One-pot synthesis of uniform carbon-coated MoO$_2$ nanospheres for high-rate reversible lithium storage

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Experimental

The MoO$_2$@C nanospheres were synthesized by hydrothermal reaction of a mixture solution of 10 mL of ammonium heptamolybdate tetrahydrate (AHM) solution (6 mM), 1 mL of ethylene glycol (EG), 10 mL of polyvinylpyrrolidone (PVP) (MW: 58,000) solution (0.1 g mL$^{-1}$) and 10 mL of deionized (DI) water in a 60 mL Teflon-lined autoclave at 180 ºC for 60 h. The final black products were collected by 3 centrifuge-disperse-rinse cycles with DI water and ethanol, and dried at 60 ºC. The as-synthesized sample was further annealed at 700 ºC for 4h in a N$_2$ flow to obtain the final product of MoO$_2$@C nanospheres. The samples were characterized by field-emission scanning electron microscope (FESEM, JEOL, JSM-6700F), transmission electron microscope
TEM, JEOL, JEM-2100F), X-ray diffraction (XRD, Bruker, D8-Advance X-ray Diffractometer, Cu Ka), nitrogen adsorption/desorption (Quantachrome Instruments, Autosorb AS-6B), thermogravimetric analysis (TGA, Shimadzu, DRG-60).

The galvanostatic charging/discharging tests were conducted on a Neware battery tester with lithium foil as the counter and reference electrodes and 1.0 M LiPF$_6$ in mixed ethylene carbonate and diethyl carbonate (EC:DEC, 1:1 by weight) as the electrolyte. A cut-off voltage window of 0.1 – 3.0 V is used. The working electrode is composed of MoO$_2$@C nanospheres, carbon black (super-P-Li) and polyvinylidene difluoride (PVDF) in a weight ratio of 8:1:1. The mass of active materials is around 1-2 mg, depending on the thickness of film formed on Cu current collector. Cyclic voltammetry (CV) study was conducted using an electrochemical workstation (CHI 660C) between 0.1 – 3.0 V at a scan rate of 0.05 mV s$^{-1}$. 
Figure S1. TGA curve of the as-prepared MoO$_2$ sample in a N$_2$ flow with a heating rate of 10°C min$^{-1}$.

Figure S2. N$_2$ adsorption/desorption isotherms of the MoO$_2$@C nanospheres before (a) and after (b) thermal annealing at 700°C in N$_2$. The corresponding pore size distribution is shown as the inset.
Figure S3. EDX spectrum of the MoO$_2$@C nanospheres. The Cu signal is from the Cu grid.

Figure S4. Simulated electron diffraction pattern of a MoO$_2$ single crystal along the <211> zone axis.
Figure S5. TGA curve of the MoO$_2$@C nanospheres in air with a heating rate of 10 °C min$^{-1}$. The weight loss before 300 °C is due to combustion of the carbon content. The weight gain from 300 °C to 400 °C is due to the oxidation of MoO$_2$ to MoO$_3$. The slight weight loss after 400 °C might be attributed to the sublimation of MoO$_3$. The weight fraction of carbon in the initial sample can be easily estimated to be about 6 % by assuming that the sample is pure MoO$_3$ at 400 °C.

Figure S6. Coulombic efficiency profile of MoO$_2$@C spheres at 0.5C and 1C rate.
Figure S7. (a) FESEM image and (b) cycling performance of the MoO$_3$ nanospheres obtained by calcining the MoO$_2$@C nanospheres in air at 400 °C for 3 h.