



Facile fabrication of graphene/nickel oxide composite with superior supercapacitance performance by using alcohols-reduced graphene as substrate



Peng Deng^a, Haiyan Zhang^{a,b,*}, Yiming Chen^{a,b}, Zhenghui Li^a, Zhikun Huang^a, Xingfa Xu^a, Yunyong Li^{a,b}, Zhicong Shi^{a,b}

^a School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, PR China

^b Guangdong Provincial Key Laboratory of Functional Soft Condensed Matter, Guangzhou 510006, PR China

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ABSTRACT

Graphene/nickel oxide composite (G/NiO) was synthesized through a facile hydrothermal method and subsequently microwave thermal treatment by using alcohols-reduced graphene as substrate. The as-prepared G/NiO was characterized by X-ray diffraction, Raman spectra, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscope and transmission electron microscope. The results indicate that the graphene oxide has been successfully reduced to graphene, and NiO nanoparticles are homogeneous anchored on the surface of graphene, forming a globule-on-sheet structure. The loading content of NiO nanoparticles anchoring on the surface of graphene nanosheets can be controlled by adjusting the hydrothermal temperature. The G/NiO displays superior electrochemical performance with a specific capacitance of 530 F g^{-1} at 1 A g^{-1} in 2 M of NaOH. After 5000 cycles, the supercapacitor still maintains a specific capacitance of 490 F g^{-1} (92% retention of the initial capacity), exhibiting excellent cycling stability.

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1. Introduction

Graphene, as a new type of two-dimensional material, has attracted tremendous attention due to its outstanding properties, including high electrical conductivity, large specific surface area and high mechanical strength [1–3]. Benefiting from such structural features, nowadays graphene has become one of the most ideal electrode materials in supercapacitor. However, there are still several inevitable drawbacks of graphene, leading to a relatively poor performance and limiting its further application [4–9]. First, chemical reduction of graphene oxide (GO) is an important method for the mass production of graphene, but most of the reduction agents such as hydrazine, hydroquinone and NaBH_4 are toxic and irritant [1]. Second, the lower energy storage capacitance of graphene compared with that available from metal oxide, cannot meet the demand of next-generation supercapacitor [10–13]. Thus, seeking a convenient and pollution-free reduction method and exploring high-energy graphene-based electrode materials are critical and urgent for the further application of graphene.

Recently, it is reported that alcohols such as methanol (MeOH), ethanol (EtOH), and benzyl alcohol (BnOH), can be used as reducing agent for GO to prepare graphene in a facile hydrothermal process [14]. Alcohols reduction method is low toxicity and environment-friendly, presenting great potential for the manufacture of graphene in large scale. Daniel et al. demonstrated that BnOH is the most effective reducing agent. BnOH-reduced graphene presents higher carbon-to-oxygen ratio and powder conductivity, which is significant for the application in energy storage devices.

Transition metal (hydro)oxides/graphene composites are reported to be potential electrode materials for supercapacitors due to their superior electrochemical performance [2]. Transition metal (hydro)oxides can supply redox reaction sites and high energy. On the other hand, graphene can enhance the electrical conductivity of electrode materials and also act as a barrier to prevent the aggregation of metal (hydro)oxides particles during charge–discharge process. The synergistic effect between graphene and metal (hydro)oxides particles makes the composites reveal high capacitance and good cycling stability.

Nickel oxide (NiO), as one of the transition metal oxides which can provide pseudocapacitance, had received great attention owing to its high theoretical specific capacitance (2573 F g^{-1}) and

* Corresponding author at: School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, PR China. Tel./fax: +86 20 39322570.

E-mail address: hyzhang@gdut.edu.cn (H. Zhang).

low cost [15]. In recent years, various methods were used to prepare graphene/NiO composites as electrode materials for supercapacitors. Huang et al. [15] prepared porous NiO-graphene hybrid film by a facile strategy combining the “on-water spreading” method and the chemical bath deposition. Zhao et al. [16] prepared graphene nanosheet/NiO nanocomposite by using a controlled refluxing and subsequent annealing. Chen et al. [17] prepared the graphene/nickel oxide (G/NiO) composites via a hydrothermal route using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the as-prepared graphene as starting material. However, the above methods are always complex as it needs extra step for preparing graphene.

In this paper, we develop a facile, effective and environment-friendly method for the fabrication of graphene/nickel oxide composite (G/NiO) using a hydrothermal method with BnOH as a reducing agent for GO. BnOH can not only effectively reduce the GO to graphene but also act as a “surfactant”, which is beneficial for the dispersion of NiO nanoparticles onto the graphene. Therefore, the obtained G/NiO presents a stable globule-on-sheet structure and demonstrates a superior supercapacitance performance.

2. Experimental and characterization

2.1. Preparation of G/NiO composite

Graphite oxide (GO) was prepared through a modified Hummers method [18]. The nanocomposites were fabricated by combining hydrothermal synthesis and subsequent microwave treatment. In a typical preparation process, 3 g of GO was dispersed into 1 L deionized water under ultrasonic condition. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution (10 g L^{-1}), BnOH and GO aqueous solution with a molar ratio of 0.2:1:1 were mixed under continuous stirring and sonication. And then the mixture was poured into an autoclave and heated at 100, 150, 200 and 250 °C for 6 h, respectively. The hydrothermal products (denoted as G/Ni(OH)₂-100, G/Ni(OH)₂-150, G/Ni(OH)₂-200 and G/Ni(OH)₂-250) were dried at 70 °C for 12 h, and were further heat treated in an industrial microwave oven at 300 °C for 1 min in ambient condition. Finally, the G/NiO composites were obtained and designated as G/NiO-100, G/NiO-150, G/NiO-200 and G/NiO-250 according to the hydrothermal temperature. For comparison, the G/NiO-200 (200 °C) was also prepared without BnOH under the same condition. To study the reduction effect of BnOH, GO was treated in hydrothermal condition at the temperature of 200 °C with/without the addition of BnOH. The hydrothermal products were labeled as rGO (with BnOH) and rGO' (without BnOH).

2.2. Structural characterization

X-ray diffraction (XRD; DMAX-Ultima IV, Rigaku Corporation, Japan) and Fourier transform infrared (FTIR; Nicolet 380, Nicolet, USA) were used to identify the chemical bands and the crystal structure of the obtained samples. The morphology of the samples were observed by scanning electron microscope (SEM; S-4800, Hitachi, Japan) and high-resolution transmission electron microscopy (HRTEM; JEM-2100F, Jeol, Japan), respectively. Raman spectra (Renishaw 2000 Confocal Raman Microprobe; Renishaw Instruments, UK) were employed to analyze the molecular vibration mode and defect of samples. X-ray photoelectron (XPS;

Amicus, Shimadzu, Japan) was used to identify the chemical state and the reduction degree of G/NiO composite. The weight percentage of NiO in the G/NiO composites was determined by thermal gravity analysis (TGA; SDT 2960, TA Instruments, American) in a temperature range of 20–700 °C at a ramp rate of 20 °C min⁻¹ in the dry air.

2.3. Electrochemical measurements

The supercapacitor electrodes were prepared by pasting the mixture of the obtained G/NiO composite, acetylene black and polytetrafluoroethylene (PTFE) with a weight ratio of 8:1:1 onto nickel foam. A 2 M NaOH aqueous solution was used as the electrolyte. The electrochemical properties of the packaged button-type supercapacitor were analyzed by cyclic voltammetry (CV), galvanostatic charge/discharge measurements (GCD) and electrochemical impedance spectroscopy (EIS). The CV measurements and EIS test were performed on a CHI660e electrochemical workstation (Chen hua, Shanghai, China) with potential from 0 to 1.0 V at the scan rate of 10 mV s⁻¹. The cycle performance was tested by a LAND battery tester (CT2001A, Wuhan LAND Corporation, China) at the current density of 1 A g⁻¹. Meanwhile, the rGO electrode was tested under the same condition as that of G/NiO composites for comparison.

3. Results and discussion

Fig. 1a shows the XRD patterns of GO, rGO, and G/NiO-200 before and after microwave thermal reduction. A characteristic peak at 11.4° can be seen from the XRD pattern of GO, which corresponds to the interlayer spacing (001) of 0.804 nm. In addition, rGO had a broad characteristic peak at 25.0°, corresponding to interlayer spacing (002) of 0.375 nm. The decreased interlayer spacing from 0.804 to 0.375 nm was attributed to the removal of bulk of oxygen functional groups from the GO sheets, indicating that GO has been successfully reduced to rGO by BnOH [1]. G/Ni(OH)₂-200 has the same diffraction peak as rGO at 25.0°. Meanwhile, the characteristic peaks at 11.4°, 22.8° and 34.2° are in good accordance with the (001), (002) and (101) crystal planes of α -Ni(OH)₂, respectively [19]. After microwave heat treatment at 300 °C, three new peaks are observed at 37.3°, 43.3° and 62.9°, which can be assigned to the (111), (200) and (220) crystal planes of cubic NiO (JCPDS No.47-1049), respectively [20,21]. This indicates that α -Ni(OH)₂ is converted to NiO during the microwave heat treatment. Fig. 1b shows the XRD patterns of hydrothermal product of rGO and rGO'. The two samples both have an obvious diffraction peak at 25.0° suggesting that they have been reduced. However the diffraction of rGO is much narrower than that of the rGO', indication of a higher degree of graphitization. It can be deduced that more functional groups were released in the presence of reducing agent BnOH, and then the stack of graphene layers is more compacted, presenting a lower interlayer spacing, and higher degree of graphitization [22,23].

Raman spectroscopy was used to analyze the molecular vibration mode and defect of samples. Fig. 2 shows the Raman spectra

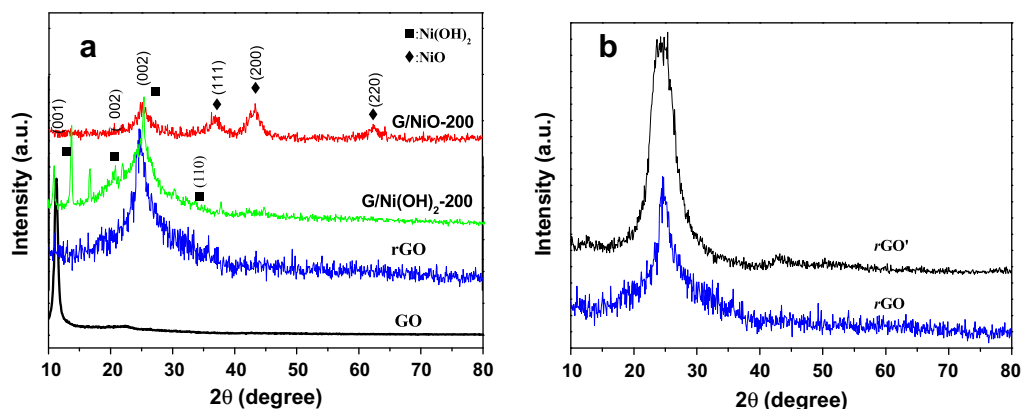


Fig. 1. XRD patterns of (a) GO, rGO, G/Ni(OH)₂-200 and G/NiO-200, and (b) rGO and rGO'.

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