Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Electronic Supporting Information

Synthesis of single crystalline hexagonal nanobricks of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ with high percentage of exposed {010} active facets as high rate performance cathode material for lithium-ion battery

Fang Fu, Gui-Liang Xu, Qi Wang, Ya-Ping Deng, Xue Li, Jun-Tao Li, Ling Huang, and Shi-Gang Sun*

State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, School of Energy Research, Xiamen University, Xiamen 361005, China

*Corresponding author, Tel & Fax: (+86)592-2180181, E-mail: sgsun@xmu.edu.cn

Experimental Section

Preparation of Materials: $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ was prepared by a solid-state reaction from lithium hydroxide ($LiOH\cdot H_2O$) and nickel-cobalt-manganese hydroxide precursor. The precursor was prepared by a surfactant-assisted coprecipitation method from 0.8 mol dm^{-3} of $NiSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, and $MnSO_4 \cdot 7H_2O$ (Co:Ni:Mn = 1:1:1 in the molar ratio) aqueous solution and 2.0 mol dm^{-3} of NaOH aqueous solution with the desired amount of NH_4OH. 1.0 g of anionic surfactant PVP as an adsorbent was also added into the solution before reaction. The solutions were mixed slowly under a nitrogen atmosphere, and the pH of the mixed solution was kept in the range of 11-12 during the precipitation process. Finally, the precipitated $Ni_{1/3}Mn_{1/3}Co_{1/3}(OH)_2$ particles were filtered, washed with water several times, and then vacuum-dried at 120 ℃ for overnight. The as-prepared $Ni_{1/3}Mn_{1/3}Co_{1/3}(OH)_2$ was then mixed with LiOH in the molar ratio of 1.0:1.06 by ball milling in the corundum vial with corundum balls for 5 h using a Retsch PM 100 planetary mill, in which 6% of excess lithium was added to compensate for the lithium evaporation during the calcinations. The speed was 500 rpm and the ball-to-material ratio was 20:1. The effect of the ball milling on the morphology of $Ni_{1/3}Mn_{1/3}Co_{1/3}(OH)_2$ nanoplates precursor has been investigated by SEM. The SEM image of the precursor after 5 h ball milling is depicted in Figure S9. The Figure S9 illustrates the precursor still keeps the original hexagonal nanoplates shape after ball milling for 5 h. The ball milling did not destroy its structure. It may be due to that the particle size of these nanoplates is relatively small, which are about 50-200 nm in edge length and 10 nm in thickness, so that the power of ball milling at a speed of 500 rpm could not destroy its structure. After suitable grinding, the mixture was annealed in air, first at 450 ℃ for 6 h, and then at 900 ℃ for 12 h. The final material was obtained by cooling them to room temperature in the furnace.

Sample Characterization: Products were thoroughly characterized by XRD (Philips X'Pert Pro Super X-ray diffractometer, Cu Kα radiation), SEM (Hitachi S-4800 SEM), and TEM (JEOL JEM-2100 microscope).

Electrochemical Tests: Electrochemical properties of the LNCM nanobrick electrodes were measured by assembling them into coin cells (type CR2025) in an argon-filled glove box. The cathode was prepared by spreading a mixture of 80 wt% active material, 10 wt% acetylene black, and 10 wt% LA132 onto an Al foil current collector. The obtained electrodes were dried at 120 ℃ for 10 h in vacuum. Lithium foil was used as anode and Celgard-2400 membrane as the separator. The electrolyte was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) / dimethyl carbonate (DMC) / diethyl carbonate (DEC) (1:1:1 in volume). The cells were galvanostatically charged and discharged in the voltage range of 2.5-4.6 V on a battery test system (LAND-V34, Land Electronic Co., Ltd., Wuhan). A 1 C rate is equivalent to 160 mA·g^{-1} in our definition.

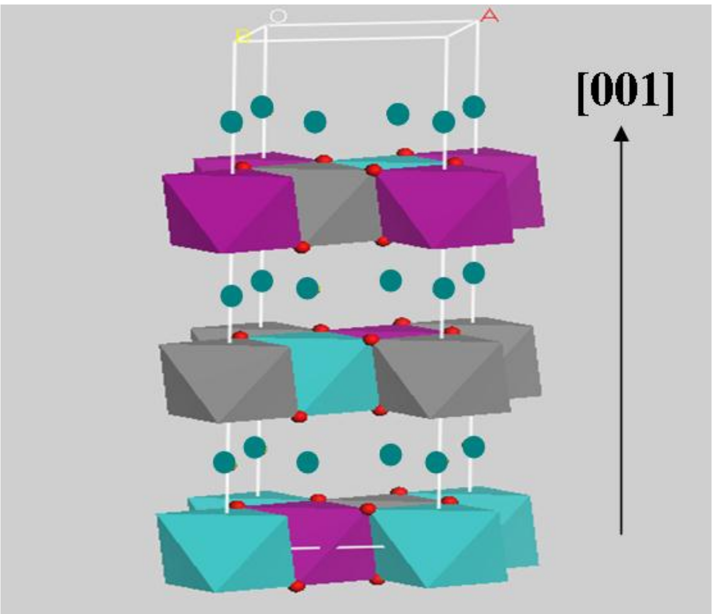

Figure S1. Crystal structure of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. The red and green spheres are oxygen and lithium atoms, respectively. The octahedra represents MO_6 unit.

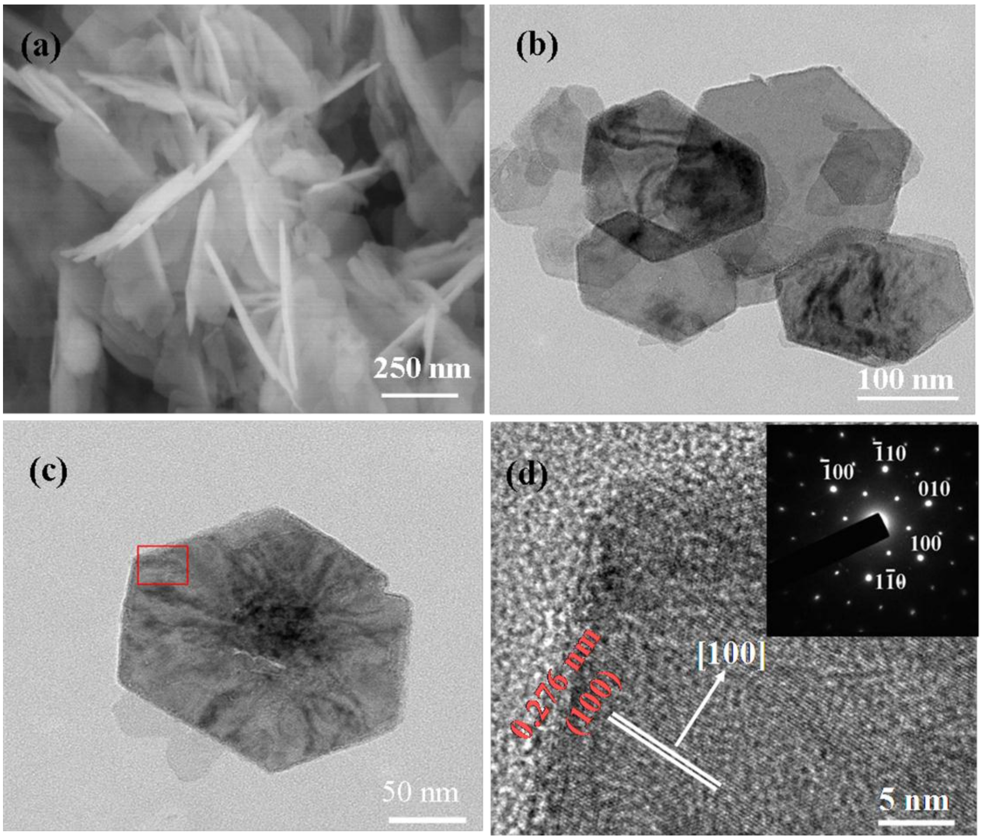

Figure S2. SEM image (a) and TEM images (b,c) of $Ni_{1/3}Mn_{1/3}Co_{1/3}(OH)_2$ hexagonal nanosheets. (d) HRTEM image of the region marked by red square in (c), inset is SAED of (c).

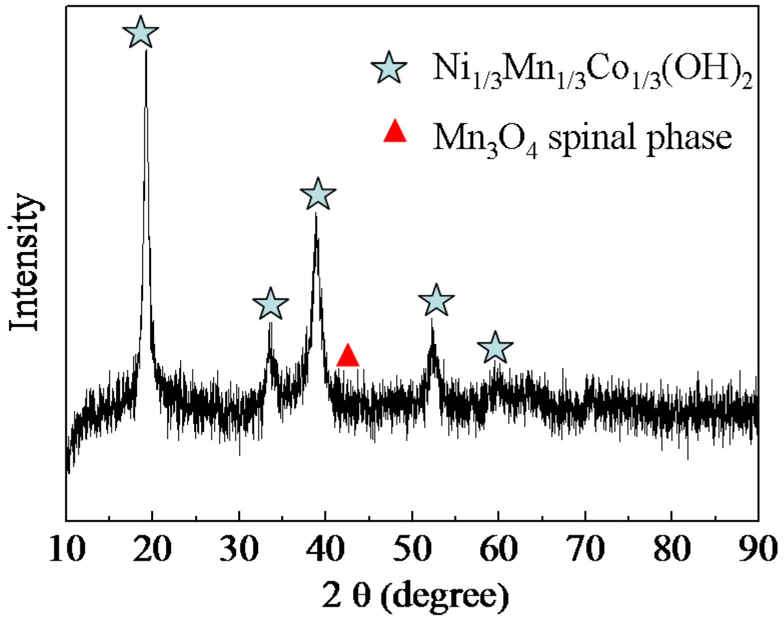

Figure S3. XRD pattern of the $Ni_{1/3}Mn_{1/3}Co_{1/3}(OH)_2$ precursor

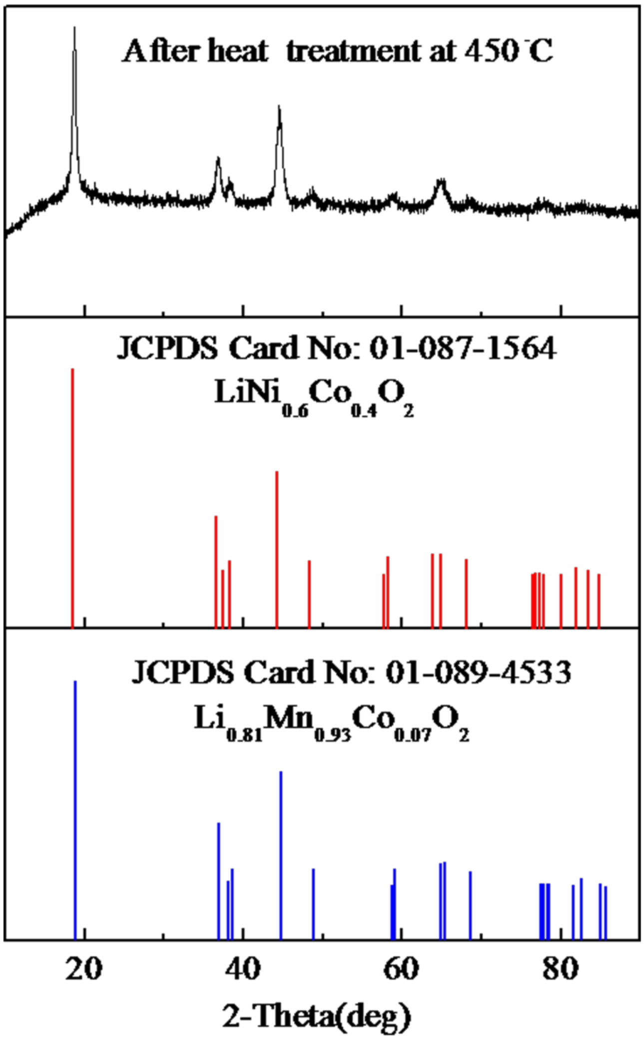

Figure S4. XRD pattern of the precursor after heat treatment at 450 ℃

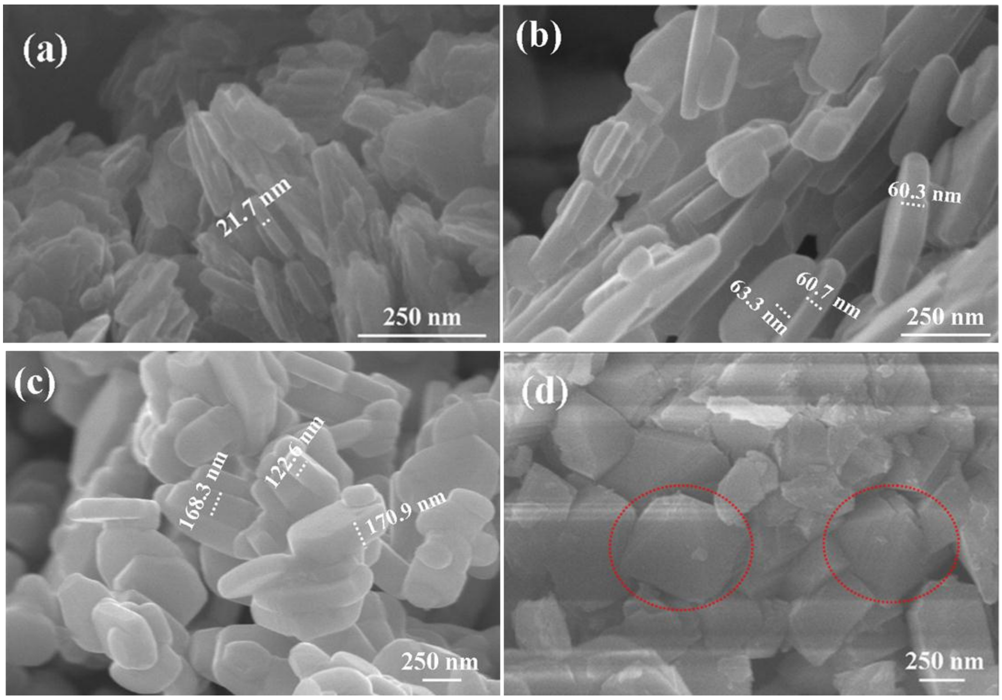

Figure S5. SEM images of the LNCM nanocrystals prepared at different temperatures (a) 450 ℃, (b) 800 ℃, (c) 900 ℃, (d) 1000 ℃.

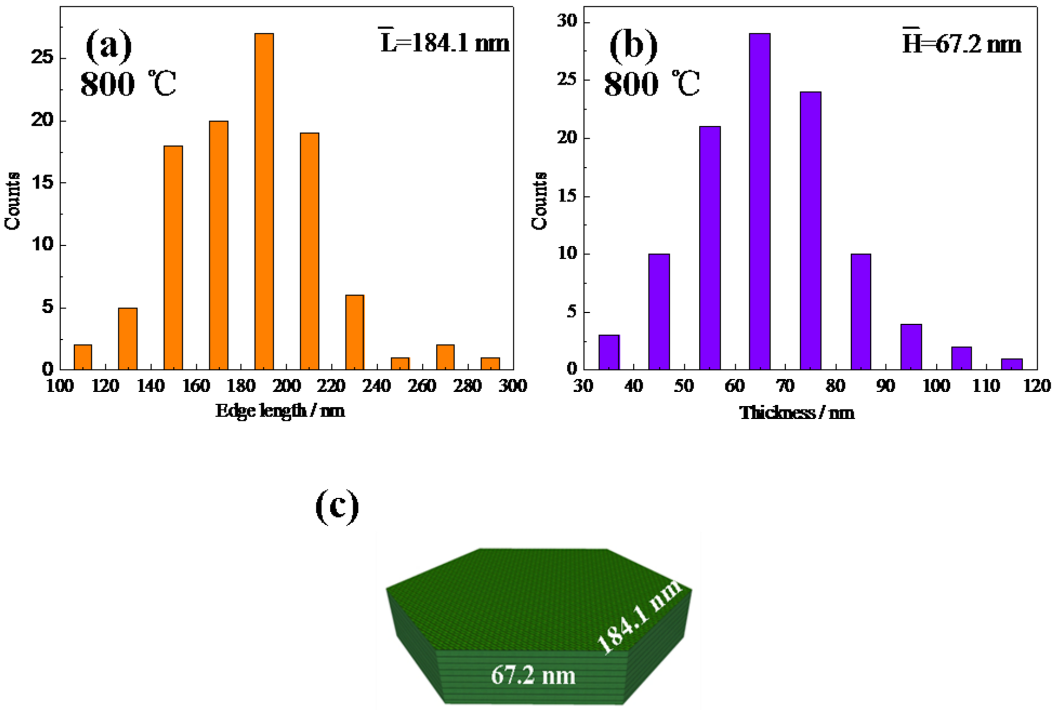

Figure S6. (a) Edge length and (b) thickness distribution of LNCM nanobricks prepared at 800 ℃. (c) Schematic drawing of a single hexagonal nanobrick.

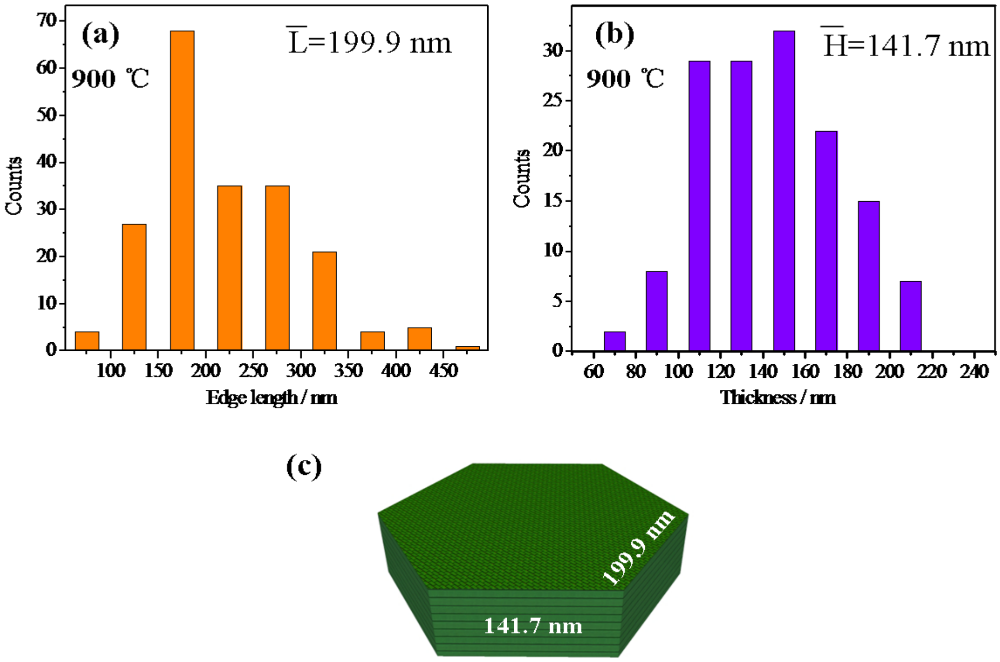

Figure S7. (a) Edge length and (b) thickness distribution of LNCM nanobricks prepared at 900 ℃. (c) Schematic drawing of a single hexagonal nanobrick.

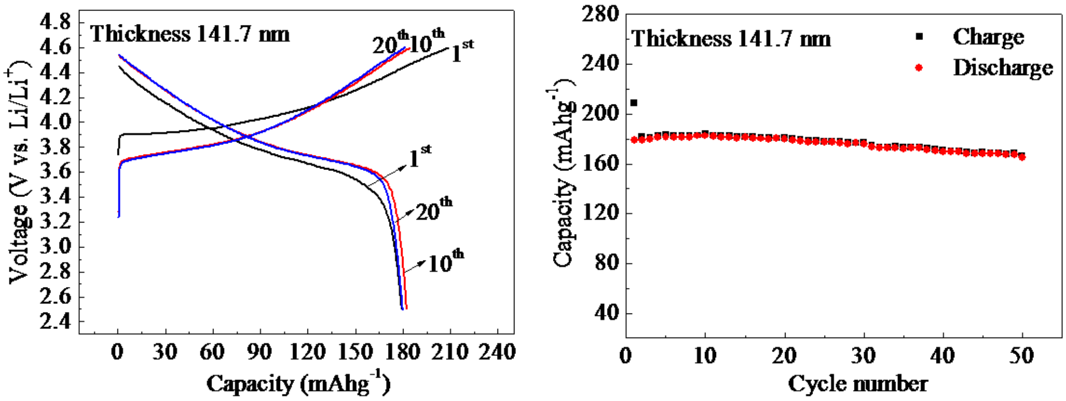

Figure S8. (a) Charge and discharge curves of the LNCM nanobricks at a rate of 1 C in the voltage range between 2.5-4.6 V. (b) Cycling performance of the LNCM nanobricks at a rate of 1 C.

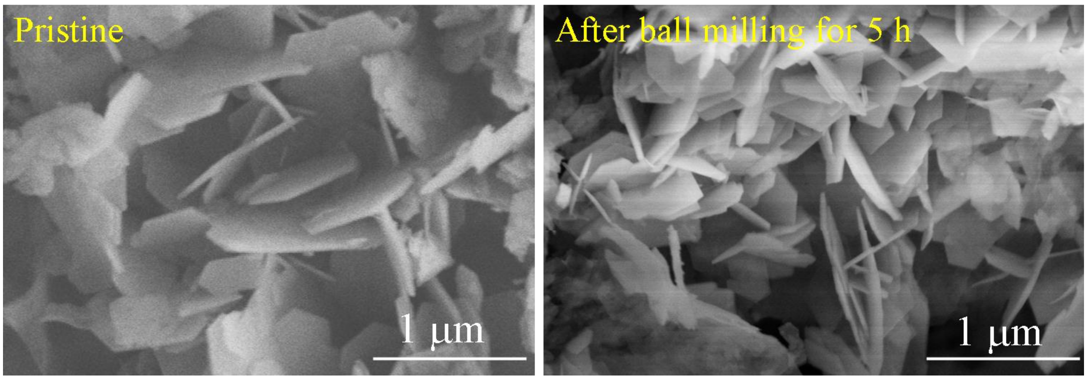

Figure S9. SEM images of the $Ni_{1/3}Mn_{1/3}Co_{1/3}(OH)_2$ nanoplates precursor before (left) and after ball milling for 5 h(right).