1. Experimental section

All the regents were analytical grade and without further purification before utilization. In a typical synthesis, A mixture of LiNO₃ and NaNO₃ (weight ratio of LiNO₃:NaNO₃=1:2) was firstly heated to 480 °C to form the molten salt. Into it MnSO₄ was added under stirring (the weight percentage of MnSO₄ in the reaction system was about 8.5 %), some red-brown gas produced and the flux gradually became black. After the reaction was conducted for 10 min, and then cooling to room temperature, the product was obtained by washing the fusion with deionized water to remove the nitrates for several times, and dried in 100 °C for 12 hrs. Electrochemical properties of the samples were studied by an assembling laboratory cell. The working electrode was fabricated by the powder pressed on the Ni net ($0.5 \times 0.5 \text{ cm}^2$) connected with a 0.2 mm Ni wire as downlead by the pressure of 15 MPa. The powder materials were made up by 85% Li₄Mn₅O₁₂ nanowires, 10% acetylene black, and 5% PTFE (tetrafluoroethylene). The weight of active materials was determined by weighing the Ni net before and after pressing the powders. The lithium foil was pressed onto the Ni net used as the reference and counter electrode. The electrolyte was 1.0 M LiPF₆ solution in ethyele carbonate (EC) and diethylene carbonater (DEC) with the volume ration of 1:1, and the water content and HF was less than 20 and 22 ppm, respectively. All the manipulations were performed at room temperature in a glove-box filled with purified argon gas.

The phase structure of the samples was determined on a Rigaku D/Max 2200 PC diffractometer with a CuK α radiation and graphite monochramator from 20 to 70° at a scanning rate 2.0 °/min. The particle size, morphology and microstructures of the resulting nanoparticles were characterized on transmission electron microscopy (TEM, JEM100-CX II), scanning electron microscopy (SEM) equipped with EDS (Oxford) and HR-TEM (GEOL-2010). IR (Nicolet 5DX FT-IR instrument, KBr pellet technique) and X-ray photoelectron spectroscopy (XPS) analyses were applied to characterize the nanocrystals' surface. The XPS spectra were recorded on a PHI-5300 ESCA spectrometer (Perkin- Elmer) with its energy analyzer working in the pass energy mode at 35.75 eV, and the AlK α line was used as excitation source. The binding energy reference was taken at 284.7 eV for the C1s peak arising from surface hydrocarbons. Charge/discharge characteristics of the cells were recorded using the LAND cell-testing system at the current density of between 2.3 and 3.3 V.

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2. Fig. S1. FT-IR spectrum of the as-prepared Li₄Mn₅O₁₂ nanowires.

The bands around 3400 cm⁻¹, 2900 cm⁻¹ and 1638 cm⁻¹ are assigned to the O-H stretching and bending modes of the absorbed water and surface hydroxyls. The adsorptions at 1380 cm⁻¹ and 1096 cm⁻¹ indicate the existence of a few of NO_3^- species on the nanowires' surface. The peaks between 700 cm⁻¹ and 400 cm⁻¹ are attributed to the vibrations of Mn-O bands.



3. Fig. S2. XRD patterns of the samples obtained at 480 °C for 10 secs (a), 30 secs (b), 1 min (c), 5 min (d), 10 min (e) and 15 min (f).





