



A simple route for fabrication of graphene nanoribbons by pulsed laser irradiation in ethanol



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ABSTRACT

Graphene nanoribbons (GNRs) are fabricated from multi-walls carbon nanotubes (MWCNTs) via an unzipping process by using pulsed laser irradiation in ethanol. We confirm the successful transformation from MWCNTs to GNRs by transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy. Related transformation mechanism is presented based on the pyrolytic and the photolytic interaction of MWCNTs with laser light.

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1. Introduction

Graphene is a planar structure of carbon atoms at one atom of thickness. It has attracted much attention due to its excellent characteristics such as unique structure, electronics, chemical, mechanical and physical properties which are useful for various applications [1]. The graphene can be divided into different types based on their structural characteristics such as graphene nanoribbons (GNRs) [2], graphene oxide [3], graphene sheet [4], graphene film [5] and reduced graphene oxide [6,7]. GNR shave smooth edges and a narrow width distribution (10–20 nm), and their electric properties show a semi-metal of zero-gap semiconductor depending on the aspect ratio, the structure (zigzag and armchair), the number of layers and edge states [8]. They have been utilized for various applications such as electronic device [9] and composite materials owing to unique electronic property [10], flexibility, high strength, high thermal property and gas barrier ability [11].

GNRs have been synthesized by lithographic [12], chemical [13], plasma methods [14], chemical vapor deposition [15] and solution based oxidative processes [16]. Nevertheless these methods have some disadvantages such as the complex step processes, long experiment time, and the use of toxic chemicals such as strong acids. Rao et al. reported a new synthesis method for GNRs by a pulse laser irradiation technique through longitudinal unzipping of MWCNTs coated on glass substrate [17]. This method is fast and simple

without using strong acid or oxidizing agent. Also, the final GNR products are quite clean without impurities. However, it has low productivity and difficult to collect the synthesized GNRs after processing due to limited laser scanning area and processing scale-up.

Another novel technique using laser irradiation is a pulsed laser irradiation (PLI) in liquid medium. The PLI process in liquid has been a one of the promising techniques for several advantages such as comparatively simple and easy processing of complex nanoparticles. [18,19] However, there is little report on the preparation of GNRs by PLI in liquid medium. In this study, we report a novel and simple transformation route for fabrication of GNRs using PLI in liquid medium. The MWCNTs (multi-wall carbon nanotubes) successfully transformed to GNRs through unzipping process. Also, transformation mechanisms of the synthesized GNRs are investigated using transmission electron microscopy (TEM), X-ray diffractometer (XRD) and Raman spectroscopy.

2. Experimental

The MWCNTs as starting materials were prepared by catalyst chemical vapor deposition (CCVD) method [20]. The diameter and purity of the MWCNTs were 10–20 nm and 99.0%, respectively. The 0.005 g of as-prepared MWCNTs was dispersed in 2 L ethanol by ultrasonic for 10 h. Subsequently, the solution of the MWCNTs (100 ml) was irradiated by pulsed laser (Nd:YAG 355 nm, Quanta Ray-LAB190) with 100 mJ/pulse for 1 h as shown in Fig. 1. The repetition rate and pulse width were 30 Hz and 10 ns, respectively. Nanostructure and morphology of the fabricated GNRs were investigated by a high resolution TEM (HR-TEM, Jeol 3010, Japan). Crystallinity was investigated by XRD (Rigaku D/MAX 2C, Japan) using Cu K α radiation (1.5406 Å). The chemical structure of the fabricated GNRs was measured by Raman spectroscopy (LabRam HR, Ar-ion laser excitation 514.5 nm, Japan).

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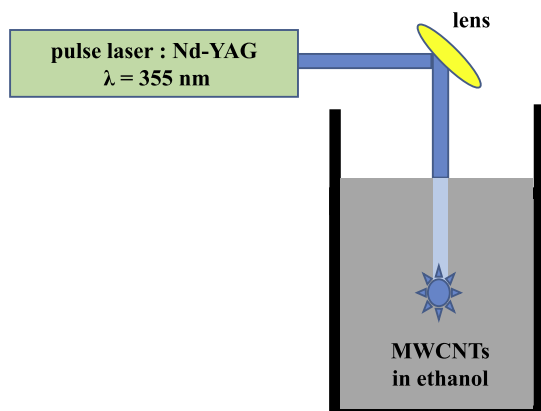


Fig. 1. A schematic diagram for pulsed laser irradiation process for fabrication of GNRs.

3. Result & discussion

The microstructures of the raw MWCNTs and PLI-processed sample are shown in Fig. 2(a) and (b). The MWCNTs have diameter of 10–20 nm with tubular structure as shown in inset of Fig. 2(a). The black arrows of Fig. 2(b) reveals that the MWCNTs successfully transformed to GNRs by the PLI process, however, the broken MWCNTs were observed as marked in white arrows. The transformed GNRs had a good edge roughness, and the width of these GNRs is around 30 nm as shown in inset of Fig. 2(b).

The possible mechanism of transformation from MWCNTs to GNRs by PLI process is distinctly illustrated in schematic diagram

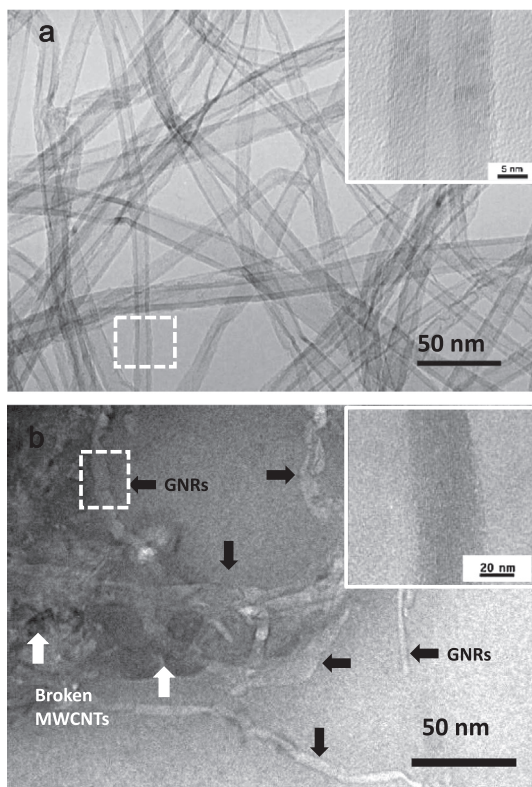


Fig. 2. (a) TEM picture of the MWCNTs raw sample. The inset shows the diameter of the MWCNT is 20 nm. (b) TEM picture of PLI processed sample for 1 h. The transformed GNRs and broken MWCNTs are marked with black and white arrows, respectively. The inset shows that the transformed GNR has a good edge roughness and width of 30 nm.

of Fig. 3. The laser irradiation is based on the interaction of laser light with matter. The interaction of material with photon can be recognized as two different phenomena: pyrolytic and photolytic processes [21]. Pyrolytic process is based on breaking of the chemical bonds by photon energy. Pyrolytic method can be applied to polymers by using ultraviolet lasers with wavelengths from 157 to 351 nm. Photon energy is converted directly in breaking chemical bonds and there is very little thermal interaction with the material. On the other hand, photolytic processes are based on a rapid thermal cycle heating, melting, and partly evaporation of the heated volume [21]. Therefore, the PLI process can be considered as a combined interactive process with the pyrolytic and the photolytic mechanism.

The pulse laser with 355 nm wavelength is absorbed mostly by MWCNTs based on the photolytic mechanism [21]. Higher energy in laser can be applied to MWCNTs compared to the breaking energy of C–C bond (248.5 eV) of walls, which attaches oxygen-containing functional groups such as carbonyls, carboxyls, epoxides or hydroxyls to the edges and surface (Fig. 3(a)) [2–6,16]. This process is analogous to the longitudinal unzipping of carbon nanotubes [22]. Once the carbon bonds with oxygen-containing functional group by laser irradiation, unzipping proceeds further along the strain induced by the carbon–carbon bond angle [23] as shown in Fig. 3 (b) and (c). Under PLI process, the pyrolytic and the photolytic process accelerate the unzipping process. Subsequently, the PLI breaks C–C bonds and generates considerable thermal vibration simultaneously, which leads to the transformation from MWCNTs to GNRs.

The transformed GNRs via unzipping process from MWCNTs are obviously observed in Fig. 4. The transformed GNRs (black arrow) and broken walls of MWCNTs (white arrow) after PLI process are shown in Fig. 4(a). Fig. 4(b) shows the unzipping process at the mid-section of the MWCNTs under PLI process [22]. The width of inner side of unzipped area is larger than that of the tip, which corresponds to the unzipping mechanism of Fig. 3(b). Fig. 4(c) presents the magnified figure of the unzipping tip showing exfoliated inner, middle and outer layer as shown in Fig. 3(c). Fig. 4(d) shows the transformed GNR layer with 61.6 nm width. The inset of Fig. 4(d) is the selected area electron diffraction (SAED) patterns of GNRs transformed from MWCNTs, it is similar to simulated SAED pattern of highly ordered pyrolytic graphite (HOPG) indexed as the (001) zone axis. The conventional SAED patterns of MWCNTs show the ring pattern or spot pattern in line to (002) direction due to poorly ordered carbon atoms among the curling layers in the multitubular structure. However, the SAED patterns of transformed GNRs are similar to HOPG due to the improved ordering of carbon atoms among the layers by curved multilayers when the tubular structure change to the planar layers structure of 2D by unzipping of MWCNTs by PLI [24] (see Fig. 5).

The carbon characteristic peaks of MWCNTs in XRD patterns are shown at 25.76° [$d(002) = 3.44 \text{ \AA}$] and GNRs at 25.86° [$d(002) = 3.41 \text{ \AA}$]. The hexagonal carbon sheets of MWCNTs have tubular structure, while the GNRs have planar structure. Thus, the interplane $d(002)$ space of MWCNTs is larger than GNRs [25,26]. It is concluded that MWCNTs is transformed to 2D structure of GNRs throughout the sample.

Fig. 6 shows the Raman spectra of the MWCNT and transformed GNRs after PLI process. The spectra show three Raman bands at 1342 cm^{-1} (D band), 1579 cm^{-1} (G band) and 2706 cm^{-1} (2D band). The G band indicates the original graphite feature due to the in-plane vibration of sp^2 carbon atoms. Also, the D band can be explained since amorphous carbon contains a certain fraction of sp^3 carbons, and disordered carbon atoms in the graphite structure [27]. The intensity ratio of the D band to the G ($I_{(D)}/I_{(G)}$) and the ratio of their sizes were employed to determine the fraction of in-plane crystallite in the graphite structure. The value of

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