Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Carve Design of MoS_2 Nanostructures by Controlling 3D MoS_2 Nanomasks

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Experimental details

Material Synthesis

Synthesis of MoO_3 nanobelts: The MoO_3 nanobelts (MoO_3 NBs) were produced according to a reported hydrothermal method.[13] Sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$, chemically pure reagent, Sinopharm, 3.36 g) was dissolved into 70 ml of deionized water. Nitric acid (chemically pure reagent, Sinopharm, 65wt%, 4 ml) was added to the solution to keep the pH value at 1. The solution was transferred into polytetrafluoroethylene lined stainless steel reactors and reacted in an oven at 180 °C for 20 h. The precipitate was collected by filtration and rinsed by deionized water several times and then dried at 60 °C to give MoO_3 nanobelts.

In situ growth of 3D MoS_2 nanomasks: The sample of MoO_3 NBs (0.32 g) was set in the middle of the CVD quartz tube and the sample of sublimed sulfur (chemically pure reagent, Sinopharm, 4 g) was put close to the inlet of the CVD quartz tube. The CVD tube was flushed by pure Ar with a flow rate of 500 sccm for 15 min and then heated to 300 °C at a heating rate of 20 °C/min in an atmosphere of pure H_2 with a flow rate of 200 sccm. The sublimed sulfur was then slowly moved to the hot area of furnace with temperature of 300 °C for 45 min and then set back to the original position. The sample was cooled to room temperature while being flushed by pure Ar with a flow rate of 100 sccm to give MoS_2 3D nanomasks on the surface of MoO_3 NBs to yield MoO_x@p-MoS_2 NBs.

Nanocarving of encapsulated molybdenum oxides: The MoO_x@p-MoS_2 NBs were annealed at 800 °C for 60 min with a heating rate of 20 °C/min in a CVD quartz tube while being flushed by pure Ar with a flow rate of 100 sccm. The sample was cooled to room temperature in an Ar atmosphere to give c-MoO_2@MoS_2 NBs.[12]

Nanocarved MoS_2 structures (MoS_2NFs@MoS_2NTs): The c-MoO_2@MoS_2 NBs (50mg) was sealed with extra amount of sublimed sulfur in an H-shape glass tube under a vacuum of 1.7×10^{-5} Pa. The sample was put in a muffle stove and heated to 500 °C with a heating rate of 1 °C/min for one week, and then cool in oven to give nanotubes with extra inside sulfur (S+MoS_2@MoS_2NTs). The extra sulfur was evacuated in a pressure-resistant bottle at 160 °C for 8 h in vacuum to give nanocarved MoS_2 flowers inside MoS_2 nanotubes (MoS_2NFs@MoS_2NTs).

Characterizations

Raman spectroscopy was taken in a backscattering geometry using a single monochromator with a microscope (Reinishaw inVia) equipped with a CCD array detector (1024 × 256 pixels, cooled to −70 °C) and an edge filter. The spectral resolution and reproducibility were determined to be better than 0.1 cm^{-1}. The samples were excited by a 633 nm He−Ne ion laser in air. The SEM images were taken by a FEI Quanta 250 scanning electron microscope. HRTEM images were acquired by a JEOL JEM-2100 transmission electron microscope (TEM; acceleration voltage: 200 kV) and a FEI Titan G^2 60-300 transition electron microscope equipped with a field-emission gun (acceleration voltage: 300 kV). X-ray diffraction patterns were obtained from a Bruker D2 PHASER using Cu/Kα radiation (λ =1.5418 Å) at 40 kV and 30 mA. N_2 adsorption−desorption isotherms were conducted on a Quantachrome Autosorb-iQ automatic surface area and pore size distribution analyzer at liquid N_2 temperature (−196 °C). The specific surface areas were determined from the linear portion of the BET plot. The average pore diameters were calculated from the desorption branch of the N_2 adsorption isotherm using the Barrett−Joyner−Halenda (BJH) method.

Electrochemical performance evaluation

The electrochemical performances of the carving designed MoS_2 nanostructures as anode materials were measured with a half cell lithium ion battery configuration. The active materials were well mixed with Super P carbon black and poly (acrylic acid) (Mx =100 000, Sigma-Aldrich) at a weight ratio of 70:20:10 on copper foil. The CR2025 coin-type cells were constructed in an argon-filled glovebox (Lab2000, Etelux, China) with both moisture and oxygen levels less than 0.1 ppm using Li foils as counter electrodes, Cellgard 2400 microporous membranes as separators, and 1.0 M $LiPF_6$ in a mixture of ethylene carbonate and dimethyl carbonate (1:1, v/v) as electrolytes. The galvanostatic charge and discharge experiments were performed on a NEWARE multichannel battery test system in a 25 °C incubator. The mass of active materials was calculated from the copper foil before and after loading. The voltage profiles of MoS_2NFs@MoS_2NTs anodes during the first, second, third, fifth, and 10th cycle were performed at a current rate of 100 mA g^{-1} between 0.01 and 3 V. Cyclic voltammetry (CV) measurements were performed on an electrochemical station (PGSTAT 302N, Metrohm, Switzerland) in a voltage window of 0.01-3.00 V at a scan rate of 0.2 mV/s.

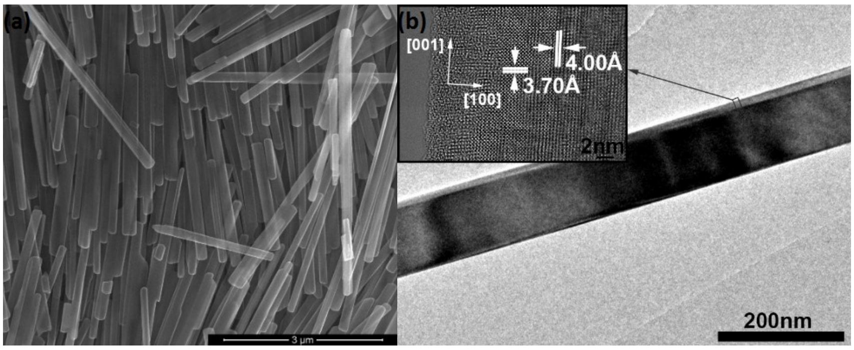

Figure S1 (a) SEM images and (b) TEM images of MoO_3 NBs

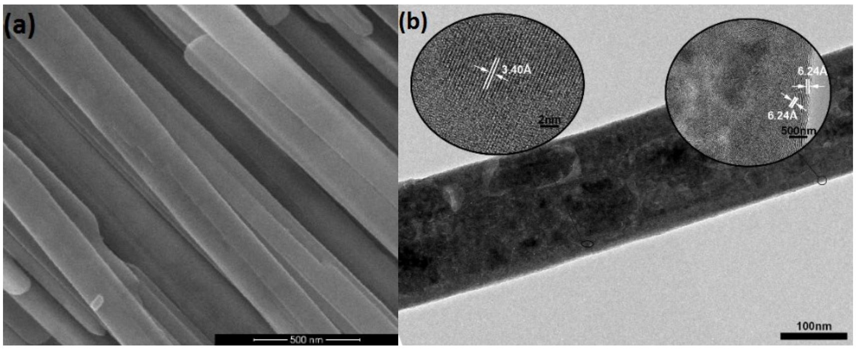

Figure S2 (a) SEM images and (b) TEM images of MoO_x@p-MoS_2 NBs

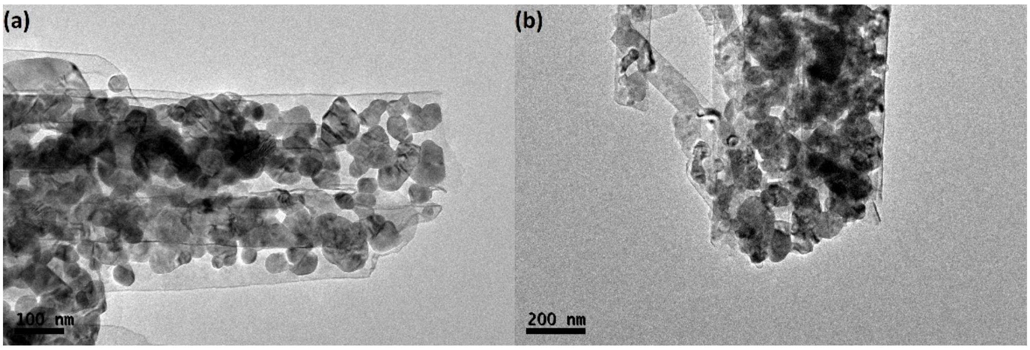

Figure S3 (a) (b) TEM images of c-MoO_2@MoS_2 NBs

Figure S4 the sublimation products attached to the glass flask

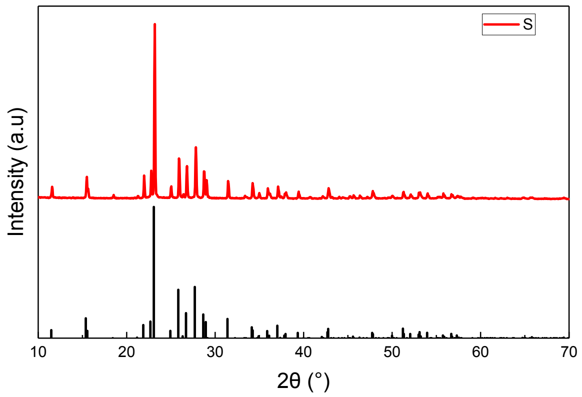

Figure S5 XRD spectra of the sublimation products attached to the glass flask and standard XRD pattern of sulfur

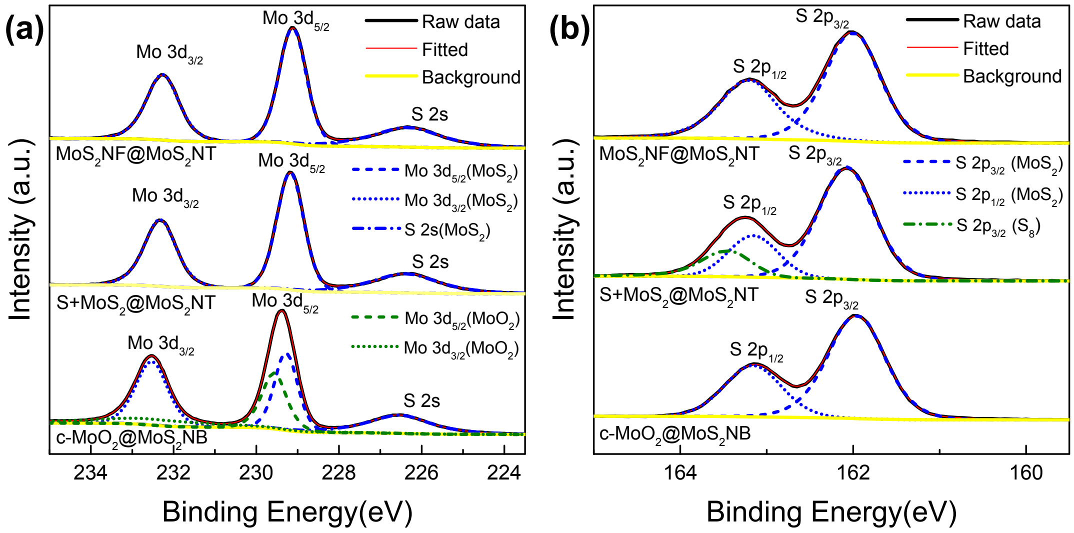

Figure S6 XPS curves of the Mo 3d (a) and S 2p (b) from c-MoO_2@MoS_2 NBs, S+MoS_2@MoS_2NTs and MoS_2NFs@MoS_2NTs.

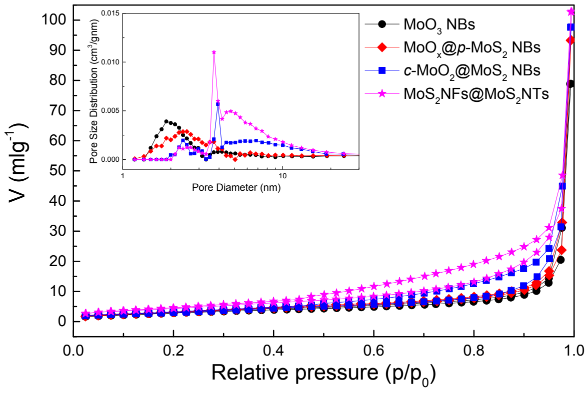

Figure S7 Nitrogen adsorption and desorption isotherms of MoO_3 NBs (black), MoO_x@p-MoS_2

NBs (red), c-MoO_2@MoS_2 NBs (blue) and MoS_2NFs@MoS_2NTs (purple). The corresponding BJH distributions are shown in the inset.

Table S1 Summaries of the specific surface areas, pore volumes and average pore diameters of MoO_3 NBs, MoO_x@p-MoS_2 NBs, c-MoO_2@MoS_2 NBs and MoS_2NFs@MoS_2NTs

Sample	BET Surface area (m^2/g)	BJH Pore volume (cm^3/g)	Average pore diameter (nm)
MoO_3 NBs	10.70	0.12	1.87
MoO_x@p-MoS_2 NBs	11.48	0.15	2.52
c-MoO_2@MoS_2 NBs	11.02	0.15	3.94
MoS_2NFs@MoS_2NTs	16.22	0.16	3.72

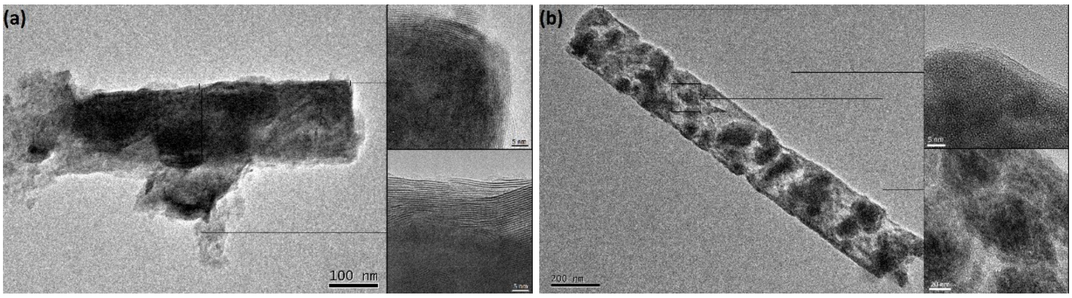

Figure S8 HRTEM images of MoS_2NFs@MoS_2NTs (a) after lithiation and (b) after delithiation.

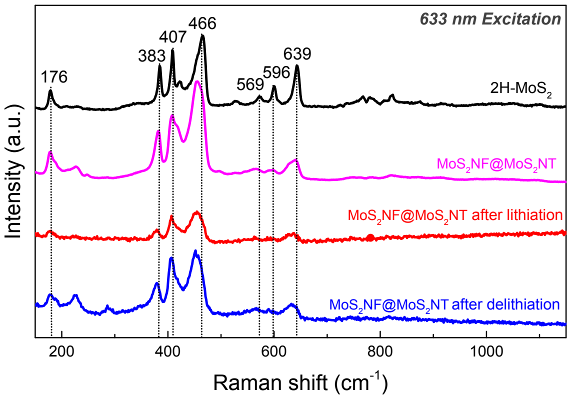

Figure S9 Raman spectra of MoS_2 (black), MoS_2NFs@MoS_2NTs (pink), MoS_2NFs@MoS_2NTs after delithiation (blue), and lithiation (red).