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High-performance asymmetric supercapacitors based on $MnFe_2O_4$/graphene nanocomposite as anode material

Bo Li [a], Yongsheng Fu [b], Hui Xia [a,*], Xin Wang [b,**]

[a] Herbert Gleiter Institute of Nanoscience, Nanjing University of Science and Technology, Xiaolingwei 200, Nanjing 210094, China
[b] Key Laboratory of Soft Chemistry and Functional Materials, Nanjing University of Science and Technology, Ministry of Education, Nanjing 210094, China

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ABSTRACT

$MnFe_2O_4$/graphene nanocomposite is synthesized and demonstrated as promising anode material for asymmetric supercapacitors. An asymmetric supercapacitor operating at 1.8 V is fabricated using $MnFe_2O_4$/graphene as anode and MnO_2/carbon nanotube as cathode. The asymmetric supercapacitor shows an energy density of 25.9 Wh kg^{-1} at a power density of 225 W kg^{-1} and an energy density of 18.1 Wh kg^{-1} at a power density of 14.4 kW kg^{-1}, indicating an excellent power capability.

1. Introduction

The energy density of commercialized supercapacitors based on two symmetric activated carbon electrodes is relatively low (~5 Wh kg^{-1}), which limits its applications in modern electronic devices and power systems [1]. The energy density of supercapacitor can be enhanced by either increasing the device capacitance with novel electrode materials or broadening the cell voltage. An effective way to increase the cell voltage is to use ionic liquids or organic electrolytes because of their wider potential windows than aqueous electrolytes. However, such electrolytes are usually cost-ineffective and not environmentally friendly, making them undesirable in practical applications. A promising alternative is fabricating asymmetric supercapacitors using aqueous electrolytes with low cost and environmental benignity [2–4].

The key to fabricate asymmetric supercapacitors is to use appropriate positive and negative electrode materials that have well-separated potential windows in the same electrolyte [5]. Many researchers chose transition metal oxides as cathode materials and carbon-based anode materials to assemble asymmetric supercapacitors. For neutral aqueous electrolyte, MnO_2-based materials have been developed as cathodes for asymmetric supercapacitors because of their excellent electrochemical performance in the positive voltage window [6,7]. However, most of asymmetric supercapacitors used activated carbon as anode material and the energy density could not be increased further.

Most recently, some metal oxides, such as MoO_3 and WO_3, have also been investigated as anode materials for asymmetric supercapacitors [8,9]. However, the poor conductivity of metal oxides limits the power density of supercapacitors. To address this issue, conductive additives, such as carbon nanotube (CNT) and graphene, were added in the metal oxides to improve the rate capability [10,11]. In the present work, $MnFe_2O_4$/graphene nanocomposite was synthesized and investigated as anode material for asymmetric supercapacitors. Graphene was used to prepare the nanocomposite becasue graphene usually provides larger surface area compared to CNTs. A 1.8 V asymmetric supercapacitor was fabricated using $MnFe_2O_4$/gaphene as anode and MnO_2/CNT as cathode in 1 M Na_2SO_4 electrolyte. The device exhibited both high energy density and power density, demonstrating that $MnFe_2O_4$/graphene nanocomposite is a promising anode material for asymmetric supercapacitors.

2. Experimental

$MnFe_2O_4$/graphene nanocomposite with 15 wt% graphene was synthesized by a hydrothermal method. In a typical synthesis, 80 mg of graphene oxide was dispersed in 80 mL ethanol with sonication for 1 h. 0.716 g of 50 wt% $Mn(NO_3)_2$ solution and 1.616 g of $Fe(NO_3)_3 \cdot 9H_2O$ were added in the above solution and stirred for 30 min at room temperature. After that, the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and

* Corresponding author. Tel.: +86 25 84315606; fax: +86 25 84315159.
** Corresponding author. Tel.: +86 25 84305667; fax: +86 25 84315054.
E-mail addresses: xiahui@njust.edu.cn (H. Xia), wxin@public1.ptt.js.cn (X. Wang).

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heated to180 °C for 20 h. Final products were separated by centrifugation and dried in a vacuum oven. MnO_2/CNT nanocomposite with 15 wt% CNT was prepared as the cathode material according to our previous work [12]. The carbon contents in the nanocomposites of $MnFe_2O_4$/graphene and MnO_2/CNT were determined by thermogravimetric analysis (TGA, Shimadzu DTG-60H).

The structure and morphology of the samples were investigated by powder X-ray diffraction (XRD, Shimadzu X-ray diffractometer 6000), field emission scanning electron microscopy (FESEM, Hitachi S4300) and transmission electron microscopy (TEM, JEOL, JEM-2010).

All electrochemical measurements were performed on a CHI660D electrochemical workstation. To prepare the electrodes, 80 wt% active material, 10 wt% carbon black, and 10 wt% polyvinylidene difluoride dissolved in N-methylpyrrolidone were mixed to form slurry. The slurry was pasted on Ti foil and dried in an electric oven. The electrochemical measurements of individual electrode (MnO_2/CNT, graphene and $MnFe_2O_4$/graphene) were performed using a three-electrode cell with a platinum foil counter electrode and an Ag/AgCl reference electrode. The mass loading of both $MnFe_2O_4$/graphene and MnO_2/CNT electrodes is in the range between 3 and 4 mg cm^{-2}. An asymmetric supercapacitor with MnO_2/CNT cathode and $MnFe_2O_4$/graphene anode was assembled in Swagelok cell using porous non-woven fabric as the separator. For both three-electrode cell and two-electrode cell, 1 M Na_2SO_4 was used as the electrolyte.

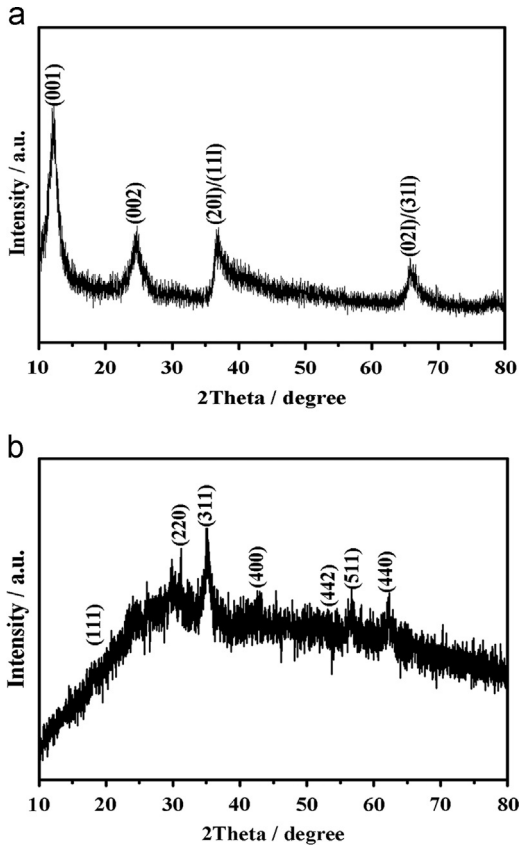

Fig. 1. The XRD patterns of (a) MnO_2/CNT and (b) $MnFe_2O_4$/graphene nanocomposites.

3. Results and discussion

As shown in Fig. 1, the XRD pattern of the MnO_2/CNT nanocomposite can be indexed to the monoclinic potassium birnessite (JCPDS no. 80-1098) [14], and the XRD pattern of the $MnFe_2O_4$/graphene nanocomposite can be indexed to the cubic type $MnFe_2O_4$ (JCPDS no. 73-1964).

Fig. 2a and c shows the FESEM and TEM images of the MnO_2/CNT nanocomposite, respectively. It can be seen that interconnected MnO_2 nanoflakes are uniformly coated on the CNT cores, forming a CNT core/porous MnO_2 shell hierarchy architecture. The inset in Fig. 2c shows clear lattice fringes with interplanar spacing

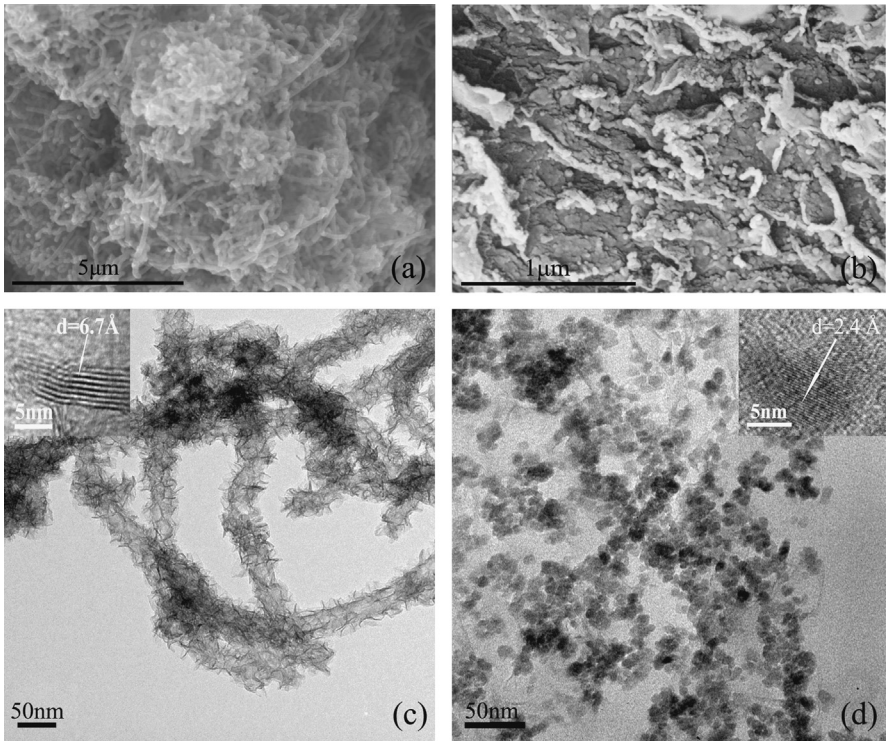

Fig. 2. FESEM images of (a) MnO_2/CNT and (b) $MnFe_2O_4$/graphene nanocomposites. TEM images of (c) MnO_2/CNT and (d) $MnFe_2O_4$/graphene nanocomposites.