Supplementary Materials:

Experimental Section

Material Synthesis

Firstly, 0.100 g ammonium molybdate tetrahydrate [(NH₄)₆Mo₇O₂₄·4H₂O] was dissolved in 37.5 mL distilled water. Then, 7.5 mL hydrochloric acid (3 M) was added into the above solution. After stirring for 10 min, 0.100 g polyvinylpyrrolidone (PVP) was then added into the as-formed solution. After complete dissolution of PVP, 0.100 g ascorbic acid (Vc) was last added into the solution, forming a light yellow solution. The as-formed solution was allowed to stir for another 30 min before it was transferred into a 65 mL Teflon-lined autoclave. Then, the autoclave was heated to 180°C and maintained for 46 h in an electric oven. The precipitate was collected by centrifugation and washed with distilled water and anhydrous ethanol for several times, and dried at 35°C for 48 h in a vacuum oven. The resulting deep blue powder was annealed at 600°C for 4 h under argon flow to obtain the final product.

Characterization

The crystalline phase of the product was determined by powder X-ray diffraction (XRD) on a Philip-X'Pert X-ray diffractometer with a Cu K α radiation (λ =1.5418 Å). The carbon content was measured on CHN-O-Rapid (Heraeus, Germany). The specific surface area is measured at 77 K on Micromeritics ASAP2020 equipment. The sample morphology was observed on scanning electron microscopy (SEM, S-4800). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and selected-area electron diffraction (SAED) were examined on JEM-2100 electron microscope (operation at an accelerating voltage of 200 kV). Fourier transform infrared absorption (FT-IR) data were collected on a Nicolet iS10 spectrophotometer

in the range 2200-1200 cm^{-1} .

Electrochemical measurement

The electrochemical properties were tested by using a CR2032-type coin cell. The working electrode consists of 80 wt% prepared powder or bulk MoO₂, 10 wt% carbon nanotube as the conductive material, 10 wt% polyvinylidene fluoride as the binder and copper foil as the current collector. The electrolyte is the mixture of 1 M LiPF₆ solution in ethylene carbonate/diethyl carbonate (EC:DEC=1:1, v/v). A coin cell is composed of lithium foil as the counter electrode, working electrode, electrolyte and Celgard 2400 as the separator. All cells were assembled in an argonfilled glove box (Mikarouna, Superstar 1220/750/900). The galvanostatic cycling test was carried out on a battery test system (Land-CT2001A) in the potential window from 0.005 to 3.0 V. Cyclic voltammetry was performed on an electrochemical workstation (CHI 660D). The rate capability were tested after the samples discharged/charged for 30 cycles at 0.5 C current density. The calculations of specific capacity had taken into account the Li⁺ insertion of carbon nanotube. As shown in Figure S1, the carbon nanotube can deliver a stable capacity of *ca*. 230 mAh·g⁻¹ before 100 cycles.



Figure S1. The specific capacity and cycling performance of multi-walled carbon nanotube.



Figure S2. N₂ adsorption/desorption isotherms of MoO₂@C hollow nanospheres. The corresponding pore size distribution curve is shown as the inset.



Figure S3. TEM images of the intermediate when the reaction time was 36 h.



Figure S4. Illustration of the lithiation and delithiation processes of MoO₂@C hollow nanosphere.



Figure S5. SEM (a) and TEM (b) images of MoO₂@C composite electrode after 100 cycles.