Experimental section

Synthesis of MoO₃/C nanofibers

In a typical synthetic process, 0.3g molybdenyl acetyacetonate ($C_{10}H_{14}MoO_6$) was firstly dissolved in 3g N, N-dimethylformamide (DMF) with stirring for 1h. Then, 0.5g PVP-10 was dissolved in above solution with stirring for 10h, followed by adding 1g ethanol to above solution. Thus, a viscous gel of mixed composite solution was obtained. As for typical electrospinning parameters, the spinneret had an inner diameter of 0.6 mm. A distance of 20 cm and a direct current voltage of 20 kV were maintained between the tip of the spinneret and the collector. After obtaining PVP-based nanofibers, the nanofibers were preliminary heat treatment in oxidizing in air from room temperature to 220 °C with a heating rate of 0.9 °C /min, and then held at 220 °C for 3h in air. Finally, MoO_3/C nanofibers were obtained through heating former precursors from room temperature to 550 °C at a rate of 3 °C/min and then held at 550 °C for 2h in argon.

Characterization

The microstructure of the as-prepared samples was characterized by X-ray diffraction (XRD; GBC MMA diffractometer) with Cu Kα radiation at a scanning rate of 2°/min. Thermogravimetric analysis (TGA) of the as-prepared MoO_3/C nanofibers was carried out with a TGA/DSC1 type instrument (METTLER TOLEDO, Switzerland) at a heating rate of 5 °C/min from 25 to 800 °C in air. The morphology of the MoO_3/C nanofibers was evaluated using a JEOL 7500FA field emission scanning electron microscope (FE-SEM, JEOL, Tokyo, Japan) and a JEOL JEM-ARM200F

transmission electron microscope (STEM, JEOL, Tokyo, Japan). Energy dispersive X-ray spectroscopy (EDX, JEOL 7500FA) was used to confirm the carbon and MoO_3 contents. X-Ray photoelectron spectroscopy (XPS) experiments were carried out on a VG Scientific ESCALAB 220IXL instrument using aluminium Kα X-ray radiation during XPS analysis.

Electrochemical Measurements

The working electrodes were prepared by mixing 80 wt% as-prepared active materials with 10 wt% carbon black and 10 wt% carboxymethylcellulose (CMC) binder in distilled water to form homogeneous slurry, which was uniformly pasted onto copper foil. The prepared working electrodes were dried in a vacuum oven at 80 °C over 12 h and were then ready for assembly in test cells after pressing. Electrochemical cells (CR2032 coin type) using the active materials (about 1.5 mg per sheet) as working electrode, Li foil as the counter electrode and reference electrode, a microporous polypropylene film as the separator, and 1 M $LiPF_6$ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte were assembled in an Ar-filled glove box (H_2O, $O_2 < 0.1$ ppm, Mbraun, Unilab, USA). The cells were galvanostatically charged and discharged over a voltage range of 0.02-3 V versus Li/Li^+ at different constant current densities based on the weight of the samples on a Land CT2001A cycler. Cyclic voltammetry (CV) was performed on an Ametek PARSTAT®2273 electrochemistry workstation.
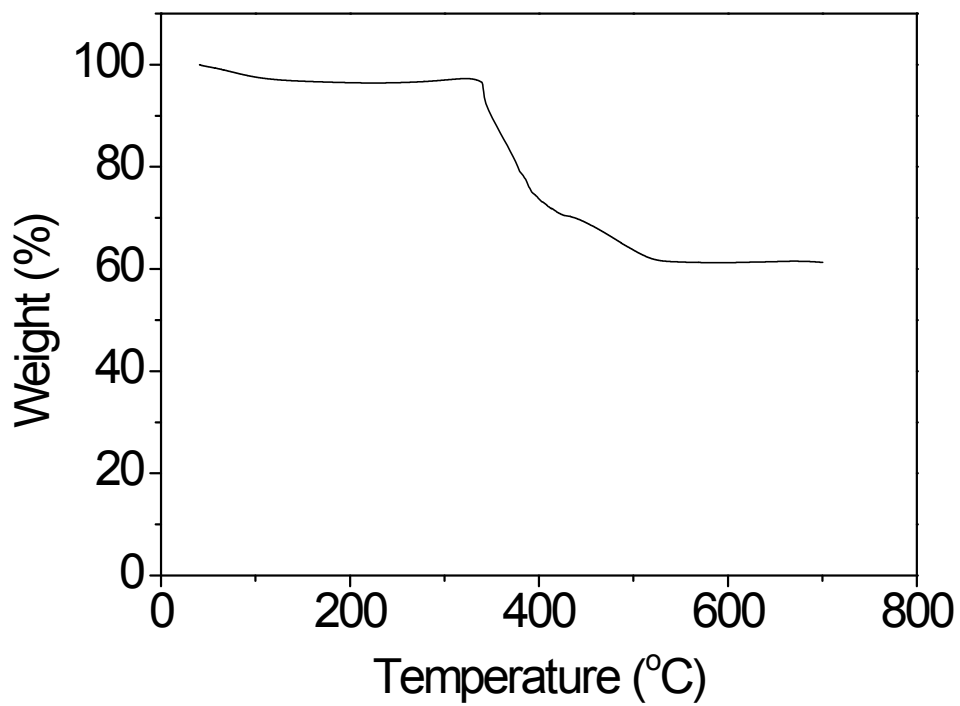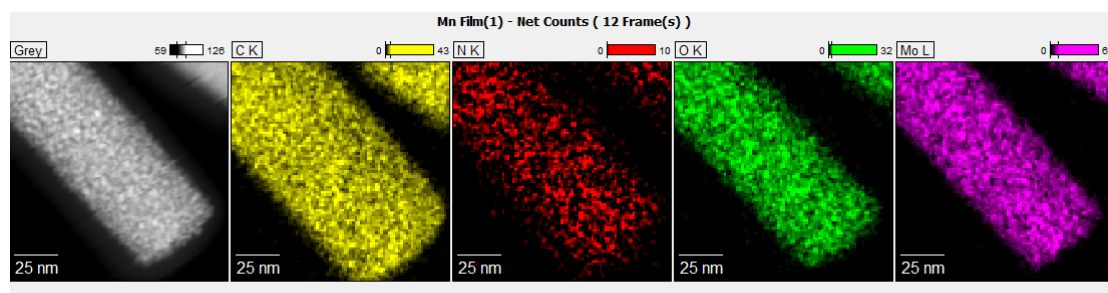
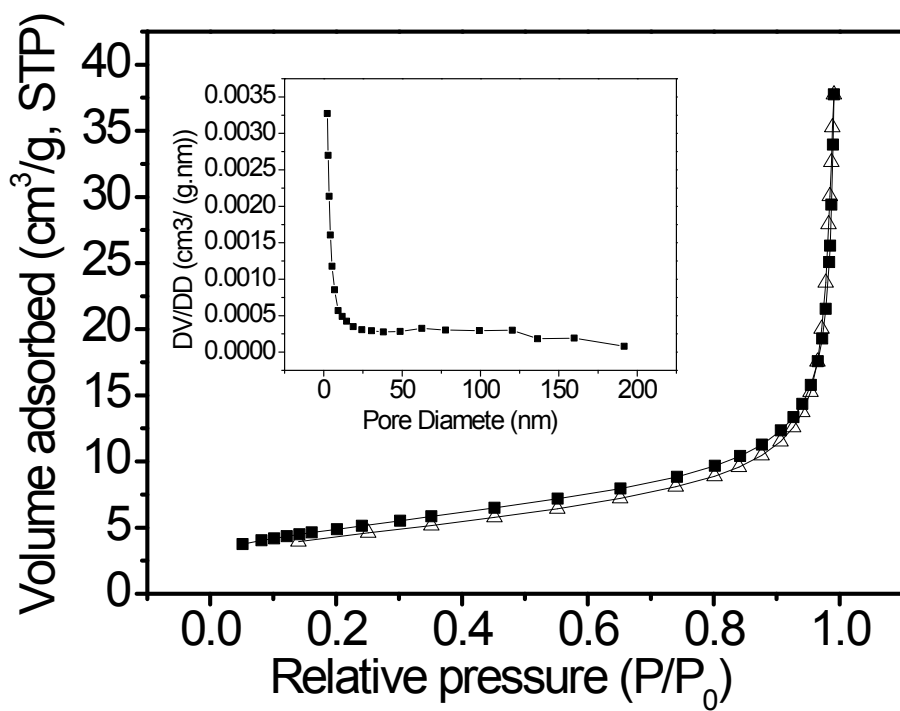**Fig. S1** TG curve of MoO$_3$@C nanofibers.
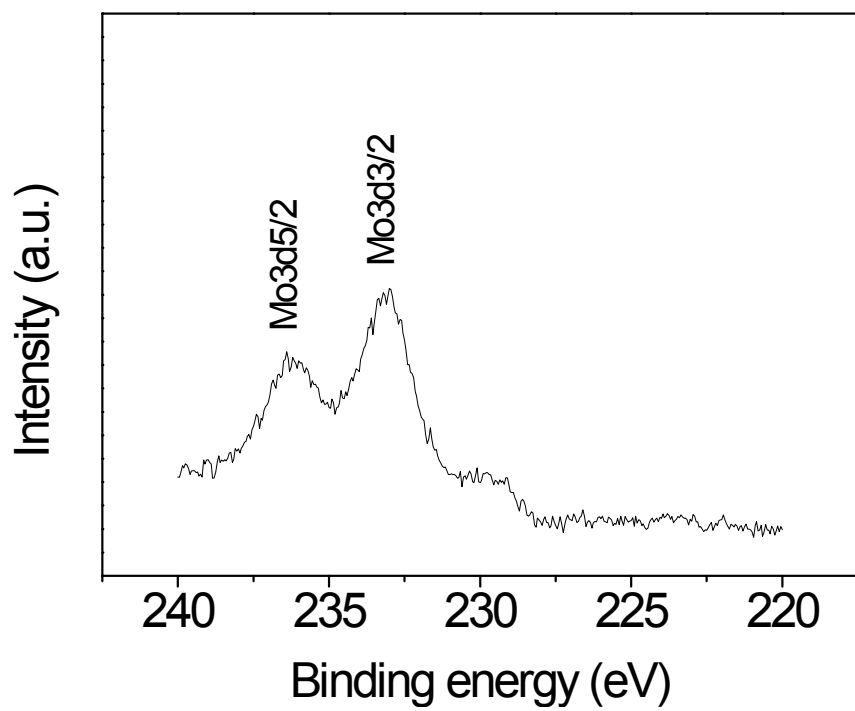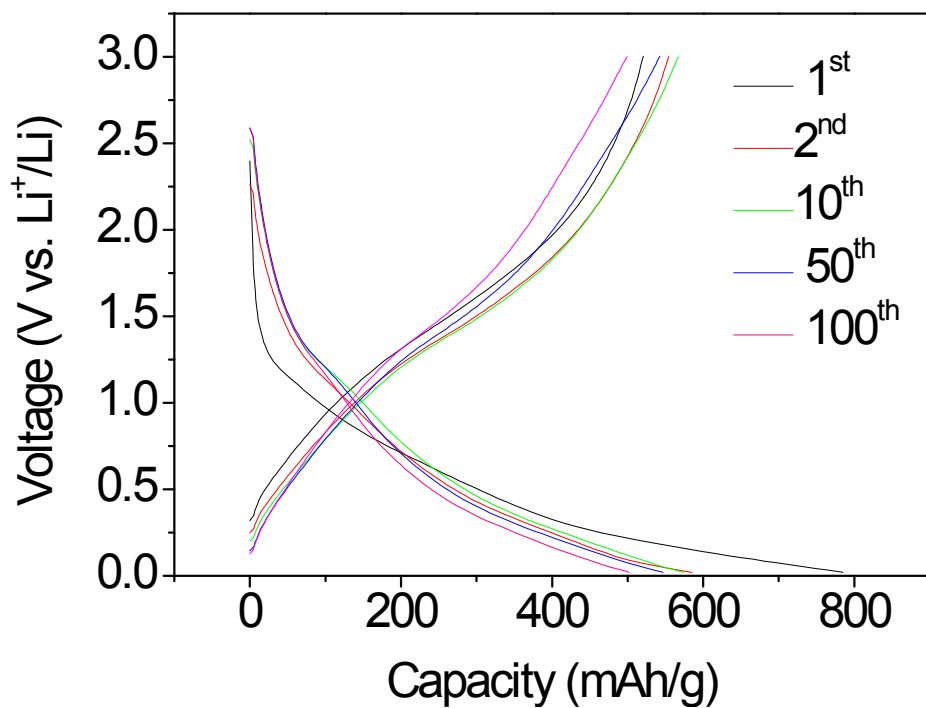
Fig. S2 XPS spectrum of Mo 3d.

S4800 5.0kV 8.7mm x10.0k SE(M)   5.00um
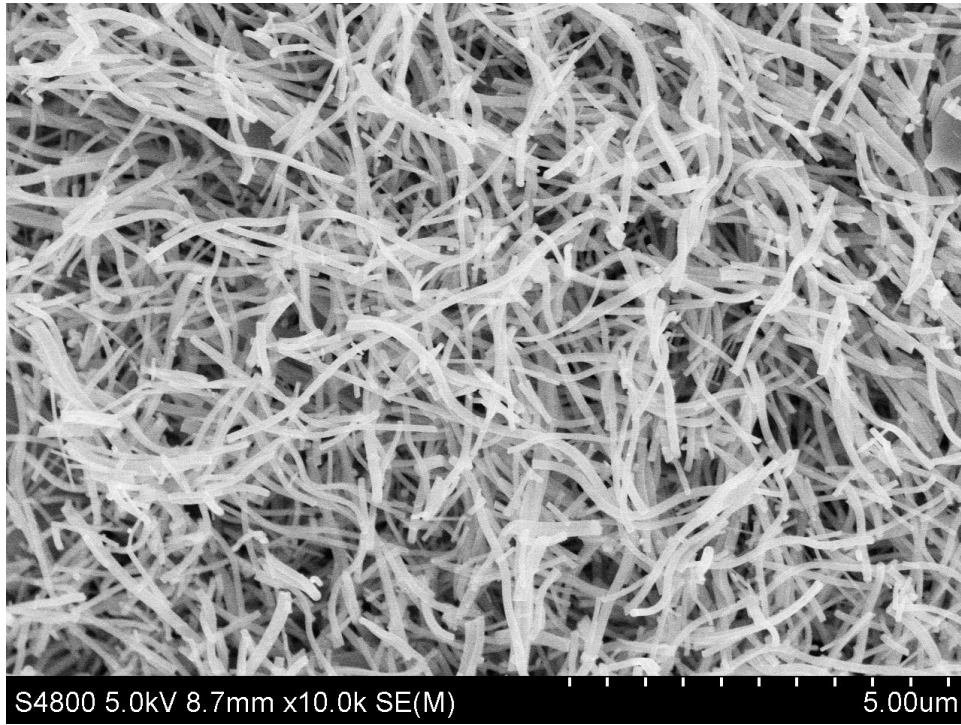
Fig. S3 Low-magnification SEM image of MoO$_3$@C nanofibers.

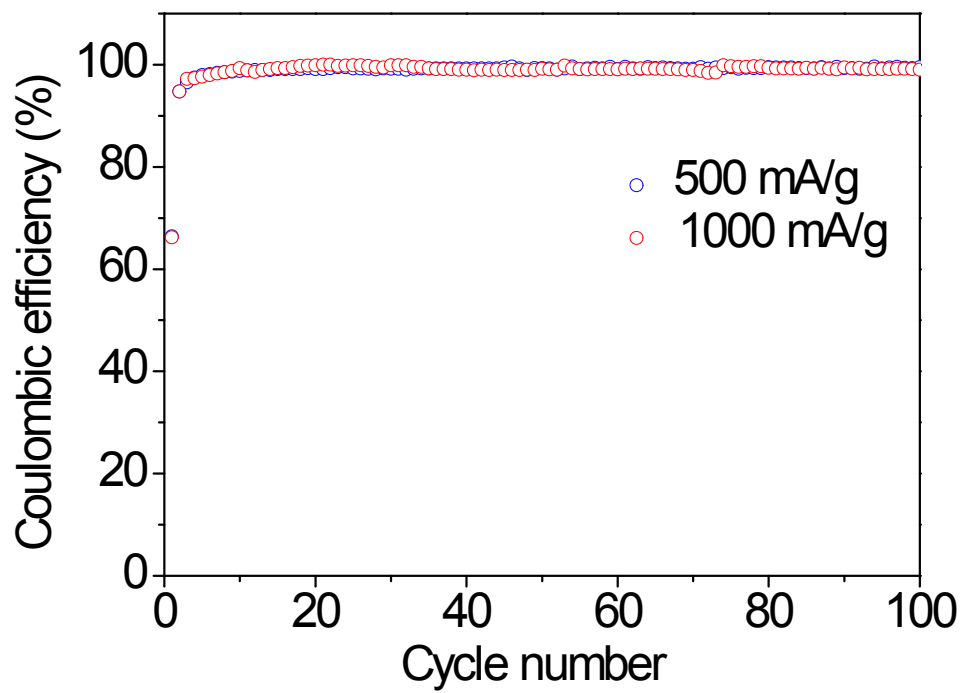**Fig. S4** Element distribution spectra of a MoO$_3$@C nanofiber.

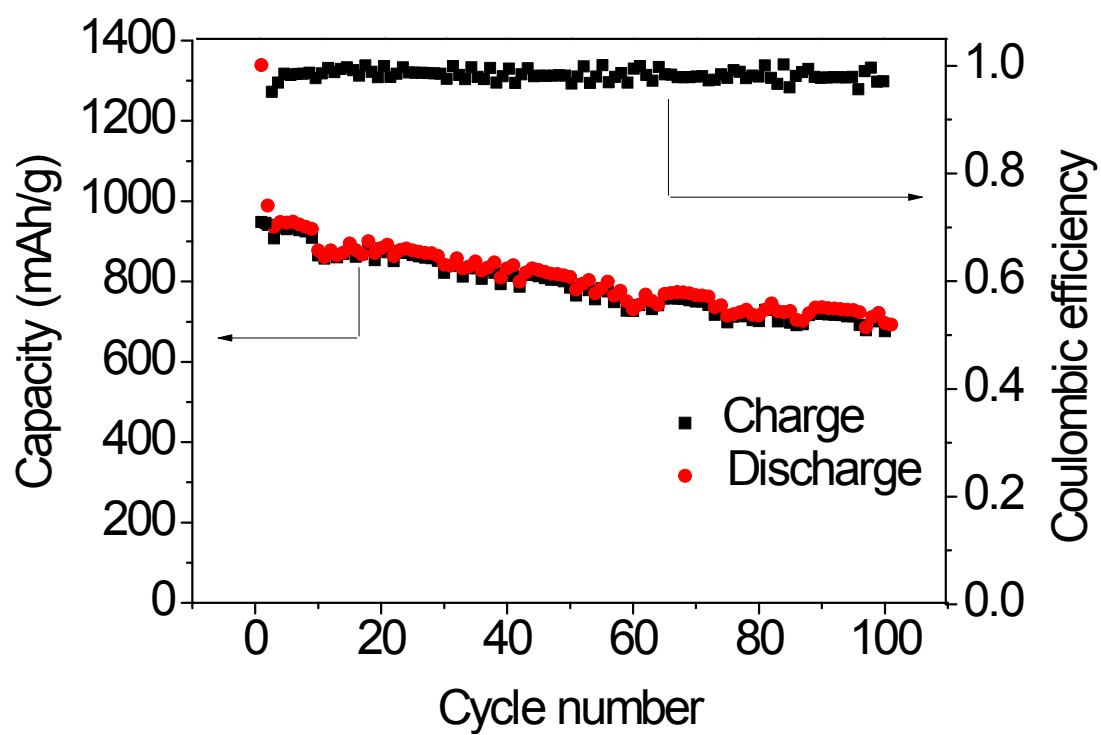**Fig. S5** N$_2$-adsorption/desorption isotherm and porous size distribution curves of MoO3@C nanofibers.

Fig. S6 Charge/discharge curves of MoO$_3$@C nanofibers at 1000 mA/g for various cycles.

Fig. S7 Coulombic efficiency of MoO$_3$@C nanofibers during cycling at 500 and 1000 mAh/g.

Fig. S8 Cycling performance of MoO$_3$@C nanofibers at 200 mA/g.

After 100 cycles, the discharge capacity is about 696 mAh/g at 200 mA/g.