

Effect of Thermal Treatment on Production of Graphene from Graphite via Exfoliation in Organic Solvent (Acetonitrile)

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Summary: Graphite flakes were divided into two equal parts Part A and Part B. Part A was thermally shocked at 800°C under inert atmosphere of argon for two min before exfoliation under sonic tip while Part B was exfoliated as such using acetonitrile (ACN) as exfoliating media in both cases at 15-20°C. The concentration of the graphene as a result of exfoliation and centrifugation at 500 rpm for 45 min in both cases were determined. After ten hours of sonication the concentration of graphene in Part A is >12mg/ml with few layered thickness while that of Part B was <5mg/ml consisting of more layers than Part A. UV spectroscopy, Raman, Transmission Electron Microscopy and Scanning Electron Microscopy (SEM) were used for the study of these nanoflakes.

Key words: Thermal treatment, Centrifuge, Concentration, Graphene layers, TEM, SEM

Introduction

Graphene is nearly a transparent, two-dimensional semimetal consisting of a single atomic lattice of hexagonally arranged sp² hybridized carbon atoms [1]. Since the isolation of graphene and the discovery of its unique properties, there have been unprecedented levels of research on this remarkable material. The work carried out by Geim and Novoselov in 2004 was a simple exfoliation method in which protrusions of highly-oriented pyrolytic graphite (HOPG) were embedded in photoresist and adhesive tape was used to successively peel off layers of graphene [2]. Although this method is tedious and cannot be scaled up to industrial level yet it opens new horizons of research in this specific field. This scotch tape method is simple and does not require any modification to environmental parameters such as temperature and pressure. In addition, this method provides high quality (high mobility and low defect) single and few layer graphene sheets with large areas as high as 100µm [3]. Usually strong acids are used for the oxidation of graphite to graphene oxide (GO) which results in stable aqueous solution of GO [4]. Then this dispersion of GO can be reduced by aqueous hydrazine as reducing agent [5, 6] or by thermal reduction under a reducing atmosphere [7-9]. Graphene growth by chemical vapor deposition (CVD) is typically carried out under ultra-high vacuum and at high temperatures [10]. In this process

volatile or gas phase carbon precursor is flowed over a metallic substrate which acts as a catalyst and nucleation site for graphene growth [11]. Graphene produced by CVD was first reported by Somani and coworkers in 2006 using nickel foil and camphor for the metallic substrate and carbon precursor respectively [12]. Graphene has been used in functionalized as well as in pristine form in order to improve the mechanical and thermal properties of different polymeric system like polyurethane, bisphenol A epoxy, ultra-high molecular weight polyethylene and polyphenylene sulfide, polyvinyl chloride and polyacrylonitrile and polyvinylalcohol [13-19]

Liquid phase exfoliation of graphite to graphene, also referred to as solution based graphene exfoliation, was first carried out by the Coleman group [20] in 2008 via sonication of graphite flakes in organic solvents such as N-methyl-Pyrrolidinone (NMP) and dimethyl formamide (DMF). Coleman's work stemmed from previous research involving dispersion of carbon nanotubes (CNTs) in organic solvents which was concerned with matching the surface energies associated with CNTs and the solvents [21].

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Likewise Rui Hao et al. used acetonitrile as exfoliating media following ball milling and sonication for monolayer and bi layers graphene production via solvo-thermal-assisted exfoliation [22]. The use of surfactants in liquid exfoliation, carried out to create aqueous dispersion of graphene, help to mitigate colloidal aggregation of graphene in solution [23, 24]. Other less common but noteworthy liquid exfoliation methods include intercalation of graphite with alkaline [25] or halogen salts [26] to form graphite intercalation compounds (GICs). The GIC's can be either directly dispersed or exfoliated in solution by sonication [25]. Likewise these can also be thermally expanded at high temperatures in which the intercalating compounds volatilize to form expanded graphite (EG) [27]. In next step these expanded graphite is subsequently exfoliated in solution via sonication [26]. Liquid exfoliation of graphite to graphene is advantageous method as compared to other methods such as CVD growth and mechanical exfoliation due to the simplicity of the process. This does not require high vacuum and high temperatures as well as the low cost of the starting materials. Although extremely high concentration of graphene in NMP has already been reported by our group, i.e. 63 mg/ml but the NMP gets degraded after six hours of tip sonication [28].

In this work, ACN is used as exfoliating media under tip sonic and graphite was divided into two equal parts (thermally treated and untreated) in order to study the thermal effects on concentration and flake size of graphene nanoflakes.

Experimental

Graphite powder and acetonitrile were purchased from Sigma-Aldrich and were used as supplied. Graphite was divided into two equal parts, 10 gms each (Part A and Part B). Both parts of graphite were dispersed in 100 ml of acetonitrile (ACN). Sonication was performed continuously for 12 hours by using sonic tip (GEX600, 48W, 24 kHz, flat head probe) running at 25% of maximum power and sonic bath (Branson 1510E-MT). Centrifugation was performed using a Hettich Mikro22R typically at 500 rpm for 45 min. After centrifugation the 70 % of top portion of dispersed solution was removed and concentration was determined by UV-Vis-IR absorption spectroscopy Varian Cary 6000i (with 1mm cuvettes). TEM was done using a Joel2100 and holey carbon grids (400 mesh). Thin film was made using porous alumina membrane (whatman Anodisc 47mm, having pore size of 0.02micron) for Raman study. Raman spectra (633 nm) were recorded on a Horiba Jobin Yvon LabRAM-HR. Scanning Electron

Microscopy (SEM) was performed in a Hitachi S-4300 field emission.

Results and Discussions

Graphite was divided into two equal parts (10 grams each), one part was thermally shocked at 800 °C in furnace under inert atmosphere of argon (Part A) while second part was not heat treated (Part B). So, through thermal treatment, we obtained expanded graphite (EG) in which the d spacing among the graphene layers was increased [22]. These materials i.e. EG and graphite flakes were then dispersed in acetonitrile separately and sonicated under tip for about 12 hours continuously at about 15-20 °C. Temperature was kept low in order to prevent the losses of ACN through evaporation. ACN has low boiling point ~ 81°C which is lower than other organic polar solvents like NMP, DMF and Dimethyl sulfoxide (DMSO) which are being used for exfoliation [20, 29]. This low boiling point polar solvent also facilitates in exfoliation process during tip sonication due to its polarity and it gets diffused into d spacing of EG and graphite [22]. Graphene layers get peeled off from EG and graphite, as sonication proceeds. Small aliquots were taken after every hour and its concentration was recorded. The both samples were processed side by side in parallel.

This process was kept continued for 12 hours and samples were taken after required interval of time. The concentration was studied through ultra violet spectroscopy using Lambert-Beer law eq. (1) [30]

$$A = \alpha Cl \quad (1)$$

where, the absorption coefficient " α " is related to the absorbance "A", "C" is concentration and is "l" the path length. We have selected " α " value equal to 3.62 ml mg⁻¹m⁻¹ [30]. The concentration was measured by recording the absorbance at 660 nm and transformed this into the concentration using eq. (1) [30]. In our prior work we reported graphene concentration in organic solvent N- methyl Pyrrolidinone (NMP) was 63 mg/ml. The exfoliation was carried out using organic solvent N-methyl Pyrrolidinone (NMP) under sonic tip. The NMP used in this work use to spoil after 6 hours which might be due to the oxidative degradation [28]. Here we tried to overcome this problem of oxidative degradation of NMP we used ACN

Before recording concentration through UV, every sample was bath sonicated for 15 min than centrifuged at 500rpm for 45 min to separate out

thick and unexfoliated graphite flakes from exfoliated one. An interesting phenomenon was observed that the concentration of Part A was rising after every passing hour while the incremental rise in Part B was not as prominent. ACN promotes the dispersion of graphene because of its strong dipole moment 3.87D [31]. No sooner did the ACN molecules get diffused into d spacing of EG and graphite, the dipole-induced dipole interaction of graphene and ACN facilitates exfoliation [22]. The ACN molecules get diffused easily in to Part A having enlarged d spacing due to thermal treatment. While in Part B case the graphene concentration does not increased to that extent which may be due to un-enhanced d spacing of graphite [22]. The process was kept continued for twelve hours but after the lapse of ten hours there was no prominent increase in concentration of both type of dispersion as shown in Fig. 1 and 2 respectively. Even after the passage of about twelve hours the concentrations of Part A and Part B were almost about 12mg/ml and about 5mg/ml respectively.

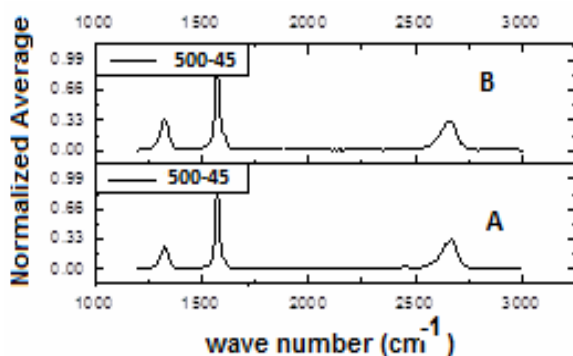


Fig. 1: Increase in the Defect peak of normalized Raman spectra of sample “A” and Sample “B”.

Raman analysis was conducted on both type of films prepared from these dispersions. A typical Raman spectrum was measured on film deposited on alumina membrane by filtering the graphene dispersion under vacuum. Sonication of nanostructured powder is complicated and not well-understood process. It has a number of effects on graphite powder. The starting crystallites are broken up into smaller crystallites [20]. Smaller flakes are formed and these small flakes are then cut up [30, 32]. It has been reported that increase in concentration is correlated with decrease in flake dimension as sonication time is increased. [30, 32]. Here in our present study, the EG with enlarged “d” spacing gave good flake size and comparatively high concentration. So, we suggest that in case of enlarged “d” spacing of EG most of the sonic energy is

utilized in peeling off the graphene layers by incorporating ACN molecules among these enlarged interlayer.

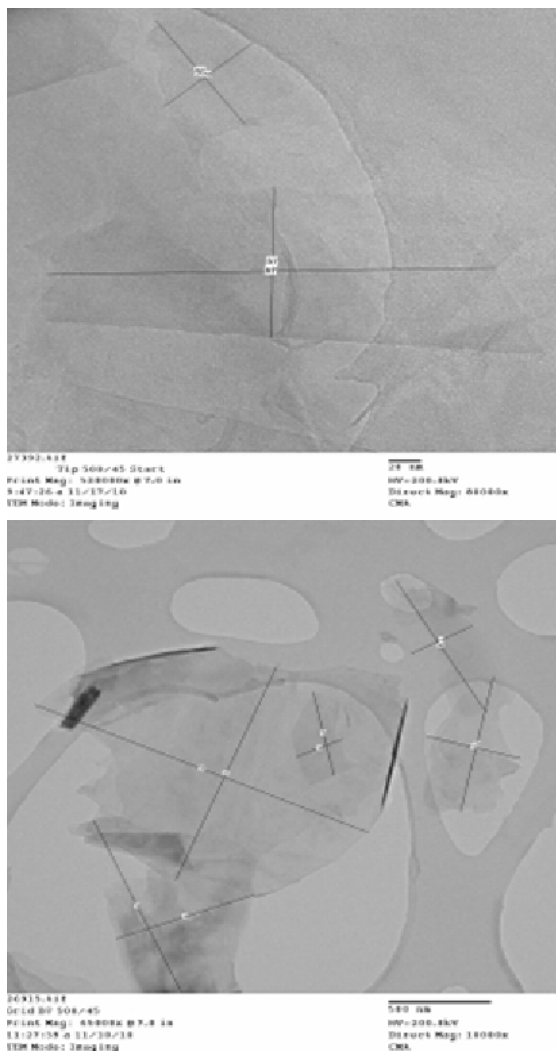


Fig. 2: TEM images of graphene nanoflakes.

Raman Spectrum of graphite materials can be characterized by certain and specific bands like D-band (1350cm^{-1}), G-band (1582cm^{-1}), and 2D-band (2700cm^{-1}) [33]. D-band shows the evidence of the presence of topological defects in sheets or edges of nanosheets [34]. For solvent exfoliated graphene the D band is associated with presence of flakes edges and can be linked to flake length by relation in eq. (2)

$$I_D/I_G - (I_D/I_G)_{\text{powder}} = k/L \quad (2)$$

where, k is constant [27] so, increase in I_D/I_G value shows decrease in flake size and vice versa. The

value of k is reported to be ≈ 0.26 , While $(I_D/I_G)_{\text{powder}}$ for graphite powder is 0.037 [35].

It is clear from Normalized Raman spectra obtained after twelve hours of sonication in Fig.1 A and B. The value of D-band (1350cm^{-1}) of sample A is less compared to sample B. In case of sample A the value of D band is below 0.33 while in case of sample B its value touches about Fig. 0.50. After the passage of 12 hours there is no appreciable rise in concentration for both cases. Why there is no appreciable rise in concentration for both cases, is not clear to us. So, we consider that sonic energy may be consumed in creating new edges at this stage (size reduction of graphene sheets) instead of exfoliation i.e. concentration is almost same even after the lapse of 12 hours. Increase in D band in case of type B is more intense and prominent compared to sample "A". It may be explained on the basis of close packing of graphene layers. In case "A" most of the sonic energy is consumed in peeling off the graphene layers from each other due to enhanced d spacing and remaining energy may have been utilized in size reduction of nanoflakes. While in case of sample "B" sonic energy is consumed in overcoming the Van der Waals forces between graphene layers in order to peel off the graphene layers and also size reduction of flakes. So, we understand in former case we obtained high concentration of graphene with better lateral dimensions as compared to later one.

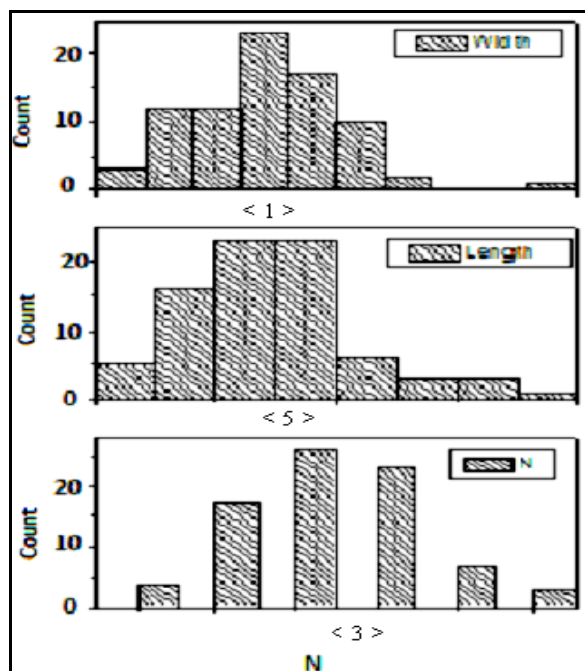


Fig. 3: Histogram of graphene nano flakes of sample "A".

Likewise TEM analysis was also conducted for exfoliated graphene. In histogram, as shown in Fig. 3 and 4, it is clear that Type A consists of less than three layers (in average) while Type B consists of more than four layers (in average) with lateral dimensions of ~ 5 and $\sim 1.2\mu\text{m}$ respectively. Similarly the width of nanoflakes in part A and part B case is $\sim 1\mu\text{m}$ and $0.3\mu\text{m}$ respectively. The difference in thickness (number of graphene layers) may be due to thermal shock which may have act like expanding agent for exfoliation of graphite. Likewise Scanning Electron Microscopy (SEM) of thin film (the segment of the film used for SEM was coated with 10-20nm of gold/palladium) also reveals that the exfoliated graphene consists of few layers as shown in Fig. 5. Scanning microscopy was conducted on part A sample only.

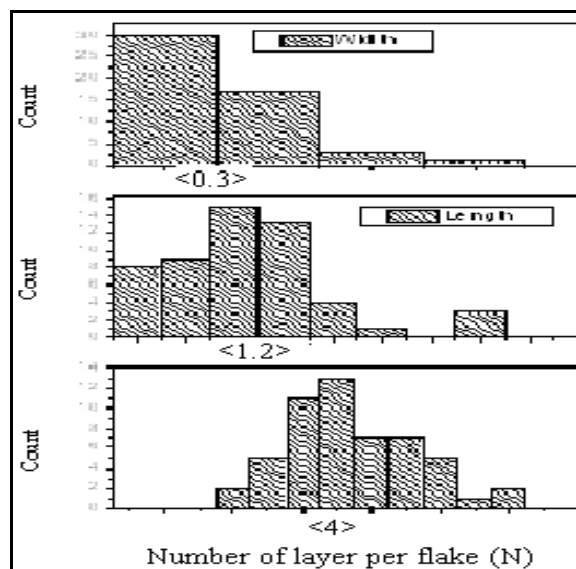


Fig. 4: Histogram of graphene nano flakes of sample "B".

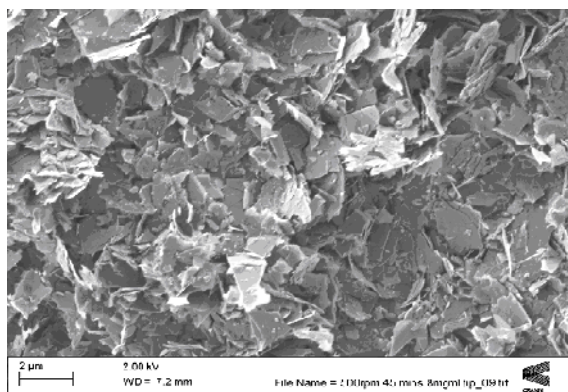


Fig. 5: SEM images of the flakes present on the interface of the free standing films prepared.

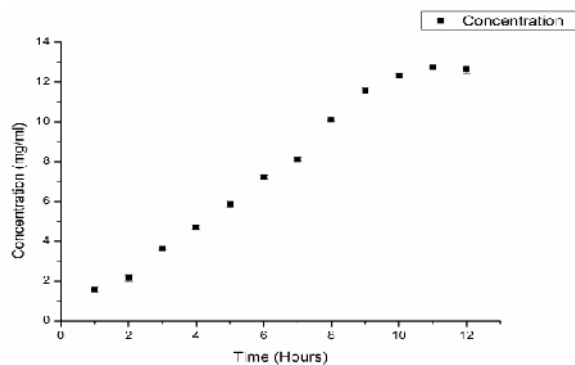


Fig. 6: Concentration of graphene of sample "A" in THF solvent determined by UV-Visible spectroscopy.

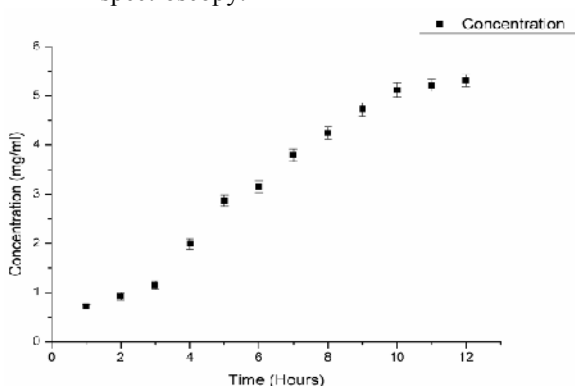


Fig. 7: Concentration of graphene of sample "B" in THF solvent determined by UV-Visible spectroscopy.

Conclusion

Optimum concentration of sodium cholate as surfactant has positive role on exfoliation of graphite to graphene in aqueous media in terms of concentration and lateral dimension of graphene sheets as reported in our previous studies [24]. Similarly heat treatment has also profound effect on exfoliation of graphite in acetonitrile as exfoliating media under sonic tip as observed in this study. Graphene nanosheets with 12mg/ml concentration, lateral dimensions of $\sim 5\mu\text{m}$ (average flake length) having few layered thickness can be obtained through this procedure in just ten hours under sonic tip. we understand that heat treatment helps to peel off the graphene layers by enhancing the interlayer spacing between graphene layers consequently sonic tip easily exfoliate the graphite with already enlarged d-spacing of graphene layers.

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References

1. R. Ruoff, Graphene: Calling all chemists, *Nat. Nanotechnol.*, **3**, 10 (2008).
2. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Electric Field Effect in Atomically Thin Carbon Films, *Science.*, **306**, 666 (2004).
3. A. H. Castro, F. Guinea, N. M. R. Peres, K. S. Novoselov, A. K. Geim, The Electronic Properties of Graphene, *Rev. Mod. Phys.*, **81**, 109 (2009).
4. S. Some, Y. Kim, E. Hwang, H. Yoo, H. Lee, Binol Salt as a Completely Removable Graphene Surfactant, *Chem. Commun.*, **48**, 7732 (2012).
5. D. Li, M. B. Müller, S. Gilje, B. K. Richard, G. G. Wallace, Processable Aqueous Dispersions of Graphene Nanosheets, *Nat. Nanotechnol.*, **3**, 101 (2008).
6. V. C. Tung, M. J. Allen, Y. Yang, R. B. Kaner, High-Throughput Solution Processing of Large-Scale Grapheme, *Nat. Nanotechnol.*, **4**, 25 (2009).
7. N. W. Pu, C. A. Wang, Y. M. Liu, Y. Sung, D. S. Wang, M. D. Ger, Dispersion of Graphene in Aqueous Solutions with Different Types of Surfactants and the Production of Graphene Films by Spray or Drop Coating, *J. Taiwan Inst Chem E.*, **43**, 140 (2012).
8. D. Yang, A. Velamakanni, G. Bozoklu, S. Park, M. Stoller, R. D. Piner, S. Stankovich, I. Jung, D. A. Field, C. A. Ventrice Jr, R. S. Ruoff, Chemical Analysis of Graphene Oxide Films After Heat and Chemical Treatments by X-Ray Photoelectron and Micro-Raman Spectroscopy, *Carbon.*, **47**, 145 (2009).
9. X. Gao, J. Jang, S. Nagase, Hydrazine and Thermal Reduction of Graphene Oxide: Reaction Mechanisms, Product Structures, and Reaction Design, *Journal of Physical Chemistry C.*, **114**, 832 (2010).
10. W. Choi, I. Lahiri, R. Seelaboyina and Y. S. Kang, Synthesis of Graphene and its Applications: a Review, *Critical Reviews in Solid State and Materials Sciences.*, **35**, 52 (2010).
11. V. Singh, D. Joung, L. Zhai, S. Das, S. I. Khondaker and S. Seal, Graphene Based Materials: Past, Present and Future, *Progress in Material Science.*, **56**, 1178 (2011).

12. P. R. Somani, S. P. Somani, M. Umeno, Planer Nano-Graphenes from Camphor by CVD, *Chemical Physics Letters.*, **430**, 56 (2006).
13. K. Nawaz, U. Khan, N. Ul-Haq, P. May, A. O'Neill, J. N. Coleman. Observation of Mechanical Percolation in Functionalized Graphene Oxide /Elastomers Composites, *Carbon.*, **50**, 4489 (2012).
14. J Gu, X Yang, Z. Lv, N. Li, C. Liang, Q. Zhang, Functionalized Graphite Nanoplatelets/Epoxy Resin Nanocomposites with High Thermal Conductivity, *International Journal of Heat and Mass Transfer*, **92**, 15 (2016).
15. J. Gu, N Li, L. Tian, Z. Lv and Q. Zhang, High Thermal Conductivity Graphite Nanoplatelet/UHMWPE Nanocomposites, *RSC Advances.*, **5**, 3634 (2015).
16. J. Gu, J. Du, J. Dang, W. Geng, S. Hu and Q. Zhang, Thermal Conductivities, Mechanical and Thermal Properties of Graphite Nanoplatelets/Polyphenylene Sulfide Composites, *RSC Advances.*, **4**, 22101 (2014).
17. K. Nawaz, M. Ayub, N. Ul. Haq, M. B. Khan, M. B. K. Niazi, A. Hussain, The Effect of Graphene Nanosheets on the Mechanical Properties of Polyvinylchloride, DOI: 10.1002/pc.23328, published online: November 2014.
18. K. Nawaz, M. Ayub, N Ul-Haq, M. B. Khan, M. B. K. Niazi, A. Hussain, Effects of Selected Size of Graphene Nanosheets on the Mechanical Properties of Polyacrylonitrile Polymer, *Fibers and Polymers.*, **15**, **2040** (2014).
19. K. Nawaz, M. Ayub, N Ul-Haq, M. B. Khan, M. B. K. Niazi and A. Hussain, The Effect of Large Area Graphene Oxide (LAGO) Nanosheets on the Mechanical Properties of Polyvinyl Alcohol DOI: 10.1515/polyeng-2015-0271, published online: August 2015.
20. Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari, J. N. Coleman, High-Yield Production of Graphene by Liquid-Phase Exfoliation of Graphite, *Nature Nanotechnology.*, **3**, 563 (2008).
21. Bergin, Nicolosi, Streich, Zhi, Tao, Ryan, Windle, Blau, Boland, Hamilton, Coleman, Sun, Carpenter, Towards Solutions of Single-Wall Carbon Nanotubes in Common Solvents. *Advanced Materials (Weinheim, Germany)*, **20**, 1876 (2008).
22. W Qian, R Hao, Y Hou, Y. Tian, C. Shen, H. Gao and X. Liang, Solvothermal-Assisted Exfoliation Process to Produce Graphene with High Yield and High Quality, *Nano. Res.*, **2**, 706 (2009).
23. A. A. Green, M. C. Hersam. Solution Phase Production of Graphene with Controlled Thickness via Density Differentiation, *Nano Letters.*, **9**, 4031 (2009).
24. K. Nawaz, M. Ayub, M. B. Khan, A. Hussain, A. Q. Malik, M. B. K. Niazi, M. Hussain, A. U. Khan, N. Ul-Haq, Effect of Concentration of Surfactant on the Exfoliation of Graphite to Graphene in Aqueous Media, *Nanomaterials and Nanotechnology.*, **6** (2016).
25. K. H. Park, B. H. Kim, S. H. Song, J. Kwon, B. S. Kong, K. Kang and S. Jeon, Exfoliation of Non-Oxidized Graphene Flakes for Scalable Conductive Film, *Nano Letters.*, **12**, 2871 (2012).
26. S. Lin, C. J Shih, M. S. Strano, D. Blankschtein, Molecular Insights into the Surface Morphology, Layering Structure, and Aggregation Kinetics of Surfactant-Stabilized Graphene Dispersions, *J. Am. Chem. Soc.*, **133**, 12810 (2011).
27. Y. A. Nikitin, M. L. Pyatkovskii, Formation and Properties of Materials Based on Thermally Expanded Graphite, *Powder Metallurgy and Metal Ceramics.*, **36**, 41 (1997).
28. U. Khan, H. Porwal,; A. O'Neill, K. Nawaz, P May, J. N. Coleman, Solvent-Exfoliated Graphene at Extremely High Concentration, *Langmuir.*, **27**, 907 (2011).
29. B. J Landi, H. J. Ruf, J. J. Worman, R. P. Raffaele, "Effects of Alkyl Amide Solvents on the Dispersion of Single Wall Carbon Nanotubes, *J. Phys. Chem. B.*, **108**, 17089 (2004).
30. U. Khan, A. O'Neill, M. Lotya, S. De, J. N. Coleman, High-Concentration Solvent Exfoliation of Graphene, *Small.*, **6**, 864 (2010).
31. J. A. Dean, Analytical Chemistry Handbook, Beijing World publishing Corporation/McGraw-Hill, Beijing, 275 (1998).
32. A. O'Neil, U. Khan, P. N. Nirmalraj, J. Boland, J. N. Coleman, High-Concentration Solvent Exfoliation of Graphene, *J. Phys. Chem. C.*, **115**, 5422 (2011).
33. A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, A. K. Geim, Raman Spectrum of Graphene and Graphene Layers, *Phys. Rev. Lett.*, **97**, 187401 (2006).
34. C. Casiraghi, A. Hartschuh, H. Qian, S. Piscanec, C. Georgi, A. Fasoli, S. Novoselov, D. M. Basko, A. C. Ferrari, Raman Spectroscopy of Graphene Edges, *Nano Lett.*, **9**, 1433 (2009).
35. U. Khan, A. O'Neill, H. Porwal, P. May, K. Nawaz and J. N. Coleman, Size Selection of Dispersed, Exfoliated Graphene Flakes by Controlled Centrifugation, *Carbon.*, **50**, 470 (2010).