

Electronic Supplementary Information of Crystallization-induced self-hollowing of molybdenum sulfide nanoparticles and their potential in sodium ion batteries

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Experimental Section

Materials

Sodium molybdate dehydrate, thioacetamide, acetic acid, hydrazine hydrate were of analytical purity and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), commercial molybdenum was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Milli-Q water (resistance 418 MΩ) was used for all experiments. All chemicals were used as received without further purification.

Synthesis

Preparation of amorphous nanospheres of molybdenum sulfide

0.24 mmol sodium molybdate, 1.74 mmol thioacetamide (TAA), and 2.1 mmol hydrazine were dissolved in 30 mL deionized water under magnetic stirring, and the pH value of solution was adjusted to 5 with acetic acid. The reaction solution was incubated at 60 °C for 10 h, and brown precipitate was obtained. The obtained product was collected by centrifugation, and then washed with deionized water, dried at 80 °C.

Preparation of hollow structured molybdenum sulfide spheres

The amorphous precursor was collected and sintered at 700 °C for 5 h in an inert atmosphere. And the amorphous precursor was sintered at different temperature from 400 °C to 900 °C for further analysis, such as TEM, XRD and Raman spectra.

Material characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy

(HRTEM) images were recorded on JEOL-2100F instruments operated at 200 kV. X-ray diffraction (XRD) data were collected on a Rigaku D/MAX-2500 instrument with Cu K α radiation at 50 kV and 250 mA. X-ray photoelectron spectroscopy data were acquired on an ESCALAB 220i-XL electron spectrometer from VG Scientific using 300 W Al K α radiation. Raman spectra were carried out on HORIBA Raman spectroscope.

Electrochemical measurements

Electrochemical performances were carried out on CR2032 coin cells, which were assembled in an argon-filled glove box. MoS₂ was used as working electrode, sodium metal was used as counter electrode, 1 M NaClO₄ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, in wt.%) was used as the electrolyte, and a glass fiber membrane (Whatman, Maidstone, UK) was used as the separator. The working electrode was prepared as a mixed slurry of 60 wt. % active materials, 20 wt. % Super P carbon black and 20 wt. % carboxymethylcellulose sodium binder in an aqueous solvent. This mixture was cast onto Cu foil (99%, Goodfellow, Cambridge, UK) and cut into circular electrodes after drying under vacuum at 80 °C for 10 h. The mass loading on the electrode was about 1 mg, and the electrode diameter was 12 mm. Galvanostatic charge/discharge tests of the assembled cells were performed using a Land CT2001A battery test system with a voltage window of 0.01-3 V at room temperature. Electrochemical impedance spectroscopy data was obtained using an Autolab test system, and all the tested cells were activated for three cycles.

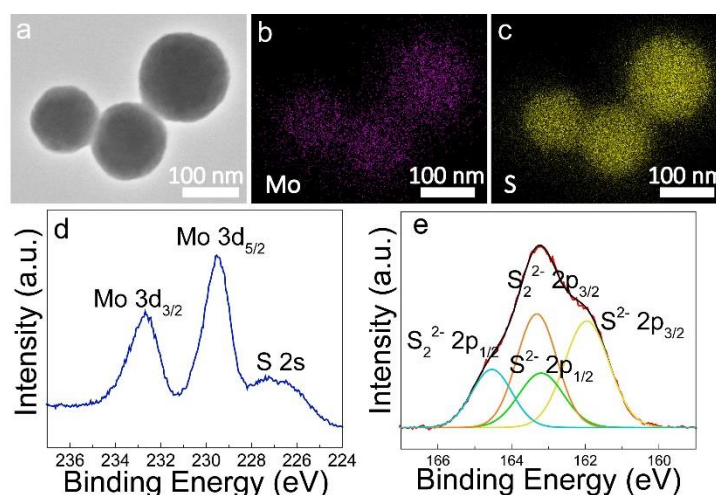


Fig. S1 STEM image (a) and elemental mapping (b-c) of pristine obtained molybdenum sulfide nanospheres. XPS pattern (d-e) of pristine obtained molybdenum sulfide sample.

Table S1. Energy dispersive spectroscopy (EDS) results of as-prepared molybdenum sulfide.

| Element | Mass fraction/% | Atomic percentage/% |
|---------|-----------------|---------------------|
| Mo | 53.70 | 27.94 |
| S | 46.30 | 72.06 |

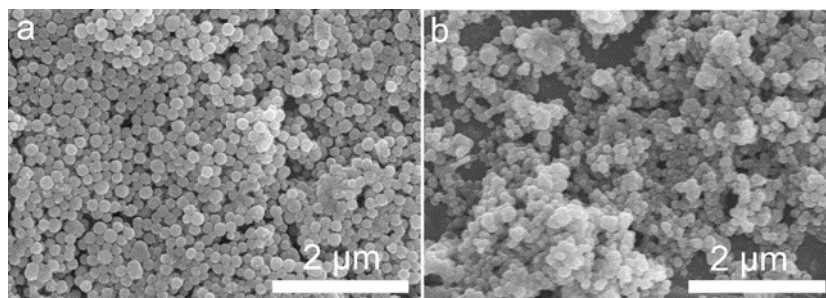


Fig. S2 SEM images of pristine sample (a) and 700 °C treated sample (b).

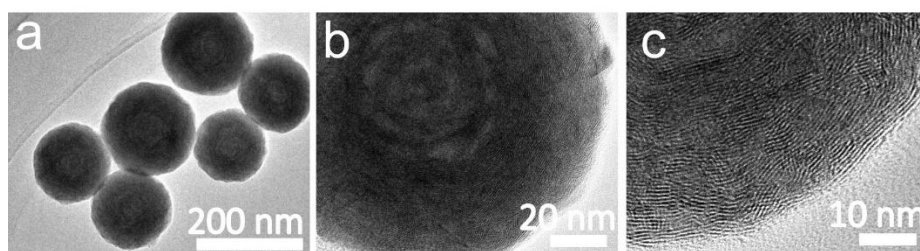


Fig. S3 TEM (a) and HRTEM (b, c) images of 600 °C treated sample.

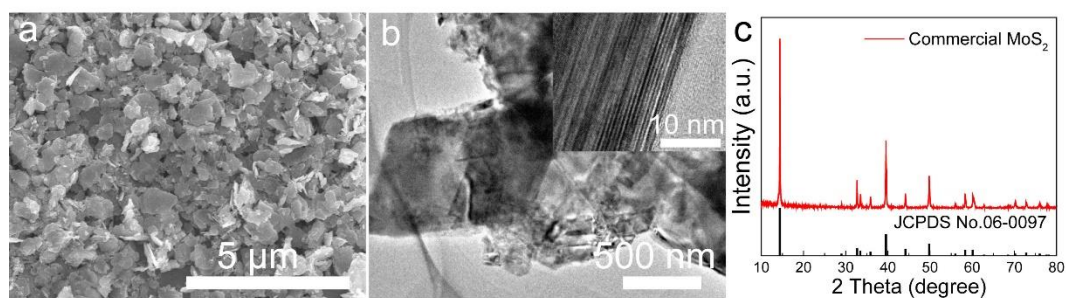


Fig. S4 SEM image (a), TEM image (b) and XRD pattern of commercial MoS₂ sample.

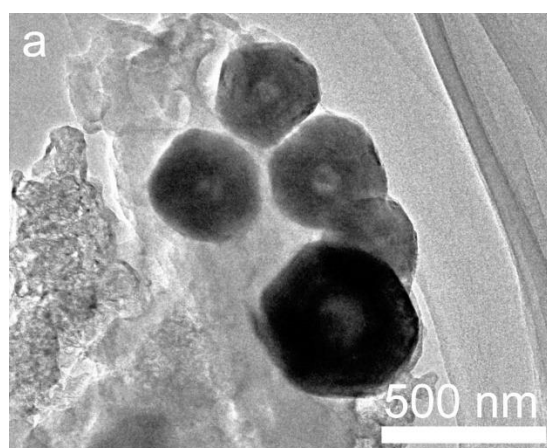


Fig. S5 TEM image of hollow MoS₂ sample after 5 cycles.

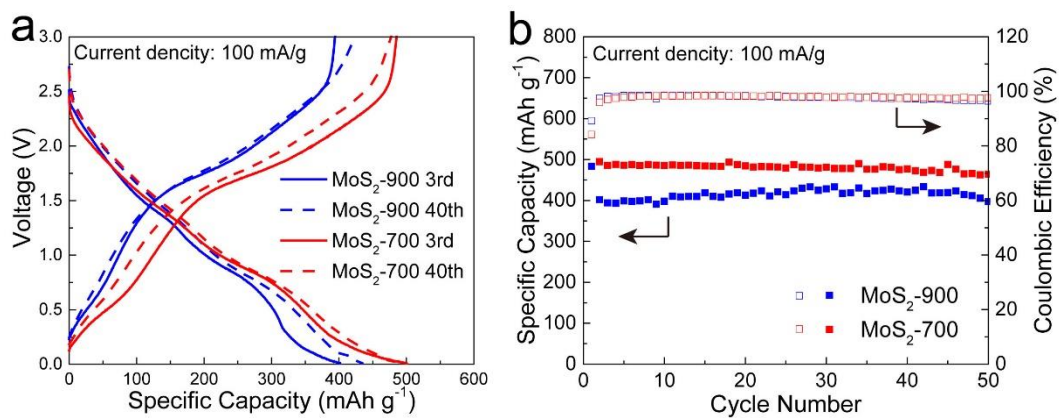


Fig. S6 Galvanostatic charge/discharge profiles of the samples treated at 700 °C and 900 °C (current density: 100 mA/g, 0.01 V-3 V) (a). Cycling performance of samples treated at 700 °C and 900 °C at current density of 100 mA/g (b).