Supplementary Information

Enhanced anode performance of manganese oxides with petal-like microsphere structures by optimizing the sintering conditions

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Experiment details

Synthesis of precursors

Mn_5Al_{95} (at.%) alloy foils (thickness about 50 μm) were prepared by melting Mn (99.9 wt.%) and Al (99.9 wt.%) in an arc-furnace and then melt-spinning under argon-protected atmosphere. In a typical synthesis, 100 mL NaOH (2 mol L^{-1}) was dropped into a mixture including 0.2 g Mn_5Al_{95} alloy foils, 72 mL water and 28 mL H_2O_2. After stirring 8 h, the product ($Na_{0.55}Mn_2O_4$) was washed with water for several times and collected by centrifugation, then dried in oven for further use.

Synthesis of petal-like MnO_2 and MnO microspheres

Petal-like MnO_2 microspheres were synthesized by heating the precursors at 500°C for 2 h in air (temperature increasing rate of 1°C min^{-1}). The corresponding MnO microspheres were obtained by sintering the as-prepared MnO_2 at 350°C for 5 h in Ar/H_2 at the same heating rate. Final product was washed with water until pH~7 in order to remove the NaOH produced and dried in vacuum for further use. In addition, MnO_x with different morphology and phase was obtained when increasing the heating rate to 5°C min^{-1} or increasing the annealing temperature to 600 °C.

Characterizations

The morphology of the samples was characterized by scanning emission microscope (SEM, Hitachi X650), transmission electron microscope (TEM, JEOL JEM-1011) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100). Thermogravimetric analysis (TGA) was measured on a Mettler Toledo TGA/SDTA851 thermal analyzer at an increasing rate of 10°C min^{-1} in flowing air. X-ray powder diffraction (XRD) measurements were performed applying a Bruker D8 advanced X-Ray diffractometer equipped with a Cu Kα radiation (λ= 1.54178 Å). X-ray photoelectron spectra (XPS) were recorded on an ESCALAB 250 X-ray photoelectron spectrometer. BET measurements were performed on a Quadrasorb SI analyzer at 77 K.

Electrochemical measurements

The electrochemical performance was investigated in coin-type cells (2032). The working electrodes were fabricated by conventional slurry-coating method on Cu foil with a mixture of active materials, acetylene black and carboxy-methylcellulose sodium (CMC) in the ratio of 70:20:10 wt.% and then dried in vacuum at 60°C overnight. Pure Li foil was used as the counter electrode, Celgard 2300 membrane and 1 mol L^{-1} $LiPF_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC = 1:1, volume ratio) were used as the separator and the electrolyte, respectively. Cyclic voltammograms (CV) tests were performed in a coin-type cell at a scan rate of 0.1 mV s^{-1} in the range of 0.05-3.0 V *vs.* Li^+/Li on an electrochemical workstation (CHI 760C, Shanghai, China). Galvanostatic discharge/charge tests were performed on a battery testing system (LAND CT-2001A, Wuhan, China) in the voltage range of 0.01-3.0 V. All the measurements were carried out at 30°C. Electrochemical impedance spectroscopy (EIS) was carried out on a PARSTAT MC electrochemical workstation (Princeton Applied Research, USA) in the frequency range of 100 kHz to 0.01 Hz.

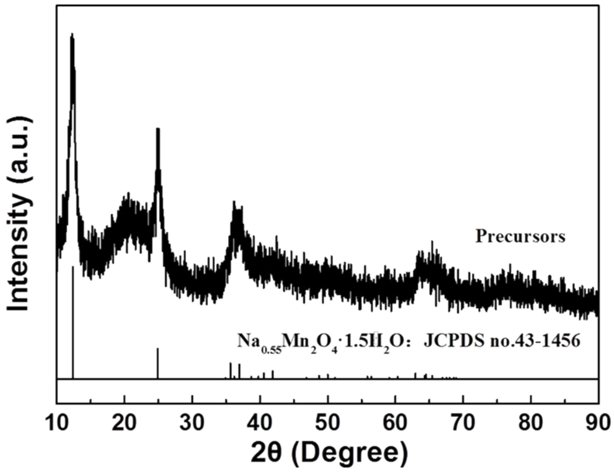

Fig. S1 XRD pattern of the precursors.

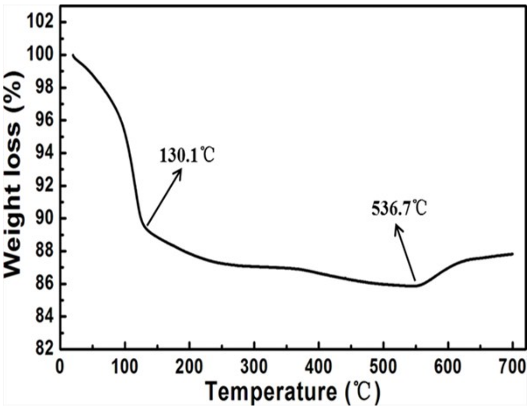

Fig. S2 TGA curve of heating the precursors at an increasing rate of 10 °C min^{-1} in flowing air.

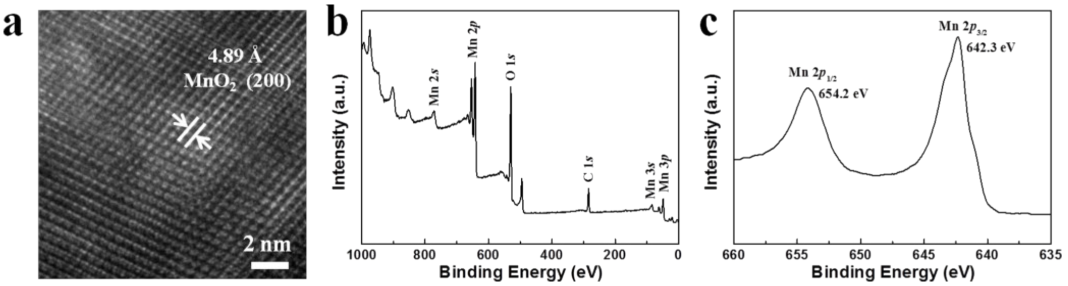

Fig. S3 HRTEM image (a), XPS spectra: survey spectrum (b) and high-resolution Mn 2*p* peaks spectrum (c) of MnO_2 microspheres.

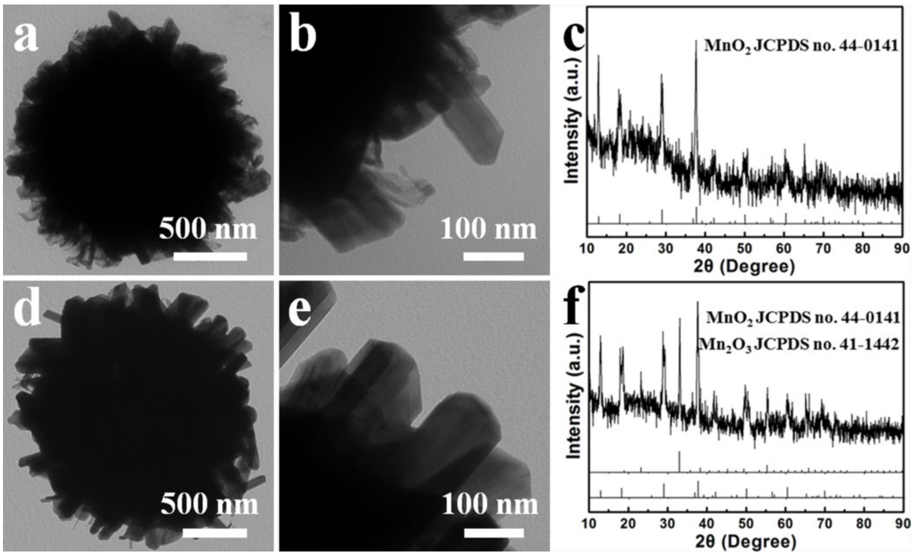

Fig. S4 TEM images of precursors after calcining at 500°C (5°C min^{-1}) (a, b) and 600°C (1°C min^{-1}) (d, e) for 2 h in air. XRD patterns of precursors after calcining at 500°C (5°C min^{-1}) (c) and 600°C (1°C min^{-1}) (f) for 2 h in air.

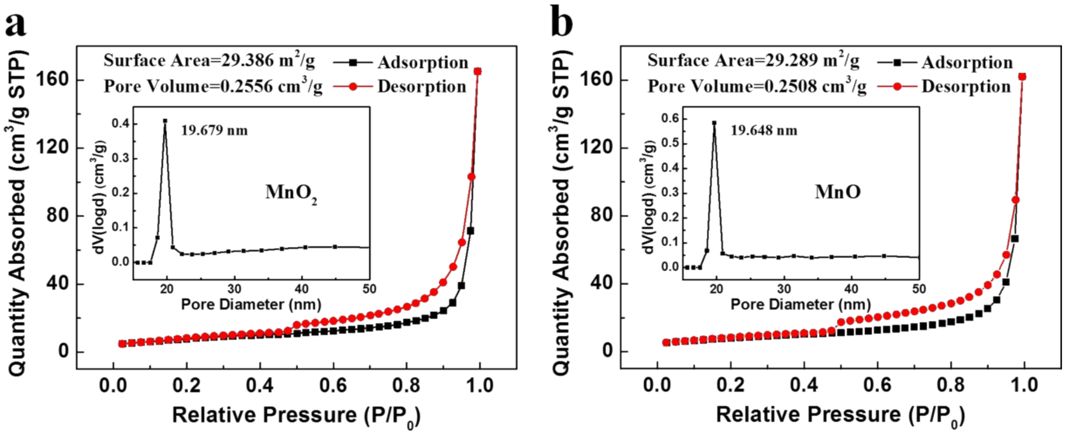

Fig. S5 The nitrogen adsorption-desorption isotherms and pore distribution curves (insert) of MnO_2 (a) and MnO (b).

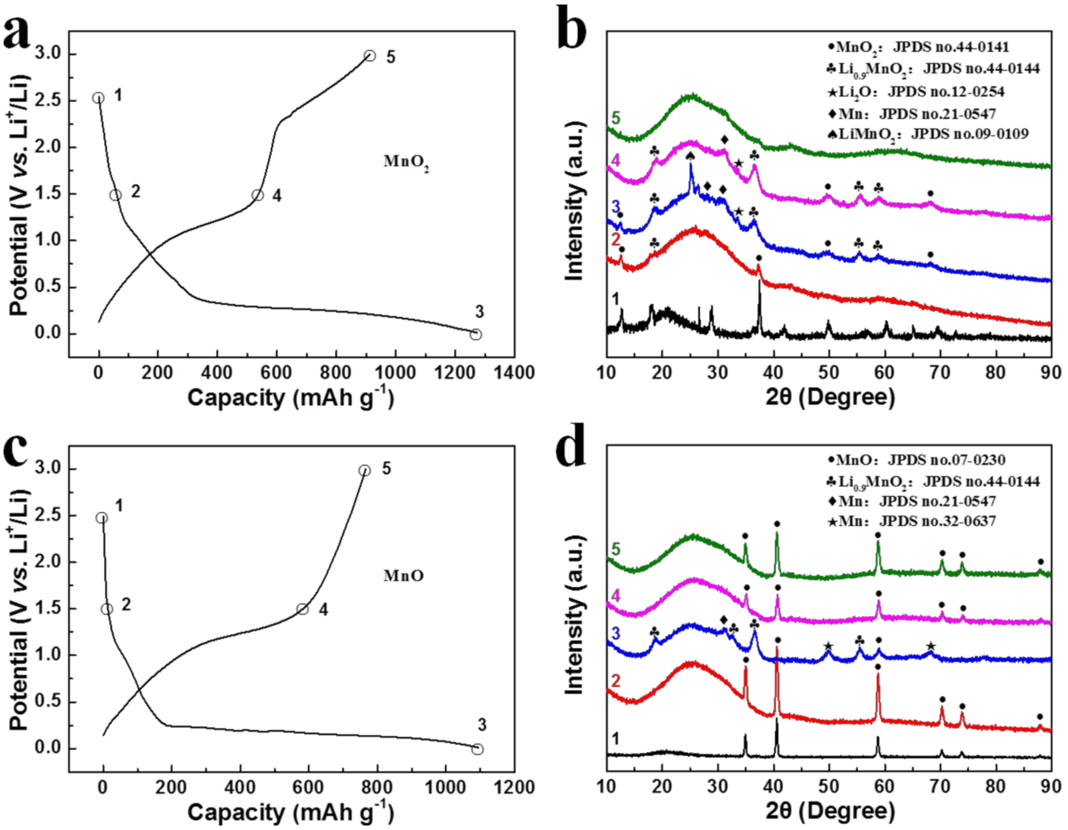

Fig. S6 The XRD patterns of MnO_2 and MnO at different charge and discharge states (1: fresh electrode, 2: half-discharged, 3: full-discharged, 4: half-charged and 5: full-charged) at 500 mA g^{-1} for the 1st cycle.

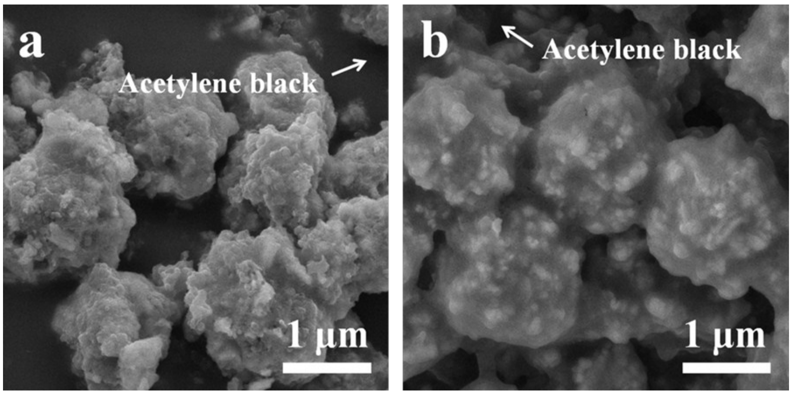

Fig. S7 SEM images of MnO_2 (a) and MnO (b) under fully charged condition at 500 mA g^{-1} after 1^{st} cycle.

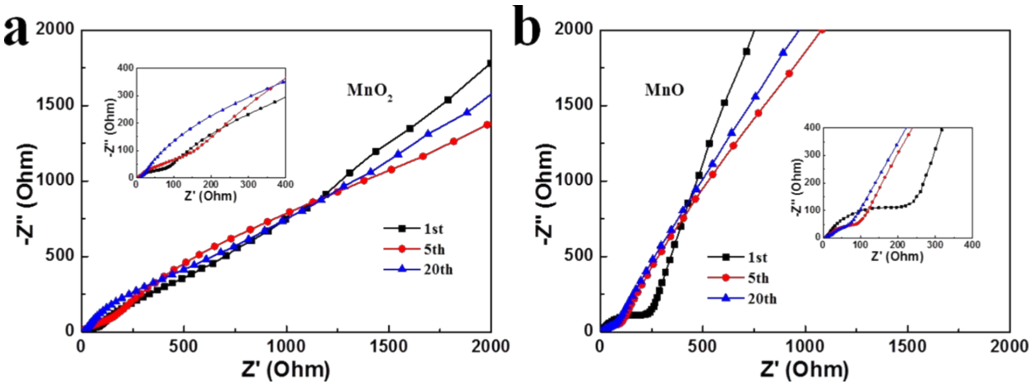

Fig. S8 EIS of the MnO_2 (a) and MnO (b) microspheres electrodes after various discharge/charge cycles at 2000 mA g^{-1} at the full charge state.