Electrochimica Acta 178 (2015) 689–698

Contents lists available at ScienceDirect

Electrochimica Acta

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

Strongly coupled graphene/Mn_3O_4 composite with enhanced electrochemical performance for supercapacitor electrode

Guizhen Jin, Xuxian Xiao*, Shun Li, Kuangmin Zhao, Yuanzhan Wu, Dan Sun, Fen Wang

College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, China

ARTICLE INFO

Article history:
Received 18 May 2015
Received in revised form 8 August 2015
Accepted 8 August 2015
Available online 12 August 2015

Keywords:
Graphene/Mn_3O_4
Composite
Polyol process
Electrochemical
Supercapacitor

ABSTRACT

Strongly coupled graphene/Mn_3O_4 (GM) composite has been synthesized via a polyol process together with a subsequent thermal annealing treatment. Mn_3O_4 nanoparticles with an average diameter of 20 nm are uniformly adhered to a substrate of graphene sheets. The electrochemical properties of the composite for supercapacitor electrode in 1.0 M Na_2SO_4 aqueous solution were investigated by cyclic voltammetry (CV) and galvanostatic charge–discharge measurements. The GM composite exhibits more remarkable capacitance (270.6 F g^{-1} at 0.2 A g^{-1}) compared with the pure Mn_3O_4 (132.0 F g^{-1} at 0.2 A g^{-1}). After 1500 cycles, the retention rates of the composite and pure Mn_3O_4 at 2.0 A g^{-1} are 91% and 71.4%, respectively. The good electrochemical performance of the GM composite could be attributed to the decreased agglomeration, enhanced conductivity, and the robust structure as a result of introducing graphene. These results render a new reasonable design of preparing nanomaterials with complex structures for supercapacitor applications.

1. Introduction

Supercapacitors (SCs) are a new type of energy storage devices that fill the energy/power gap between batteries and electrostatic capacitors [1]. In recent years, SCs have attracted intensive research attention in view of their prominent advantages of fast charging-discharging, long cycling life and convenient operation over a wide temperature range [2,3]. As a consequence, SCs have been widely applied in hybrid electric vehicles (HEVs), backup power and other energy storage devices which require a quick and high power output in a short time [4,5]. Based on the different charge storage mechanisms, SCs can be categorized into two types: (i) electrical double-layer capacitors (EDLCs) and (ii) pseudocapacitors [2,6]. The properties of electrode materials are key factors for the performance of SCs, many intense researches have been focused on various electroactive materials in order to improve the performance of SCs [3]. Up to now, the carbon-based materials, including graphene, activated carbon (AC) and carbon nanotubes (CNTs), have been intensively studied for EDLCs in light of their readily accessible mesopores, low cost, eco-friendliness, and stability [7,8]. However, EDLCs are plagued by their relatively low energy density, and their capacitance are typically in the range of 75 – 175 F g^{-1} due to the restriction of the specific surface area and the pore-size distribution [2]. In contrast, pseudocapacitors can offer far higher specific capacitance and energy density [5]. At present, the pseudocapacitors electrode materials generally involve various metal oxides [9–11], metal hydroxides [12,13], metal sulphides [7,14] and conductive polymers [12,14]. Among these materials , transition metal oxides, in terms of achieving high specific capacitance in SCs, are regarded as excellent pseudocapacitors materials [15].

During the past few decades, the manganese oxides have received much attention as suitable electrode materials for SCs [16]. Among these manganese oxides, hausmannite (Mn_3O_4) has been considered as one of the promising electrode materials for SCs owing to its natural abundance, low cost, environmental compatibility, satisfactory energy storage performance [17,18], and relatively broad work potential window in aqueous solution [8]. However, the drawbacks of pure Mn_3O_4, such as poor electronic conductivity (10^{-5}-10^{-6} S cm^{-1}) and inferior cycling stability, limit its application. Therefore, many efforts have been devoted to overcoming these problems. At present, the common strategy is either embedding Mn_3O_4 nanoparticles (NPs) into or depositing Mn_3O_4 NPs on a highly conductive porous substrate to form composite [8]. For example, one effective way to solve the inherent defects of Mn_3O_4 is to synthesize hybrid nanostructures by electrically wiring them up with a highly conductive underlying substrate such as carbon cloth or carbon nanotubes (CNTs) [16].

Among numerous carbon materials, graphene, which is a flat monolayer of carbon atoms with a tight packing honeycomb lattice,

* Corresponding author. Fax: +86-731-88879616.
E-mail address: lushangzhuimeng@163.com (X. Xiao).

http://dx.doi.org/10.1016/j.electacta.2015.08.032
0013-4686/

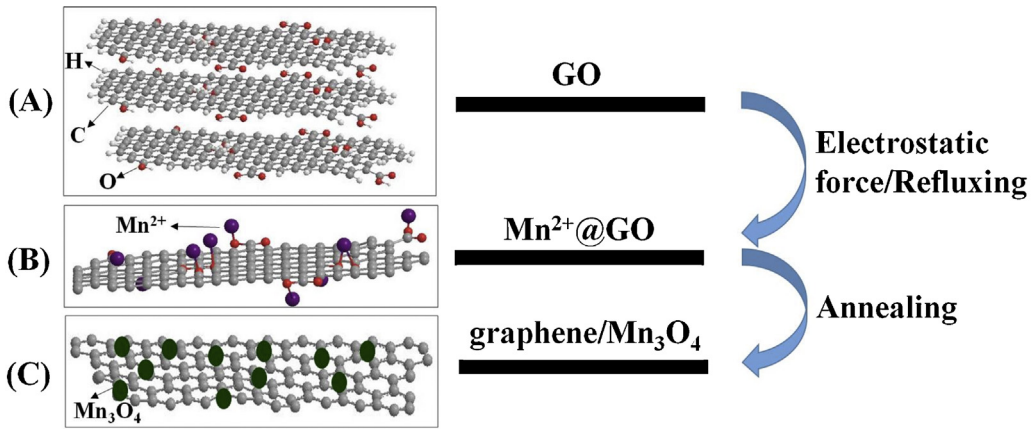

Fig. 1. Scheme of the effective synthesis of graphene/ Mn_3O_4 (GM) composite by a two-step strategy involving a polyol process together with a subsequent thermal annealing treatment.

has attracted extensive attention due to its excellent electrical conductivity, ultrahigh specific surface area and excellent chemical stability [7,9,19,20]. In addition, graphene is also drawing increasing attention to owing to its ultrathin flexible sheets can offer a support to adhere to metal oxide NPs and reckon as a highly conductive substrate [21–23]. Currently, graphene/metal oxide composites, such as graphene/Co_3O_4, graphene/Fe_3O_4, graphene/MnO_x, graphene/SnO_2 and graphene/$Ni(OH)_2$ nanocomposites [8,24–27], have been successfully synthesized as electrode materials for SCs. Furthermore, graphene/Mn_3O_4 composites have been prepared by various methods [8,18,28]. However, these composites did not demonstrate a whole improvement in methods or electrochemical performances, such as using toxic precursors and low increasement in capacitance. The low capacitance can be ascribed to the fact that the GM composite is unstable and just an intermediate product [8]. Hence, it will be of great significance to develop an effective method to synthesize better performance graphene/Mn_3O_4 composite.

As is well known, the morphology and structure of materials, which have an important effect on the electrochemical properties, are much depended on the fabrication strategy. Herein, we adopt an effective two-step strategy to synthesize hybrid sheets by growing small Mn_3O_4 nanocrystals on reduced graphene oxide (RGO) sheets. As the formation process shown in Fig. 1, in situ growth of Mn_3O_4 on the surface of RGO results in the intimate combination of the conductive graphene network with uniformly dispersed Mn_3O_4 NPs, which not only improves the electrochemical utilization of Mn_3O_4, but also increases the double layer capacitance of the graphene sheets when used as supercapacitor electrodes. The GM composite exhibit remarkable capacitance of 270.6 F g^{-1} at 0.2 A g^{-1} as well as outstanding cycling stability of 91% after 1500 cycles at 2.0 A g^{-1}, which are much superior than the pure Mn_3O_4. In this connection, our method may be very appealing for the large-scale and environmentally-friendly production of graphene/MnO_x composite.

2. Experimental

2.1. Preparation of graphene/Mn_3O_4 (GM) composite

All of chemical reagents used in this experiment were of analytical grade without any further purification. The graphene oxide (GO) was prepared from natural graphite (Sigma-Aldrich) by a modified Hummers method [29]. The synthesis of GM hybrid structure involves an effective two-step process. Firstly, 50 mg of GO powder was added to 50 mL of ethylene glycol, and then the mixture was sonicated for 1 h to achieve a homogeneous dispersion. Next, 5 mmol of manganese acetate tetrahydrate ($Mn(CH_3COO)_2{\cdot}4H_2O$) was dissolved into the above mixture. After stirring for 30 min, the mixture was transferred to a flask and then heated up to 165 °C using an oil bath. After reaction for 2 h, the solution was cooled down naturally. Subsequently, the product of the Mn-glycolate-RGO hybrid was collected by centrifugation and washed with deionized (DI) water and ethanol for several times. In order to obtain GM hybrid structure, the Mn-glycolate-RGO was annealed at 320 °C for 4 h in air with a slow heating rate of 1 °C min^{-1}. And the final product was denoted as 1.0-GM composite. In other two experiments, samples were synthesized by 0.5 mg mL^{-1} and 2.0 mg mL^{-1} GO suspension with same conditions of sample 1.0-GM composite, their products were denoted as 0.5-GM composite and 2.0-GM composite, respectively. For comparison, pure Mn_3O_4 and reduced graphene oxide (RGO) were prepared by the similar procedure, the physical mixture of RGO and pure Mn_3O_4 was also prepared, denoted as graphene+Mn_3O_4 mixture.

2.2. Materials characterizations

The structural phases of the products were measured by powder X-ray diffraction (XRD) experiments on a MXPAHF X-ray diffractometer from 10° to 80° with Cu Kα radiation (λ=1.54056 Å). Thermogravimetric analysis (TGA) was performed on a thermogravimeter analyzer (TGA, DTA-50, Shimazu, Japan) from room temperature to 600 °C at a heating rate of 10 °C min^{-1} in air flux. Fourier transform infrared (FT-IR) spectra of the samples were recorded on a VECTOR-22 (Bruker) spectrometer with KBr pellet ranging from 400 to 4000 cm^{-1}. Raman spectra were examined with an Ar ion CW laser (514.5 nm) as the excitation source by using a LabRAM HR UV/vis/NIR spectrometer (Horiba Jobin Yvon, france). X-ray photoelectron spectroscopy (XPS) was used to verify the valence states of Mn in the product with a Thermo VG Scientific SiRGa Probe spectrometer. The morphology was analyzed by using scanning electron microscope (SEM, JEOL JSM-6360) and field-emission scanning electron microscopy (FE-SEM, FEI Nova Nano-230). The structural informations of the product were characterized by high-resolution transmission electron microscope (HR-TEM, JEOL-2010).

2.3. Preparation of electrodes

To fabricate the working electrodes, the prepared active material, acetylene black, and a 10 wt % polytetrafluoroethylene (PTFE) binder were mixed at a weight ratio of 80:10:10, and then the