Electronic Supplementary information

Lithiation Mechanism of Hierarchical Porous MoO₂ Nanotubes Fabricated through One-step Carbothermal Reduction

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Fig. S1 (a) Low-angle XRD pattern, (b) SEM, and (c, d) TEM images of CMK-3.



Fig. S2 Nitrogen adsorption/desorption isotherm and the corresponding pore size distribution curve (insert) of CMK-3.



Fig. S3 (a) SEM and (b) TEM image of MoO₂ nanotubes.

The tubular structure can be observed from the open MoO_2 nanotubes. The diameter of the tube is less than 100 nm. A lot of MoO_2 nanoparticles are coated by a thin carbon layer as shown in the following TEM image. It is believed that thin carbon layer increases the electronic conductivity of these MoO_2 nanotubes and structure stability. Therefore, both the residual carbon and the hierarchical structure contribute to the good cycling performance of these MoO_2 nanotubes.



Fig. S4. *In situ* XRD patterns of the electrode before the first cycle and discharged to 0.01 V at the first cycle.



Fig. S5 *Ex situ* XRD pattern of the electrode after 30 cycles at a current density 40 mA/g. The diffraction peak of Li_2O can be detected while the diffraction peak of $Li_{0.98}MoO_2$ can't be observed.



Fig. S6. Galvanostatic charge/discharge curves of the hierarchical porous MoO_2 at a current density of 0.5 A/g between 0.01~3.0 V. The two discharge plateaus (1.5 V and 1.3 V) and two charge plateaus (1.4 V and 1.7 V) of $Li_{0.98}MoO_2$ cannot be observed after 30 cycles.