Understanding hydrothermal transformation from $\text{Mn}_2\text{O}_3$ particles to $\text{Na}_{0.55}\text{Mn}_2\text{O}_4\cdot1.5\text{H}_2\text{O}$ nanosheets, nanobelts, and single crystalline ultra-long $\text{Na}_4\text{Mn}_9\text{O}_{18}$ nanowires

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Manganese oxides are one of the most valuable materials for batteries, fuel cells and catalysis. Herein, we report the change in morphology and phase of as-synthesized $\text{Mn}_2\text{O}_3$ by inserting $\text{Na}^+$ ions. In particular, $\text{Mn}_2\text{O}_3$ nanoparticles were first transformed to 2 nm thin $\text{Na}_{0.55}\text{Mn}_2\text{O}_4\cdot1.5\text{H}_2\text{O}$ nanosheets and nanobelts via hydrothermal exfoliation and $\text{Na}$ cation intercalation, and finally to sub-mm ultra-long single crystalline $\text{Na}_4\text{Mn}_9\text{O}_{18}$ nanowires. This paper reports the morphology and phase-dependent magnetic and catalytic (CO oxidation) properties of the as-synthesized nanostructured Na intercalated Mn-based materials.
for Na-ion rechargeable batteries. Several methods have been used to synthesize the material, including sol-gel/high-temperature calcinations, solid-state reaction, thermal-conversion of a precursor, polymer-pyrolysis, and hydrothermal method. Hosono et al. used a hydrothermal method (Teflon-lined autoclave at 205 °C for 2 days) using MnO powder in a 5.0 M NaOH solution and obtained single-crystalline Na0.44MnO2 nanowires with superior capacity of 120 mAh/g and high charge-discharge cyclability. In these cases, the efficiency of the material was shown to be dependent on the surface area and morphology; hence, an understanding of the change in morphology during Na (or Li and K) ion-insertion is very important. Liu et al. prepared Na0.44MnO2 nanorods with recipes of MnSO4, KMnO4 and NaOH solutions by a hydrothermal method. Le et al. reported a change in morphology (from nanosheets to nanowires) and crystal structure (from Mn2O3 to birnessite and Na0.44MnO2) after the hydrothermal reaction of Mn2O3 powder in a 5.0 M NaOH solution. Although many studies have reported the electrochemical properties of Na-inserted MnOx materials, this study examined the undiscovered Na-insertion and morphological behaviors of Mn2O3 nanoparticles during a hydrothermal reaction process.

This paper reports a facile process to control the morphology and phase of alkali metal intercalated Mn oxides using a simple hydrothermal technique. Three different alkali metals (Li, Na, and K) were intercalated into the Mn2O3 powder (particles) to nanosheets, nanobelts and nanowires. In particular, quantum-thick Na0.55Mn2O4·1.5H2O nanosheets, nanobelts and single crystalline ultra-long Na4Mn9O18 nanowires were produced by inserting Na with different concentrations and reaction durations. The magnetic and catalytic (CO oxidation) properties of the as-synthesized Mn oxides are reported in detail. In addition to the new findings of the morphological behaviors (by Na-insertion)/detailed characterization and magnetic properties, the laser-induced Na-deinsertion behavior was also examined by Raman spectroscopy. The present study provides several new insights into the development of alkali metal ion intercalated Mn materials.

Results and Discussion

Figure 1 presents powder XRD patterns and scanning electron microscopy (SEM) images of the starting materials (Mn3O4 and Mn2O3) and the synthesized Na-intercalated Mn oxides by varying the reaction conditions. The insets show the corresponding SEM images (left) and Rietveld refinement powder XRD patterns of a mixed phase sample (top right). The additional Figures are provided in the Supporting Information (Figs S1, S2, and S3a, S3b) to understand the change in the crystal phase with varying reaction conditions. The reaction time was written on the right of the corresponding XRD.

Figure 1. XRD patterns of the starting materials (Mn3O4 and Mn2O3) and the synthesized materials according to the reaction time in the 1.0 and 10 M NaOH solution. The insets show the corresponding SEM images (left) and Rietveld refinement powder XRD patterns of a mixed phase sample (top right).
12.5° and 25.1° 2θ decreased in intensity. After a reaction for 3 weeks, the newly appeared peaks (γ) were mainly present, which matched orthorhombic (Pbam) Na₄Mn₉O₁₈ (JCPDS 27-0750) (Supporting Information Fig. S1 and S2). This suggests a complete change in the crystal phase of Na₀.₅₅Mn₂O₄·1.₅H₂O to Na₄Mn₉O₁₈ with increasing hydrothermal reaction duration to 3 weeks in 10 M NaOH at 200 °C. The high purity Na₄Mn₉O₁₈ nanowires were finally obtained after the intermediate mixture; a mixture of Na₀.₅₅Mn₂O₄·1.₅H₂O and Na₄Mn₉O₁₈ followed by a mixture of Na₀.₅₅Mn₂O₄·1.₅H₂O and Mn₂O₃. High purity Na₀.₅₅Mn₂O₄·1.₅H₂O nanosheets were not observed in the hydrothermal method.

Rietveld analysis was performed for a sample with mixed crystal phases (Na₀.₅₅Mn₂O₄·1.₅H₂O:Na₄Mn₉O₁₈ = 22.7%:77.3%). The inset in Fig. 1 shows the observed and Rietveld refinement XRD patterns (see Supporting Information, Fig. S3). The crystal structures were fully refined, and the detailed structural parameters are provided in the Supporting Information Fig. S3, Tables S1 and S2.

The SEM and TEM/HRTEM images of the corresponding samples were examined to further understand the recrystallization mechanism of Mn₂O₃ NPs in a NaOH solution under hydrothermal conditions at 200°C for the specified duration. Figure 2 shows SEM images of the starting materials (Mn₃O₄ and Mn₂O₃) and the synthesized materials prepared by a hydrothermal method in 1.0 M NaOH, LiOH and KOH solutions for 24 hrs. The starting Mn₃O₄ and Mn₂O₃ showed particle morphologies with different sizes. On the other hand, after a hydrothermal reaction (1.0 M NaOH) at 200°C, the surface morphology had changed entirely to ultrathin nanosheets. Under LiOH and KOH solution conditions, the surface morphologies were also changed to nanosheets, but were thicker than those prepared in the NaOH solution. Supporting Information, Fig. S4 provides additional SEM images of the nanosheets obtained by Na, Li and K intercalation. The SEM images and the XRD patterns (Fig. 1) indicate that the sheet morphology originated from the monoclinic Na₀.₅₅Mn₂O₄·1.₅H₂O phase, which was formed by the exfoliation of Mn₂O₃ upon Na and H₂O concomitant intercalation. On the other hand, the presence of a Mn₂O₃ phase for the samples prepared in a short duration (< 3 weeks in 1 M NaOH or < 3 days in 10 M NaOH) was attributed to the incomplete conversion of Mn₂O₃ present primarily in the core part of the powder, whereas the surface consisted mainly of ultra-thin nanosheets (Fig. S5,SI). TEM, HRTEM images and electron diffraction patterns were also obtained for the ultrathin nanosheets, as shown in Fig. 2. The TEM image (top right, Fig. 2) supports the nanosheet morphology shown in the SEM images. High resolution TEM (HRTEM) (bottom right, Fig. 2) revealed the continuous lattice, indicating the crystalline nature of the nanosheets with a lattice spacing of 0.25 nm, corresponding to the (200) plane of monoclinic Na₀.₅₅Mn₂O₄·1.₅H₂O. The selected area electron diffraction (SAED) patterns of the distinct spots on the rings shown as an inset of the HRTEM image further confirmed the crystalline
nature of these nanosheets. More TEM and HRTEM images were provided in the Supporting Information, Fig. S5. For comparison, Ma et al. employed a similar hydrothermal (170 °C for 12 hrs to 1 week) method using Mn₂O₃ powder in a 10 M NaOH solution⁵⁷. On the other hand, they reported Na⁺-ion free birnessite-related layered MnO₂ nanobelts (5–15 nm width), which is inconsistent with the present study.

To measure the accurate thickness of the ultrathin nanosheets discussed above, a more skillful technique was employed, as described in Fig. 3. The nanosheets were first sandwiched between epoxy supported by disks, as illustrated in the Figure. Various treatment steps such as bonding, slicing, disk cutting, and ion milling, were then performed to make a suitable TEM specimen. The thickness of the TEM specimen was finally less than 5 μm. TEM, HRTEM and high-angle annular dark field (HAADF) images were taken, which clearly showed the edge of the nanosheets. Mn in the nanosheets edge was also confirmed by an EDX profile (Supporting Information, Fig. S6).

The HRTEM image showed lattice fringes with neighboring distances of 0.25 nm, corresponding to the (200) plane of monoclinic Na₀.₅₅Mn₂O₄·1.₅H₂O as mentioned above. The thickness of the nanosheet edge was measured to be 2 nm, which is close to the unit cell thickness (also see Supporting Information, Fig. S7).

Because the crystal phase of Mn₂O₃ was not completely changed using 1.0 M NaOH, the NaOH concentration was increased to 10.0 M and a hydrothermal reaction was performed for various reaction durations. The morphologies and microstructures of the samples obtained by the hydrothermal treatment of Mn₂O₃ in 10 M NaOH for 20h at 200 °C were examined further by SEM and TEM/HRTEM, as shown in Figs 4 and 5. The Mn₂O₃ particles initially changed to nanosheets and nanobelts with a few nanowires (or nanothreads) for a reaction duration of less than 1 week (Supporting Information, Fig. S8), whereas the Mn₂O₃ nanoparticles were still present in the synthesized samples. This was supported by the corresponding XRD patterns (Fig. 1). As the reaction time increased, the nanobelts evolved slowly to ultra-long nanowires. Mixed morphologies were observed in the SEM images (Supporting Information, Fig. S9). For the corresponding XRD results (Fig. 1), the XRD patterns (Δ) of Na₀.₅₅Mn₂O₄·1.₅H₂O were diminished slowly and those (α) of Na₆Mn₁₄ were remarkable. Upon the reaction for 3 weeks, the SEM
image in Fig. 5 showed mostly ultra-long (sub-mm) nanowires (also see Supporting Information, Fig. S10). The corresponding optical microscopy images showed that the black color of the Mn$_2$O$_3$ (with particle morphology) changed to a brown color as the crystal phase changed to Na$_{0.55}$Mn$_2$O$_4$·1.5H$_2$O and Na$_4$Mn$_9$O$_{18}$ (Supporting Information, Fig. S10).
The morphology appeared as nanofibers for the final Na-intercalated Mn product. HRTEM images of the nanobelts showed a clear lattice spacing of 0.23 nm, corresponding to the (200) plane of monoclinic Na$_{0.55}$Mn$_2$O$_4$·1.5H$_2$O (Fig. 4). This was also observed for the ultrathin nanosheets (Figs 2 and 3), suggesting a similar growth direction of nanosheets and nanobelts. The SAED pattern confirmed the single crystal nature of the Na$_{0.55}$Mn$_2$O$_4$·1.5H$_2$O nanobelts. Supporting Information, Fig. S12 shows the corresponding simulated diffraction patterns. A structure projection model in Fig. 4 displays the corresponding [011] planes of Na$_{0.55}$Mn$_2$O$_4$·1.5H$_2$O. Figure 5 shows representative SEM, TEM, and HRTEM images of the Na$_4$Mn$_{18}$O$_{36}$ nanowires obtained using 10 M NaOH at 200 °C for 3 weeks. The HRTEM image shows a lattice spacing of 0.442 nm for the nanowires, which is in accordance with the (200) plane of orthorhombic Na$_4$Mn$_{18}$O$_{36}$. The spot SAED pattern confirms the single crystal structure of these nanowires. The wire grew along the [100] direction. Figure 6 shows the corresponding structure projections and crystal models of the Na-intercalated samples. In the case of the Na$_{0.55}$Mn$_2$O$_4$·1.5H$_2$O nanobelts, H$_2$O and Na cations were concomitantly intercalated between the skeletons of Mn-O sheets. For the $ab$ plane structure of the Na$_4$Mn$_{18}$O$_{36}$ nanowires, Na was embedded in the Mn-O tunnel, which is consistent with the Mn$_2$O$_3$ square pyramids and MnO$_6$ octahedra. The Na cations are situated in two different sites (with a unique tunnel structure) and the c-axis is the charge-discharge paths of Na cation diffusion. The SAED and simulated patterns of the starting material, i.e. Mn$_2$O$_3$, are provided in the Supporting Information, Fig. S13.

The magnetic properties of Mn$_2$O$_3$ were measured at various temperatures from 5 K to 300 K and magnetic fields from 0 to 50 kOe. An ideal linear plot of the magnetization curve was observed because of the high resistance.

The surface resistance of Na$_4$Mn$_{18}$O$_{36}$ nanowires was measured as a function of temperature (Supporting Information, Fig. S20). The resistance of 12.5 MΩ at room temperature decreased linearly to 1.0 MΩ with increasing temperature to 200 °C. For the Mn$_2$O$_3$ powder samples, the surface resistance could not be measured because of the high resistance.

The CO oxidation activities (Supporting Information, Fig. S21) of Mn$_2$O$_3$ (in Fig. 2), Mn$_3$O$_4$ (in Fig. 2), and Na$_{0.55}$Mn$_2$O$_4$·1.5H$_2$O nanosheets (Mn$_2$O$_3$@Na$_{0.55}$Mn$_2$O$_4$·1.5H$_2$O core-shell structures; sample prepared with NaOH solution in Fig. 2) was tested for catalytic applications, such as CO oxidation using low power plasma sources.
cost materials. In the first CO oxidation runs, the CO oxidation onsets were observed in the order of Mn$_2$O$_3$ (200 °C) < Na$_{0.55}$Mn$_2$O$_4$·1.5H$_2$O (250 °C) < Mn$_3$O$_4$ (280 °C). The T$_{10\%}$ (the temperature at 10% CO conversion) for Mn$_2$O$_3$, Mn$_3$O$_4$ and Na$_{0.55}$Mn$_2$O$_4$·1.5H$_2$O was observed at 240 °C, 280 °C and 320 °C, respectively. In the second runs, the order was the same as the onset temperatures of 180 °C (Mn$_2$O$_3$), 260 °C (Na$_{0.55}$Mn$_2$O$_4$·1.5H$_2$O) and 300 °C (Mn$_3$O$_4$). The T$_{10\%}$ for Mn$_2$O$_3$, Mn$_3$O$_4$ and Na$_{0.55}$Mn$_2$O$_4$·1.5H$_2$O was observed at 230 °C, 320 °C and 365 °C, respectively. Only the Mn$_3$O$_4$ nanoparticles showed an increase in CO oxidation activity in the second run. The Na-insertion into Mn$_2$O$_3$ (forming Na$_{0.55}$Mn$_2$O$_4$·1.5H$_2$O nanosheets on the surface) showed no synergistic effect for CO oxidation. Ji et al. prepared α- Mn$_2$O$_3$ nanowires (by a molten salt method), Mn$_3$O$_4$ nanoparticles and mixed Mn$_2$O$_3$/Na$_3$Mn$_3$O$_{16}$ (a ratio of 9/1) samples, and tested their CO oxidation activities. They reported that α- Mn$_2$O$_3$
nanowires (T_{10\%} \approx 180^\circ C) showed much catalytic activity than the others (T_{10\%} \approx 220^\circ C) and Na$_2$Mn$_8$O$_{16}$ did not relate to their high catalytic activity. Their conclusions are in good agreement with the present study.

**Conclusion**

Na-ion intercalation into Mn$_2$O$_3$ was initially transformed into ultra-thin monoclinic Na$_{0.55}$Mn$_2$O$_4$·1.5H$_2$O nanosheets and nanobelts. The nanobelts were then evolved to single crystalline ultra-long orthorhombic Na$_4$Mn$_9$O$_{18}$ nanowires with a (Na-ion mobile) tunnel structure. This synthesis process was extended further to other alkali metals (Li and K) using a simple hydrothermal method in a Mn$_2$O$_3$-dispersed alkali hydroxide (LiOH, NaOH and KOH) solution. SEM and TEM confirm the transformation of the morphology. XRD and HRTEM were used to examine the crystal phase change and microstructure. Detailed crystal structural parameters were obtained

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Figure 7. Raman spectra of the Na$_4$Mn$_9$O$_{18}$ nanowires with increasing laser power. The inset shows an image of the analyzed area.

Figure 8. High resolution Mn 2p, O 1s, N 1s, and Na KLL photoelectron spectra of the Mn$_2$O$_3$ particles and Na$_4$Mn$_9$O$_{18}$ nanowires.
by Rietveld refinement analysis. XPS confirmed the presence of inserted Na cation. Moreover, high power laser irradiation readily induces the irreversible Na-deinsertion behavior from Na₄Mn₉O₁₈ to Mn₂O₃, as confirmed by Raman spectroscopy. The Na₄Mn₉O₁₈ nanowires exhibited ferromagnetic behavior at temperatures below 25 K and paramagnetic behavior at above that temperature. The surface resistance of Na₄Mn₉O₁₈ nanowires was 12.5 MΩ at room temperature and decreased linearly to 1.0 MΩ with increasing temperature to 200 °C. The CO oxidation activity (T₁₀% = 230 °C) of the Mn₂O₃ nanoparticles was substantially decreased after Na-intercalation. The very detailed transformation mechanism and the new fundamental characterization provide new insights into the development of alkali metal cation intercalated Mn oxides.

Methods

Material synthesis. Mn₃O₄ was synthesized by a hydrothermal method, as described below. Briefly, 10 mL of 0.1 M Mn(II) nitrate tetrahydrate (Sigma-Aldrich, > 97.0%) was mixed with 10 mL of deionized water (18.2 MΩ cm resistivity) in a Teflon jar (120 mL capacity), and 1.0 mL of an ammonia solution was then added to obtain the precipitates. The reaction jar was capped tightly and placed in an oven (120 °C) for 12 hours, after which the oven was cooled naturally to room temperature. The brown precipitate was collected after washing with deionized water followed by ethanol, and then dried in an air convection oven (80 °C). Bulk Mn₂O₃ was obtained by the post-annealing of Mn₃O₄ at 750 °C for 4 hrs. To synthesize the Na(or Li and K)-intercalated Mn materials, the Mn₂O₃ (~25 mg) was dispersed in a 20.0 mL 1.0 M (or 10 M) NaOH (or LiOH and KOH) solution. The solution in a Teflon-lined stainless autoclave was placed at 200 °C for a reaction time, which was varied from 12 hrs to 3 weeks. After a specified time (12 hrs, 1 day, 3 days, 1, 2 and 3 weeks were selected to show in the present article), the oven was stopped and cooled naturally to room temperature and the powder product was collected by centrifuging. The powder was finally washed and dried for further characterization. Although the slow reaction process took time and patience (and somewhat industrially impractical) we employed the slow process to disclose new findings and to carefully examine change in morphology which has never been reported for Mn oxide material.

Material characterization. The surface morphology of the synthesized powder samples was examined by field emission scanning electron microscopy (FE-SEM, Hitachi SE-4800). High resolution transmission electron microscopy (HRTEM) and the electron diffraction patterns were obtained using a FEI Tecnai G2 F20 at an operating voltage of 200 kV. The powder X-ray diffraction (XRD) patterns were obtained using a PANalytical X’Pert Pro MPD diffractometer operated at 40 kV and 30 mA using Cu Kα radiation. The Rietveld refinement was performed using the TOPAS software program (ver. 4.2, Bruker 2005). Further details are described elsewhere61. The Fourier-transform infrared (FT-IR) spectroscopy was performed using a Thermo Scientific Nicolet iS10 spectrometer in ATR (attenuated total reflectance) mode. The X-ray photoelectron spectra were obtained using a ThermoScientific K-alpha X-ray photoelectron spectrometer with a monochromated Al Kα X-ray source, a pass energy of 20.0 eV, and an analyzed spot size of 400 μm. Confocal Raman microscopy (PRISM, NOST Co., South Korea) was conducted to take the Raman spectra for the powder samples at a laser wavelength of 532 nm and a 100 ×, 0.9NA microscope objective. The laser intensity was varied from 0.004 mW to 2.7 mW. All the Raman spectra were referenced to the Raman spectrum of cyclohexane. The magnetic properties of the Na₄Mn₉O₁₈ nanowires were examined using a MPM5-XL-7 superconducting quantum interference device (SQUID) magnetometer (Quantum Design, Inc.) at various temperatures.

Figure 9. Mass-normalized FC and ZFC curves of Na₄Mn₉O₁₈ nanowires from 5 to 300 K in H = 100 Oe. The inset show the magnetization (M – H) curves measured at various temperatures.
CO oxidation and surface resistance tests.  The CO oxidation experiments were performed on a continuous flow quartz U-tube reactor with a 10 mg sample. A mixed gas (1% CO and 2.5% O2 in N2) balance was introduced into the reactor at a flow rate of 40 mL/min. The temperature heating rate was fixed to 20 °C/min. The reaction gas products were analyzed using a SRS RGA200 quadrupole mass spectrometer. The surface resistance of the pelletized sample was measured using a home-built four-probe resistance measurement instrument.

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Author Contributions
Y.S. designed the main experimental concepts and prepared the manuscript. Y.P. mainly performed the material synthesis. S.W.L. contributed to structural analysis. Y. et al. performed HRTEM measurements. K.H. Kim performed magnetic measurements and analysis. B.K.M. performed the thickness measurement. A.K.N. acknowledge the Raman measurements by NOST Co., Ltd.

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