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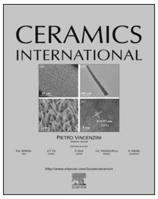

Synthesis of Mn_3O_4/N-doped graphene hybrid and its improved electrochemical performance for lithium-ion batteries

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ABSTRACT

Mn_3O_4/N-doped graphene (Mn_3O_4/NG) hybrids were synthesized by a simple one-pot hydrothermal process. The scanning electron microscopy (SEM), transition electron microscopy (TEM), X-ray powder diffraction (XRD), Thermogravimetric analysis (TG), Raman Spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to characterize the microstructure, crystallinity and compositions. It is demonstrated that Mn_3O_4 nanoparticles are high-dispersely anchored onto the individual graphene nanosheets, and also found that, in contrast with pure Mn_3O_4 obtained without graphene added, the introduction of graphene effectively restricts the growth of Mn_3O_4 nanoparticles. Simultaneously, the anchored well-dispersed Mn_3O_4 nanoparticles also play a role as spacers in preventing the restacking of graphene sheets and producing abundant nanoscale porous channels. Hence, it is well anticipated that the accessibility and reactivity of electrolyte molecules with Mn_3O_4/NG electrode are highly improved during the electrochemical process. As the anode material for lithium ion batteries, the Mn_3O_4/NG hybrid electrode displays an outstanding reversible capacity of 1208.4 mAh g^{-1} after 150 cycles at a current density of 88 mA g^{-1}, even still retained 284 mAh g^{-1} at a high current density of 4400 mA g^{-1} after 10 cycles, indicating the superior capacity retention, which is better than those of bare Mn_3O_4, and most other Mn_3O_4/C hybrids in reported literatures. Finally, the superior performance can be ascribed to the uniformly distribution of ultrafine Mn_3O_4 nanoparticles, successful nitrogen doping of graphene and favorable structures of the composites.

1. Introduction

As the promising energy storage system and important power sources, rechargeable lithium ion batteries (LIBs) have been widely used in portable electronics, electric vehicles and other areas due to their high energy density, better cyclability, low maintenance, and dramatically low self-discharge [1–3]. However, as a traditional anode material, graphitic carbon can only deliver a theoretical specific capacity of 372 mAh g^{-1}, which is difficult to meet the pressing high energy density and power density demand [4,5]. To further improve the performance of LIBs, many efforts have been made to explore new anode electrode materials. Transition metal oxides (TMOs) with high theoretical capacities have been widely investigated and regarded as potential anode materials [6,7]. Among them, manganese oxide (Mn_3O_4) has been paid great attention due to its high theoretical specific capacity (937 mAh g^{-1}), environmental friendliness and relatively low cost [8]. Furthermore, the oxidation potential of Mn_3O_4 (~1.25 V) is lower than many other transition metal oxides like (~2.0 V for Co_3O_4 [9]; ~2.25 V for NiO [10] , etc.), resulting in remarkably lower voltage polarization and higher energy density [9]. Nonetheless, there are still some obstacles which needed to be overcame. Firstly, the extremely low electrical conductivity (~10^{-7} to 10^{-8} S cm^{-1}) of Mn_3O_4 may cause low rate capability. In other hand, the significant volume change and severe particle aggregation of Mn_3O_4 during Li^+ insertion-desertion process deteriorate cycle performance and shorten lifetime [11]. Therefore, it is still urgent and challenging to develop Mn_3O_4-based electrode material to solve the above-mentioned problems.

Decoration of Mn_3O_4 on a carbon material matrix should be an alternative way to address the above problems, wherein graphene with excellent electronic conductivity, high theoretical surface area (2630 m^2 g^{-1}), and good mechanical properties is a good candidate [12,13]. Specifically, the ultrathin flexible graphene layers can effectively prevent the volume expansion and aggregation of nanopar-

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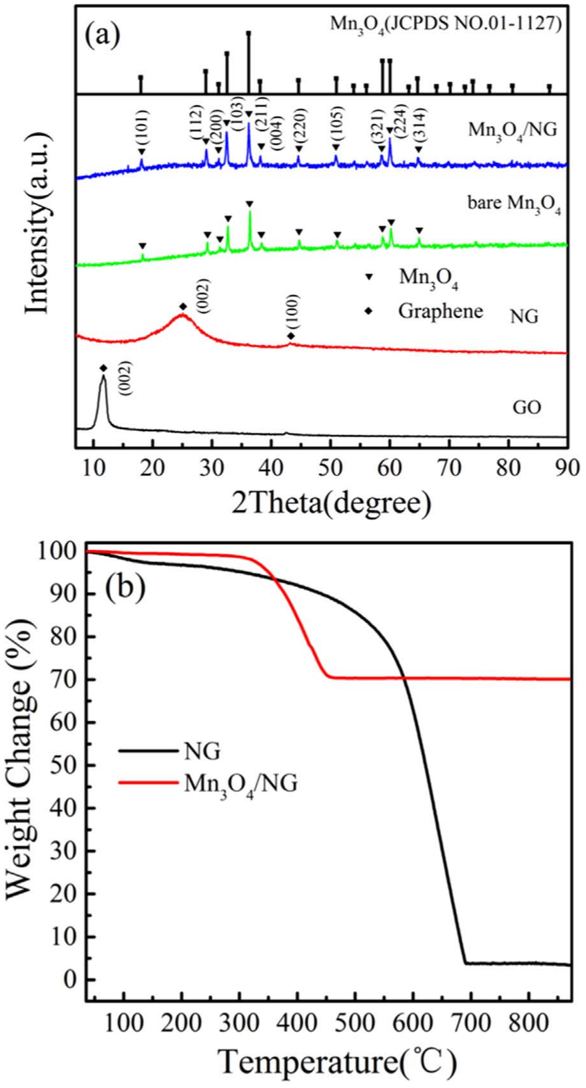

Fig. 1. (a) XRD patterns of Mn_3O_4/NG, pure Mn_3O_4, NG and GO; (b) TGA curve of Mn_3O_4/NG hybrid and pure NG.

ticles (NPs) during lithium ion insertion-desertion process [14]. Meanwhile, the deposited NPs in turn reduce the restacking of graphene sheets and ensure the full utilization of graphene. In addition, graphene has a much higher theoretical capacity of 744 mAh g^{-1} compared with that of graphite (372 mAh g^{-1}), due to the formation of Li_2C_6 [15,16]. For instance, Ayhan et al. [17] produced Mn_3O_4/rGO hybrid by adding $KMnO_4$ into the mixture of $MnCl_2$ and graphene oxide (GO) suspension followed by a hydrazine hydrate reduction process, and the resulting hybrid exhibited a reversible capacity of about 550 mAh g^{-1} after 40 cycles at a current density of 120 mA g^{-1}. Li et al. [18] also synthesized the composite of Mn_3O_4 nanoparticles wrapped in graphene sheets using a microwave-assisted hydrothermal method, which exhibited a reversible capacity more than 900 mA g^{-1} after 50 cycles at 40 mA g^{-1}. To further enhance the electrochemical performance, doping heteroatoms (e.g., nitrogen) in graphene has been proven to be an effective strategy to improve the surface wettability and electrical conductivity of graphene [19–22]. Park et al. [19] prepared Mn_3O_4/N-doped graphene composite using hydrazine monohydrate as nitrogen source and reported a reversible lithium storage capacity as high as 703 mAh g^{-1} at 200 mA g^{-1} after 40 cycles. However, all the above-mentioned Mn_3O_4/graphene anodic materials perform relatively low reversible capacity, or obvious decline trends after few tens of charge/discharge cycles. By now, few efforts have been made on Mn_3O_4/N-doped graphene hybrids as anode material for LIBs, and it is highly desirable to synthesize Mn_3O_4/N-doped graphene hybrids with improved electrochemical performance in LIBs application.

Herein, a facile one-pot approach coupling the reducing and nitrating process of GO precursors with simultaneously Mn_3O_4 on-plane decorating of graphene was developed to synthesize Mn_3O_4/N-doped graphene hybrid. The obtained Mn_3O_4/N-doped graphene hybrid exhibits superior LIB performance with large reversible capacity, high Coulombic efficiency, good capacity retention, and excellent rate capability, which can be reasonably ascribed to the synergistic effect of Mn_3O_4 NPs and N-doped graphene components.

2. Experimental

2.1. Synthesis of Mn_3O_4/N-doped graphene hybrid

To obtain the Mn_3O_4/N-doped graphene hybrid, graphene oxide was firstly prepared from natural flake graphite (Shanghai Graphite Co., Ltd., China) according to the reported procedure with a slight modification [23]. Concisely, 5g of flake graphite was dispersed into a mixture of H_2SO_4 (200 mL, 98%) and H_3PO_4 (40 mL, 85%) under magnetic stirring in an ice bath. After 1 h, $KMnO_4$ (25g) was carefully added into and dissolved within 30 min. Then, the ice bath was removed, and the oxidation of graphite last for another 6.5 h in 40 °C water bath. Subsequently, the black slurry was cooled and poured slowly into cold water (600 mL) containing 40 mL of 35% H_2O_2 under stirring. The bright yellow GO suspension was left overnight. As for the purification procedure, the supernatant of the yellow GO dispersion was decanted, and the precipitate was dispersed in 5 wt% HCl (1 L). Large unexfoliated graphite particles were removed by centrifugation at 4000 rpm for 5 min and GO was separated by centrifugation at 7200 rpm for 15 min. Subsequently, GO precipitate was re-dispersed in deionized water (3 L), and followed by consecutively centrifugation-dispersion cycles at 7200 rpm until the pH reaches ~6. The resulting GO was stored in the form of powders by freeze-drying method.

In order to prepare the Mn_3O_4/NG hybrid, 0.15g of GO was dispersed in 60 mL deionized water by sonication for 0.5 h to obtain a homogeneous GO suspension. Then, 1.078g of $Mn(NO_3)_2$ aqueous solution (50 wt%) was slowly dropped into the GO suspension under vigorous stirring for 0.5 h. Subsequently, 15 mL of ammonia (28%) was added into the above mixture under stirring for another 0.5 h. The final mixed solution was transferred into a 100 mL Teflon lined stainless steel autoclave and kept at 180 °C for 6 h. After cooled to room temperature, the resultant black product was collected by centrifugation, and rinsed with deionized water and ethanol for removing of impure ions. Finally, the obtained sample was dried at 80 °C overnight in an oven. For comparison, the bare Mn_3O_4 nanoparticles and nitrogen-doped graphene were prepared according to the same procedure in the absence of GO or $Mn(NO_3)_2$, respectively.

2.2. Materials characterization

X–ray diffraction (XRD) patterns were obtained on a Panalytical X′Pert PRO system, applying scans from 5° to 90° (2θ) with Cu Kα (λ=1.5418 Å) radiation. Thermogravimetric analysis (TGA) was conducted in air atmosphere with a NETZSCH STA 409/PC instrument in the 35–900 °C temperature range. The morphology was characterized with a field-emission scanning electron microscopy (SEM) (JSM-6700F, JEOL, Japan). The transmission electron microscopy (TEM) was performed on a JEM-2010F (JEOL, Japan) with an acceleration voltage of 200 kV. Surface areas of the samples were measured on an adsorption system (SSA-7300, China) at −196 °C. Raman spectra was obtained using Renishaw in Via-Reflex with 532 nm wavelength incident laser light. The surface chemical states of the samples were analyzed by X-ray photo electron spectroscopy (XlESCALAB 250Xi electron spectrometer) with a monochromatic Al Kα radiation.