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Raman spectroscopy investigations of chemically derived zigzag edge graphene nanoribbons

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We fabricated graphene nanoribbons (GNRs) chemically derived from expandable graphite. All GNRs exhibit atomically smooth edges that extended over their entire length. We investigated four of the fabricated GNRs using Raman spectroscopy. Two of the investigated GNRs show Raman spectra with a missing D-band peak, while D-band peaks can be clearly observed for the other two GNRs. The two GNRs which do not show the D-band peak are GNRs with zigzag edges, and the two other GNRs which show clearly the D-band peaks are possibly GNRs with armchair edges. © 2013 Au-thor(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4821281]

Graphene, a single layer or sometimes a few stacked layers of sp^2 carbon honeycomb lattice, has attracted considerable attention for its unconventional electronic structure of massless Dirac fermions.^{1,2} From the viewpoint of potential applications, opening the bandgap between the valence and conduction bands of graphene is expected to accelerate the realization of next generation ultrafast graphene devices. There are several approaches to introduce a bandgap in graphene; these include the application of a perpendicular electric field to bilayer graphene,³ introducing nanoscale holes into a graphene sheet (graphene nanomesh),⁴ and fabricating long and narrow graphene strips (graphene nanoribbons: GNRs).⁵ It is theoretically predicted that a significant variation would be observed in the electric and magnetic properties of GNRs according to variation in their edge structures and width.⁶ The fabrication of GNRs with smooth and well controlled edges is a technical challenge. In this letter, we report the fabrication of chemically derived zigzag edge GNRs free from structural disorder for a long distance. The Raman spectra of our zigzag edge GNRs exhibit no D-band peak. The fabrication of such GNRs can significantly contribute to the development of future GNR devices and applications.

In the preparation of the GNR samples, we primarily followed the method developed by Li *et al.*⁷ We used the expandable graphite, GrafGuard 160-80 NC (GrafTech International, Cleveland, OH), as the original material. The material 160-80 NC provided us a better GNR yield than 160-50 N, which is a similar type of GrafGuard expandable graphite that was used in the study by Li *et al.*⁷ The main difference between their expandable graphite and ours is the particle size before expansion: 250 μ m for 160-80 NC and 350 μ m for 160-50 N. The exfoliation of the graphite was carried out by heating the expandable graphite at 1000°C for 1 min in a 97% He + 3% H₂ forming gas atmosphere with a pressure of 1 × 10³ Pa. In order to obtain a high yield of GNRs, it is required that the material undergo a large temperature change in a very short time span. After the heating,



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FIG. 1. (a) AFM image of fabricated GNRs. Two straight and unbroken GNRs with lengths of 33 μ m and 6 μ m are visible. The address marks were deposited on the wafer with spacings of 5 μ m between each mark. (b) Enlarged image of the area indicated by the rectangle in (a). The edge structures appear smooth within this resolution. The smooth edges extend over the entire length of the GNRs. The width is 100 nm for both GNRs at any position. The measured thickness is 0.8 nm, and this corresponds to a single layer GNR.

we obtained an expanded graphite yield that was a few hundred times larger than the initial volume. The expanded graphite was dispersed by using a ultrasonic cleaner in a solution containing 0.1 mg m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene (PmPV) in 1 ml of 1,2-dichloroethane (DCE). For the dispersion, we used a commercially available ultrasonic cleaner for 30 min under moderate operating power; large oparating values of ultrasonic power can cause breakage of the GNRs into smaller pieces. The dispersed solution was centrifugated for 5 min at 14,000 krpm. We extracted the top clean layer containing the desired GNRs suspended by PmPV molecules. The GNRs were deposited onto a Si wafer covered with 300 nm of SiO₂ on which address marks with spacing 5 μ m were subsequently deposited. In order to deposit the GNRs on the wafer, we soaked the wafer in the solution for 10 min; the solution can also be dripped onto the wafer surface. It is to be noted that the complete removal of PmPV residue from the wafer surface is difficult even after the heating treatment. The soaking method leaves behind a relatively less quantity of PmPV residue than that obtained by the dripping method; however, the GNR yield is reduced. In our study, we employed both methods for GNR deposition. The wafer was subsequently dried under ambient conditions for 30 min and cleaned by acetone in an ultrasonic cleaner, followed by isopropyl alcohol rinsing. We heated the wafer to 400°C in air for 10 min to burn off the PmPV residue. The wafer was subsequently heated to 600°C in vacuum for 10 min for further cleaning.

Since GNRs are not visible under an optical microscope, we used a field-emission scanning electron microscope (FE-SEM) to locate the position of the fabricated GNRs. Next, we used an atomic force microscope (AFM) for the characterization of each GNR. Figure 1 shows AFM images of our typical GNRs. A long GNR (33 μ m) and a short one (6 μ m) are clearly visible in the image. Our GNRs are straight and exhibit uniform width and smooth edges over their entire length. The size distributions of our GNRs ranged from 1.0 to 100 μ m in length, 10 to 500 nm in width, and 0.8 to 4.0 nm in apparent thickness. The GNR with length of 100 μ m is the longest one ever reported. The apparent GNR thickness of 0.8 nm indicates that they are single-layer GNRs. The difference between the obtained apparent thickness and the expected single-layer thickness of 0.337 nm may be caused by chemical and Van der Waals contrasts.¹

Raman spectroscopy has been considered as a very powerful tool to investigate graphite and other similar materials.⁸ In the Raman spectra of general sp^2 carbon-based materials such as graphite, carbon nanotubes, and graphene, the following peaks are prominent: a Raman-active G-band peak centered at ~1580 cm⁻¹ induced by lattice vibration, an intra-valley double resonance 2D-band peak centered at ~2700 cm⁻¹, and an inter-valley double resonance D-band peak centered at ~1350 cm⁻¹. It is well established that the D-band peak is induced by elastic scattering at disorders in the crystal lattice. Thus, a strong D-band peak is observed for small crystallites, while it is absent for the flat surface of Highly Oriented Pyrolytic Graphite. The intensity ratio of the G- and D- band peaks is



FIG. 2. (a) AFM image of GNR. The width of the GNR is 500 nm and the apparent thickness is 0.8 nm. The circles marked 1, 2, and 3 represent the locations where the Raman spectra shown in (b) were measured. The diameter of the circles ($\sim 1 \mu m$) almost corresponds to the spot size of the excitation laser. (b) Raman spectra of the GNR shown in (a). It is significant that the D-band peak is missing for all three measured points. The absence of the D-band peak indicates that the edges of the GNR consist of a zigzag structure and are free from roughness.

often used to estimate the quality of crystal alignment. It is to be noted that the edges can play a role of lattice disorder and contribute to the formation of a D-band peak. Therefore, in order to investigate the edge structure of the fabricated GNRs, we carried out Raman spectroscopy measurements. Since our sample was of an extremely small size to enable proper adjustment of its position under the laser spot, we employed a scanning Raman mapping technique. The excitation light was linear polarized and the wavelength was 532 nm, with an operating power of several mW and a spot size of approximately 1 μ m. For the case of the GNR with a width of 100 nm, the GNR section under the laser spot scanned in 0.5 μ m step over an area of 8 μ m × 8 μ m for a laser exposure time of 5 min at every step. An exposure time of 10 s is sufficient for a 500 nm-wide GNR. On the other hand, GNRs with widths less than 100 nm may require considerably longer exposure times. Too much laser power or too long exposure time may cause local heating and results in down shifts of the Raman peaks, ^{9,10} however, this effect does not influence our following discussions.

Figure 2 shows the AFM image (a) and Raman spectrum (b) of the 500 nm-wide, 0.8 nm-thick GNR. The narrow (FWHM $\sim 60 \text{ cm}^{-1}$) and symmetric line shape of the 2D-band peak ensures that the GNR is single layer. For few layer GNR, the 2D-band may appear as a broad and distorted shape because it consists of a sum of several peaks.^{11,12} It is noteworthy that the D-band peak is absent in the Raman spectrum. If we suppose that the D-band peak is hidden in the noise, the intensity ratio of the D- and G-band peaks: I_D/I_G could be well below 0.1. To the best of our knowledge, all the reported Raman spectra of GNRs exhibit a clear D-band peak.^{12–16} Since the excitation laser spot size of about 1 μ m is sufficiently large to cover the GNR width, as shown by the circles in Fig. 2, that the Raman spectrum must be influenced by the edges. However, although electron scattering at the edges is an origin of the D-band peak, the D-band peak of the GNR in Fig. 2 is still missing. Moreover, the D-band peak is missing at all three measured points indicated by the circles in Fig. 2. This is not the only GNR whose D-band peak in the Raman spectrum is missing. It is reported that the D-band peak intensity strongly depends on the angle between the excitation laser polarization and the edge.¹⁷ On the other hand, clear D-band peaks are observed for the two GNRs shown in Fig. 3. The peak amplitude of the D-band is comparable to that of the G-band for both GNRs. We investigated the four GNRs using Raman spectroscopy, and the sptctra for two GNRs showed a missing D-band peak while the other two GNRs exhibited a clear D-band peak.

The appearance or non-appearance of the D-band peak is influenced by the structure of the edges. It is known that the D-band peak is observed for armchair edges, while it is absent for zigzag edges because the scattering at an armchair edge can connect inequivalent valleys (K and K' points of the reciprocal lattice) as opposed to scattering at a zigzag edge.¹⁹ Accordingly, the GNRs that do not exhibit the D-band peak are inferred to the those with zigzag edges. Moreover, the zigzag edges continue over several micrometers (the distance between points 2 and 3 in Fig. 2) without exhibiting



FIG. 3. (a) AFM image of two GNRs whose Raman spectra are shown in (b). The widths and the apparent thicknesses of GNRs A and B are 100 nm, 0.8 nm, and 150 nm, 1.3 nm, respectively. (b) Raman spectra of GNRs A (bottom) and B (top). The clear D-band peak is measured to be as strong as the G-band peak for the both GNRs, in contrast with D- and G- band peak strengths in the Raman spectrum shown in Fig. 2.

roughness. The AFM inspection indicates that the GNR is straight and its edges are smooth, and therefore, the zigzag edges probably extend over the entire length of the GNR. The edge structure of the GNRs exhibiting the D-band peak can be armchair-structured; however, this area requires further investigation. The GNRs with edge orientations between zigzag and armchair show the D-band peak, too. So we cannot determine that the edge structure of two GNRs exhibiting the D-band peak is armchair. It is interesting that the 2D-band peak is not observed for the GNRs shown in Fig. 3. We speculate that this is because the GNRs in this case are narrow, and the signal resolution was not sufficient, or the 2D-band peak is too broad. In H. Dai group,¹⁸ the clearly Raman signal of very narrow GNRs with 10–30 nm width was obtained using the polarized Raman spectroscopy. In order to improve the signal to noise ratio for GNRs with widths of 100 nm or less, the laser exposure time is required to be greater than 5min; however, the increase in exposure time for each point results in an enormous increase in scanning time, or we need to try the polarized Raman spectroscopy.

To summarize, we fabricated straight GNRs with smooth edges and length as great as 100 μ m by using a previously reported chemical method.⁷ We investigated the fabricated GNRs using Raman spectroscopy. Two of the fabricated GNR samples do not exhibit the D-band peak in the Raman spectrum. The missing D-band peak in the spectra of these GNR samples is attributed to their zigzag edge structure. The zigzag edge structure continues over a length scale of several micrometers, and it possibly extends over the entire GNR length. Though this study cannot obtain proof, we are likely to have armchair GNR samples, which show clear D-peak. So, we possibly obtain both zigzag and armchair GNR samples with straight and smooth edges. Our future study will examine the detail; for example, transmission electron microscope (TEM) will make it possible to observe directly the atomic edge structure of our GNRs.

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