

# Production of Surfactant Assisted Graphene by Liquid Phase Exfoliation via Probe Tip Sonication

Arti Sharma<sup>1</sup>, Gaurav Verma<sup>2</sup> and Amrit Pal Toor<sup>3</sup>

<sup>1</sup>Centre for Nano Science and Nanotechnology Panjab University, Chandigarh

<sup>2</sup>Centre for Nano Science and Nanotechnology Panjab University, Chandigarh

<sup>3</sup>Dr. S S Bhatnagar University Institute of Chemical Engineering and Technology Panjab University, Chandigarh

E-mail: <sup>1</sup>artisharma3@gmail.com, <sup>2</sup>gauravvermas@gmail.com, <sup>3</sup>aptoor@yahoo.com

**Abstract**—Graphene having  $sp^2$  hybridization of carbon atoms arranged in a honeycomb lattice is the parent of all 2D carbon allotropes. Owing to its extremely wonderful physical and chemical properties, it has attracted wide interest in recent years. Graphene majorly made by two completely different approaches i.e. top-down and bottom up. The top-down approach depends on exfoliation of carbon to provide graphene. Liquid phase exfoliation is more classified in to primarily two categories one is surfactant free and another is surfactant aided Liquid part exfoliation. Due to the versatility and the up-scalability of liquid phase exfoliation techniques, it is becoming more interesting in last few years. In this paper we have reported the liquid phase exfoliation of surfactant assisted graphene via probe tip sonication followed by centrifugation. The liquid dispersion has been characterized by spectroscopic techniques. The graphene dispersion produced by liquid phase exfoliation technique is a good candidate for many applications i.e. photovoltaics, optoelectronics, conductive transparent electrodes, thin film transistors etc.

## 1. INTRODUCTION

These Graphene two dimensional material having  $sp^2$  bonded carbon atoms arranged in a honeycomb lattice [1] and parent of all two dimensional carbon allotropes e.g. fullerenes, carbon nanotubes etc. Graphene has attracted wide interest since last decade because of its extraordinary electrical, chemical and optical properties high intrinsic mobility, ( $200000 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ ), high Young's modulus ( $\sim 1 \text{ TP}$ ) and thermal conductivity ( $5000 \text{ W m}^{-1} \text{ K}^{-1}$ ), quantum hall effect, tunable band gap, optical transmittance (97.75) [3-7] which make it promising for various devices such as solar cells, fuel cells, supercapacitors, liquid crystal devices and nanocomposites [8] etc. Graphene is the hexagonal network of single graphite basal plane and Graphite comprised of graphene sheets held together by weak Vander Waal's forces between the  $\pi$ - $\pi$  stacked graphene having interlayer spacing of 0.34nm [2]. The molecular forces between the adjacent layers of graphite are weak [10] and can also be weakened by increasing interlayer distance between the graphite layers to produce graphene. Thus mono and multilayer graphene produced by Scotch tape [1] method and ball milling techniques etc. [11]. Exfoliation of graphite in

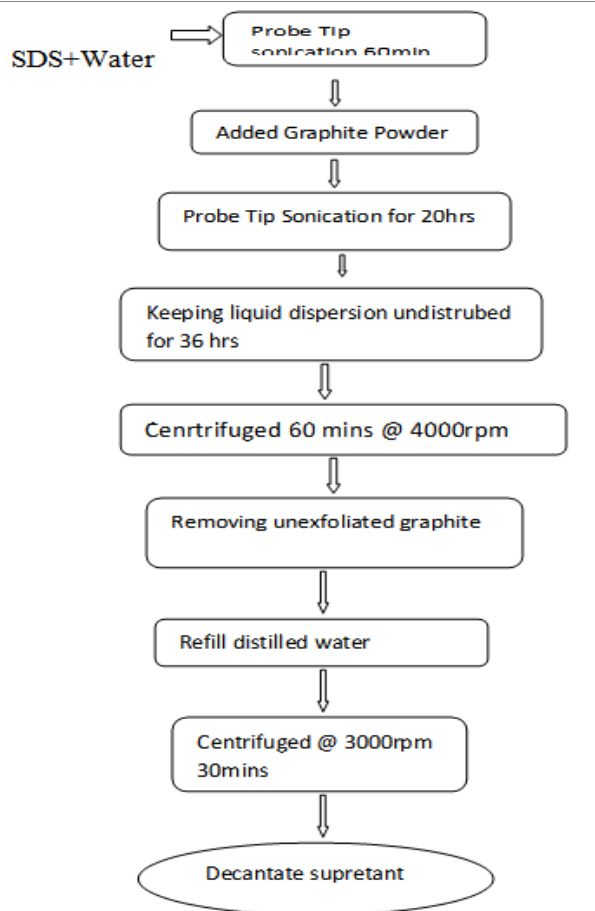
water surfactant solution increases the d-spacing due the presence of polar functional group [12].

The quality and quantity of graphene production directly affect the performance of applications related to photovoltaic, optoelectronic devices etc. Graphene majorly produced by two completely different approaches i.e. top-down and bottom up. In bottom-up approach techniques like chemical vapor growth, electrical discharge, plasma enhanced CVD, epitaxial growth on SiC substrates [9], solution based chemical-oxidation of graphite and electric discharge methods have been reported to produce graphene [13-19]. The top-down approach depends on exfoliation of carbon to provide graphene. Liquid phase exfoliation is more classified into primarily two categories one is surfactant free and another is surfactant aided Liquid phase exfoliation. Liquid phase exfoliation was first carried out by Coleman group Liquid phase exfoliation is the simple and the cost effective technique to produce graphene on large scale and involves the dispersion of graphite powder to particular solvent e.g. in ionic liquids [20], organic solvents [21-23] or surfactant solutions [24-26] and then exposed this dispersion to sonication. As water has high surface energy so it does not allow the dispersion and exfoliation of graphite, so surfactants are used to promote the exfoliation of graphite into graphene [26]. Exfoliation of graphene in water is quite challenging due to its hydrophobic nature, this kind of challenge is overcome by adding surfactant into water which helps to decrease the surface tension of water so that its surface tension match with that of graphene and also helps to stabilize the graphene. In this paper, we report the liquid phase exfoliation of graphite in water/surfactant solution to produce graphene. The obtained graphene flakes have been characterized by spectroscopy and microscopy techniques.

## 2. EXPERIMENTAL WORK

### 2.1 Materials

The surfactant SDS (Sodium dodecyl sulfonate) purchased from Sigma Aldrich. Graphite powder was purchased from commercial sources and was used without any purification.



**Fig. 1: Schematic of Exfoliation of graphite powder in SDS/Water solution**

## 2.2 Exfoliation Process

The exfoliation process is shown in Fig. 1. This exfoliation process involves three steps i.e. mixing, exfoliation and washing. 0.1mg of SDS powder was dissolved in 10ml of distilled water and surfactant/water solution was produced by sonication for 60mins via probe tip sonication to get clear solution.

Graphite powder dispersed into the surfactant/water solution and sonicated via probe tip sonication for 20hrs.

After sonication the liquid suspension was left to stand undisturbed for 36hrs to allow any unstable aggregates to form and then it was centrifuged at 4000rpm for 60 mins to remove large particles and this resulted in dark grey colored homogeneous suspension. In order to wash the surfactant the liquid dispersion was refilled with water and again centrifuged at 3000 rpm for 30mins. After centrifugation the resultant stable graphene suspension was obtained after pipetting off supernatant.

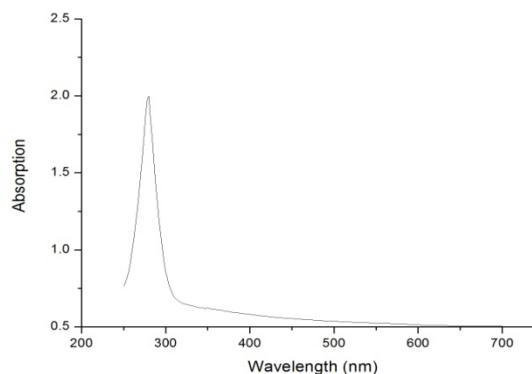
## 2.3 Characterisation

Chemical analysis of graphene dispersion was carried out by UV-VIS spectroscopy which was measured by using UV-Vis spectrophotometer in 200-700 nm wavelength region (Lambda 35, Perkin Elmer, USA) and fourier transform infrared spectroscopy (FTIR) were recorded on a Perkin Elmer Spectrum 100 spectrometer in the 4500–500 region. Morphology of graphite powder and liquid dispersion was examined by field emission scanning electron microscopy (SEM, Hitachi S-4800). X-Ray diffraction pattern was studied by using X-ray diffractometer (D8 FOCUS, Bruker, Germany) with Cu K $\alpha$  line (1  $\frac{1}{4}$  0.15405 nm) operated at 35 kV and 30 mA. Fluorescence was studied by using Spex FluorologII, having 450 watt Xenon lamp.

## Results and Discussion

### 3.1 UV-VIS Spectroscopy

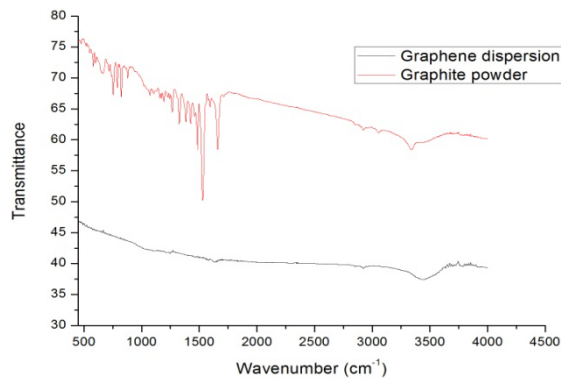
UV-VIS spectra of liquid dispersion is shown in the Fig. 2. UV-VIS spectra of liquid dispersion after 20hr probe sonication shows strong absorption peak at 270nm which is characteristic of  $\pi$ - $\pi$  interaction between SDS surfactant and graphene i.e. molecules interact with graphene sheet through  $\pi$ - $\pi$  interaction thus exfoliation graphene in water [27,28]. This  $\pi$ - $\pi$  interaction facilitate the formation of graphene dispersion.



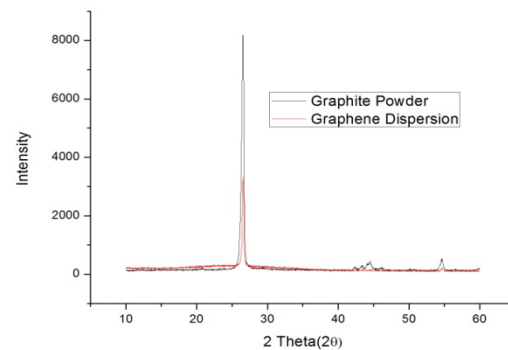
**Fig. 2: UV-VIS Spectra of Liquid Dispersion**

### 3.2 FTIR Spectroscopy

Fig. 3, show the FTIR spectrum for natural graphite powder (red) and liquid dispersion after sonication (black) in the full range (500-4500  $\text{cm}^{-1}$ ). FTIR spectra confirms the oxidation of graphite and also confirms the presence of different types of oxygen functionalities. Graphite powder shows sharp peaks between 1660-1081  $\text{cm}^{-1}$  and broad peak 3335  $\text{cm}^{-1}$ , but there is disappearance of peaks in graphene dispersion and it shows broad peak between 3320-3600  $\text{cm}^{-1}$  which is attributed to the stretching vibration of C-OH and water [29,30].



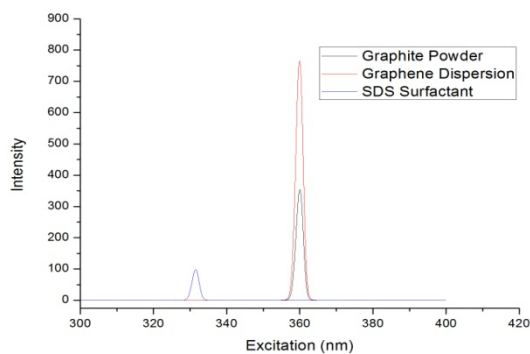
**Fig. 3: FTIR Spectra of graphite powder (red) and Liquid Dispersion (black)**



**Fig. 5: FTIR Spectra of graphite powder (red) and Liquid Dispersion (black)**

### 3.3 Fluorescence Measurement

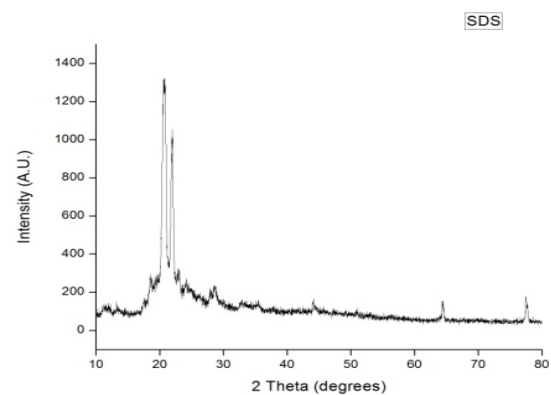
Fluorescence measurements of SDS surfactant, Graphite powder and graphene dispersion is shown in the Fig. 4. This measurement is the finger print of interaction between surfactant molecules and the graphene. And has a great importance for optoelectronic materials. Fluorescence of graphene is completely quenched which means that there is excess of molecules in the solution.



**Fig. 4: Fluorescence measurements of SDS surfactant, Graphite powder, Graphene Dispersion**

### 3.4 X-Ray Diffraction

Powder XRD pattern of graphite powder (black) and the graphene dispersion (red) is shown in Fig. 5 and XRD of SDS surfactant is shown in fig 6. XRD peak related to the structure of graphite at  $2\theta=26.52^\circ$  and also shows peaks at  $2\theta=42.23^\circ$ ,  $44.42^\circ$ ,  $54.04^\circ$  but graphene dispersion shows one peak at  $2\theta=26.52^\circ$  and a broad peak at  $2\theta=23.52^\circ$  which indicate the partial restacking of exfoliated graphene layers. The disappearance of other peaks attributed to the exfoliation of graphite and it confirms that the surfactant has successfully entered between the layered structure of graphite and the crystalline order of graphene dispersion has been decreased as compared with graphite powder.



**Fig. 6: XRD pattern of SDS surfactant**

### 3.5 Morphology

SEM was performed to see the effect of sonication on the liquid dispersion. The samples were prepared by drop casting method that is dripping off few drops of liquid dispersion of graphene onto clean glass substrate and was dried at  $250^\circ\text{C}$  for 2 hours. It can be seen from Fig. 7 that the liquid suspension shows good dispersive graphene flakes having diameter  $1\mu\text{m}$ .



**Fig. 6: SEM image of Graphite powder**

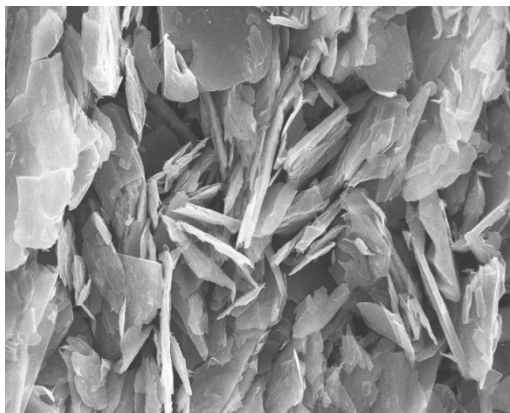


Fig. 7: SEM image of Graphene Dispersion

### 3. CONCLUSIONS

Liquid phase exfoliation technique is becoming more interesting because of its versatility and up-scalability to produce good quality of graphene. We found that graphene produced by Liquid Phase Exfoliation of graphite via probe tip sonication is a stable suspension. SEM confirms the presence of thin graphene flakes. UV-VIS spectra shows peak at 270nm and FTIR confirms the shifting of groups. This method results in large-scale production of stable graphene dispersions. The film formed by this method is conductive. This method is cost effective method to produce stable graphene dispersions on large scale and is good candidate for many applications i.e. photovoltaics, conductive transparent electrodes, thin film transistors etc.

### 4. ACKNOWLEDGEMENTS

One of the Author is greatly thankful to Rita Sharma and Shaveta Sharma from Guru Nanak Dev University, Amritsar for their kindly help.

### REFERENCES

- [1] Novoselov K. S., Geim A. K., Morozov S. V., Jiang D., Zhang Y., Dubonos S. V., Grigorieva I. V. and Firsov A. A., *Science*, 306, 2004, 666–669.
- [2] Chung D. D. L., *J. Mater. Sci.*, 37, 2002, 1475–1489.
- [3] Chae H. K., Siberio-Perez D. Y., Kim J., Go Y., Eddaoudi M., Matzger A. J., Keeffe M. O' and Yaghi O. M., *Nature*, 427, 2004, 523–527.
- [4] Stoller M. D., Park S., Zhu Y., An J. and Ruoff R. S., *Nano Lett.*, 8, 2008, 3498–3502.
- [5] Rao C. N. R., Sood A. K., Subrahmanyam K. S. and Govindaraj A., *Angew. Chem., Int. Ed.*, 48, 2009, 7752–7777.
- [6] Zhang Y., Tan Y.-W., Stormer H. L. and Kim P., *Nature*, 438, 2005, 201–204.
- [7] Cai M. Z., Thorpe D., Adamson D. H. and Schniepp H. C., *J. Mater. Chem.*, 22, 2012, 24992–25002.
- [8] Nair R. R., Blake P., Grigorenko A. N., Novoselov K. S., Booth T. J., Stauber T., Peres N. M. R. and Geim A. K., *Science*, 320, 2008, 1308.
- [9] Berger C., Song Z.M., Li X.B., Brown N., Naud C., Mayou D., Li T.B., Hass J., Marchenkov A.N., Conrad E.H., First P.N. and de Heer W.A., *Science*, 312, 2006, 1191–1196.
- [10] Brandt N. B., Chudinov S. M. and Ponomarev Y. G., *Semimetals, Graphite and Its Compounds*, North-Holland, Amsterdam, 1988.
- [11] Yao Y. G., Lin Z. Y., Li Z., Song X. J., Moon K. S. and Wong C.-P., *J. Mater. Chem.*, 2012, 22, 13494–13499.
- [12] Stankovich S., Dikin D. A., Piner R. D., Kohlhaas K. A., Kleinhammes A., Jia Y., Wu Y., Nguyen S. B. T. and Ruoff R. S., *Carbon*, 45, 2007, 1558–1565.
- [13] Li X., Cai W., An J., Kim S., Nah J., Yang D., Piner R., Velamakanni A., Jung I., Tutuc E., Banerjee S. K., Colombo L. and Ruoff R. S., *Science*, 324, 2009, 1312–1314.
- [14] Kim K. S., Zhao Y., Jang H., Lee Y. S., Kim J. M., Kim K. S., Ahn J. H., Kim P., Choi J. Y. and Hong B. H., *Nature*, 457, 2009, 706–710.
- [15] Malesevic A., Vitchev R., Schouteden K., Volodin A., Zhang L., Teneloo G. V., Vanhulsei A. and C. V. Haesendonck C. V., *Nanotechnology*, 19, 2008, 305604.
- [16] Vlassiouk I., Regmi M., Fulvio P., Dai S., Datskos P. and Eres G., *ACS Nano*, 5, 2011, 6069–6076.
- [17] Dreyer R. D., Park S., Bielawski C. W. and Ruoff R. S., *Chem. Soc. Rev.*, 39, 2010, 228–240.
- [18] Keidar v, Shashurin A., Volotskova O., Raitses Y. and Beilis I. I., *Phys. Plasmas*, 17, 2010, 057101.
- [19] Kuila T., Bose S., Mishra A. K., Khanra P., Kim N. H. and Lee J. H., *Prog. Mater. Sci.*, 57, 2012, 1061–1105.
- [20] Nuvoli D., Valentini L., Alzari V., Scognamillo S., Bon S.B., Piccinini M., Illescas J., Mariani A., *J. Mater. Chem.* 21 (2011) 3428–3431.
- [21] Choi E.Y., Choi W.S., Lee Y.B., Noh Y.Y., *Nanotechnology* 22, 2011, 365601–365606.
- [22] Liu W., Wang J., *Chem. Commun.* 47, 2011, 6888–6890.
- [23] O'Neill A., Khan U., Nirmalraj P.N., Boland J., Coleman J.N., *J. Phys. Chem.* 115, 2011, 5422–5428.
- [24] Lin S., Shih C., Strano M.S., Blankschtein D., *J. Am. Chem. Soc.* 133, 2011, 12810–12823.
- [25] Guardia L., Fernández-Merino M.J., Paredes J.I., Solís-Fernández P., Villar-Rodil S., Martínez-Alonso A., Tascón J.M.D., *Carbon* 49, 2011, 1653–1662.
- [26] Lotya M., Hernandez Y., King P.J., Smith R.J., Nicolosi V., and Karlson L.S., *J. Am. Chem. Soc.*, 131, 2009, 13611–13620.
- [27] Abergel, Fal'ko, *Physical Review B*, 75, 2007, 155430.
- [28] Ebertin, Bangert, Nari, Jones, Gass, Bleloch, Novoselov, Geim, Briddo, *Physical Review B*, 77, 2008, 233406.
- [29] Si. Y, Samulski E.T. *J Nano Lett* ,8, 2008, 1679–1682.
- [30] Zhang T., Zhang D., Shen M.A., *J Mater Lett* ,63, 2009, 2051–2054.