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Effect of sonication energy on the yield of graphene nanosheets by liquid-phase exfoliation of graphite

Rakhee Durge\textsuperscript{a}, R. V. Kshirsagar\textsuperscript{a}, Pankaj Tambe\textsuperscript{b}\textsuperscript{*}

\textsuperscript{a}Department of Electronics and Telecommunication Engineering, Priyadarshini College of Engineering, Nagpur-440019, India
\textsuperscript{b}School of Mechanical and Building Sciences, VIT University, Vellore-632014, India

Abstract

We demonstrate the high concentration exfoliation of graphene nanosheets in dimethyl formamide (DMF) as a solvent from graphite powder. UV-Vis-NIR spectroscopy shows low power bath sonication yields less concentration of graphene nanosheets exfoliation, whereas the high power probe sonication yields high concentration graphene nanosheets exfoliation. The concentration of graphene nanosheets exfoliation depends on amount of energy supplied, and there exists a linear relationship between the concentration of graphene and energy supplied during sonication. TEM micrograph confirms the exfoliation of graphene nanosheets. AFM studies shows; high power sonication for longer time reveals graphene exfoliation with fewer graphene layers. The strategy of bath sonication followed by probe sonication of graphite solution shows the stable suspension of graphene nanosheets even after one month.

Keywords: Graphene; dimethyl formamide (DMF)

\textsuperscript{*} Corresponding author Pankaj Tambe Tel.: +91-7708235023
E-mail address: pankajtambe@vit.ac.in
1. Introduction

The remarkable mechanical, electrical and thermal properties of graphene have created a great interest, and possibly make the graphene as the fastest emerging topic for research in recent years [1-5]. The initial groundbreaking experiments have been carried out on micromechanically cleaved monolayers, [6] but limitation of this method of processing is low yield. In order to utilize graphene for future industrial applications required large-scale, and high-throughput processing methods are required [7]. At present the preferred scalable method for preparation of graphene is reduction of graphene oxide. In this method, the oxidation of graphite by following Hummers modified method, followed by exfoliation of graphite oxide in water, to give aqueous dispersions of graphene oxide (GO), [8, 9] and further the oxidation can be removed by thermal or chemical reduction. Moreover, the reduction of graphene oxide creates many structural defects and these defects disrupt the band structure resulting in deterioration of mechanical, electrical and thermal properties which make graphene unique.

In this regard, several groups have demonstrated the method to exfoliate graphite powder for obtaining graphene in the liquid medium without defect formation for addressing the issues associated with graphite oxidation followed by its reduction [10, 11]. The liquid phase exfoliation method relies on the exfoliation and stabilization of graphene using special solvents and suffers from none of the problems associated with graphite oxidation followed by its reduction. However, these methods have one critical disadvantage of relatively low concentration exfoliation of graphene which is typically <0.01 mg/ml [10]. In order to exploit the full advantage associate with dispersions of pristine graphene in solvents using solvent-exfoliation route, it is necessary to obtain the maximum obtainable concentration while maintaining the pristine graphitic lattice of the graphene nanosheets. In this work we studied the effect of sonication energy on the extent of exfoliation of graphene nanosheets in the solvent. Low power bath and high power probe sonicator’s were used in this study. The acoustic power delivered to the graphene suspension was determined using calorimetric method and the actual energy transferred was quantified and correlated with quantified values of graphene nanosheets dispersion.

2. Experimentation

2.1 Materials

Graphite (99% carbon content) was kindly supplied by Stellar Material Corporation, Bangalore. Dimethyl formamide (DMF) was of analytical grade and used without further purification, purchased from S. D. Fine Chemicals, India.

2.2 Liquid phase exfoliation of graphene

Graphene dispersion was prepared by sonicating natural graphite powder in the DMF using low power bath sonicator and high power probe sonicator. Initially, 3 mg/ml graphite powder was mixed with DMF and sonicated for various sonication times using both type of sonicator. After sonication, the obtained dark dispersion was left to stand for 8 h for the sufficient sedimentation of large particles. Then the upper less dark dispersion was centrifuged at 3500 rpm for 15 min with a centrifuge to remove any largish flakes, eventually resulting in homogeneous colloidal suspension of graphene sheets in the DMF.

In order to evaluate the graphene concentration with an absorbance, we have to measure an absorption coefficient of the graphene suspensions. For this purpose, we prepared the suspension containing graphene with the concentration of 0.1 mg/ml by adding 10 mg of the as-received graphene material into 100 ml of DMF, without centrifugation. This suspension was then diluted into seven different concentrations between 0.005–0.03 mg/ml by adding DMF. By using the optical path length of 1 cm cuvette, the absorbance was measured with increasing the graphene concentration, producing an absorption coefficient of the graphene suspensions from the Beer–Lambert law [12].
2.3 Characterization

The morphology of the graphene was examined by JEOL JEM 2100 high resolution transmission electron microscope (HRTEM). FTIR spectroscopic analysis was carried out with (IRAffinity-1, SHIMADZU, resolution 0.5 cm\(^{-1}\)) for the powder samples in the scanning range of 400 to 4000 cm\(^{-1}\). UV-Vis-NIR spectroscopy analysis was carried out with HITACHI U-2800 spectrophotometer. Scanning electron microscopy (SEM) analysis was performed with Hitachi S3400, operated at 15 KV with gold sputtering on the powder samples. Atomic force microscopy was carried out using Nanosurf Easyscan 2.

3. Results and discussion

![Figure 1](image1.png)

**Figure 1:** (a) Photograph of graphene suspensions at different bath sonication time (b) UV-Vis-NIR spectra of graphene suspensions at different bath sonication time

The exfoliation of the nanoparticle in the solvent is occurred due to the strong interaction between the solvent and nanoparticles, means that the energetic penalty for exfoliation and subsequent salvation become small [13]. During sonication of graphite flakes in the solvent, initially the lager flakes is exfoliated into smaller flakes, and subsequently with more amount of energy supplied result in few layers or monolayer with high concentration

![Figure 2](image2.png)

**Figure 2:** (a) Photograph of graphene suspensions at different probe sonication time (b)UV-Vis-NIR spectra of graphene suspensions at different probe sonication time
dispersion of graphene in the solvent. To test this hypothesis, we dispersed the 3 mg/ml of graphite powder in DMF solvent, and sonicated using the low power bath and high power probe sonicator. Fig. 1a shows the photograph of the graphene suspensions which are bath sonicated over different bath sonication time followed by centrifugation. It is clear from the photograph, as the sonication time increases the colour of suspension changes, which depict higher concentration graphene exfoliation. At 90 minutes of bath sonication, the colour of suspension appear grey, while at 120 minutes of bath sonication, the colour appears darker exhibiting greater extent of graphene exfoliation.

To monitor the degree of exfoliation of graphene nanosheets from the graphite, UV-Vis-NIR spectroscopy was employed. UV-Vis-NIR spectra were taken for the graphene suspensions for various sonication time followed by centrifugation, to qualitatively probe the dispersion of graphene. Fig. 1b shows the UV-Vis-NIR spectra of graphene suspensions for various sonication time followed by centrifugation. The peak centered on 272 nm is the characteristic peak of graphene. As the bath sonication time increases, the absorption value at 272 nm also increases, which depict the high concentration exfoliation of graphene.

Fig. 2a shows the photograph of the graphene suspensions, which are sonicated using high power probe sonicator over different sonication time followed by centrifugation. It is clear from the photograph, as the sonication time increases, the colour of suspension changes, which depict higher concentration of graphene exfoliation. At 120 minutes of probe sonication, the suspension appears darker, exhibiting greater extent of graphene exfoliation. UV-Vis-NIR spectra were taken for the graphene suspensions for various probe sonication time followed by centrifugation, to qualitatively probe the dispersion of graphene. Fig. 2b shows the UV-Vis-NIR spectra of graphene suspensions for various probe sonication time followed by centrifugation. As the probe sonication time increases, the absorption value at 272 nm also increases, which depict the high concentration exfoliation of graphene. The absorption values of graphene suspension sonicated using high power probe sonication are much higher as compared with the graphene suspension sonicated using low power bath sonication. Thus, it is clear from this observation that higher the sonication energy results in higher concentration exfoliation of graphene.

Figure 3: TEM images of (a, b) graphene and (d) Electron diffraction pattern of graphene
TEM microscopy was carried out for the low power bath sonicated graphene suspension by dropping a single drop on the carbon grid. Fig. 3 shows the TEM micrograph of the graphene. It is clearly seen from the TEM micrograph that graphene nanosheets exfoliation takes place, (Fig. 3a) and consist of number of layers. Fig. 3b shows the wrinkles for the graphene nanosheets. Electron diffraction pattern of the graphene nanosheets reveal the clear hexagonal pattern, (Fig. 3c) which further confirm the presence of graphene nanosheets. The multiple hexagonal patterns confirm the presence of multilayer graphene nanosheets. In addition, Atomic force microscopy (AFM) is the tool to probe the 3D topographic images. AFM were carried out on the selected graphene suspension to qualitatively access the number of layers after sonication. It is expected that at high concentration dispersion of graphene nanosheets in the solvent must have few layers of graphene nanosheets, while low concentration dispersion of graphene nanosheets in the solvent must show the more number of layers of graphene nanosheets. Fig. 4a shows the AFM of graphene suspension sonicated using low power bath sonication for 60 minutes. It is clearly seen that the multilayer graphene nanosheets are present. 3D image of the graphene suspension shows the Z axis height as approximately 36 microns. While the graphene suspension probe sonicated for 120 minutes, shows the less number of graphene nanosheets as compared to the graphene suspension bath sonicated for 60 minutes (Fig. 4b). 3D image of the graphene suspension shows the Z axis height as approximately 13 microns. Fig. 5 shows the SEM micrographs of graphite and graphene powder. SEM of graphene nanosheets shows the flakes of graphene. Further, FTIR spectroscopy had been performed to confirm that the long hour of sonication results in graphene nanosheets formation and not something else. Fig. 6 shows the FTIR spectra of graphite and graphene nanosheets sonicated for the 120 minutes using high power probe sonicator. FTIR spectra of graphene show no significant difference from the graphite spectra, thus confirming the presence of graphene.

![AFM topographic scan of a graphene and its mean fit](image)

**Figure 4:** AFM topographic scan of a graphene and its mean fit (a) Bath sonicated (b) Probe sonicated
Figure 5: SEM images of (a) Graphite (b) Graphene

Figure 6: FTIR spectra of graphite and graphene

Figure 7: Absorbance versus graphene concentration

Figure 8: Normalized temperature versus time
In order to quantitatively evaluate the amounts of the graphene dispersed in the DMF suspensions, the absorption coefficients of graphene should be calculated first [14]. The initial graphene suspensions were prepared by adding 10 mg of the as-received graphene product into 100 ml of DMF solution. The graphene suspensions with the initial concentration of 0.1 mg/ml were serially diluted into seven low graphene concentrations in the range of 0.005–0.03 by adding DMF. Centrifugation was not performed on these suspensions because we would like to know the exact concentrations of graphene in the suspensions. The absorbance of these diluted suspensions with different graphene concentrations measured at a wavelength of 450 nm using UV–Vis–NIR spectroscopy and is shown in Fig. 7. The absorbance showed an exactly linear dependency on the graphene concentrations and the slopes of the straight lines are obtained by linear least square regression. The absorption coefficients of the graphene suspensions is calculated from the slope by using the Beer–Lambert law at a wavelength of 450 nm and found out to be 2932 ml mg⁻¹ m⁻¹.

![Figure 9: Effect of sonication energy on dispersion concentration of graphene](image)

a) Bath sonication b) Probe sonication
In order to quantity the actual amount of acoustic energy delivered to the graphene suspension, the increase in temperature of the suspension with time was recorded and is shown in Fig. 8. The amount of acoustic energy delivered was calculated using equation as $P = (dT/dt)MC_p$, where $P$ is the delivered acoustic power (W), $T$ and $t$ are temperature (K) and time (s), respectively, $C_p$ is the specific heat of the liquid (J/g·K) and $M$ is the mass of liquid (g) [15]. Further, the total amount of energy delivered to the suspension was calculates as $E = P \times t$. In addition, the graphene concentration ($C_f$) in the stabilized suspension is estimated by using the Beer-Lambert law, $C_f = A/e\ell$, where $A$, $e$ and $\ell$ are absorbance, absorption coefficient, and optical path length, respectively, at a specific wavelength [14]. The quantified graphene concentration was calculated at different sonication time for both bath and probe sonicated suspensions and is plotted against the sonication energy which is shown in Fig. 9. The concentration increases steadily with time using both type of sonicator. The exfoliation of graphene nanosheets concentration is higher by using high power probe sonication as compared to low power probe sonication. Empirically the concentration and energy supplied exhibit linear relationship. The concentration of $\sim 0.12$ mg/ml of graphene was achieved by sonicating using bath sonication for 120 minutes, while, sonication using probe sonicator yield graphene of $\sim 1.2$ mg/ml for 120 minute of probe sonication. This shows that probe sonication yield is 10 time higher than that of yield obtained using bath sonicator.

In order to use the high concentration suspension of few layers or monolayer graphene for several applications, the graphene suspension must exhibit long term stability. In this regards, stability of graphene suspensions were judged for a month by using following two strategies, which are, (a) low power bath sonicator and (b) low power bath sonicator followed by high power probe sonication. It is observed that graphene suspension sonicated using low power bath sonicator followed by high power probe sonication shows that the graphene suspension was stable even after 30 days, while the graphene suspension sonicated using low power bath sonicator showing the sedimentation of the graphene nanosheets (Fig. 10). Thus, the sonication strategy of low power bath sonication followed by high power probe sonication is an effective strategy to obtain the long term stability of graphene suspension.

4. Conclusions

Graphene was successfully prepared by using liquid phase exfoliation route. Dimethyl formamide (DMF) is
used as a solvent for the exfoliation of graphene nanosheets from graphite. UV-Vis-NIR spectroscopy shows low power bath sonication yield less concentration of graphene nanosheets exfoliation, whereas the high power probe sonication yields high concentration graphene nanosheets exfoliation. TEM micrograph confirms the exfoliation of graphene nanosheets and electron diffraction pattern confirms the hexagonal structure of the graphene nanosheets. In addition, AFM studies reveal high power sonication for longer time reveal graphene exfoliation with fewer graphene layers. Bath sonication followed by probe sonication of graphene solution results in stable suspension even after one month.

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