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Nanocrystal manganese oxide (Mn_3O_4, MnO) anchored on graphite nanosheet with improved electrochemical Li-storage properties

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ABSTRACT

Graphite nanosheet anchored with nanocrystal manganese oxide (Mn_3O_4, MnO) was synthesized by a facile in situ one-pot solvothermal route. It was found that nanosized Mn_3O_4 and MnO particles (30–50 nm) were homogeneously anchored on graphite nanosheet. During the hydrothermal reaction, the reduction of graphite oxide to graphite nanosheet and the formation of manganese oxide occur simultaneously, forming a manganese-oxide/graphite nanosheet sandwich structure. In this sandwich structure, the electrochemical properties of Mn_3O_4 and MnO can be obviously improved because of the buffering, confining and conducting effects of the graphite nanosheet. The good electrochemical performance of manganese-oxide/graphite nanosheet composites makes them potential application as anodes in Li-ion batteries.

1. Introduction

In the early 1980s, transition metal oxides, such as CoO [1], Fe_2O_3 [2], and CuO [3], have been used as cathodes in primary batteries. In recent years, these oxides have received a renewed interest since they show potential use as anode for Li-ion batteries through a reversible conversion reaction as first reported by Tarascon et al. [4–7]. Compared with other oxides [8,9], manganese oxides exhibit a low conversion potential, abundance, low cost and environmental benignity, which is desirable for the practical application in full cells. These materials, however, generally show a rapid capacity fade because of the large volume changes and severe particle aggregation which leads to the particle pulverization and exfoliation during the conversion reaction [10–13]. Great effort has been made to improve the electrochemical properties of these oxides. Stable cycling could be achieved for manganese oxides by using nanostructured [14,15], porous [16] and thin-film materials [17] with mitigated volume changes.

Constructing a composite with carbon materials has proved to be a useful strategy to improve the cycling stability of the transition metal oxides because of their unique buffering ability. In addition, they also contribute to the overall capacity. Various forms of carbon, such as amorphous carbon [16,18–20], carbon nanofibers [21], and carbon nanotubes [22], have been suggested as the matrices to support manganese oxides. Recently, graphene has also received a special interest as the potential matrix since first reported by Novoselov et al. [23]. Graphene, a flat monolayer of sp^2-bonded carbon atoms, is considered as an ideal matrix to disperse nanoparticles due to its advantages such as large specific surface area, high electronic conductivity, and high mechanical strength. With this in mind, intensive researches have been carried out to investigate the effect of graphene on the electrochemical performance of iron oxides [24–32], cobalt oxides [33–38,31], and copper oxides [39,40]. The results have shown that the cycling stability of these oxides could be considerably improved by loading them onto graphene.

The effect of graphene on the electrochemical Li-storage properties of manganese oxides, however, has been rarely reported [41]. In the above work, an improved electrochemical performance was also realized for Mn_3O_4 by forming a Mn_3O_4/graphene composite using a two-step solution route. In this work, we will systematically investigate the effect of graphite nanosheet on the electrochemical performance of two manganese oxides, Mn_3O_4 and MnO. The Mn_3O_4/graphite nanosheet (Mn_3O_4/GN) composite was synthesized by a facile one-step in situ hydrothermal route. The MnO/graphite nanosheet (MnO/GN) composite, which has not been reported yet, was prepared by simply heating Mn_3O_4/GN in N_2/H_2. It was found that both the nanocomposites exhibited obviously improved electrochemical properties compared with bare oxides.

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2. Experimental

2.1. Preparation of Mn_3O_4/GN and MnO/GN

In a typical synthesis of Mn_3O_4/GN, 20 mg of graphite oxide, prepared by a modified Hummer's method [42], was dispersed in deionized (DI) water with sonication for 1 h to form graphene oxide. Then, 1 mmol of $Mn(CH_3COO)_2 \cdot 4H_2O$ was added into the above solution. When it was dissolved completely, 28 mg of poly(ethylene glycol) was introduced into the solution, followed by adding 20 mL of NaOH aqueous solution (0.2 M) slowly under stirring. The NaOH was used to adjust the pH of the reaction solution. It was found that Mn_3O_4 is difficult to form by the one-pot route without adding NaOH. The mixed solution was transferred to a Teflon-lined stainless steel autoclave (100 mL) and heated in an electric oven at 180 °C for 12 h. The resultant product was separated by centrifugation, washed with DI water and dried at 60 °C under vacuum for 8 h. MnO/GN was obtained by heating Mn_3O_4/GN at 400 °C for 2 h in flowing N_2/H_2 (10% H_2). For comparison, bare Mn_3O_4 and MnO were also prepared using the similar route without adding graphite oxide in the precursors.

2.2. Materials characterization

X-ray diffraction (XRD) patterns of the products were collected on a Rigaku D/Max-2550pc powder diffractometer equipped with Cu K_α radiation ($\lambda = 1.541$ Å). X-ray photoelectron spectroscopy (XPS) analyses were performed on a KRATOS AXIS ULTRA-DLD spectrometer with a monochromatic Al K_α radiation ($h\nu = 1486.6$ eV). The microstructures were observed by field emission scanning electron microscopy (FE-SEM) on a FEI-sirion microscope and transmission electron microscopy (TEM) on a JEM 2100F microscope. Raman spectra were recorded on a Jobin-Yvon Labor Raman HR-800 system using 514.5 nm Ar-ion laser. Brunauer–Emmett–Teller (BET) specific surface areas of the products were determined by N_2 absorption/desorption isotherms on an AUTOSORB-1-C apparatus. Thermogravimetric analysis (TGA) was conducted on a DSCQ1000 instrument from 45 to 650 °C at a heating rate of 10 °C min^{-1} under air.

2.3. Electrochemical measurements

Electrochemical properties of the products (Mn_3O_4/G, Mn_3O_4, MnO/G, and MnO) were evaluated using CR2025-type coin cells. The electrode slurry was made by mixing the active material, acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 75:15:10 (for the composites, the part of 75 is referred to the masses of both manganese oxide and graphite nanosheet) in N-methyl pyrrolidone (NMP) with stirring for 2 h. The working electrodes were made by spreading the slurry onto Ni foam current collector and dried at 100 °C under vacuum overnight. Half cells were assembled in an Ar-filled glove box using Li foil as the counter electrode and polypropylene microporous sheet (Celgard 2300) as the separator. The electrolyte was 1 M $LiPF_6$ dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v). The cells were galvanostatically charged and discharged between 0.05 and 3 V (vs. Li/Li^+) on a Neware BTS-5V10 mA battery cycler (Shenzhen, China). Cyclic voltammetry (CV) measurements were performed on an Arbin BT2000 system in the voltage range 0.05–3.0 V (vs. Li/Li^+) at 0.1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were conducted on a CHI660C electrochemistry workstation by applying an ac voltage of 5 mV amplitude in the frequency range from 10 mHz to 100 kHz. All of the electrochemical measurements were carried out at room temperature.

3. Results and discussion

Graphite oxide can be fully exfoliated into graphene oxide sheets in water. Graphene oxide nanosheets can be considered as macromolecules containing epoxyl and hydroxyl functional groups on

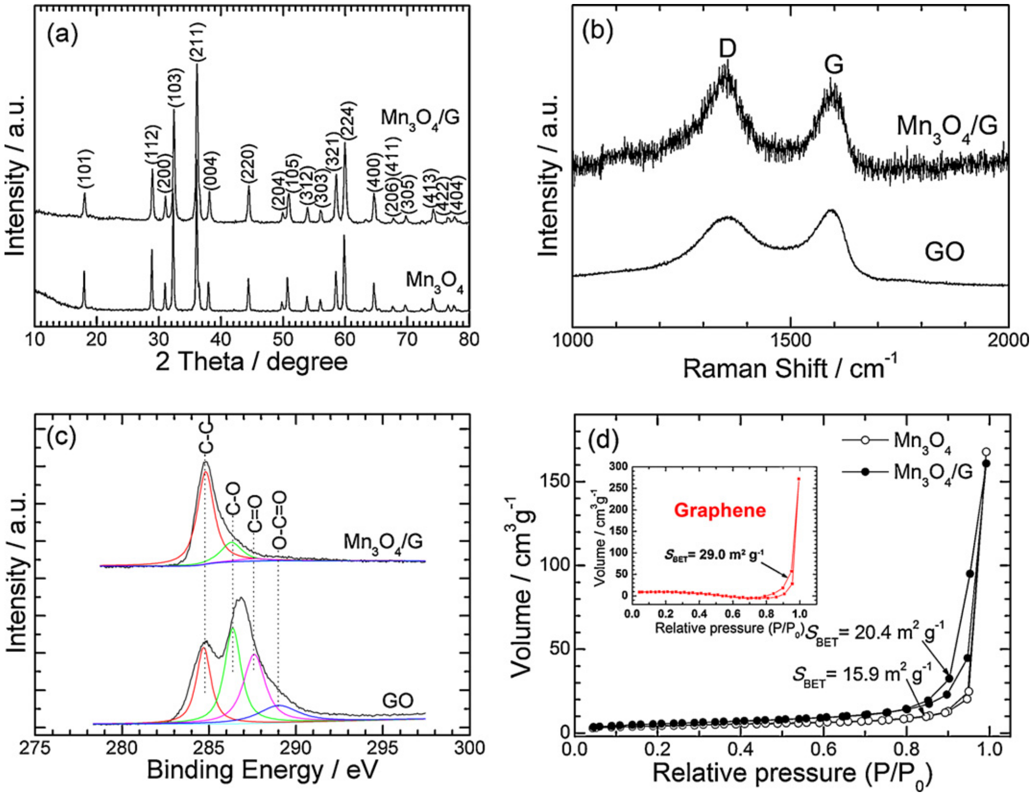

Fig. 1. (a) XRD patterns of Mn_3O_4/GN and Mn_3O_4, (b) Raman spectra of Mn_3O_4/GN and graphite oxide, (c) C 1s XPS of Mn_3O_4/GN and graphite oxide, and (d) nitrogen adsorption/desorption isotherms of Mn_3O_4/GN, Mn_3O_4 and bare graphite nanosheet.