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Electrical and Structural Feature of Monolayer Graphene Produced by Pulse Current Unzipping and Microwave Exfoliation of Carbon Nanotubes

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The electrical conductivity and structural properties of monolayer graphene (MLG) have been studied. MLG is fabricated from single-walled carbon nanotubes (SWCNTs) using high direct current pulse and microwave irradiation. Transformed MLG initially obtained from SWCNTs was not a stable planar structure because of its high surface energy. Therefore, they became stacked together to form the few-layer graphene structure. With the exfoliation process using an alkali metal, the stacked structure changes to a monolayer structure. A variety of characterizing techniques, such as a field emission scanning electron microscopy, high resolution transmission electron microscopy, high resolution Raman spectroscopy, and X-ray photoelectron spectroscopy were used for the analysis of MLG structures.

Introduction

Graphene has highly desirable electrical properties, such as low electronic scattering rates and high electron transport.[1−3] Because graphene has these electrical properties, it has great potential for the future electronics and extensive commercial applications, such as ballistic transistors, field-effect transistors, quantum interference devices, and flexible transparency electrodes.[4]

Recently, synthesis of a controlled graphene layer has become important because of its potential for electrical device applications, since the number of graphene layers influences its electrical properties and also transparency of light in the visible range.[5] The single layer carbon structure in graphene has over 90% transparency for visible light. Although graphene is strongly transparent to light, this transparency decreases as the number of graphene layers is increased. Therefore, for future electronic and extensive commercial applications, the fabrication techniques for controlling the growth of graphene layers becomes important for graphene research.

To make graphene, several fabrication methods have been reported, such as mechanical cleavage,[1,2] silicon carbide sublimation,[6] solvothermal synthesis,[7] chemical vapor deposition (CVD),[4] plasma etching,[8] and unzipping of carbon nanotubes (CNTs).[9]

In this paper, we report the structural and electrical feature of monolayer graphene (MLG) fabricated from single-walled carbon nanotubes (SWCNTs) using high direct current (DC) pulse unzipping and microwave exfoliation. Because the SWCNTs have single layer carbon structure with rolling carbon structure, SWCNTs can be possible to convert the graphene layer from the unzipping process of SWCNTs. For the unzipping process of SWCNTs, high direct current is used. From the unzipping process from SWCNTs to graphene, few layer graphene (FLG) is fabricated from accumulation of SWCNTs. After fabricating the FLG, monolayer graphene is synthesized from the exfoliation process using alkali metal intercalation and microwave irradiation. Alkali metals such as potassium are well-known to form graphite

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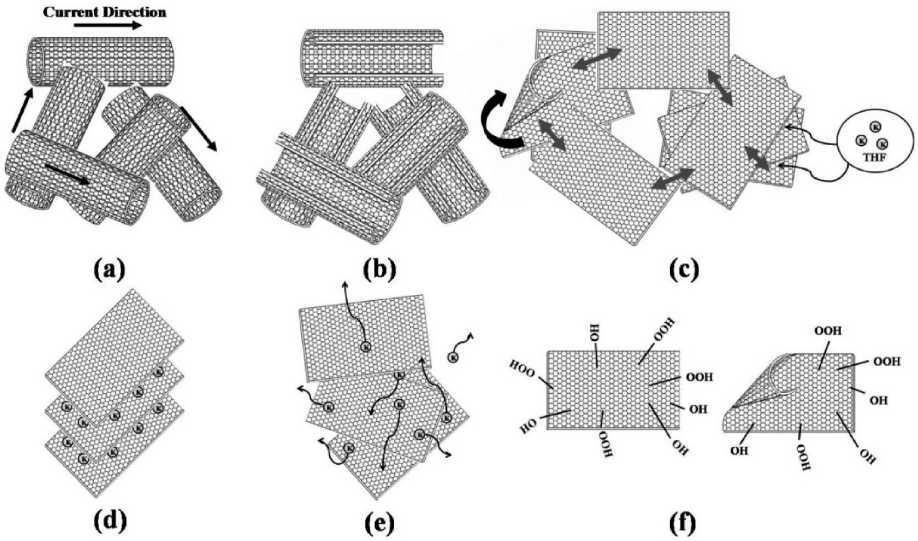

Figure 1. Schematic illustration of the transformation model of SWCNTs to graphene layer by high DC pulse: (a) nonuniform arrayed SWCNTs as starting materials before current flowing, (b) C−C bonding broken along the current path, (c) broken SWCNTs stretched away by curvature tension. To reduce the surface energy, they were stacked on top of each other by van der Waals force, (d) the intercalation compound of potassium and FLG, (e) the exfoliation by microwave irradiation, and (f) the planar MLG and the partially scrolled MLG.

intercalation compounds.[10] Alkali metals can easily penetrate the interlayer space of FLG. With molecule vibration and rapid heating with microwave irradiation, the intercalated alkali metals get out from FLG and overcome the van der Waals force among the graphene layers. Using this method, we can fabricate the high quality and large scale MLG in a very short time.

Experimental Details

We use SWCNTs (Hanwha Nanotech, ASP-100F, Korea) as the starting material. They are transformed to FLG with 2 to 3 atomic layer thickness by a high direct current (DC) pulse in the pulse current sintering (PCS) process.[11] The FLG were produced in vacuum (mechanical pump) using a Dr. sinter model SPS-515S PCS system (Sumitomo Coal mining Co., Japan). Contacts were placed between two graphite rams in a cylindrical graphite (ISO-63) die having an inner diameter of 10 mm with 1 g SWCNTs. The pellets are heated to 2000 °C at a heating rate of 100 °C per minute with a pressure of 100 MPa between the rams, and the applied DC is about 700 A (voltage < 5 V) with a pulse duration of 12 ms and pulse interval of 2 ms during 10 min. Potassium organic solution is prepared by adding a stoichiometric amount of potassium hydroxide (KOH), 0.5 mol to 200 mL of tetrahydrofuran (THF) organic solvent. FLG is dispersed in this solution by ultrasonification for 20 min. At the same time, the dissolved potassium ion in the solvent is intercalated at the interlayer space of FLG. The dispersion is irradiated by rapid microwave heating for 60 s using 60 Hz with 1000 W. Then, we can get the exfoliated graphene layer from the irradiated dispersion of alkali metal intercalated FLG. They are finally observed with scanning electron microscopy (SEM) using an FEI-Nova NanoSEM200 instrument with a field emission gun. High resolution transmission electron microscopy (HR-TEM) investigations were carried out using a JEOL-4010 microscope operating at 400 keV. X-ray photoelectron spectroscopy (XPS) was performed using a VG Multilab ESCA 2000 system, and Raman spectra were taken at room temperature under ambient condition using a LabRam HR (Jobin-Yvon) with a laser excitation of 514.5 nm (Ar-ion laser). The current−voltage ($I-V$) characteristic of the FLG and its comparisons was measured by the two probe method within an applied voltage ranging from −1.0 to 1.0 V using a source meter (Keithley Model 2400, OH, USA). In order to exclude the metal substrate, samples were measured on the quarts substrate using Pt patterned electrode.

Results and Discussion

A pictorial representation of the transformation from SWCNTs to graphene layers by the high pulse current unzipping of SWCNTs and the exfoliation process, as illustrated in Figure 1. PCS is a field activated sintering technique based on the electrical spark discharge phenomenon, which is a high-energy and low voltage sparking pulse-current momentarily generating spark plasma at high localized temperatures. During the PCS process, high DC pulse flows on the surface of the SWCNTs (Figure 1a), and simultaneously, high DC pulse is the breaking of sp^2 carbon bonding starting at the tip of SWCNT following the current direction. This phenomenon leads to the breakage of C−C bonds along the current path (Figure 1b). The broken SWCNTs in a straight line were stretched away by curvature tension on the surface of the SWCNT and then transformed into the graphene layer.[11] The transformed monolayer graphene (MLG) has a large surface area (the theoretical surface area of individual carbon sheet can be up to 2630−2965 m^2/g).[12,13] The individual carbon sheet could not exist in a

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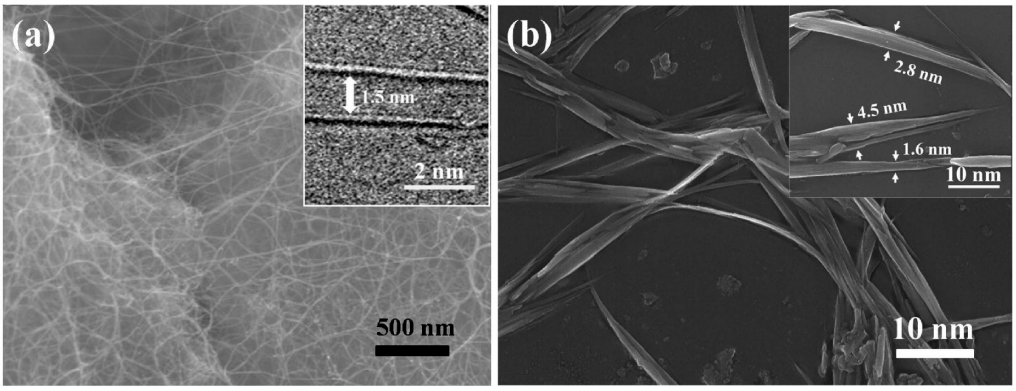

Figure 2. FE-SEM of SWCNTs: (a) the pristine SWCNTs (inset is HR-TEM of individual SWCNT) and (b) the SWCNTs treated with pulse current (inset shows the edge of unzipped SWCNTs).

planar structure because of the large surface area.[14] Thus, to reduce the large surface area, they are combined promptly by van der Waals force. The combined graphenes are stacked on each other and, then, form the FLG structure (Figure 1c). Intercalation of FLG is carried out using potassium instead of the lighter alkali metals, lithium and sodium, because potassium's ionization potential (4.34 eV) lies below the electron affinity of graphite (4.6 eV), thus enabling a direct reaction that does not require high temperature or pressure. Lithium (5.39 eV) and sodium (5.14 eV) have ionization potentials above the electron affinity of graphite. Therefore, potassium will intercalate FLG at relatively low temperature and ambient pressure.[15] Thus, the ionized potassium in THF solvent is easily intercalated into the interlayer space of FLG at room temperature and ambient pressure (Figure 1d). The intercalated potassium is put out from interlayer space of FLG by molecule vibration and rapid heating of microwave irradiation. This phenomenon leads to exfoliation of FLG by the breaking of van der Waals bonding among the layers (Figure 1e). In spite of the large surface area, the exfoliated MLG can exist as a planar structure by the combination with −OH and −OOH functional groups in THF organic solvent; these combinations stabilize the unstable surface energy (Figure 1f).[16,17] At the edge area without these combinations, to reduce the surface area, they are rolled up.[14] These chemical and physical phenomena prohibit the restacking and rolling of exfoliated MLG.

Figure 2 shows the field emission scanning electron microscopy (FE-SEM) images of starting materials. Figure 2a is the pristine SWCNTs before high DC pulse flowing. They have a length of several micrometers and tubular structure with diameter of 1 to 2 nm (inset). After treatment of high DC pulse, their tubular is changed to nanoscroll or the stacked graphene structure. Figure 2b shows FE-SEM image of the unzipped SWCNTs by PCS process. We confirm that the edge of unzipped SWCNTs has the rolled carbon sheet structure and their diameter is increased (inset).

Figure 3 shows HR-TEM image of FLG which is fabricated from SWCNTs using high DC pulse unzipping and the exfoliated MLG from FLG using the chemical and microwave treatment. When SWCNTs are unzipped by high pulsed current, their surface area is increased to about 2900 m^2/g. Therefore, to reduce their increasing surface area and energy, the unzipped SWCNTs (namely graphene) are combined and stacked promptly because of van der Waals forces. This momentary combination and the nonuniform arrayed starting materials (SWCNTs) produce the irregular stacked graphene structure. Figure 3a shows the stacked planar carbon sheets with width of several nanometers, which are fabricated from SWCNTs with diameter distribution of 1 to 2 nm. The cross section image (Figure 3b) reveals that the average thickness of FLG is double or triple atomic layers with interlayer spacing of 0.34 nm (inset). Figure 3c shows the MLG after the exfoliation process of FLG. A small edge of the MLG has the scroll structure. Those are not perfectly combined with functional groups in organic solvent. Thus, to reduce the surface area, they formed into a scroll structure. Figure 3d shows a HR-TEM image of MLG. It has planar structure with monolayer, not the scroll shape such as nanotubes. We confirmed that MLG could be fabricated from SWCNTs using this method.

The C1s XPS spectra of SWCNT, FLG, and MLG is shown in Figure 4a. Through the transformation from SWCNTs to FLG, the binding energy of the C−C sp^2 bonding is assigned at 284.6 eV as the same, but after exfoliation from FLG to MLG, chemical shifts of +1.4, +2.4, and +4.0 eV are found for the C−OH, C═O, and O═C−OH typical functional groups of graphene oxides at 286, 287, and 288.6 eV,[16,17] and the 2p3/2 binding energy of the intercalated potassium at interlayer space of FLG is shown at 293 eV. The exfoliated MLG combine with −OH and −OOH functional groups in THF organic solvent; this combination can reduce the unstable surface energy.[18] These results prohibit the restacking such as FLG, and an individual planar carbon sheet such as

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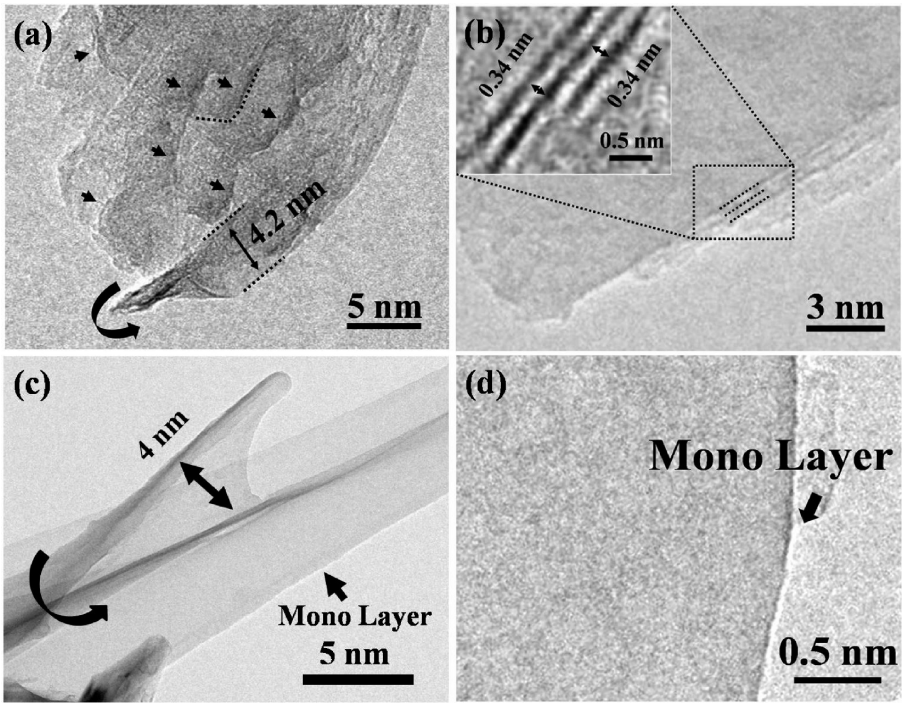

Figure 3. HR-TEM of FLG and the exfoliated graphene from FLG: (a) the transformed FLG from SWCNTs, (b) the cross section image of the stacked graphenes with 2 to 3 layers (inset shows the interlayer spacing of FLG), (c) the exfoliated graphene with the rolled MLG, and (d) the exfoliated graphene with the planar MLG.

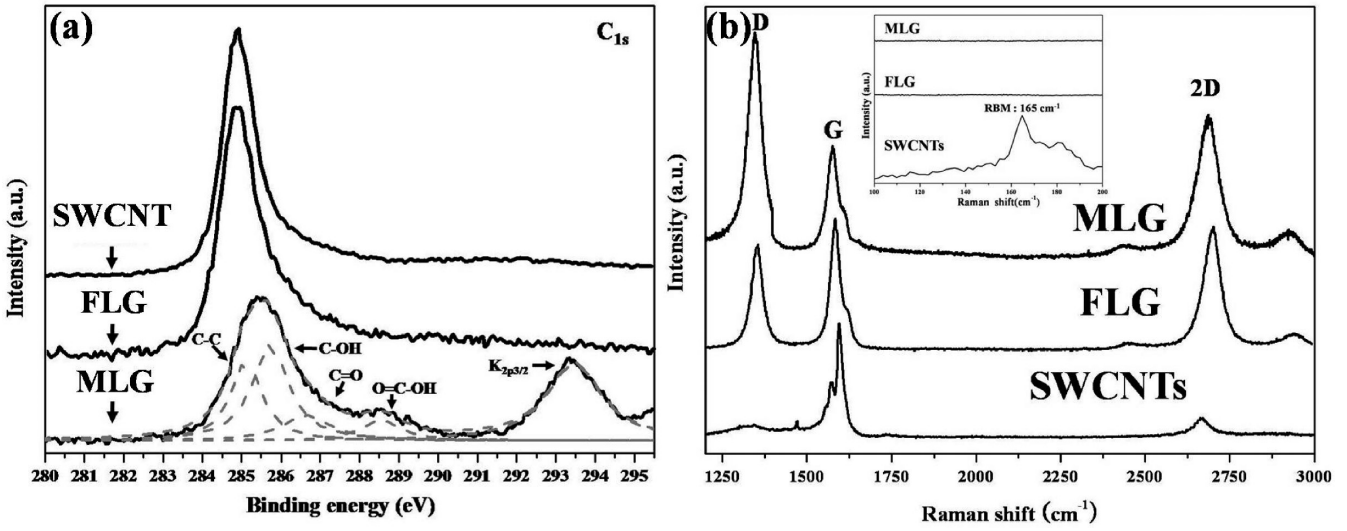

Figure 4. (a) XPS carbon 1s spectra of exfoliated graphene layer. (b) Raman spectra at 514 nm of exfoliated graphene layer; inset is RBM. The comparison is SWNCT and FLG.

MLG can exist. Figure 3b shows the Raman spectra of the exfoliated graphene, FLG, and SWCNTs. These spectra show mainly three Raman bands at ~165 cm^{-1} (RMB), ~1355 cm^{-1} (D band), ~1585 cm^{-1} (G band), and ~2707 cm^{-1} (2nd order band).[19,20] The G band indicates the original graphite features by in-plane vibration of sp^2 carbon atoms, and the D band has been explained as amorphous carbon contains a certain fraction of sp^3 carbons.[21] Therefore, the intensity of the G band depends on the thickness or number of layers in graphene. With the increasing number of layers, Raman intensity of the G band increases.[22] The intensity ratio of D band to the G band (I_D/I_G) and the proportion of their dimension were noted for evaluation factor of the in-plane crystallite in the graphite structure.[22,23] The value of I_D/I_G for the SWCNTs

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is 0.11, and the transformed FLG from SWCNTs is 0.85. It reveals that the local disorder was generated by the unzipping process under high DC pulse and high temperature. It has been influenced in the increasing I_D/I_G intensity ratio.[24] With the exfoliation of FLG to MLG, the value of I_D/I_G of MLG is increased up to 2.12. The prominent D peak is from the structural imperfections created by the attachment of hydroxyl and epoxide groups on the graphene structure,[16,17] and radial breathing mode (RBM) at 150−200 cm^{-1} of SWCNTs has disappeared after applying high pulse DC; it reveals the transformation from 1D tubular structure to 2D planar structure (inset of Figure 4b). Through the I_{2D}/I_G ratio, we can confirm the thickness and electrical properties of graphene.[21,25,26] The value of I_{2D}/I_G for SWCNTs is 0.17 and FLG is 0.94. This result proves that the mixture of semiconducting and metallic electrical properties in SWCNTs change to metallic property.[25] After the exfoliation of FLG, the value of I_{2D}/I_G is increased up to 1.31, and the position of 2D band is shifted from 2707 to 2686 cm^{-1}. These results reveal that the number of layers in graphene is reduced by exfoliation, compared with starting materials.[26,27]

To examine the electrical resistance of MLG, we measured the current−voltage characteristic. As can be seen in Figure 5, all samples exhibit linear $I-V$ relation within the experimental condition (from −1.0 to 1.0 V), and we use the Pt patterned glass device; the distance of two electrodes is 3 μm, and the width of electrode is 3 μm. It is well-known that SWCNTs were formed by various structures, such as zigzag, armchair, and chiral. These mixed structures caused the mixture of semiconducting and metallic electrical properties of SWCNTs. When SWCNTs are unzipped, SWCNTs changes to a metallic state because of the transformation of the graphene layer; the $I-V$ slope of FLG is increased by transformation compared with SWCNTs. However, after transformation, the local disorder has been created by high DC pulse and high temperature. This local disorder leads to the decrease of $I-V$ slope compared with highly ordered pyrolytic graphite (HOPG). On the other hand, the $I-V$ slope of MLG is decreased by the bonding of functional groups (C−OH, C═O, and O═C−OH) on the graphene structure. The XPS and Raman results are corroborated by FT-IR spectra (inset). With the exfoliation of unzipped SWCNTs, a new FT-IR spectrum is confirmed. The spectrum of MLG illustrates the presence of C−O (epoxy or alkoxy) at ~1070 cm^{-1}, C−OH (carboxyl) at ~1380 cm^{-1}, and C═O in carboxylic acid and carbonyl moieties at ~1740 cm^{-1}. These results confirm the bonding of functional groups of MLG. These attachments of functional groups reduced the electrical conductance of MLG.

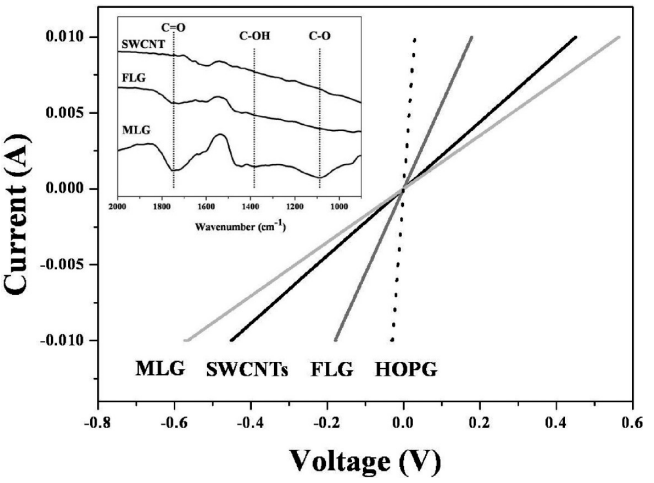

Figure 5. Current−voltage curves of MLG. The comparisons are HOPG, FLG, and SWCNTs; inset is FT-IR spectra.

Conclusion

In summary, we fabricated MLG using pulse current unzipping and the intercalation of alkali metals and microwave exfoliation of SWCNTs. We confirmed the structural properties of graphene by FE-SEM, HR-TEM, and Raman analysis, and in spite of a large surface area, the exfoliated graphene could exist as the planar structure with monolayer. With XPS analysis, we identified that hydroxyl and epoxide groups (C−OH, C═O, O═C−OH) were attached on the exfoliated graphene. Those prohibited the rebonding among the layers and rolling up of graphene for reducing the surface area, but these attachments of hydroxyl and epoxide groups reduced the electrical conductivity of MLG. This method could fabricate the high quality MLG in a large scale for a very short time. Therefore, this technique shows great potential for MLG fabrication and commercial applications.

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