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Millimeter-long multilayer graphene nanoribbons prepared by wet chemical processing

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ABSTRACT

Millimeter long multilayer graphene nanoribbons were prepared by a chemical treatment of graphite oxide (GO). To our knowledge, this is the very first report to harvest ultralong graphene ribbons with length dimension >1 mm using a wet chemical process. Scanning electron microscope (SEM) images reveal the nanoribbon length larger than 1 mm and width ~10 μm. X-ray photoelectron spectroscopy (XPS) analysis shows that oxygen-containing functional groups decreased as the extent of the chemical treatment increased. X-ray diffraction (XRD) and Raman spectroscopy studies confirmed the XPS result and unveil more graphitic sheet like structure formed as GO was reduced by more concentrated NaOH. It is found that by adjusting NaOH/GO mass ratio during the chemical treatment, we can produce >1 mm long multilayer graphene nanoribbons and achieve controllable degree of reduction to the GO material. It is expected that this technique will make ultralong graphene nanoribbons readily available for research and applications.

1. Introduction

Since its discovery in 2004 [1], graphene, a one-atom-thick two-dimensional (2-D) carbon nanosheet structure, has revealed exceptional characteristics in mechanical, thermal, electronic and optical properties [2], demonstrating its potential to revolutionize applications ranging from flexible displays, solar cells, supercapacitors, terahertz frequency manipulation to various sensor applications [3–5]. Already important achievements have been made in fabricating graphene (including graphene-based materials such as graphene oxide, exfoliated graphite, chemically modified graphene, etc.) and its analogous 2-D composite materials [6,7]. A variety of synthesis techniques have been developed including: chemical vapor deposition (CVD) [8–11], micromechanical exfoliation [12], epitaxial growth, and reduction of chemically extracted graphene oxide [13–17], etc.

As GO can be made readily available in relatively large quantity from natural graphite powder [18], synthesis of graphene from the GO has been attempted and successfully achieved with a variety of methods, including: applying electrical field using an AFM probe [19], dispersion followed by chemical reduction [20,21], electrochemical reduction [22,23], reduction using solvothermal techniques [24,25], electromagnetic radiation [26], vacuum thermal technique [27], and rapid thermal exfoliation/reduction [28,29], and rapid

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thermal processing using an aerosol-through-plasma approach [14], etc.

Mechanical exfoliation of highly oriented pyrolytic graphite (HOPG) provided the first well-ordered but millimeter-sized graphene monolayers and multilayer flakes in small quantities just sufficient for fundamental studies [12]. Recently, CVD technique has been used to fabricate larger area graphene sheets on metal-foil substrates [10,30–32] and successfully transferred onto soft surfaces [33].

In contrast to the exfoliation and CVD method, wet chemical synthesis needs no complicated equipment, it remains to be the most accessible and the most economic method to produce large amount of graphene material. Indeed, graphene materials with low-oxygen content (9–10%) and high surface area (600–900 m^2/g) have been prepared [14]. Moreover, its easy accessibility has made graphene a very popular candidate in many applications [2,3,34–36]. For example, Miller et al. developed supercapacitors using oriented and relatively sparsely distributed graphene flakes grown on nickel by CVD [37,9,20]. Ruoff et al. prepared highly conductive and porous graphene oxide films by chemical activation of reduced graphene oxide using KOH [7]. It is believed that the KOH treatment created an open pore structure in the graphene oxide sheet, leading to a specific surface area as high as 2400 m^2/g, the highest for a freestanding carbon film. Using the films as electrodes for high-power supercapacitors, they demonstrated an excellent high-frequency response, an extremely low equivalent series resistance, and a high-power delivery while simultaneously maintaining excellent specific capacitances and energy densities. They further proposed that the combination of high conductivity, high surface area, open pore structure, chemical stability, and flexibility would make the porous graphene films suitable for applications such as lithium ion batteries, conducting substrates for composites, photocatalysis, and so on.

However, up to now, all graphene materials harvested from the wet chemical methods are in nanosheet or nanoflake forms with width and length limited to micrometer scale. In order for graphene to be effectively used in microelectronics and many other applications, larger length dimension is necessary. Here, we describe our success in obtaining millimeter long graphene nanoribbon material using a simple wet chemical process. To our knowledge, this represents the very first realization to harvest graphene ribbons with large length dimension >1 mm using a simple wet chemical process. Our methodology involved two steps: (1) to prepare GO from natural graphite powder, and then (2) to chemically reduce GO to produce millimeter long graphene nanoribbons. Herein, we describe detailed processes for the reduction of GO sheets using NaOH and characterization of the resultant material. In particular, we systematically investigated modification of graphene by NaOH with controlled degree of reduction.

2. Experimental

2.1. Preparation of graphite oxide

GO was synthesized from natural graphite powder using an in house modified Hummers method [38]. Specifically, graphite powder (3 g) was slowly added into concentrated H_2SO_4 (98%, 120 mL) in a 1000 mL beaker at about 0 °C in an ice bath. Then $KMnO_4$ (15 g) was added gradually under continuous magnetic stirring and cooling. The rate was carefully controlled to keep reaction temperature to 0–4 °C. After stirring for 2 h, the mixture was moved to a 35 °C water bath and continue to stir for 1 h. Then raise reaction temperature and add distilled water (250 mL) slowly with vigorous stirring to hold temperature at 60 ± 3 °C. After 30 min, distilled water (500 mL) and 30% H_2O_2 solution (30 mL) were added with active stirring. The resultant suspension was centrifuged and repeatedly washed with 10% HCl aqueous solution for many cycles until the suspension became pH neutral. The product was then carefully dried under freeze drying at −50 °C for 24 h. GO was harvested as a golden color sponge material.

2.2. Preparation of ultralong graphene nanoribbon

The ultralong graphene nanoribbons were prepared using following procedure: (1) GO was dispersed in distilled water by ultrasonication at room temperature for half hour to prepare 1 mg/mL GO suspension. (2) Add 1 M NaOH solution slowly into the suspension to prepare different mass ratio of NaOH–GO mixture. (3) The NaOH–GO mixture was then refluxed under constant stirring at 100 °C in an oil bath until it was thickened into an "ink-paste". (4) The mixture was then filtrated and washed with distilled water until pH = 7. (5) The solid product was dried at about 80 °C in vacuum for 24 h. (6) Finally, the dried powder was moved into an atmospheric tube furnace (50-mm diameter) with active argon flow at 150 sccm. It was first heated at 280 °C for 30 min, then the temperature was increased at a rate of ~5 °C/min to 800 °C. Keep it at 800 °C for an hour before it was allowed to cool down to room temperature. The final product was harvested as graphene nanoribbons.

2.3. Characterization

The morphology and microscopic feature of the samples were observed using a Quanta 200 environmental SEM and a Tecnai G^2 F20 S-TWIN transmission electron microscope. The crystallographic structure was determined by a powder XRD system (DX2000, Cu-K_α radiation). The XPS characterization was carried out on a PHI 1600 spectrometer equipped with a monochromatic Al K_α X-ray source. Raman spectra were recorded using a French U-1000 laser Raman spectrometer with Ar^+ laser excitation at 514 nm.

3. Results and discussion

3.1. Morphological studies

As the degree of chemical etching was controlled by the mass ratio of NaOH/GO, a series of graphene oxide films were prepared using NaOH/GO mass ratio 0, 10, 26 and 33, and the corresponding samples labeled GO, GO-10, GO-26 and GO-33 respectively. Detailed analyses were conducted to investigate how NaOH/GO mass ratio would affect shape and morphology of the final graphene products. Table 1 summarizes