Supporting Information

Hydrothermal synthesis of hollow Mn_2O_3 nanocones as anode material for Li-ion batteries

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1. Materials Characterizations:

The morphologies and structures of the as-prepared samples were characterized by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and powder X-ray diffraction (XRD) measurements. XPS and TG analysis of the as-prepared samples were also measured.

2. Electrochemical Measurements:

The electrodes were prepared by spreading a mixture of 80 wt % Mn_2O_3 active material, 10 wt % acetylene black and 10 wt % poly(vinylidene fluoride) (PVDF) onto a copper foil current collector. The as-prepared electrodes were dried at 120 °C in vacuum oven for 24 h and pressed under 10 MPa. The loading mass and thickness of the films are about 0.26 mg and ~ 50 μm, respectively. Electrochemical properties

of the electrodes were measured by assembling them into coin cells (type CR2016) in an argon-filled glove box (MIKROUNA, Super (1220/750/900)) with water and oxygen contents less than 0.5 ppm. Li foil was used as the counter electrode and polypropylene (PP) film (Celgard 2400) as the separator. The electrolyte was made from $LiPF_6$ (1 M) in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) in a volume ratio of 1:1 with 2 wt % vinylene carbonate (VC) as additive. The cells were galvanostatically charged and discharged in a battery test system (LAND-V34, Land Electronic Co., Ltd., Wuhan) for a cut-off voltage of 0.02-3.0 V (vs. Li+/Li) at room temperature. Cyclic voltammetry (CV) studies of hollow Mn_2O_3 nanocones were carried out in the potential range from 3.0 to 0.02 V vs. Li^+/Li at a sweeping rate of 0.1 mV/s by Metrohm Autolab, PGSTAT302N. Electrochemical impedance spectroscopy (EIS) was conducted on constant voltage mode by sweeping the frequency from 10 MHz to 0.1 Hz.

3. Mechanism analysis:

The formation of hollow nanocones may be proposed to an Ostwald ripening process. This ripening process involves "the growth of larger crystals from those of smaller size which have a higher solubility than the larger ones" (IUPAC Compendium of Chemical Terminology, 2nd edition, 1997).[s1] Upon ripening, interior spaces can be created in accordance to matter state and agglomerative pattern of pristine crystallites. For example, to lower the total energy of a system, smaller, less crystalline, or less dense particles in a colloidal aggregate will dissolve gradually and re-grow into the larger, better crystallized, or denser particles.[s2-s4] Based on the results of different

reaction time, it can be seen that the nanocone with a solid interior is formed in the first 2 h. With the increase of reaction, the ripening process gradually happens. When the time is 6 h, a total hollow interior is formed. A detailed formation mechanism needs further investigation, which will be proceeded in the subsequent works.

S1 W. Z. Ostwald, *Phys. Chem.* 1900, 34, 495-503.

S2 H. G. Yang, H. C. Zeng, *J. Phys. Chem. B* 2004, **108**, 3492.

S3 B. Liu, H. C. Zeng, *Small* 2005, **1**, 566.

S4 J. Li, H. C. Zeng. *J. Am. Chem. Soc.* 2007, **129**, 15839.

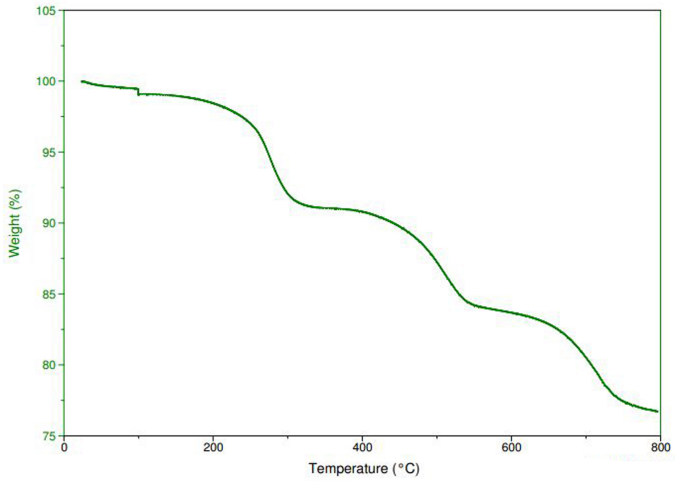

Fig. S1 TGA curves of as-prepared MnO_2 nanocone/CNTs composite. The first weight loss of 9% from room temperature to ~300 °C can be attributed to the removal of surfactant that may be from the unclean part after washing, while the second significant weight loss of 17% in the temperature range of 300-550 °C is most likely due to the reduction of MnO_2 into Mn_2O_3 and combustion of CNTs and the adsorbed organic species. Thus 550 °C is chosen for thermal treatment. The Mn_2O_3 has been gradually converted into Mn_3O_4 in the temperature range of 650-750 °C, that is, $Mn_2O_3 = 2/3Mn_3O_4 + 1/2O_2$.

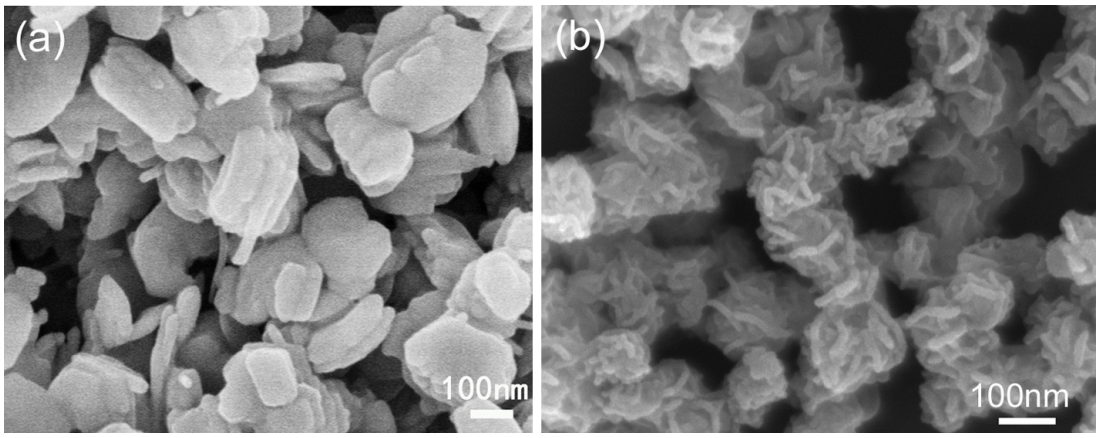

Fig. S2 SEM images of as-prepared MnO_2 (a) without the addition of P123, (b) without the addition of CNTs.

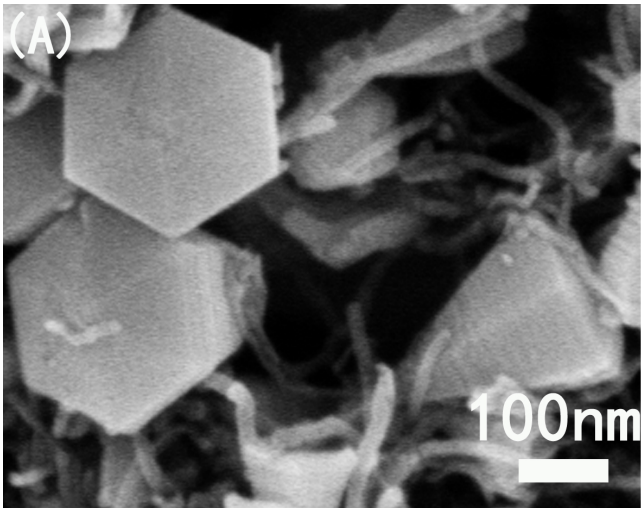

Fig. S3 SEM image of MnO_2 nanocones/CNTs composite grown at different reaction times of 2 h at 120 °C.

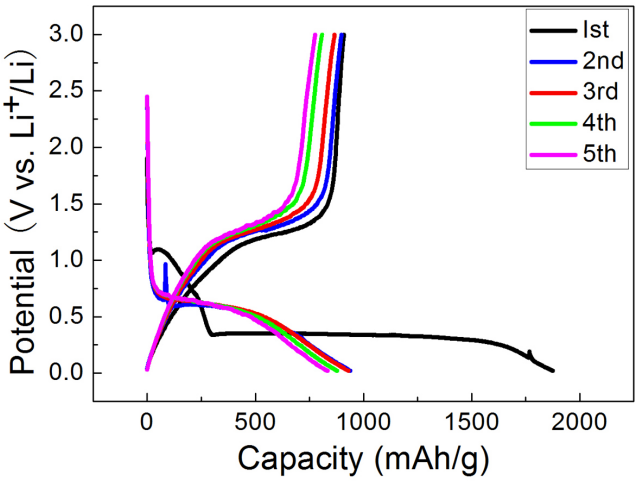

Fig. S4 The first five discharge-charge curves of the hollow Mn_2O_3 nanocones between 0.02 and 3.0 V (vs. Li^+/Li) cycled at a constant current density of 50 mA g^{-1}. Several reasons should be responsible for the irreversible capacity in the first cycle. Part of Mn_2O_3 may be dissolved into electrolyte during the complete formation of SEI layer ($Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$), which is the main reasons for the large irreversible capacity. In addition, some irreversible capacities also result from acetylene black, irreversible surface absorption and so forth. These side effects are mainly attributed to the capacity loss.

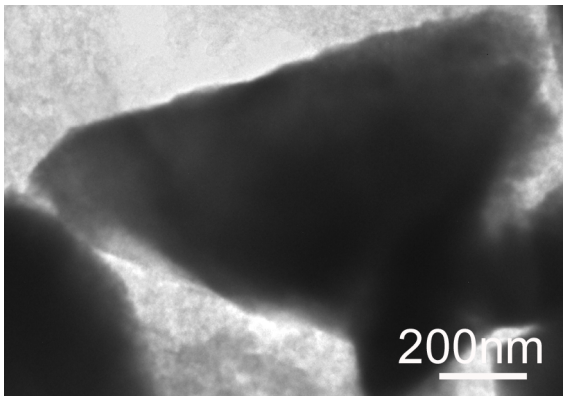

Fig. S5 SEM image of the as-prepared Mn_2O_3 after cycles.

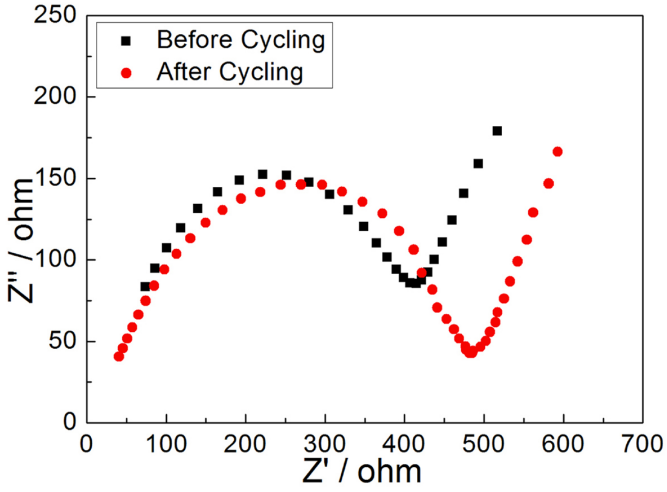

Fig. S6 Electrochemical impedance spectroscopy (EIS) curves of the Mn_2O_3 electrode.