Room-Temperature Solution Synthesis of $ZnMn_2O_4$ nanoparticles for advanced electrochemical lithium storage

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Experiments:

Synthesis of $ZnMn_2O_4$ nano-particles

All chemicals utilized in this work were of analytical grade and were used without further purification. Easily, ZnO and MnO hybrid materials (molar ratio: 3:1), mixed by ball mill, were poured into 5 M KOH aqueous solution with continuously stirring for 24 h at room temperature. Finally, the products were washed with deionized water and ethyl alcohol for several times before drying overnight in air oven at 60 °C. For comparison, the raw samples of ZnO and MnO are also as the electrodes for Li-ion battery to be measured.

Material characterizations

The phases of as-prepared $ZnMn_2O_4$ materials and the two raw samples were investigated by XRD on a Rigaku diffractometer (D/Max2500) with Cu Kα (λ=1.5406 Å) radiation at 40 kV and 250 mA, meanwhile, the phases were further verified by the Raman and X-ray photoelectron spectroscopy. The morphological and the crystal structure were characterized by SEM, TEM and HRTEM.

Electrochemical characterizations

The anode slurry was carried out with $ZnMn_2O_4$ (or ZnO, MnO), acetylene black, and carboxymethyl cellulose sodium at a mass ratio of 7:2:1 and was casted on copper foil with doctor blade. The loading of active material is 1.0-1.2 mg cm^{-2}. The batteries of CR2025-type coin cells were assembled in Ar-filled gloveboxwith lithium as counter and reference electrodes. The electrolyte was a solution of 1 M $LiPF_6$ dissolved in ethylene carbonate, ethylmethyl carbonate and dimethyl carbonate (1:1:1 v/v/v). Celgard 2400 membrane was used as a separator. Discharge/charge measurements were characterized at the potential range of 0.01-3.00 V (*vs.* Li/Li^+) with LAND battery test system (CT2001A) at the room temperature of 25°C. EIS in a frequency from 10 mHz to 100 KHz and cyclic voltammetry (CV) at a scanning rate of 0.1 mV s^{-1} between 0.01 and 3.00 V were tested on a CHI660E electrochemical workstation.

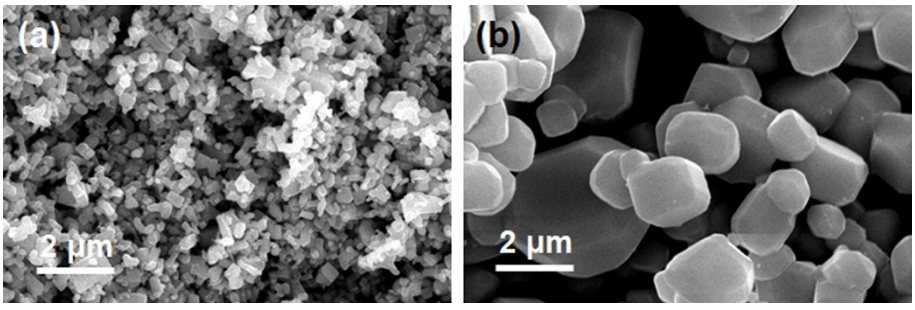

Figure **S1** The morphology of ZnO (a) and MnO (b).

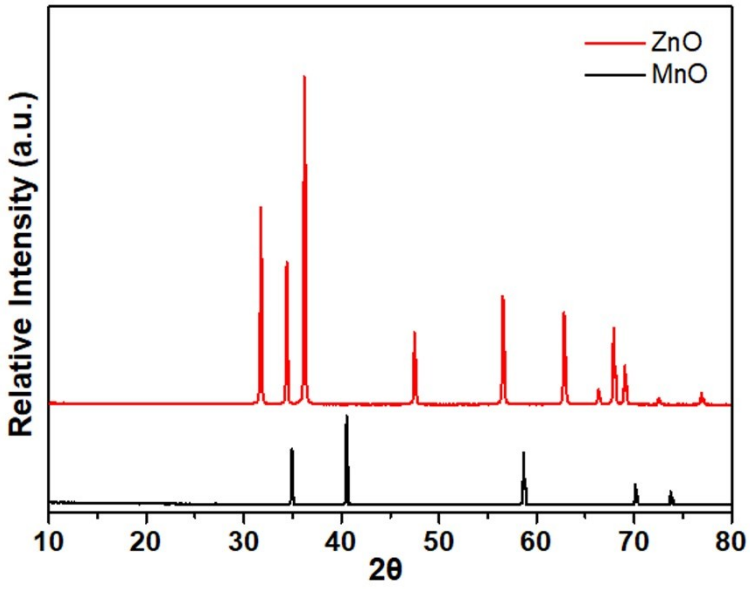

Figure **S2** The XRD patterns of ZnO and MnO materials.

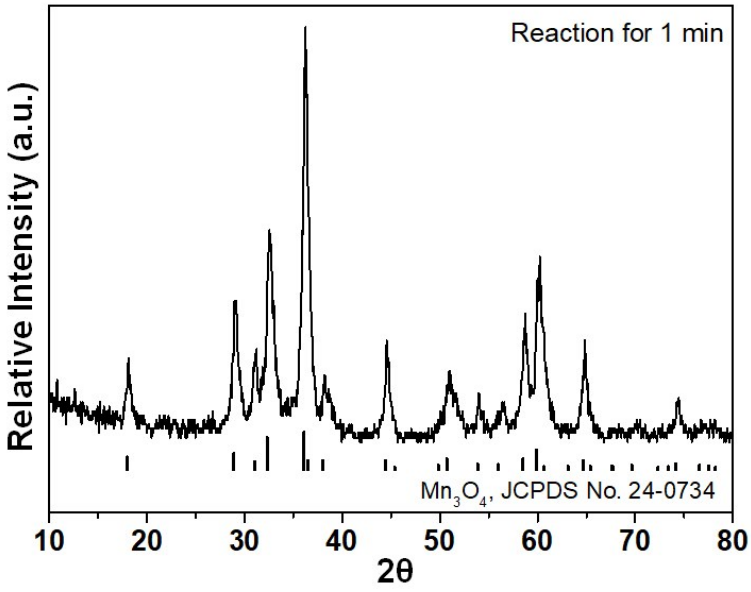

Figure **S3** The XRD results of the reaction for 1min.

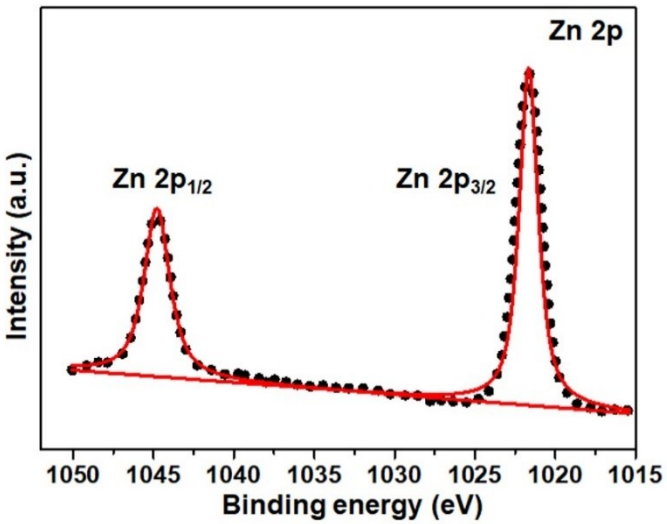

Figure **S4** The XPS spectrum of Zn 2p.

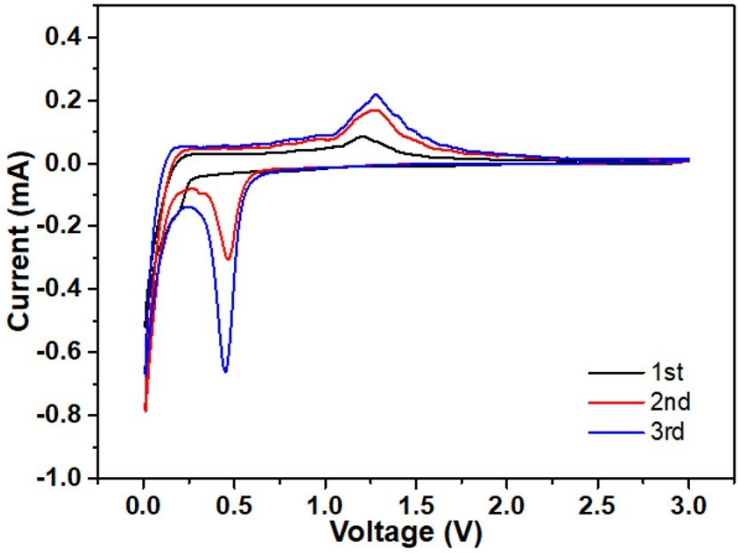

Figure **S5** The CV results of MnO.

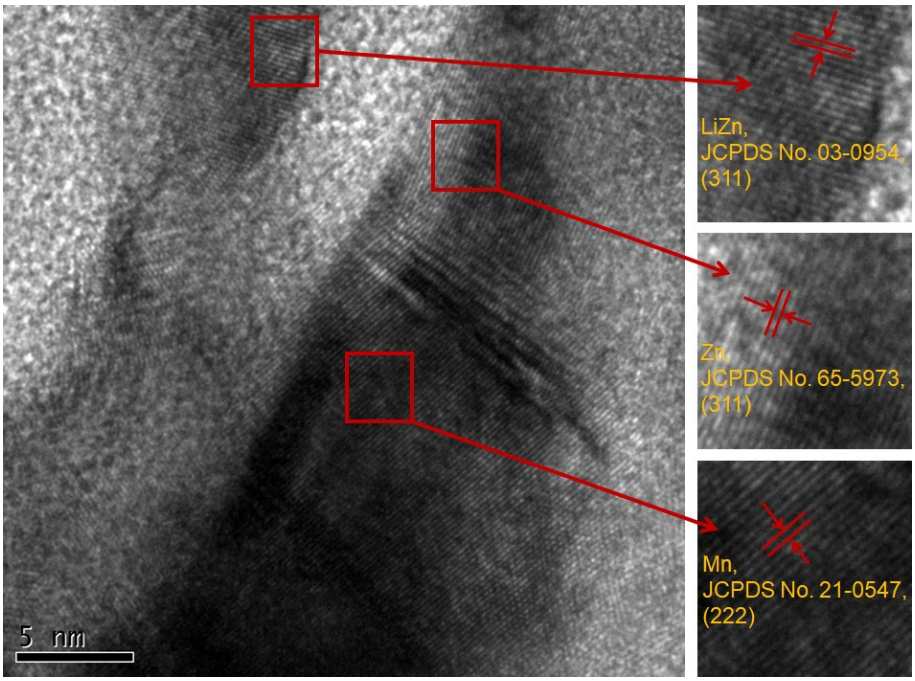

Figure **S6** The HRTEM results of $ZnMn_2O_4$ after discharging to 0.01 V.