Journal of Ceramic Processing Research. Vol. 13, Special. 1, pp. s42~s46 (2012)

J O U R N A L O F
Ceramic Processing Research

The effect of various parameters for few-layered graphene synthesis using methane and acetylene

Jungrok Kim[a], Jihoon Seo[b], Hyun Kyung Jung[c], Soo H. Kim[d,*] and Hyung Woo Lee[b,*]

[a]*Department of Mechanical Engineering, Pusan National University, san 30, Jangjeon-dong, Geumjung-gu, Busan 609-735, South Korea*

[b]*National Core Research Center for Hybrid Materials Solution, Pusan National University, San 30, Jangjeon-dong, Geumjung-gu, Busan 609-735, South Korea*

[c]*Department of Diagnostic Radiology, College of Medicine Inje University, Haeundae Paik Hospital, Busan 612-030, South Korea*

[d]*Department of Nanomechatronics Engineering, Pusan National University, San 30, Jangjeon-dong, Geumjung-gu, Busan 609-735, South Korea*

The effect of the parameters for few-layered graphene growth by thermal CVD on nickel substrate was investigated. Graphene can be synthesized by using different strategies. Chemical vapor deposition (CVD) has known as one of the most attractive methods to produce graphene due to its good film uniformity, compatibility and large scale production. The control of parameters such as temperature, growth time and pressure in CVD process has been widely recognized as the most important process in graphene growth. Different carbon precursors, methane and acetylene, were introduced in the quartz tube with a variety of growth conditions. Raman spectroscopy was used to confirm the presence of a few- or multi-layered graphene.

Key words: Graphene, Chemical vapor deposition, Raman spectroscopy, Hydrogen, Methane, Acetylene.

Introduction

Graphene is one-atom-thick film of carbon arranged in a two-dimensional hexagonal lattice. Due to its outstanding electrical, mechanical, and chemical properties [1-4], it has recently become a promising candidate for various high-tech applications such as transparent and flexible displays, high speed transistors, electric devices and biological sensors [5-10]. Lots of methods such as mechanical and chemical exfoliation from graphite, and epitaxial growth on SiC substrate were used for graphene synthesis [11-13]. One of the most common methods for thin film graphene growth is chemical vapor deposition (CVD) [14-16]. In comparison to other methods, graphene growth on metal catalyst by CVD has the distinct advantages in terms of large area graphene and transferring onto other targeted substrates. Ni and Cu have received the most attention as a metal catalyst for graphene synthesis. Because its surface chemistry with hydrocarbons has been well investigated [17-19], the discussion of this paper will be limited to graphene synthesis. The nickel substrate, where the carbon solubility is higher than Cu, is used as a metal catalyst for decomposition of a carbon source gas. In general graphene synthesis mechanism, the carbon atoms segregated on the nickel or diffused into the bulk substrate by increasing temperature, and then they are precipitated to the surface during the cool-down process [20-21]. With this general growth mechanism, the graphene synthesis is affected by various parameters such as the growth temperature, insert gas ratio, growing time, and so on. For obtaining the desired graphene with high quality and controlled few-layer, the mentioned parameters should be controlled to find the optimal conditions. In this paper, we demonstrate that a single or a few layers of graphene can be grown by the thermal decomposition of methane and acetylene by controlling the process parameters and compare the effect of hydrocarbon source gases. The synthesized graphene was investigated with Raman spectroscopy and high resolution transmission electron microscopy (HR-TEM).

*Corresponding author:
Tel : +82-55-350-5287 ; +82-51-510-3160
Fax: +82-55-350-5653 ; +82-51-518-3360
E-mail: sookim@pusan.ac.kr ; LHW2010@pusan.ac.kr

Experiments

Chemical vapor deposition (CVD) is a synthesis technique that offers a number of advantages such as good film uniformity, high deposition rates and scalability from laboratory to production systems. In this work, the hybrid vacuum machine combined with plasma enhanced chemical vapor deposition (PE-CVD) and thermal CVD to synthesize few-layered graphene (Black Magic II, Aixtron Co.). This experiment was implemented under various temperatures, pressures, gases mixing ratio

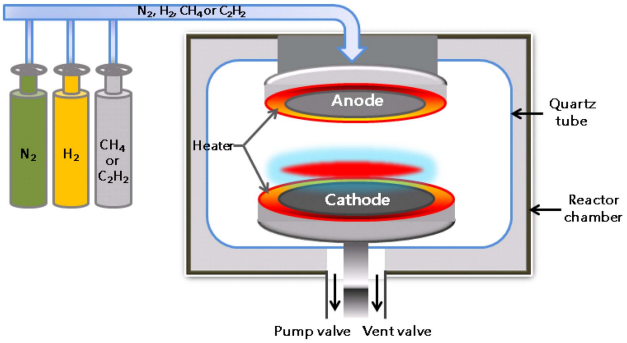

Fig. 1. A schematic diagram of the hybrid vacuum system for synthesizing carbon nanotubes and graphene.

(H_2:C_2H_2, H_2:CH_4), and growth time. For a metal catalyst, a 300 nm thick Ni film sputtered onto 100 nm thick SiO_2 coated Si wafer was prepared. Fig. 1 shows the schematic diagram of the hybrid CVD machine. The substrate was placed on the reactor cathode in a vacuum chamber which connected to a vacuum pump and pressure control systems. The quartz tube had a diameter of 12 inches and the gases were introduced into the reactor from top to bottom to get a uniform flow. A Raman spectroscopy (Horiba Co.) operating at a wavelength of 532 nm was used to analyze the graphene synthesis. Raman spectroscopy is known as a very useful technique, providing information about the quality and number of layers of graphene [22-25]. The G-band at ~1582 cm^{-1} is common to all sp^2 carbon forms. The stretching of the C-C bond in graphitic materials gives rise to the G-band Raman feature. The 2D-band which appears in the range around 2600-2800 cm^{-1} is shown in all sp^2 carbon materials. The ratio of G-band to 2-D band indicates the number of layer of graphene, thus it is an important factor to determine a mono layer graphene. The D-band which appears at ~1340 cm^{-1} shows the presence of defect in sp^2 -hybridized carbon systems and the quality of graphene.

Results and Discussion

The characteristics of graphene synthesis according to the various growing parameters such as active temperature, growing time, reacting gas ratio, and pressure were investigated and analyzed. Fig. 2(a) shows the Raman spectra of the graphene grown at various active temperatures by methane and Fig. 2(b) shows the Raman spectra by acetylene on Ni substrate. A few-layered graphene could be obtained at a ratio of 15:1 (H_2:C_xH_y) which can be explained by over one of the intensity ratio of G peak to 2D (I_G/I_{2D}). As shown in Fig. 2, the D peak was reduced gradually by increasing growing temperature. The high temperature caused a stable structured and high quality graphene synthesis. Fig. 2(a) shows that it is not easy to synthesize the graphene at 750 °C by methane, while few-layered graphene was obtained at 750 °C by acetylene due

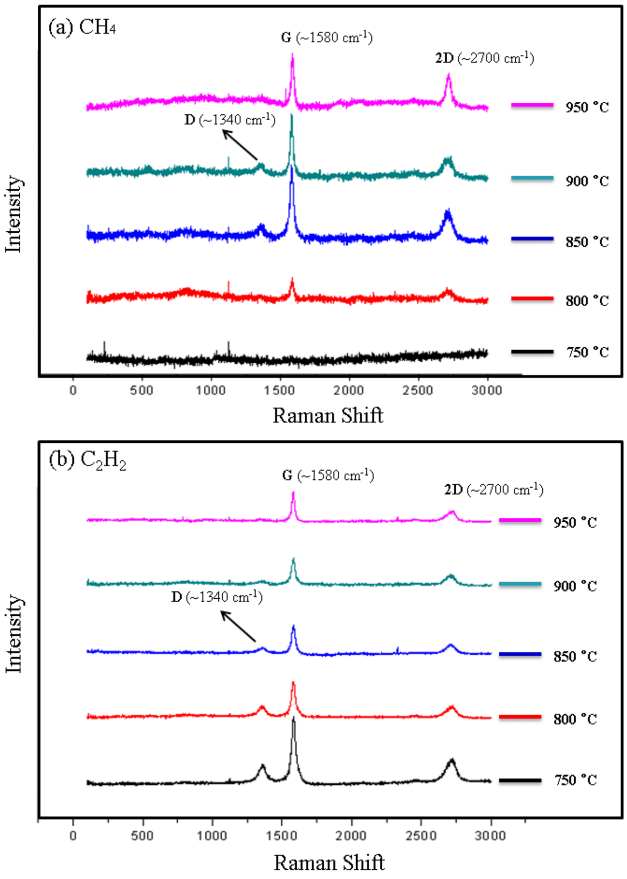

Fig. 2. Raman spectra of the graphene synthesized at various active temperatures with (a) 15:1 (H_2:CH_4) and (b) 15:1 (H_2:C_2H_2) of gas mixing ratio.

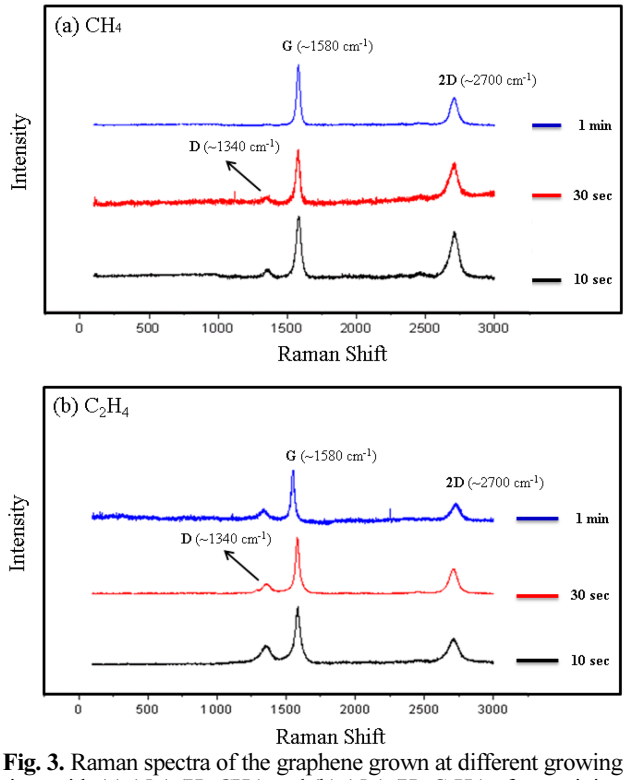

Fig. 3. Raman spectra of the graphene grown at different growing time with (a) 15:1 (H_2:CH_4) and (b) 15:1 (H_2:C_2H_2) of gas mixing ratio at 950 °C.

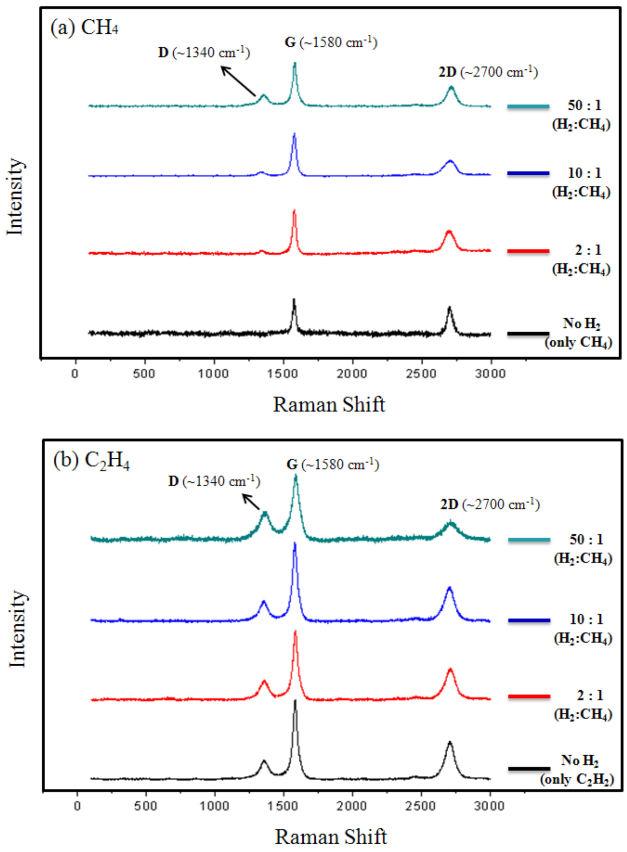

Fig. 4. Raman spectra for the graphene films synthesized at various gas mixing ratio (H_2:CH_4) by (a) methane (growing time: 10 sec, temperature: 950 °C) and (b) acetylene (H_2:C_2H_2) (growing time: 10 sec, temperature: 950 °C).

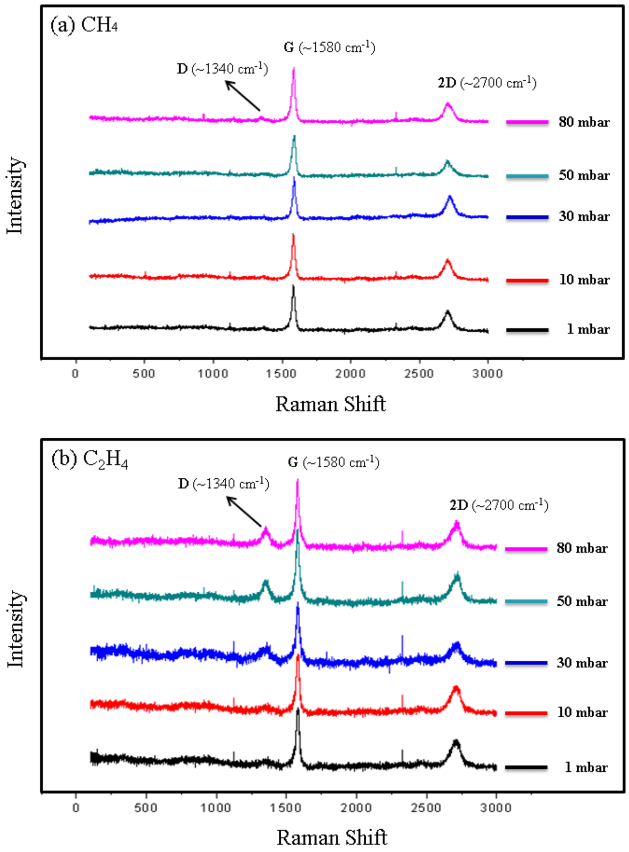

Fig. 5. Raman spectra for the graphene film grown at different pressures by (a) methane (growing time: 1 min, temperature: 950 °C), (b) acetylene (H_2:C_2H_2) (growing time: 1 min, temperature: 950 °C).

to their different dissociation temperature. This result can be explained that methane and acetylene have a different dissociation temperature, because the barrier energy for breaking the C-C bond is lower than for C-H bonds [26-28]. Therefore, graphene can be synthesized at lower growing temperature with acetylene than methane as experimental results. Most of the results show that multilayer graphene was synthesized. This is because nickel substrate has a high solubility and carbon diffuses into the metal first before segregating and precipitates to the surface. Fig. 3 shows the Raman spectra of the graphene formed at various growth times using methane and acetylene. The synthesis temperature was 950 °C and 900 °C, respectively, providing 15:1 (H_2:C_xH_y) of gas mixing ratio. In both cases, D peak was gradually reduced by increasing growing time. In a short growing time, bi- or few-layered graphene with defects such as grain boundary and crack can be synthesized and D peak will be appeared in Raman spectra as shown in Fig. 3. By increasing growing time, upper layer might be covered on a defected part of a bottom layer and D peak will be reduced. However, the number of layer was increased from 2~3 to over 15. Fig. 4 shows the Raman spectra of the graphene formed at various gases mixing ratio of H_2:CH_4 and H_2:C_2H_2. The D peak was increased by increasing the proportion of H_2 to C_xH_y. Because hydrogen not only controls the graphene shape and size, but etches the graphene [29], the high proportion of hydrogen to C_xH_y might cause more defects of graphene. Since graphene synthesis and etching processes occur simultaneously in graphene growth mechanism, the high quality of graphene can be synthesized by optimizing the conditions of gas mixing ratio. In Fig. 4 (a), the bottom Raman spectrum (black color) shows 2~3 layered graphene grown at 950 °C growing temperature and 10 second growing time without hydrogen, just with methane. The synthesis of high quality graphene is more controllable by the gas mixing ratio in methane than in acetylene. Since the dissociation temperature of acetylene is lower than methane, acetylene is more sufficiently dissociated into C atoms than methane at 950 °C. Because the graphene synthesis in inadequate carbon condition under methane is more reactive to hydrogen etching, D peak-free graphene might be obtained under methane more easily than under acetylene through the optimazation. Fig. 5 shows the Raman spectra of the graphene formed at different pressures by methane and acetylene, respectively. In case of methane, there is no remarkable change in a range from 80 mbar to

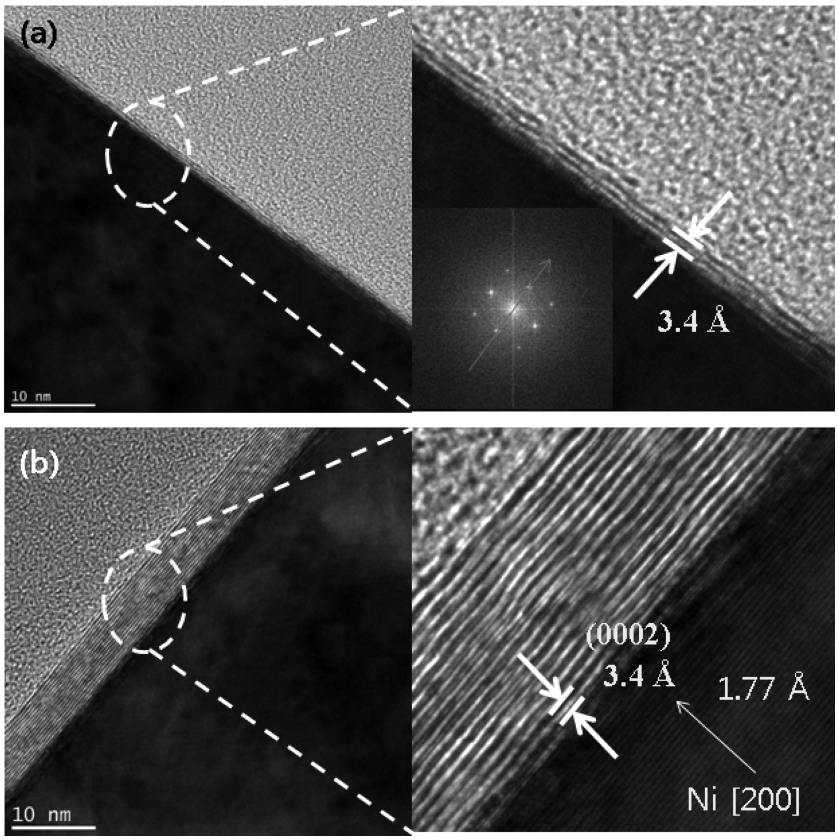

Fig. 6. HR-TEM images of graphene having 0.34 nm of interlayer spacing grown at 950 °C by methane (a) for 10 sec, 2~3 layers (b) for 3 min , 15~18 layers.

1 mbar. On the other hand, D peak of graphene grown by acetylene was gradually reduced by reducing pressure. We verified the number of graphene layer by high resolution transmission electron microscopy. Fig. 6 shows HR-TEM images of graphene grown at 950 °C by methane. Through optimizing growing conditions, as shown in Fig. 6(a), we obtained 2~3 layered graphene with 10 sec growing time, 950 °C growing temperature and 15:1 (H_2:CH_4) gas mixing ratio. It was well synthesized having 0.34 nm of interlayer spacing. Fig. 6(b) shows over 15 layers of graphene with 1 minute growing time.

Conclusions

It was investigated the effect of various parameters such as growing temperature, growing time, gas mixing ratio, and pressure for growing few-layered graphene by methane and acetylene. Graphene was synthesized by thermal CVD for good film uniformity and large scale production. For synthesizing a graphene, a 300 nm thick Ni film on 100 nm thick SiO_2/Si wafer was used as a metal catalyst. The D peak of Raman spectra was gradually reduced by increasing growing temperature. In contrast to methane, few-layered graphene was obtained with acetylene at 750 °C. It might be caused that the dissociation temperature of acetylene is lower than methane. Increasing growing time can reduce the D peak gradually. However, the number of layer was increased from 2~3 to over 15. By decreasing the proportion of hydrogen to C_xH_y, intensity of D peak was reduced. Especially, D peak-free graphene was grown without hydrogen by methane. In contrast to methane, D peak of graphene grown by acetylene was gradually reduced by reducing growing pressure.

Lots of growing parameters were coupled each other. Temperature, growth time, gas ratio and pressure are the important factors to produce high quality graphene. The optimization of these parameters to control the number of layer and quality of graphene is needed to implement the graphene into bio-, nano-device fabrication.

Acknowledgements

This work was supported by a 2-Year Research Grant of Pusan National University and also supported by NCRC (National Core Research Center) program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (2011-0006257).

References

1. A.H.C. Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, and A.K. Geim, Rev. Mod. Phys. 81 (2009) 109-162.
2. A.K. Geim and K.S. Novoselov, Nature Mater. 6 (2007) 183-191.

3. A.K. Geim, Science. 324 (2009) 1530-1534.
4. M.J. Allen, V.C. Tung, and R.B. Kaner, Chem. Rev, 110 (2010) 132-145.
5. G. Eda, G. Fanchini and M. Chhowalla, Nat. Nanotechnol. 3 (2008) 274.
6. Z. Yin, S. Sun, T. Salim, S. Wu, X. Huang, Q. He, Y.M. Lam and H. Zhang, ACS Nano. 4 (2010) 5263-5268.
7. C. Biswas and Y.H. Lee, Adv. Funct. Mater. 21 (2011) 3806-3826.
8. Y. Wu, Y. Lin, A.A. Bol, K.A. Jenkins, F. Xia, D.B. Farmer, Y. Zhu, and P. Avouris, Nature. 472 (2011) 74-78.
9. Y. Zhu, Z. Sun, Z. Yan, Z. Jin, and J. M. Tour, ACS Nano. 5 (2011) 6472-6479.
10. Z. Wang, Y. Chen, P. Li, X. Hao, J. Liu, R. Huang, and Y. Li, ACS Nano. 5 (2011) 7149-7154.
11. K. Novoselov, A. Geim, S. Morozov, D. Jiang, Y. Zhang, S. Dubonos, I. Grigorieva, and A. Firsov, Science. 306 (2004) 666-669.
12. M. Choucair, P. Thordarson, and J.A. Stride, Nat. Nanotechnol. 4 (2009) 30-33.
13. L. Gao, J.R. Guest and N.P. Guisinger, Nano Lett. 10 (2010) 3512-3516.
14. A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. Dresselhaus and J. Kong, Nano Lett. 9 (2009) 30-35.
15. X. Wang, H. You, F. Liu, M. Li, L. Wan, S. Li, Q. Li, Y. Xu, R. Tian, Z. Yu, D. Xiang and J. Cheng, Chem.Vap. Deposition. 15 (2009) 53-56.
16. A. Ismach, C. Druzgalski, S. Penwell, A. Schwartzberg, M. Zheng, A. Javey, J. Bokor and Y. Zhang, Nano Lett. 10 (2010) 1542-1548.
17. H.H. Madden, J. Kuppers, and G. Ertl, J. Chem. Phys. 58 (1973) 3401-3410.
18. Y. Gamo, A. Nagashima, M. Wakabayashi, M. Terai, and C, Oshima, Surf. Sci. 374 (1997) 61-64.
19. R.V. Vang, K. Honkala, S. Dhal, E.K. Vestergaard, J. Schadt, E. Laegsgaard, B.S. Clausen, J.K. Norskov, and F. Besenbacher, Nat. Mater. 4 (2005) 160-162.
20. X.S. Li, W.W. Cai, L. Colombo, and R.S. Ruoff, Nano Lett. 9, (2009) 4268-4272.
21. Q.J. Yu, S. Lian, S. Siriponglert, H. Li, Y.P. Chen, and S. Pei, Appl. Phys. Lett. 93 (2008) 113103.
22. A.C. Ferrari, J.C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K.S. Novoselov, S. Roth, and A.K. Geim, Phys. Rev. Lett. 97 (2006) 187401.
23. D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold, and L. Wirtz, Nano Lett. 7 (2007) 238-242.
24. L.M. Malarda, M.A. Pimentaa, G. Dresselhaus, M.S. Dresselhaus, Physics Reports. 473 (2009) 51-87.
25. M.S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus, and R. Saito, Nano Lett. 10 (2010) 751-758.
26. G. Nandamuri, S. Roumimov, and R. Solanki, Nanotechnology. 21 (2010) 145604-145607.
27. C.N.R. Rao, K.S. Subrahmanyam, H.S.S.R. Matte, B. Abdulhakeem, A. Govindaraj, B. Das, P. Kumar, A. Ghosh, and D.J. Late1, Sci. Technol, Adv. Mater. 11 (2010) 040502.
28. R.V. Vang, K. Honkala, E.K. Vestergaard, J. Schadt, E. Laegsgaard, B.S. Clausen, J.K. Norskov, and F. Besenbacher, Nat. Mater. 4 (2005) 160-162.
29. I. Vlassiouk, M. Regmi, P. Fulvio, S. Dai, P. Datskos, G. Eres, and S. Smirnov, ACS Nano. 5 (2011) 6069-6076.