

Supporting information

## Nanotube $\alpha$ -MnO<sub>2</sub>: High Surface Area and Enhanced Lithium Battery Properties

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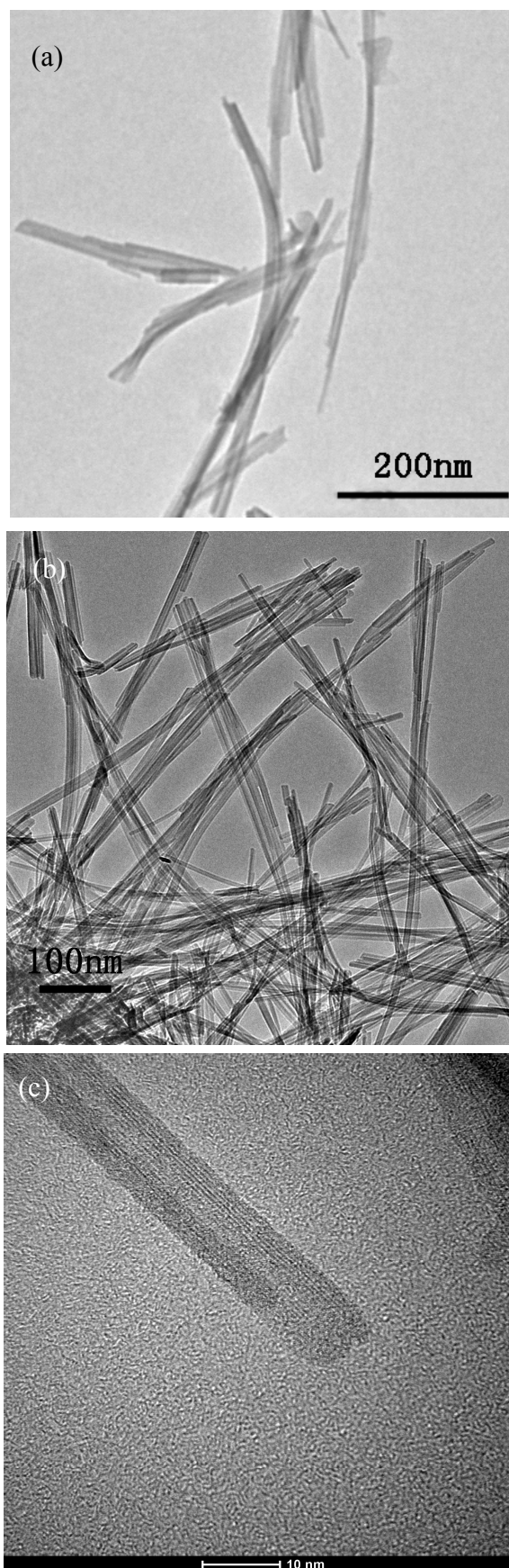
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### Experimental:

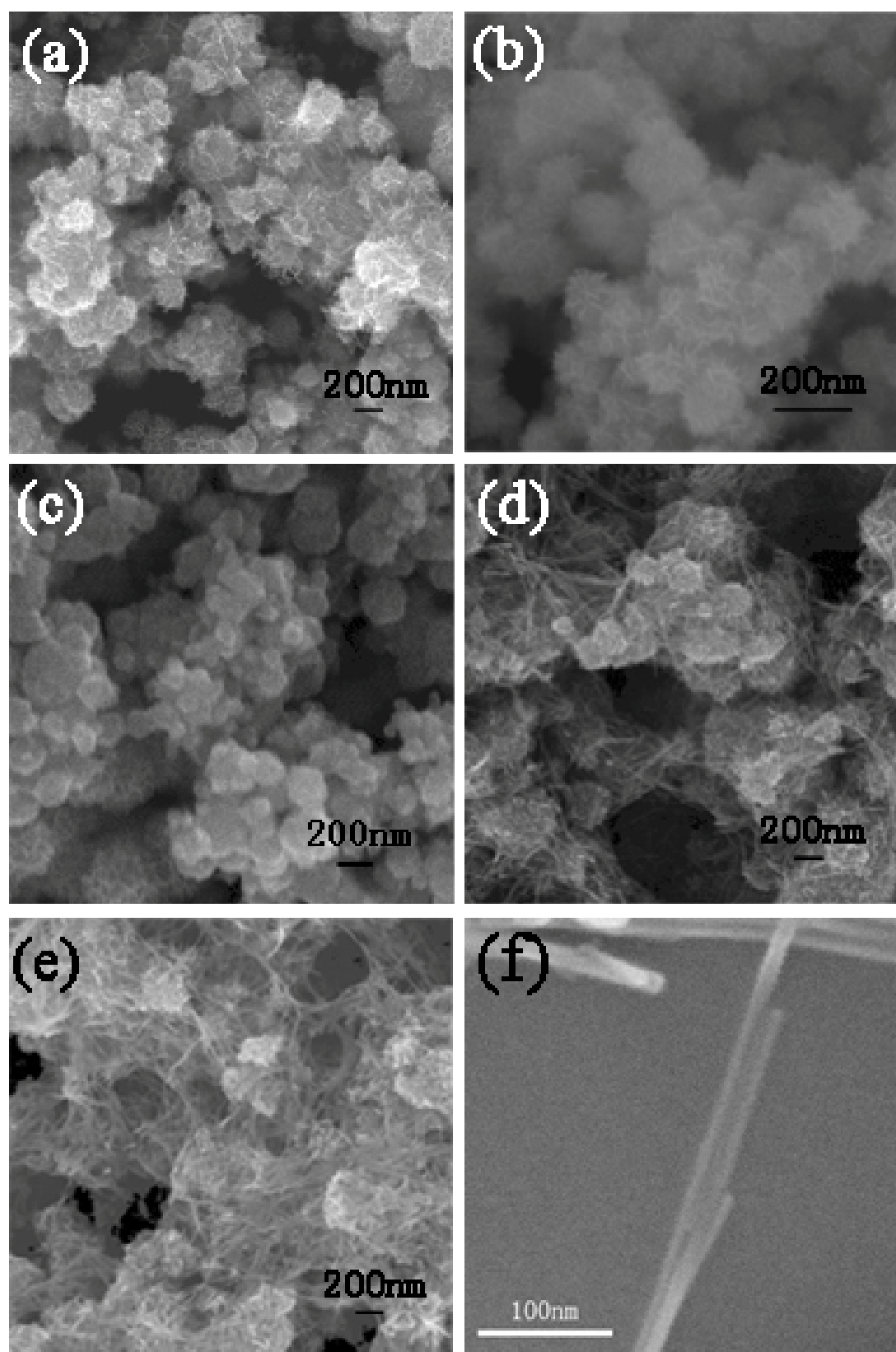
The  $\alpha$ -MnO<sub>2</sub> nanotubes were prepared by a hydrothermal approach. In a typical experimental procedure, 8 mmol KMnO<sub>4</sub>, 0.4 mmol concentrated NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and 1.5  $\mu$ mL 10% aqueous tetra-(n-butyl) ammonium hydroxide (TBAOH) were added to 35 mL deionized water to form the precursor solution, which was then transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 mL. The autoclave was sealed and hydrothermally treated at 180 °C for 48 h. After the autoclave was cooled down to room temperature naturally, the products were collected by centrifugation and washed several times by deionized water to remove possible impurities or excess ions. The as-prepared sample was then dried overnight. All the reagents were of analytical purity and purchased from Beijing Chemical Reagents Company.

The structure of the samples was characterized by x-ray diffraction patterns (XRD, Model Rikagu D/max 2500 with CuK $\alpha$  radiation), and their microstructure of the samples was observed using a field-emission scanning electron microscope (FE-SEM, Model ZIESS SUPRA 55). High-resolution transmission microscopy (HRTEM) image was recorded on a microscope (FEI Tecnai G2 F20 S-Twin) with an accelerating voltage of 200 kV. Transmission electron microscopy (TEM) observations were performed on a transmission electron microscope (model: JEM-6301F at 100 kV, JEOL, Japan). Nitrogen physisorption experiments were carried out using a Quantachrome Autosorb-1 analyser at -196 °C. Before the measurement, degassing was conducted at 100 °C for 6h to remove possible moisture. Raman-scattering data were collected in the frequency range of 100-1100 cm<sup>-1</sup> using a Raman spectrometer (Model JYT6400, Jobin Yvon, France).

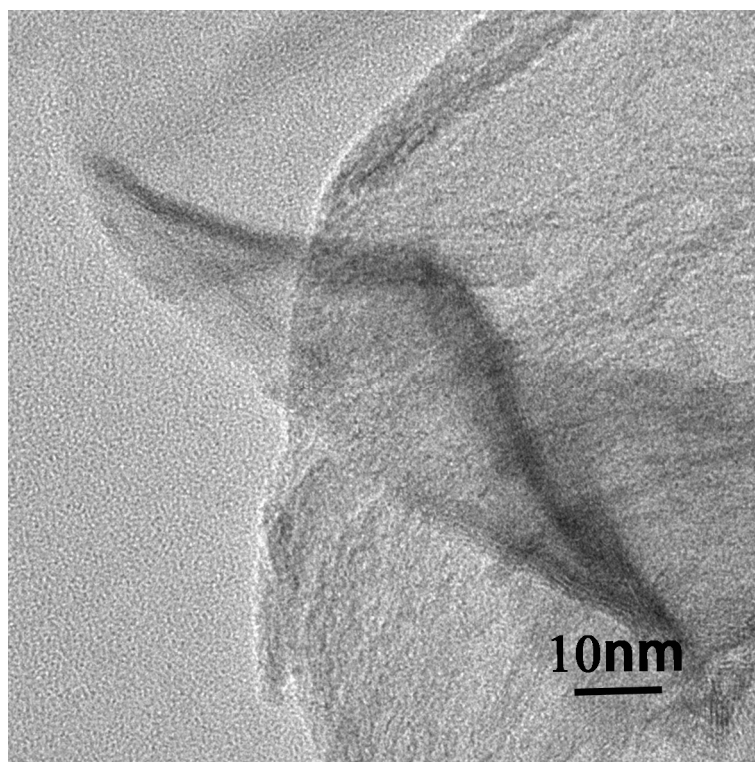
The test electrode was composed of active material (80 wt%), carbon black (10 wt%) and polyvinylidene fluoride (PVDF) (10 wt%). Cu foil was used as the current collector and Li foil was used as the counter electrode and 1M LiPF<sub>6</sub> dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) (Shanghai Topsol Ltd., H<sub>2</sub>O <10 ppm) was used as the electrolyte. A Swagelok-type two-electrode cell was constructed for electrochemical test. The cell was assembled in an argon-filled glove box and cycled between 10mV and 3.25V using a Land automatic battery tester. Galvanostatic intermittent titration technique (GITT) experiment was performed using an automatic battery tester (Arbin Instruments, Tianjin Co., Ltd.) by the cell for about 35days for the 300 charging/discharging cycles at a rate of 200 mA g<sup>-1</sup>.



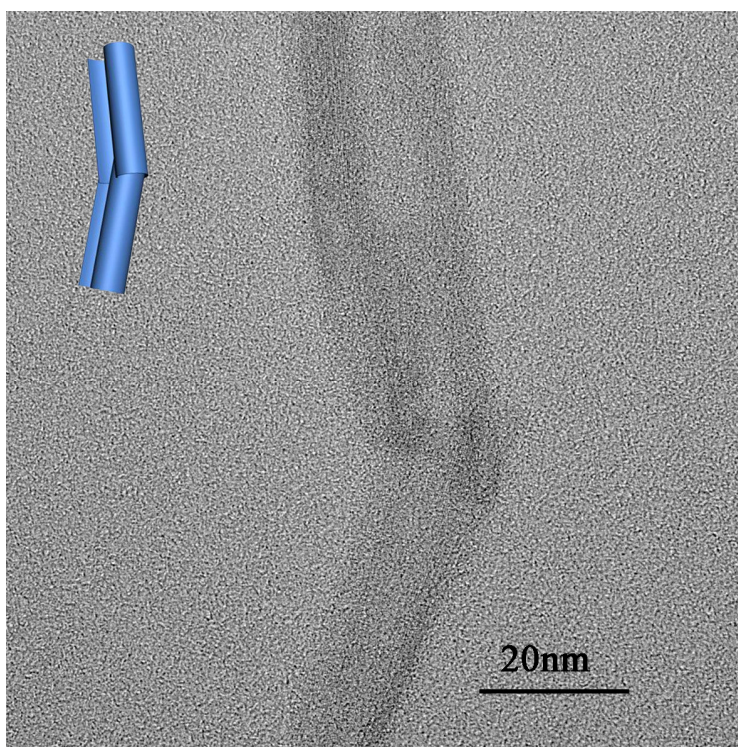
**Fig. S1** TEM images of the as-prepared  $\text{MnO}_2$  treated via hydrothermal method for (a) 24h and (b) 48 h, and (c) HRTEM images for 48 h.



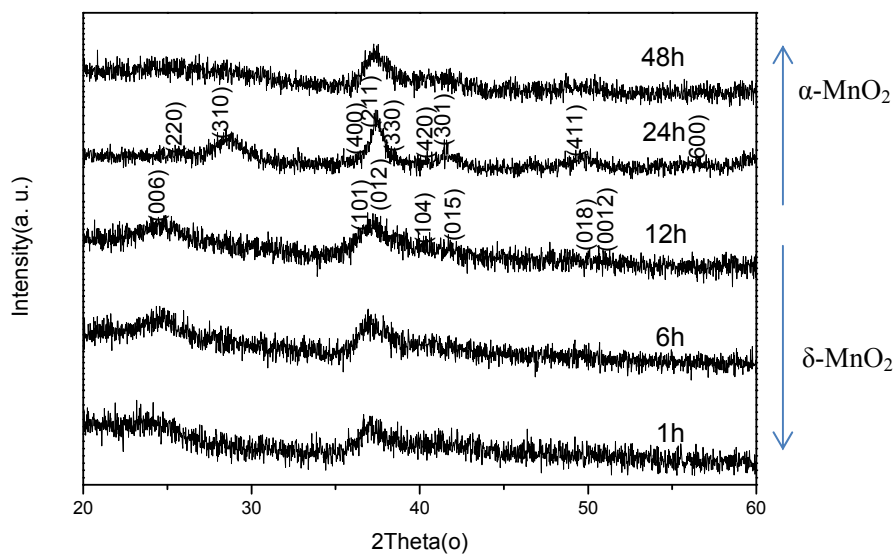
**Fig. S2** SEM images of the as-prepared MnO<sub>2</sub> treated via hydrothermal method for (a) 1h, (b) 6h, (c) 12h, (d) 24h, and (e, f) 48h.



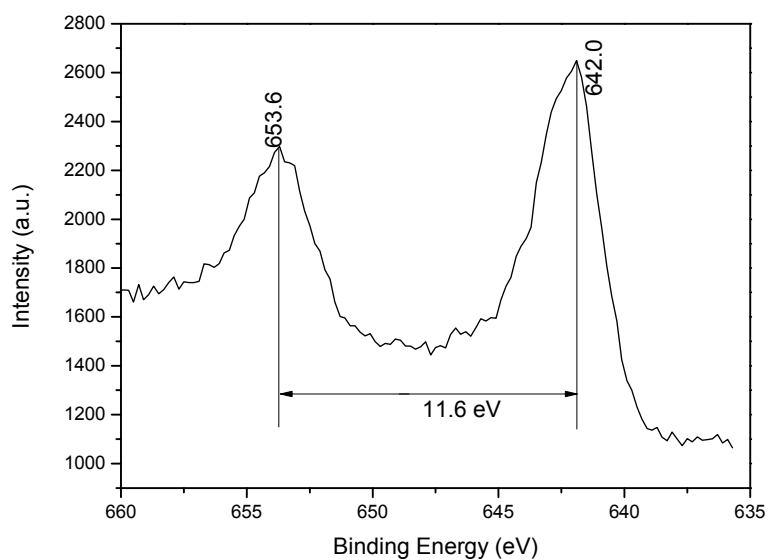
**Fig. S3** HRTEM image of the as-prepared MnO<sub>2</sub> treated via hydrothermal method with TBAOH for 12h. It was found that the platelet trend to be exfoliated to thinner platelet and to scroll.



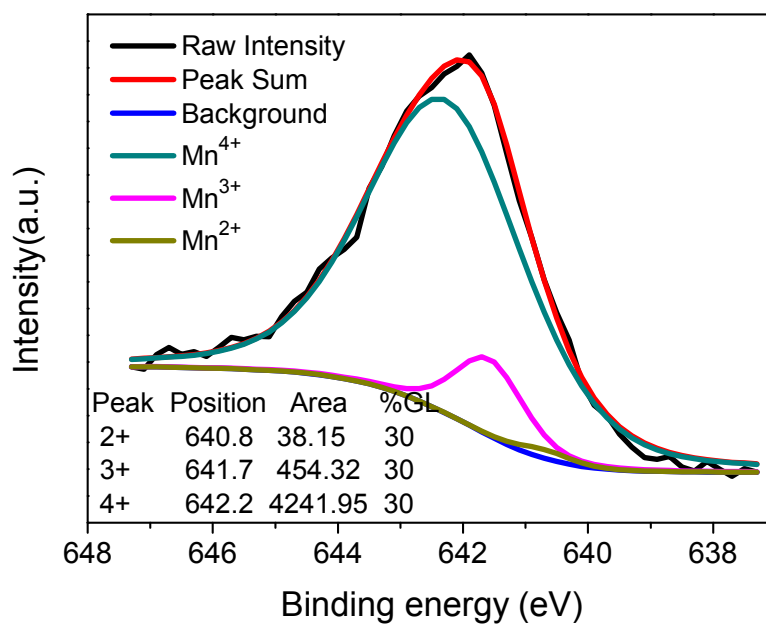
**Fig. S4** HRTEM image of the as-prepared  $\text{MnO}_2$  treated via hydrothermal method with TBAOH for 24h. The tubes were likely to be connected with ends, so the length of nanotube was larger than the lateral size of  $\delta\text{-MnO}_2$  nanoplate.



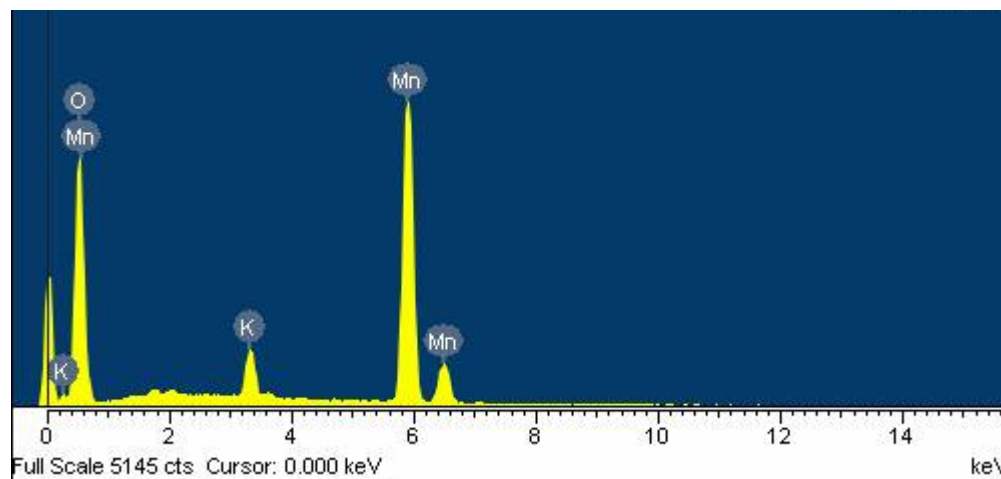
**Fig. S5** X-ray diffraction (XRD) of the as-prepared MnO<sub>2</sub> treated via hydrothermal method with TBAOH for 1h, 6h, 12h, 24h, and 48h. It is found that δ-MnO<sub>2</sub> was obtained before 24h, while the α-MnO<sub>2</sub> formed with the reaction time increased.



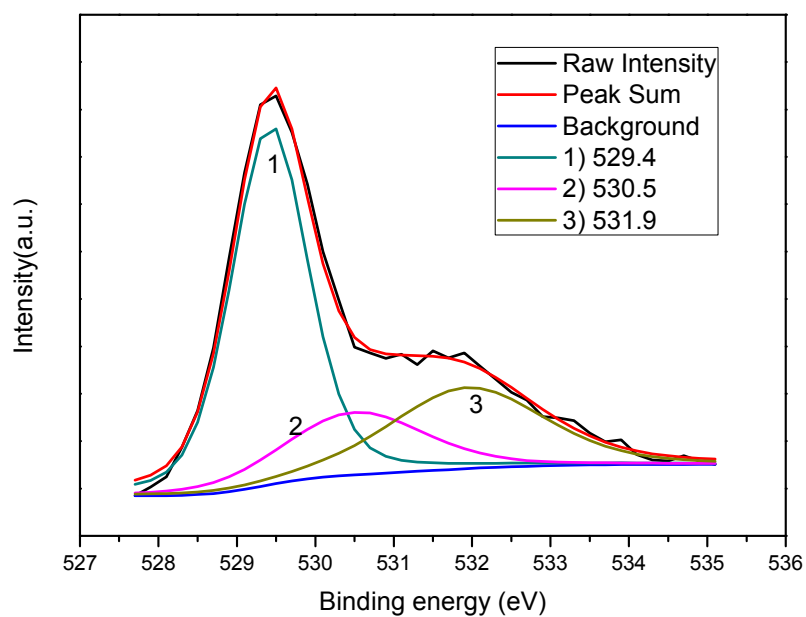
**Fig. S6** XPS survey spectra of Mn 2p of the as-prepared α-MnO<sub>2</sub> nanotube.



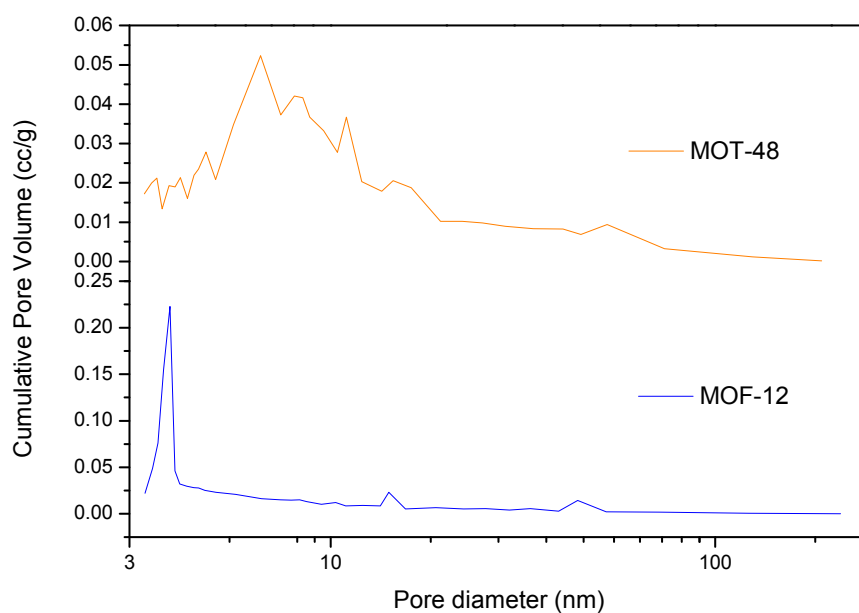
**Fig. S7** The fitted spectra of Mn2p<sub>3/2</sub>.



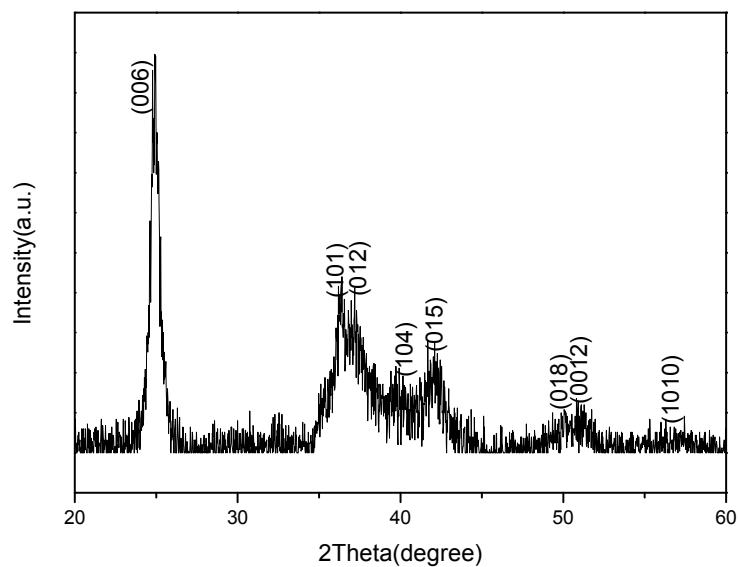
**Fig. S8** The EDS image of MOT-48.



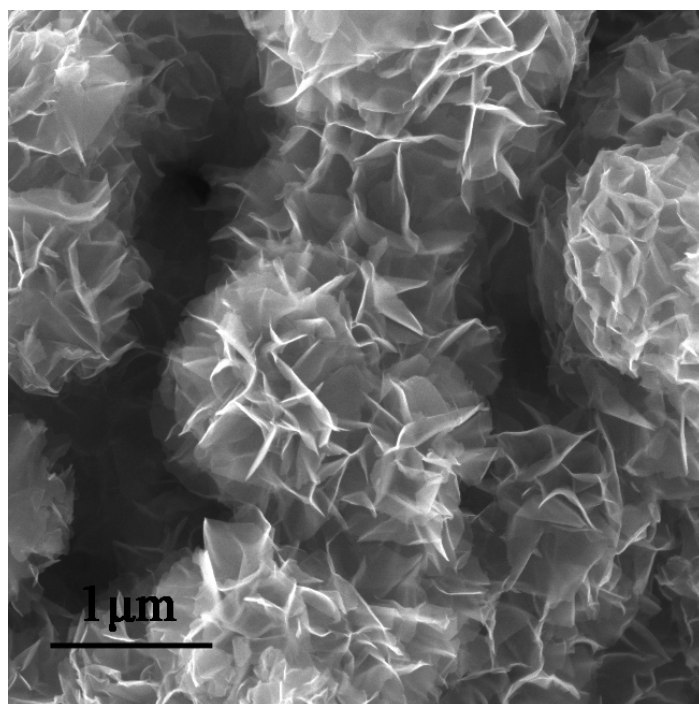
**Fig. S9** The fitted spectra of O1s.



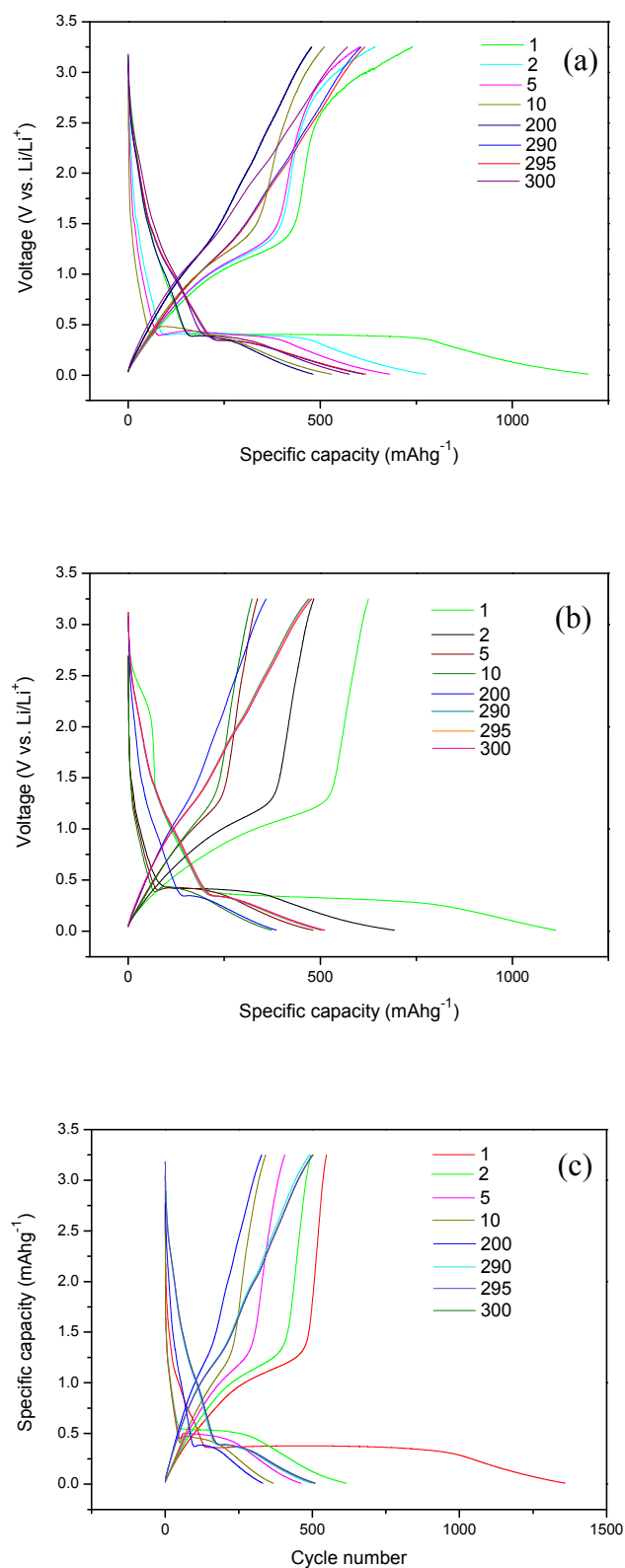
**Fig. S10** The pore size distribution curves of MOF-12 and MOT-48



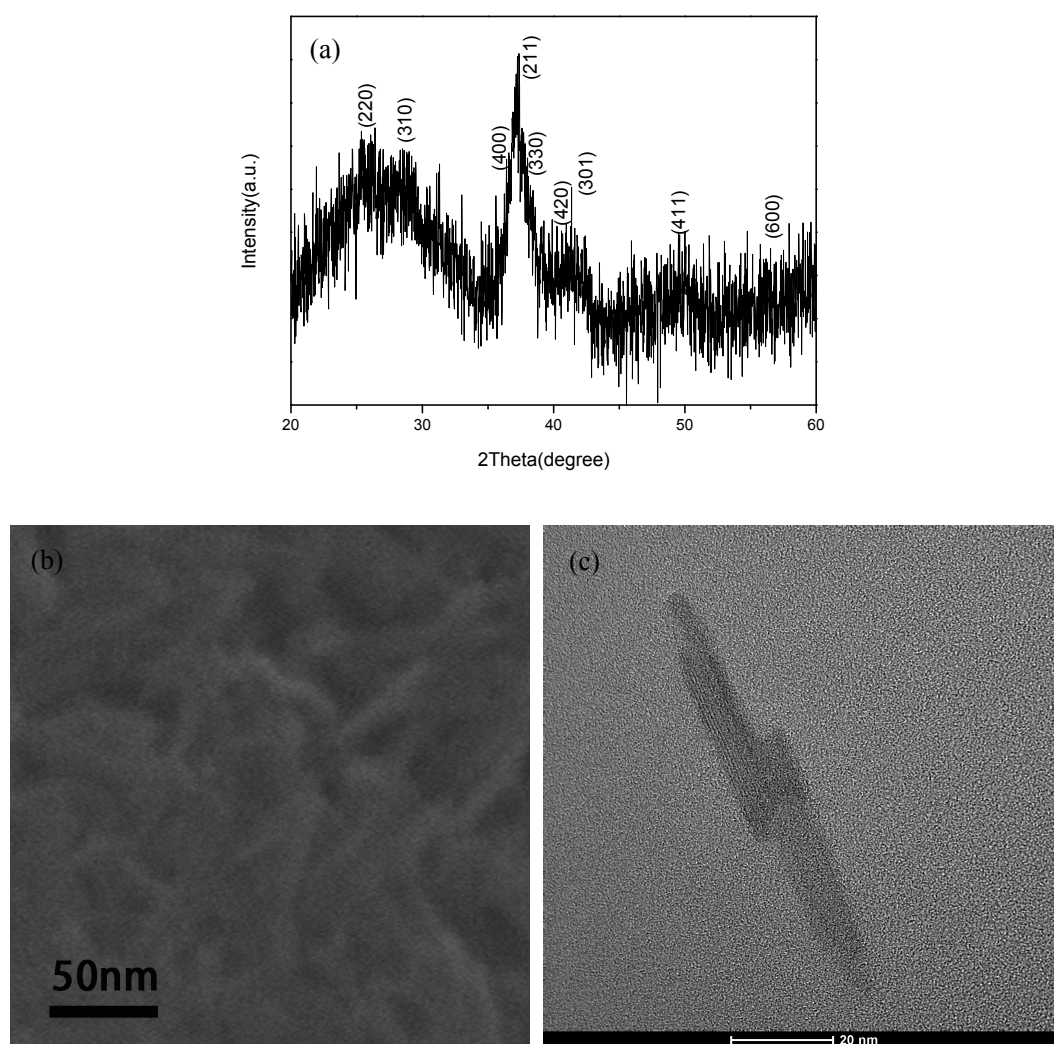
**Fig. S11** X-ray diffraction (XRD) of the as-prepared  $\text{MnO}_2$  treated without TBAOH for 48h. The large  $\text{MnO}_2$  micro-flowers were obtained with the rhombohedral phase of  $\delta\text{-MnO}_2$  (JCPDS no. 86-666).



**Fig. S12** SEM image of the as-prepared  $\text{MnO}_2$  treated without TBAOH for 48h. The  $\delta\text{-MnO}_2$  is micro size and is much larger and thicker than that obtained with TBAOH.



**Fig. S13** The charge-discharge voltage profiles of the MOT at constant current densities of (a) 200 and (b) 800 mA g<sup>-1</sup> and (c) that of MOF at constant current densities of 200 mA g<sup>-1</sup> are shown in Figure S6



**Fig. S14** (a)XRD pattern, (b) SEM image, and (c) HRTEM image of the MOT after 50 discharge-charge cycles. It was confirmed that, the nanotubes were obtained with tetragonal phase of  $\alpha$ -MnO<sub>2</sub> (JCPDS no. 81-1947). The nanotubes are stable under electrochemical environment.