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Hydrothermal synthesis of reduced graphene oxide-Mn_3O_4 nanocomposite as an efficient electrode materials for supercapacitors

Hidayat Ullah Shah[a], Fengping Wang[a,*], Muhammad Sufyan Javed[b,c], Nusrat Shaheen[b,c], Muhammad Saleem[d], Yan Li[a]

[a] Department of Physics, School of Mathematics and Physics, University of Science and Technology Beijing, Beijing 100083, PR China
[b] Department of Applied Physics, Chongqing University, Chongqing 400044, PR China
[c] Department of Physics, COMSATS Institute of Information Technology, Lahore 54000, Pakistan
[d] Department of Physics, Khwaja Freed University of Engineering and Information Technology, Rahim Yar-Khan 64200, Pakistan

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ABSTRACT

Mn_3O_4 nanoparticles (NPs) are decorated with reduced graphene oxide nanosheets (rGO-Mn_3O_4) through a facile and eco-friendly hydrothermal method. The as-synthesized composite was characterized by XRD, SEM, TEM and Raman spectroscopy. The electrochemical properties of (rGO-Mn_3O_4) nanocomposite were studied as electrode materials for supercapacitors. The rGO-Mn_3O_4 nanocomposite exhibit high specific capacitance of 457 Fg^{-1} at 1.0 A/g in 1 M Na_2SO_4 aqueous electrolyte. The rGO-Mn_3O_4 exhibits good capacitance retention by achieving 91.6% of its initial capacitance after 5000 cycles. The excellent electrochemical performance is attributed to the increased electrode conductivity in the presence of graphene network.

1. Introduction

During the past decades, numerous efforts have been made to explore new energy storage devices with high energy and high power density that can be used in electric vehicles. Supercapacitor emerges as a promising energy storage device, which exhibits various advantages such as high power density, long cycle life, fast charge/discharge ability and high stability [1,2]. However, its energy density is not so high as compared to conventional batteries. So the hot topic of supercapacitors is improving its energy density without apparent damage to its power performance [3]. Graphene, a unique single layer of carbon atoms tightly packed into 2-dimensional honeycomb sp^2 carbon lattice has been attracted considerable attention due to their wonderful properties and potential application in many technological fields such as sensors, energy storage and electronic devices. Graphene also exhibits excellent chemical and physical properties such as high surface area, high electronic conductivity and excellent mechanical strength [4,5]. As compared to other carbon matrixes such as graphite, carbon black, and carbon nanotubes; graphene is an emerging as one of the most appealing carbon materials because of these unique properties [6]. It has been suggested that graphene is an excellent candidate as an electrode material for energy conversion/storage systems as a result of the above-mentioned characteristics. Reduced graphene oxide (rGO) is one of the exciting topics in many research fields especially in the field of nanotechnology during the last few years [7,8]. rGO, a kind of graphene derivative, exhibits excellent electrical, thermal, mechanical properties, a flexible porous structure with mesopores and microspores, high surface area, high conductivity, high energy density and excellent electrochemical stability [9,10]. As a result of these features, graphene nanosheets can acts better as matrices for hosting active nanomaterials to improve the electrochemical properties of the composite materials [11].

Transition metal oxides are usually considered the best candidates for electrode materials in supercapacitors owing to their large specific capacitance and fast redox kinetics. Hausmannite Mn_3O_4 has drawn particularly colossal research attention due to its distinctive structural features combined with fascinating physicochemical properties, which are of great interest in magnetic, energy storage and catalyst applications [12]. Several studies have been done with Mn_3O_4 as the supercapacitor electrode material. However, the poor conductivity of MnO_x hinders the practical applications. One useful approach to enhance electrical conductivity is to make composites with highly conductive materials, such as carbon/graphene [11]. Combining Mn_3O_4 with other conducting substrates such as carbon nanotubes and activated carbons would lead to enhance the electrochemical performance of the resulting electrode [13]. Therefore, the development of a convenient and feasible method to prepare Mn_3O_4 based composite with improved electrochemical performance will be a great significance.

* Corresponding author.
E-mail address: fpwang@ustb.edu.cn (F. Wang).

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Herein, we report a simple and robust approach for the synthesis of rGO-Mn_3O_4 nanocomposite with enhanced electrochemical performance as a supercapacitor electrode. The as-synthesized composite was characterized by XRD, SEM, TEM and Raman spectroscopy. The rGO-Mn_3O_4 delivered high capacitance of 457 Fg^{-1} at 1 A/g with high rate capability and good retention after 5000 charge/discharge cycles.

2. Experimental section

2.1. Synthesis of GO, rGO and rGO-Mn_3O_4

2.1.1. Synthesis of graphite oxide (GO)

Graphite oxide was synthesized from graphite powder by modified Hummer's method [14]. In brief, 2.5 g of graphite powder was first added into 150 mL concentrated H_2SO_4 at room temperature. After 2 h, 6 g of $KMnO_4$ was added gradually to the above solution while keeping the temperature less than 10 °C to prevent overheating and explosion. 100 mL distilled water was added to the mixture, stirred for 1 h and further diluted to approximately 300 mL with distilled water. After 6 h stirring, 20 mL of 30% H_2O_2 was added to the mixture to reduce the residual $KMnO_4$. The resulting GO powder was collected after washing the solid material successively with 10% HCl, ethanol and water to remove metal ions until the pH was 6. The GO was dried at 45 °C for 24 h.

2.1.2. Synthesis of reduced graphite oxide (rGO)

rGO was prepared by the reduction of the as-prepared GO with ascorbic acid. 2 g GO with 50 mg L-ascorbic acid was ultrasonicated in 40 mL H_2O for 30 min. Then, the mixture solution was transferred into a 40-mL Teflon autoclave and kept in a muffle furnace at 180 °C for 6 h. The product was washed with a water and ethanol mixture and dried at 60 °C. The colors of rGOs changed from brown to black, which is the evidence of the reduction process converting GO into rGO [14].

2.1.3. Synthesis of rGO-Mn_3O_4 nanocomposite

rGO-Mn_3O_4 was achieved by dissolving 1.5 g $MnCl_2$, 1.5 g GO powder and 1.0 g NaOH in 40 mL deionized water. The mixture was magneticlally stirred for 2 h. Finally, the mixture was sealed in a Teflon-lined stainless steel autoclave for hydrothermal reaction at 180 °C for 18 h. The final product was washed several times with water and ethanol and then dried at 90 °C for 6 h. Mn_3O_4 nanoparticles were also prepared under the same conditions but without the presence of rGO. The synthesis procedure for the synthesis of the rGO-Mn_3O_4 nanocomposite is schematically shown in Scheme 1.

2.2. Characterization

The structural properties of the materials were characterized by X-ray diffractometer (X'Pert MPD-XRD). The surface morphology of the as-prepared products were studied by field emission scanning electron microscopy (FESEM, ZEISS SUPRA™ 55), high-resolution transmission electron microscopy (HRTEM), energy dispersive spectroscopy (EDS, OXFORD 55-XMX) and Raman spectroscopy to examine the structural properties.

2.3. Electrode preparation and electrochemical characterization

The rGO-Mn_3O_4 based electrodes were prepared as follows; a conducting filler of acetylene black (20 wt%) and a binder of polyvinylidene fluoride (10 wt%) was mixed with rGO-Mn_3O_4 (70 wt%) as an active material. The mixture was milled to a homogeneous gel and pasted into a nickel foam (1 × 1 cm^2) current collector substrate. All electrochemical measurements were carried out with a three-electrode cell with Pt foil (1 × 1 cm^2) as the counter electrode, silver/silver chloride electrode (Ag/AgCl) as the reference electrode and the rGO-Mn_3O_4 as working electrode. The mass loading density of the active material on the current collector substrate is 1.25 mg/cm^2. Potential sweep cyclic voltammetric (CV), galvanostatic charge-discharge (GCD) measurements and electrochemical impedance performance spectroscopy (EIS, 100 kHz-0.01 Hz) were studied respectively.

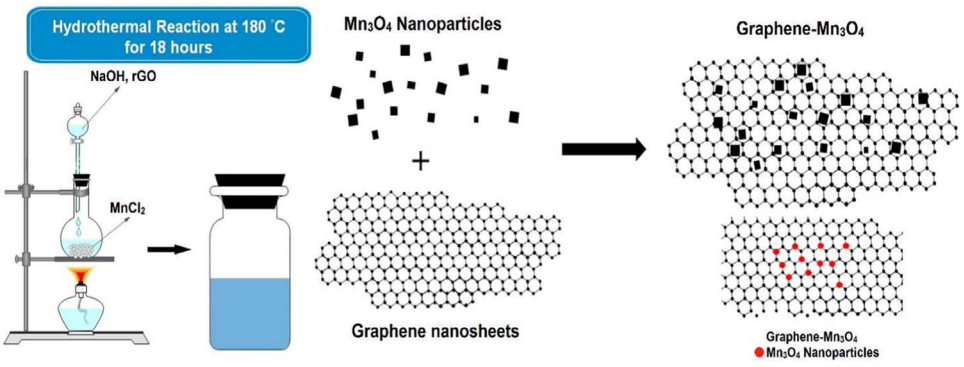
3. Results and discussion

Fig. 1(b) shows the XRD patterns of pure Mn_3O_4-NPs, rGO and rGO-Mn_3O_4 nanocomposite. All the diffraction peaks can be quickly indexed to Hausmannite Mn_3O_4 (JCPDS no. 80–0382). No additional peaks were detected, which indicates the high purity of the samples. Furthermore, EDX analysis has proved that the product is mainly comprised of three elements: C, O and Mn as shown in Fig. 1(c).

Raman spectroscopy is one of the most common and effective techniques for analyzing the structure changes of graphene-based materials, including disorder and defect structures, defect density and doping levels [14]. Two prominent features are usually observed in the Raman spectra of graphene, namely the G band (~1580 cm^{-1}) and the D band (1270–1450 cm^{-1}, depending on laser wavelength [15]). G band relating to the graphite carbon structure is corresponding to the first order scattering of E_{2g} phonon of sp^2 C atoms at the Brillouin zone center, while the D band, indicating typical defects attributed to the structural edge effects, is arising from a breathing mode of rings or K-point photons of A_{1g} symmetry [15]. Raman spectra of the rGO-Mn_3O_4 nanocomposite are shown in [Fig. 1(c) inset]. Four characteristic peaks at 302, 353, 372 and 642 cm^{-1} were observed which are attributed to crystalline Mn_3O_4 and corresponds to the skeletal vibrations [16]. Two broad peaks were observed at 1337 and 1593 cm^{-1}, which are assigned to the graphene D and G bands, respectively [17,18].

These results suggest that the rGO-Mn_3O_4 nanocomposite is composed of pure graphene nanosheets and crystalline Mn_3O_4-NPs.

Fig. 2(a) shows the FE-SEM image of Mn_3O_4-NPs, which indicate the homogenous and uniform size of NPs. Fig. 2(b-c) shows the FE-SEM images rGO-Mn_3O_4 nanocomposite, and it can be observed that Mn_3O_4-NPs are well ordered distributed on the surface of graphene nanosheets. TEM and HRTEM images (Fig. d, e, f) reveal the existence of Mn_3O_4-NPs



Scheme 1. The schematic diagram of the synthesis process of the rGO-Mn_3O_4 nanocomposite.