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High performance graphene/manganese oxide hybrid electrode with flexible holey structure

Qian Yang[a,b], Qi Li[a,b], Zhe Yan[a,b], Xiaona Hu[a,b], Liping Kang[a,b], Zhibin Lei[a,b], Zong-Huai Liu[a,b,*]

[a] *Key Laboratory of Applied Surface and Colloid Chemistry (Shaanxi Normal University), Ministry of Education, Xi'an, 710062, PR China*
[b] *School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, 710062, PR China*

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ABSTRACT

Graphene with flexible holey structure (HRGO) is firstly prepared by a wet chemical method in mild acid oxidation, and then graphene/manganese oxide hybrid nanocomposite with holey structure (HRGO/α–MnO_2) is prepared by hydrothermally treating an isopropyl alcohol suspension of HRGO, $MnCl_2 \cdot 4H_2O$, and $KMnO_4$ at 90 °C for 1 h. α–MnO_2 with needle–like morphology is uniformly dispersed on the surface of HRGO nanosheets, which prevents the restacking of the graphene nanosheets and allows graphene nanosheets to exist in a complete exfoliation state in HRGO/α–MnO_2 hybrid material. The self–assembly between HRGO nanosheets and α–MnO_2 particles can increase the specific surface area of the prepared material (about 196 $m^2\,g^{-1}$). The HRGO nanosheets improve the utilization efficiency of α–MnO_2 in the hybrid electrode, while the holey structure provides a high density of porosity to facilitate charges and ions transport. The prepared electrode material exhibits a high specific capacitance of 348 F g^{-1} at 5 mV s^{-1} in 1 mol L^{-1} Na_2SO_4 electrolyte with a capacitance retention of 86% after 1000 cycles at a constant current density of 10 A g^{-1}. This preparation method may open new opportunity for preparing other types of graphene–based hybrid materials for technological applications.

1. Introduction

With the environmental problem increase and the depletion risk of fossil fuels, there is an urgent need for efficient, clean, and sustainable source of energy, as well as new technology associated with energy conversion and storage [1]. Electrochemical capacitors (ECs) are considered as the most effective and practical technology one of the energy conversion and storage [2]. In comparison with conventional dielectric capacitors, ECs offer a promising approach to meet the increasing power demands of energy storage systems in the twenty first century due to the high power capability and relatively large energy density [3–7]. Moreover, ECs can bridge the critical performance gap between the energy density of battery and high power density of conventional dielectric capacitor, which makes the rapid storage and release of energy become possible [8]. Research results indicate that the capacitive property of the ECs is strongly affected by the electrode materials, electrolyte, and the assembled devices, with the most important factor being the electrode materials [9]. Many efforts have been devoted to design advanced new materials for high–performance and manufacture of electrochemical supercapacitors [10–12].

Although great progress in the theoretical and practical research and development of ECs has been yielded by a large number of research articles and technical reports [13–18], ECs still suffer from the low energy and high production cost. In order to increase the energy density of ECs while retaining their intrinsic high power density, many researchers have focused attention on the development of the new electrode materials including carbon–based nanostructures and transition metal oxides. In the carbon–based electrode, energy is stored based on the electrical double layer capacitance at the interface of the electrode/electrolyte. In this case, ECs usually display excellent rate capability, good reversibility, and superior stability, but their capacitance values are not high [19,20]. On the other hand, pseudocapacitor is stored energy through fast Faraday redox reaction for transition metal oxide electrodes. Although the transition metal oxide electrodes show high specific capacitances, most of them suffer from poor rate capability and reversibility during the charge/discharge process [21–23]. Therefore, carbon–metal oxide hybrid electrode materials are given wide attentions, and the electrodes with high capacitive performance and good stability will be expected.

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[*] Corresponding author. Tel.: +86 29 81530716; fax: +86 29 81530702.
E-mail address: zhliu@snnu.edu.cn (Z.-H. Liu).

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Graphene (RGO) is a unique carbon material with potential for electrochemical energy storage device applications due to its high thermal and chemical stabilities, large theoretic surface area, and high electrical conductivity [24]. It can be used to improve the electrical conductivity of the electrode materials by improving the electron transfer from the graphene nanosheets [25]. However, the capacitive behavior of pure RGO is much lower than its theoretic value because of the agglomeration during preparation [26]. In order to improve the low power output of the graphene electrodes, vertically oriented design of graphene stacks with a preponderance of exposed edge planes and enlarged interlayer space is constructed [27,28]. Also for the sake of large specific surface area and high capacity of graphene, graphene nanosheets with holey structure have been prepared by a wet chemical method combined ultrasonic vibration and mild acid oxidation, and the holey graphene can provide a high density of porosity to facilitate charges and ions transport [29]. Moreover, in order to improve the capacitance of RGO while retaining its good charge transport and electrical conductivity, a series of metal oxides are doped on the RGO surface and many promising RGO/metal oxide hybrid electrode materials have been prepared [30–32]. As one of the potentially excellent electrode materials in supercapacitors, manganese dioxide shows a potential application due to its low cost, relatively environmentally benign properties, and high theoretical specific capacitance ($\sim$1370 F g^{-1}) [33]. However, the bulk manganese oxides have a small specific surface area and low electrical conductivity, which largely limit their application as the electrode materials of electrochemical capacitors [34]. Therefore, graphene/manganese oxide hybrid electrode materials with high specific capacitance and high electrical conductivity are expected to be obtained.

In the present work, HRGO/MnO_2 hybrid electrode with flexible holey structure (HRGO/α–MnO_2) was fabricated through a simple soft chemical route and followed by hydrothermal treatment. The electrochemical properties of the prepared HRGO/α–MnO_2 electrodes were characterized by cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) in 1 mol L^{-1} Na_2SO_4 electrolyte. α–MnO_2 with needle–like morphology was loaded on the surface of the graphene nanosheets with flexible holey structure, which could significantly improve the electrical performance of RGO/α–MnO_2 hybrid electrodes.

2. Experimental

2.1. Materials preparation

Graphite oxide (GO) was prepared from natural graphite by a modified Hummer's method [35]. The as–prepared GO was then treated by ultrasonication treatment using a KQ–600kDE Digital Ultrasonic cleaning device (600 W, 80% amplitude) in a water bath for 2 h at room temperature to better evenly dispersed, GO homogeneous dispersion (0.5 mg mL^{-1}) was obtained. The prepared GO homogeneous dispersion (0.5 mg mL^{-1}, 150 mL) was dispersed in a mixed acid solution (300 mL) containing a mixed solution of 70% concentrated HNO_3 (60 mL) and 83% concentrated H_2SO_4 (240 mL). After ultrasonic treatment of the suspension at room temperature for 6 h (600 W, 70% amplitude), a holey graphite oxide (HGO) was obtained. HGO homogeneous dispersion (0.5 mg mL^{-1}, 300 mL) was mixed with a solution of hydrazine solution (0.21 mL) and ammonia solution (2.4 mL) and followed by stirring for 10 min, then heated at 95 °C, and stirred for 1 h. HGO was reduced into graphene with holey structure (HRGO) and the stable holey graphene dispersion was obtained.

Holey graphene/manganese dioxide hybrid materials (HRGO/α–MnO_2) with different mass ratios of HRGO to α–MnO_2 were prepared by a simple soft hydrothermal technology. In a typical preparation, 0.0625 g $MnCl_2 \cdot 4H_2O$ and 0.0262 g HRGO were firstly dispersed in isopropyl alcohol (12.5 mL), with ultrasonication treatment (600 W, 70% amplitude) for 1 h. Then, 0.0375 g $KMnO_4$ dissolved in 1.25 mL of deionized water was added to the above suspension. After being vigorously stirring for another 10 min, the obtained suspension was transferred into an autoclave and was heated at 90 °C for 1 h. Finally, the resulted precipitate was washed with distilled water for several times, dried in room temperature, and HRGO/α–MnO_2 hybrid electrode material with holey structure was obtained, which was abbreviated as HRGO(1.5)/α–MnO_2. By changing the amount of HRGO, HRGO/α–MnO_2 hybrid electrode materials with different HRGO amounts were obtained using the same procedure, and the obtained samples were abbreviated as HRGO(0.5)/α–MnO_2, HRGO(1.0)/α–MnO_2, and HRGO(2.0)/α–MnO_2, respectively. In comparison with HRGO/α–MnO_2 hybrid electrode, pure α–MnO_2 electrode material was also prepared using the same procedure.

2.2. Characterization

X–ray diffraction (XRD) measurements were carried out using a D/Max–3c X–ray diffractometer with Cu Kα (λ=0.154 nm), using an operation voltage and current of 40 kV and 30 mA, respectively. Transmission electron microscope (TEM) images were collected by using a JEM–2100 microscope. Samples for TEM observation were prepared by dispersing the material into alcohol by an ultrasonic treatment for several minutes. X–ray photoelectron spectroscopy (XPS, AXIS ULTRA Kratos Analytical Ltd.) of the as–prepared materials was performed using an Omicron ESCA probe equipped with an electron flood gun. The Al Kα radiation (1486.6 eV) was used as an excitation source, and the binding energy scale was calibrated with respect to adventitious carbon (C1s). A Beckman coulter–type N_2 adsorption–desorption apparatus (ASAP 2020 M) was used to investigate the pore property degassing at 150 °C for 6 h below 10^{-3} mmHg. Mn and K contents in samples were determined by atomic absorption spectrometry (AAS) after the obtained materials were dissolved in a mixed solution of HCl and H_2O_2.

2.3. Electrochemical measurement

An IVIUMSTAT electrochemical workstation (Ivium Technologies BV Co., Holland) was used for electrochemical measurement. Electrodes were prepared by mixing the obtained materials (90 wt%) as active materials with acetylene black (5 wt%) and polyvinylidene fluoride (5 wt%). The first two components were mixed together to obtain a homogeneous powder. Then the polyvinylidene fluoride solution (0.02 g mL^{-1}, in N–methyl–ketopyrrolidine) was added and grinded evenly. A rubber–like paste was eventually obtained, then it was coated on a Ni mesh (typical surfaces: 2 cm^2). The mesh was dried at 110 °C in air for 12 h for removal of the solvent. The loading mass of each active material was about 2–3 mg.

The cyclic voltammetry (CV), galvanostatic charge–discharge test, and the electrochemical impedance spectroscopy (EIS) were conducted in above work system. CV tests were performed at a potential window of −0.2–0.8 V with different scan rates in 1 mol L^{-1} Na_2SO_4 solution. Galvanostatic charge–discharge curves were measured at different current densities and EIS measurements were done in a frequency range from 100 kHz to 0.01 Hz at open circuit potential with an alternating current perturbation of 5 mV [36]. The specific capacitance C (F g^{-1}) of the electrode was determined by means of galvanostatic charge–discharge cycles and cyclic voltammetry (CV) as follows:

$$C = {}^{It}\!/_{(\Delta V)m} \qquad (1)$$