Supporting Information

Controllable Synthesis of Hierarchical Ball-in-Ball Hollow Microsphere for High Performance Layered Li-Rich Oxide Cathode Material

Fu-Da Yu, Lan-Fang Que, Zhen-Bo Wang,* Yuan Xue, Yin Zhang, Bao-Sheng Liu and Da-Ming Gu*

MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, No. 92 West-Da Zhi Street, Harbin, 150001, China

** Corresponding author. Tel.: +86-451-86417853; Fax: +86-451-86418616;*

E-mail: wangzhb@hit.edu.cn (Z. B. Wang); gudmaing@hit.edu.cn (D. M. Gu).

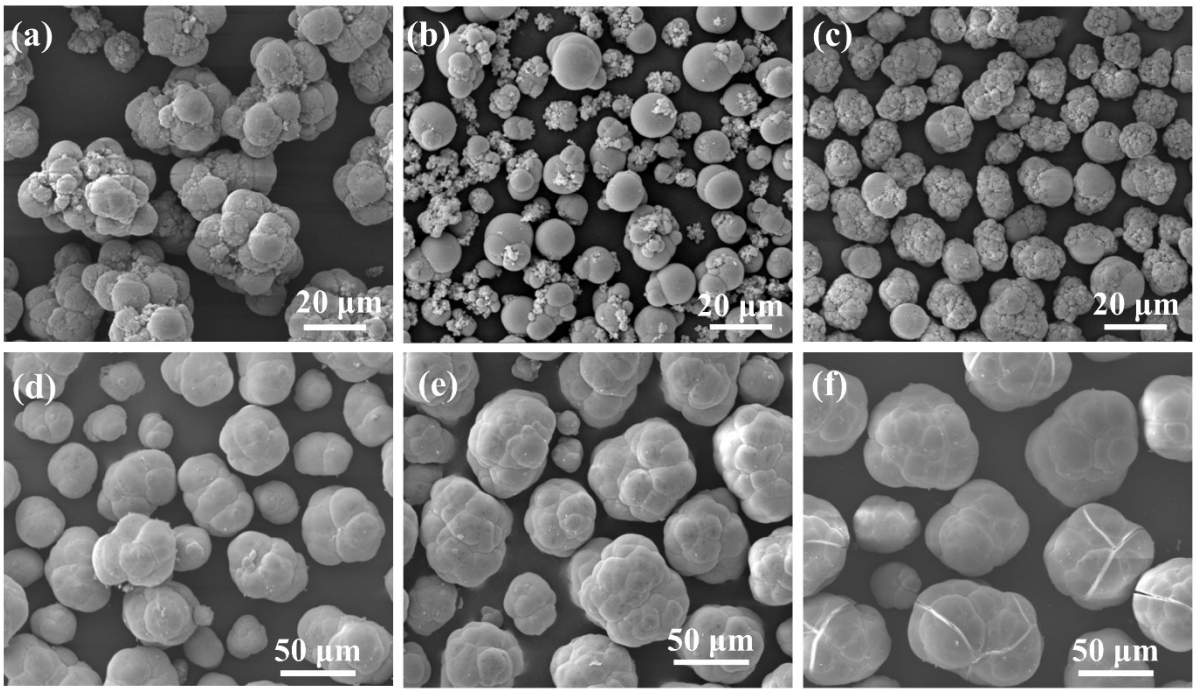

Figure S1. Typical SEM images of $Mn_{4/6}Ni_{1/6}Co_{1/6}CO_3$ precursor. The molar ratio of NH_4HCO_3 and $NH_3 \cdot H_2O$ is (a) 0:10, (b) 1:9, (c) 2:8, (d) 3:7, (e) 5:5, (f) 10:0. The co-precipitation process was carried out with a fixed pH of 7.5 at a constant temperature of 50 ^oC for 5h.

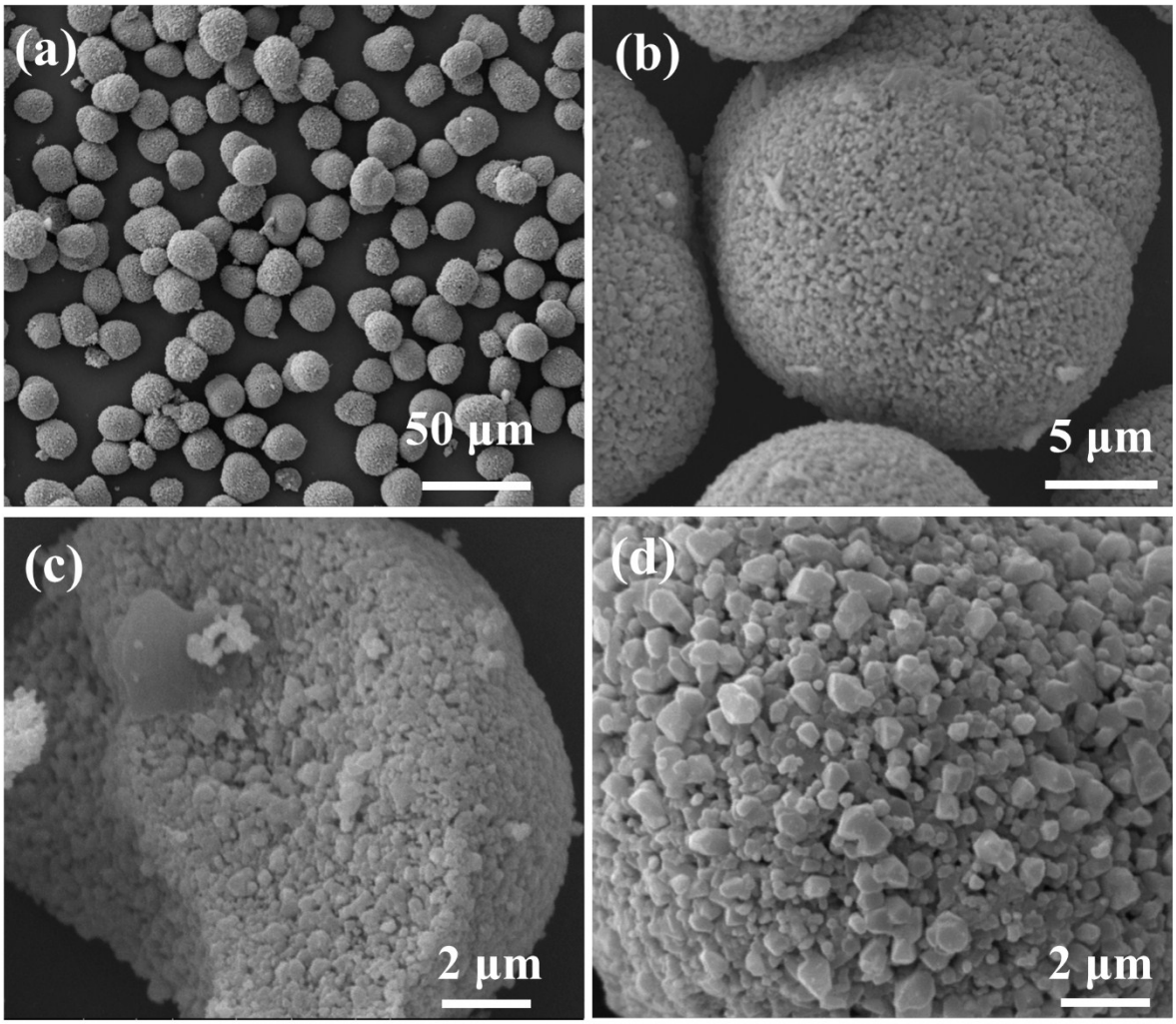

Figure S2. (a-d) Typical SEM images of S-LLRO. In (c), solid interior structure of S-LLRO is showed.

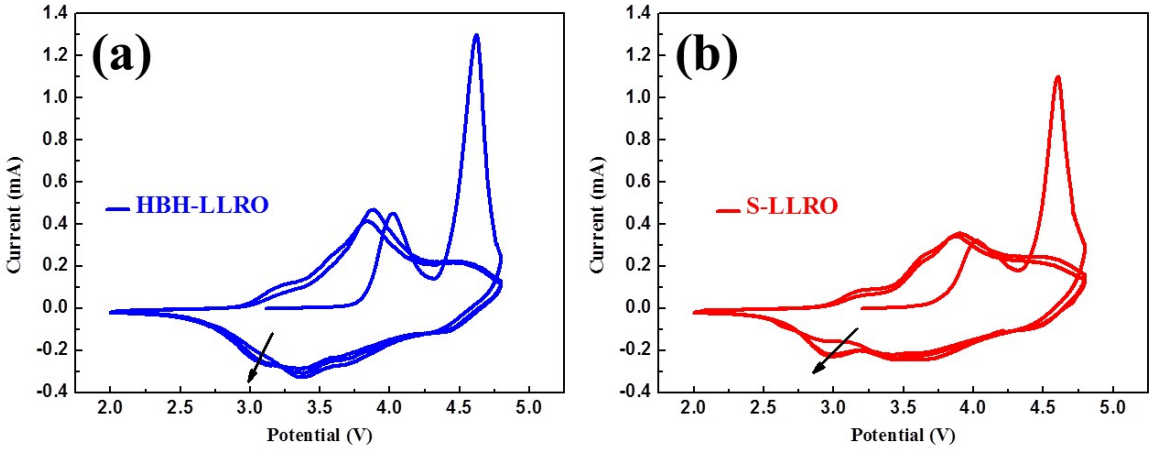

Figure S3. The CV curves of the (a) HBH-LLRO and (b) S-LLRO samples during first to third cycle in a potential range of 2.0-4.8 V at a scan rate of 0.1 mV s^{-1}, and the arrows show the lattice transformation.

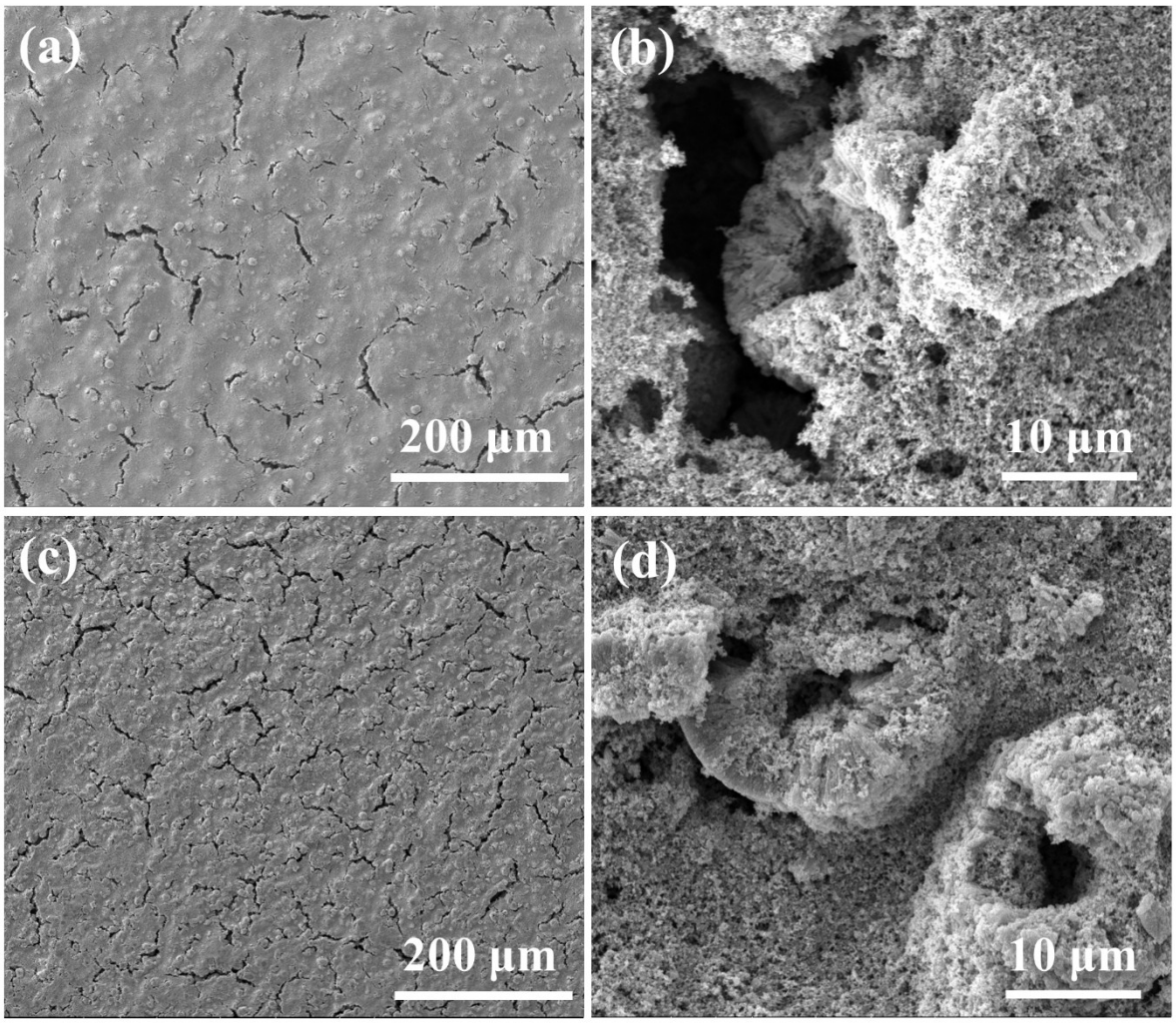

Figure S4. Typical SEM images of (a, b) pristine and (c, d) cycled electrode of HBH-LLRO. In (c, d), the cycled electrode of HBH-LLRO for 200 cycles at 1 C still shows a clear surface of the secondary particles and the hierarchical hollow structure of microsphere is also well preserved during long-term prolonged cycling, indicating the good structural stability of HBH-LLRO.

Table S1. The lithium storage properties for reported LLRO cathode materials.

LLRO cathode materials	Discharge capacities (mAh g^{-1}) at different C-rate			Cycle life at different C-rate	Capacity retention
	1C	5C	10C		
Hierarchical ball-in-ball hollow LLRO microsphere (This work)	223	170	132	400 cycles @3C	87.6%
Spinel-layered LLRO nanoparticle [1]	N/A	~120	~108	300 cycles@0.04C	~53%
Core-shelled $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ [2]	126	37	N/A	100 cycles @0.5C	83.6%
Dual-coated LLRO nanoparticle [3]	~212	~150	~130	300 cycles @10C	~83%
Graphene/$AlPO_4$ modified LLRO nanoparticle [4]	~170	~110	N/A	100 cycles @1C	70.8%
$LiFePO_4$-coated $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ [5]	201	125	N/A	120 cycles @1C	88.2%
Li_2MnO_3-coated LLRO nanoparticle [6]	219	156	121	45 cycles @0.1C	88.8%
Fusiform-like micro/nano $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ [7]	217	158	N/A	100 cycles @1C	94%
Porous LLRO microrod [8]	226	172	N/A	50 cycles @5C	79.4%
$Li_{1.2}(Mn_{0.4}Co_{0.4})O_2$ nanorod [9]	~185	~148	~102	50 cycles @0.1C	89.9%
MnO_2 nanosheets coated LLRO nanoparticle [10]	226	157	N/A	50 cycles @0.5C	93%
Nanotube assembled 3D LLRO hierarchitecture [11]	219	140	94	200 cycles @1C	80.4%

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