Investigation on the Electrochemical Performances of Mn$_2$O$_3$ as a Potential Anode for Na-Ion Batteries

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Currently, the development of the sodium-ion (Na-ion) batteries as an alternative to lithium-ion batteries has been accelerated to meet the energy demands of large-scale power applications. The difficulty of obtaining suitable electrode materials capable of storing large amount of Na-ion arises from the large radius of Na-ion that restricts its reversible capacity. Herein, Mn$_2$O$_3$ powders are synthesised through the thermal conversion of MnCO$_3$ and reported for the first time as an anode for Na-ion batteries. The phase, morphology and charge/discharge characteristics of Mn$_2$O$_3$ obtained are evaluated systematically. The cubic-like Mn$_2$O$_3$ with particle sizes approximately 1.0–1.5 µm coupled with the formation of Mn$_2$O$_3$ sub-units on its surface create a positive effect on the insertion/deinsertion of Na-ion. Mn$_2$O$_3$ delivers a first discharge capacity of 544 mAh g$^{-1}$ and retains its capacity by 85% after 200 cycles at 100 mA g$^{-1}$, demonstrating the excellent cyclability of the Mn$_2$O$_3$ electrode. Therefore, this study provides a significant contribution towards exploring the potential of Mn$_2$O$_3$ as a promising anode in the development of Na-ion batteries.

Sodium-ion (Na-ion) batteries have been introduced as a possible alternative to lithium-based ion batteries due to several reasons, including abundant supply, low cost and less toxicity$^{1,2}$. However, sodium cannot be simply swapped with lithium as sodium has a larger ion size (1.02 Å for Na$^+$ as compared to 0.76 Å for Li$^+$) and slightly different chemistry, resulting in sluggish reaction kinetics that usually causes low capacity, poor rate capability and poor cyclability$^{3-5}$. Therefore, challenges still exist to find suitable anode materials for the development of Na-ion batteries and scientists are searching for the best material among a vast number of materials using the trial-and-error approach.

Among the various types of materials, metal oxides have been explored extensively for lithium-ion (Li-ion) batteries. Similar to Li-ion batteries, metal oxides can potentially be used as large capacity anodes for Na-ion batteries because of their high theoretical capacities resulting from conversion reaction in most cases. For example, one-step conversion reaction of metal oxide with Na-ions can deliver high theoretical specific capacities of >600 mAh g$^{-1}$ according to the reaction described in Eq. (1)$^{6,7}$.

$$\text{MO}_x + 2x\text{Na} + 2xe^- \leftrightarrow x\text{Na}_2\text{O} + M(M = \text{Co}, \text{Fe}, \text{Mn}, \text{Cu}, \text{etc.})$$  \(\text{(1)}\)

Among different conversion-type transition metal oxides for anodes, manganese oxides exhibit advantages of high capacity, natural richness, low cost and environmental benignity. Even though manganese oxides including mono, Mn$_3$O$_4$, Mn$_2$O$_3$, MnO$_2$ and their carbon-based composites with different nanostructures have been found technologically important in Li-ion batteries$^8$, the use of manganese oxides in Na-ion batteries is rarely reported. In 2014, Jiang et al.$^9$ synthesised Mn$_2$O$_3$ and investigated its reactivity as anode towards sodium for the first time.
Subsequently, Weng et al. prepared MnO$_2$ using a SiO$_2$-templated hydrothermal approach, which was used as conversion-type anode for Na-ion batteries. However, rapid irreversible fading of capacities following the cycling process is a common problem with MnO$_2$ and Mn$_3$O$_4$ phases due to volume expansion and aggregation as well as low electronic conductivity. To tackle these problems with transition metal oxide anodes, nanostructure engineering is widely adopted, where structural parameters including particle size, crystal size and morphology act as critical factors in achieving maximum electrochemical performance. By adopting nanostructure engineering, much improvement of sodium storage properties was realised with MnO$_2$ anode by the development of new structures such as MnO$_2$ nanorods and nanoflowers.

In this study, Mn$_2$O$_3$ is synthesised by combining a hydrothermal and a thermal decomposition method and used as Na-ion battery anode for the first time. We developed a cubic structure of Mn$_2$O$_3$ by simple thermal decomposition of manganese carbonate (MnCO$_3$) precursor through controlled calcination temperatures. The crucial feature of this structure is that cubic particles of Mn$_2$O$_3$ are approximately 1–2 µm in size and are composed of numerous nanoparticles (sub-units) of 40–50 nm grown on the surface, leading to more accessible sites for electrolyte penetration into the bulk of the electrode, which facilitates ion transportation thereby promoting the insertion/deinsertion of Na-ions. The obtained Mn$_2$O$_3$ anode prepared at 600 °C demonstrates an impressive capacity of 130 mAh g$^{-1}$ at 100 mA g$^{-1}$ after 200 cycles with a remarkable rate capability of 120 mAh g$^{-1}$ at a very high current of 1000 mA g$^{-1}$ even without any cation doping or carbon coating.

**Results and Discussion**

To verify the nature of decomposition and the formation temperature of Mn$_2$O$_3$, TGA analysis of both MnCO$_3$ precursors (synthesized MnCO$_3$ (S) and commercially available MnCO$_3$ (MnCO$_3$ (C) was performed. It is clearly observed that the nature of decomposition of MnCO$_3$ (S) and MnCO$_3$ (C) precursors within the same temperature range is different, as shown in Fig. 1. One-step decomposition is realised with MnCO$_3$ (S), whereas MnCO$_3$ (C) precursor shows the two-step decomposition. Generally, the initial undulation appeared with initial weight loss of ~3 wt.% caused by the loss of hydrated water from MnCO$_3$. The weight loss appeared between 250 and 350 °C for MnCO$_3$ (C), presumably due to the formation of MnO$_2$ which is further confirmed by XRD analysis (Fig. S1). The commercial MnCO$_3$ (C) was heated up to temperature 300 °C in air for 2 h and the obtained product was analysed by XRD. The XRD pattern shows the presence of MnO$_2$ and MnCO$_3$ (C) in the product, suggesting partial decomposition of MnCO$_3$ (C) and formation of MnO$_2$. It is obvious that the weight loss between 400 and 600 °C is attributed to the formation of Mn$_2$O$_3$ and the release of O$_2$.

Reducing the decomposition step of MnCO$_3$ (S) indicates that the conversion process is favourable since the kinetic process is shortened to obtain clear facet of Mn$_2$O$_3$.

Figure 2 shows the XRD patterns along with the Rietveld refinement profiles for MnCO$_3$ and Mn$_2$O$_3$. Figure 2(a) shows the refinement patterns for MnCO$_3$ (C) and MnCO$_3$ (S) precursors. All the diffraction peaks could be indexed to the rhodochrosite phase of MnCO$_3$ (JCPDS card No: 044-1472) with R-3c space group (rhombohedral unit cell). The refined lattice parameters for MnCO$_3$ (C) were $a = 4.8045$ (2) Å, $c = 15.6892$ (8) Å, and the unit cell volume was 313.636 Å$^3$ (Table S1). For MnCO$_3$ (S), the lattice parameters were smaller than MnCO$_3$ (C) with $a = 4.8019$ (3) Å, $c = 15.6798$ (1) Å and a unit cell volume of 313.103 Å$^3$ that are consistent with the previous report. However, a small diffraction peak appeared at 20 value of 28.5° for MnCO$_3$ (S), which is attributed to impurity that could have formed due to incomplete utilisation of manganese precursor during the hydrothermal process. Furthermore, the average crystallite sizes ($L$) of MnCO$_3$ were calculated according to the Scherrer’s equation as shown in Eq. (3):

$$2 \text{MnCO}_3 + \text{O}_2 \rightarrow \text{Mn}_2\text{O}_3 + 2\text{CO}_2$$ (2)
\[ L = \frac{k}{\beta \cos \theta} \]

where, \( k \) is the constant (0.9394), \( \lambda \) is the X-ray wavelength of Cu-K\( \alpha \) (1.5148 Å), \( \beta \) is the FWHM of the XRD peak in radian and \( \theta \) is the angle of diffraction. The calculated average crystallite sizes of the MnCO\( _3 \) (C) and MnCO\( _3 \) (S) samples were ~36 nm and ~35 nm, respectively, which is in good agreement with reported result\(^{21}\). Figure 2(b) shows quantitative analysis of the Rietveld refinement fit profiles along with the observed XRD patterns of Mn\( _2 \)O\( _3 \) (C600), Mn\( _2 \)O\( _3 \) (S500), Mn\( _2 \)O\( _3 \) (S600) and Mn\( _2 \)O\( _3 \) (S700) samples. All the diffraction peaks matched well and could be indexed to a cubic Mn\( _2 \)O\( _3 \) with the space group of \( \text{la}-3 \) (JCPDS card no.041-1442). No other diffraction peaks of any impurities have been detected. As the calcination temperature increases, the intensity of the diffraction peaks of Mn\( _2 \)O\( _3 \) increased, indicating improved crystallinity\(^{22}\). No changes were observed in the crystallite size of Mn\( _2 \)O\( _3 \) (~23 nm) at the calcination temperature of 500 and 600 °C, whereas it was ~31 nm at 700 °C based on the (222) peak. Nevertheless, crystal size decreases during transformation of MnCO\( _3 \) to Mn\( _2 \)O\( _3 \). The details of lattice parameter, goodness of fit and other related fitting parameters of Mn\( _2 \)O\( _3 \) obtained from crystal structure refinement are consistent with other reports\(^{23,24}\). Clearly, the lattice parameter of Mn\( _2 \)O\( _3 \) increases as the calcination temperature increases due to the expansion during crystal growth.

Figure 3(a) shows FTIR spectra of D-glucose, MnCO\( _3 \) and Mn\( _2 \)O\( _3 \) samples. The FTIR spectrum of D-glucose shows the existence of a strong and broad absorption peak at 3391 cm\(^{-1} \) indicating the presence of \( \nu(\text{OH}) \) group stretching vibration. A small peak at 2920 cm\(^{-1} \) was attributed to the absorption peak of \( \nu(\text{CH}_2) \) group, and the bands at 1475 cm\(^{-1} \) and 1328 cm\(^{-1} \) were assigned to the bending vibration of \( \nu(\text{CH}) \). The \( \nu(\text{C}–\text{O}) \) and \( \nu(\text{C}–\text{C}) \) stretching bands were observed at 1132 and 1007 cm\(^{-1} \), respectively\(^{25,26}\). During hydrothermal process, the D-glucose peaks (O–H bond at 3391 cm\(^{-1} \) and C–H bond at 1475 cm\(^{-1} \)) were completely vanished due to the formation of MnCO\( _3 \) (S) with the presence of C–O bending vibration at 1384, 860 and 721 cm\(^{-1} \)\(^{27}\). When MnCO\( _3 \) was heated at high temperature, the carbonate peaks diminished. The presence of three absorption peaks located at 487, 559 and 655 cm\(^{-1} \) for Mn\( _2 \)O\( _3 \) may be attributed to Mn–O and Mn–O–Mn, confirming the formation of Mn\( _2 \)O\( _3 \)\(^{23,27,28}\), which is consistent with the Raman spectroscopy results as shown in Fig. 3(b). Raman active bands located at 170–1000 cm\(^{-1} \) may be due to the Mn–O vibration modes of manganese oxides\(^{29,30}\). The Raman bands at 310, 366 and 655 cm\(^{-1} \) are corresponding to the bending modes of Mn\( _2 \)O\( _3 \), the asymmetric stretch of Mn–O–Mn and an asymmetric stretch of Mn\( _2 \)O\( _3 \) corresponding to Mn (III)–O mode vibration group, respectively\(^{28}\).

Surface morphologies of MnCO\( _3 \) (C) and MnCO\( _3 \) (S) precursors were examined using SEM analysis, as depicted in Fig. S2. SEM analysis reveals that particles are agglomerated clusters and non-uniformly distributed with a size of 0.5–1.5 \( \mu \)m. It is clearly observed that Mn\( _2 \)O\( _3 \) (C600) obtained from MnCO\( _3 \) (C) precursor possesses irregular shape with an approximate particle size between 0.5 and 1.3 \( \mu \)m (Fig. 4(a)). Conversely, well-defined cubic particles of Mn\( _2 \)O\( _3 \) were formed through the calcination of MnCO\( _3 \) (S) precursor (Fig. 4(b–d)). Mn\( _2 \)O\( _3 \) (S500) consists of inhomogeneous cubic particles in the range of 1.0–1.2 \( \mu \)m in sizes (Fig. 4(b)), Mn\( _2 \)O\( _3 \) (S600)
exhibits larger cubic particles (0.9−1.7 µm sizes) (Fig. 4(c)) with numerous nanoparticles (sub-units) observed on the surface. Moreover, cubic Mn$_2$O$_3$ are organised by nanosized sub-units (40−50 nm) with distinct voids between the sub-units (Fig. S3). The d-spacing of 0.38 nm of the sample corresponded well with (211) lattice plane of Mn$_2$O$_3$ (Fig. S4). Clearly, well-defined cubic particles of Mn$_2$O$_3$ were observed with an average size of approximately 1.1−1.7 µm, when the precursor was calcined at a high temperature of 700 °C (Fig. 4(d)). Moreover, a porous-like structure is clearly visible at the surface of the cubic at 700 °C. This type of structure is often formed if metal carbonate is used as a precursor because it releases O$_2$ and CO$_2$ from the interior of the metal carbonate, which possibly leads to a finer or porous structure$^{13,14,16}$. The obtained electron microscopy results demonstrate that one-step decomposition of the synthesised MnCO$_3$ precursor produces a clear facet with well-defined cubic Mn$_2$O$_3$ structures compared to the two-step decomposition of the commercial MnCO$_3$. The hysteresis loops (Fig. S5) reveal that these materials exhibit type IV isotherm, indicating a disordered mesoporous structure with average pore diameter between 5 and 60 nm. The calculated BET specific surface area for the Mn$_2$O$_3$ powders are tabulated in Table S2. It is well known that nanostructures play a crucial role in electrochemical processes due to their capability to enhance mass diffusion and transportation such as electrolyte penetration or ion transport$^{31}$. Moreover, porous-like nanostructures can allow an electrolyte to diffuse smoothly within the lattice fringes of the crystals, providing more active sites and shortened ion route. Such structures are also beneficial because they relieve the stress and buffer the volume changes caused by pulverisation and aggregation process during redox reaction$^{32,33}$. Therefore, the structure of Mn$_2$O$_3$ obtained from MnCO$_3$ (S) precursor is likely to enhance Na-ion storage performance.

The galvanostatic charge/discharge measurements of the Mn$_2$O$_3$ electrodes at a current density of 100 mA g$^{-1}$ within the potential range of 0.01−3.00 V (vs. Na/Na$^{+}$) are shown in Fig. 5. At the first cycle, irreversible capacities...
Figure 4. SEM images of (a) Mn$_2$O$_3$ (C600), (b) Mn$_2$O$_3$ (S500), (c) Mn$_2$O$_3$ (S600) and (d) Mn$_2$O$_3$ (S700).

Figure 5. Galvanostatic charge/discharge profiles of (a) Mn$_2$O$_3$ (C600), (b) Mn$_2$O$_3$ (S500), (c) Mn$_2$O$_3$ (S600), and (d) Mn$_2$O$_3$ (S700).
observed in all electrodes may be attributed to the undesirable growth of a surface passivation layer of solid electrolyte interphase (SEI). The discharge/charge potential profile of the Mn\textsubscript{2}O\textsubscript{3} (S600) electrode was further supported by CV analysis as demonstrated in Fig. S6. However, the SEI formation plateau for the Na/Na\textsuperscript{+} system is not as sharp/long as compared to the Li-ion cell\textsuperscript{34,35}. Conversely, no distinct plateau observed in the charge/discharge curves after the first cycle, typically seen and consistent with other metal oxides anode in the Na/Na\textsuperscript{+} system\textsuperscript{10,12,36–38}. During cathodic process, Mn and Na\textsubscript{2}O were observed from the \textit{ex-situ} XRD patterns (Fig. S7), whereas, re-formation of Mn\textsubscript{2}O\textsubscript{3} was observed during anodic process. It is important to note that the evidence of Mn phase formation is hardly found in the XRD patterns because of significant overlap of this Mn peak with very strong peak from copper (Cu) current collector. Therefore, the formation of Mn and Na\textsubscript{2}O and the re-formation of Mn\textsubscript{2}O\textsubscript{3} can be expressed by the following electrochemical reversible conversion reaction in Eq. (4).

\[
\text{Mn}_2\text{O}_3 + 6\text{Na}^+ + 6e^- \leftrightarrow 2\text{Mn} + 3\text{Na}_2\text{O}
\] (4)

Figure 6 shows the cycling performance of the Mn\textsubscript{2}O\textsubscript{3} electrodes. Figure 6(a) compares cycling stability and Coulombic efficiency among the electrodes measured at a current density of 100 mA g\textsuperscript{-1} up to 200 cycles. All electrodes exhibit high initial discharge capacity of 544 mAh g\textsuperscript{-1} for Mn\textsubscript{2}O\textsubscript{3} (S600), 429 mAh g\textsuperscript{-1} for Mn\textsubscript{2}O\textsubscript{3} (C600), 331 mAh g\textsuperscript{-1} for Mn\textsubscript{2}O\textsubscript{3} (S700) and 163 mAh g\textsuperscript{-1} for Mn\textsubscript{2}O\textsubscript{3} (S500). High initial discharge capacity could be related to the formation of SEI layer and the electrolyte decomposition itself\textsuperscript{39}. For Mn\textsubscript{2}O\textsubscript{3} (S600) electrode, the discharge capacity increased after the 2\textsuperscript{nd} cycle and then started to decrease after ~15 cycles. Similar trends were observed for Mn\textsubscript{2}O\textsubscript{3} (S700) electrode, where the discharge capacity increased gradually and then started to decrease after 140 cycles, which was possibly due to the activation and stabilisation processes within the electrode\textsuperscript{40–44}. Nevertheless, the capacity depletion behaviour was noticed in Mn\textsubscript{2}O\textsubscript{3} (S500) and Mn\textsubscript{2}O\textsubscript{3} (C600) electrodes. At 2\textsuperscript{nd} cycle, the Mn\textsubscript{2}O\textsubscript{3} (S600) electrode exhibited the highest discharge capacity of 294 mAh g\textsuperscript{-1} and gradually decreased to 130 mAh g\textsuperscript{-1} after 200 cycles. For the Mn\textsubscript{2}O\textsubscript{3} (S700) electrode, the discharge capacity was 137 mAh g\textsuperscript{-1} at 2\textsuperscript{nd} cycle and reached 116 mAh g\textsuperscript{-1} after 200 cycles. In the case of Mn\textsubscript{2}O\textsubscript{3} (S500) and Mn\textsubscript{2}O\textsubscript{3} (C600) electrodes, the discharge capacity at the 2\textsuperscript{nd} cycle was 243 and 162 mAh g\textsuperscript{-1}, respectively. After 200 cycles,
both electrodes had the lowest discharge capacity, i.e. 66 mAh g$^{-1}$ and 89 mAh g$^{-1}$. After the initial cycle, all electrodes showed very high Coulombic efficiency of approximately 100% throughout the cycles.

Rate capability of the Mn$_2$O$_3$ electrodes were also measured at different charge/discharge current densities and sustained for 11 cycles for each current density (Fig. 6(b)). At the initial 11th cycle, the Mn$_2$O$_3$ (S600) electrode delivered a high discharge capacity of 207 mAh g$^{-1}$ at 200 mA g$^{-1}$. When the current density increased, the electrode exhibited high retention of 166 mAh g$^{-1}$ at 400 mA g$^{-1}$, 143 mAh g$^{-1}$ at 600 mA g$^{-1}$, 126 mAh g$^{-1}$ at 800 mA g$^{-1}$ and 115 mAh g$^{-1}$ at 1000 mA g$^{-1}$. Moreover, consecutive cycling performances of Mn$_2$O$_3$ (S500), Mn$_2$O$_3$ (S700) and Mn$_2$O$_3$ (C600) electrodes were not as good as Mn$_2$O$_3$ (S600). Returning to 200 mA g$^{-1}$ after it had been exposed to different discharge rates, the Mn$_2$O$_3$ (S600) electrode was able to restore the discharge capacity of 197 mAh g$^{-1}$, which represents above 90% capacity recovery.

All the above results show that cubic-like Mn$_2$O$_3$ demonstrates a possible insertion/deinsertion of Na-ion with a reasonable capacity and cycling stability. The key factor that contributes to the improved performances may be offered by the special morphology of Mn$_2$O$_3$ itself. It is well known that the surface area is proportional to the insertion sites for ions movements$^{47}$ and this could be ameliorated by downsizing the materials or porous architectures. The Mn$_2$O$_3$ synthesised here is cubic-like particles with nanoparticles (sub-units) embedded on their surfaces which in turn improve the electrochemical performances of the battery. Such Mn$_2$O$_3$ structure can be obtained by thermal decomposition of high quality starting metal source. Thermal decomposition of commercial MnCO$_3$ produced irregular shapes of Mn$_2$O$_3$ whereas, hydrothermally synthesised MnCO$_3$ resulted in cubic-like Mn$_2$O$_3$ particles. It is important to highlight that the use of glucose as reducing agent gives advantages to the precursor for growth in a required direction, thus developing well-crystallised MnCO$_3$ particles via the simple route with good reproducibility. Without using any scarifying template to form porous-like structure, this method is practical for scaling-up production in the industry. Clearly, the electrochemical characteristics of Mn$_2$O$_3$ in Na-ion storage is promising and needs to be further explored. The cubic-like Mn$_2$O$_3$ with nanoparticles on its surface provides more accessible sites for electrolyte penetration into inner Mn$_2$O$_3$ and exposes a large area for Na-ions transportation. Meanwhile, a short ion diffusion path could facilitate the charge-transfer and greatly improve the rate capability of the Na-ions. Additionally, porous-like structure of Mn$_2$O$_3$ could suppress the stress created by volume changes during insertion/deinsertion process. Overall, the electrochemical activity, i.e. synthesis process, discharge capacity and rate capability, demonstrated by Mn$_2$O$_3$ in this study is quite impressive. The performance of Mn$_2$O$_3$ anode can be further improved by controlled synthesis of highly porous nanostructured with high surface area. Such a porous nanostructured needs to be integrated with conductive matrix such as surface carbon coating or hybrid formation with graphite or graphene or carbon nanotubes$^{40-44}$. These carbon materials will not only enhance electrical conductivities of the Mn$_2$O$_3$ electrodes, but also will prevent agglomeration of nanostructured Mn$_2$O$_3$ active materials during repeated cycling, leading to much improved electrochemical performance in terms of capacity, stability, and rate capability. The findings obtained from this research create opportunities for other researchers to explore this material as an anode for Na-ion batteries.

Materials and Methods
Synthesis of MnCO$_3$ and Mn$_2$O$_3$. Scheme 1 shows the synthesis strategy of Mn$_2$O$_3$ from the starting materials. To prepare MnCO$_3$, 0.3 mmol D-(+)-glucose (C$_6$H$_{12}$O$_6$, Merck Millipore) and 0.3 mmol KMnO$_4$ (Sigma-Aldrich, 97%) were dissolved in 60 ml deionised water at room temperature and stirred to form a homogeneous solution. Then, the homogeneous mixture was transferred into a 125 ml stainless steel autoclave, sealed and heated at 150 °C for 10 h. During the hydrothermal reaction, MnO$_4^{−}$ was reduced by glucose and Mn$^{2+}$ ions generated, leading to the formation of MnCO$_3$ according to the Eq. (5)$^{49,50}$.

$$24\text{KMnO}_4 + 5\text{C}_6\text{H}_{12}\text{O}_6 = 24\text{MnCO}_3 + 6\text{K}_2\text{CO}_3 + 12\text{KOH} + 24\text{H}_2\text{O}$$

(5)

The precipitates were collected, washed several times with absolute ethanol and deionised water and dried overnight under vacuum. The dried sample is marked as (MnCO$_3$ (S)). To obtain Mn$_2$O$_3$, MnCO$_3$ (S) was calcined at 500, 600 and 700 °C in air for 2 h and denoted as Mn$_2$O$_3$ (S500), Mn$_2$O$_3$ (S600) and Mn$_2$O$_3$ (S700), respectively. For comparison purpose, as-received MnCO$_3$ (Sigma-Aldrich, 98%) marked as MnCO$_3$ (C) was also used in this study. MnCO$_3$ (C) was calcined at 600 °C in air for 2 h and later denoted as Mn$_2$O$_3$ (C600).

Scheme 1. A schematic presentation for the formation of Mn$_2$O$_3$. 

![Scheme 1](image.png)
Materials characterization. The phase purity and structure of MnCO₃ and Mn₂O₃ samples were determined by X-ray diffraction (XRD, Rigaku Minillex II) with monochromatic CuKα radiation at a wavelength (λ) of 1.5406 Å. The morphology of the samples was observed through scanning electron microscopy (SEM, JSM-6360LV) and transmission electron microscopy (TEM, Tecnai G2 F20) with an accelerating voltage of 200 kV. The thermogravimetric analysis (TGA) was conducted on Mettler-Toledo thermogravimetric analysis/differential scanning calorimetry (TGA/DSC 1) Star® System at a heating rate of 10 °C min⁻¹ in air. The Fourier transform infra-red (FTIR) spectroscopy was recorded on an IR Tracer-100. Raman spectra were collected on Raman spectroscopy (Renishaw, 532 nm radiation) extended with 0.1 power laser measurement.

Electrochemical measurements. To investigate the electrochemical performances of Mn₂O₃ samples, the active materials, carbon black (Sigma-Aldrich, >99.95%) and polyvinylidene fluoride (PVDF, Sigma-Aldrich), in a weight ratio of 75:20:5 were dissolved in an N-methylpyrrolidone (NMP). The slurry was casted onto a copper (Cu) foil with an approximate active material loading of ~2 mg cm⁻². The electrodes were then dried at 100 °C overnight under vacuum. Subsequently, the electrode was cut to 1 cm × 1 cm size. Coin-type cell (CR 2032) was assembled in an Argon-filled glove box (Mbraun, Unilab, Germany) using sodium metal (Sigma-Aldrich, 99.9% trace metals basis) as the counter electrode. A Whatman glass fibre (GF/D) was used as a separator, and the electrolyte 1 M NaClO₄ (Sigma-Aldrich, 98%) was dissolved in propylene carbonate (PC) (Sigma-Aldrich, anhydrous, 99.7%) with the addition of 5 wt.% of fluoroethylene carbonate (FEC) (Sigma-Aldrich, 99%). The cycling performance of the electrodes was conducted by Neware battery tester at room temperature.

Conclusion
The cubic-like Mn₂O₃ was successfully obtained through thermal decomposition of the hydrothermally synthesized MnCO₃. For comparison, Mn₂O₃ obtained through thermal conversion of commercial MnCO₃ was also investigated. The synthesis method employed in this study offers a simple and practical approach to industrial production. A microstructure of cubic-like Mn₂O₃ with nanoparticles (sub-units) embedded on its surface was obtained. The electrochemical results indicate that the Mn₂O₃ electrode can deliver a promising discharge capacity, cyclability and rate capability during the insertion/deinsertion of Na-ions. The Mn₂O₃ electrode exhibited high initial discharge capacity of 544 mAh g⁻¹ at 100 mAg⁻¹ and reached 130 mAh g⁻¹ after 200 cycles. The obtained Mn₂O₃ structure promotes electrolyte penetration into the interior of Mn₂O₃, provides large sites to facilitate fast ion transportation and thus, expedites the charge-transfer within the electrode. Therefore, the results demonstrate strong evidence for its application in Na-ion batteries.

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Author contributions
N.H.I. and N.F.M.Y. conceived the idea and designed the experiments, and wrote the manuscript. N.F.M.Y. carried out most of the experimental work. M.F.M.D., S.R.M., N.A.H. and M.M.R. assists the experimental work and data analysis. All authors involved in the discussion to finalize the manuscript.

Competing interests
The authors declare no competing interests.

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