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A novel reduction synthesis of the graphene/Mn_3O_4 nanocomposite for supercapacitors

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ABSTRACT

Graphene/Mn_3O_4 nanocomposite is successfully synthesized from graphene oxide (GO)/MnO_2 precursor using dilute hydrazine hydrate assisted hydrothermal reaction (DAH method). X-ray photoelectron spectroscopy (XPS) and Raman characterizations confirm the decrease of oxygen-containing functional groups of GO. The results indicate that GO have been reduced to graphene to a large degree to increase the electronic conductive channels. The morphology and the phase transformation of MnO_2 can be ascribed to the “dissolution-recrystallization” mechanism. Such nanocomposite, as electrode material for supercapacitor, exhibits a high specific capacitance of 326.9 F g^{-1}, almost 4 times that of GO/MnO_2 precursor (81.3 F g^{-1}). The good cycle stability of 94.6% capacitance retention after 1000 cycles, can be explained by the firm interfacial cohesion between graphene and Mn_3O_4 nanoparticle. This soft chemical DAH process could be readily extended to the preparation of other classes of hybrids.

1. Introduction

Supercapacitors (SCs), as charge-storage devices with the ability to store large amounts of energy, transport high power loads within a very short period and excellent reversibility and cycle-ability, are considered as promising candidates for energy storage [1,2]. The characteristic performance of supercapacitors as energy storage devices is closely related to the physical and chemical features of their electrode materials. The electrode materials usually contain carbonaceous materials, conductive polymers, and transition metal oxides [3,4]. Among these, manganese oxide is generally considered to be the most promising transition metal oxide for the next generation of supercapacitors by virtue of its high energy density, low cost, environmental friendliness, and natural abundance [5,6].

Unfortunately, in spite of the high theoretical specific capacitance and long life cycle of electrode materials, MnO_2 possesses unique advantages and shortcomings for application in supercapacitors. Its poor electronic conductivity and low electron transport rate limits the electrochemical performance in supercapacitors, such as specific capacitance. Therefore, in order to tackle these issues and obtain excellent capacitive property, the corresponding graphene composite has attracted tremendous interest due to its large surface area, high electrical conductivity, favorable mechanical flexibility and the high thermal/chemical stability [7–10]. The graphene is composed of monolayers of carbon atoms arranged in a honeycomb network and is an ideal substrate to grow and anchor nanoparticles for excellent functional materials. Intensive studies involving adjustment of composition and structure of graphene/MnO_2 with various synthesis procedures have been investigated. In general, all synthesis procedures can be summarized as a one-step approach and two-steps approach. For instance, Fan et al. [11] have prepared the capacitive graphene/MnO_2 nanoparticles with 205.7 F g^{-1} by one-step hydrothermal process. On the other hand, many other reports have been focused on two-steps approach to achieve the transformation from GO/MnO_2 to graphene/MnO_2 by the soft-chemical reduction. Especially, Kim [12] has synthesized the graphene/MnO_2 nanorod composite by reduced the GO/MnO_2 precursor in the relative concentrated hydrazine hydrate, and the highest capacitive performance could up to 383.82 F g^{-1}. However, the hydrazine hydrate is poisonous, environmental detrimental and explosive. Hydrothermal synthesis is beneficial to making smaller particles, but it requires quite high temperature to complete the reaction [13]. Thus, combination of the dilute hydrazine hydrate and hydrothermal reaction is expected to increase the kinetics of crystallization by promoting rapid nucleation and growth, as well as decrease the environmental pollution and improve the electrochemical performance.

In this paper, we report the preparation of graphene/Mn_3O_4 nanocomposites using two-steps approach from the GO/MnO_2 precursor for the first time. The dilute hydrazine hydrate (0.4 mM) assisted by hydrothermal reaction (DAH process) has been utilized. The structure, chemical composition and electrochemical performance are investigated in details. The possible mechanism of

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conversion from MnO_2 nanoneedles to Mn_3O_4 nanoparticles is derived. Most importantly, our experiments suggest that DAH method is a much more effective reducing candidate to improve the electrochemical properties in many factors.

2. Experimental

2.1. Synthesis of GO/MnO_2 precursor

Graphene oxide (GO) was synthesized using the modified Hummers method as described previously [14]. Then, GO (0.14 g) and $MnCl_2 \cdot 4H_2O$ (0.54 g) were dispersed in isopropyl alcohol (100 mL) by ultrasonication for 0.5 h, and the mixture was heated to approximately 85 °C in a water-cooled condenser under vigorous stirring. Subsequently, $KMnO_4$ (0.30 g) dissolved in 10 mL deionized water was added rapidly into the above boiling solution. After refluxing for 0.5 h, the mixture began to cool to room temperature. The composite was centrifuged, washed, and finally dried at 60 °C overnight.

2.2. The preparation of graphene/Mn_3O_4 composites

The Graphene/Mn_3O_4 composite (labeled as DAH-rGO/Mn_3O_4) was obtained by the DAH process. Typically, 0.05 g GO/MnO_2 precursor was dispersed into 0.4 mM hydrazine hydrate solution (20 mL) under ultrasonication for 1 h. Then, the as-obtained mixture was transformed to a 50 mL Teflon-lined autoclave at 120 °C for 12 h. After cooling to room temperature slowly, the product was filtered, washed and dried in a vacuum oven at 90 °C for 24 h. For comparison, the CH-rGO/MnO_2 composite only reduced by the relative concentrated hydrazine hydrate (20 mM) is carried out with the method described in the literature [6].

2.3. Characterization methods

XRD analyses were performed on a Bruker D8 Advance diffractometer with Cu-K radiation (1.54 Å). The morphologies of the samples were characterized using transmission electron microscope (TEM, JEOL JEM2010) at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a thermos scientific ESCALAB 250 (Thermo Fisher Scientific, UK). Raman spectra were recorded at ambient temperature on a WITeck ALPHA300M Raman System (excitation at 532 nm, 2.33 eV). The Brunauer-Emmett-Teller (BET) surface areas of as-synthesized samples were calculated using adsorption data of N_2 at 77 K on a Quantachrome autosorb-1 analyzer.

2.4. Preparation and characterization of the supercapacitor

The electrochemical properties were measured in a typical three-electrode setup [12]. Before the electrochemical test, the prepared electrode was soaked in a 0.5 M Na_2SO_4 solution overnight. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests were performed in a potential window ranging from -0.12 V to 0.88 V using a CHI660D electrochemical working station. Electrochemical impedance spectroscopy (EIS) was conducted by applying an AC voltage with an amplitude of 5 mV in a frequency range from 0.01 Hz to 100 kHz.

3. Results and discussion

The XRD patterns of GO (Fig. 1a) reveal that the most intensive peak of GO (around $2\theta = 10.2°$) corresponds to the (002) reflection. The interlayer spacing (0.87 nm) is much larger than that of pristine graphite (0.34 nm) due to the introduction of oxygen-containing functional groups on the graphite sheets [15]. The diffraction peaks of as-synthesized GO/MnO_2 (Fig. 1(b)) are similar to those of a nanotetragonal phase of α-MnO_2 (JCPDS 44-0141). However, the (002) reflection peak of layered GO almost disappeared, which is the result of the growth of MnO_2 on the surface of GO. This result correlates well with the previous report [16]. After the CH reduction, there is no obvious difference in XRD patterns, except that these peaks are much narrower and sharper, indicating that the crystalline growth of MnO_2 is promoted. For the DAH-rGO/MnO_2 material as shown in Fig. 1(d), a series of new peaks are observed and the diffraction peaks can be indexed to Mn_3O_4 (JCPDS 18-0803). The transformation of MnO_2 to Mn_3O_4 has been induced during the DAH process.

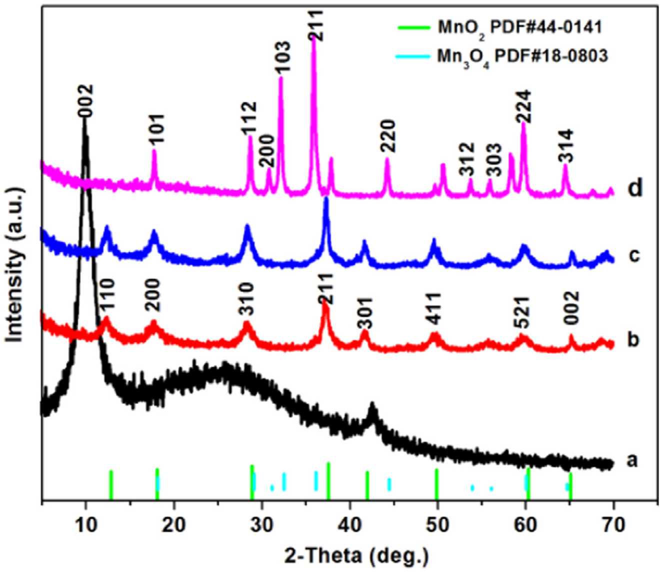

Fig. 1. XRD patterns of (a) GO, (b) GO/MnO_2, (c) CH-rGO/MnO_2 and (d) DAH-rGO/Mn_3O_4.

Raman spectroscopy is used to investigate the vibrational properties of GO in the reference samples (Fig. 2). The G band at 1590 cm^{-1} represents the in-plane bond-stretching motion of the pairs of C sp^2 atoms (the E_{2g} phonons), while the D band at 1350 cm^{-1} corresponds to breathing modes of rings or K-point phonons of A_{1g} symmetry [17,18]. The intensity ratio between the D and G bands (I_D/I_G) has been widely used to evaluate the quality

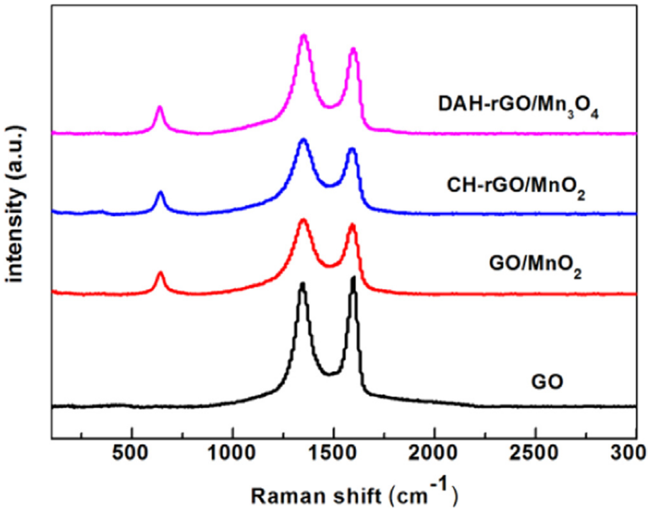

Fig. 2. Raman spectra of different composites.