Materials Letters 143 (2015) 163–166

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Facile and economic synthesis of nitrogen doped graphene/manganese dioxide composites in aqueous solution for energy storage devices

Jun Mei, Long Zhang *

Jilin Provincial Engineering Laboratory for the Complex Utilization of Petro-Resources and Biomass, Changchun University of Technology, Changchun 130012, PR China

ARTICLE INFO

Article history:
Received 11 November 2014
Accepted 19 December 2014
Available online 31 December 2014

Keywords:
Carbon materials
Nanocomposites
Electrical properties

ABSTRACT

Nitrogen doped graphene/manganese dioxide (N-GR/MnO_2) composites were fabricated by a facile and economic method involving one-step hydrothermal reaction at low temperature (90 °C) in aqueous solution. Characterization and systematic investigations of the samples by X-ray diffraction and X-ray photoelectron spectroscopy confirmed that MnO_2 nanoparticles were assembled with a small mass fraction of GR flakes and the incorporation of nitrogen atoms into GR skeleton was accomplished synchronously. The so-obtained MnO_2-loaded and nitrogen-doped novel composites exhibited a capacitance as high as 171.65 F g^{-1} at a current density of 2 mA cm^{-2}. Moreover, they exhibited good rate performances with long cycling stability for energy storage. Thus, these high-performance materials could act as promising candidates for energy storage devices.

1. Introduction

The increasing demand for a clean, sustainable, and renewable energy storage system has been motivated by energy needs and environmental awareness. Compared to battery or fuel cells, highly reliable and easy to maintain supercapacitors possess high power density with long cycle life and rapid charge/discharge rates [1,2]. The low-cost and environment-friendly manganese dioxide (MnO_2) has been considered as the most promising pseudocapacitive material [3,4]. However, poor conductivity of MnO_2 is still the biggest obstacle for its extended applications.

To overcome the above mentioned problem, extensive research efforts have been devoted to investigate the composite structures where MnO_2 is combined with highly conductive materials [5–11]. In particular, GR, with outstanding structural features of superior electronic conductivity, has attracted significant attention as ideal building blocks for energy storage materials [12]. Unfortunately, the binding force between GR and MnO_2 nanoparticles is weak for its intrinsic properties, leading to low electrochemical cyclic stability.

Therefore, to further enhance the cyclic stability of GR-based materials, tremendous research efforts have been focused on the structural modification of GR. Among them, doping with heteroatoms, in particular, nitrogen atoms, is a facile and effective method. In traditional doping methods, such as heat treatment (over 600 °C) and hydrothermal or solvothermal reactions (over 160 °C) [13,14], high temperature leads to additional costs and complex assembling process for nitrogen doped GR (N-GR) and MnO_2 nanoparticles, for which the crystal forms are sensitive to temperature. In general, N-GR is prepared in advance and then hybridized with different morphologies of MnO_2 nanoparticles. Therefore, to obtain a facile and economic method in green solvent to fabricate N-GR/MnO_2 composites is imminent for the further development of electrode materials in energy storage devices.

In this study, nitrogen doped reduced graphene oxide (N-RGO)/MnO_2 composites were fabricated by one-pot hydrothermal reaction at low temperature (90 °C) with water as solvent, and the electrochemical performances were also investigated.

2. Experimental

The GO solid was prepared according to a modified Hummers' method [15]. Functionalized GR (RGO) was prepared by reducing GO by the following method. First, the as-prepared GO solid was re-dispersed into deionized water (50 mL, 0.5 mg mL^{-1}) by an ultrasonic vibration for 90 min. Then, $(NH_4)_2CO_3$ (2.5 g) and $CO(NH_2)_2$ powder (1.8 g) were added into the brown colloidal dispersion and stirred for 30 min. Subsequently, $KMnO_4$ powder (1.2 g) was added and the contents were stirred for another 10 min. Then, the mixture was transferred into 80 mL Teflon-lined autoclave and maintained at 90 °C for 24 h. After cooling to room temperature, the solid so-obtained was filtered, and washed with distilled water and ethanol successively for three times. Finally, the collected solid was dried in

* Corresponding author. Tel.: +86 431 8571 7216; fax: +86 431 8571 6328.
E-mail address: zhanglongzhl@163.com (L. Zhang).

http://dx.doi.org/10.1016/j.matlet.2014.12.095
0167-577X/

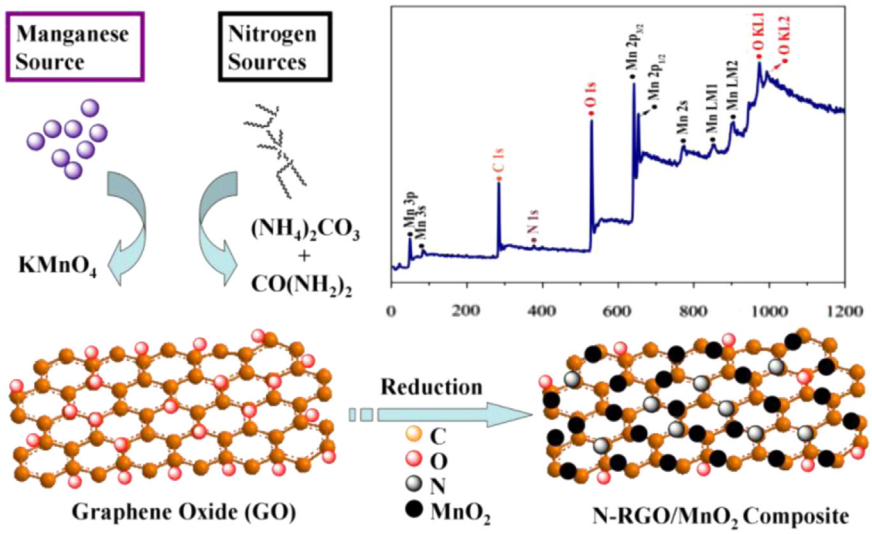

Fig. 1. Schematic of the fabrication process and XPS survey spectrum of (N-RGO)/MnO_2 composites.

a vacuum oven at 65 °C for 12 h. The mass fraction of graphene (3.1%) was calculated based on the weight of the final product. For comparison, the MnO_2 and RGO/MnO_2 composites were synthesized without GO and $(NH_4)_2CO_3$, respectively. The RGO was synthesized with GO and $(NH_4)_2CO_3$. (Details of preparation of electrodes and electrochemical test methods in the ESI.)

3. Results and discussions

In this study, (N-RGO)/MnO_2 composites were successfully fabricated by the aid of reducing-doping agents and Mn source at low temperature, as shown in Fig. 1. Low-cost GO and $KMnO_4$ were selected as raw materials and $(NH_4)_2CO_3$ and $CO(NH_2)_2$ as reducing-doping agents. The reducing-doping system was crucial to reduce GO and $KMnO_4$ which were reduced into RGO and MnO_2, respectively. Simultaneously, N-RGO was obtained with nitrogen atoms embedded by assistance of abundant nitrogen resources in aqueous solution. The free charge-carrier density could be enriched and ion transportation could be accelerated with the incorporation of nitrogen atoms. Initially, pH of the reaction system is high, which has an inhibitory effect on the hydrolysis of $CO(NH_2)_2$. Instead, $(NH_4)_2CO_3$ can be rapidly decomposed into NH_3 and CO_2 in the alkaline condition at low temperature. One of the products, NH_3, will react with the oxygen-containing functional groups of GO flakes for reduction. The residual CO_2 makes the pH of the systems lower. Therefore, the hydrolysis rate of $CO(NH_2)_2$ is accelerated. The produced NH_3 is consumed immediately until the reactions are completed. By the mutual effect, nitrogen atoms are embedded into graphene skeletons successfully. The composites exhibited good electrical performances and stability with low requirement of mass fraction of GR.

The evidence for nitrogen doping in GR was obtained by X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250), a powerful tool to identify the elements' states in bulk material. Fig. 1 shows the survey spectrum obtained by XPS revealing that the as-prepared composites contain only four elements, namely, C, O, Mn, and N. Furthermore, the deconvoluted N 1s spectrum (Fig. 2a) also shows that the N atoms are doped into GR lattices in three different valence states. The N 1s peaks of three components at 398.3, 399.4, and 401.7 eV are ascribed to pyridinic-N, pyrrolic-N, and quaternary-N, respectively. The pyridinic-N and quaternary-N can be attributed to the formation of C–N and N–O bonds. The pyrrolic-N, where the nitrogen atoms are incorporated into the five membered heterocyclic rings, is a crucial part responsible for the increased electrical conductivity and improved electrochemical performance. It possessed higher electron mobility in GR to enhance capacitances of the entire composites.

The morphology of MnO_2 in the as-synthesized composites is confirmed by X-ray diffraction (XRD, Rigaku D/max-2500) analysis (Fig. 2b), which shows the typical peaks corresponding to birnessite-type MnO_2 at about 12.73, 37.61, and 66.00°. The intensity of diffraction peaks indicate poorly crystallized composites due to the existence of GR flakes.

The capacitive performances of the obtained (N-RGO)/MnO_2 composites were evaluated by cycle voltammetry (CV) and galvanostatic charge/discharge techniques. Fig. 3a shows CV curves at different scan rates ranging from 1 to 10 mV s^{-1} in 1.0 M Na_2SO_4 electrolyte within a potential window from 0 to 1 V (vs SCE). The composites exhibit perfect capacitive behavior with a fairly rectangular shape at different scan rates. Fig. 3b shows the results of the galvanostatic charge/discharge measurements performed to obtain further information. All the curves are highly linear and symmetrical at different scan densities from 2 to 20 mA cm^{-2} indicating excellent electrochemical reversibility. The specific capacitance (C, F g^{-1}) at various current densities can be calculated according to the following equation: $C = I \times \Delta t / \Delta V \times m$, where I (A) is the discharge current, Δt (s) is discharge time, ΔV (V) is the voltage change, and m (g) represents the mass of the active materials in the electrode. The calculated specific capacitances at 2, 5, 10, and 20 mA cm^{-2} are 171.65, 157.25, 144.86, and 122.91 F g^{-1}, respectively (Fig. 3c). With the increasing charge/discharge current density, the specific capacitances show a slight decay because nitrogen-doping of GR improves the conductivity of the entire composite. Long cycling life is an important requirement for supercapacitors. Therefore, the cyclic stability was further investigated by galvanostatic charge/discharge cycling test between 0 and 1.0 V at a current density of 2 mA cm^{-2} (Fig. 3d). The cycling life runs over 500 cycles demonstrate a relatively good capability at a certain specific current. The 3.1% GR doping contributes to the (N-RGO)/MnO_2 composites with a stable capacitance of about 124.68 F g^{-1}. This results are higher than these of pure MnO_2 (96.32 F g^{-1}), GR (98.71 F g^{-1}) and RGO/MnO_2 composites (114.90 F g^{-1}). The above mentioned results demonstrated that this composite is a promising material for energy storage. Thus, N-RGO/MnO_2 could act as potential candidate for the high performance electrochemical energy storage devices for practical applications.