

Layered $\text{Li}_{0.88}[\text{Li}_{0.18}\text{Co}_{0.33}\text{Mn}_{0.49}]\text{O}_2$ Nanowires for Fast and High Capacity Li-ion Storage Material

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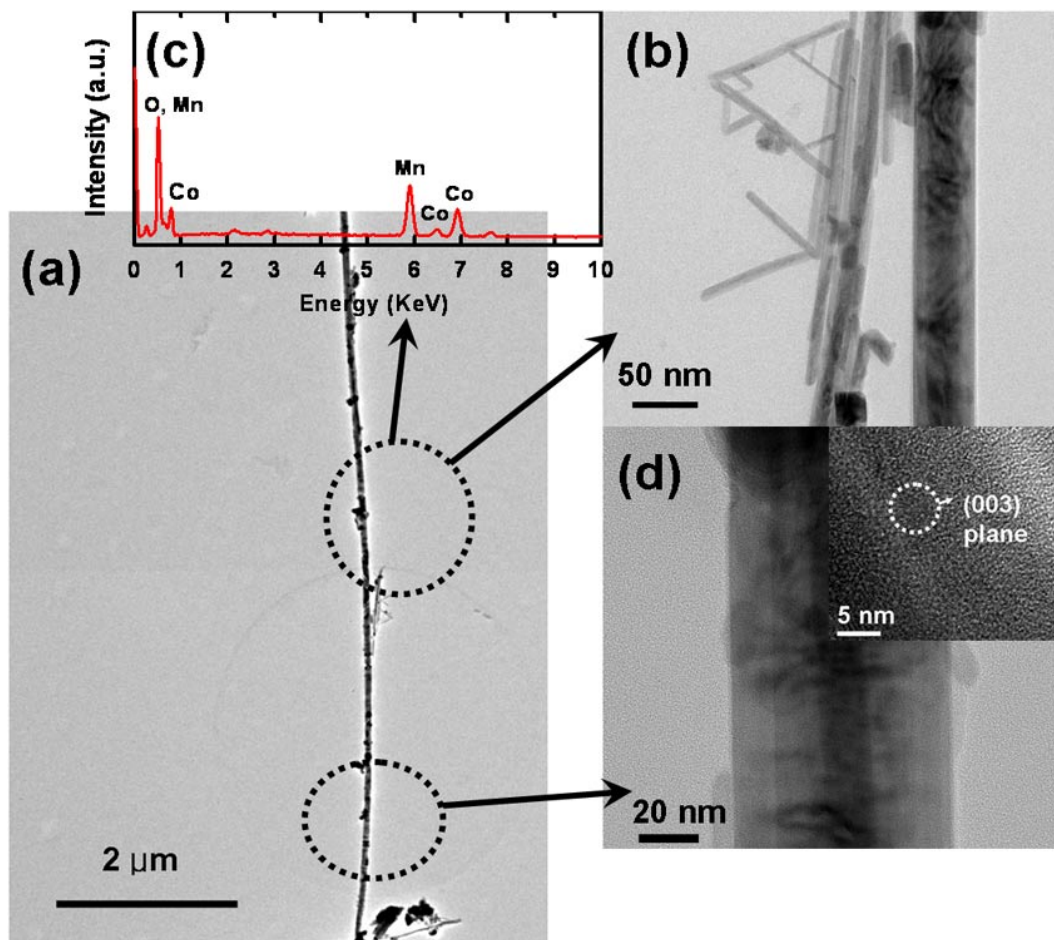
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Experimental methods

A solution containing 7.2 g of KMnO_4 and 200 ml of distilled water was slowly stirred for 30 min at 40°C and added to 2.1 g of fumaric acid which resulted in a rapid, exothermic reaction, forming a brown gel. This gel was further annealed at 400°C and 700°C for 6 and 12 h, respectively, and the resulting dark black powders were thoroughly washed with water 6 times, followed by vacuum-drying at 200°C overnight. Inductively coupled plasma mass spectrometry (ICP-MS) analysis of the sample confirmed $\text{K}_{0.3}\text{MnO}_2$. As-prepared K-birnessite was mixed with $\text{Co}(\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$: $\text{K}_{0.3}\text{MnO}_2$ with a weight ratio of 8:1 in 100 ml of distilled water, and kept it in the autoclave for 5 days at 200°C, and finally washed with water 6 times in order to remove residues that did not participate in the reaction and dissolved K ions. ICP-MS analysis of the sample confirmed formation of $\text{Co}_{0.4}\text{Mn}_{0.6}\text{O}_2$. Finally, $\text{LiNO}_3 \cdot \text{H}_2\text{O}$ and $\text{Co}_{0.40}\text{Mn}_{0.60}\text{O}_2$ were combined with weight ratios of 4:1 were mixed in 100ml of distilled water, and transferred in an autoclave, maintaining it at 200°C for 2 days. As-prepared powders were rinsed with water, and dried under vacuum at 120°C. Cathodes for battery test cells were made from the active material (~20 mg), super P carbon black (MMM, Belgium), and a polyvinylidene fluoride (PVdF) binder (Kureha Company, Japan) at a weight ratio of 90:5:5.

A cathode-slurry was prepared by thoroughly mixing an *N*-methyl-2-pyrrolidene (NMP) solution with the PVdF, the carbon black and the powdery cathode-active material. The electrodes were prepared by coating the cathode-slurry onto an Al foil, followed by drying at 130°C for 20 min. Coin-type battery-test cells (size 2016) containing a cathode, a Li metal anode, and a micro-porous polyethylene separator were prepared in a helium-filled glove box. The electrolyte used was 1 M LiPF₆ with ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (EC/DEC/EMC) (30:30:40 vol. %) (Cheil Industries, Korea). After addition of the electrolyte, the test cells were aged at room temperature for 24 h before commencing the electrochemical tests.

HRTEM samples were prepared by the evaporation of the dispersed nanoparticles in acetone or hexane on carbon-coated copper grids. The field-emission electron microscope was a JEOL 2010F operating at 200 kV. Powder X-ray diffraction measurements were carried out with a Cu-target tube. Inductively coupled plasma- mass spectroscopy (ICP, ICPS-1000IV, Shimadzu) was used for checking the stiochiometry of the as-prepared nanowires. Mn and Co K-edge X-ray absorption spectra were recorded on a BL7C1 beam line from a Pohang light source (PLS) with a ring current of 130-185 mA at 2.5 GeV. A Si(111) double-crystal monochromator was employed to monochromatize the X-ray photon energy. The data were collected in transmission mode with N₂ gas-filled ionization chambers as detectors. Higher-order harmonic contamination was eliminated by detuning to reduce the incident X-ray intensity by ~30 %.



S1. TEM images of (a and c) abnormally grown $\text{Li}_{0.88}[\text{Li}_{0.18}\text{Co}_{0.33}\text{Mn}_{0.49}]\text{O}_2$ nanowires, and (c) Corresponding EDS spectrum of image a, and (d) High-resolution TEM image of a single nanowire of (a).