

Supporting information for

Enhanced Li Storage Performance of Ordered Mesoporous MoO₂ via Tungsten Doping

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Experimental

Mesoporous W-doped MoO₂ was obtained using mesoporous silica KIT-6 as a hard template. PTA and PMA ($W_{\text{PTA}}/(W_{\text{PMA}}+W_{\text{PTA}}) = 0.25$) were adopted as the tungsten and molybdenum sources respectively and filled into the mesopore of KIT-6 template. The prepared precursors@template composite was then heated up to 700 °C at a rate of 5 °C min⁻¹ in a mixed gas flow of 10% H₂ and 90% Ar. During this treatment, the PTA and PMA precursors decomposed and the tungsten and molybdenum atoms were reduced in-situ from 6+ to 4+, forming crystalline dioxide product inside the mesopore of the KIT-6 template. Mesoporous silica template was removed using 4 wt% HF as etchant, and highly ordered mesoporous crystalline W-doped MoO₂ was collected as the final product. Meanwhile, for comparison, mesoporous MoO₂ was synthesized in the same way which has been reported in our earlier paper.

Chemicals: Triblock poly (ethylene oxide)-*b*-poly (propylene oxide)-*b*-poly (ethylene oxide) copolymer Pluronic P123 ($M_w = 5800$, EO₂₀PO₇₀EO₂₀), n-butanol, tetraethyl orthosilicate (TEOS), phosphotungstic acid H₃PW₁₂O₄₀·xH₂O (PTA), phosphomolybdic acid H₃PMo₁₂O₄₀·xH₂O (PMA), hydrochloric acid (38 wt%) and hydrofluoric acid (48 wt%) were purchased from Aldrich Chemical Inc.. Micro-sized WO₂ was obtained from Aldrich Chemical Inc. Premixed 10% hydrogen diluted with 90% argon gas were purchased from Praxair, Inc.. All chemicals were used as received without any further purification. Millipore water was used in all experiments.

Synthesis of KIT-6 hard template material: Mesoporous silica KIT-6 was prepared according to the literature report and used as the hard template in our synthesis: 23.5 g of triblock copolymer P123 was dissolved in the mixture of 850 mL of water and 38.0 mL of 38 wt.% HCl with stirring overnight to get a clear solution. The solution was heated to 35 °C and then 23.5 g of n-butanol was added. After 2 h stirring, 48.0 g of TEOS was poured in with rigorously stirring, and the mixture was kept at the same temperature for another 24 h. The above mixture was then transferred into a Teflon lined stainless steel autoclave and heated up to 110 °C for 2 days for hydrothermal treatment. The white solids were recovered by filtration and dried in a 65 °C oven. Thereafter, the products were calcined at 500 °C for 2 h with a heating rate of 1.5 °C min⁻¹ in air to remove the P123 surfactant.

Synthesis of mesoporous W-doped MoO₂: 4.2 g of precursor, composed of PTA and PMA with weight ratio 25:75, was added into 20 mL of ethanol in an open crucible, leading to a homogenous clear yellow solution. 1.0 g of mesoporous silica KIT-6 hard template was then added into the solution under stirring at room temperature in a fume

hood. After ethanol solvent was evaporated up after about 5 - 8 h, the obtained yellow powders were loaded on a quartz boat and heated to 700 °C in a tube furnace at a rate of 5 °C min⁻¹ under 10% H₂/90% Ar atmosphere (150 mL min⁻¹) for a desired time. The obtained W-doped MoO₂@KIT-6 composite was treated with 60 mL 4 wt% HF aqueous solution to remove the silica template.

Synthesis of micro-sized MoO₂: 5 g of micro-sized MoO₃ without any mesoporous silica template was directly reduced to micro-sized MoO₂ by Ar-diluted H₂ gas flow at 600 °C for 5 h.

Characterizations: Powder X-ray diffraction (XRD) patterns were collected on a Scintag PADX diffractometer with Cu K α radiation (45 kV, 35 mA). Transmission electron microscopy (TEM) images were taken using a FEI Tecnai T20 Sphera electron microscope operating at 200 keV. Scanning electron microscopy (SEM) images were acquired on a FEI XL30 Sirion FEG Digital Scanning electron microscope. Nitrogen sorption isotherms were measured at 77 K on a Micromeritics Tristars 3000 analyzer (USA).

Electrochemical performance: Electrochemical experiments were carried out using home-made two-electrode cells. The working electrodes were prepared by mixing the active materials, carbon black and poly(vinylidene difluoride) (PVDF) at a weight ratio of 80:10:10. The slurry was pasted on pure Cu foil and dried under vacuum at 100 °C for 12 hours. A polypropylene film (Celgard 2300) was used as a separator. Pure lithium foil was used as a counter electrode. The electrolyte consisted of a solution of 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume) obtained from Ferro Corporation. The cells were assembled in an argon-filled glove box. Galvanostatic discharge-charge experiments were tested at a current rate of 0.1C in the voltage range of 0.01-3 V on a Land BT2000 battery test system (Wuhan, China).

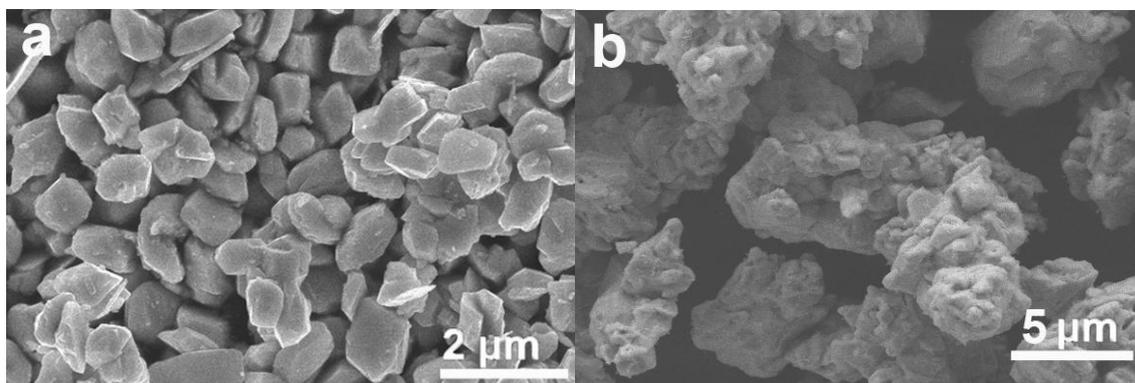


Fig. S1 SEM images of micron-sized MoO₂ (a) and micron-sized WO₂ (b).