Paper No.
CL25

# Laser ablation of suspended graphite powder to obtain few-layered graphene in bulk quantities

**Ravi Kiran Gadde**

School of Engineering Sciences and Technology (SEST), University of Hyderabad, Gachibowli, Hyderabad 500046, Telangana, India

swati364@gmail.com(S.G.Acharyya)

**Chandu Byram, Swati G. Acharyya, Venugopal Rao Soma,Vadali V. S.S. Srikanth**

School of Engineering Sciences and Technology (SEST), University of Hyderabad, Gachibowli, Hyderabad 500046, Telangana, India

ACRHEM, University of Hyderabad, Gachibowli, Hyderabad 500046, Telangana, India

## ABSTRACT

Few-layered Graphene (FLG) has emerged as a unique material in various fields due to its outstanding mechanical, electrical, and optical properties. The main aim of this work is to synthesis the FLG in bulk with high quality in a simple method which can be applicable for the protective coatings as well as liners in oil refineries etc. Here, we report a simple technique for bulk synthesis of few layered graphene (FLG) from graphite powder (suspended in ethanol)by employing ultrafast laser ablation in liquids (ULAL) technique without the requirement of controlled environment. Graphite powder (average particle size of <20 μm) was suspended uniformly in ethanol and exfoliated at room temperature using a femtosecond laser (wave length is ~800 nm and beam diameter is ~8 mm) followed by ultrasonication to obtain few layer graphene with a lateral size of ~1 μm. Raman spectroscopy and high resolution transmission electron microscopy (HRTEM)

confirmed the nature and morphology of the FLG. The quality and number of layers in FLG could be controlled by tuning the laser parameters.

Keywords: Laser; Carbon material; few layer graphene

## INTRODUCTION

Surface oxidation and corrosion are the two prime concerns in metal based materials research as they degrade the metal structures and their mechanical strength [1]. Owing to these,the researchers have invested sustained efforts in developing more environmental friendly and cheaper corrosion resistant materials which will provide alternative conduits to the existing anticorrosion technologies as thesegenerate large amounts of toxic liquid waste [1]. For example, in the industries such as oil refineries a sudden damage or gradual wear and abrasion in pipes could result due to the continuous flow of high temperature fluids (700°C - 900°C). Hence, a protective coating material which can withstand at high temperatures and improves the strength of the material is desirable for all such industries in a large scale.

Graphene is a well-studied two dimensional $sp^2$ hybridized honey comb material [3-5] withnumerousoutstanding mechanical, electrical, thermal and optical properties [2-4]. Few layer graphene (FLG) became an attractive material for the researchers owing to its several applications in diverse fields such as sensors, solar cells and novel protective coatings [5]. Few layered graphene can be synthesized chemically (Hummers method) [2], mechanically (scotch tape method) and by thermal decomposition [2-3]. However,bulk synthesis of high quality FLG for industrial applicationsis still remain as a challenge for researchers. Most recently, an attempt was made by the researchers by utilizing the laser based graphene deposition and patterning on the metallic and non-metallic substrates [2,3]. Porous graphene quantum dots and graphene nano-ribbons have been developed from highly oriented pyrolic graphite (HOPG)upon laser irradiation [2,7,8]. From the previous studies it is clear that a quality and fast growth of few layer graphene can be produced in close environments (chemical vapor deposition, physical vapor deposition)[4,5] thoughtheseare not suitable for industrial applications. Nanosecond laser pulses with very high laser energies (12 J) were utilized in these studies [2,6]. R. Kumar et al., [2] illustrated the fabrication of graphene by using lasers and also comprehended the recent progress in exploiting lasers for micro-patterning of graphene. In this work, we present a very simple procedure for production of FLG in bulk with a lateral size of ~1 μm under ambient conditions towards the coating applications using a femtosecond laser.

## EXPERIMENTAL PROCEDURE

A suspension of graphite powder (99.5% pure, average particle size <20 μm) in ethanol was prepared (concentration of 30mg/ml). The suspension was constantly stirred using a magnetic stirrer while a femtosecond laser beam (~50 fs duration, 800 nm, 1 kHz, input beam diameter of 8 mm) was simultaneously focused on the suspension.The experiment was performed at two different energies of laser viz., ~200 μJand ~400 μJ. The suspension was irradiated with laser energy of ~200 μJ and~400 μJ for 60 minutes in separate experiments and the sample thus obtained is labelled as $S_1$ and $S_2$. Then the laser processed solutions were ultrasonicated for 60 minutes followed by probe sonication for 15 min with an amplitude of <60%. The suspension was then allowed to rest for 24 h.

## Characterization of few layer Graphene

The suspension was characterized using Transmission electron microscopes (TEM) operated at accelerating voltages of 5 V and 200 KV, respectivelyare used to characterize the suspension to study the morphology of the samples.Raman spectra are obtained using 532nm green laser excitation source.

## RESULTS

Low magnification TEM images of different samples obtained at two irradiances are shown in Figure 1, which clearly shows that in all the cases the final product (FLG) is transparent to electrons. Figure 1 also exhibits that the sheets have lateral dimensions in the range 0.8 -1 μm. Representative electron diffraction pattern [Inset of Fig. 1(a)] clearly shows that the atoms in the material are arranged in six folded symmetry of graphene (hexagonal). The decrease in intensity of the higher order diffraction spots indicates layered nature of the material.

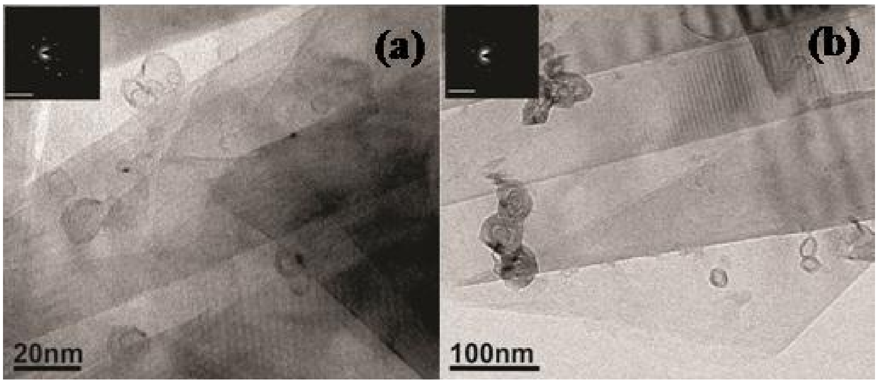


**Figure 1 TEM image (a) exhibits the planar graphene sheets with hexagonal arrangement of carbon atoms from $S_1$ with SAED pattern shown in inset (b) illustrating planar graphene sheets (length ~ 1μm) with edge defectsfrom $S_2$ with SAED pattern shown in inset.**

To further understand the layered-nature of the synthesized materials, High resolution TEM images of the samples are recorded and shown in Fig 2. Figure 2 (a) depict the HRTEM image of sample $S_1$respectively revealing the number of layers of graphene produced. Figure 1(a) shows the TEM image of sample $S_1$ with a corresponding SAED image showing planar sheets of the produced graphene.

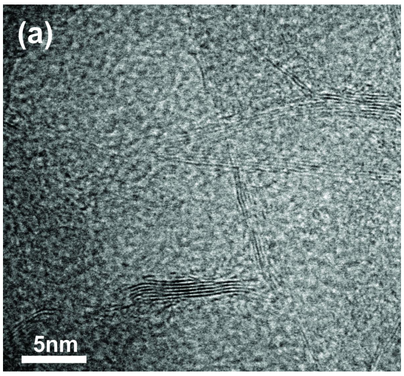


**Figure 2 (a) High Resolution TEM (HRTEM)image of $S_1$**

At higher magnification hexagonal arrangement of carbon atoms is also evident. In both the cases, interplanar spacing of ~0.35 nm, which is representative of FLG has been observed with a length of 0.8–1 μm. HRTEM images of $S_1$ demonstrate the formation of three layered graphene with inter layer spacing of 0.35 nm [Figure 2 (a)]. In case of $S_2$, the graphene sheets possessing a length of 0.8-1 μm were formed, but contained defects. Interestingly, the end product consisted of direct graphene from graphite as ethanol from the suspension evaporated and there was minimal material loss and contamination.

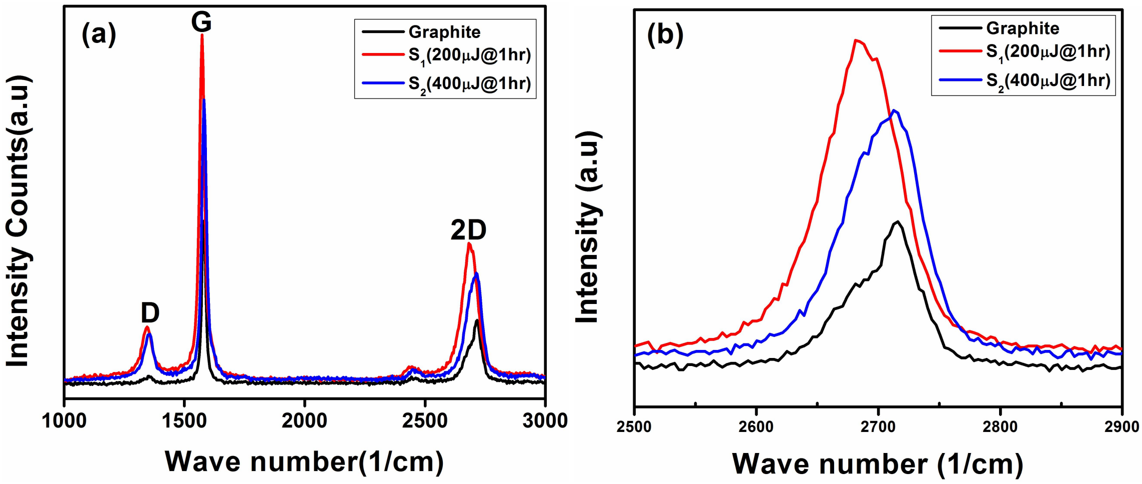


**Figure 3 (a) Raman Spectra of $S_1$, $S_2$ (b) magnified view of 2D band for $S_1$, $S_2$**

Figure 3 shows the Raman spectra of as received graphite, $S_1$and $S_2$. Three signature peaks of FLG namely D, G, and 2D bands, appeared at 1350 $cm^{-1}$, 1580 $cm^{-1}$, 2700 $cm^{-1}$, respectivelyin the corresponding Raman spectra [10-12]. Furthermore, the $I_G/I_{2D}$ ratios were 1.84, 1.73 for $S_1$, $S_2$ respectively indicating the presence of several graphene walls [12]. This is consistent with the observations made from the HRTEM images (Fig. 2). As received graphite depicted 2D and G bands whereas in the laser treated samples a new D peak emerged as shown in Figure 3(a). In the case of laser ablated sample $S_1$ the position of D peak shifted left at a range of 1341 $cm^{-1}$ but in sample $S_2$the D peak shifted right at 1352 $cm^{-1}$. The 2D band was nearly symmetric for $S_1$sample whereas it was completely asymmetric for the $S_2$. The peak positions of 2D band were at 2681 $cm^{-1}$and 2712 $cm^{-1}$ [Figure 3(b)]. The G band provides information regarding quality and thickness of graphene layers [11]. The G band for samples $S_1$, $S_2$ was in the 1573 $cm^{-1}$ and 1582 $cm^{-1}$ range due to in plane vibration of $sp^2$ hybridized neighbor atoms on carbon layers [6]. Hence, planar graphene sheets could be produced simply by irradiation of graphite suspension using femtosecond laser pulses.

Here we could observe that force induced physical exfoliation makes a key role in breaking the graphite particles during the laser ablation of solid liquid interface. Subsequently followed by probesonication also favor for further exfoliation [9]. R. Kumar et.al [2] explained that the laser interaction with sample, leads to production of energetic high frequency radiation owing from the breakdown of chemical bonds (photochemical effect), opening the possibility to initiate chemical reactions, ionization, or desorption of surface molecules when the operation is performed at lower laser powers. However, since the pulses are ultrashort (~ 50 fs), multi-photon absorption, resulting from large fluencies (peak intensities) of ~ 100 $J/cm^2$ (~$10^{14}$ $W/cm^2$), is possible leading to direct photochemical bond breaking. This is clear that 200µJ laser energy and time of exposure (1hr) is sufficient for formation of few layer graphene with low defects. The experiment is in the initial stage and needs few improvisations for developing the coating material and further detailed studies are yet to be performed to optimize the quality and yield of the graphene, such as increasing exposure time at same energy, etc.

## CONCLUSIONS

FLG has been synthesized under room conditions by irradiation of graphite powder suspended in ethanol using femtosecond laser pulses. The FLG had a lateral size of ~0.8-1 µm and contained 2-10 graphene layers. Electron microscopy and Raman scattering clearly indicated the formation of FLG, which is explained on the basis of force-induced physical exfoliation. The quality and number of layers in FLG could be controlled by tuning the input laser parameters. Characterisation techniques reveals that the fluence has influence in the graphene layer formation. The laser energy used in this study was probably sufficient to ablate the graphite into graphene sheets. The effect of the exposure time is to be studied in coming future.Further detailed studies are needed to completely understand the mechanism of graphene formation by laser ablation of suspended graphite.

## ACKNOWLEDGMENTS

All authors acknowledge the Defence Research and Development Organization (DRDO), India for providing the funding (ASL/31/14/4051/CARS/051, dated: 02/02/2015 and through ACRHEM) required to do this work. The authors would like to thank the Center for nanotechnology (CFN), University of Hyderabad for allowing us to use the TEM facility.

## REFERENCES

1. Dumée, Ludovic F., et al. "Growth of nano-textured graphene coatings across highly porous stainless steel supports towards corrosion resistant coatings." Carbon 87 (2015): 395-408.

2. Kumar, Rajesh, et al. "Laser-assisted synthesis, reduction and micro-patterning of graphene: Recent progress and applications." Coordination Chemistry Reviews (2017).

3. Kalsoom U, Rafique MS, Shaheen R, Fatima K. Metal based synthesis of Graphene by pulsed laser deposition technique. Int. J. Sci. Engg. Res., 2014; 5: 1200-1204

4. Park HJ, Meyer J, Roth S, Skakalova S, Growth and properties of few-layer graphene prepared by chemical vapor deposition. Carbon 2010; 48:1088-1094.

5. Ye X, Long J, Lin Z, Zhang H, Zhu H, Zhong M. Direct laser fabrication of large area and patterned graphene at room temperature. Carbon 2014; 68: 784–790.

6. Park JB, Xiong W, Gao Y, Qian M, Xie ZQ, Mitchell M, et al. Fast growth of graphene patterns by laser direct writing. Appl. Phys. Lett. 2011; 98:123109.

7. Ren XD, Liu R, Zheng LM, Ren YP, Hu ZZ, and He H. Morphology selective preparation and formation of graphene nanoribbons from graphite by liquid phase pulsed laser ablation. Appl. Phys. Lett. 2016; 108: 071904.

8. Russo, Paola, et al. "Femtosecond laser ablation of highly oriented pyrolytic graphite: a green route for large-scale production of porous graphene and graphene quantum dots." Nanoscale 6.4 (2014): 2381-2389.

9. Ciesielsk A and Samori P. Graphene via sonication assisted liquid-phase exfoliation. Chem. Soc. Rev. 2014; 43: 381-398.

10. Maximova K, Aristov A, Sentis M and Kabashin A V. Size –controllable synthesis of bare gold nanoparticles by femtosecond laser fragmentation in water. Nanotechnology 2015; 26: 065601.

11. Dresselhaus MS, Jorio A, Hofmann M, Dresselhaus G, and Saito R. Perspectives on Carbon Nanotubes and Graphene Raman Spectroscopy. Nano Lett. 2010; 10: 751-758.

12. Das A, Chakraborty B, Sood AK. Raman spectroscopy of graphene on different substrates and influence of defects. Bull. Mater. Sci. 2008; 31 (3):579-584