



Functionalized graphene nanosheets decorated on carbon nanotubes networks for high performance supercapacitors

Bing Ding^a, Dong Guo^a, Yahui Wang^a, Xiaoliang Wu^{a,*}, Zhuangjun Fan^b

^a Department of Chemistry, College of Science, Northeast Forestry University, 26 Hexing Road, Harbin, 150040, PR China

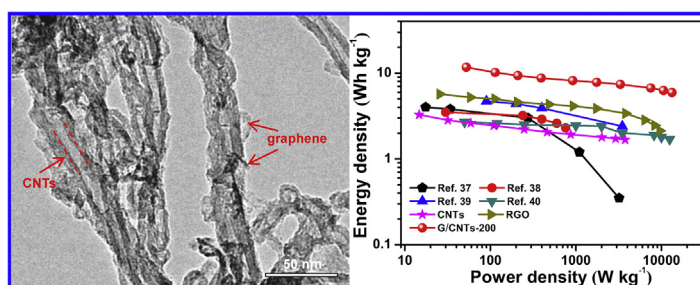
^b Key Laboratory of Superlight Materials and Surface Technology, Ministry of Education, College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin, 150001, PR China



HIGHLIGHTS

- G/CNTs-200 is consisted of 1D carbon nanotubes and 2D graphene nanosheets.
- G/CNTs-200 delivers high specific capacitances and good rate performance.
- The symmetric supercapacitor delivers high energy density.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Carbon nanotubes
Graphene nanosheets
Oxygen functional groups
Supercapacitor

ABSTRACT

We report a simple and convenient method for the synthesis of functionalized graphene nanosheets/carbon nanotubes networks (G/CNTs-200) through chemical oxidation followed by low temperature treatment reduction. The G/CNTs-200 sample has the unique hybrid structure consisting of 1D carbon nanotubes as the continuous conductive networks and 2D functionalized graphene nanosheets as pseudocapacitive materials. Significantly, such unique hybrid structure ensures high surface area and suitable oxygen functional groups without obviously sacrificial conductivity. As a result, the G/CNTs-200 electrode exhibits a specific capacitance of 202 F g^{-1} at a current density of 0.5 A g^{-1} , which is almost five times higher than that of pure CNTs (40 F g^{-1}). Interestingly, it can keep a high capacitance retention ratio of 60% at a current density of 50 A g^{-1} in 6 mol L^{-1} KOH aqueous electrolyte. More importantly, a symmetric device based on G/CNTs-200 electrodes delivers an energy density of 11.7 Wh kg^{-1} and excellent electrochemical stability in 1 mol L^{-1} Na_2SO_4 aqueous electrolyte. Therefore, this work holds a great promise for the design and large-scale production of CNTs-based electrode materials for high performance supercapacitors.

1. Introduction

Owing to their fast charge-discharge characteristic, high power density, and excellent electrochemical stability, supercapacitors have drawn considerable attention around the world in recent years [1–4]. Among various electrode materials, carbon materials are widely used as

electrode materials for supercapacitors due to their large surface area, moderate cost and excellent chemical stability [5–9]. It is well known that the electrochemical performance of carbon materials is mainly determined by the specific surface area and pore size distribution, as well as the surface characteristic of carbon materials. Generally, activated carbon materials (ACs) have a high surface area range from 2000

* Corresponding author.

E-mail address: wuxiaoliang90@163.com (X. Wu).

<https://doi.org/10.1016/j.jpowsour.2018.07.063>

Received 27 April 2018; Received in revised form 28 June 2018; Accepted 15 July 2018

0378-7753/ © 2018 Elsevier B.V. All rights reserved.

to $3000 \text{ m}^2 \text{ g}^{-1}$ by physical and/or chemical activation. However, with an increase of specific surface area, the conductivity of ACs becomes worse, resulting in poor rate performance and power density.

Graphene has been considered as the promising electrode material for supercapacitors because of its excellent electrical conductivity and large theoretical specific surface area [10–13]. Compared with ACs, the high specific surface area of graphene mainly comes from the solid surface. Unfortunately, graphene usually suffers from the irreversible aggregation due to the strong interlayer van der Waals force and dramatically decreases the surface area, thus resulting in low specific capacitance. Additionally, the high manufacturing cost and complex production process seriously restrict its commercial application [14–17]. Carbon nanotubes (CNTs) possess readily accessible surface area, straight large pore channels, excellent electrical conductivity and moderate cost, enabling them to be regarded as the candidate for high power electrode materials [6]. However, CNTs materials usually exhibit unsatisfactory specific capacitances due to their relative low surface area (generally $< 200 \text{ m}^2 \text{ g}^{-1}$) [18–22]. Recent studies have developed to longitudinally unzip CNTs into graphene nanoribbons through chemical oxidation method [23–25]. After chemical oxidation, the surface of graphene nanoribbons contains a large number of oxygen-containing functional groups, which can provide extra pseudocapacitance during charge-discharge process [26–28]. However, the introduction of massive oxygen functional groups and the destruction of tubular structures often lead to poor electrical conductivity, and thus resulting in poor rate performance and power density.

Herein, we report a simple and convenient method for the synthesis of functionalized graphene nanosheets/carbon nanotubes networks (G/CNTs-200) through chemical oxidation followed by low temperature treatment reduction. Benefiting from its unique hybrid structure consisting of 1D carbon nanotubes as the continuous conductive networks and 2D functionalized graphene nanosheets as pseudocapacitive materials, the G/CNTs-200 electrode exhibits high specific capacitance (202 F g^{-1} at a current density of 0.5 A g^{-1}) and good rate performance (retain 60% at a high current density of 50 A g^{-1}) in 6 mol L^{-1} KOH aqueous electrolyte. In addition, a symmetric device based on G/CNTs-200 electrodes delivers an energy density of 11.7 Wh kg^{-1} and excellent electrochemical stability (102% of its initial capacitance after 20,000 cycles) in 1 mol L^{-1} Na_2SO_4 aqueous electrolyte.

2. Experimental section

2.1. Synthesis of functionalized graphene nanosheets/carbon nanotubes networks

0.3 g CNTs were added into 60 mL concentrated H_2SO_4 and stirred for 30 min. Then, 1.8 g KMnO_4 was slowly added into the above suspension and stirred for 6 h at room temperature. Next, 300 mL distilled water containing 20 mL of 30% H_2O_2 was slowly added into the above suspension under vigorous stirring. The suspension was stirred for 12 h at room temperature. Then, the mixture was washed with deionized water to neutral and then freeze-dried. The obtained sample was denoted as G/CNT. Finally, the G/CNT samples were sealed in a tubular furnace and heated at different temperatures (200, 300, 600 and 800) for 2 h under the N_2 flow, and the obtained sample was denoted as G/CNT-x, where x refers to the temperature of heating. For comparison, samples prepared at different reaction times (4 h and 8 h) were prepared under the same conditions as described with G/CNT, the obtained sample was denoted as G/CNT-4h and G/CNT-8h. Samples prepared with different mass of potassium permanganate (2.4 g) were prepared under the same conditions as described with G/CNT, the obtained sample was denoted as G/CNT-1-8.

2.2. Synthesis of hydrazine reduced graphene

Graphene oxide (GO) was synthesized from purified natural

graphite (300 μm , Qingdao Graphite Company) by a modified Hummers method [29]. In a typical procedure for chemical conversion of GO to graphene, the GO dispersion (1 mg mL^{-1} , 100 mL) was adjusted to $\text{pH} = 10$ using sodium hydroxide and mixed with 20 mL of hydrazine solution, then the suspension refluxed at $100 \text{ }^\circ\text{C}$ for 24 h. Finally, the solid was filtered, and washed several times with distilled water and alcohol, dried at $100 \text{ }^\circ\text{C}$ for 12 h in a vacuum oven.

2.3. Material characterization

The morphology and microstructure of the obtained samples were investigated by transmission electron microscope (TEM, JEOL JEM2010). Structural characterization of samples was measured by Raman spectrometer (Jobin-Yvon HR800) with the wavelength of 458 nm. X-ray photoelectron spectroscopy (XPS) measurements were performed by a PHI5700ESCA spectrometer using a monochromatic ($\text{K}\alpha$ radiation) source. FTIR spectroscopy investigated by a Perkin-Elmer Spectrum 100 spectrometer in a range of $500\text{--}4000 \text{ cm}^{-1}$. Nitrogen adsorption/desorption isotherms were measured on a NOVA 2000 (Quantachrome, USA). The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method.

2.4. Electrochemical characterization

The mixture containing 75 wt% electroactive material, 20 wt% carbon black and 5 wt% poly (tetrafluoroethylene) were added into ethanol to form a slurry and then coated onto the Ni foam ($1 \text{ cm} \times 1 \text{ cm}$) and dried under vacuum at $80 \text{ }^\circ\text{C}$ for 12 h. The mass loading of the electrode materials was about 3 mg cm^{-2} . The electrochemical measurements of the individual electrode were carried out using a three-electrode cell in 6 mol L^{-1} KOH aqueous electrolyte. Ni foam coated with electroactive materials, platinum foil and Hg/HgO electrode were used as the working electrode, the counter and reference electrodes, respectively. CV tests of the three-electrode system were recorded between -1 and 0 V (vs. Hg/HgO) at various scan rates. Galvanostatic charge-discharge was performed in the same potential range of CV test at the current densities ranging from 0.5 to 50 A g^{-1} . Electrochemical impedance spectra (EIS, Nyquist plots) were carried out at an open circuit potential of 5 mV and a frequency range of $0.01 \text{ Hz--}100 \text{ kHz}$. The symmetrical supercapacitor device was fabricated with two G/CNTs-200 electrodes with the same mass (both positive and negative electrodes are made of the G/CNTs-200 electrode materials) and separated by a glassy fibrous separator. The whole system was immersed in 1 mol L^{-1} Na_2SO_4 aqueous electrolyte for electrochemical measurements. All of the above electrochemical measurements were performed by a CHI 660 E electrochemical work station at room temperature.

The gravimetric specific capacitance of the single electrode was calculated through the following equation:

$$C = \frac{I\Delta t}{m\Delta V} \quad (1)$$

Where I is the current density, Δt is the discharge time, ΔV is the discharge potential, and m is the mass of the electroactive materials.

The gravimetric specific capacitance, energy density (E) and power density (P) of the symmetric supercapacitor were calculated based on the following equations:

$$C = \frac{\int IdV}{\nu mV} \quad (2)$$

$$E = 0.5CV^2 \quad (3)$$

$$P = E/\Delta t \quad (4)$$

Where I is the current density, V is the working potential, ν is the scan

Download English Version:

<https://daneshyari.com/en/article/7724735>

Download Persian Version:

<https://daneshyari.com/article/7724735>

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