



Short communication

Tailoring nanostructured MnO₂ as anodes for lithium ion batteries with high reversible capacity and initial Coulombic efficiencyLifeng Zhang^{a,*}, Jiajia Song^a, Yi Liu^a, Xiaoyan Yuan^a, Shouwu Guo^{a,b,**}^a School of Materials Science & Engineering, Shaanxi University of Science & Technology, Xi'an 710021, PR China^b Department of Electronic Engineering, School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

HIGHLIGHTS

- Nanostructured MnO₂ is tailored from nanorod to nanoparticle.
- MnO₂ nanoparticles exhibit excellent electrochemical performance.
- The high capacity is attributed to numerous active sites and interspaces.

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ABSTRACT

Developing high energy storage lithium ion batteries (LIBs) using manganese oxides as anodes is an attractive challenge due to their high theoretical capacity and abundant resources. However, the manganese oxides anodes still suffer from the low initial Coulombic efficiency and poor rate performance. Herein, we demonstrate that nano-sized morphological engineering is a facile and effective strategy to improve the electrochemical performance of the manganese dioxide (MnO₂) for LIBs. The tailored MnO₂ nanoparticles (NPs) exhibit high reversible capacity (1095 mAh g⁻¹ at 100 mA g⁻¹), high initial Coulombic efficiency (94.5%) and good rate capability (464 mAh g⁻¹ at 2000 mA g⁻¹). The enhanced electrochemical performance of MnO₂ NPs can be attributed to the presences of numerous electrochemically active sites and interspaces among the NPs.

1. Introduction

For advanced energy storage devices, lithium ion batteries (LIBs) have received growing attention due to the rapidly growing demand for the sustainable and renewable power storage resources [1–3]. As anode materials for LIBs, nanostructured manganese dioxide (MnO₂) is remarkably attractive due to its high theoretical capacity (1230 mAh g⁻¹) [4], low cost and environmentally benign [5–7]. Unfortunately, MnO₂ anode materials still suffer from some annoying issues, such as the low initial Coulombic efficiency, poor rate performance and rapid capacity fading [8–10]. Many efforts have been devoted to fabricating nanostructured MnO₂ composites with conductive carbon materials, resulting in the significantly enhanced cycling performance for LIBs. However, the initial Coulombic efficiencies (ICE) of these composites are still low (< 70%) [11–16]. Such a result was attributed to the poor reversibility of the conversion reaction of lithiated MnO₂, which is probably because of the aggregation of nano-sized electrode materials, resulting in a structural deterioration, hindering the free extraction of Li⁺ ion

[17,18]. Therefore, the rational design and facile fabrication of nanostructured MnO₂ with unobstructed channels for fast insertion/extraction of Li⁺ ion is still of importance, but greatly challenging.

Herein, we have controllably prepared the nanostructured MnO₂ from nanorods to nanoparticles (NPs) via a facile sol–gel method, in which the typical 2D carbon materials graphene oxide (GO) was employed as a morphology-control agent to facilitate the uniform and controllable growth of MnO₂ crystals. The GO was demonstrated that can effectively confine and slice the MnO₂ crystals to form NPs, owing to its thin 2D nanosheets structure, ultrahigh specific surface area and well-dispersion in water [19–21]. More importantly, it was identified that the remaining interspaces among the as-synthesized MnO₂ NPs after removing GO are beneficial to improve the initial Coulombic efficiency for LIBs.

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2. Experimental section

2.1. Sample preparation

All the chemical reagents are of analytical grade and were used without further purification. GO was fabricated according to the modified Hummers methods as previously reported [22]. For the synthesis of MnO₂, manganese acetate (Mn(CH₃COO)₂ 99% TCI) and citric acid (C₆H₇O₈ 99% Merck) with a molar ratio of 1:2 were dissolved in the dispersion solutions of GO, adjusting the pH value to 4.0 by addition of ammonia. The solution was heated at 90 °C until the wet gel appeared, then the wet gel was dried at 110 °C followed by calcinations in air at 400 °C for 5 h. The calcined product was acid treated in 2 M H₂SO₄ solution with stirring at 80 °C for 2 h. For comparison, the concentration of GO was adjusted to 0 mg mL⁻¹, 0.3 mg mL⁻¹, 0.7 mg mL⁻¹ and 1.4 mg mL⁻¹ and the other experimental conditions were the same with the above procedure. The corresponding products were denoted as M0, M1, M2 and M3 according to the different concentration of GO.

2.2. Characterization

The crystal structure of the products was characterized by X-ray diffraction (XRD, Rigaku D/max-2200/PC) using Cu K α radiation at a scanning rate of 10° min⁻¹ with 2 θ ranging from 10° to 80°. X-ray photoelectron spectroscopy (XPS, Kratos AXIS Supra, UK) was conducted to identify the chemical composition of the samples. The morphology and microstructure of the samples were further investigated by field emission scanning electron microscopy (FESEM, Hitachi, S-4800) and transmission electron microscopy (TEM, FEI Tecnai F20, USA). The Brunauer-Emmett-Teller (BET) specific surface areas of the products were calculated according to the nitrogen adsorption-desorption isotherms measured with a NOVA 2200e analyzer (Quantachrome Co., USA) at 77 K.

2.3. Electrochemical measurements

Lithium storage performance of as-prepared MnO₂ was measured with CR2032 coin-type cells assembled in a glovebox under argon atmosphere (LABstar, MBRAUN, Germany), where both the moisture content and oxygen content were maintained below 0.5 ppm. The anode was prepared by mixing 80 wt % active materials, 15% acetylene black and 5 wt% polyvinylidene difluoride (PVDF, Alfa Aesar), which was dissolved in N-methyl-2-pyrrolidinone (NMP, TCI). The resultant homogenous slurry was coated on a copper foil substrate, followed by drying in a vacuum oven at 120 °C for 12 h. Lithium foil was used as counter electrode separated by a microporous polypropylene film (Celgard 2400). The electrolyte was consisted of LiPF₆ (1 M) dissolved in ethylene carbonate and dimethyl carbonate with the volume ratio of 1:1. Galvanostatic charge/discharge characteristics of the as-assembled cells (actually half cells) were determined between 0.01 and 3 V on a BTS battery test system (Neware, Shenzhen, China). The cyclic voltammetry (CV) profiles were obtained from the CHI660E electrochemical workstation (Chenhua, Shanghai, China) in the voltage range of 0.01–0.3 V vs. Li/Li⁺ at a scanning rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurement was carried in the frequency range from 0.01 Hz to 100 Hz on a CHI660E electrochemical workstation.

3. Results and discussion

Fig. 1a describes the morphology evolution of MnO₂, which changed from nanorods to nanoparticles. It is clearly that the increase of GO promotes the formation of MnO₂ NPs owing to the slicing effect of GO nanosheets. The corresponding SEM images of as-prepared MnO₂ are shown in Fig. 1b–e. Without GO, only the MnO₂ nanorods were observed (Fig. 1b), whose average diameter is ca. 20 nm. Subsequently,

when the GO was present, the MnO₂ nanorods became shorter and thinner, and little NPs begin to appear (Fig. 1c). Increasing the GO dosage, the morphology of as-synthesized MnO₂ has changed to irregular NPs. However, a small quantity of MnO₂ nanorods can be still observed (Fig. 1d). Fig. 1e illustrates a typical morphology of near-spherical MnO₂ NPs with the diameter of ca. 19 nm, and no obvious MnO₂ nanorods were observed, indicating that the MnO₂ crystals are completely sliced during their growing process.

The TEM images of as-synthesized MnO₂ are shown in Fig. 1f–i. In the initial stage (without GO, sample M0), MnO₂ crystals freely developed to form interlaced MnO₂ nanorods (Fig. 1f). For the sample M1, the as-prepared MnO₂ has a hybrid nanostructure consisted of nanorods and NPs (Fig. 1g). With the increasing of GO, sample M2 changed to irregular MnO₂ NPs accompanying some short nanorods (Fig. 1h). Subsequently, as shown in Fig. 1i, only near-spherical NPs can be observed, and the clear lattice fringe spacing of 0.39 nm corresponds to the (131) lattice plane of MnO₂ (the inset of Fig. 1i). These results are in good agreement with the tunable MnO₂ morphologies analyzed by the SEM images.

Fig. 2a shows the X-ray diffraction (XRD) patterns of as-synthesized MnO₂. The diffraction peaks located at 2 θ = 22.4°, 37.1°, 42.6°, 56.1° and 68.9° could be indexed to the crystal planes of (120), (131), (300), (160) and (421) of γ -MnO₂ standard data (JCPDS No. 14-0644). This result is similar to that of the γ -MnO₂ reported in the literature [23–25]. Raman spectroscopy was further employed to investigate the structures of products (Fig. 2b). The band at 641 cm⁻¹ is attributed to the Mn-O stretching vibration in the basal plane and symmetric vibrational mode of the MnO₆ group [26,27]. It is worth mentioning that the characteristic bands of GO at about 1300 cm⁻¹ and 1600 cm⁻¹ are not detected in the Raman spectra. Combining the negligible content of C element in the product, as shown in the energy dispersive X-ray spectroscopy and elemental mapping (Fig. S1), it is clearly that the GO was almost depleted by the calcinations of samples in air atmosphere. Brunauer-Emmett-Teller (BET) measurements were further carried out to investigate the textural characteristics of the prepared MnO₂. The BET specific surface areas of M0–M3 are respectively 98.42, 113.97, 151.36 and 185.62 m² g⁻¹ (Fig. 2c). The increased specific surface area of M3 can be attributed to the regular and well-distributed NPs. In addition, the specific surface area of M3 is also much higher than that of previously reported MnO₂ produced by other methods [20,21,28]. In order to determine the oxidation state of manganese ions in the samples, XPS was further conducted and the multiplet splitting of Mn 2p core level spectra are shown in Fig. 2d. The peaks of Mn 2p_{1/2} and Mn 2p_{3/2} are respectively located at 638.3 and 650.1 eV with a spin energy of separation of 11.8 eV, which are in good agreement with the previously reported data for the Mn⁴⁺ state [11,15].

The electrochemical performances of as-prepared MnO₂ as anode for LIBs were compared by the discharge-charge experiments at a current density of 100 mA g⁻¹, and the results were presented in Fig. 3. It is clear that sample M0 and M1 both exhibit drastic capacity fading (Fig. 3a). The reversible capacities after six cycles are only 107 mAh g⁻¹ (for M0) and 198 mAh g⁻¹ (for M1), respectively (Fig. 3b), even though their Coulombic efficiencies are over 80% after six cycles. Although sample M2 is capable of delivering 379 mAh g⁻¹ after 80 cycles, its capacity and initial Coulombic efficiency (37%) is still low. By contrast, the MnO₂ NPs (M3) shows the high reversible capacity of 813 mAh g⁻¹ after 80 cycles. Its capacity decreases slightly between the 6th and 80th cycles. In addition, the initial Coulombic efficiency of the MnO₂ NPs is 94.5%, which is much higher than the MnO₂ hybrid consisted of nanorods and NPs (M2) and many reported MnO₂ anode materials (Fig. 3a, Table S1). The high reversible capacity and initial Coulombic efficiency of the as-synthesized MnO₂ NPs can be attributed to the regular spherical NPs with abundant interspaces, which provide not only a sufficient number of electrochemically active sites, but also many unobstructed channels for lithiation/delithiation. Furthermore, the well-distributed MnO₂ NPs can reduce the lithium concentration

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