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A facile one-step hydrothermal method to produce α-MnO_2/graphene sheet composites and its electrochemical properties

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ABSTRACT

A composite of graphene sheet (GNS) supported by nanotube-like MnO_2 nanocrystalline (α-MnO_2/GNS composites) has been fabricated through a facile one-step hydrothermal method. The nanosized MnO_2 particles were homogeneously distributed on GNS, which have been confirmed by transmission electron microscopy analysis (TEM). The structure, composition and electrochemical properties of α-MnO_2/GNS composites were investigated by means of selective-area electron diffraction (SAED), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), cyclic voltammetry (CV) curves and Galvanostatic charge–discharge curves. α-MnO_2/GNS composites exhibited a high specific capacitance of 116 $F \cdot g^{-1}$ in 1 M Na_2SO_4 electrolyte. In addition, the α-MnO_2/GNS composite electrode shows good long-term cycle stability (only 11.99% decrease of the specific capacitance is observed after 1000 charge–discharge cycles).

1. Introduction

Over the past few years, considerable effort has been devoted to the development of alternative energy storage/conversion devices with high power and energy densities because of the ever-increasing environmental problems and the up-coming depletion of fossil fuels [1]. Graphenes have attracted increasing interest due to their amazing properties with various promising potential applications since they were discovered in 2004 [2,3]. These fantastic properties include its high surface area, excellent mechanical properties, and conductivity [4,5]. Graphene oxide (GO) is a single sheet of graphite oxide bearing oxygen functional groups on the basal planes and edges, and it exhibits good performance. GO can be obtained by the exfoliation of graphite oxide. The tunable oxygen functional groups of GO facilitate surface modifications and make it a promising material for preparation of composites [6].

Manganese oxide (MnO_2) is a widely used material featuring low-cost, high energy density, environmental pollution-free and nature abundance [7,8]. Li et al. [9] synthesized alpha-MnO_2 nanorod by chemical precipitation with surfactant as the structure-directing agent. It showed regular capacitive behaviors and good cycling stabilities in 1 M Na_2SO_4 aqueous. Zhu et al. [10] synthesized delta-MnO_2 by low-temperature hydrothermal method and found that it was an excellent electrode material for the supercapacitor in a 1 mol/LNa_2SO_4 aqueous electrolyte. Therefore, MnO_2 with high specific capacitance, good cyclic stability and low fabrication cost is expected to be synthesized. Recently, much efforts have been focused on the synthesis of nanoscale MnO_2/CNT (graphene or graphene oxide or porous carbon) hybrids due to their significant electrochemical applications [11–14], such as supercapacitors. Yu et al. [15] and Qian et al. [16] have reported that MnO_2/graphene as electrode materials for supercapacitors. However, such methods were complicated, time/energy-consuming processes.

In this paper, we reported a rapid and facile method to prepare α-MnO_2/GNS composites as novel electrode materials by hydrothermal method. The schematic illustration of the structure of this hybrid material is shown in Fig. 1. GO contains a large number of C═O, C–OH and –COOH. In the process of hydrothermal reaction, C═O converts to CO_2, at the same time, GO loses functional groups and generates GNS in situ. For this composite, GNS serves mainly as a highly conductive support, which can also provide a large surface for the deposition of nanoscale MnO_2 nanotubes with outer diameter about 20–25 nm. The excellent interfacial contact and increased contact area between MnO_2 and GNS can significantly promote the electrical conductivity of the electrode due to the high electrical conductivity of graphene. Besides, the easy surface accessibility of this composite by the electrolyte, and the improved electrochemical utilization of MnO_2, resulted from the small particle size, could provide the high reversible pseudocapacity [12]. Our experimental results show that the composite exhibits overall specific capacitance of 116 $F \cdot g^{-1}$. Furthermore, the composite exhibits good long-term cycle stability.

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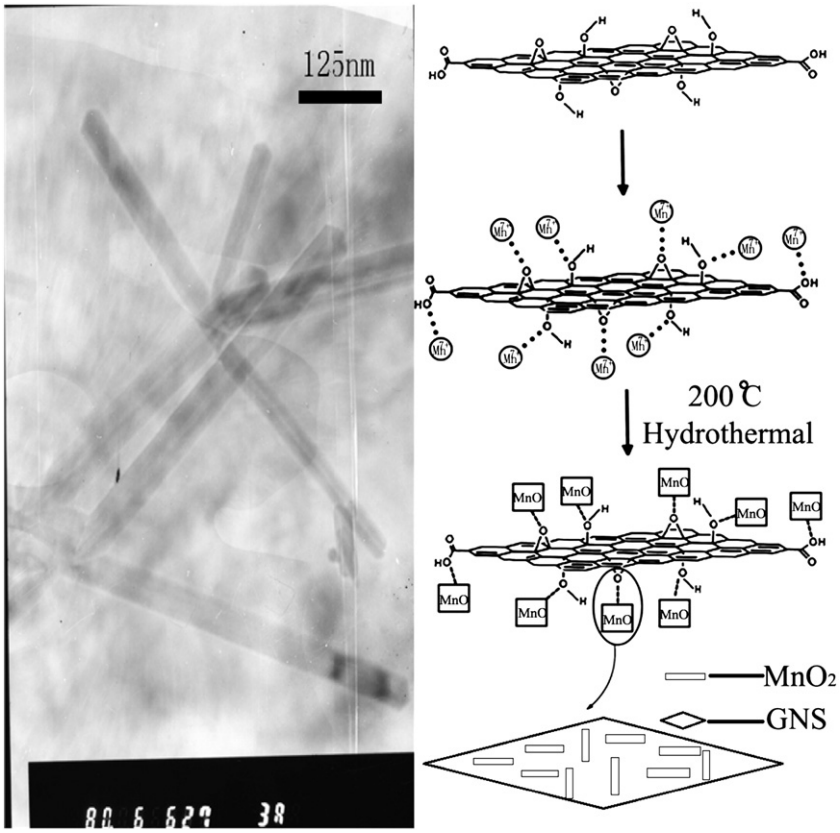

Fig. 1. Schematic illustration for the synthesis of α-MnO_2/GNS composites.

2. Experiments

2.1. Synthesis of α-MnO_2/GNS composites

GO was synthesized from natural graphite powder according to the modification of Hummers' method [17] and the method presented by Yang Yonghui et al. [18]. α-MnO_2/GNS composites were prepared by redox reaction between GO and $KMnO_4$ under hydrothermal condition. A typical synthesis of α-MnO_2/GNS composite materials was carried out as follows: The prepared GO (excessive) was dispersed in deionized water (40 mL) with vigorous stirring to get a homogeneous dispersion. $KMnO_4$ (0.608 g) was then added to the above solution. After stirring for 10 min, the mixture was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 50 mL for hydrothermal treatment at 200 °C for 3 h. After the autoclave cooling down to room temperature naturally, the precipitate was separated by suction filter separation, washed with distilled water, and dried under vacuum at 60 °C for 2 h.

2.2. The electrode preparation and characterization

To measure the electrochemical performance of the as synthesized α-MnO_2/GNS composites, α-MnO_2/GNS composites (80 wt.%) were mixed with a binder (10 wt.%) (polyvinylidene fluoride) and acetylene black (10 wt.%). The mixing active materials were made more homogeneous slurry. The slurry was pressed on nickel sheet to form a uniform film that was vacuumed-dried at 60 °C for 12 h. A square piece of the film (1 cm^2) was cut to form the working electrode. Weight of the electrode was measured by a balance with an accuracy of 0.01 mg. The exposed apparent surface area is 1 cm^2 and the typical loading of α-MnO_2/GNS composite is about 0.4 mg. For comparison, the electrochemical performance of pure α-MnO_2 is measured by the same method. The typical loading of α-MnO_2 is about 0.49 mg.

Electrochemical studies were carried out in a three-electrode system, the freshly prepared α-MnO_2/GNS composites or pure α-MnO_2 on nickel sheet, a platinum electrode (2 cm × 2 cm, Aldrich), and a saturated calomel electrode were used as working electrode, counter electrode and reference electrode, respectively. The electrolyte was 1 M Na_2SO_4 solution. CV and galvanostatic charge–discharge in different potential ranges were performed using CHI660 electrochemical working station system (Shanghai, China) at the room temperature.

3. Results and discussion

3.1. XRD analysis

The XRD spectrums of the as-synthesized α-MnO_2 and α-MnO_2/GNS are shown in Fig. 2. Pure α-MnO_2 was synthesized according to J. Luo' method [19]. All the diffraction peaks can be indexed to the α-MnO_2 phase, and no other characteristic peaks from impurities are observed. This demonstrates the high purity of the sample [20]. Whereas it can be noted that XRD peaks for α-MnO_2/GNS composite combined the diffraction peaks from α-MnO_2 nanotubes at $2\theta = 12.61°$, 17.87°, 25.49°, 28.68°, 37.44°, 38.87°, 41.88°, 47.00°, 49.84°, 56.04°, 60.02°, 65.27°, 69.41°, 72.90°, and 78.64° despite some differences in intensity. There are no other clear sharp peaks coincident with those peaks of other impurities. The broad peak from the GNS was located in the range of 22–27° and centered at $2\theta = 23°$, which was the characteristic peak of amorphous GNS with somewhat of a change in intensity and position compared to the XRD pattern in the literature [21]. This characteristic peak of GNS appeared in α-MnO_2/GNS composite. These results indicate that