Supplementary Materials:

Experimental Section

Material Synthesis

Firstly, 0.100 g ammonium molybdate tetrahydrate \([(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot4\text{H}_2\text{O}]\) 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 Kα 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 MoO\(_2\), 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 LiPF\(_6\) 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 argon-filled 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 \(ca. 230 \text{ mAh} \cdot \text{g}^{-1}\) before 100 cycles.
Figure S1. The specific capacity and cycling performance of multi-walled carbon nanotube.

Figure S2. N$_2$ adsorption/desorption isotherms of MoO$_2$@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 MoO$_2$@C hollow nanosphere.
Figure S5. SEM (a) and TEM (b) images of MoO$_2$@C composite electrode after 100 cycles.