

Supporting Information for

Mesoporous ZnMn₂O₄ microtubules derived from a biomorphic strategy for high performance lithium/sodium ion batteries

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Experimental details

The ZMO-MT is prepared via a biomorphic route as illustrated in Figure 1. In a typical synthesis process, both 1 mmol $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 2 mmol $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were first dissolved in 15 mL deionized water, followed by constant magnetic stirring for 1 h to obtain a transparent solution. Next, 0.5 g piece of natural cotton was immersed in the solution and the wet cotton was dried at 75 °C for overnight. The ZMO-MT was finally obtained by calcination of the precursor at 700 °C for 3h in air atmosphere by heating at the rate of 2 °C min⁻¹. For comparison, bulk ZnMn_2O_4 was synthesized in a similar procedure to the preparation of ZMO-MT, but without using cotton.

Scanning electron microscope (SEM, Tecnai-450, FEI), transmission electron microscope (TEM, Talos F200X, FEI), infrared spectroscopy (IR) (TENSOR27 spectrophotometer, Bruker) and X-ray diffraction diffractometer (XRD, D8-Advance, Bruker) were used to study the structure and morphologies of the sample. The 2θ ranges from 10° to 80° with a scan rate of 4°/min and a step width of 0.02°. The valance states of ZMO-MT were investigated by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher). Thermogravimetric analysis (TG, Netzsch STA-449F3) was conducted in air between room temperature and 800 °C while heating at a rate of 10 °C min⁻¹. The Brunauer-Emmett-Teller (BET) surface area and pore size distribution of sample were recorded by a surface area analyzer (ASAP 2020 HD88, Micromeritics).

The lithium/sodium storage performances of the ZMO-MT and bulk ZnMn_2O_4 were studied using CR2032 coin-type cells. The working electrodes were obtained as follows. First, ZMO (70 wt%), acetylene black (20 wt%) and polyvinylidene fluoride

(10 wt%) were mixed in N-Methyl pyrrolidone (NMP) solvent, and then, the resulting slurry was used to coat a Cu foil, which was dried at 80 °C for 12h in a vacuum atmosphere. Typically, the loading mass of the active materials is about 1.8-2.3 mg/cm². LIBs were prepared in following manner: as the anode, the as-prepared working electrode was used; as the counter, a metallic lithium was used; as the separator, a Celgard Brand polymer membrane was used; and as the electrolyte, a solution of 1M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, volume ratio) was used. SIBs were prepared as follows: as the counter, a sodium foil was used; as the separator, a Whatman glass microfiber filters membrane was used; and as the electrolyte, a solution of 1M NaClO₄ dissolved in a mixture of ethylene carbonate (EC) and propylene carbonate (PC) (1:1, volume ratio) with 5% fluoroethylene carbonate (FEC) was used. The cyclic voltammograms and galvanostatic charge-discharge data of the sample were recorded in the potential range of 0.01 to 3.00 V (vs. Li⁺/Li or Na⁺/Na) by an electrochemical workstation (CHI 660E, Chenhua) and a battery testing system (CT 2001A, Land), respectively.

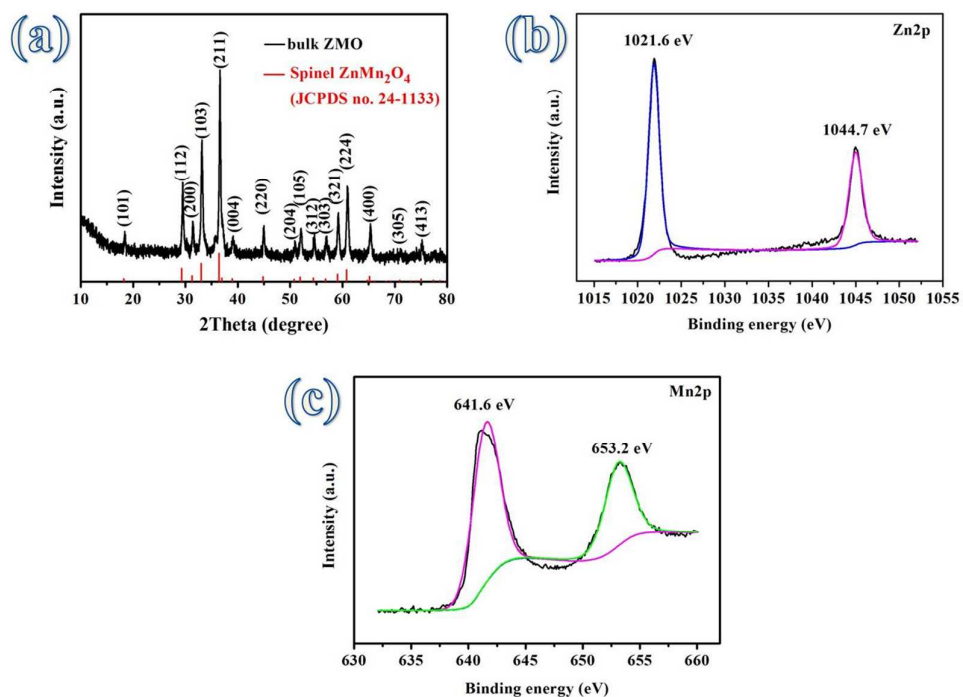


Figure S1 (a) XRD pattern; and (b) XPS spectrum of Zn2p, (c) Mn2p for bulk ZnMn₂O₄

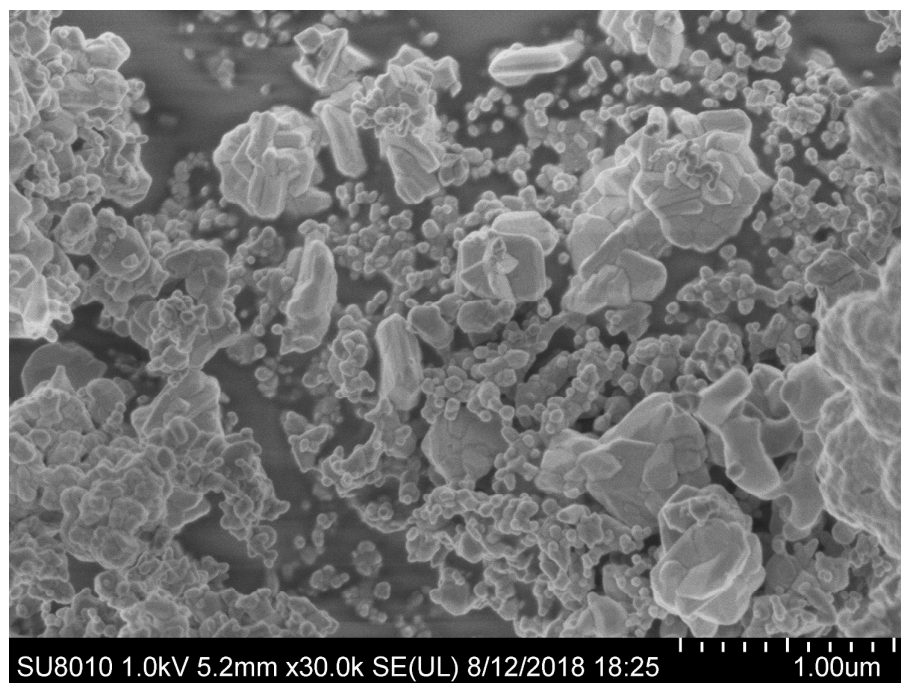


Figure S2 SEM image of bulk ZnMn₂O₄

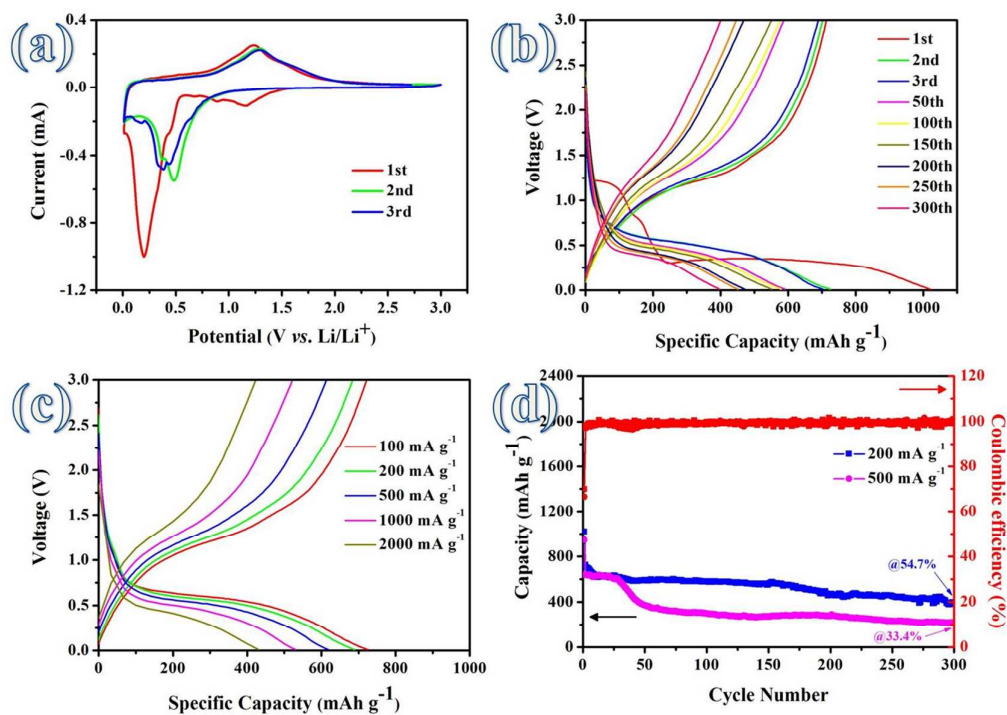


Figure S3 Electrochemical performances in LIBs: (a) Cyclic voltammetry curves; (b) charge-discharge profiles at 200 mA g^{-1} ; (c) rate capabilities at various current densities; (d) cyclic life for bulk ZnMn_2O_4

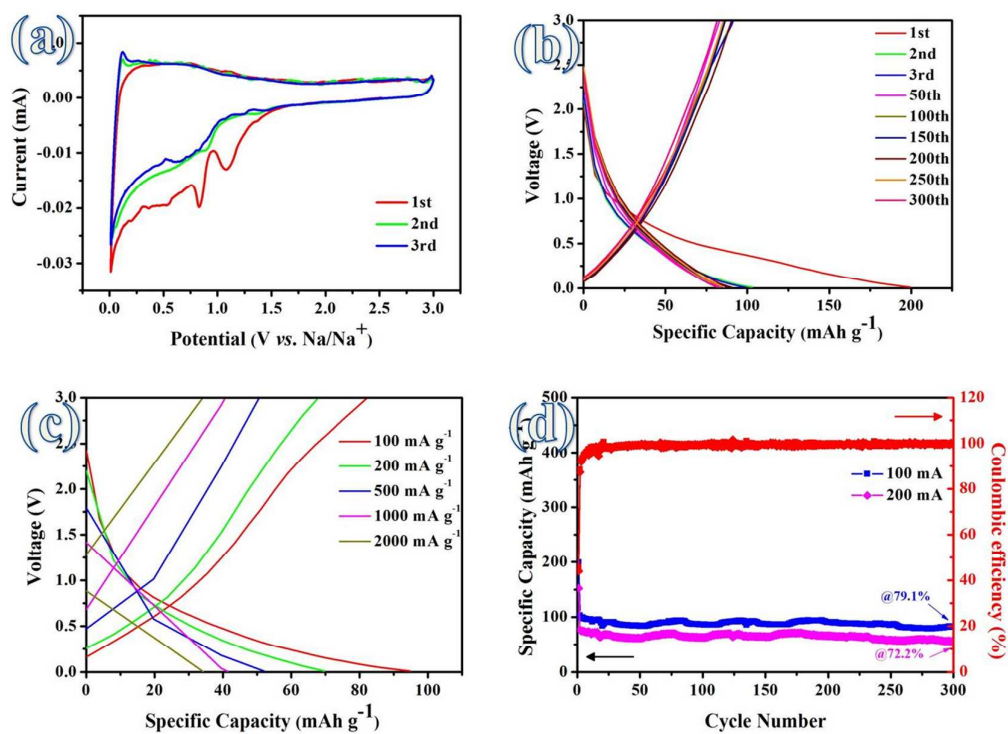


Figure S4 Electrochemical performances in SIBs: (a) Cyclic voltammetry curves; (b) charge-discharge profiles at 100 mA g⁻¹; (c) rate capabilities at various current densities; (d) cyclic life for bulk ZnMn₂O₄

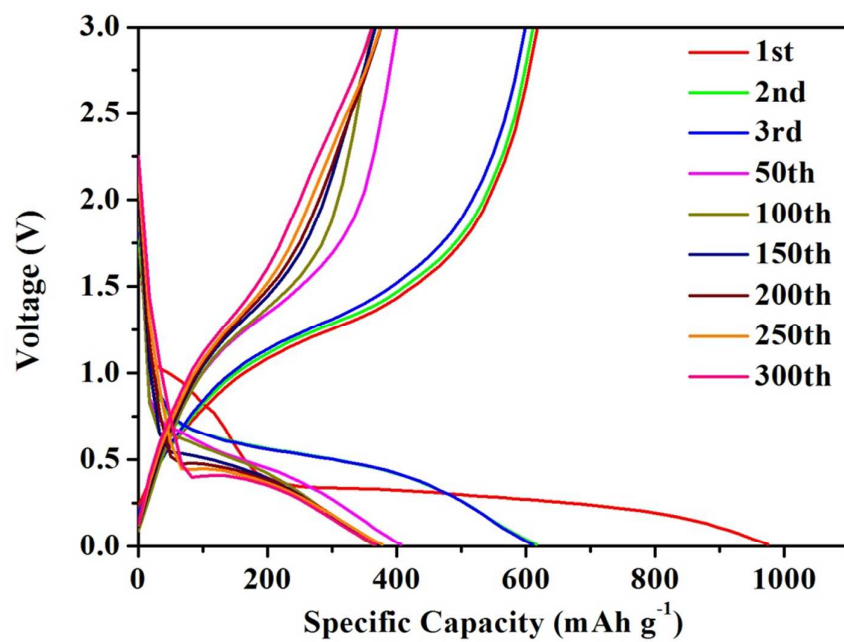


Figure S5 Charge-discharge profiles at 1 A g⁻¹ for 300 cycles of ZMO-MT