Journal of the Taiwan Institute of Chemical Engineers 45 (2014) 2762–2769

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

A unique two-step Hummers method for fabricating low-defect graphene oxide nanoribbons through exfoliating multiwalled carbon nanotubes

Chih-I Chang, Kuo-Hsin Chang, Hsiao-Hsuan Shen, Chi-Chang Hu *

Laboratory of Electrochemistry & Advanced Materials, Department of Chemical Engineering, National Tsing Hua University, Hsin-Chu 30013, Taiwan

ARTICLE INFO

Article history:
Received 10 January 2014
Received in revised form 27 May 2014
Accepted 29 May 2014
Available online 15 June 2014

Keywords:
Graphene oxide nanoribbon
Unzipping
Exfoliation
Multiwalled carbon nanotube
Two-step Hummers method

ABSTRACT

A unique two-step modified Hummers method is developed to unzip and exfoliate multiwalled carbon nanotubes (MWCNTs) into low-defect graphene oxide nanoribbons (GONRs). From the X-ray diffraction (XRD), Raman spectroscopic (RS), X-ray photoelectron spectroscopic (XPS), Fourier transform infrared spectroscopic (FTIR), and transmission electron microscopic (TEM) results, a mechanism involving multilayer-unzipping followed with rapid local peeing-off (*i.e.*, exfoliation) is proposed for this two-step Hummers procedure which provides a guide for obtaining high-quality GONRs. In the two-step procedure, both multilayer-unzipping of MWCNTs and oxidative exfoliation of multilayer GONRs are accelerated by a freshly prepared, concentrated $KMnO_4$ medium. This action reduces the random damage on the basal plane of resultant GONRs, which is commonly found in the ineffective, time-wasting, oxidant-consuming, one-step strategy. Consequently, low-defect GONRs can be efficiently fabricated in this two-step process.

1. Introduction

Graphene, a single layer of graphitic carbon, has received great interest because of the unusual physicochemical properties for applications in energy storage/conversion devices, electronics, and sensors [1–7]. Especially, synthesis of graphene nanoribbons (GNRs), *i.e.*, strips of graphene with a high length-to-width ratio and straight edges, becomes one of important topics in graphene researches due to its one-dimensional conduction. From the literature [4,8–12], small amount GNRs have been produced by several methods such as lithographic [8,9], chemical methods [4,10,11], and plasma etching of multiwalled carbon nanotubes (MWCNTs) partially imbedded in a layer of polymer [12]. In contrast, Campos-Delgado et al. [13] proposed to produce considerable quantities of GNRs through a chemical vapor deposition (CVD) method. On the other hand, the Hummers method, a wet oxidative exfoliation process, is the most common method for producing graphene oxide (GO) nanosheets from graphite [14–19] and carbon nanotubes (CNTs) [20,21]. The latter two studies, in fact, reported a high-yield production method with large amounts of GNRs through oxidative exfoliation of MWCNTs.

Although the oxidative longitudinal unzipping of MWCNTs has been achieved and the unzipping mechanism was also proposed [20], the inside exfoliating mechanism for preparation of low-defect GNRs is still not clarified. Moreover, the physicochemical properties of graphene and GO are exceptionally sensitive to lattice imperfections and functional groups [7,22], while damages and high-density defects on the graphene chemically reduced from suspended GO are unavoidable because GO was obtained through supersonic exfoliation of graphite oxidized by strong oxidants (*i.e.*, the Hummers method). Accordingly, how to modify the Hummers method for effectively improving the quality of reduced graphene oxide (RGO) is a crucial demand.

This work demonstrates a very unique two-step procedure of the Hummers method for powerfully unzipping and exfoliating MWCNTs into graphene oxide nanoribbons (GONRs) with low defects. The produced GONRs through this high-yield process show fewer defects but maintain acceptable aspect ratios. Furthermore, a mechanism involving multilayer-unzipping and local peeling-off steps is also proposed in this work and the differences in the exfoliating mechanism for MWCNTs between one-step and two-step procedures are discussed.

2. Experimental

Preparation of GONRs follows the modified Hummers method through either the one-step or the two-step procedure. MWCNTs

* Corresponding author. Tel.: +886 3 5736027; fax: +886 3 5736027.
E-mail address: cchu@che.nthu.edu.tw (C.-C. Hu).

http://dx.doi.org/10.1016/j.jtice.2014.05.030
1876-1070/

were used as received from Seedchem Company PTY LTD, Australia. In a typical one-step Hummers procedure, 0.2 g MWCNTs and 0.2 g $NaNO_3$ were suspended in 20 ml of concentrated H_2SO_4 for 1–12 h under stirring. Next, 1 g $KMnO_4$ (*i.e.*, 500 wt%) was added slowly to the solution and the mixture was allowed to stir for 1 h at room temperature. Then, the mixture was heated to 70 °C for 1–8 h (*e.g.*, 8 h for the 2 g $KMnO_4$ (1000 wt%) solution) with ultrasonic vibration. During the above $KMnO_4$ addition and heating periods, $KMnO_4$ was continuously consumed, probably via $4KMnO_4 + 3C + 4HNO_3 \Rightarrow 4MnO_2 + 3CO_2 + 4KNO_3 + 2H_2O$. When the above oxidation step was completed, 20 ml deionized water was added into the solution, followed by heating the solution to 100 °C. The solution was removed from the heat source and cooled in the ice bath. Next, the 10 ml deionized water with 30% H_2O_2 was added to the solution until cessation of gas evolution. This solution was filtered with a polytetrafluoroethylene (PTFE) membrane with a pore size of 0.4 μm. The filtered powders were removed, stirred in deionized water for 15 min, and then bath-sonicated for 30 min. The solid was filtered with a PTFE membrane with a pore size of 0.2 μm again. The final filtered powders were washed several times by deionized water, and dried in a vacuum oven at 80 °C overnight. Preparation of GO nanosheets from graphite nanoparticles for comparisons completely follows the above procedure.

For GONRs prepared from the two-step process, MWCNTs were treated with the modified Hummers method twice. The total time reacted with $KMnO_4$ in this two-step process is less than or equal to that in the one-step procedure. For example, the total reaction time for the first 1-g $KMnO_4$ (500 wt%) and second 2-g $KMnO_4$ (1000 wt%) steps is equal to 3 h which is shorter than 8 h for the one-step 1000 wt% $KMnO_4$ case. Here GONRs made from MWCNTs by the one-step Hummers method with 500, 1000, and 2000 wt% $KMnO_4$ are denoted as GONR500, GONR1000 and GONR2000, respectively, while those prepared through the two-step Hummers procedure with 500 and 1000 wt% $KMnO_4$ in the first and second steps, respectively, are denoted as GONR500-1000.

The X-ray diffraction (XRD) measurements were carried out with a Rigaku diffractometer (Cu *K*α radiation; X-ray wavelength, λ = 1.54 Å; operating energy, 40 keV; cathode current, 40 mA; scan rate, 1° min^{-1}). Raman spectroscopy was performed on a HOROBA, Lab RAM HR Raman Microscope using a 532 nm HeNe laser. The functional groups of GO nanosheets and GONRs were measured by a high-resolution X-ray photoelectron spectrometer (XPS, Kratos Axis Ultra DLD), employed Al monochromator ($h\nu$ = 1486.69 eV) irradiation as the photosource. The FTIR spectra of GONRs were measured by Horiba FT-720 spectrometer. The zeta potentials (denoted as E_Z) of GONRs were performed by Zetasizer Nano ZS. The atomic force microscopic (AFM) images were obtained with a Digital Instruments NS3a controller with D3100 stage (Digital Instruments/Veeco Metrology, Inc.). The transmission electron microscopic (TEM) imaging was performed on a FEI Tecnai F20 G2 FE-TEM microscope. Samples were prepared by dispersing the nanoribbons in deionized water and dropped onto 300 mesh holey, lacey carbon grids on copper support (Ted Pella).

3. Results and discussion

Due to the strong graphite structure of MWCNTs, conventional oxidative exfoliation of MWCNTs for producing GONRs is a relatively ineffective, time-wasting, and oxidant-consuming process although crystalline GONRs and resultant graphene sheets may be derived from this well-crystalline carbon material. In a typical, one-step Hummers procedure, very concentrated (*e.g.*, 1000 wt%) $KMnO_4$ was used to rip MWCNTs open in a long continuous supersonic exfoliation process (8 h), while the resultant GONRs were seriously damaged. The high intensity ratios

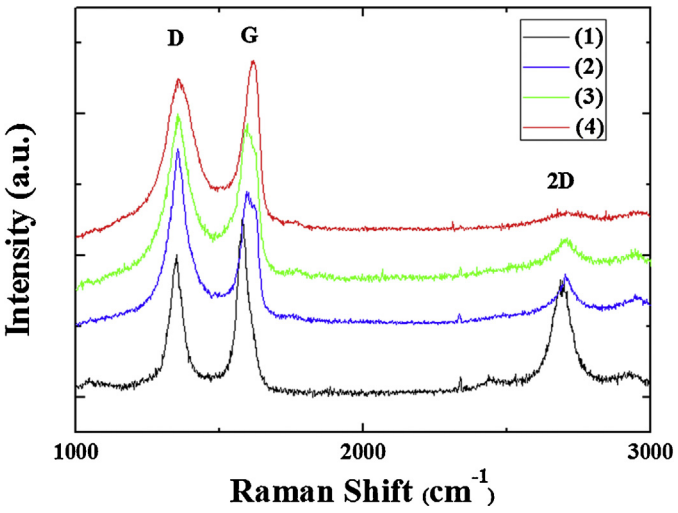

Fig. 1. Raman spectra of (1) MWCNTs, (2) GONR1000, (3) GONR2000, and (4) GONR500-1000.

Table 1
D-band and G-band analyses of Raman spectra from various carbon sources.

Sample	I_D/I_G
MWCNTs	0.81
GONR500	1.15
GONR1000	1.26
GONR2000	1.04
GONR500-1000	0.92

between D and G bands on the Raman spectra for the one-step-derived GONRs in Fig. 1 and Table 1 indicate a significant increase in the defect density of the graphite structure. The lower I_D/I_G value (1.04) of GONR2000 (2000 wt% $KMnO_4$) in comparison with GONR1000 (I_D/I_G = 1.26; 1000 wt% $KMnO_4$) suggests that MWCNTs can be more effectively unzipped and exfoliated into GONRs with a lower defect density in the medium containing more concentrated oxidants, probably due to a shorter exfoliation period (4 h). The

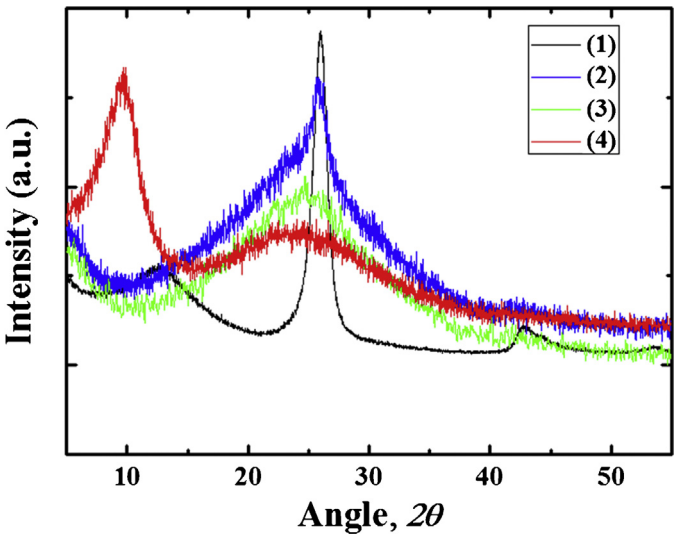

Fig. 2. XRD patterns of (1) MWCNTs, (2) GONR1000, (3) GONR2000, and (4) GONR500-1000.