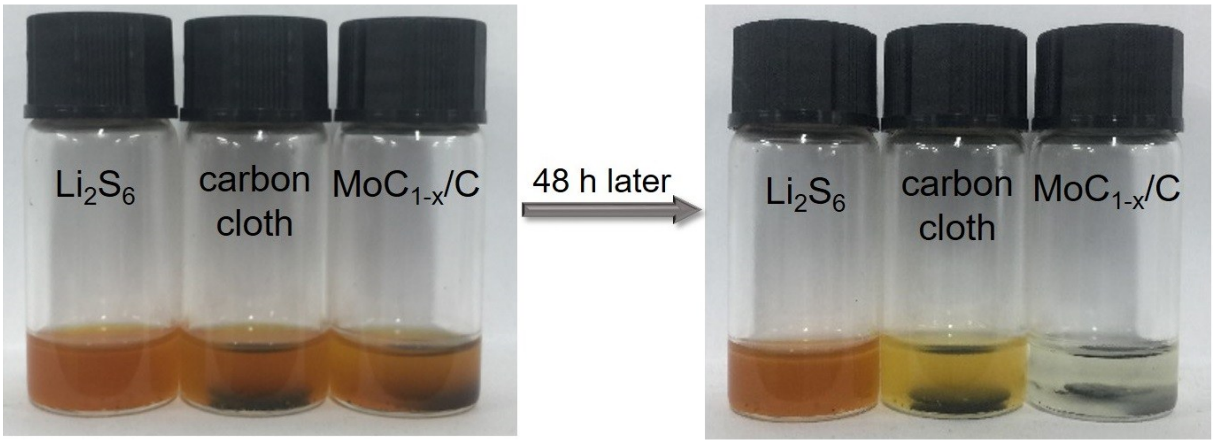

**Fig. S5.** Photographs showing the adsorption capability of $MoC_{1-x}/C$ toward $Li_2S_6$.

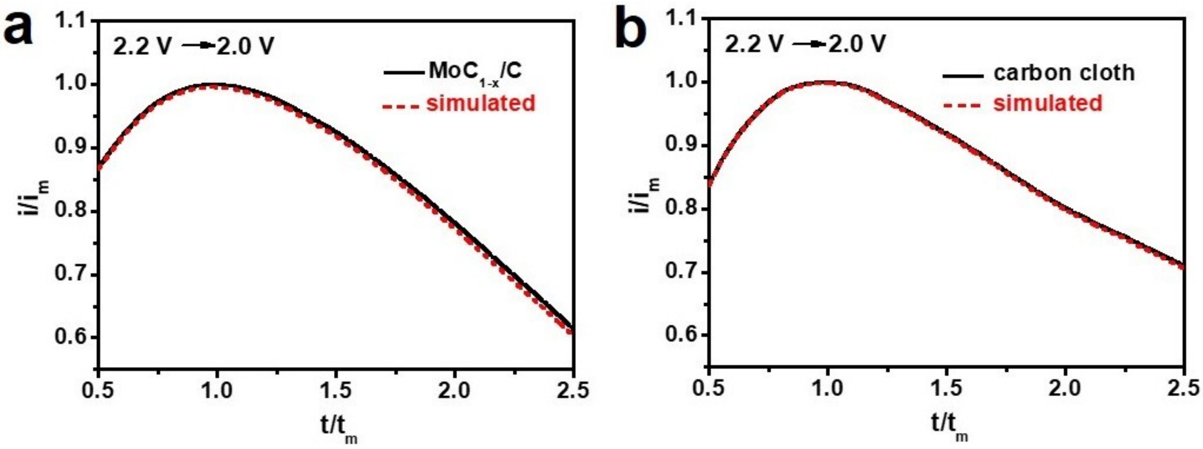

**Fig. S6.** Replotting and fitting the transient current curves reported in Fig. 3c with the two-dimensional instantaneous (2DI) nucleation model:

$$\frac{i}{i_m} = \frac{t}{t_m} \cdot e^{\frac{t^2 - t_m^2}{2t_m^2}}$$

where $i_m$ is the maximum current, and $t_m$ is the corresponding time when the current reaches the maximum.

**Table S1.** A detailed comparison of the electrochemical performances of $MoC_{1-x}$/C to other cathode catalysts in Li-sulfur/polysulfide batteries reported previously.

| Cathode catalyst | S loading [mg $cm^{-2}$] | Areal capacity [mAh $cm^{-2}$] | Rate capability [mAh $g^{-1}$] (1 C=1600 mA $g^{-1}$) | Reference |
|---|---|---|---|---|
| **$MoC_{1-x}$/C** | **6** | **3.6 at 1.6 mA $cm^{-2}$** | **800 at 2 C** | **This work** |
| $W_2C$ | 1 | 1.2 at 0.64 mA $cm^{-2}$ | 650 at 2 C | *Nano Lett*. 2018, **18,** 1035. |
| $Mo_2C$ | 1 | 1.1 at 0.64 mA $cm^2$ | 450 at 2 C | |
| TiC | 1 | 1.0 at 0.64 mA $cm^2$ | 430 at 2 C | |
| $MoS_{2-X}$ | 1.5 | 0.9 at 1.6 mA $cm^2$ | 800 at 8 C | *Energy Environ. Sci.* 2017, **10**, 1470. |
| VN | 3 | 3.9 at 0.64 mA $cm^2$ | 700 at 3 C | *Nat. Commun.* 2017, **8**, 14627. |
| $TiO_2$-TiN | 4.3 | 1.5 at 3.2 mA $cm^2$ | 650 at 2 C | *Energy Environ. Sci.* 2017, **10**, 1694. |
| Phosphorene | 5 | 3.5 at 4.8 mA $cm^2$ | 800 at 3 C | *Adv. Mater*. 2017, **29**, 1602734. |
| Pt/graphene | 1.21 | 0.9 at 0.16 mA $cm^2$ | 750 at 0.2 C | *J. Am. Chem. Soc.* 2015, **137**, 11542. |
| NiO-$NiCo_2O_4$@C | 0.8 | 0.6 at 1.6 mA $cm^{-2}$ | 700 at 2 C | *Adv. Energy Mater.* 2018, **8**, 1800709 |
| MoP | 1 | 0.2 at 0.32 mA $cm^{-2}$ | 650 at 2 C | Nano Res. 2017, **10**, 3698. |
| $Nb_2O_5$ | 1.5 | 1.5 at 1.6 mA $cm^{-2}$ | 900 at 5 C | *Energy Environ. Sci.* 2016, **9**, 3230. |
| Te | 0.58 | 0.4 at 10 mA $cm^{-2}$ | 580 at 12.5 C | *ACS Energy Lett.* 2018, **3**, 420. |
| FeP | 3.5 | 1.4 at 3.2 mA $cm^{-2}$ | 630 at 3 C | Nano Energy 2018, **51**, 340. |
| $WS_2$ | 3 | 3.0 at 1.6 mA $cm^2$ | 700 at 5 C | *Adv. Energy Mater.* 2017, **7**, 1602567. |
| $Ni_3FeN$ | 4.8 | 3.8 at 1.6 mA $cm^2$ | 840 at 3 C | *Angew. Chem., Int. Ed.* 2018, **131**, 3819. |
| Co−N/G | 6 | 5.0 at 0.64 mA $cm^{-2}$ | 580 at 4 C | *J. Am. Chem. Soc.* 2019, **141**, 3977. |
| NCNT@Co-$SnS_2$ | 3 | 3.0 at 1.3 mA $cm^{-2}$ | 740 at 1.6 C | *Adv. Funct. Mater.* 2019, **29**, 1806724. |
| $CoSe_2$/G | 4.35 | 3.9 at 3.64 mA $cm^{-2}$ | 890 at 6 C | *Adv. Energy Mater.* 2019, **9**, 1802768. |
| CoOOH | 4.35 | 2.5 at 0.64 mA $cm^2$ | 520 at 2 C | *Adv. Funct. Mater.* 2019, **29**, 1901051. |

| | | | | |
|---|---|---|---|---|
| TiO$_{2-x}$ | 8.6 | 5.4 at 0.16 mA cm$^{-2}$ | 400 at 5 C | *Adv. Energy Mater.* 2019, **9**, 1900953 |
| black phosphorus | 8 | 4.0 at 0.32 mA cm$^{-2}$ | 810 at 4 C | *Nat. Commun.* 2018, 9, 4164. |
| B$_4$C@CNF | 10.3 | 7.2 at 0.64 mA cm$^{-2}$ | 400 at 4 C | *Adv. Mater. 2018,* **30**, 1804149. |
| CNTs/CoS-NSs | 1.5 | 1.7 at 0.64 mA cm$^{-2}$ | 550 at 5 C | *ACS Nano* 2018, **12**, 4868. |

**Table S2.** Estimated energy efficiency of our Li-polysulfide batteries using MoC$_{1-x}$/C as the cathode electrocatalyst.

| **S loading [mg cm$^{-2}$]** | **Current density [mA cm$^{-2}$]** | **Energy efficiency (%)** |
|---|---|---|
| 2 | 1.6 | 90.3% at 500th cycle |
| 2 | 3.2 | 86.6% at 200th cycle |
| 4 | 1.6 | 88.2% at 120th cycle |
| 6 | 1.6 | 91.0% at 120th cycle |