



Facile synthesis of reduced graphene oxide/NiMn₂O₄ nanorods hybrid materials for high-performance supercapacitors



Zhongbing Wang*, Zihao Zhu, Chunlei Zhang, Chengqiao Xu, Chunnian Chen

School of Chemistry & Chemical Engineering, Anhui Key Laboratory of Controllable Chemistry Reaction & Material Chemical Engineering, Hefei University of Technology, Hefei, Anhui 230009, PR China

ARTICLE INFO

Article history:

Received 13 November 2016

Received in revised form 31 January 2017

Accepted 5 February 2017

Available online 6 February 2017

Keywords:

Hybrid materials
NiMn₂O₄ nanorods
Graphene
Supercapacitors

ABSTRACT

We report a mild strategy to synthesize reduced graphene oxide/spinel nickel manganese oxide (rGO/NiMn₂O₄) nanorods composites. The rGO/NiMn₂(C₂O₄)₃ precursors were prepared via coprecipitation method in ethanol-water system and the composites were obtained by calcining the precursors in air. The hybrid materials have been characterized by X-ray powder diffraction, Raman spectra, X-Ray photoelectron spectroscopy, high-resolution transmission electron microscopy and field emission scanning electron microscopy. Different electrochemical measurements have been used in a three electrode system to study the electrochemical performance such as cyclic voltammetry, galvanostatic charge/discharge, and electrochemical impedance spectroscopy. The typical hybrid materials (30 wt% rGO) display a high specific capacitance (693.00 F g⁻¹ at 1 A g⁻¹) and prominent cycling stability (91.38% capacitance retention after 2000 cycles at 5 A g⁻¹), indicating that the composites possess potential application as excellent electrode material.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

With the exhaustion of fossil energy, global warming and pollution, renewable energy resources have attracted a vast amount of attention. Electrochemical supercapacitors exhibit a promising application as energy storage devices [1], as a result of its relatively high power density, high energy efficiency, rapid charge/discharge characteristics and outstanding cycle stability [2]. In recent years, different kinds of electrode materials have been reported, for instance, carbon materials (carbon nanotubes [3], mesoporous carbons [4], graphene [5], etc.), metal oxides (CuO₂ [6], MnO₂ [7,8], NiO [9], MoO₃ [10], etc.) and conducting polymers (polypyrrole [11], polyaniline [12], polythiophene [13], etc.). In comparison with conducting polymers and carbon materials, transition metal oxides (TMO) attracted tremendous interest owing to its superior redox activity, abundant reserves, high theoretical capacity and low cost. Binary metal oxides, which can handle the synergistic effect of different TMO, improve electrochemical performance such as conductivity, stability and potential window [14]. Many researches have been reported on binary metal oxides such as NiMnO₃ [15], MnCo₂O₄ [16], CoMoO₄ [17], CoFe₂O₄ and ZnMn₂O₄ [18]. NiMn₂O₄, which

has a unique spinel crystal structure, is a potential electrode material with excellent electrochemical performance as a result of its various advantages, for instance, lower cost, environmental benignity and easy preparation. Some developments based on NiMn₂O₄ materials have been carried out, Miao Zhang and co-workers have reported NiMn₂O₄ with a mesoporous structure [19], Nan's groups have prepared a NiMn₂O₄@CNT nano composites [20], and K.Vijaya Sankar's groups have investigated the electrochemical intercalation/de-intercalation mechanism of it for supercapacitor [21]. However, as the same as other transition metal oxides, its applications are limited by relatively poor conductivity, low specific surface area and bad dispersity [22]. In order to overcome above drawbacks, we pay attention to incorporation with carbon materials for promising electrode materials.

Graphene, an important carbon material, has a hexagonal 2D layer structured consisted of sp² carbon atoms [23]. Owing to its unique structure, graphene exhibits anticipated properties including large surface area, outstanding electrical conductivity, excellent chemical and thermal stability, and wide potential window [24], which make it a promising candidate for hybrid hierarchical nanostructures composites with TMO. Significant efforts have been devoted to develop graphene/TMO hybrid materials up to date, such as graphene/MnO₂ [25], graphene/V₂O₅ [26], graphene/NiO [27], etc. These hybrid materials exhibit better electrochemical

* Corresponding author. Tel.: +86 551 62901451; fax: +86 551 62901450.
E-mail address: zbwang@hfut.edu.cn (Z. Wang).

performance than individual component because of synergistic effects of graphene and TMO. Graphene offers a 2D support to build conductive network, suppresses the volume change and agglomeration of TMO, and ensures good electrical contacts between graphene and TMO by oxygen-containing groups [28]. Without doubt graphene/ NiMn_2O_4 composite materials are worth expecting to possess better electrochemical performance although there are few reports about NiMn_2O_4 /graphene composites for supercapacitors to the best of our knowledge.

In addition, factors that determine the realization of a high-performance supercapacitor electrode are surface area, electrical conductivity, chemical and electrochemical stability. Designing with nanostructures supplies a potential strategy to manipulate aforementioned factors effectively [29]. Much efforts have been expended on the designing with nanostructures such as nanowires [30], nanotubes [31], nanosheets [32], and so on. For the past few years, the one-dimensional nanostructured materials exhibit appealing potential in the field of energy storage devices due to their unique structures and properties. Li's groups have prepared V_2O_5 nanorods encapsulated into carbon for lithium-ion batteries [33], the hybrid materials possess excellent electrochemical performances because of the shorter Li^+ and electron diffusion paths. Shaheen and his co-workers have successfully synthesized rGO/MoO₃ nanowire@C composites for high-performance supercapacitors [34], the nanowires provide a high surface area due to their high aspect ratio. Beyond these, the 1-D nanostructured materials exhibit stronger competitive power in various application fields such as solar cells [35,36], sensors [37], and catalysis [38].

In this work, we adopt a mild method to synthesize reduced graphene oxide/ NiMn_2O_4 (rGO/ NiMn_2O_4) composites from rGO and 1-D NiMn_2O_4 nanorods. The $\text{NiMn}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ precursors were prepared by coprecipitation method in ethanol-water system [39], which graphene oxide dispersed in. The precursors attached to graphene oxide during precipitation process at room temperature. After that, the mixture was calcined in the air to obtain rGO/ NiMn_2O_4 composites successfully. The product prepared by a mild, facile and low cost strategy exhibits good electrochemical performance and chemical stability. Electrochemical test revealed that the composites possess the highest specific capacitance of 693.00 F g^{-1} , good supercapacitors performance, and prominent cycling stability.

2. Experiment section

2.1. Preparation of rGO/ NiMn_2O_4 nanorods composites

All the reagents used in this work were obtained from Sinopharm Chemical Reagent Co. Ltd. The reagents were of

analytical grade and used directly without any more purification. In a typical synthesis procedure, 250 mg nickel acetate tetrahydrate ($\text{C}_4\text{H}_6\text{NiO}_4 \cdot 4\text{H}_2\text{O}$), 492 mg manganese acetate tetrahydrate ($\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$) and 30 ml of GO aqueous suspension (2 mg/ml) were dissolved in 120 ml of ethanol with ultrasonically stirring for 20 min to form solution I. At the same time, 379 mg oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) and 20 ml of GO aqueous suspension (2 mg/ml) were dissolved in 80 ml of ethanol with ultrasonically stirring for 20 min to form solution II. The solution II was poured into the solution I and kept at room temperature with ultrasonically stirred for 6 h. The $\text{NiMn}_2(\text{C}_2\text{O}_4)_3/\text{GO}$ precursors were obtained through evaporating the solvent in air at 80°C overnight. The precursors were calcined at 250°C for 8 h in air and the heating rate was of 2°C min^{-1} . The final rGO/ NiMn_2O_4 nanorods composites were obtained after calcining and marked as GMN-30. The NiMn_2O_4 nanorods and the rGO/ NiMn_2O_4 composites in the different mass ratio (15 wt%, 50 wt% rGO) were prepared by changing the mass of rGO while keeping other parameters constant, and were noted as GMN-0, GMN-15, GMN-50, respectively.

2.2. Characterization

X-ray powder diffraction (XRD) were used to analyze the composition and structure of the as-obtained samples on a PANalytical B.V. X'Pert PRO MPD using a $\text{Cu K}\alpha$ radiation source ($\lambda = 1.54056 \text{ \AA}$) worked at 40 kV and 40 mA. Field emission scanning electron microscopy (FESEM) images were acquired with a Hitachi SU8020 at an acceleration voltage of 5.0 kV. The morphologies of the composites were characterized by high-resolution transmission electron microscopy (HRTEM) with a JEOL JEM-2100 at an acceleration voltage of 200 kV. Specimens for FESEM and HRTEM observation were pretreated by ultrasonically diffusing the composites powder into anhydrous ethanol. X-Ray photoelectron spectroscopy (XPS) measurement was performed on a Thermo Scientific ESCALAB250Xi with a focused monochrome $\text{Al K}\alpha$ X-ray source. Raman scattering spectra were carried out on a HORIBA JOBIN YVON HR Evolution with a 534 nm argon ion laser.

2.3. Electrochemical measurements

The working electrodes were prepared by mechanically mixing rGO/ NiMn_2O_4 active material powder with conductive additive (acetylene black) and binder (polyvinylidene fluoride) in the mass ratio of 80: 10: 10. After that, the mixture was dissolved in N-methyl pyrrolidone to form homogeneous slurry and coated on a piece of nicked foil current collector. The loading mass of the as-prepared sample on nicked foil was approximately 1.0–2.0 mg with an area of 1 cm^2 . The current collector was dried at 60°C in vacuum overnight. The electrochemical performance were evaluated with a

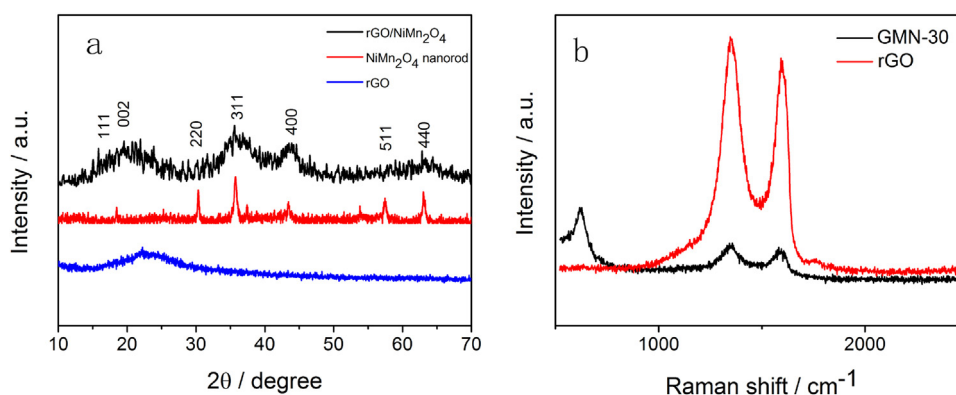


Fig. 1. (a) XRD patterns of rGO, NiMn_2O_4 nanorods and rGO/ NiMn_2O_4 hybrid composites and (b) Raman spectra of rGO and GMN-30.

Download English Version:

<https://daneshyari.com/en/article/6471451>

Download Persian Version:

<https://daneshyari.com/article/6471451>

[Daneshyari.com](https://daneshyari.com)