

## Supporting Information

### **Uniform LiMO<sub>2</sub> assembled microspheres as superior cycle stability cathode materials of high energy and power Li-ion batteries**

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#### Experimental Section

*Sample synthesis:* LiMO<sub>2</sub> assembled microspheres were prepared using a solvothermal-precursor method followed by a heat treatment process. Analytical grade chemicals of lithium acetate (CH<sub>3</sub>COOLi·2H<sub>2</sub>O), manganese acetate (Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O), cobalt acetate (Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O), nickel acetate (Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O) and urea were chosen as the starting materials. The stoichiometric ratio of CH<sub>3</sub>COOLi·2H<sub>2</sub>O (5 mol% excess), Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O together with 1.42 g urea were dissolved in 65 mL diglycol to form mixed solutions. After stirring for about 1 h, the diglycol solution was moved into a 100 mL Teflon-lined autoclave and kept at 180 °C for 12 h. Finally, after filtering and several times washing with ethanol, the precursors were calcined in air at 900 °C for 12 h, and then quenched to room temperature to gain target products.

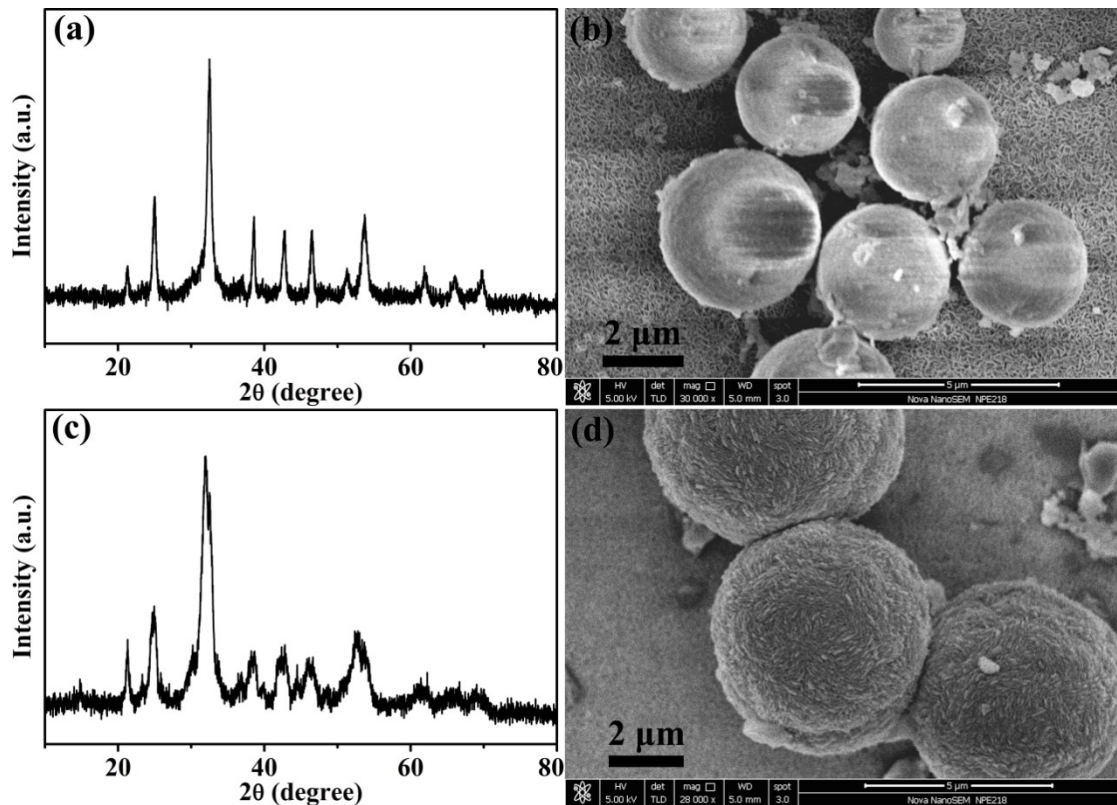
For comparison, a commercial LiMn<sub>1/3</sub>Co<sub>1/3</sub>Ni<sub>1/3</sub>O<sub>2</sub> taken from Amperex Technology Limited (Ningde city, Fujian, P. R. China) was used as a reference sample.

*Sample characterization:* Crystalline phases of the synthesized materials were identified by X-ray diffraction measurement (XRD, Rigaku, D/max-Rbusung Cu K radiation) laser Raman spectroscopy (Renishaw in Via). The particle morphology and

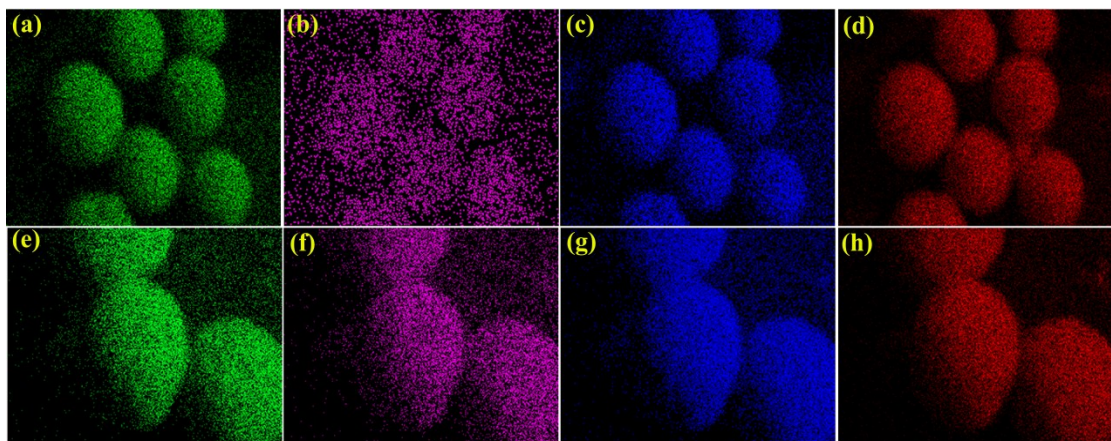
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size of the samples were determined by field emission scanning electron microscopy (SEM) on a JEOL JSM-7401F instrument under an acceleration voltage of 5 kV. The energy-dispersive X-ray (EDX) mapping was detected under an acceleration voltage of 12 kV. The composition and state of samples were further investigated by X-ray photoelectron spectroscopy (XPS) experiments measured on an AXIS ULTRA DLD instrument, using aluminum K X-ray radiation.

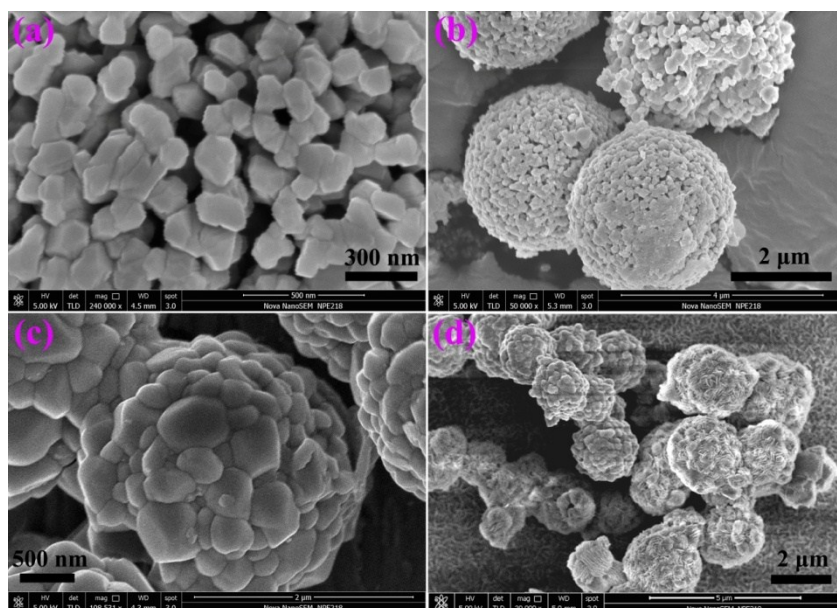
*Electrochemical test:* Electrochemical performance of the samples was measured using the CR-2016-type coin cell. The cathode materials were prepared as follows: 80 wt% of synthesized powders, 10 wt% of carbon black, and 10 wt% polyvinylidene fluoride (PVDF) were mixed using N-methyl pyrrolidinone (NMP) as a solution. The resulting slurry was coated on Al foil by a doctor blade technique and vacuum dried at 110 °C for 12 h. The loading of the active materials on the Al foil is about 2 mg cm<sup>-2</sup>. The cells were assembled in an argon-filled glove box (H<sub>2</sub>O and O<sub>2</sub> < 1 ppm) using lithium foil as the anode, a polymer separator and 1 M LiPF<sub>6</sub> in EC:DMC (1:1 in volume) as the electrolyte. The cell was charged and discharged galvanostatically on a CT2001a cell test instrument (LAND Electronic Co.) at room temperature. The voltage ranges of charge-discharge tests are 3.0-4.4 V for LiMn<sub>0.075</sub>Co<sub>0.775</sub>Ni<sub>0.15</sub>O<sub>2</sub> cathode and 2.5-4.6 V for LiMn<sub>1/3</sub>Co<sub>1/3</sub>Ni<sub>1/3</sub>O<sub>2</sub> cathode.



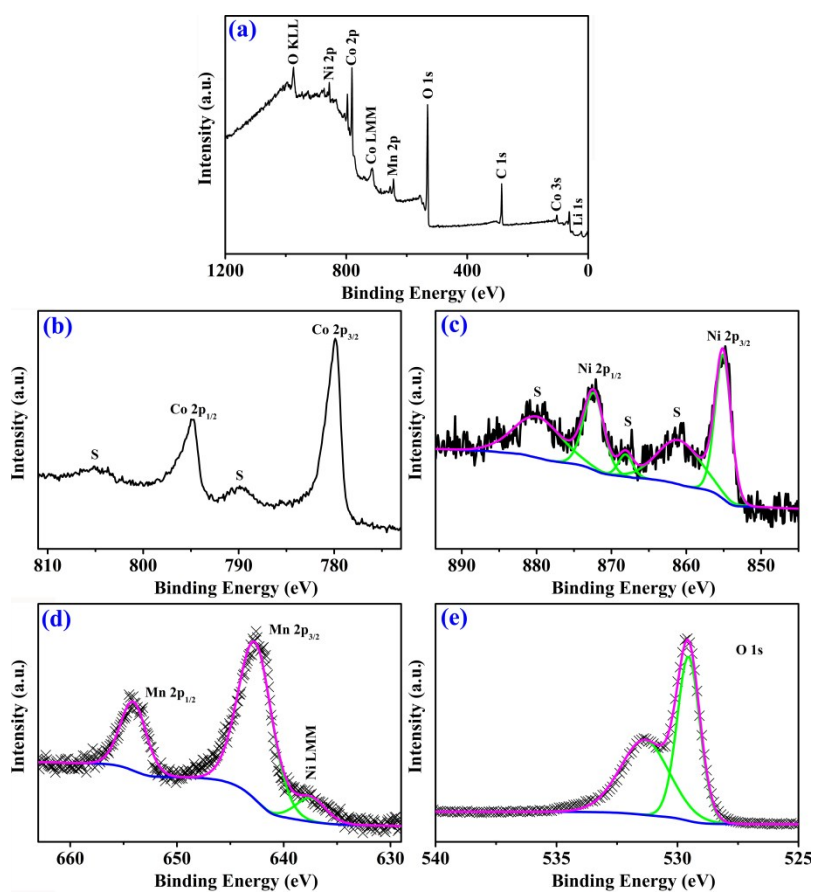
**Fig. S1** (a,c) XRD patterns and (b,d) SEM images for precursors of the samples  $\text{LiMn}_{0.075}\text{Co}_{0.775}\text{Ni}_{0.15}\text{O}_2$  and  $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$ .



**Fig. S2** EDX-mapping of Co, Mn, Ni and O for carbonate precursors of (a-d)  $\text{LiMn}_{0.075}\text{Co}_{0.775}\text{Ni}_{0.15}\text{O}_2$  and (e-h)  $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$ .

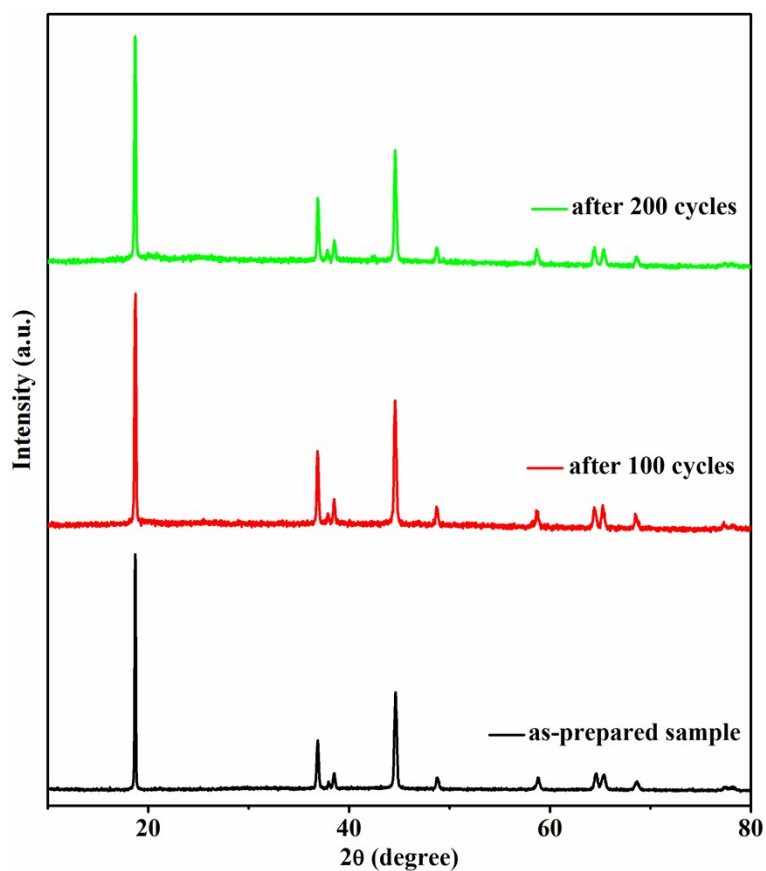


**Fig. S3** SEM images of (a,b)  $\text{LiMn}_{0.075}\text{Co}_{0.775}\text{Ni}_{0.15}\text{O}_2$  and (c,d)  $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$ .



**Fig. S4** XPS spectra of  $\text{LiMn}_{0.075}\text{Co}_{0.775}\text{Ni}_{0.15}\text{O}_2$  microspheres: (a) survey spectrum, (b) Co 2p, (c) Ni 2p, (d) Mn 2p, and (e) O 1s.

Detailed XPS data for Co 2p, Ni 2p and Mn 2p are shown in Fig. S4(b-d). The  $2p_{3/2}$  peaks of these three elements are located at 780.64, 855.31 and 642.89 eV respectively, and one of satellite peaks of Co 2p locates at 789.9 eV. It indicates that the valence states of Co, Ni and Mn ions in the  $\text{LiMn}_{0.075}\text{Co}_{0.775}\text{Ni}_{0.15}\text{O}_2$  sample are +3, +2 and +4, respectively.[1-3] Additionally, we also detect the O 1s spectrum of the  $\text{LiMn}_{0.075}\text{Co}_{0.775}\text{Ni}_{0.15}\text{O}_2$  sample. As shown in Fig. 3e, the O 1s spectrum composed of two peaks. One (peak I) at  $\sim 529.6$ - $530.1$  eV is assigned to oxygen atoms of  $\text{LiMn}_{0.075}\text{Co}_{0.775}\text{Ni}_{0.15}\text{O}_2$  lattice, and the other (peak II) at ca. 531.4 eV can be attributed to oxygen-containing species.[4]



**Fig. S5** XRD pattern of  $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$  microspheres after 100 and 200 cycles, XRD pattern of as-prepared  $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$  microspheres is displayed again for convenient compare.

**Table S1.** The comparison of cycle performance between this work and the literatures

Sample	Test condition	Initial capacity	Cycle times	Capacity retention ratio	reference
$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$	2.5-4.6 V, 300 mA g <sup>-1</sup>	195.5 mA h g <sup>-1</sup>	200/300	96.5%/90.7%	This work
	2.5-4.6 V, ~360 mA g <sup>-1</sup>	159.1 mA h g <sup>-1</sup>	100	89%	Ref.[5]
	2.5-4.6 V, ~100 mA g <sup>-1</sup>	209 mA h g <sup>-1</sup>	200	90.9%	Ref.[6]
	2.5-4.5 V, 200 mA g <sup>-1</sup>	178.1 mA h g <sup>-1</sup>	50	85.1%	Ref.[7]
	2.8-4.3 V, ~150 mA g <sup>-1</sup>	156 mA h g <sup>-1</sup>	80	88%	Ref.[8]
	2.5-4.5 V, 100 mA g <sup>-1</sup>	188 mA h g <sup>-1</sup>	100	84%	Ref.[8]
	2.8-4.4 V, 20 mA g <sup>-1</sup>	173 mA h g <sup>-1</sup>	50	94%	Ref.[10]

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