ISSN: 2586-7652 | 2635-7607 Vol. 02, No. 02 September 2019

International Journal of Advanced Engineering

Source: http://ictaes.org

Manuscript received: August 12, 2019; Revised : September 9, 2019 ; Accepted : September 20, 2019



Synthesis of Chemical Vapor Deposition of Twisted and Collapsed Graphene Tubes with Doping Behaviour

Krishna Bahadur Rai

Department of Physics, Patan Multiple Campus, Tribhuwan University, Nepal

krishnarai135@gmail.com

Abstract

Graphene is a planar atomic layer of carbon atoms arranged in hexagonal structures. In this work, we have demonstrated the simple cost-effective and lithography-free fabrication method for the synthesis of the Chemical Vapor Deposition (CVD) twisted, collapsed graphene tube which is a new structure of graphene. A characterized wavy surface is also found by the wrinkling of the folded, twisted and collapsed graphene tubes. The twisted, collapsed graphene tube obtained was confirmed by the Raman spectra similar to that of planar graphene.The values of I_{2D}/I_G ratio for twisted collapsed graphene on SiO_2/Si and the self-supporting twisted graphene are 1.93 and 1.62 respectively and inform that twisted collapsed graphene on SiO_2/Si is less doped than the self-supporting twisted graphene. The amplitude ratio of D peak to the G peak suggests that the structural defects in twisted, collapsed graphene tubes are relatively insignificant such that the degree of crystallization of twisted, collapsed graphene tube is relatively good. On the other hand, long twisted graphene tube in millimeter (mm) length is obtained as self-supportive and can be hung vertically. The self-supporting twisted, collapsed (partially) graphene tube synthesized in our work might have potential application in the field of mechanical, electrical, thermal and chemical properties.

Keywords: *Graphen; Chemical Vapor Deposition (CVD); twisted graphene; collapsed graphene tube; self-supportive graphene.*

1. Introduction

Graphene is a planar atomic layer of carbon atoms arranged in hexagonal structures [1]. Graphene

Corresponding Author: Krishna Bahadur Rai
Author's affiliation: Department of Physics, Patan Multiple Campus, Tribhuwan University, Nepal
Email: krishnarai135@gmail.com

nanoparticles, carbon nanotubes (CNTs) and nanofibers (CNFs) being carbon nanomaterials have been extensively used as the reinforcement of composites on account of their remarkable combination of strength, stiffness and high surface to volume ratio [2]. Carbon fibers generally have high thermal and chemical stabilities in the absence of the oxidizing agent, low densities, excellent creep resistance, good thermal and electrical conductivities and excellent tensile properties [3].

The low energy dispersion in graphene is linear which makes charge carriers in graphene behave like massless Dirac fermions [4]. This linear dispersion also gives the extremely large mean free path in graphene at room temperature [5]. Chemical and geometrical modifications of this material allow different electronic and optical properties. The band gap is opened in hydrogenated [6] and fluorinated [7] graphene. Besides the band gap, other novel electronic properties [8] can be also found in graphene nano-ribbons. Nanoholes in periodic arrangements can induce magnetic behavior [9] or bandgap opening [10].

The micromechanical cleavage was the cheap, straightforward and first method to produce planar single layer graphene. However, it has a low material yield and often generates small sized graphene flakes [11]. So, for such method to have success, highly experienced and skilled personal are required. On the other hand, chemical intercalation gives the synthesis of planar graphene with higher yields. However, it suffers from the poor control of the shape, size, and defects introduced during the chemical reaction [12].

Over the past decades, considerable efforts have been devoted to exploring various structures because some modifications to the physical properties are expected from their interactions. The carbon nanotube eventually collapses under radial deformation and this collapsed state is more stable than the tubular geometry [13] when the radius becomes greater than a crossover value. More interestingly, graphene can be grown on copper with many shapes such as balls, wires or tubes. In some cases, collapsed induces metallic carbon nanotubes to become semiconducting and vice-versa [14]. The application of graphene requires versatile patterns such as strips, ribbons or other defined shapes for high strength materials and for high electrical transport. Kwonjae Yoo et. al., [15] attempted to grow micrometer size graphene tubes using a copper wire of 15 μm diameter. Number of Chemical Vapor Deposition (CVD) growth of graphene on metal plate substrates such as Cu [11], Ni [16], Pt [17] Ir [18], Ru [19] etc. have been reported and they can be easily chemically wet etched such that it is easy to transfer as grown graphene to another substrate. However, achieving CVD growth of twisted and collapsed graphene tube on twisted copper wires templates (like a rope) has not been produced and it remains still challenging but it might have importance in future applications. So, we explore a simple cost-effective and lithography-free fabrication method for the synthesis of the CVD twisted, collapsed graphene tubes as fibers which are a new structure of graphene.

2. Experiment

Mechanical exfoliation of graphite is not good for producing large area high-quality graphene as compared with CVD technique. In this work, we grow thin layers of twisted graphene tubes on twisted copper wires template like a rope structure by CVD method. For this, three wires, each having diameter 56 μm (Alfa-Aesar), were twisted to make the twisted structure of copper wires like a rope in figure 1(a). And these were then employed as a template for the subsequent growth of twisted single-layer graphene via CVD into the silica chamber of the system. The thermal CVD silica chamber was pumped to the base vacuum pressure (about 10 - 2 Torr). Then it was heated by allowing the Ar gas at the flow rate 99 sccm (sccm- standard cubic centimeters

per minute) till the temperature reached to 950 ºC and it was again adjusted to reach the temperature 1020 ºC. At the time of rising temperature from 950 ºC to 1020 ºC, when the temperature reached to around 1003 ºC, H_2 gas (99 sccm) was started to pass for 1 hour into the hot chamber. After 1 hour cleaning with H_2 gas, methane (CH_4) gas at the flow rate 21 sccm was passed for 15 minutes at around 9.7 Torr pressure to carry out the growth of twisted graphene wires. Finally, the sample was fast cooled to room temperature under Ar ambient atmosphere.

After spin coating with poly(methyl methacrylate) PMMA on the twisted graphene wires on the twisted copper wires, it was etched using ferric chloride ($FeCl_3$) by normally like that of planner graphene and by specially hanging for other samples too. Therefore, the twisted and collapsed graphene tube is obtained from laid etching (horizontal etching) when metallic core copper is removed by chemical etching. Then this PMMA/graphene was rinsed with deionized (DI) water more than five times (for approximately 30 minute each). The cleaning of PMMA film on the twisted graphene wires was removed by immersing the samples into acetone for 30 minutes. At last, that normally cleaned twisted, collapsed graphene tubes left are transferred on SiO_2/Si.

When the samples were etched by hanging vertically with the help of other horizontal supportive wire, self-supporting twisted collapsed (partially) graphene tubes were obtained and it was washed with deionized water. For removing PMMA, it was also dipped into the acetone and then taken out using previously used supportive wires with still hanging.

After this, Raman spectrum and optical microscope were used to characterize the morphologies and properties of our twisted and collapsed graphene tubes. Raman analysis is also used to show the presence of a small level of defects of CVD grown graphene.

3. Result and Discussion

Here a method to synthesize twisted, collapsed graphene tube by CVD using methane as a precursor at growth temperature around 1020 ºC on twisted copper wires has been reported. Figure 1(b) shows the optical image of the twisted copper wires after synthesis of the graphene layer and it seems like continuous graphene covers the whole surface of twisted Cu wires.

Raman spectroscopy is a powerful and versatile tool for finding graphene structures, single layer, bilayer, multilayer graphene and for detecting the electronic properties of graphene [20]. Besides these, it is also sensitive to the doping level [21], defects [22] and strains [23]. So, Raman analysis was carried out to confirm a graphene layer and defects by taking Raman spectrum using Inviva (50X objective length) Raman system with 1800 lines/mm grating, 532 nm excitation laser. The laser power was kept sufficiently lower than the damage threshold of graphene to avoid any heat-induced effects. Ensuring that the high-quality graphene is synthesized on the surface of the twisted copper wires as evidence in figure 1(c), Raman spectrum shows the peaks for the G and 2D bands at 1584 cm^{-1} and 2683 cm^{-1} respectively due the individual bond stretching and compression (G band) and breathing modes of hexagonal rings of carbon atoms (D band) [20]. There is also a small D peak intensity at 1349 cm^{-1} and it shows the amount of defects in the graphene structure. The defect density in the synthesized graphene on twisted copper wires was found to be very low i.e. $I_D/I_G = 0.79$ ($I_D/I_G < 1$, figure 1(c)). Moreover, the sharpness of the G and 2D bands and the intensity ratio of 2D to G peak is I_{2D}/I_G

= 1.21 and it confirms the monolayer graphene [11].

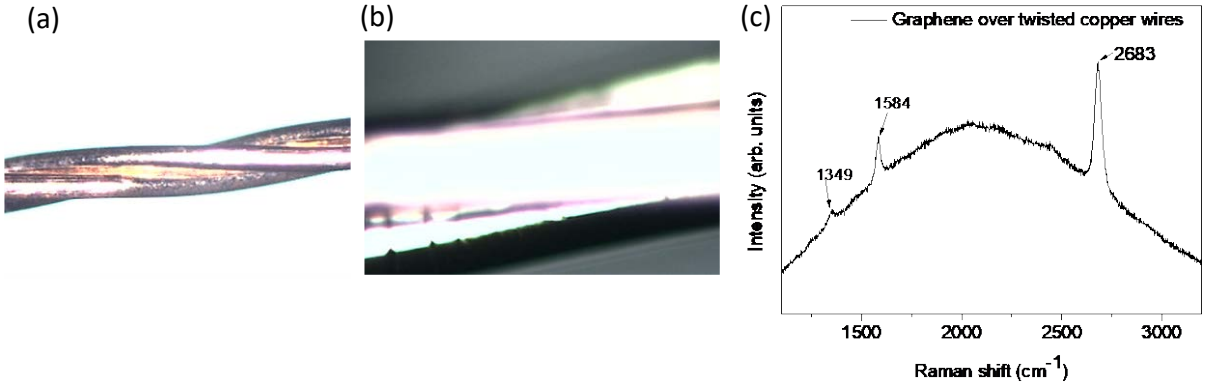


Figure 1. (a) Optical image of twisted copper wires (each having 56 µm diameter) before CVD process (b) optical image of twisted graphene covered twisted copper wires after CVD process (c) Raman spectrum of the twisted graphene on twisted copper wires obtained by 532 nm photoexcitation.

Figure 2(a) shows the optical image of the transferred twisted, collapsed graphene strips on 300 nm SiO_2/Si. It can be seen that some residues and wrinkles were unavoidably obtained at the surface and groove of the twisted, collapsed graphene tubes. It is also inevitable that some part of the graphene is also removed in the etching step leaving the twisted, collapsed strips of graphene tube and the width of the obtained collapsed strips is around 70 – 80 µm which is smaller than the initial diameter of the collective twisted wires (56+56+56) µm. A characterized wavy surface is also found by the wrinkling of the folded, twisted and collapsed graphene tubes. The G peak for figure 2(b) of the twisted, collapsed graphene tube is located at 1593 cm^{-1} and is near with the G peak position value of planar graphene. The position and shape of the G peak provide the sp^2 phase carbon which is indeed the formed graphene [24]. Except for this G peak, there is also the presence of D peak at 1347 cm^{-1} which is common in CVD grown graphene films due to the attribution of structural defects in the material [25]. The amplitude ratio of D peak to the G peak suggests that the structural defects in twisted, collapsed graphene tubes which are relatively insignificant such that the degree of crystallization of twisted, collapsed graphene tube is relatively good. However, the only difference observed is a more intense D peak in figure 2(b) than in figure 1(c) which is explained by folding and cracking of the layers during the wet transfer process, thus increasing defect density and the intensity of the D peak [26]. Finally, we focus on the 2D peak located at 2688 cm^{-1}. In this case, the ratio of I_{2D}/I_G =1.93 suggests that single layer and folded graphene due to collapsed is formed after etching the twisted copper wires with ferric chloride.

The self-supporting twisted, collapsed (partially) graphene tube was adjusted with the help of the substrate such as glass as supportive material on the non-etched part of graphene covered twisted copper wires. In such case, the self-supporting twisted collapsed graphene with some millimeter in length (figure 3(a)) was freely suspended like one side supported beam.

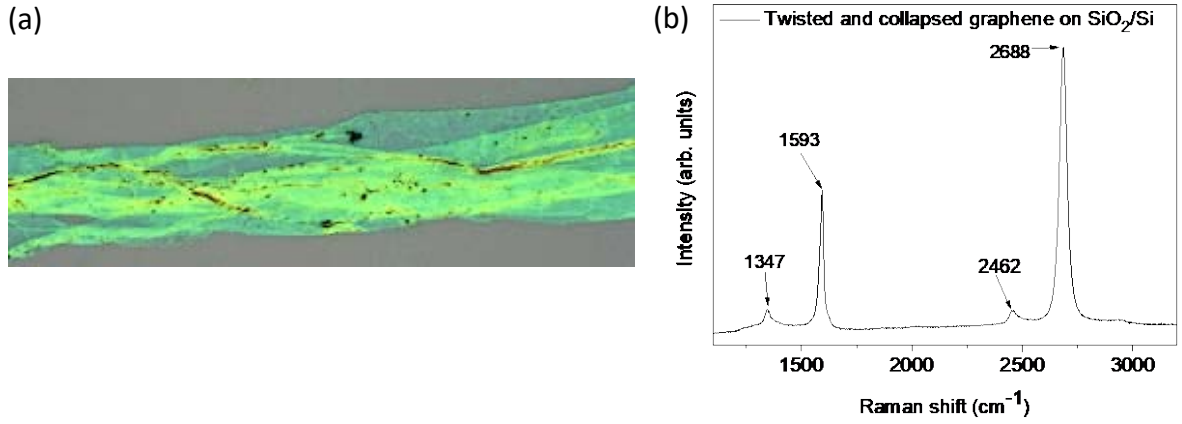


Figure 2. (a) Optical image of transferred twisted collapsed graphene tube on SiO_2/Si (b) Raman spectrum of transferred twisted collapsed graphene tube on the SiO_2/Si substrate obtained by 532 nm photoexcitation.

Figure 3(a) shows an optical image of twisted collapsed graphene suspending with the help of support. In which one side looks like a thread of graphene due to etching and the other side having bigger diameter is the non-etched twisted copper wire with graphene covered. So using this bigger side, it can be taken to the Raman tool or optical microscope.

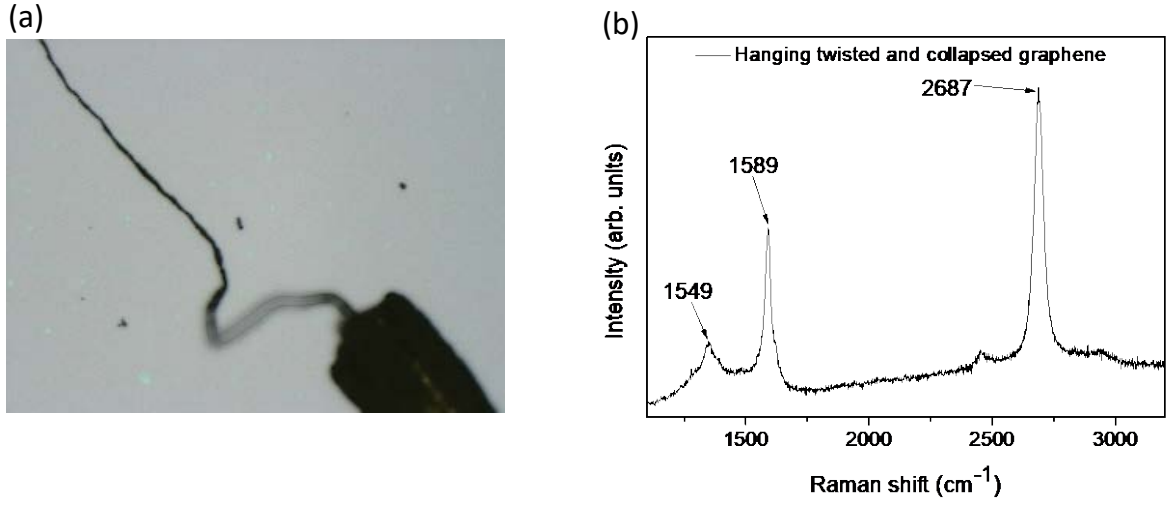


Figure 3(a): Optical image of self-supporting twisted collapsed graphene taken from the objective lens of 5X (b) Raman spectrum of hanging and self-supporting twisted collapsed graphene obtained by 532 nm photoexcitation.

A typical Raman spectrum from figure 3(b) for this self-supporting sample shows G and 2D peak at 1589 cm^{-1} and 2687 cm^{-1} respectively. The ratio between their intensity i.e. $I_{2D}/I_G = 1.62$ confirms that the sample is a monolayer. To verify the consistency of the monolayer graphene after wet etching, we collected Raman spectra at four different locations such that the G peak is 1592 ± 3 cm^{-1} and 2 D peak is 2689 ± 2 cm^{-1}. As reported, I_{2D}/I_G is an indicator of doping level where a larger I_{2D}/I_G corresponds to a lower doping level [27]. Here figures 2(b) and 3(b) have I_{2D}/I_G ratios 1.93 and 1.62 respectively. So it can be inferred that twisted collapsed graphene on SiO_2/Si is less doped than the self-supporting twisted graphene. Therefore it indicates

that the self-supporting graphene might have some etchant or acetone inside it even after cleaning several times. By this etchant or acetone, the twisted graphene may not be completely collapsed in figure 3(a) and more intense Raman D peak at 1349 cm^{-1} was observed. It is like the graphene transferred on to a SiO_2/Si wafer coated with the hydrophobic PDMS film has fewer defects compared to those in graphene transferred on to a bare SiO_2/Si wafer [28]. So the self-supporting twisted and partially collapsed graphene behaves like a graphene transferred in bare SiO_2/Si.

4. Conclusion

In this work, we have demonstrated the twisted collapsed graphene tubes synthesized on the surface of twisted copper wires. We optimized the process conditions for twisted, collapsed graphene tube and this was confirmed by the Raman spectra similar to that of planar graphene. On the other hand, long twisted graphene tube in millimeter (mm) length is obtained as self-supportive and can be hung vertically. In this case, the preparation of twisted collapsed graphene tube does not need conventional lithography process in which there might have residual photoresists. This may be useful study for getting cleanly twisted collapsed graphene tube. The self-supporting twisted, collapsed (partially) graphene tube synthesized in our work might have potential application in the field of mechanical, electrical, thermal and chemical properties.

References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, (2004). Electric Field Effects in Atomically Thin Carbon Films. Science, 306 (5696), 666-669

[2] A. Needleman, T. L. Borders, L. C. Brinson, V. M. Flores, L. S. Schadler, (2010). Effect of an Interphase region on debonding of a CNT reinforced Polymer Composites. Composites Science and Technology, 70(15), 2207-2215

[3] X. Huang, Materials, (2009). Fabrication and Properties of Carbon Fibers. 2(4), 2369-2407

[4] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov , (2005).Two-dimensional Gas of massless Dirac Fermions in graphene. Nature, 438, 197-200

[5] A. K. Geim, K. S. Novoselov, (2007). The Rise of Graphene. Nature Materials, 6(3), 183-191

[6] J. O. Sofo, A. S. Chaudhari, G.D. Barber, (2007). A Two-Dimensional Hydrocarbon. Phys. Rev. B, 75(15), 153401-153404

[7] R. R. Nair, W. Ren, R. Jalil, I. Riaz, V. G. Kravets, L. Britnell, P. Blake, F. Schedin, A. S. Mayorov, S. Yuan, M. I. Katsnelson, H. M. Cheng, W. Strupinski, L. G. Bulusheva, A. V. Okotrub, I. V. Grigorieva, A. N. Grigorenko, K. S. Novoselov, A. K. Geim, (2010). Fluorographene: A Two dimensional Counterpart of Teflon. Small, 6(24), 2877-2884

[8] X. Wang, Y. Ouyang, L. Jiao, H. Wang, L. Xie, J. Wu, J. Guo and H. Dai, (2011). Graphene Nanoribbons with Smooth Edges behave as Quantum Wires. Nat. Nanotechnol., 6(9), 563-567

[9] D. Yu, E. M. Lupton, M. Liu, W. Liu, F. Liu, (2008). A Unified Geometric Rule for designing Nanomagnetism in Graphene. Nano Research, 1(6), 497-501

[10] W. Lu, Z. F. Wang, Q. W. Shi, J. Yang, F. Liu, (2009). Band-gap scaling of graphene nanohole superlattices. Phys. Rev. B, 80(23), 233405-233408

[11] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, R. S. Ruoff, (2009). Large-Area Synthesis of High Quality and Uniform Graphene Films on Copper Foils. Science, 324(5932), 1312-1314

[12] Z. Luo, Y. Lu, L. A. Somers, A. T. C. Johnson, (2009). High Yield Preparation of Macroscopic Graphene Oxide Membranes. J. Am. Chem. Soc.,131(3), 898-899

[13] G. Gao, T. Cagin, W. A. Goddard, (1998). Energetics, Structure, Mechanical and Vibrational Properties of Single-Walled Carbon Nanotubes. Nanotechnol., 9(3), 184-191

[14] P. E. Lamert, P. Zhang, V. H. Crespi, (2000). Gapping by Squashing: metal-insulator and insulator-metal Transition in Collapsed carbon Nanotubes. Phys. Rev. Lett., 84(11), 2453-2456

[15] K. Yoo, E. K. Seo, S. J. Kim, W. Kim, M. G. Park, H. Yu, C. Hwang, (2012). Electrical Transport Properties of graphene-covered-Cu wires grown by Chemical vapor deposition. Current Applied Physics, 12(1), 115-118

[16] Q. Yu, J. Lian, S. Siriponglert, H. Li, Y. P. Chen, S. S. Pei, (2008). Graphene segregated on Ni surfaces and transferred to insulators. Appl. Phys. Lett., 93, 113103-113105

[17] P. Sutter, J. T. Sadowski, E. Sutter, (2009). Graphene on Pt(111): Growth and Substrate Interaction. Phys. Rev. B, 80(24), 245411-245420

[18] J. Coraux, A. T. N'Diaye, C. Busse, T. Michely, (2008). Structural Coherency of Graphene. Nano Lett., 8(2), 565-570

[19] K. F. McCarty, P. J. Feibelman, E. Loginova, N. C. Bartelt, (2009). Kinetics and Thermodynamics of carbon Segregation and Graphene growth on Ru(0001). Carbon,47(7) 1806-1813

[20] A. C. Ferrari, J. C. Meyer, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, A. K. Geim, (2006). Raman Spectrum of Graphene and Graphene Layers. Phys. Rev. Lett., 97(18), 187401-187404

[21] A. Das, S. Pisana, B. Chakraborty, S. Piscanec, S. K. Saha, U. V. Waghmare, K. S. Novoselov, H. R. Krishnamurthy, A. K. Geim, A. C. Ferrari, A. K. Sood, (2008). Monitoring Dopants by by Raman Scattering in an electrochemically Top-gated graphene Transistor. Nat. Nanotechnol., 3(4), 210-215

[22] J. L. Chen, W. G. Cullen, C. Jang, M. S. Fuhrer, E. D. Williams, (2009). Defect Scattering in graphene. Phys. Rev. Lett., 102(23), 236805-236808

[23] Z. H. Ni, Y. Y. Wang, T. Yu, Z. X. Shen, (2008). Raman Spectroscopy and imaging of graphene. Nano Res., 1(4), 273-291

[24] M. S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus, R. Saito, (2010). Perspectives on Carbon Nanotubes and Graphene Raman Spectroscopy. Nano Lett. 10(3), 751-758

[25] A. Ismach, C. Druzgalski, S. Penwell, A. Schwartzberg, M. Zheng, A. Javey, J. Bokor, Y. Zhang, (2010). Direct Chemical Vapor Deposition of Graphene on Dielectric Surfaces. Nano Lett., 10(5), 1542-1548

[26] X. Liang, B. A. Sperling, I. Calizo, G. Cheng, C. A. Hacker, Q. Zhang, Y. Obeng, K. Yan, H. Peng, Q. Li, X. Zhu, H. Yuan, A. R. Hight Walker, Z. Liu, L. Peng, C. Richter, (2011). Toward Clean and Crackless Transfer of Graphene. ACS Nano, 5(11), 9144-9153

[27] D. M. Basko, S. Piscanec, A. C. Ferrari, (2009). Electron-electron interactions and doping dependence of the two-phonon Raman intensity in graphene. Phys. Rev., B, 80(16), 165413-165422

[28] K. B. Rai, I. B. Khadka, E. H. Kim, S. J. Ahn, H. W. Kim, (2018). Influence of Hydrophobicity on the Chemical Treatments of Graphene. Journal of the Korean Physical Society, 72(1), 107-110