



A green and efficient method to produce graphene for electrochemical capacitors from graphene oxide using sodium carbonate as a reducing agent

Yuhong Jin, Shuo Huang, Mei Zhang, Mengqiu Jia*, Dong Hu

Laboratory of Electrochemical Process and Technology for Materials, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

ARTICLE INFO

Article history:

Received 20 November 2012
Accepted 2 January 2013
Available online 9 January 2013

Keywords:

Sodium carbonate
Graphene oxide
Graphene
Electrochemical capacitors

ABSTRACT

The green and efficient synthesis of graphene using sodium carbonate (Na_2CO_3) as a chemical reducing agent was studied. Extensive characterization confirmed the formation of graphene from graphene oxide using a Na_2CO_3 solution. The C/O atomic ratio of the as-prepared graphene has increased from 2.48 to 8.15 after reduction as determined by X-ray photoelectron spectroscopy. The conductivity of as-prepared graphene sheets is as high as 10 S m^{-1} . After electrochemical measurements, gravimetric capacitances of 228 and 166 F g^{-1} at current densities of 5 and 25 mA cm^{-2} , respectively, were obtained with KOH electrolyte.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Graphene, which is a monolayer of sp^2 hybridized carbon atoms arranged in a honeycomb lattice, has given rise to intense attention due to its extraordinary electronic, thermal, optical and mechanical properties arising from its interesting two-dimensional structure [1,2]. Various applications have been demonstrated for graphene, such as nanoelectronics [3], sensors [4], supercapacitors [5], polymer composites [6], hydrogen storage [7], solar cell [8] and transparent electrode [9].

Graphene can be produced by seven different methods, including micromechanical exfoliation of graphite [1], epitaxial growth on the electrically insulating surfaces [10], chemical vapor deposition method of hydrocarbons on the transition metal substrates [11], electric arc discharge [12], direct sonication [13], unzipping carbon nanotubes [14] and solution-based graphene oxide (GO) of chemical reduction [15]. So far, the chemical reduction method has received the most attention as it is considered as the possible route for industrial production due to its simple procedure and low cost. Typically, graphene is prepared from oxidation of graphite powder by a modified Hummers method and subsequent reduction process. Many attempts have been devoted to the reduction of GO and various methods have been used. Chemical reduction of GO is considered as an effective method to produce graphene on a large-scale at low cost. Hydrazine hydrate is widely considered to be the most

efficient reduction agent to date. Unfortunately, hydrazine hydrate is highly hazardous and explosive. They also leave oxygen atoms remaining on the graphene and can introduce additional functional groups during chemical reduction, which results in a decrease of the properties of graphene [15,16]. Recently, different reducing agents have been reported to substitute hydrazine hydrate. Fernandez-Merion et al. [17] and Zhang et al. [18] reported the chemical reduction of GO using vitamin C as an ideal substitute for hydrazine. However, expensive vitamin C and long experimental time limit practical application. Therefore, it is still a great challenge to develop a green, low-cost and effective chemical reducing agent.

In this work, we report the efficient synthesis of graphene directly from GO dispersion using Na_2CO_3 as a previous unreported reducing agent. Graphene was characterized by fourier transform infrared (FT-IR) spectrometry, X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS). Electrochemical properties of as-prepared graphene were tested by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Materials and synthesis

Graphite flakes were used as received from Qingdao Ruisheng Graphite Co., Ltd. (China). Graphite oxide flakes were prepared by a modified Hummers method [19,20]. In brief, 100 mg graphite oxide

* Corresponding author. Tel.: +86 10 64413808; fax: +86 10 64413808.
E-mail address: jjmq@mail.buct.edu.cn (M. Jia).

flakes were dispersed in 50 ml water to form brown GO dispersion. This was then sonicated for 30 min, transformed to a flake and stirred with 2.0 g Na_2CO_3 dissolved with 20 ml distilled water for 4 h at 80 °C. The resulting black mixture was filtered and washed with water. Finally, the product was dried at 60 °C under vacuum for 24 h. The as-prepared graphene was named as Na_2CO_3 -graphene.

2.2. Characterization methods

Material's crystallographic structure was determined by XRD measurement with a D/Max 2500 V/PC diffractometer (Rigaku Corporation, Japan) and Cu K α targets ($\lambda = 0.154$ nm), at a scanning rate of $0.0202 \theta \text{ s}^{-1}$, chart speed of 10. Operation voltage was 40 kV and current was 100 mA. FT-IR spectra (Thermoscientific, USA) in the range of $4000\text{--}500 \text{ cm}^{-1}$. XPS was undertaken on an AXIS-NOVA analyzer (Kratos Analytical Ltd., UK), using an unmonochromated Al-K α X-ray source (1486.6 eV), where the pass energy of the hemisphere analyzer was set at 160 eV for the wide scan and 40 eV for the narrow scan, while the pass pressure and dwell time were 5.2×10^{-9} Torr and 100 ms, respectively. The thermal stability of samples was characterized using the thermal gravimetric analysis technique on a Shimadzu DTG-60AH analyzer. The measurement was carried out under N_2 atmosphere from the room temperature to 700 °C with a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$. HRTEM measures were performed on a JEM-2200 FS (JEOL, Japan) microscopy at an acceleration voltage of 200 kV. For HRTEM measurements, the aqueous solutions of the samples were ultrasonicated for 10 min followed by drop-casted onto a fresh copper grid. Optical properties of as-prepared materials were characterized by absorbance spectroscopy (UV-2501PC, Shimadzu, working in 200–900 nm range) at the room temperature. Raman spectroscopy was recorded from 800 to 3600 cm^{-1} on a Renishaw 1000 confocal Raman microprobe (Renishaw instruments) using a 514 nm argon ion laser. The electrical conductivity of graphite, GO and as-prepared graphene films was tested by four-point probe method (SB100A/2, Qianfeng).

2.3. Preparation of electrodes and electrochemical measurements

The test electrodes were prepared by mixing 85 wt% active material with 10 wt% acetylene black as a conductive agent and 5 wt% polytetrafluoroethylene dissolved in ethanol as a binder to form a slurry, coating onto a foam nickel, drying under vacuum at 60 °C for 24 h. All electrochemical experiments were carried out using a three-electrode system, in which the sample was used as the working electrode, graphite electrode as the counter, Hg/HgO electrode as a reference electrode, and 6 M KOH was used as electrolyte. GCD measurements were carried out at $5\text{--}25 \text{ mA cm}^{-2}$ rate over a voltage of $-0.7\text{--}0.3 \text{ V}$. CV was carried out at $5\text{--}50 \text{ mV s}^{-1}$ rate over a voltage of $-0.7\text{--}0.3 \text{ V}$. For EIS measurements, the frequency range was from 10^{-2} to 10^5 Hz .

3. Results and discussion

3.1. Possible reducing mechanism

Previous reports show that exfoliated graphite oxide can be deoxygenated under alkaline condition. Fan et al. [21] reports a green route to prepare graphene using NaOH or KOH as a reducing agent. Although the mechanism remains unclear, they think the deoxygenation of exfoliated GO under alkaline conditions appears to the reverse of the oxidation reaction of graphite in strong acids. This mechanism is supported by the pH dependency of this deoxygenation reaction – the higher pH of the exfoliated GO suspension, the faster the reaction. Notably, the reaction can even start at temperatures as low as 15 °C, when the pH of the suspension is high enough. Our experiment is based on this possible mechanism. We

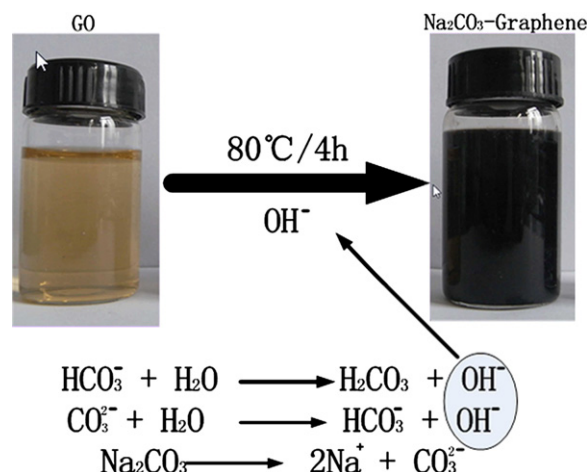


Fig. 1. Illustration of preparation of graphene based on Na_2CO_3 reduction.

use Na_2CO_3 as a new chemical reducing agent for the reduction of GO dispersion. Na_2CO_3 can produce sodium ions and carbonate ions in the aqueous solution, then carbonate ions hydrolysis and yield hydroxide ions and bicarbonate ions, and bicarbonate ions can further hydrolysis and produce hydroxide ions. The hydroxide ions can create alkaline conditions. The yellow brown color of GO rapidly darkens within 4 h in the presence of hydroxide ions at 80 °C, as shown in Fig. 1. This experimental phenomenon can prove that GO dispersion is reduced under alkaline conditions.

3.2. FT-IR characterization

Since the oxygenated functional groups are infrared active, FT-IR spectra can give a qualitative measure of the deoxygenating reaction [22]. Fig. 2 shows the typical FT-IR spectra of GO and Na_2CO_3 -graphene. The peaks at $3387, 1730, 1630, 1222, 1056 \text{ cm}^{-1}$ in the FT-IR spectra of GO are attributed to hydroxyl stretching groups on the plane, carboxyl groups located at the edges of sheets, aromatic C=C bonds, epoxy C–O stretching vibration, the stretching vibration of alkoxy C–O, respectively [18,23]. After reducing with Na_2CO_3 , the peak at $1730, 1222, 1056 \text{ cm}^{-1}$ almost disappears and the peak for OH stretching bonds at 3387 cm^{-1} weakens obviously, indicating that oxygen containing functional groups are removed from GO using Na_2CO_3 as a reduction agent.

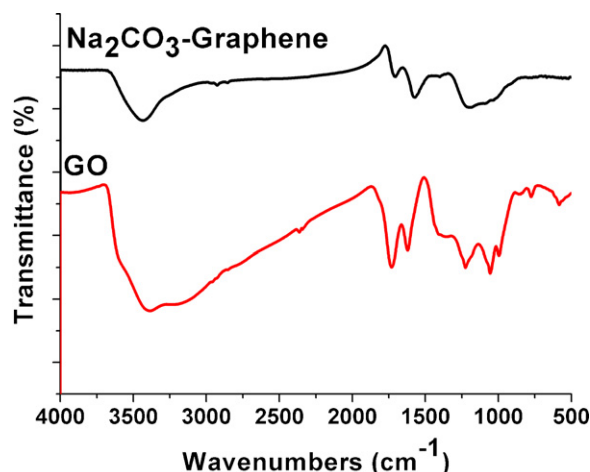


Fig. 2. FT-IR spectra of GO and Na_2CO_3 -graphene.

Download English Version:

<https://daneshyari.com/en/article/5360696>

Download Persian Version:

<https://daneshyari.com/article/5360696>

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