Synthesis of ultrasmall Li–Mn spinel oxides exhibiting unusual ion exchange, electrochemical, and catalytic properties

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The efficient surface reaction and rapid ion diffusion of nanocrystalline metal oxides have prompted considerable research interest for the development of high functional materials. Herein, we present a novel low-temperature method to synthesize ultrasmall nanocrystalline spinel oxides by controlling the hydration of coexisting metal cations in an organic solvent. This method selectively led to Li–Mn spinel oxides by tuning the hydration of Li\(^{+}\) ions under mild reaction conditions (i.e., low temperature and short reaction time). These particles exhibited an ultrasmall crystallite size of 2.3 nm and a large specific surface area of \(371 \pm 15 \text{ m}^2 \text{ g}^{-1}\). They exhibited unique properties such as unusual topotactic Li\(^{+}\)/H\(^{+}\) ion exchange, high-rate discharge ability, and high catalytic performance for several aerobic oxidation reactions, by creating surface phenomena throughout the particles. These properties differed significantly from those of Li–Mn spinel oxides obtained by conventional solid-state methods.

Metal oxide crystal structures and compositions are expected to lead to numerous applications. Manganese-based binary oxides have attracted tremendous research interest because of their potential use as electrode materials1–10, adsorbents11–21, catalysts22–27, catalyst supports28,29, and oxidants30–33. Specifically, Li–Mn spinel oxides (LMOs) have served as cathode materials for lithium-ion batteries1–10 and Li\(^{+}\) ion-selective adsorbents11–14,18 because these ions can be chemically and/or electrochemically extracted from and inserted into the spinel structure. Nanocrystalline metal oxides offer large specific surface areas and short ion diffusion lengths that may contribute to the efficient surface reaction and rapid ion extraction/insertion3–9 required to achieve high functional materials. Nanocrystalline manganese oxides are typically synthesized by hydrothermal methods5,10,34–39 involving harsh conditions such as elevated temperatures, high pressures, and long reaction times, limiting control over product crystal structures and morphologies.

Manganese-based binary oxides exhibit three-dimensional frameworks, comprising MnO\(_6\) octahedral units and metal cations and form different crystal structures such as tunnels as well as layered and spinel structures according to the nature of the coexisting metal cations acting as templates for these structures40–44. Layered manganese-based binary oxides that consist of a large interlayer space between MnO\(_6\) octahedral units and hydrated cations as templates are often synthesized at relatively low temperatures44,37,45–47. On the other hand, spinel structure formation typically requires relatively high

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temperatures and long reaction times (Supplementary Table 1) because spaces between \( \text{MnO}_6 \) octahedral units are too small to accommodate hydrated cations in these structures.

To control both morphologies and crystal structures, a synthetic method was designed to synthesize complex oxides such as LMO. This method assumed that spinel structures can be synthesized at low temperatures using non-hydrated metal cations as templates. Therefore, the cation hydration state was tuned by combining an organic solvent and an organic solvent-soluble manganese precursor. In this study, the rational one-pot low-temperature synthesis of LMO was achieved by controlling the Li\(^{+}\) ion hydration in an organic solvent (Fig. 1a). Amorphous Li–Mn binary oxide nanoparticles were initially prepared by room temperature reduction of tetra-\( n \)-butylammonium permanganate salt (TBAMnO\(_4\)) in 2-propanol, which simultaneously acted as a reductant for MnO\(_4^{-}\) and a solvent. Subsequently, the amorphous nanoparticles crystallized within 30 min when the temperature was increased to up to 86 °C while stirring. The method produced ultrasmall LMO particles with an average crystallite size of 2.3 nm (LMO(2.3 nm)) and an elevated average specific surface area of 371 ± 15 m\(^2\) g\(^{-1}\). The LMO(2.3 nm) particles showed unique characteristics such as unusual topotactic Li\(^{+}\)/H\(^{+}\) ion exchange property, high-rate discharge ability applicable to cathode material for lithium-ion battery, and high catalytic performance for several oxidation reactions. These properties differed significantly from those of Li–Mn spinel oxides obtained by conventional solid-state methods (LMO(bulk)).

**Results**

**Synthesis of Li–Mn spinel nanoparticles using dehydrated Li\(^{+}\) ions in an organic solvent.** The low-temperature synthesis of LMO hinged on suppressing the hydration of Li\(^{+}\) ions and was consequently performed in an organic solvent using the organic solvent-soluble TBAMnO\(_4\) salt as an LMO precursor. TBAMnO\(_4\) readily dissolved in a 2-propanol-based LiCl solution to yield a purple mixture. The purple color, characteristic of MnO\(_4^{-}\) ions, completely disappeared when the mixture was stirred for 5 min at room temperature; a brown slurry consisting of amorphous Li–Mn oxide nanoparticles was obtained. The slurry was subsequently heated at 86 °C for 30 min to generate nanoparticles. Peak positions and intensities of X-ray diffraction (XRD) pattern of these nanoparticles were in good agreement with those of LMO structures, but all observed peaks were very broad (Fig. 1b). Crystallite size estimated with Scherrer equation using width of 111 peak was 2.3 nm. On the basis of the average Mn oxidation state of 3.62 ± 0.065, which was estimated from a redox titration and the composition of LMO(2.3 nm) (Li/Mn = 0.463 (mol/mol)), which was from elemental analyses, the empirical formula of LMO(2.3 nm) was determined to be Li\(_{0.825}\)(Mn\(_{0.966}\)Li\(_{0.034}\))O\(_4\). Transmission electron microscopy (TEM) images also showed that LMO(2.3 nm) consisted of small nanoparticles averaging 2.55 nm in size with a main particle size distribution of 2–3 nm (standard deviation (\( \sigma \)) = 19.4% (0.49 nm), Fig. 1c,e). These TEM images displayed...
clear lattice fringes throughout the particles (Fig. 1c). Electron diffraction and XRD patterns did not present any obvious halo pattern (Fig. 1b,d). These results indicated the crystallinity of LMO(2.3 nm) and absence of an amorphous phase in the sample. The LMO(2.3 nm) nanoparticles exhibited large Brunauer–Emmett–Teller (BET) surface areas (371 ± 15 m$^2$ g$^{-1}$), consistent with their small size. These observations demonstrate that mild synthetic conditions (i.e., low temperature and short reaction time) have led to LMO(2.3 nm) with the ultrasmall particle sizes. These nanoparticles displayed smaller sizes and larger specific surface areas than previously reported LMOs (Supplementary Table 1).

Due to the ultrasmall particle size and the large specific surface areas of LMO(2.3 nm), the surface structure of LMO(2.3 nm) is expected to be different from those of LMOs with large particle sizes. Thus, we next performed the surface characterization of LMO(2.3 nm) and LMO(bulk). LMO(bulk) exhibited an average particle size of 410 nm (according to the BET surface area). The average oxidation states of LMO(2.3 nm) and LMO(bulk) were 3.62 ± 0.065 and 3.48 ± 0.018, respectively, indicative of the mixed valency of Mn. Electron paramagnetic resonance (EPR) spectra of LMO(2.3 nm) showed only a very broad and low intensity peak, and the characteristic six-peak hyperfine structures due to Mn$^{2+}$ species were not observed (Supplementary Fig. 1). Thus, LMOs are predominantly composed of Mn$^{4+}$ and Mn$^{3+}$ species. The XPS spectra of LMO in the Mn 2p region showed no significant difference between LMO(2.3 nm) and LMO(bulk) (Supplementary Fig. 2). This indicated that the relative concentration of Mn$^{4+}$ (Mn$^{3+}$) species on the surface of LMO(2.3 nm) was almost the same as that of LMO(bulk). On the other hand, the XPS spectrum of LMO(2.3 nm) in the O 1s region was much different from that of LMO(bulk) (Supplementary Fig. 3). Each O 1s spectrum can be deconvoluted into three peaks corresponding to the three types of oxygen species; the low (around 530 eV), medium (around 531 eV), and high binding energy peaks (around 533 eV) are possibly ascribed to the coordinatively saturated oxygen species (lattice oxygen, described as $O_{\text{sat}}$), the coordinatively unsaturated oxygen species (surface adsorbed oxygen, OH groups on the surface, or oxygen vacancy, described as $O_{\text{unsat}}$), and adsorbed H$_2$O molecule, respectively. The curve-fitting analyses showed that the $O_{\text{unsat}}$/$O_{\text{sat}}$ values for LMO(2.3 nm) and LMO(bulk) were 0.38 and 0.13, respectively, indicating that the Mn and O species on the surface of LMO(2.3 nm) are in lower coordination environments in comparison with those of LMO(bulk). This may contribute to the enhancement of the surface reactivity of LMO(2.3 nm) (e.g. catalytic reactions).

This low-temperature synthesis of nanocrystalline LMO assumed the effectiveness of water exclusion using an organic solvent. To assess its effect on the product structure, water was incrementally added to the solvent during the synthesis of nanocrystalline LMO. Spinel phase was predominantly formed only in the absence of water (H$_2$O/Li ≈ 0 (mol/mol)) (Fig. 2c). Diffraction peaks characteristic of the spinel structure disappeared when a specific amount of water corresponding to a H$_2$O/Li molar ratio of 10 was added to the solvent (Fig. 2d). The product showed diffraction peaks assignable to the birnessite-type layered manganese oxide when the H$_2$O/Li molar ratio increased up to 20 (Fig. 2e). Further increases

Figure 2. The effect of water addition to organic solvents on product phases. Literature data for (a) LiMn$_2$O$_4$ (JCPDS 35-0782) and (b) Li-birnessite (JCPDS 50-0009). XRD patterns of products synthesized using H$_2$O/2-propanol mixtures as solvents ((c) H$_2$O/Li molar ratios of 0, (d) 10, (e) 20, (f) 200, and (g) 500).
in water amounts (H\textsubscript{2}O/Li\textsuperscript{+} = 200 or 500 (mol/mol)) afforded the well-developed birnessite-type structure (Fig. 2f,g). These results clearly show that product phases can be controlled by manipulating the amounts of water added to the solvent. In spinel structures, Li\textsuperscript{+} ions occupy tetrahedral sites surrounded by closely packed O\textsuperscript{2–} species. Therefore, highly hydrated Li\textsuperscript{+} ions likely present relatively large hydration radii, preventing their incorporation into spinel structures. In contrast, these highly hydrated Li\textsuperscript{+} ions are readily integrated into layered structures displaying a larger interlayer space. This suggests that a precise control of the Li\textsuperscript{+} ion hydration in organic solvents is essential for the low-temperature synthesis of nanocrystalline LMOs. To the best of our knowledge, this is the first low-temperature nanocrystalline spinel oxide synthesis achieved by the concept of controlling the hydration of coexisting metal cations.

Furthermore, this low-water approach using TBAMnO\textsubscript{4} in 2-propanol could be applied to the syntheses of other manganese-based binary spinel nanoparticles such as Co–Mn spinel oxides (CMOs) and Zn–Mn spinel oxides (ZMOs) by using CoCl\textsubscript{2} or ZnCl\textsubscript{2} instead of LiCl (Fig. 3). The products showed the XRD patterns assignable to the CMO and ZMO structures (Fig. 3b,d). The CMO and ZMO nanoparticles obtained by the present procedure also showed the small crystallite sizes (CMO: 2.78 nm, ZMO: 2.97 nm) and the large BET surface areas (CMO: 257 m\textsuperscript{2} g\textsuperscript{−1}, ZMO: 110 m\textsuperscript{2} g\textsuperscript{−1}). The TEM image of CMO indicated that CMO consisted of the small crystalline nanoparticles (Fig. 3e).

These results revealed that the crystallization into the spinel phase does not require a temperature as high as that previously employed (higher than 180°C in most cases, Supplementary Table 1). The use of an organic solvent canceled the energetic demands related to the coexisting metal cation (e.g. Li\textsuperscript{+}, Co\textsuperscript{2+}, and Zn\textsuperscript{2+}) dehydration and structural transformation of birnessite-type layered intermediates into the spinel phase to possibly reveal the actual requirements of the crystallization. This understanding enabled temperature and reaction time optimization to give the smallest manganese-based binary spinel nanoparticles, which may be applicable to a wide range of (binary) metal oxides.

**Specific ion exchange properties of Li–Mn spinel nanoparticles.** In general, Li\textsuperscript{+} ions can be extracted from LMOs with aqueous acidic solutions to produce a spinel-type λ-manganese oxide that acts as an Li\textsuperscript{+} ion-selective adsorbent\textsuperscript{11–14,18}. This acid-mediated extraction from bulk LMO predominantly involves a redox reaction, concomitant with the disproportionation of Mn\textsuperscript{3+} species, resulting in dissolution of formed Mn\textsuperscript{2+} species and increasing the average oxidation state of the oxide manganese species (Fig. 4a, upper)\textsuperscript{14}. Alternatively, it was reported that an Li\textsuperscript{+}/H\textsuperscript{+} ion exchange reaction is possible at the particle surfaces (Fig. 4a, lower)\textsuperscript{19}. Therefore, surface reactions may proceed throughout the particle upon LMO particle size reduction.

**Figure 3.** Synthesis of CMO and ZMO under controlled Li\textsuperscript{+} ion hydration in an organic solvent. (a) Simulated pattern of CMO, (b) XRD pattern of CMO, (c) simulated pattern of ZMO, and (d) XRD pattern of ZMO. (e) TEM image of CMO.
The acid-mediated Li\(^+\) ion extraction was investigated for LMO samples with various particle sizes (Supplementary Fig. 4 and Supplementary Table 2). LMO samples were dispersed in an aqueous nitric acid at pH 2 and stirred for 30 min at room temperature. This acid treatment extracted about 90% of Li\(^+\) ions from all spinel structures (Fig. 4b and Supplementary Fig. 5). We confirmed that all reactions reached their equilibria within 30 min. (b) Li\(^+\) ion extraction (black) and Mn dissolution ratios (red) for LMOs stirred in nitric aqueous solution (pH 2) at room temperature as a function of particle size. (c) Average oxidation states of Mn in LMOs before (black) and after acid treatment (red). (d) Li\(^+\) ion extraction by ion exchange reaction. (e) Ion exchange reaction as a function of pH. Data shown in (b), (c), and (d) are plotted against crystallite sizes for LMO(2.3 nm), LMO(6.7 nm), LMO(13 nm), and LMO(40 nm) and against particle sizes calculated from the BET surface area for LMO(bulk). In (d) and (e), “ion-exchange-type” means the contribution of ion exchange reaction to Li\(^+\) ion extraction reaction from LMOs. (e) For LMO(bulk), the Li\(^+\) ion extraction hardly proceeded (Supplementary Table 4) under weakly acidic conditions (pH > 5). At pH 7, LMOs were dispersed in neutral water without pH adjustment.
Electrochemical properties of Li–Mn spinel nanoparticles. Because of the possible electrochemical Li\(^+\) extraction from and insertion into its spinel structure, LMO has attracted significant interest as a cathode material for lithium ion batteries\(^1\)–\(^10\). The electrochemical properties of LMO particles in different sizes (Supplementary Fig. 4 and Supplementary Table 2) were investigated by collecting their voltage curves during charge and discharge corresponding to Li\(^+\) ion extraction and insertion processes, respectively. The charge/discharge rate amounted to 0.1 C (1 C = 148 mA g\(^{-1}\)). Typical charge/discharge curves of LMOs show plateau regions at around 4 V (region I) and 3 V (region II)\(^50\). Plateau regions I and II correspond to the Li\(^+\) insertion into (or extraction from) the spinel structure and biphasic region comprising spinel and rock-salt structures, respectively. The area below region II corresponds to the Li\(^+\) insertion into (or extraction from) the rock-salt structure\(^50\). Figure 5a shows the LMO charge/discharge voltage curves for a first charge reaching 4.3 V. Smaller LMO particles presented smaller discharge capacities in the plateau region approximating 4 V and larger capacities below this plateau (Fig. 5a). While this tendency associated with the cathode materials size reduction was consistent with the previous studies\(^5\)–\(^3\), region I was almost undetectable in LMO(2.3 nm) charge/discharge curves. The Li\(^+\) site energy distribution, which is usually only within a few nanometers of conventional particle surfaces\(^2\), appeared throughout the LMO(2.3 nm) particle. As a result, voltage changes stemmed from the variations in the site energy distribution (Supplementary Fig. 10). The existence of plateau at around 3 V (region II) suggests that excess Li\(^+\) inserted into the spinel structure via biphasic spinel/rock-salt state formation (Fig. 5a).

The short Li\(^+\)-diffusion length and high electrochemical surface area of the nanoparticles are expected to impart high discharge rate capability to the resulting electrode. However, the tendency of LMO(2.3 nm) to form dense aggregates (Supplementary Fig. 11) may result in high electrode resistance, limiting electrochemical performance such as discharge rate capabilities. In fact, LMO(2.3 nm) displayed smaller first charge/discharge capacities than theoretical values (theoretical charge capacity: 148 mAh g\(^{-1}\), theoretical discharge capacity: 296 mAh g\(^{-1}\)) (Fig. 5a). To improve the electrochemical property of LMO(2.3 nm), a Li–Mn spinel nanoparticles–graphene composite (LMO–G) was prepared by adding graphene to the LMO synthetic solution to prevent LMO particle aggregation and promote electronic conduction (Fig. 5d and Supplementary Fig. 11). Electrochemical performance improvements were assessed by measuring the discharge rate of LMO–G. Charge and discharge capacities were expressed based on the LMO weight in the composite after subtracting the graphene contribution from the observed capacities. Figure 5b demonstrated that LMO delivered an extremely high discharge capacity of 134 mAh g\(^{-1}\) even at 100°C. Electrode elemental analyses provided a Li/Mn molar ratio of 0.37 for Li\(^+\) ion extraction during the first discharge at 100°C, consistent with that calculated from the LMO discharge capacity (Li/Mn = 0.45 (mol/mol)). The difference between these ratios may result from the electric double layer capacitance contribution of the high-surface-area LMO to the discharge capacity. No plateau was observed for the spinel/rock-salt biphasic region in Fig. 5b. Therefore, the LMO–G discharge at 100°C corresponded to Li\(^+\) ion insertion into the spinel structure without transformation into a rock-salt structure although the cell was discharged to 2 V. This originated from the large ohmic resistance-related voltage drop due to such high current density, as indicated by the low initial voltage of the discharge curves (Fig. 5b). Hence, LMO–G did not undergo any phase transition, which often causes poor cycle durability, and exhibited good capacity retention (Fig. 5c). These high discharge rate capabilities arose from the short Li\(^+\)-diffusion length and high electrochemical surface area of the small LMO particles.

Catalytic performance of Li–Mn spinel nanoparticles. Because Mn adopts various oxidation states, its oxides can act as oxidants\(^20\)–\(^30\) and catalysts\(^22\)–\(^27\) for several oxidative functional group transformations. The catalytic activities of different LMO particles (Supplementary Fig. 4 and Supplementary Table 2) were initially investigated for the oxidative homocoupling of cyclohexanethiol into dicyclohexyl disulfide at 0°C. Nanoparticles displaying the smallest particle sizes and highest BET surface areas exhibited the
highest catalytic activity for the homocoupling (Fig. 6a). Initial reaction rates were almost proportional to the nanoparticles BET surface areas (Fig. 6a). On the other hand, when the reaction time was prolonged, differences in catalytic activities increased depending on particle size. Dicyclohexyl disulfide was obtained in only 0.66% yield after 10h using LMO(bulk) whereas the reaction was completed within 2h in the presence of LMO(2.3 nm) under the conditions described in Fig. 6a. A smooth redox reaction of the metal (in particular, re-oxidation of the reduced metal by O₂ species) becomes important in manganese-based oxide-catalyzed transformations. When catalyst particle sizes decrease and BET

Figure 5. Electrochemical properties of LMO. (a) First charge (black) and discharge (red) curves of LMO with crystallite sizes of 2.3, 6.7, 13, and 40 nm and LMO(bulk) at a constant charge and discharge rate of 0.1 C (14.8 mA g⁻¹) between 2 and 4.3 V. (b) Charge and discharge curves of LMO–G. The cell was fully charged to 4.3 V at 0.1 C and subsequently discharged to 2 V at 100C. (c) Discharge capacity of LMO in LMO–G at 100C. The cell was fully charged to 4.3 V at 0.1 C and subsequently discharged to 2 V at 100C. Charge and discharge capacities were calculated based on the weight of LMO by subtracting the graphene capacity from the LMO–G capacity. The graphene capacity in LMO–G was estimated by electrochemical tests performed on graphene electrode under the corresponding charge and discharge conditions. (d) TEM images of LMO–G at (left) low and (right) high magnifications.
Under the optimized reaction conditions, the LMO(2.3 nm) particles acted as an efficient homocoupling catalyst for various kinds of structurally diverse thiols including alkyl, aromatic, and heteroaromatic ones, typically selectively producing the corresponding disulfides in high yields within only 1 min (Fig. 6b). In addition, they could be reused at least twice for the homocoupling of cyclohexanethiol to give dicyclohexyldisulfide in high yields (yields for the first reuse: 99%, the second reuse: 95%) and retained their spinel structure after these experiments (Supplementary Fig. 13). To date, several efficient catalytic activities of LMOs for oxidation reactions. (a) Reaction profiles (left) and initial rates (right) for cyclohexanethiol homocoupling in the presence of LMO exhibiting different particle sizes. Reaction conditions: LMO (20 mg), substrate (1.25 mmol), acetonitrile (5 mL), 0 °C, air (1 atm). (b) LMO(2.3 nm)-catalyzed oxidative thiol homocoupling. Reaction conditions: LMO(2.3 nm) (20 mg), substrate (0.25 mmol), acetonitrile (1 mL), 30 °C, O2 (1 atm), 1 min. (c) LMO(2.3 nm)-catalyzed sulfide oxidation. Reaction conditions: LMO(2.3 nm) (50 mg), substrate (0.5 mmol), o-dichlorobenzene (1 mL), 150 °C, O2 (5 atm). (d) LMO(2.3 nm)-catalyzed alkylarene oxidation. Reaction conditions: LMO(2.3 nm) (50 mg), substrate (0.5 mmol), o-dichlorobenzene (1 mL), 150 °C, O2 (5 atm). (e) LMO(2.3 nm)-catalyzed oxidative amidation. Reaction conditions: LMO(2.3 nm) (50 mg), substrate (0.25 mmol), 28% aqueous ammonia (50 μL), 1,4-dioxane (1 mL), 150 °C, O2 (3 atm), 1 h. Product yields were determined by gas chromatography using naphthalene as an internal standard.
catalytic systems for aerobic oxidative homocoupling of thiols have been developed. In comparison with the previously reported catalysts, the present LMO(2.3 nm) catalyst possesses several noteworthy features; for example, (i) use of recyclable LMO(2.3 nm), (ii) simple operations, (iii) use of the greenest oxidant of O2, (iv) wide substrate scope, (v) mild reaction conditions, and/or (vi) very short reaction times.

Furthermore, LMO(2.3 nm) could catalyze aerobic oxygenation of various sulfides and alkylarenes (Fig. 6c,d). Oxygenation of sulfides to sulfoxides and/or sulfones is an important reaction, and catalytic oxygenation of sulfides has generally been performed by using hydrogen peroxide or tert-butyl hydroperoxide as the oxidant. Although several homogeneously catalyzed systems for aerobic oxygenation of sulfides have been reported, to date there have been only a few reports on heterogeneously catalyzed aerobic oxygenation of sulfides.

Finally, we demonstrated the use of LMO(2.3 nm) for oxidative amidation of primary alcohols to primary amides using O2 as the oxidant and aqueous NH3 as the nitrogen source. The oxidative amidation is a recently developed reaction by us and composed of the following four relay steps; (i) oxidative dehydrogenation of primary alcohols to aldehydes, (ii) dehydrative condensation of the aldehydes with NH3 to aldlimines, (iii) oxidative dehydrogenation of the aldlimines to nitriles, and (iv) hydration of the nitriles to form the corresponding primary amides. In order to realize the oxidative amidation as the efficient one-pot procedure, both oxidation and hydration abilities should be needed for the catalysts, and we utilize a manganese oxide octahedral molecular sieve (OMS-2) as the catalyst in the previous study. Notably, in the presence of LMO(2.3 nm), various kinds of primary alcohols could quantitatively be converted into the corresponding primary amides within 1 h (Fig. 6e). It typically required at least 3 h to complete these reactions when using OMS-2. Under the present conditions, LMO(bulk) did not produce benzamide at all (benzamide: <1%, benzaldehyde: 8%). The high performance of LMO(2.3 nm) is likely due to the smooth redox property (for oxidation) and the surface coordinately unsaturated oxygen species (for hydration). The catalysis of LMO(2.3 nm) was truly heterogeneous, and LMO(2.3 nm) could be reused for the oxidative amidation of benzyl alcohol without an appreciable loss of its catalytic performance; for the reuse experiment, benzamide was obtained in 98% yield.

Discussion
In summary, a novel low-temperature method was developed to synthesize Li–Mn spinel oxide (LMO) by suppressing the hydration of Li+ in an organic solvent. This mild procedure produced ultrasmall LMO particles and moreover was applicable to other manganese-based binary spinel nanoparticles such as Co–Mn spinel oxides and Zn–Mn spinel oxides. The product phase was controlled by tuning the amount of water added to the solvent, giving birnessite in the presence of large water quantities. The LMO(2.3 nm) particles exhibited unusual ion exchange between Li+ and H+ in addition to specific charge/discharge curves because of their Li+ site energy distribution. Furthermore, their combination with graphene led to a cathode material displaying high discharge rate capability. The properties of LMO(2.3 nm) are much more significant than those expected simply by the increase in the surface area, which is due to uniqueness of surfaces for insertion–extraction materials. Because the present synthetic method is specifically useful for the size control of insertion–extraction materials, controlling the hydration state of the templates, these findings are quite meaningful as a novel concept for the development of highly functional insertion–extraction materials. Also, LMO(2.3 nm) effectively catalyzed several aerobic oxidation reactions, such as homocoupling of thiols to disulfides, oxygenation of sulfides to sulfoxides and sulfones, oxygenation of alkylarenes to ketones, and oxidative amidation of primary alcohols to primary amides.

These results demonstrated that the new approach provided ultrasmall LMOs exhibiting unique properties, such as ion exchangeabilities, electrochemical properties, and catalytic activities, by creating surface phenomenon throughout the particles. This method offers structural control and functional design for various metal oxide nanoparticles at low temperatures.

Methods
Materials. KMnO4, 2-propanol, ethanol, acetone, nitric acid, ethylene carbonate (EC), and dimethyl carbonate (DMC) were purchased from Kanto Chemical. Tetraethylammonium bromide (TBABr) was purchased from TCI. LiCl, MnCO3·nH2O, Li2CO3, and naphthalene were acquired from Wako. Graphene was obtained from Graphene Laboratories, Inc. The 1 M LiPF6 solution in 1:1 EC/DMC (v/v) was acquired from Kishida. Solvents and substrates for thiol homocoupling, sulfide oxidation, alkylarene oxidation, and oxidative amidation were purchased from Kanto, TCI, Wako, and Aldrich. All reagents were used as received without purification.

Instruments. X-ray diffraction (XRD) patterns were recorded using a Rigaku SmartLab instrument under CuKα radiation (λ = 1.5418 Å, 45 kV, 200 mA). Elemental analyses were performed by inductively coupled plasma–atomic emission spectroscopy using a Shimadzu ICP-AES-8100 apparatus. The average oxidation states of Mn were determined by redox titration, during which Mn in the sample was reduced with excess Fe(NH3)6(SO4)2 and unreacted Fe2+ was titrated with KMnO4 aqueous solution. This redox titration was repeated three times for each sample and average oxidation states were defined as average value ± standard deviation. Brunauer–Emmett–Teller (BET) surface areas were measured by N2 adsorption at −196°C using a micromeritics ASAP 2010 instrument. Transmission electron microscopy (TEM) images were obtained using JEOL JEM-2800 or JEM-2000EX II at an acceleration voltage of 200 kV. TEM
was subsequently heated to ca. 82 °C and stirred at 82 °C for 12 h. The precipitates were collected by membrane filtration (average pore size: 0.2 μm) under reduced pressure and successively washed with deionized water before drying at 120 °C.

Synthesis of LMO(2.3 nm). TBAMnO₄ (1.50 mmol) was added to a LiCl solution (2 M, 50 mL) in 2-propanol and stirred at room temperature for 5 min to give a brown precipitate. The resulting slurry was subsequently heated to 86 °C and stirred at 86 °C for 30 min. The precipitates were collected by membrane filtration (average pore size: 0.2 μm) under reduced pressure and successively washed with deionized water before drying at 120 °C.

Effect of water on the product phase. The effect of water on the product phase was investigated using 2-propanol/H₂O mixtures as solvents for reaction time of 3 h. Synthetic solution compositions are shown in Supplementary Table 7.

Synthesis of CMO and ZMO. TBAMnO₄ (0.15 mmol) was added to a LiCl solution (0.015 M, 5 mL) in 2-propanol and stirred at room temperature for 5 min to give a brown precipitate. The resulting slurry was subsequently heated to ca. 82 °C and stirred at 82 °C for 12 h. The precipitates were collected by membrane filtration (average pore size: 0.2 μm) under reduced pressure and successively washed with deionized water and acetone before drying at 120 °C.

Synthesis of LMO with different particle sizes. LMO(6.7 nm), LMO(13 nm), and LMO(40 nm) were synthesized by a hydrothermal method. The organic reducing agent (1.1 equiv. to Mn) was added to a mixture (91 mL) containing LiOH (0.1 M) and KMnO₄ (0.077 M) and the solution was stirred at room temperature for 1 min. The organic reducing agent was ethanol for LMO(6.7 nm) and acetone for LMO(13 nm) and LMO(40 nm). The reaction mixture was transferred into a polytetrafluoroethylene-lined stainless steel autoclave and heated at 180 °C for 5 h to give LMO(6.7 nm) and LMO(13 nm) or 72 h to generate LMO(40 nm). Precipitates were collected by membrane filtration (average pore size: 0.2 μm) under reduced pressure, washed with deionized water and dried at 120 °C overnight. LMO(bulk) was synthesized by a conventional solid state method. MnCO₃•nH₂O and Li₂CO₃ were mixed and ground in an agate mortar (Li/Mn molar ratio = 1:2) before successive calcinations at 700 °C for 21 h and 825 °C for 21 h.

Li⁺ ion extraction from LMO in aqueous acid solutions. Li–Mn spinel oxide (200 mg) was added to an aqueous nitric acid solution (40 mL) and the solution pH was kept constant for 30 min at room temperature. We confirmed that all reactions in Fig. 4 reached their equilibria within 30 min. The products were collected by membrane filtration (average pore size: 0.2 μm) under reduced pressure, washed with deionized water several times, and dried at 120 °C overnight. Then, the products were characterized.

Li⁺ ion insertion into λ-MnO₂ nanoparticles. λ-MnO₂ nanoparticles obtained by extracting Li⁺ ions from LMO by acid treatment at pH 2 (30 mg) were added to a mixture of LiCl (0.1 M) and LiOH•H₂O (0.1 M) and stirred at room temperature for 30 min or 6 h. The product was collected by membrane filtration (average pore size: 0.2 μm) under reduced pressure, washed with deionized water several times, and dried at 120 °C overnight. Then, the products were characterized.

Synthesis of LMO–G. Graphene powder (28 mg) was dispersed in 2 M LiCl in 2-propanol (10 mL) and TBAMnO₄ was added to the solution at room temperature. Subsequently, the slurry was stirred at room temperature for 5 min and heated at 86 °C for 30 min. The resulting precipitates were collected by membrane filtration (average pore size: 0.2 μm) under reduced pressure and washed with deionized water (ca. 30 mL) and acetone before drying at 120 °C overnight. The amount of LMO in LMO–G was estimated by elemental analysis.
Electrochemical measurements of LMO. Cathodes were prepared by mixing LMO (or LMO–G) with acetylene black and PTFE according to compositions shown in Supplementary Table 8. The mixture was pressed on an Al-mesh (100 mesh) current collector and the resulting electrode was dried at 120 °C overnight prior to use. Lithium metal was used as an anode while 1 M LiPF₆ in 1:1 EC/DMC (v/v) acted as electrolyte solution. The 2032-type coin cells were assembled from the LMO-based cathode, lithium metal anode, electrolyte solution, glass filter as a separator, and metallic lithium in an Ar-filled glove box. Cells were charged to 4.3 V at a current density of 0.1 C and discharged to 2.0 V at required current densities (0.1 or 100 C). The current density of 1 C rate was defined as 148 mA g⁻¹ based on the weight of LMO. Electrochemical measurements were performed at 25 °C using a HJ1001SD8 battery charge/discharge system (Hokuto Denko Corporation). Charge/discharge capacities were calculated based on the weight of LMO by subtracting the graphene capacity from the observed LMO–G capacity. The graphene capacity in LMO–G was estimated by performing independent electrochemical tests on graphene electrodes under similar charge/discharge conditions.

Oxidative homocoupling of thiols using LMOs as catalysts. Substrate (0.25 or 1.25 mmol), acetoni­trile (1 or 5 mL), LMO (20 mg), and naphthalene (GC internal standard) were placed in a Pyrex glass reactor with a Teflon-coated magnetic stir bar. The reaction mixture was stirred at 0 or 30 °C and ca. overnight prior to use. Lithium metal was used as an anode while 1 M LiPF₆ in 1:1 EC/DMC (v/v) acted as electrolyte solution. Glass filter as a separator, and metallic lithium in an Ar-filled glove box. Cells were charged to 4.3 V at a current density of 0.1 C and discharged to 2.0 V at required current densities (0.1 or 100 C). The current density of 1 C rate was defined as 148 mA g⁻¹ based on the weight of LMO. Electrochemical measurements were performed at 25 °C using a HJ1001SD8 battery charge/discharge system (Hokuto Denko Corporation). Charge/discharge capacities were calculated based on the weight of LMO by subtracting the graphene capacity from the observed LMO–G capacity. The graphene capacity in LMO–G was estimated by performing independent electrochemical tests on graphene electrodes under similar charge/discharge conditions.

Oxidation of sulfides and alkylarenes using LMO(2.3 nm) as a catalyst. LMO(2.3 nm) (50 mg), substrate (0.5 mmol), o-dichlorobenzene (1 mL), and naphthalene (GC internal standard) were charged into a PTFE-lined stainless-steel autoclave. The reaction was carried out at 150 °C under O₂ atmosphere (5 atm) and LMO(2.3 nm) was filtered off upon completion. Products were quantified by GC and identified by GC-MS.

Oxidative amidation of alcohols using LMO(2.3 nm) as a catalyst. LMO(2.3 nm) (50 mg), substrate (0.25 mmol), 28% aqueous ammonia (50 μL, ca. 2.6 equiv.), 1,4-dioxane (1 mL), and naphthalene (GC internal standard) were charged into a PTFE-lined stainless-steel autoclave. The reaction was carried out at 150 °C under O₂ atmosphere (3 atm) and LMO(2.3 nm) was filtered off upon completion. Products were quantified by GC and identified by GC-MS.

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Under the direction of Y.K., K.Y. and N.M., Y.M. conducted the ion exchange experiments and wrote the manuscript. Under the direction of N.S. and Y.I., H.O. performed the TEM observations.

This work was partly supported by the Japan Society for the Promotion of Science (JSPS) through its “Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)” and Grants-in-Aid for Scientific Research from Ministry of Education, Culture, Sports, Science and Technology (MEXT). A part of this work was conducted in Research Hub for Advanced Nano Characterization, The University of Tokyo, under the support of “Nanotechnology Platform” (project No.12024046) by MEXT, Japan.

Acknowledgements

This work was partly supported by the Japan Society for the Promotion of Science (JSPS) through its “Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)” and Grants-in-Aid for Scientific Research from Ministry of Education, Culture, Sports, Science and Technology (MEXT). A part of this work was conducted in Research Hub for Advanced Nano Characterization, The University of Tokyo, under the support of “Nanotechnology Platform” (project No.12024046) by MEXT, Japan.

Author Contributions

Y.M. and Y.K. synthesized the materials, collected and interpreted the XRD and elemental analysis data and wrote the manuscript. Under the direction of N.S. and Y.I., H.O. performed the TEM observations. Under the direction of Y.K., K.Y. and N.M., Y.M. conducted the ion exchange experiments. Under the direction of M.H., K.Y. and N.M., Y.M. investigated the electrochemical performance of the LMOs. Y.M.,...
T.U. and K.Y. evaluated the catalytic properties. N.M., K.Y., M.H. and K.S. supervised the experiments and carefully proofread the manuscript.

**Additional Information**

*Supplementary information* accompanies this paper at http://www.nature.com/srep

**Competing financial interests:** The authors declare no competing financial interests.

**How to cite this article:** Miyamoto, Y. *et al.* Synthesis of ultrasmall Li—Mn spinel oxides exhibiting unusual ion exchange, electrochemical, and catalytic properties. *Sci. Rep.* 5, 15011; doi: 10.1038/srep15011 (2015).

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