Electrochemical Sodiation/Desodiation into Mn$_3$O$_4$ Nanoparticles

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ABSTRACT: Mn$_3$O$_4$ is considered to be a promising anode material for sodium-ion batteries (SIBs) because of its low cost, high capacity, and enhanced safety. However, the inferior cyclic stability of the Mn$_3$O$_4$ anode is a major challenge for the development of SIBs. In this study, a one-step solvothermal method was established to produce nanostructured Mn$_3$O$_4$ with an average particle size of 21 nm and a crystal size of 11 nm. The Mn$_3$O$_4$ obtained exhibits a unique architecture, consisting of small clusters composed of numerous tiny nanoparticles. The Mn$_3$O$_4$ material could deliver high capacity (522 mAh g$^{-1}$ at 100 mA g$^{-1}$), reasonable cyclic stability (158 mAh g$^{-1}$ after 200 cycles), and good rate capability (73 mAh g$^{-1}$ at 1000 mA g$^{-1}$) even without further carbon coating, which is a common exercise for most anode materials so far. The sodium insertion/extraction was also confirmed by a reversible conversion reaction by adopting an ex situ X-ray diffraction technique. This simple, cost-effective, and environmentally friendly synthesis technique with good electrochemical performance shows that the Mn$_3$O$_4$ nanoparticle anode has the potential for SIB development.

1. INTRODUCTION

Sodium-ion batteries (SIBs) are considered as a low-cost alternative to lithium-ion batteries (LIBs) because of the suitable redox potential ($E_{\text{Na}^+/\text{Na}} = 0.33$ V vs $E_{\text{Li}^+/\text{Li}} = 0$ V) and inexpensive raw materials available. Nevertheless, unsatisfactory electrochemical performance is a major challenge with SIBs because of the much larger radius of the Na ion (1.02 Å) than the Li ion (0.76 Å), which causes structural and phase instability and sluggish transport properties. Furthermore, the low energy density of SIBs is another disadvantage owing to the much heavier sodium (23 g mol$^{-1}$) than lithium (6.9 g mol$^{-1}$) and the higher standard electrode potential [$-2.71$ V vs the standard hydrogen electrode (SHE) for sodium as compared to $-3.04$ V vs the SHE for lithium]. Therefore, it is a challenge to discover appropriate electrode materials to enhance the overall electrochemical performance of SIBs.

Among various electrode materials, conversion-type materials, particularly transition metal oxides (TMOs), are attractive candidates as anode materials for SIBs, owing to their intrinsically low cost, high capacity, and enhanced safety. However, TMOs exhibit numerous problems during electrochemical reactions, which limit their application. The swelling and shrinking of active particles on the insertion and extraction of Li$^+$ or Na$^+$ ions are the most common problems, which induce poor contact because of pulverization between active materials and conducting agents, leading to low electrical and ionic conductivities. As a result, electrodes suffer from poor cycling stability and rate capability, which need to be solved. Although many research groups have already explored various TMOs as anodes for SIBs with greatly improved cycling stability and rate capability, not much work has been conducted on manganese oxide based materials, specifically Mn$_3$O$_4$ so far. In 2014, Jiang et al. synthesized thin-film Mn$_3$O$_4$ and investigated its electrochemical reaction with sodium for the first time, with an initial discharge capacity of...
257 mAh g\(^{-1}\) at a 100 mA g\(^{-1}\) current. However, its cycling stability was unsatisfactory, with a capacity retention of 61% over 200 cycles.

Basically, to achieve a stable cycle life and high rate capability of the cells, both the ionic and electrical conductivities of the electrodes must be improved. Among different strategies, coating with conductive carbon and reducing the particle size have been utilized widely to improve the ionic and electrical conductivities of the electrodes.\(^{11−13}\) However, even though carbon coating or the formation of a composite with carbon is the most popular strategy, the incorporation of carbon into the electrode materials constitutes half the weight of the composites in most cases, which leads to several disadvantages: \(^{14−16}\) (i) the overall energy density is decreased because of the addition of low-capacity carbon, (ii) multiple complex steps are involved in preparing the composites, (iii) the surface carbon coating decreases the electrodes’ kinetics because of the thick and nonporous intact coating, and (iv) carbon can manage only inadequate accommodation, so the composites either must be porous to provide preformed voids or require inactive oxides to buffer the volume change, which increases the effects of the other three disadvantages. \(^{14}\) Therefore, discovering a high-performance, economical anode material without a carbon coating is always preferred for energy-storage devices, particularly for LIBs and SIBs.

To further advance Mn\(_3\)O\(_4\) materials as anodes for SIBs, we have synthesized nanostructured Mn\(_3\)O\(_4\) with a unique architecture of tiny clusters composed of numerous nanoparticles, by adopting a solvothermal technique without any additional carbon coating, surfactant, or template. The sodium storage performance of the Mn\(_3\)O\(_4\) electrode is improved significantly, which is superior to the results reported previously. \(^{10}\) When used as an SIB anode, the Mn\(_3\)O\(_4\) electrode (synthesized at 160 °C) delivers the first discharge capacity of 522 mAh g\(^{-1}\), with a capacity retention of 158 mAh g\(^{-1}\) at a 100 mA g\(^{-1}\) current after 200 cycles. The rate capability is also commendable at 73 mAh g\(^{-1}\) at a very high current rate of 1.0 A g\(^{-1}\). Furthermore, the electrochemical sodiation/desodiation process in the Mn\(_3\)O\(_4\) system is also determined by an ex situ X-ray diffraction (XRD) technique.

2. RESULTS AND DISCUSSION

The Rietveld-refined fit of the Mn\(_3\)O\(_4\) structural models to the XRD data is shown in Figure 1 and Table 1. All diffraction peaks of the Mn\(_3\)O\(_4\) samples prepared at 150, 160, 170, and 180 °C are well matched with the commercially available product denoted as Mn\(_3\)O\(_4\) (C) and diffraction peaks can be indexed to the tetragonal phase of Mn\(_3\)O\(_4\) (JCPDS card no. 024-0734) with the \(I\_4/amd\) space group (haussmannite unit cell), which is consistent with the reported literature. \(^{17}\) The Rietveld refinement results show that our solvothermal technique is capable of producing high-purity Mn\(_3\)O\(_4\).

Rietveld-refined parameters and parameters fit for the samples prepared at 150 °C (Mn\(_3\)O\(_4\) (S150)) and 170 °C (Mn\(_3\)O\(_4\) (S170)) can be found in Table S1 and Figure S1 (Supporting Information), respectively. Besides, the characteristic peaks were very sharp, indicating that the Mn\(_3\)O\(_4\) products obtained are highly crystallized. From this XRD pattern, the crystallite sizes (\(D\)) of all samples were calculated from the dominant (211) diffraction peak at 36° using the Debye–Scherer equation as described below:

\[
L = \frac{k\lambda}{\beta\cos\theta}
\]

where \(k\) is the constant (0.9394), \(\lambda\) is the X-ray wavelength of Cu Ka (1.5148 Å), \(\beta\) is the full width at half-maximum of the XRD peak in radian, and \(\theta\) is the angle of diffraction. The calculated crystallite sizes of commercial Mn\(_3\)O\(_4\) (C) and synthesized Mn\(_3\)O\(_4\) (S) samples are summarized in Tables 2 and S2. It was observed that Mn\(_3\)O\(_4\) with very small crystal sizes between 10 and 21 nm could be synthesized within the temperature range of 150–180 °C, which were much smaller than that of the commercial Mn\(_3\)O\(_4\) (C) (~87 nm).

To further verify the nature of the Mn\(_3\)O\(_4\) samples, Raman spectroscopy was carried out (Figure 2). The Raman spectra of each Mn\(_3\)O\(_4\) sample were recorded in the range of 200–1000 cm\(^{-1}\). A common active band located at ~654 cm\(^{-1}\) was observed for all samples, which confirms the crystalline nature of the sample corresponding to the Mn–O stretching vibrations of Mn\(^{2+}\) in tetrahedral coordination. \(^{18,19}\)
particular, the vibrational mode corresponding to the bending modes of Mn$_3$O$_4$ at 654 cm$^{-1}$ is a representative characteristic of the tetragonal Mn$_3$O$_4$ structure, which is found in the mineral hausmannite as well as in both chemically prepared samples and commercial powder. The results are further supported by XRD results. \(^{22-23}\) Furthermore, two other peaks located at 314 and 367 cm$^{-1}$ were assigned to the out-of-plane bending modes of Mn−O (the $E_g$ symmetry mode) and the asymmetric stretch of the bridge oxygen species Mn−O−Mn, respectively. All peaks in the spectrum represent the tetragonal structure of Mn$_3$O$_4$. The Raman spectra of the Mn$_3$O$_4$ (S150) and Mn$_3$O$_4$ (S170) samples can be found in Figure S2 (Supporting Information).

To obtain more insights into the synthesized Mn$_3$O$_4$ nanoparticles, Fourier transform infrared (FTIR) analysis was conducted. Figure 3 compares the FTIR spectra obtained for the commercial Mn$_3$O$_4$ (C) and synthesized Mn$_3$O$_4$ (S160) samples. The FTIR spectra for the Mn$_3$O$_4$ (S150) and Mn$_3$O$_4$ (S170) samples were compared with the commercial Mn$_3$O$_4$ (C) sample. The FTIR spectra for the Mn$_3$O$_4$ (S160) sample, whereas the commercial Mn$_3$O$_4$ (C) sample shows an agglomerated large cluster composed of nanoparticles with an average particle size of ~102 nm. The Mn$_3$O$_4$ (S160) sample was further investigated by TEM analysis (Figure 4d,e). The bright-field TEM image in Figure 4d shows that the Mn$_3$O$_4$ (S160) sample consists of small clusters composed of numerous tiny nanoparticles, with particle sizes between 15 and 25 nm. A high-resolution transmission electron microscopy (HRTEM) image of an individual Mn$_3$O$_4$ (S160) particle reveals that the sample has strong crystallinity with a lattice $d$ spacing of 0.25 nm, which corresponds to the crystallographic direction of (211) (Figure 4e). The crystalline structure of the Mn$_3$O$_4$ (S160) sample was also verified by the selected area electron diffraction (SAED) pattern as presented in the inset of Figure 4e. The corresponding SAED patterns of the Mn$_3$O$_4$ (S160) sample obtained display diffraction spots and rings consistent with the high crystallinity of the sample. The nanoparticle histograms of the particle size distribution according to the FESEM images for the Mn$_3$O$_4$ (S160) sample are demonstrated in Figure 4f. The highest particle size distribution of nanoparticles was observed in the range of ~23 nm.

The Brunauer−Emmett−Teller (BET) surface area of the samples was examined using nitrogen adsorption−desorption isotherms measured at 77.3 K (Figure 5). According to the IUPAC nomenclature, all Mn$_3$O$_4$ samples exhibit type-IV isotherms, indicating the presence of slit-shaped pores with a mesoporous structure \(^{24}\) (Figure 5a−c). The pore size and pore volume distribution curves were determined from desorption of the isotherm using the Barrett−Joyner−Halenda (BJH) method, as shown in the inset of Figure 5a−c. The N$_2$ adsorption−desorption isotherms and BJH pore size distribution curves for the Mn$_3$O$_4$ (S150) and Mn$_3$O$_4$ (S170) samples are depicted in Figure 5S (Supporting Information). The highest BET surface area of 64.5 m$^2$ g$^{-1}$ with a total pore volume of 0.21 cm$^3$ g$^{-1}$ was measured for the Mn$_3$O$_4$ (S160) sample, whereas the BET surface areas were 54.8 m$^2$ g$^{-1}$ for Mn$_3$O$_4$ (S150), 49.4 m$^2$ g$^{-1}$ for Mn$_3$O$_4$ (S170), 31.3 m$^2$ g$^{-1}$ for Mn$_3$O$_4$ (S180), and 3.23 m$^2$ g$^{-1}$ for Mn$_3$O$_4$ (C). The measured pore volumes of the samples were 0.15 cm$^3$ g$^{-1}$ for Mn$_3$O$_4$ (S150), 0.14 cm$^3$ g$^{-1}$ for Mn$_3$O$_4$ (S170), 0.13 cm$^3$ g$^{-1}$ for Mn$_3$O$_4$ (S180), and 0.14 cm$^3$ g$^{-1}$ for Mn$_3$O$_4$ (C).
for Mn$_3$O$_4$ (S180), and 0.002 cm$^3$ g$^{-1}$ for Mn$_3$O$_4$ (C). The highest surface area with the mesoporous structure of the Mn$_3$O$_4$ (S160) sample can shorten the diffusion paths for charge carriers in the electrode–electrolyte interphases, facilitate the mass transfer of Na$^+$, and thus reduce the internal resistance and efficiently improve the rate capability.\textsuperscript{29,30} Moreover, the nanoparticles obtained are beneficial in facilitating the fastest migration of Na$^+$, leading to the high rate performance of the sample.

To evaluate the electrochemical performance, cyclic voltammetry (CV) tests of the Mn$_3$O$_4$ (C), Mn$_3$O$_4$ (S160), and Mn$_3$O$_4$ (S180) electrodes were performed within the potential range of 0.01−3.0 V versus Na/Na$^+$ at a scan rate of 0.3 mV s$^{-1}$ (Figure 6). The CV curves for Mn$_3$O$_4$ (S150) and Mn$_3$O$_4$ electrodes are depicted in Figure S6 (Supporting Information). During the first discharge (first cathodic scan), all electrodes exhibited a broad peak $\sim$0.6 V, which can be attributed to a solid electrolyte interphase (SEI) film and an initial reduction of Mn$_3$O$_4$ to MnO.\textsuperscript{31,32} In addition, a tiny peak was located at the lower potential of $\sim$0.4 V, which can be associated with the complete reduction of MnO to metallic Mn. From the second cycle onward, the reduction peaks shift to $\sim$0.8 V, indicating improvements in reaction kinetics after the first sodiation.\textsuperscript{33,34} During the charge process (reverse sweep), a small anodic peak located at $\sim$0.1 V is ascribed to the reoxidation of metallic Mn to the oxide counterpart, while
Figure 5. N$_2$ adsorption–desorption isotherms and BJH pore size distribution curves (inset) for the samples of (a) Mn$_3$O$_4$ (C), (b) Mn$_3$O$_4$ (S160), and (c) Mn$_3$O$_4$ (S180).

Figure 6. CV measurements of (a) Mn$_3$O$_4$ (C), (b) Mn$_3$O$_4$ (S160), and (c) Mn$_3$O$_4$ (S180) at a scan rate of 0.3 mV s$^{-1}$ (vs Na/Na$^+$).
the broad anodic peak located at \( \sim 0.8 \text{ V} \) is attributed to the reoxidation of MnO to Mn\(_3\)O\(_4\).\(^{35}\) The cycles were observed to almost overlap with each other for all the samples, which indicates good electrochemical reversibility of the electrodes. The reversible conversion reaction can be expressed as follows:

\[
\text{Mn}_3\text{O}_4 + 8\text{Na}^+ + 8\text{e}^- \leftrightarrow 3\text{Mn} + 4\text{Na}_2\text{O}
\]  

(2)

To define the Na storage mechanism in Mn\(_3\)O\(_4\), ex situ XRD measurements were performed on electrodes at various discharge–charge states (Figure 7). When an electrode is discharged to 0.8 V, the XRD pattern demonstrates the formation of MnO and Na\(_2\)O as discharge products. When discharge is carried out to 0.4 V, the formation of Mn and Na\(_2\)O was confirmed. However, in the anodic sweep, two peaks were obtained around 0.1 and 1.0 V, which are assigned to the oxidation of metallic Mn and the decomposition of Na\(_2\)O. The ex situ XRD data obtained confirm that the Mn\(_3\)O\(_4\) electrode undergoes a reversible conversion reaction during the sodiation/desodiation process, which is in good agreement with the CV results.

Figure 7. Ex situ XRD patterns of Mn\(_3\)O\(_4\) at different discharge and charge states.

Discharge curves for Mn\(_3\)O\(_4\) (S150), Mn\(_3\)O\(_4\) (S160), and Mn\(_3\)O\(_4\) (C) materials and electrodes are shown in Figure S8 (Supporting Information). The initial Coulombic efficiencies of the Mn\(_3\)O\(_4\) (S150), Mn\(_3\)O\(_4\) (S160), and Mn\(_3\)O\(_4\) (C) electrodes are 94%, 90%, and 88%, respectively. After a few initial cycles, all electrodes exhibited a high Coulombic efficiency of \( > 99\% \). An additional examination of the electrochemical performance of the electrodes is shown in Figure 9b. The consecutive cycling behavior at different charge–discharge rates, measured after 11 cycles in ascending steps from 0.2 to 1.0 A g\(^{-1}\), and a return to 0.2 A g\(^{-1}\), is presented in Figure 9b. The Mn\(_3\)O\(_4\) (S160) electrode delivers capacities of 176, 126, 97, 79, 73, and 146 mAh g\(^{-1}\) at current densities of 0.2, 0.4, 0.6, 0.8, 1.0, and returning 0.2 A g\(^{-1}\), respectively. On the other hand, the consecutive cycling performance for the different electrochemical performance of the other electrodes was unsatisfactory. After 66 cycles with different charge–discharge rates, the discharge capacity of the Mn\(_3\)O\(_4\) (S160) electrode at 0.2 A g\(^{-1}\) was still 146 mAh g\(^{-1}\), which represents around 83% capacity recovery. The cyclic performance, Coulombic efficiency, and rate capability of the Mn\(_3\)O\(_4\) (S150) and Mn\(_3\)O\(_4\) (S170) electrodes are shown in Figure S8 (Supporting Information).

Figure 8 shows the typical discharge–charge potential profiles of the Mn\(_3\)O\(_4\) (C), Mn\(_3\)O\(_4\) (S160), and Mn\(_3\)O\(_4\) (S180) electrodes for the selected 1st, 2nd, 5th, 10th, 20th, 50th, and 100th cycles at a current density of 0.1 A g\(^{-1}\). The discharge–charge potential profiles of the Mn\(_3\)O\(_4\) (S150) and Mn\(_3\)O\(_4\) (S170) electrodes are depicted in Figure S7. Clearly, the first discharge curves are different from the subsequent discharge curves for all electrodes, suggesting SEI layer formation during the first sodiation. As a result, all electrodes exhibit irreversible capacity lost in the first cycle, which leads to low initial Coulombic efficiency. However, the SEI layer formation voltage of the metal oxide electrodes is different for Na-ion and Li-ion systems. The SEI formation plateau for the Na\(^+\)/Na\(_2\)\(^-\) system is not as sharp/long as that for the Li-ion cell.\(^{37,38}\) On the contrary, after the first cycle, no discrete plateau was observed in the discharge–charge curves, which is consistent with the CV results.

Figure 9a compares the cycling performance of the Mn\(_3\)O\(_4\) (S160) and Mn\(_3\)O\(_4\) (S180) electrodes with that of the commercial Mn\(_3\)O\(_4\) (C) electrode at a current density of 0.1 A g\(^{-1}\). The initial discharge capacities were measured to be 522 mAh g\(^{-1}\) for Mn\(_3\)O\(_4\) (S160), 51 mAh g\(^{-1}\) for Mn\(_3\)O\(_4\) (S180), and 299 mAh g\(^{-1}\) for Mn\(_3\)O\(_4\) (C) electrodes. After 200 cycles, a retained discharge capacity of 158 mAh g\(^{-1}\) was measured for the Mn\(_3\)O\(_4\) (S160) electrode, whereas it was negligible for the Mn\(_3\)O\(_4\) (C), Mn\(_3\)O\(_4\) (S150), Mn\(_3\)O\(_4\) (S170), and Mn\(_3\)O\(_4\) (S180) electrodes. The discharge capacity of the Mn\(_3\)O\(_4\) (S160) electrode declined after the second cycle (337 mAh g\(^{-1}\)) and continued over the 200 cycles. Nonetheless, the capacity value obtained was still high compared to the other electrodes. Such an initial capacity loss may be attributed to the activation process restricted by the gradual wetting of the electrode materials by the electrolyte.\(^{35}\) Similar trends were also observed for the Mn\(_3\)O\(_4\) (S150), Mn\(_3\)O\(_4\) (S170), Mn\(_3\)O\(_4\) (S180), and Mn\(_3\)O\(_4\) (C) electrodes. The Coulombic efficiencies of the electrodes are demonstrated in Figure 9a. The initial Coulombic efficiencies were measured to be 49% for Mn\(_3\)O\(_4\) (S150), 32% for Mn\(_3\)O\(_4\) (S160), 50% for Mn\(_3\)O\(_4\) (S170), 28% for Mn\(_3\)O\(_4\) (S180), and 31% for Mn\(_3\)O\(_4\) (C) electrodes. After a few initial cycles, all electrodes exhibited a high Coulombic efficiency of \( > 99\% \). The overall electrochemical performance of the Mn\(_3\)O\(_4\) material synthesized at 160 °C (Mn\(_3\)O\(_4\) (S160)) reported here is superior compared to that of the Mn\(_3\)O\(_4\) (S150), Mn\(_3\)O\(_4\) (S170), Mn\(_3\)O\(_4\) (S180), and Mn\(_3\)O\(_4\) (C) materials and also superior to the results reported previously (Table 3).\(^{10}\) The BET surface area, morphology, particle size, and crystal size have a great impact on the electrochemical performance of the Mn\(_3\)O\(_4\) materials. The use of nanoparticles not only overcomes the issue of low ionic conductivity but also minimizes excessive stress developing in the electrode on charge and discharge. The smaller particles are generally able to tolerate the repeated expansion and contraction better, leading to better structural stability of the electrode. The Mn\(_3\)O\(_4\) (S160) material obtained showed much smaller nanoparticles of 21 nm than that of the other electrodes. Therefore, the Mn\(_3\)O\(_4\) (S160) material is expected to deliver better structural stability in the electrodes, thus improving capacity and cyclic stability. In addition, the high surface area of 64.5 m\(^2\) g\(^{-1}\) with the mesoporous structure of the Mn\(_3\)O\(_4\) (S160) sample accelerates electrolyte diffusion into the bulk of the electrode, providing much easier Na\(^+\) ion transfer across.
the electrolyte-electrode interface, thus reducing the internal resistance and efficiently improving the rate capability.29,30

3. CONCLUSIONS
A relatively simple and direct solvothermal method was employed to produce Mn$_3$O$_4$ nanoparticles with an irregular shape without any carbon coating. A wide range of characterization techniques, including XRD, BET, FTIR spectroscopy, Raman spectroscopy, FESEM, and TEM, were employed to identify the phases and structures, chemical composition, surface area, and morphology of the materials produced. Among all the materials synthesized, the Mn$_3$O$_4$ material obtained at 160 °C exhibited small particle size and high surface area. When this Mn$_3$O$_4$ was used as the SIB anode, it underwent reversible sodium insertion/extraction, with an average operational potential of ∼1.25 V (vs Na/Na$^+$) with greatly improved electrochemical performance. The improved electrochemical performance of Mn$_3$O$_4$ creates new opportunities in the development of high-performance Mn$_3$O$_4$-based electrodes for SIBs.

4. EXPERIMENTAL SECTIONS
4.1. Synthesis of Mn$_3$O$_4$ Nanoparticles. In a typical procedure, Mn$_3$O$_4$ nanoparticles were synthesized via a
solvothermal method, as illustrated in Scheme 1. First, 0.3 mmol of manganese acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O, Sigma-Aldrich) was dissolved in 60 mL of ethanol and homogenized under a magnetic stirrer until dissolved. The resultant solution was transferred into a Teflon-lined stainless steel autoclave (125 mL), and heat treatment was carried out in an oven at a temperature range of 150–180 °C for 24 h. Finally, the resultant Mn₃O₄ particles were collected by filtration and washed carefully with deionized water several times. The products obtained were then dried in a vacuum oven at 60 °C overnight and denoted according their heat treatment temperature, respectively, as Mn₃O₄ (S150), Mn₃O₄ (S160), Mn₃O₄ (S170), and Mn₃O₄ (S180). During the solvothermal process, Mn(CH₃COO)₂·4H₂O undergoes hydrolysis and is decomposed into Mn₃O₄ according to the following equation:

\[3\text{Mn(CH}_3\text{COO)}_2\cdot4\text{H}_2\text{O} + 5\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{Mn}_3\text{O}_4 + 11\text{CH}_3\text{CHO} + 14\text{H}_2\text{O}\]  

(3)

**4.2. Material Characterization.** The phase purity of the materials obtained was revealed by XRD on a Rigaku MiniFlex II system, with monochromatic Cu Kα radiation (λ = 1.5406 Å). The pattern was obtained in 2θ ranges between 5 and 80°. The morphologies of the materials were examined under a field emission electron scanning microscope using a Jeol JSM 7600 and a HRTEM system equipped with a TECNAI G2 F20 microscope operated at a voltage of 200 kV. FTIR spectroscopy results of the Mn₃O₄ material were recorded with a KBr pellet on an FTIR Thermo Nicolet spectrophotometer ranging from 400 to 4000 cm⁻¹. Raman spectra were collected using Raman spectroscopy (Renishaw, 532 nm radiations) extended with a 0.1 power laser measurement. The surface area and pore size of the Mn₃O₄ materials were investigated using nitrogen adsorption–desorption isotherms, BJH pore size distribution, CV, and electrochemical performances of Mn₃O₄ (PDF).

**ASSOCIATED CONTENT**

*Supporting Information*

Additional details for Rietveld refinements results, calculated crystallite size, Raman spectroscopy, FTIR, FESEM, N₂ adsorption–desorption isotherms, BJH pore size distribution, CV, and electrochemical performances of Mn₃O₄ (PDF).

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![Scheme 1. Schematic Illustration for the Synthesis Procedure of Mn₃O₄ Nanoparticles](https://pubs.acs.org/journal/acsodf)
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Notes

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