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Nanorod Mn_3O_4 anchored on graphene nanosheet as anode of lithium ion batteries with enhanced reversible capacity and cyclic performance

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ABSTRACT

Nanorod Mn_3O_4 anchored on graphene nanosheet (Mn_3O_4@GNS) using GNSs and $MnSO_4 \cdot H_2O$ as precursor materials have been prepared by a simple, effective and scalable method. The nanorod Mn_3O_4@GNS as anode materials in lithium-ion batteries exhibits the better electrochemical properties in the composite than the bare nanorod Mn_3O_4 owing to its special structure, including a maximum reversible specific capacity of 1155.2 mA h g^{-1} at 100 mA g^{-1}, and the extraordinary cycling stability, with no decay in capacity for up to 100 cycles. The nanorod Mn_3O_4@GNS could be a promising candidate material for high reversible specific capacity, stable columbic efficiency, long cycle life and outstanding rate capacity. This study would offer a new method to improve the properties of insulating materials, holding a promising potential for high-performance lithium-ion batteries in energy storage fields.

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1. Introduction

Rechargeable lithium-ion batteries have achieved great success in the portable electronics and electronic vehicles owing to their high energy density, better cycle stability, low maintenance, and dramatically low self-discharge [1–3]. Lately, many studies have been reported that the nanomaterials of metal oxides can achieve a higher specific capacity than graphite [4,5]. Among them, Mn_3O_4 shows high theoretical specific capacity of 937 mA h g^{-1} and has a stable crystal structure. What's more, it has been a key topic for its environmental benignity, natural abundance and low price. Therefore, the Mn_3O_4 has extensive applications as electrode materials for lithium-ion batteries. However, its low electrical conductivity (10^{-7}~10^{-8} S cm^{-1}) cause rather low rate capability, which prohibit the further application in excellent performance lithium-ion batteries. On the other hand, the large volume variation and severe particle aggregation during the charge-discharge process, greatly reduce its rate capability performance and cycling stability. Consequently, it is highly desirable to develop Mn_3O_4-based underlying conducting substrate for improving the electrochemical performance of the Mn_3O_4 [6–8]. In order to tackle these problems, a variety of methods have been studied, including the use of carbon-based composites and unique structure of Mn_3O_4 [9].

Graphene, as a rising star in materials science, exhibits exceptional electrical conductivity, mechanical robustness, chemical stability. What's more, its high theoretical surface area can make it an excellent substrate for growth of functional nanomaterials [10–13]. Because of these characteristics, graphene can be used in a composite with metal oxide (Fe_2O_3, Mn_3O_4, Co_3O_4) to improve the electrochemical performance when used as electrode materials for lithium-ion batteries [14–16]. For the nanocomposite, a good dispersion of the Mn_3O_4 nanoparticles on graphene sheets can effectively avoid the aggregation of graphene sheets, and the graphene not only provides the efficient electron transfer channels for Mn_3O_4, but also relieves the volume expansion in the charge-discharge cycles [17–20]. Such as, Gao et al. [7] prepared the sponge Mn_3O_4 used a simple coprecipitation method, which exhibited a reversible capacity of about 800 mA h g^{-1} after 40 cycles, although the electrochemical performance of the bare Mn_3O_4 could be better in 40th cycle. It is necessary to improve its cycling stability, thus should be coated with conductive agent on the surface such as carbon materials. While, West et al. [21] produced

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Mn_3O_4/Co-doped hybrid by solid phase thermal method, and the result showed that the capacity really have been improved, but, the actual growth of capacity is not obvious, far less than its theoretical capacity (936 mA h g^{-1}) [22]. In 2017, Chen et al. [23] synthesized the Mn_3O_4/NG by a simple one-pot hydrothermal process, the results displayed an excellent capacity of 1208.4 mA h g^{-1} after 150 cycles at a current density of 88 mA g^{-1}, even still remained 284 mA h g^{-1} at a high current density of 4400 mA g^{-1} after 10 cycles. Cui et al. [15] prepared nanocomposite of Mn_3O_4 nanoparticles/Reduced graphene oxide by two-step solution-phase reactions, exhibited a reversible capacity (~900 mA h g^{-1}), with good rate capacity performance and cyclic stability. At present, there are few reports on lithium-ion batteries based on different morphology Mn_3O_4/graphene composites.

As reported, there are many methods for the preparation of metal oxide/graphene hybrids, chemical in situ deposition [24,25], sol–gel processes [26] and solid phase sintering process [27] and so on. They not only could control their morphologies and size, but also could be some complicated synthetic strategies.

In this paper, we use the GNSs and $MnSO_4 \cdot H_2O$ as precursor materials, and adopt a simple, effective and scalable method of solvothermal to prepare the nanorod Mn_3O_4@GNS. This method not only effectively control various multifunctional nanomaterials with attractive morphologies, such as nanorods, but also make nanorod Mn_3O_4 uniformly anchored on the graphene substrate. Owing to the special nanorod structure, volume variation and severe particle aggregation of the Mn_3O_4 can be avoid during the charge-discharge process. The nanorod Mn_3O_4@GNS as anode materials in lithium-ion batteries exhibits high reversible specific capacity, attractive columbic efficiency, long cycle life and excellent rate capacity performance, and shows the extensive application background.

2. Experimental

2.1. Synthesis of GNSs

GO was synthesized from natural graphite powder according to a modified Hummers method [28]. Briefly, the 1.5 g $NaNO_3$ was gradually added into concentrated H_2SO_4 (15 mL) under stirring in an ice bath. Then 3 g natural graphite powder were added to the solution with keeping the mixture solution in an ice bath and stirring for 15 min. Afterward, 9 g $KMnO_4$ was gradually added in above solution in 5 min under stirring, and the temperature of mixture heated up to 98 °C. Then, the mixture solution were keeping at 98 °C for 15 min. The temperature of the obtained uniformly solution cooled down to 35 °C and keeping for 1 h. Then, deionized water (420 mL, 50 °C) was added followed by a slow additional of H_2O_2 (30 mL) and the solution become yellow from brown. The suspension was first centrifuged at 4000 rpm for 5 min. The mixture solution was filtered and washed with 5% HCl (700 mL) to remove metal ions. The precipitate was collected and added deionized water (500 mL), then ultrasonic for 1.5 h. Subsequently, the suspension was washed with water and concentrated HCl to remove the impurities by centrifuge. The Sol liquid was centrifuged and the GO was obtained and finally dried at 65 °C for 36 h in air. Then, the GNS was prepared by GO undergo calcination in muffle furnace at 1000 °C for around 1 min.

2.2. Synthesis of nanorod Mn_3O_4

The synthesis of bare nanorod Mn_3O_4 were carried out in a Teflon-lined autoclave. Firstly, 0.0877 g $MnSO_4 \cdot H_2O$ and 0.3 g CTAB were added into the deionized water (25 mL) and ethanol (25 mL). Then, an aqueous solution of NaOH (2 mg/mL) was gradually added into the obtained well-mixed solution under magnetic stirring at room temperature. The as-obtained suspension were transferred into a 100 mL-capacity Teflon-lined stainless steel autoclave sealed, and heated under autogenous pressure to 135 °C for 18 h. After the end of reaction, the reactant naturally cooled to room temperature. The brown solid product was collected, then washed with excess deionized water and ethanol to remove remaining ions in the products. After being freeze-drying, the nanorod Mn_3O_4 was obtained.

2.3. Synthesis of nanorod Mn_3O_4@GNS

Nanorod Mn_3O_4@GNS were synthesized via a simple solvothermal route. Firstly, the 20 mg as-prepared GNSs were dispersed in deionized water (25 mL) and ethanol (25 mL), besides, exfoliated by ultrasonication for approximately 2 h and stirred for 1 h. Afterward, 0.0877 g $MnSO_4 \cdot H_2O$ and 0.3 g CTAB were added into the uniform solution of GNSs. The 40 mg NaOH (2 mg/mL) gradually added to the obtained well-mixed solution under magnetic stirring at room temperature until form a uniform solution. Then the whole mixture was transferred into a 100 mL capacity Teflon-lined stainless steel autoclave sealed, and heated to 135 °C for 18 h under autogenous pressure. After the end of reaction, the reactant naturally cooled to room temperature. The resulting black solid product was collected, washed with excess deionized water and ethanol to remove remaining ions in the products. After freeze-drying, the nanorod Mn_3O_4@GNS was obtained.

For comparison, the nanorod Mn_3O_4@GNS with different mass percentages of GNS were synthesized according to the same procedure. The nanorod Mn_3O_4@GNS were labelled as nanorod Mn_3O_4@GNS-X, where the X represented the mass percentages of GNSs in the nanorod Mn_3O_4@GNS.

2.4. Characterization of materials

The morphologies of the as-prepared powder samples were characterized by a scanning electron microscope (SEM; Hitachi S-4700) and transmission electron microscopy (TEM, JEOL JEM-3010). The crystalline structure was characterized by X-ray diffraction (XRD; Rigaku D/max-2500B2+/PCX). Fourier transform-infrared spectra (FTIR) is recorded in the range of 200–3000 cm^{-1} (Thermo Nicolet-6700). Surface functional groups and bonding characterization were performed by using X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB250xi). Thermo gravimetric analysis (TGA) was conducted in air atmosphere with a Mettler Toledo in the 800 °C temperature.

2.5. Electrochemical measurements

The as-prepared electrode materials made into polar plates were tested in the configuration of CR 2032 (3 V) type Coin cells to characterize the performance of lithium storage, and which was assembled in an Ar-filled glove box. A Celgard 2500 micropore membrane and 1 M $LiPF_6$ was used as a separator and electrolyte, respectively. The electrodes were constructed by mixing active materials, acetylene black and sodium alginate with ratio of 7:2:1, and then the mixing materials were coated on a copper foil. The electrode dried in a vacuum oven at 80 °C for 24 h, and next, assembled into half-cell. Galvanostatically charge-discharge were measured on a battery test system (LAND, Wuhan), and the voltage range were among 0.01–3.00 V at room temperature. Electrochemical workstation (CHI660b) were used to test the cyclic voltammetry at 0.01 mV s^{-1} and the electrochemical impedance spectroscopy (EIS) from 0.01 Hz to 100 kHz with signal amplitude of 5 mV.

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