

Review Article

A Review on the Synthesis of Manganese Oxide Nanomaterials and Their Applications on Lithium-Ion Batteries

Xiaodi Liu, Changzhong Chen, Yiyang Zhao, and Bin Jia

College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang, Henan 473061, China

Correspondence should be addressed to Xiaodi Liu; liuxd1983@yahoo.com.cn

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Most recently, manganese oxides nanomaterials, including MnO and MnO₂, have attracted great interest as anode materials in lithium-ion batteries (LIBs) for their high theoretical capacity, environmental benignity, low cost, and special properties. Up to now, manganese oxides nanostructures with excellent properties and various morphologies have been successfully synthesized. Herein, we provide an in-depth discussion of recent development of the synthesis of manganese oxides nanomaterials and their application in the field of LIBs.

1. Introduction

Nanomaterials, having a length scale less than 100 nm, have received increasing interest owing not only to their fundamental scientific significance but also to the potential applications that derive from their fascinating electrical, magnetic, and catalytic properties [1]. Compared to bulk active electrode materials, the corresponding nanomaterials possess more excellent electrochemical activity, such as higher capacities, larger surface areas, and lower current densities, thereby, nanomaterials have widely potential application in electrochemistry field. Manganese oxides, including MnO, MnO₂, and Mn₃O₄, are intriguing composites and have been used in wastewater treatment, catalysis, sensors, supercapacitors, and alkaline and rechargeable batteries [2–6]. Particularly, MnO and MnO₂ nanomaterials have attracted great interest as anode materials in lithium-ion batteries (LIBs) for their high theoretical capacity, low cost, environmental benignity, and special properties [7–9].

It is known that the phases, sizes, and morphologies of nanomaterials have great influence on the properties and applications; therefore, many research efforts have focused on rational control of phase, shape, size, and dimensionality of nanomaterials [14]. Several novel and effective routes have been devoted to prepare manganese oxides nanomaterials with various shapes and excellent properties, such as hydrothermal method [15–18], sol-gel synthesis [19], wet

chemical route [12, 20, 21], pulsed laser deposition method [22], and precursor technique [23]. Moreover, lots of successes on the properties and applications of manganese oxides nanomaterials have been reported in the last few years, for example, a hydrothermal method has been used to synthesize sea urchin shaped α -MnO₂ [24]; Wu et al. have prepared γ -MnO₂ hexagon-based layer-cake-like and intertexture-like nanoarchitectures *via* a hydrothermal route [25]; Liu and coworkers have found MnO₂ nanoparticle-enriched poly(3,4-ethylenedioxythiophene) nanowires that could maintain high specific capacitance at high charge-discharge rates [26]. Thus, it is necessary to review the development of manganese oxides nanomaterials to keep the readers abreast of the rapid development. In this paper, we review the synthesis of manganese oxides nanomaterials with various morphologies and their application on LIBs; furthermore, the future prospects have also been discussed.

2. Synthesis of Manganese Oxide Nanomaterials

2.1. Synthesis of MnO₂ Nanomaterials. It is known that MnO₂ can exist in different structural forms, α -, β -, γ -, δ -, ϵ - and λ -types and so forth, when the basic structural unit ([MnO₆] octahedron) is linked in different ways. Based on the different [MnO₆] links, MnO₂ can be divided into three

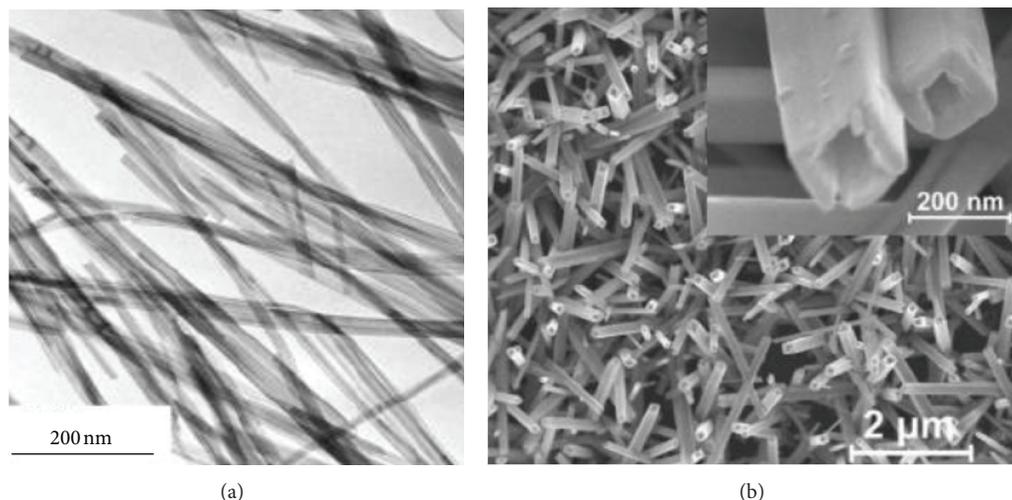


FIGURE 1: (a) TEM image of α - MnO_2 nanowires and (b) SEM image of α - MnO_2 nanotubes [10, 11].

categories: the chain-like tunnel structure such as α -, β -, and γ -types, the sheet or layered structure such as δ - MnO_2 , and the 3D structure such as λ -type [27]. The properties of MnO_2 are significantly affected by their phases and morphologies; moreover, the operating properties of LIBs also depend on the phase of MnO_2 . In this regard, a great effort has been directed toward the preparation of MnO_2 with different phases and various shapes [28]. Generally, MnO_2 nanostructures could be synthesized through the oxidation of Mn^{2+} , reduction of MnO_4^- , redox reactions between Mn^{2+} and MnO_4^- , or direct phase transformation from other manganese oxides.

1D MnO_2 may provide the possibility of detecting the theoretical operating limits of LIBs, so various 1D MnO_2 nanomaterials have been synthesized [29, 30]. Chen et al. have synthesized MnO_2 with different crystal structures (α -, γ -) and morphologies *via* quick precipitation of Mn^{2+} and Mn^{7+} in water isopropanol without using templates or surfactants [31]. In a typical synthesis, MnCl_2 (0.18 g) mixed with isopropanol (50 mL) was heated to 83°C in a refluxing process, and then KMnO_4 (0.10 g) dissolved in DI water (5 mL) was added to the solution. Finally, MnO_2 nanoneedles were obtained. Singly-crystal nanowires of α - and β - MnO_2 have been prepared in a hydrothermal procedures employing Mn^{2+} with oxidizing reagents such as $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or KMnO_4 [28, 32]. Ma group have used a hydrothermal method for MnO_2 nanobelts, which have narrow size dispersions and can be self-assembled into bundles [6]. In a typical procedure, Mn_2O_3 powders (2 g) were dispersed in NaOH aqueous solution ($10 \text{ mol}\cdot\text{dm}^{-3}$), and then the solution was sealed and heated at 170°C for 12 h to 1 week. Sui et al. have synthesized α - MnO_2 nanowires and β - MnO_2 nanorods *via* molten salt method [10]. In the synthesis, KNO_3 , NaNO_3 , and LiNO_3 are applied as the reaction media. α - MnO_2 is a (2×2) and (1×1) tunnel structure, and large ions (K^+) are needed to support the framework; thus, KNO_3 is used as molten salt to prepare α - MnO_2 nanomaterials (Figure 1(a)). β - MnO_2 is a (1×1) tunnel structure, so a mixture of NaNO_3 and

LiNO_3 with smaller cation is selected. Zheng et al. have prepared β - MnO_2 nanotubes using MnSO_4 as reagent, PVP as morphology directing agent and NaClO_3 as oxidant [33]. α - MnO_2 nanotubes have been synthesized by a hydrothermal treatment of KMnO_4 in HCl solution [11]. As shown in Figure 1(b), the obtained nanotubes have an average outer diameter of 100 nm and the wall thickness of 30 nm, and the length is up to several microns. It is found that the nanotubes are formed *via* solid nanorods involving in chemical etching process.

Other special shapes, such as nanowalls [34], nanodisks [35], urchin-like nanoballs [27], multipods [36], and nanosheets [37], have been fabricated. Some successes discussed above can be summarized in Table 1.

Compared to 1D/2D nanostructures, 3D MnO_2 hierarchical structures often produce more active sites or possess more interesting properties, so great interests have been given to well-defined MnO_2 architectures with controlled crystal structures [38]. Six-branched ϵ - MnO_2 architectures have been synthesized *via* an aqueous chemical route without any organic templates (Figure 2(a)). The growth rate along the six-fold c -axis is faster than along the other axes for the crystal structure of ϵ - MnO_2 , which results in the elongated twinned pyramidal shape of the crystals. Consequently, the edges of the adjacent facets of the pyramid become the nucleation sites, and the sprouted branches form the central core [13]. Jana et al. have used a green method for the synthesis of hierarchical flower-like Ag-doped β - MnO_2 nanostructures at 300 K. As displayed in Figure 2(b), the flowery nanostructures are composed of tiny nanopetals (500 nm in diameter and $1.25 \mu\text{m}$ in length) [12]. Fei group have reported a controlled synthesis of hollow microspheres and microcubes of hierarchical MnO_2 superstructures using MnCO_3 crystals as the templates [39]. MnCO_3 microspheres and microcubes are synthesized by the reaction of MnSO_4 and NH_4HCO_3 , and MnO_2 hollow microspheres and microcubes are prepared by mixing KMnO_4 and the solid MnCO_3 crystals. In

TABLE I: Synthesis of MnO₂ with different morphologies.

Method	Morphology	Size	Year
Molten salt route	Nanowires	Length of several microns and diameter of 15–30 nm	2009 [10]
	Nanorods	Length of 500 nm–2 μ m and diameter of 20–40 nm	
Hydrothermal method	Urchin-like nanoballs	Diameter of 1 μ m	2010 [27]
Microemulsion method	Nanodisks	Size of 1–2 μ m and thickness of 50–100 nm	2007 [35]
Hydrothermal method	Nanotubes	Outer diameter of 100 nm, wall thickness of 30 nm, and length of several microns	2008 [11]
Hydrothermal method	Multipods	The legs of the multipods are 200–600 nm in width and several microns in length	2006 [36]

the synthesis, a microscale Kirkendall effect is used for the synthesis of hollow microstructures. Other hierarchical architectures with novel morphologies have also been prepared [20, 40–44], such as λ -MnO₂ nanodisks assembled from nanoparticles *via* a novel wet chemical route [20] and MnO₂ microspheres composed of nanodisks [41].

2.2. Synthesis of MnO Nanomaterials. MnO, a simple binary metal oxide, has an *Fm-3m* rock-salt structure with a lattice constant of 4.445 Å at 300 K and has attracted strong interest for its application as catalysts [45], contrast enhancement for magnetic resonance imaging (MRI) [46], and LIBs materials [47]. Currently, several methods have been developed for the fabrication of MnO nanostructures with well-controlled shapes, such as nanocrystals [48], nanofibers [49], and nanosheets [50]. Monodisperse MnO nanocrystals have been synthesized by thermal decomposition of manganese oleate using the hot-injection method or thermal decomposition of manganese acetate in the presence of oleic acid [51, 52]. Park et al. have prepared MnO nanospheres (sizes of 5–40 nm) and nanorods (diameters of 7–10 nm and lengths of 30–140 nm) by the thermal decomposition of Mn-surfactant complexes [53]. Nanoscale MnO octahedrons have been prepared by decomposing manganese oleate in octadecene and S at high temperature [54]. Xie and coworkers have fabricated supercrystals (SCs) assembled of octahedral MnO nanocrystals (NCs) [55]. In the synthesis, octahedral MnO NCs are synthesized by thermal deposition of Mn(OOC₂H₅)₂ assisted by a mixed solvent of TOA and OA, and then microscale cubic SCs built by NCs are created *via* direct crystallization in ethanol (Figures 3(a) and 3(b)). Other unusual shapes, such as nanoclusters, nanocube, and nanoflake, have also been fabricated [56–59]. Besides rock-salt structure, MnO has another crystal structure, which is hexagonal wurtzite. Nam et al. have reported the synthesis of wurtzite MnO on a carbon template, which may offer an extra degree of freedom in the design of sensors and energy storage devices (Figure 3(c)) [60, 61].

Hybrid nanostructures consisting of two or more different functional units possess novel and enriched properties for magnetic, optical, and catalytic applications. As to MnO, several hybrid nanomaterials have been fabricated, such as porous C-MnO disks, MnO/C nanotubes, MnO/SiO₂ core-shell nanoparticles, and MnO/C core-shell nanoplates [16, 62–64].

3. Applications of Manganese Oxide Nanomaterials on Lithium-Ion Batteries (LIBs)

Lithium-ion batteries (LIBs) are regarded as a promising rechargeable power sources for hybrid electric vehicles (HEVs) and portable electronic devices for their high specific capacity, long cycle life, and lack of memory [65]. Electrode materials play an important role in the performance of LIBs. It was found that transition metal oxides nanomaterials are very appealing anode materials owing to their higher theoretical capacities than that of commercial graphite (372 mA·h·g⁻¹) [66]. Among them, nanoscale MnO and MnO₂ have attracted more and more attention due to the high theoretical capacities, environmentally benign, low cost, and special properties.

Zhao et al. have synthesized nanoporous γ -MnO₂ hollow microspheres and nanocubes with high initial capacities and excellent cycle performance in LIBs. The γ -MnO₂ architectures provide more possibility to serve as an ideal host material for the insertion and extraction of lithium ions for the nanoporous structure. After 20 cycles, the capacities of the γ -MnO₂ microspheres and nanocubes are 602.1 and 656.5 mA·h·g⁻¹ [67]. Interconnected porous MnO nanoflakes have been prepared on Ni foam. The obtained nanoflakes retain a capacity of 708.4 mA·h·g⁻¹ at the 200th charge-discharge cycle after cycling with different current densities up to 2460 mA·g⁻¹ and deliver a capacity of 376.4 mA·h·g⁻¹ at 2460 mA·g⁻¹. The special morphology of the porous MnO nanoflake affected its electrochemical property: (I) the nanomaterials have a large specific area and offer a large material/electrolyte contact area; (II) the structure can supply enough space to buffer the volume change caused by the electrochemical reaction; (III) the nanosize of flakes leads to a shortened electronic and ionic transport length [59]. In addition, Chen et al. have reported the best cycle performance of MnO anode material, which deliver a capacity of 650 mA·h·g⁻¹ after 150 cycles at 35.5 mA·g⁻¹ [68].

Despite the above successes, there are still many challenges in using MnO₂ and MnO as anode materials for LIBs, such as poor cycling performance and poor electrical conductivity. It has been demonstrated that electrode materials with a deliberately designed nanostructure can partly accommodate the strains of Li⁺ intercalation and deintercalation [62]. The electrical conductivity of manganese oxide can be enhanced by mixing them with electrolytes

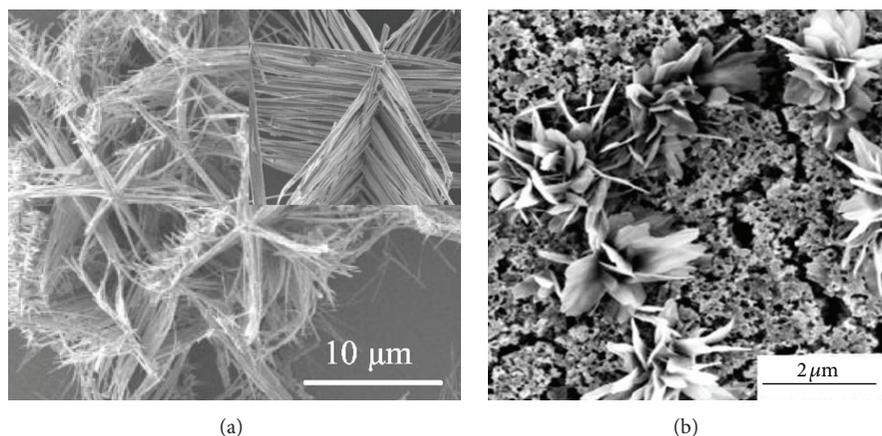


FIGURE 2: (a) SEM image of hierarchical ϵ - MnO_2 architectures, the inset is high-magnification SEM image of one architecture, and (b) SEM image of hierarchical flower-like Ag-doped MnO_2 nanostructures [12, 13].

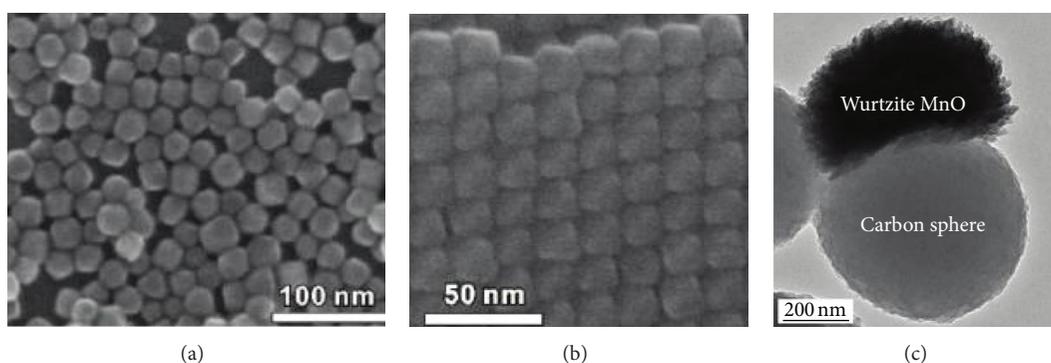


FIGURE 3: (a) SEM image of disperse MnO octahedral NCs, (b) SEM image of well-oriented MnO SCs, and (c) TEM image of hexagonal wurtzite MnO on the carbon sphere template [55, 61].

[69]. For instance, amorphous MnO_2 in a mild KCl aqueous electrolyte has been proved to be an excellent electrode for the faradaic electrochemical capacitor [70]. More importantly, a common strategy for improving the poor electrical conductivity is combining them with carbon to form composites. After Raymundo-Piñero et al. have studied the electrical conductivity and the capacity of the manganese oxide/ C nanotubes composites for the first time, several groups have researched the electrical conductivity of different MnO/C composites [71]. For example, MnO/C core-shell nanoplates with a C -shell thickness of about 8.1 nm display a high reversible capacity of $770 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ at $200 \text{ mA}\cdot\text{g}^{-1}$ [60]. C - MnO disks exhibit a capacity of $534.6 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 250 cycles at a relatively high current density of $1000 \text{ mA}\cdot\text{g}^{-1}$. The high capacity and excellent cycling stability can be attributed to the assembled nanoarchitecture including 3D interconnected nanopores, carbon modification, and the small particle sizes of MnO nanocrystals [64]. Porous MnO/C nanotubes can deliver a reversible capacity as high as $763.3 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 100 cycles at a charge/discharge current

density of $100 \text{ mA}\cdot\text{g}^{-1}$. The superior cyclability and rate capability are attributed to the hollow interior, porous structure, 1D structure, and the uniformly dispersed carbon in the porous MnO/C nanotubes [16]. MnO/C nanoparticles have a reversible capacity of $470 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after the 50th cycle, when tested at $75 \text{ mA}\cdot\text{g}^{-1}$ [72]. Additionally, it has been found that nanopainting metal oxides with a thin layer of conducting polymers can improve their lithium storage capabilities. Xiao et al. have synthesized porous spheres assembled from polythiophene-coated MnO_2 nanosheets. The electrochemical measurements show that the obtained nanocomposites can deliver a capacity of $500 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 100 cycles at a current density of $500 \text{ mA}\cdot\text{g}^{-1}$. The high-rate lithium storage capability of the nanocomposites might be explained by the special structure: (I) the ultrathin nanosheets entail a high effective electrolyte/electrode contact area and a short solid-state diffusion length of Li^+ ions; (II) the mesopores enable fast ionic transport throughout the electrode; (III) the hierarchical structure is beneficial for the stability of the electrode; (IV) the polythiophene “nanopaint” not only enhances the electrical conductivity but also acts as a buffer

layer for the large volume change and drastic structural or textural alterations during charge/discharge cycling [73].

4. Conclusions

In summary, we have briefly reviewed the recent development of manganese oxide nanomaterials. In the near future, we will face some challenges in spite of the successes discussed above. For instance (I) manganese oxide nanomaterials have recently been synthesized in the labs, and they should be applied in industry. Therefore, we should explore simple and effective methods for the synthesis of manganese oxide nanomaterials with high surface areas and good dispersity, and (II) the application of manganese oxide in the field of electrochemistry is still in its infancy; moreover, some data and conclusions are controversial. Thus, the electrochemical mechanism of manganese oxide nanomaterials should be deeply understood. In short, we hope that this paper will not only show the development of manganese oxide nanomaterials but also give the readers some inspiration to explore novel routes for the synthesis of manganese oxide nanomaterials.

Acknowledgments

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