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Synthesis of graphene nano-sheet without catalysts and substrates using fullerene and spark plasma sintering process

Tae-Sung Jun*,†, No-Hyung Park**, Dea-Sup So***, Joon-Woo Lee***, Hak-Sang Lim****, Heon Ham*,***** and Kwang Bo Shim*****

**Korea National University of Transportation, Civil. Environmental and Transportation Engineering, Chungju 380-702, Korea*
***Department of Textile Convergence of Biotechnology & Nanotechnology, Korea Institute of Industrial Technology, Ansan 426-910, Korea*
****National Nanotechnology Policy Center, Korea Institute of Science and Technology Information (KISTI), Seoul 130-741, Korea*
*****Department of Bio & Environmental Engineering, Semyung University, Jecheon 390-711, Korea*
******Division of Materials Science and Engineering, Hanyang University, Seoul 133-791, Korea*

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Abstract Catalyst-free graphene nano-sheets without substrates have been synthesized using fullerene and a high direct current (dc) pulse in the spark plasma sintering (SPS) process. Graphene nano-sheets were synthesized directly in the gas phase of carbon atoms which are generated from fullerene at a temperature of 600°C. Characterization has been carried out by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM), Raman spectroscopy (Raman), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD).

Key words Graphene, Fullerene, Nano-sheet, Substrate free, SPS

1. Introduction

With remarkable physical, chemical and electrical properties of graphene nano-sheets, graphite nano-sheets can possible to use in wide range of industrial applications, including energy storage, gas detection, conducting electrodes and etc [1-3].

With technical development of synthesis of graphene nano-sheets, pure solid carbonaceous sources of carbon nanotubes have been interested in synthesis of graphene nano-sheets [4-9]. Although the earliest efforts focused on graphene nano-sheets conversion from carbon nanotubes have been studied using unzipping techniques of carbon nanotubes, because of advantage of control of layers, width and length of graphene nano-sheet, carbon nanotubes were used for gaseous carbonaceous to synthesize graphene nano-sheets in spark plasma sintering process [10-13].

Because most of natural graphite forms from natural carbon sources at temperatures in the neighborhood of 750°C under high pressure and long time without transition metal catalysts, catalyst-free synthesis of graphene nano-sheets using pure solid carbon sources have interested.

Although low temperature synthesis of graphene have been reported on Cu foil at 600°C using gaseous hydrocarbon sources and chemical vapor deposition method, but catalyst-free synthesis of graphene nano-sheets using pure solid carbon without catalyst at temperatures in the neighborhood of 600°C have not been reported [14, 15]. Up to now, for graphene nano-sheets synthesis using solid carbon source of carbon nanotubes (CNTs), CNTs need over 2400°C to evaporate gaseous carbon from CNTs. Thus, low temperature synthesis of graphene nano-sheets has been interested.

In this paper, catalysts-free synthesis of graphene nano-sheets without substrate has been synthesized using fullerene and a spark plasma sintering process at a temperature of 600°C.

2. Experimental

Fullerene (1~2 nm diameter, with > 98 % purity) were purchased from SES Research Co. The pellets of fullerene were produced in a vacuum chamber (10^{-5} torr) using a Dr.sinter®model SPS-2080 pulse current sintering system (Sumitomo Coalmining Co., Japan). Contacts

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†Corresponding author
Tel: +82-43-841-5601
Fax: +82-43-849-1500
E-mail: tsjun@ut.ac.kr

were placed between two graphite rams in a cylindrical graphite (ISO-63) die with an inner diameter of 20 mm with 2 g fullerene. The pellets were heated to 600°C at a heating rate of 10°C/min with a pressure of 100 MP a between the rams, and the applied direct current was about 1500 A (voltage < 5 V) with a pulse duration of 12 ms and pulse interval of 2 ms during 10 min [16]. The thickness of compact sintered samples was about 2 mm. After polishing using SiC abrasive paper, they were finally subjected to scanning electron microscopy (SEM) observation using a Hitachi-S5700 instrument with a field emission gun. High resolution transmission electron microscopy (HR-TEM) investigations were carried out using a JEOL-3010 micro scope operating at 300 kV. 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). X-ray diffraction (XRD) was using copper Kα radiation (Rigaku D/MAX 2C, Japan).

3. Results and Discussion

Fig. 1 shows HR-TEM images of few-tens-nanometer graphene nano-sheet formed from gaseous carbon atoms which directly evaporated from fullerene at a temperature of 600°C. Fig. 1(a) shows an HR-TEM image of few-tens-nanometer graphene nano-sheet formed in the SPS process. During the SPS process, gas-phase carbon atoms were directly generated by the Joule heating when the current flows on the surfaces of fullerene. After that process, gaseous carbon atoms gradually formed graphene nano-sheet as the temperature decreased. Fig. 1(b) shows magnified lattice-resolved TEM image of graphene nano-sheet with a lattice spacing of about 0.35 nm, which is a few ten nanometers in size and were synthesized without catalysts and substrates. Fig. 1(c) shows SEAD pattern of graphene nano-sheet, which shows ordered graphite lattice structure.

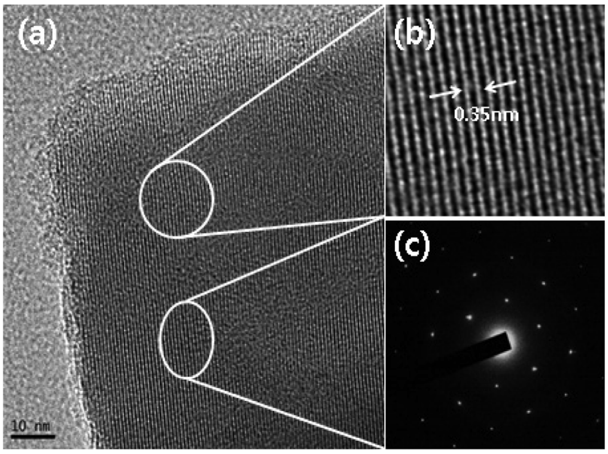

Fig. 1. (a) An HR-TEM image of few-tens-nanometer graphene nano-sheets. (b) shows magnified lattice-resolved TEM image of graphene nano-sheet with a lattice spacing of about 0.35 nm. (c) shows SEAD pattern of graphene nano-sheet.

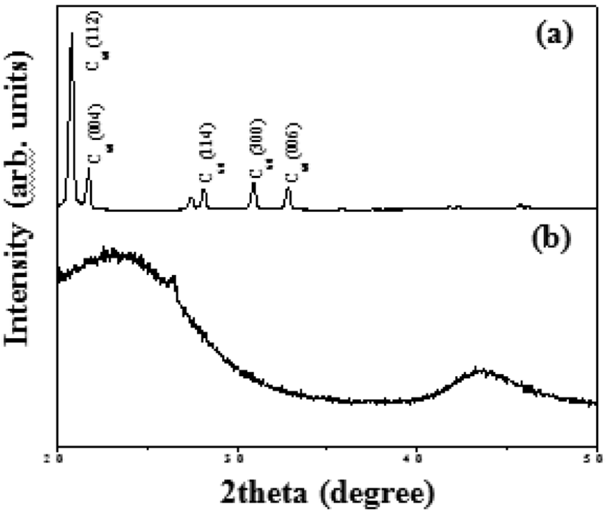

Fig. 2. XRD spectrum of (a) pure fullerene, (b) graphene nano-sheet converted from fullerene at 600°C.

Fig. 2(a) shows the XRD patterns of the fullerene and graphene nano-sheets, The XRD pattern in Fig. 3(a) shows that the diffraction peaks at 2θ = 20.753°, 21.622° and 28.059°, 30.632°, 32.682° correspond to the inter-planar spacing of fullerene {112}, {004} and {114}, {300}, {006}, respectively. Fig. 2(b) shows the X-ray diffraction patterns of graphene nano-sheets which converted from fullerene after the heat-treatment at 500°C, and then showed two peaks at 26° and 44.7°. Appearance of turbostratic stacking of the graphene nano-sheets planes

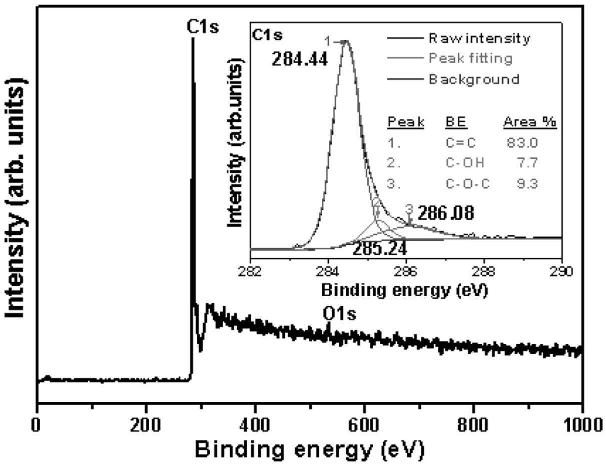

Fig. 3. XPS spectrum of graphene nanosheet, and the enlarged figure which shows the result of resolution of the C1s peak.

is indicated at 26°. The graphene nano-sheets show a (002) diffraction peak at 26°, corresponding to a d-spacing of 0.34 nm, which is almost the same as that of graphite (JCPDS No. 75-1621). The 44.7° (100) diffraction peak originates from the two-dimensional in-plane symmetry along the graphene sheets [17, 18].

Fig. 3 shows the XPS spectrum of the graphene nanosheets that exhibited two intense and narrow peaks at 284.44 eV and 532.0 eV, which correspond to C1s and O1s core levels, respectively. The relative atomic concentrations of carbon and oxygen estimated from XPS were 98 and 2 %, respectively. The result of resolution of the C1s core level peak is also shown in Fig. 3. The C1s core level peak can be resolved into three contributions appearing at 284.44, 285.24, and 286.8 eV. The resolution was carried out using an asymmetric peak analogous to that observed for graphite at 284.44 eV and two Gaussian peaks are centered at 285.24 eV, and 286.08 eV. The main peak at 284.44 eV was assigned to sp^2-hybridized graphite-like carbon atoms and to sp^2 carbon atoms bound to hydrogen. The peak at 285.3 eV appeared because of sp3-hybridized carbon atoms as in diamond-like carbon. Peaks at 286.2 eV, 287.2 eV and 288.9 eV were typical of carbon atoms bound to one oxygen atom by single bonds (C-OH, C-O-C), and double bond (C=C), respectively. The oxygen was present at trace level, as shown by the very weak intensity of O1s peak centered at 532.0 eV [19, 20].

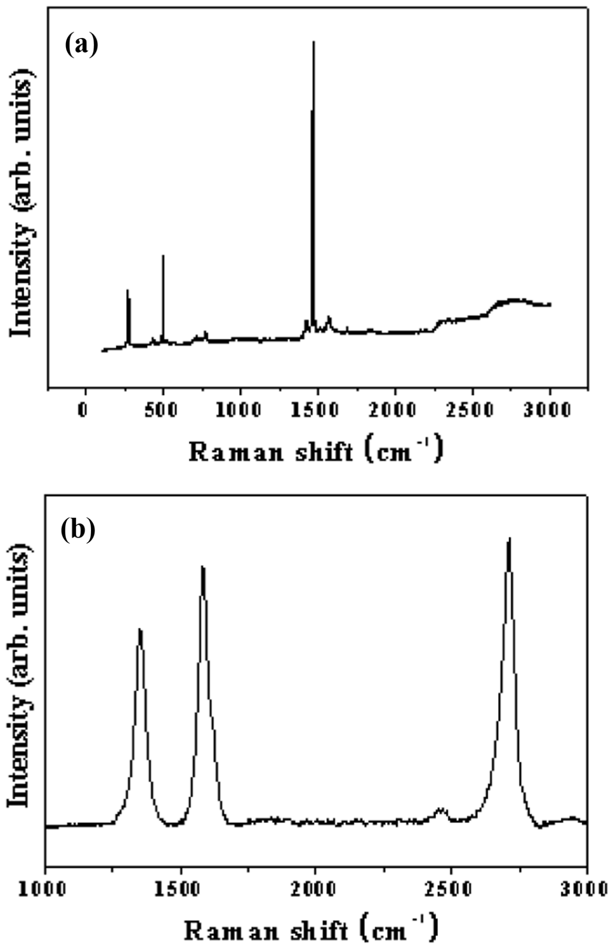

Fig. 4. (a) Raman spectrum of fullerene, (b) graphene nano-sheet converted from fullerene at 600°C.

Fig. 4 shows Raman spectra of fullerene and graphene nano-sheet. The Raman spectra of pure C60 fullerene sample are shown in Fig. 4(a). The three main lines of fullerene were obtained at the shift of 269, 494 and 1466 cm^{-1}, which are the Ag(1), Hg(1), and Ag(2) characteristic modes of pure C60 fullerene molecules [9, 10]. Fig. 4(b) shows the Raman spectrum of graphene nano-sheet which converted from fullerene by plasma sintering process at 600°C for 30 min. This spectrum shows two Raman bands at ~1318 cm^{-1} (D band), ~1580 cm^{-1} (G band) of graphite, 2600 cm^{-1} (2D band). The G band indicates the original graphite feature because of the in-plane vibration of sp^2 carbon atoms, and the D band is due to amorphous carbons which have a certain fraction of sp^3 carbon bonding structures. Therefore, the intensity of the G band depends on the thickness or number of layers in graphene. The intensity ratio of the D band to the G (I_D/I_G) was employed to determine the fraction of in-plane crystallite in the graphite structure [21, 22]. The value of I_D/I_G of the graphite is 0.82. The second-order Raman feature, namely the 2D band (second-order of the D band) at 2600 cm^{-1}, is very sensitive to the stacking order of the graphene sheets along the c-axis as well as to the number of layers, and shows greater structure with increasing number of graphene layers [21-23].

4. Conclusions

Catalyst-free graphene nano-sheets without substrates have been synthesized using fullerene and a high direct current (dc) pulse in the spark plasma sintering (SPS) process. Graphene nano-sheets were synthesized directly in the gas phase of carbon atoms which are generated from fullerene at a temperature of 600°C. The Raman spectra of fullerene and graphene nano-sheets show that the I(D)/I(G) was increased via the generation of graphene nano-sheets in conjunction with the consumption of starting fullerene. From analysis of the XPS spectrum of the graphene nano-sheets, the relative atomic concentrations of carbon and oxygen were 98 and 2 %, respectively.

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References

[1] D.R. Dreyer, R.S. Ruoff and C.W. Bielawski, "From conception to realization: An historial account of graphene and some perspectives for its future", Angewandte Chemie International Edition 49 (2010) 9336.

[2] X. Li, H. Zhu, K. Wang, A. Cao, J. Wei, C. Li, Y. Jia, Z. Li, X. Li and D. Wu, "Graphene-on-silicon schottky junction solar cells", Adv. Mater. 22 (2010) 2743.

[3] S. Bae, H. Kim, Y. Lee, X. Xu, J. Park, Y. Zheng, J. Balakrishnan, T. Lei, H.R. Kim, Y.I. Song, Y. Kim, K.S. Kim, B. Ozyilmaz, J. Ahn, B.H. Hong and S. Iijima, "Roll-to-roll production of 30-inch graphene films for transparent electrodes", Nat. Nanotechnol. 5 (2010) 574.

[4] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva and A.A. Firsov, "Electric field effect in atomically thin carbon films", Science 306 (2004) 666.

[5] A.K. Geim and K.S. Novoselov, "The rise of graphene", Nature Mater. 6 (2007) 183.

[6] D. Wei and Y. Liu, "Controllable synthesis of graphene and its applications", Adv. Mater. 22 (2010) 3225.

[7] T.G. Kim, Y.H. Shin, H. Cho and J.K. Kim, "Synthesis of transparent diamond-like carbon film on the glass by radiofrequency plasma enhanced chemical vapor deposition", J. Korean Crystal Growth and Crystal Technology 22(4) (2012) 190.

[8] K.H. Choi, I.J. Yoo, H.S. Lee, K.H. Lee and D.C. Lim, "Fabrication of various carbon nanostructures by using different catalysts", Journal of the Korean Crystal Growth and Crystal Technology 20(3) (2010) 133.

[9] W. Kratchmer, L.D. Lamb, K. Fostiropoulos and D.R. Huffmann, "Solid C60: a new form of carbon", Nature 347 (1990) 354.

[10] J.B. Howard, J.T. McKinnon, Y. Makarovsky, A.L. Laeur and M.E. Johnson, "Fullerenes C60 and C70 in flames", Nature 352 (1991) 139.

[11] J.B. Howard, K.D. Chowdhury and J.B. Vander Sande, "Carbon shells in flames", Nature 370 (1994) 603.

[12] B. Chase and P.J. Fagan, "Substituted C60 molecuels: a study in symmetry reduction", J. Am. Chem. Soc. 114 (1992) 2252.

[13] B. Chase, N. Herron and E. Holler, "Vibrational spectroscopy of fullerenes (C60 and C70) temperature dependent studies", J. Phys. Chem. 96 (1992) 4262.

[14] B. Zhang, W.H. Lee, R. Piner, I. Kholmanov, Y. Wu, H. Li, H. Ji and R.S. Ruoff, "Low-temperature chemical vapor deposition growth of graphene from toluene on electropolished copper foils", ACS Nano 6(3) (2012) 2471.

[15] Z. Li, P. Wu, C. Wang, X. Fan, W. Zhang, X. Zhai, C. Zeng, Z. Li, J. Yang and J. Hou, "Low-temperature growth of graphene by chemical vapor deposition using solid and liquid carbon sources", ACS Nano 5(4) (2011) 3385.

[16] H. Ham, N.-H. Park, I. Kang, H.W. Kim and K.B. Shim, "Catalyst-free fabrication of graphene nanosheets without substrates using multiwalled carbon nanotubes and a spark plasma sintering", Chem. Commun. 48 (2012) 6672.

[17] S. Dimovski, A. Nikitin, H. Ye and Y. Gogotsi, "Synthesis of graphite by chlorination of iron carbide at moderate temperatures", J. Mat. Chem. 14 (2004) 238.

[18] M. Armandi, B. Bonelli, I. Bottero, A.C. Otero and E. Garrone, "Synthesis and characterization of ordered porous carbons with potential applications as hydrogen storage media", Microporous Mesoporous Mater 103 (2007) 150.

[19] C.N. Mbileni, F.F. Princloo, M.J. Witcomb and N.J. Covile, "Synthesis of mesoporous carbon supports via liquid impregnation of polystyrene onto a MCM-48 silica template", Carbon 44 (2006) 1476.

[20] K. Qin, S.Y. Xie, Z.Y. Jiang, X.H. Zhang, Z.X. Xie, R.B. Huang and L.S. Zheng, "Low temperature solvothermal synthesis of crumpled carbon nanosheets", Carbon 42 (2004) 1737.

[21] D.V. Kosynkin, A.L. Higginbotham, A. Sinitskii, J.R. Lomeda, A. Dimiev, B.K. Price and J.M. Tour, "Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons", Nature 458 (2009) 872.

[22] L. Jiao, L. Zhang, X. Wang, G. Diankov and H. Dai, "Narrow graphene nanoribbons from carbon nanotubes", Nature 458 (2009) 877.

[23] A. Gupta, G. Chen, P. Joshi, S. Tadigadapa and P.C. Eklund, "Raman scattering from high-frequency phonons in supported n-graphene layer films", Nano Lett. 6 (2006) 2667.