

One-pot synthesis of uniform carbon-coated MoO₂ nanospheres for high-rate reversible lithium storage

Zhiyu Wang,^{a,b,c} Jun Song Chen,^a Ting Zhu,^a Srinivasan Madhavi,^{b,c,*}
and Xiong Wen Lou^{a,c,*}

^a*School of Chemical and Biomedical Engineering, Nanyang Technological University, 70 Nanyang Drive, 637457 (Singapore) E-mail: xwlou@ntu.edu.sg; Tel: +65 63168879*

^b*School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798 (Singapore) E-mail: madhavi@ntu.edu.sg; Tel: +65 67904606*

^c*Energy Research Institute @ NTU, Nanyang Technological University, 50 Nanyang Drive, 637553 (Singapore)*

Experimental

The MoO₂@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 °C for 60 h. The final black products were collected by 3 centrifuge-disperse-rinse cycles with DI water and ethanol, and dried at 60 °C. The as-synthesized sample was further annealed at 700 °C for 4h in a N₂ flow to obtain the final product of MoO₂@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 LiPF₆ 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 MoO₂@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.

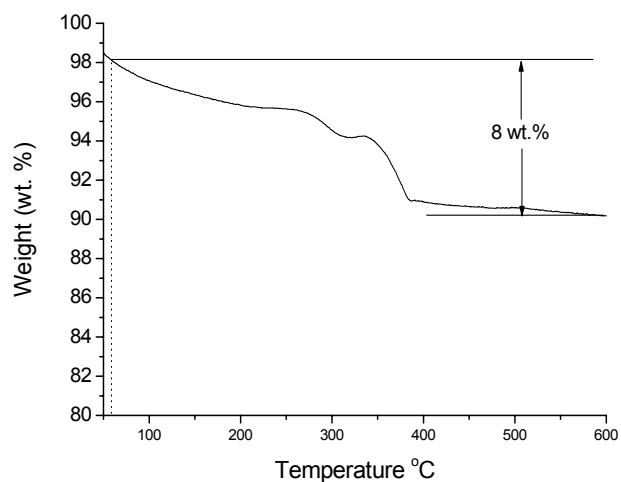


Figure S1. TGA curve of the as-prepared MoO₂ sample in a N₂ flow with a heating rate of 10 °C min⁻¹.

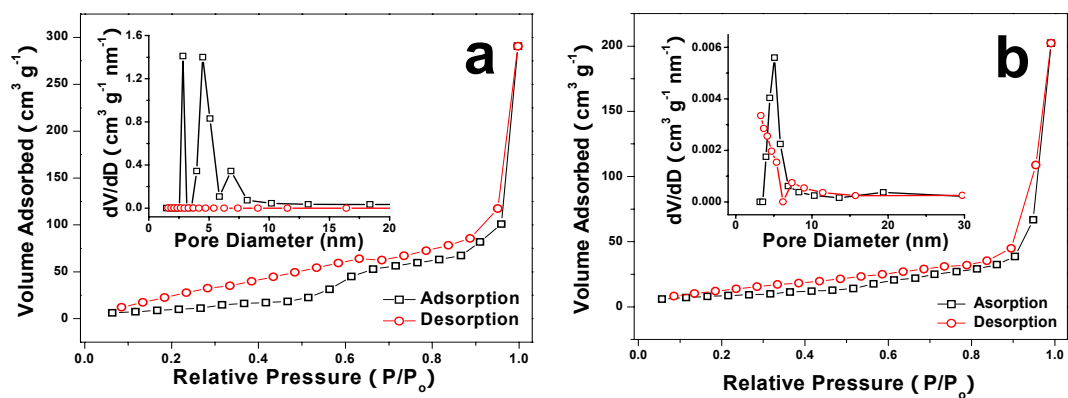


Figure S2. N₂ adsorption/desorption isotherms of the MoO₂@C nanospheres before (a) and after (b) thermal annealing at 700 °C in N₂. The corresponding pore size distribution is shown as the inset.

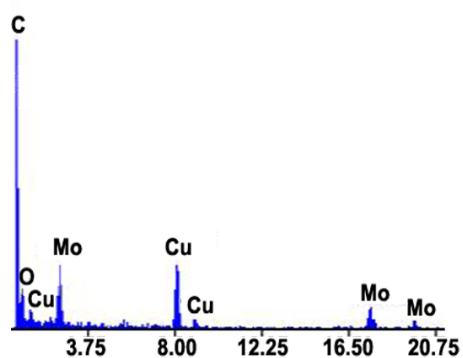


Figure S3. EDX spectrum of the $\text{MoO}_2@C$ nanospheres. The Cu signal is from the Cu grid.

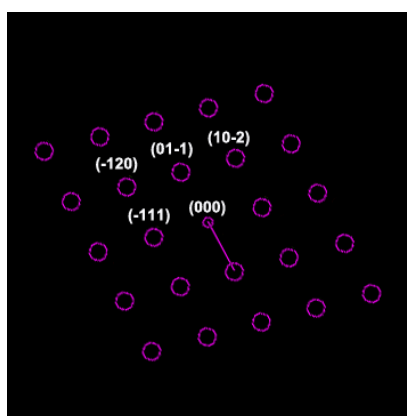


Figure S4. Simulated electron diffraction pattern of a MoO_2 single crystal along the $\langle 211 \rangle$ zone axis.

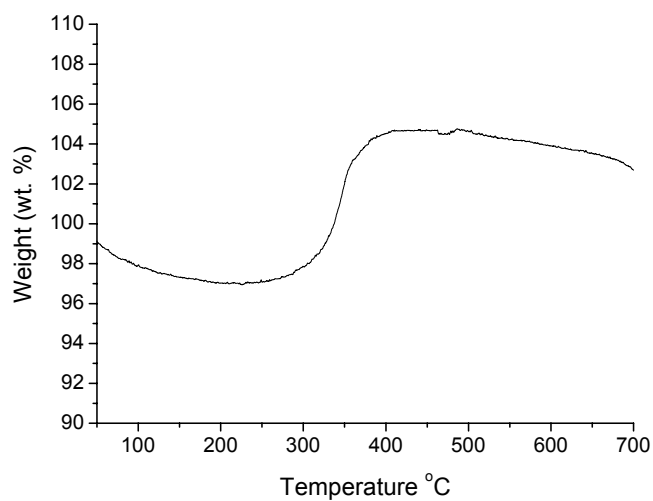


Figure S5. TGA curve of the $\text{MoO}_2@\text{C}$ nanospheres in air with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The weight loss before $300\text{ }^\circ\text{C}$ is due to combustion of the carbon content. The weight gain from $300\text{ }^\circ\text{C}$ to $400\text{ }^\circ\text{C}$ is due to the oxidation of MoO_2 to MoO_3 . The slight weight loss after $400\text{ }^\circ\text{C}$ 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 $400\text{ }^\circ\text{C}$.

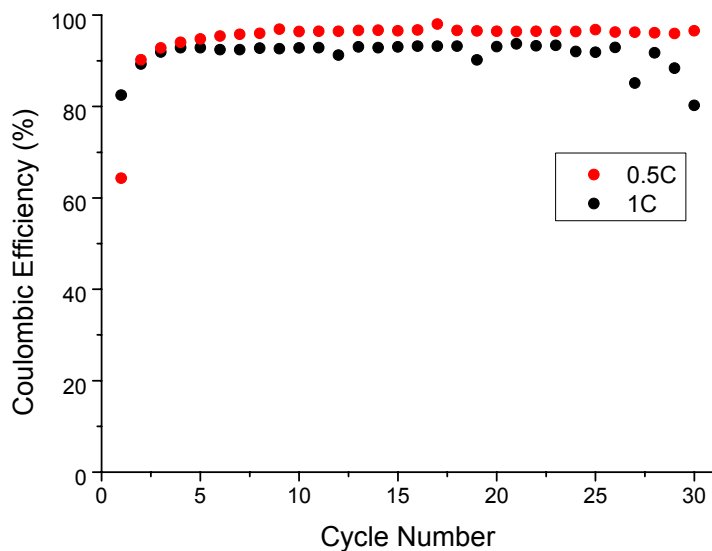


Figure S6. Coulombic efficiency profile of $\text{MoO}_2@\text{C}$ spheres at 0.5C and 1C rate.

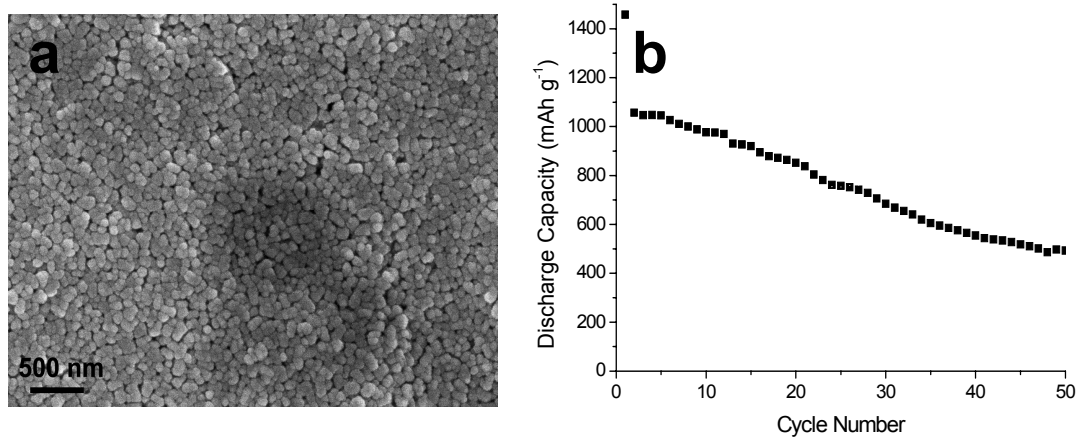


Figure S7. (a) FESEM image and (b) cycling performance of the MoO₃ nanospheres obtained by calcining the MoO₂@C nanospheres in air at 400 °C for 3 h.