Template-Free Synthesis of $Li[Ni_{0.25}Li_{0.15}Mn_{0.6}]O_2$ Nanowires for High Performance Lithium Battery Cathode

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S1. Experimental Section

Synthesis of K-birnessite. After stirring a solution containing 4 g of $KMnO_4$ and 100 ml of distilled water for 1 hr at 40°C, we added the solution to 1 g of fumaric acid, resulting in the formation of a brown gel. This gel was annealed at 700°C for 8 h. The resultant dark black powders were washed with water three times and vacuum-dried at 200°C for overnight. By using inductively coupled plasma (ICP)-mass spectrometry (MS) to analyze the sample, we confirmed the presence of $K_{0.33}MnO_2$.

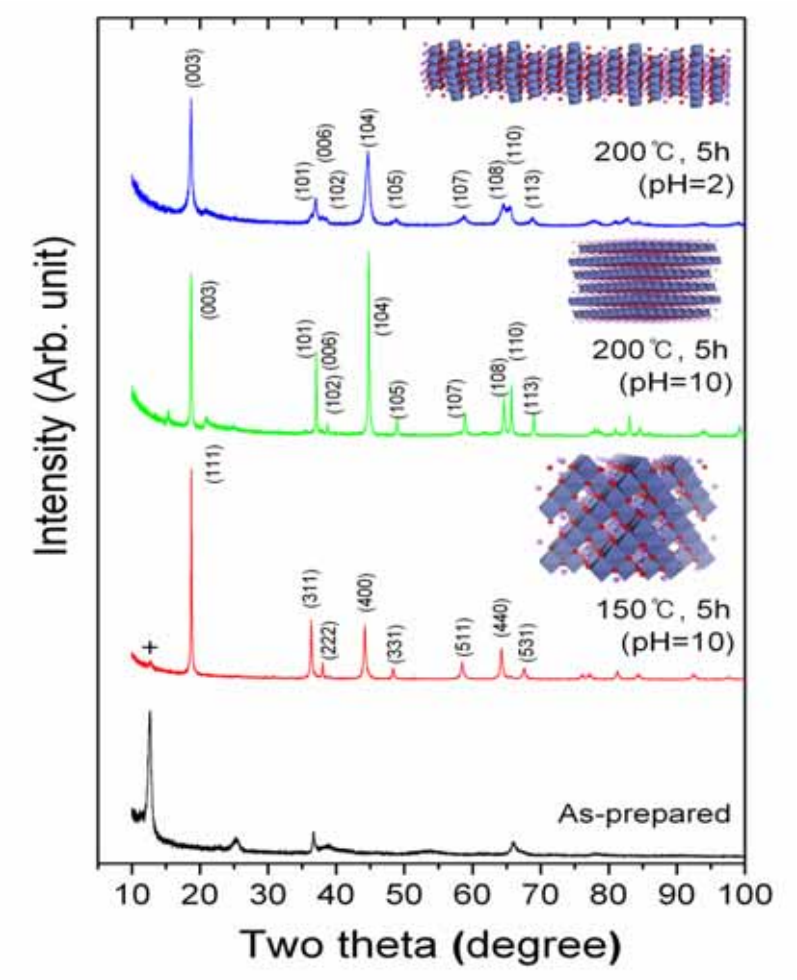
Synthesis of $Ni_{0.3}Mn_{0.7}O_2$. The as-prepared K-birnessite was mixed with $NiCl_2{\cdot}6H_2O$: $K_{0.33}MnO_2$ with a weight ratio of 17:1 in 100 ml of distilled water at 21°C. The mixture was stirred for 8 days at room temperature and finally washed with water four times in order to remove any residues that did not participate in the reaction.

Synthesis of $Li[Ni_{0.25}Li_{0.15}Mn_{0.6}]O_2$ nanowires. After dissolving $LiNO_3{\cdot}H_2O$ into the distilled water solute and $Ni_{0.3}Mn_{0.7}O_2$ powder was added (pH was controlled by the amounts of the water and $LiNO_3{\cdot}H_2O$ and was adjusted at 2), the combination was transferred to an autoclave where it was maintained at 200°C for 1 h to 5 h. The obtained products were rinsed with water several times and dried under vacuum at 200°C for 24h. ICP-MS analysis revealed that the sample had a $Li_{1.14}Ni_{0.24}Mn_{0.61}O_2$ stoichiometry.

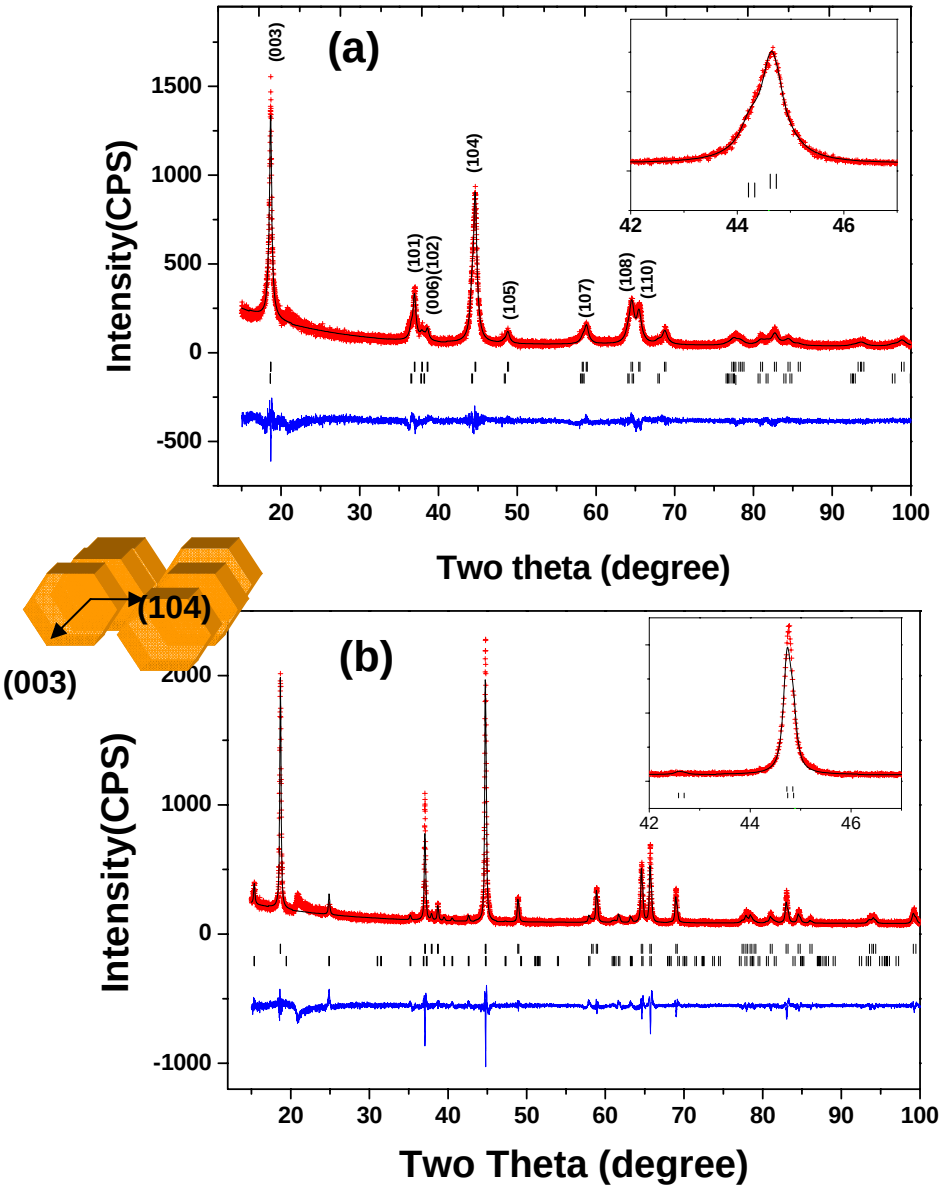
Characterization. Powder X-ray diffraction measurements were taken with a Rigaku DMax/2000PC with a Cu-target tube. We then used an ICP mass spectroscope (ICPS-1000IV, Shimadzu) to determine the metal contents. For the field-emission transition electron microscopy (TEM), which enabled us to investigate the microstructure of the samples, we used a JEOL 2100F microscope at 200 KV.

Electrochemical characterization. Coin-type half-cell tests were conducted on samples which had different C rates between 2 V and 4.8 V and the same discharge and charge rates were used. We made the cathodes for the battery test cells from the active material (approximately 25 mg), super P carbon black (MMM, Belgium), and a polyvinylidene fluoride binder (Solef) in a weight ratio of 80:10:10. Next, we prepared a cathode slurry by thoroughly mixing a *N*-methyl-2-pyrrolidene solution with the polyvinylidene fluoride, the

carbon black, and the powdery cathode-active material. To prepare the electrodes, we coated Al foil with the cathode slurry and left it to dry at 150^{o}C for 20 min. The coin-type battery test cells (size 2016R), each of which contained a cathode, an Li metal anode, and a microporous polyethylene separator, were prepared in a helium-filled glove box. The electrolyte used was 1.15 M $LiPF_6$ with ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (3/3/4 vol%) (Cheil Ind. Korea).



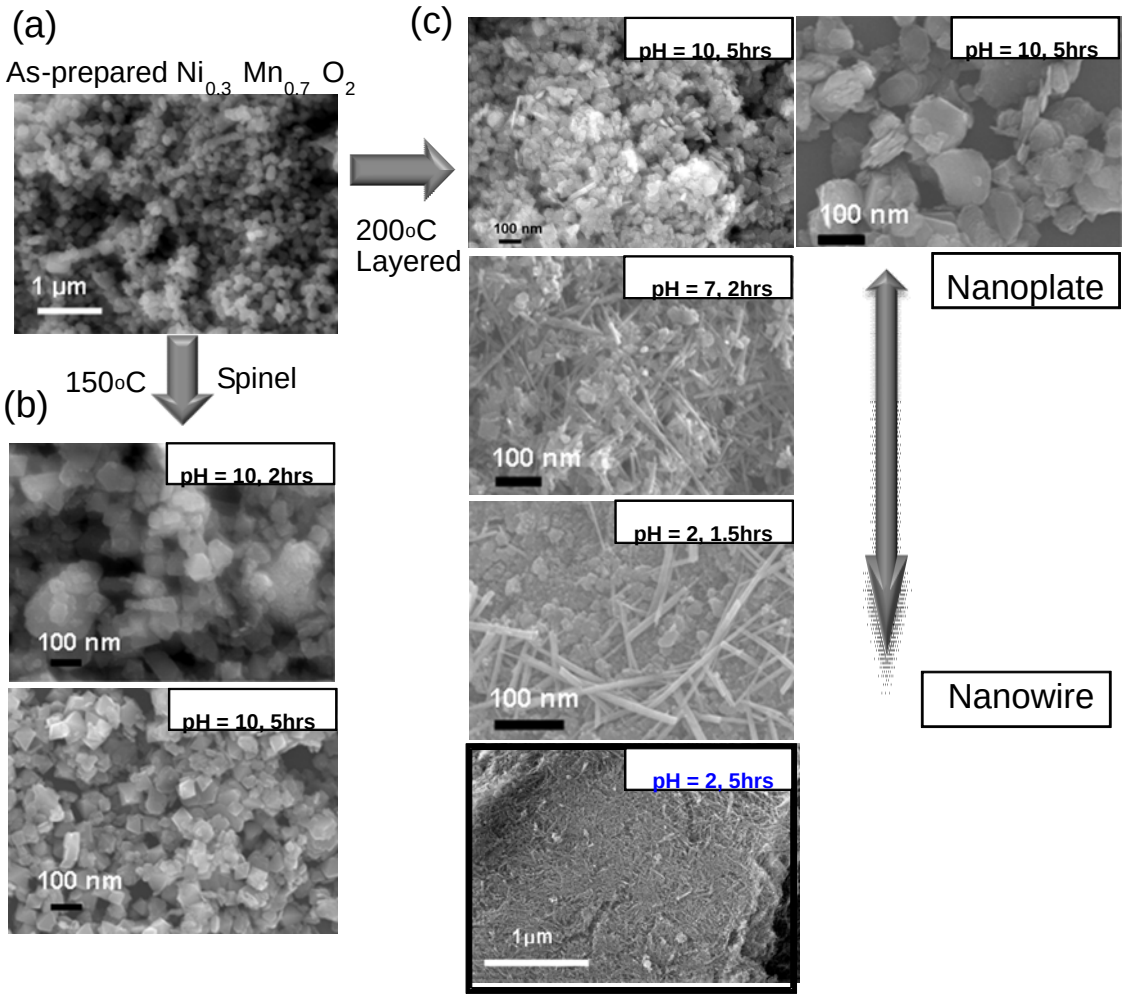
S2. XRD patterns for the $Ni_{0.3}Mn_{0.7}O_2$ precursor after hydrothermal heating at different temperatures and pHs.



S3. Rietveld analysis results of the $Li[Ni_{0.25}Li_{0.15}Mn_{0.6}]O_2$ (a) nanowire and (b) nanoplate. Inset figures are expanded characteristic diffraction peak.

S4. The lattice constants, R factors, and relative percentages of the phase for $Li[Ni_{0.25}Li_{0.15}Mn_{0.6}]O_2$.

	Phase	a /Å	b /Å	c / Å	R_p (%)	R_{wp} (%)	Relative %
Nanowire	phase 1	2.8510(3)		14.251(2)	16.6	17.2	83
	phase 2	2.8912(8)		14.312(7)			17
Nanoplate	phase	2.8403(1)		14.234(1)	15.9	17.5	82
	o-$LiMnO_2$	2.8405(8)	5.7625(5)	4.5601(6)			18
Nanowire after cycling	phase 1	2.8560(3)		14.252(6)	16.6	35	81
	phase 2	2.8931(9)		14.409(9)			19



S5. Evolution of the morphologies of the $Ni_{0.3}Mn_{0.7}O_2$ precursor after treating at different pHs, hydrothermal heating temperatures and times. The pHs were controlled by the relative amounts of $LiNO_3$ or LiOH and distilled water. (a) SEM images of (a) $Ni_{0.3}Mn_{0.7}O_2$ precursor, (b) after 150^{o}C heating at pH = 10 and (c) after 200^{o}C heating at pHs = 10, 7, and 2, in addition to high resolution TEM image of the $Li[Ni_{0.25}Li_{0.15}Mn_{0.6}]O_2$ nanowires.