



# Nitrogen-doped graphene prepared by pyrolysis of graphene oxide/polyaniline composites as supercapacitor electrodes

Wen-Dong Wang, Xiao-Qiang Lin, Hai-Bo Zhao, Qiu-Feng Lü\*

College of Materials Science and Engineering, Fuzhou University, 2 Xueyuan Road, Fuzhou 350116, People's Republic of China

## ARTICLE INFO

### Article history:

Received 11 July 2015

Received in revised form 11 April 2016

Accepted 17 April 2016

Available online 22 April 2016

### Keywords:

Nitrogen-doped graphene

Pyrolysis

Polyaniline

Supercapacitor

## ABSTRACT

Three polyaniline/graphene oxide (PANI/GO) composites were fabricated by means of an in-situ polymerization of aniline monomers in the presence of graphene oxide (GO). And then, nitrogen-doped graphene was prepared by pyrolysis of the PANI/GO composite. The structures and morphologies of the samples were characterized by using different techniques, and the electrochemical performances of the nitrogen-doped graphene samples were further investigated. When PANI/GO10 (the GO feed content in PANI/GO is 10 wt.%) was used as a precursor, and the pyrolysis temperature is 800 °C, nitrogen content of the as-prepared nitrogen-doped graphene (i.e., NG10-800) is 9.2 at.%. The specific capacitance of NG10-800 is up to 206 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup>, indicating an excellent electrochemical performance. After 1000 cycles at a scan rate of 50 mV s<sup>-1</sup>, the capacitance retention of NG10-800 is about 92.5% of the initial value, suggesting an excellent cycling stability.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Supercapacitors, as devices to store charges in the electrode/electrolyte interface, arouse considerable interests due to their outstanding performances such as fast charge-discharge rate, long cycle life, high power density as well as high reliability. As a new member of various carbon materials, graphene has drawn much attention in the energy storage devices due to its remarkable physical and chemical properties such as excellent electrical and thermal conductivity, high surface area, super mechanical property and good chemical stability. More significantly, when used as a supercapacitor, the ideal specific capacitance value of graphene can reach up to 550 F g<sup>-1</sup> [1,2], if the whole surface area (2675 m<sup>2</sup> g<sup>-1</sup>) develops its full potential. However, the individual graphene nanosheets are prone to restack due to the strong interaction between graphene layers, with the surface area of final product decreasing, which limits electron and ion transport, leading to poor specific capacity of graphene. In order to avoid the restacking problem, various methods have been applied to prepare graphene with different structures, such as graphene foam, graphene fiber, and three-dimensional graphene. The efficient method is to introduce foreign stuff including metal oxides, small organic molecules [3,4], and conducting polymers [5] into the layers of graphene sheets, because of the hydrogen bond interactions or  $\pi$ - $\pi$  stacking

effects between graphene sheets and foreign materials. However, the introduced materials would fall from graphene during the repetitive electrochemical behavior, resulting in the aggregation of graphene and poor cycling stability.

Incorporating heteroatoms into graphene lattice is another efficient method to modify the structure and property of graphene [6,7]. Among different kinds of doped graphene, nitrogen-doped graphene has been given special attention. Theoretical computational study clearly demonstrated that nitrogen doping can lead to significant enhancement in capacitance and electrocatalytic activity of the graphene electrode [8,9]. Recently, nitrogen-doped graphene has been widely studied in applications such as supercapacitors [10–12], Li-ion batteries [13,14], catalysts for oxygen reduction reaction [15,16], catalyst supports [17,18], and adsorbents [19]. Simple methods to obtain nitrogen-doped graphene are through high temperature pyrolysis [20–25] or hydrothermal reaction [26] processes. High temperature pyrolysis is usually carried out via carbonization treatment of graphene oxide at atmospheric pressure in the presence of nitrogen sources. The nitrogen sources of high temperature pyrolysis method are usually urea [20,21], melamine [22], ammonia [23,24], polypyrrole [25] and so on. The introduction of nitrogen atoms into the graphene lattice can tune the electronic structure of graphene, realizing the improved electrochemical performance.

Polyaniline (PANI), as a low cost conducting polymer, has attracted great attention in the field of graphene-based composite electrodes for supercapacitors. However, most of the PANI/graphene composites usually only fabricated without fur-

\* Corresponding author.

E-mail addresses: [qiufenglv@163.com](mailto:qiufenglv@163.com), [qiufenglvfzu@gmail.com](mailto:qiufenglvfzu@gmail.com) (Q.-F. Lü).

ther treatment, so that the composite had a poor cycle stability because of the shrinkage and swelling of PANI during practical usage [27]. To solve this problem, through simple pyrolysis of graphene oxide/PANI multilayer wrapped polystyrene nanospheres, nitrogen-doped graphene hollow spheres have been successfully prepared as a supercapacitor electrode material [28], which possess unique hollow structure and nitrogen content about 8.7 at.%. The synergistic effect of hollow nanostructure and nitrogen doping makes a high specific capacitance of this electrode material. In addition, PANI as a low cost nitrogen source, can also be used to prepare nitrogen-doped graphene [29] and nitrogen-doped porous carbon [30].

In this work, uniformed polyaniline/graphene oxide (PANI/GO) composites, in which PANI nanorods arrayed on both sides of GO sheets, was firstly prepared via an in-situ polymerization by optimizing the GO feed contents. Then, the PANI/GO composite as a precursor was directly carbonized at desired temperature to obtain nitrogen-doped graphene (NG). Compared with other nitrogen-doped graphene prepared from a mixture of PANI and graphene oxide, this NG samples were highly dispersed, and the graphene sheets were uniformly covered with a layer of carbon nanorods from pyrolytic PANI. Moreover, the NG samples exhibits excellent electrochemical behaviors, and shows great promise for use as supercapacitor electrodes.

## 2. Experimental

### 2.1. Materials

Aniline was obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and purified by distillation under reduced pressure prior to use. Expansive graphite (100 meshes), sulphuric acid ( $\text{H}_2\text{SO}_4$ ), potassium permanganate ( $\text{KMnO}_4$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), ammonium persulfate (APS), and other solvents were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used without further treatment.

### 2.2. Preparation of PANI/GO

Graphene oxide (GO) was prepared from expansive graphite by a modified Hummers' method [31,32], followed by ultrasound treatment. PANI/GO was synthesized by in-situ polymerization of aniline monomers on both sides of GO in the solution. The typical polymerized procedure of PANI/GO10 (GO feed content of 10 wt.%) was performed as follows: 0.186 g GO was first dispersed in 70 mL of HCl (1.0 M) aqueous solution with the aid of ultrasonic wave. Then, 1.83 mL aniline was added into the above solution and stirred for 30 min. Meanwhile, 4.564 g APS was dissolved into another 30 mL of HCl solution and kept in an ice water bath for 30 min to obtain the oxidant solution. Then, the APS solution was added into the mixture of GO and aniline in drops. Subsequently, the final mixture was statically kept in the ice water bath for 24 h, with the color of the mixture gradually turning from yellow into dark green. The final product was washed with deionized water until the filtrate turned into colorless and then dried at 60 °C for 24 h under vacuum. The product was denoted as PANI/GO10. When the GO feed contents was 15 wt.% and 30 wt.%, PANI/GO15 and PANI/GO30 composites were prepared according to the same procedure above. Pure PANI was synthesized according to the same procedure in the absence of GO. The fabrication procedure of PANI/GO was shown in Scheme 1.

### 2.3. Carbonization of PANI/GO

In a typical pyrolysis experiment, PANI/GO was placed in a closed crucible, and then the sample was heated up to 800 °C by programmed temperature control method with a heating rate of

3 °C min<sup>-1</sup> under nitrogen flow, and kept at 800 °C for 2 h. When PANI/GO10, PANI/GO15 and PANI/GO30 were used as precursors, the obtained products were labelled as NG10-800, NG15-800 and NG30-800, respectively. In addition, pure GO and PANI were treated under the same condition in order to prepare rGO and P-800. Furthermore, NG10-700 and NG10-900 samples were obtained from PANI/GO10 at 700 °C and 900 °C for 2 h, respectively.

### 2.4. Characterization

Morphological measurements of the samples were performed using a field emission scanning electron microscopy (FE-SEM, Carl Zeiss ULTRA 55) and transmission electron microscopy (TEM, FEI TECNAI F20). FT-IR spectra were recorded on a Nicolet FT-IR 5700 spectrophotometer in KBr pellets. Raman spectra were performed on a confocal Raman spectrometer (LabRAM HR UV-NIR, HORIBA Jobin-Yvon) with an excitation wavelength of 532 nm. Wide-angle X-ray diffraction scan was obtained using an Ultima III X-ray model diffractometer (Rigaku, Tokyo, Japan) with Cu K $\alpha$  radiation at a scan rate of 10° min<sup>-1</sup> in reflection mode over a 2 $\theta$  range from 5° to 90°. The X-ray photoelectron (XPS) spectra were measured on an X-ray photoelectron spectrometer (ESCALAB 250, Thermo Scientific) with a monochromatic Al K $\alpha$  source (1486.6 eV) under ultrahigh vacuum. Brunauer-Emmett-Teller (BET) surface area was measured with a Quantachrome NOVA 4200e surface area detecting instrument by N<sub>2</sub> adsorption at 77.3 K. Pore size distribution was calculated using BJH (Barrett-Joyner-Halenda) method.

### 2.5. Electrochemical measurements

Electrochemical measurements were carried out using a three-electrode system in 6 M KOH electrolyte at room temperature. Ag/AgCl electrode full of saturated KCl solution and platinum wire were used as reference electrode and the counter electrode, respectively. A working electrode was fabricated by pellet method. The as-prepared sample (active material), acetylene black (as a conducting agent) and polytetrafluoroethylene (PTFE, 5 wt.%, as a binder) were firstly mixed according to mass ratio of 85:10:5. Then, the mixture was ground with tiny amounts of deionized water in a mortar to form a homogeneous paste. The paste (1 cm × 1 cm) containing about 5 mg active material was covered with two pieces of foam nickel current collector, then pressed with a pressure of 10 MPa, and finally dried in a vacuum oven at 60 °C for 12 h. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectra (EIS) were measured on a CHI660E electrochemical workstation (Chenhua Instruments Co, Shanghai, China). CV was carried out in a voltage range from at different scan rates. GCD measurements were measured from -1.0 to 0 V at current densities of 0.1, 0.2, 0.5 and 1.0 A g<sup>-1</sup>. The specific capacitance (F g<sup>-1</sup>) was calculated from GCD curves according to the following equation:

$$C_s = \frac{I \times \Delta t}{\Delta V \times m}$$

where  $I$  is the current of the charge-discharge process (A),  $\Delta t$  is the discharge time (s),  $\Delta V$  is the potential change during the discharge process (V),  $m$  is the mass of active material in a single electrode (g). EIS was obtained in the swept frequency range from 10<sup>5</sup> to 0.01 Hz at open circuit potential with AC voltage amplitude of 5 mV. The cycle stability of electrode material was carried out using CV at a scan rate of 50 mV s<sup>-1</sup> for 1000 cycles.

Download English Version:

<https://daneshyari.com/en/article/1196525>

Download Persian Version:

<https://daneshyari.com/article/1196525>

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