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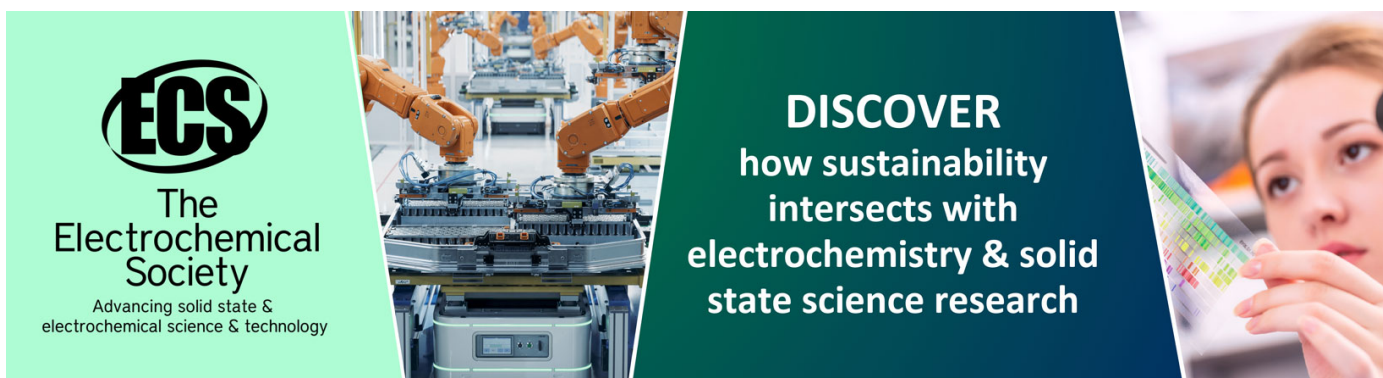
Experimental investigation of concentration yields of liquid phase exfoliated graphene in organic solvent media

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Experimental investigation of concentration yields of liquid phase exfoliated graphene in organic solvent media

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Abstract. The main purpose of this work is to experimentally investigate the concentration yields of exfoliated Graphene in organic solvents with the variation of different centrifugation speeds (rpm). Graphene was effectively fabricated by one of the most convenient chemical processing approach liquid-phase exfoliation (LPE) of graphite in two different organic solvent N-Methyl-2-Pyrrolidone (NMP) and N, N-dimethylformamide (DMF). After exfoliation separated supernatant dispersions were preserved into the other tube as product. Similar procedure was repeated with same parameter and same graphite for both of the solvents. FESEM analyses of the exfoliated Graphene samples revealed the presence of few layers of Graphene flakes stacking. Analysis of the Raman spectrum of the samples it was revealed that the precursor graphite flakes was converted to Graphene sheets. Concentrations of graphene suspensions in both solvents were measured from separately prepared standard graphs using Beer's law with the aid of UV-vis absorbance spectroscopy. Estimated exfoliated graphene concentration was acquired higher for lower centrifugation (rpm) for both of the solvent. It was also seen that for the same rpm concentration of Graphene was higher in NMP than that of in DMF.

1. Introduction

Graphene is one or several planar sheets of carbon atoms and these are united with sp^2 bond. It possesses unique physical and chemical properties such as, extremely high mobility of charge carriers, and thermo-electrical conductivity, enormously large surface area and high mechanical strength. It is now becoming the most widely used carbon based nanomaterial [1]. Different types of graphene have been fabricated using different techniques. Such as chemical vapour growth technique [2], bottom-up growth by wet ball-milling technique [3] and burning of Mg metal in solid CO_2 (dry ice) technique [4]. In these techniques macromolecules are suffered from the happening of side reactions. Moreover, containing of impurities with the end products, complicated and time consuming initial rig setup limits their implementations [5]. Besides, these techniques have very low final yielding of graphene. Exfoliation of expanded graphite has also been used to produce graphene [6] however; intercalated compounds limit the end application of this graphene. Current efforts have emphasized on the chemical processing of graphite, which shown the most anticipation to produce graphene suspension in organic solvents [7]. Significant quantity of graphene is prepared by one of the most convenient chemical processing approach LPE of graphite by organic solvents [8, 9, 10]. It has ability to produce enormous amount of graphene sheets. It is very simple, direct and one-step method to yield graphene by dispersing the available graphite powder in organic solvents [5]. Although some work has been



conducted to produce Graphene using LPE technique in organic solvents, however, till now it has not been investigated the concentration yields of exfoliated Graphene in organic solvents with the variation of different centrifugation speeds (rpm).

1.1. Liquid-Phase Exfoliation (LPE) for Graphene Production

Microcrystalline graphite particles can exfoliate into separate graphene flakes by the interaction with solvent. To exfoliate the graphite into individual layers two types of mechanical force are needed to be activated. Application of shear force along the graphene surface is effectively responsible for the exfoliation of graphite [11]. The enthalpy of mixing is dependent on the balance of surface energies of Graphene and the solvent [12]. Graphite surface energy is defined as the energy per unit area minimum required to overcome the van der Waals forces when peeling two sheets apart. A successful occurring of exfoliation depends on the small net energetic cost of the whole process [8]. The matching of the surface energies of Graphene and the solvent is one of the most prominent criterions for a successful exfoliation process. During the exfoliation process, if the surface energy of the solvent closer to the surface energy of Graphene then the enthalpy of mixing will be smaller and the degree of exfoliation will be higher [13]. The solvents NMP and DMF are properly fulfilling the criteria of mothering of surface energy with the Graphene. Thus, these solvents are intensely recommended for the successful exfoliation to graphene sheets [14].

Sonication parameters such as sonication time have been used from 30 minutes to 1000 hours. Intense tip sonication is relatively ineffective for the exfoliation graphene from graphite [15]. Sonication generates the shear forces and creates cavitation in the solvent liquid [11]. Due to the fluctuations of pressure small micro-sized voids or bubbles is created, grown and simultaneously those are collapsed in the liquids. It induces shock waves that surround the graphite and persuade exfoliation into graphene sheets [16]. Sedimentation-based separation (SBS) approach could divide the suspended flakes on the basis of degree of sedimentation due to the effect of centrifugal force on the flakes. Centrifugation of 500 rpm is sufficient to remove all the existing graphitic crystallites [8] from the dispersed flakes [15]. Thus controlled centrifugation is the potential mechanism to get the controlled concentration of graphene suspension from sonication assisted exfoliation dispersion. Suitable range of centrifugation speeds is from 4000 to 500 rpm for the analysis of sonication assisted exfoliated graphene concentration [15].

2. Materials and Equipment Used

Graphene flakes were fabricated using an easy and effective LPE technique. In this technique graphite flakes of molecular weight (MW), 12.011C (g/mol) were used in all experiments as the precursor material. They were purchased from Fisher Scientific (M) Sdn. Bhd (product code: 385030010, Lot: A0335167, CAS: 7782-42-5). Organic solvent NMP (C₅H₉NO, MW: 99.13) 99.9+% and DMF (C₂H₇NO, MW: 73.09) 99.8+%, were also supplied by Fisher Scientific (M) Sdn. Bhd (NMP product code: 390680010, Lot: A0333185, CAS: 872-50-4 and DMF product code: 423640010, Lot: A0340988, CAS: 68-12-2). Chemical was used as provided. Bath sonication was performed using a BRANSONIC (ultrasonic cleaner), model- 3510E-MTH, 100 W, 42 kHz. The supernatant was separated from sediment by removing the top ~80% of the dispersion by pipette. Centrifugation was carried out using an Eppendorf Centrifuge 5804 for 45 min in all cases. After exfoliation morphology of the exfoliated Graphene flakes were investigated using field emission scanning electron microscopy (FESEM) (Model JEOL JSM-6700F). Besides, exfoliated Graphene were also characterized by Raman Spectroscopy. It was performed on the prepared films on silicon wafer using an InVia Reflex, Renishaw, UK Raman Spectroscope. Concentrations of Graphene suspensions in solvents were estimated from the standard graphs prepared using Beer's law with the aid of ultra-violet visible (UV-vis) absorbance spectroscopy (Thermo Scientific, Multiskan GO, Version-1.00.40. 96-grid transparent micro-plates).

2.1. Experimental Procedures

First, 200 mg of graphite flakes was weighted using analytic balance and 200 ml of NMP was taken by a measuring cylinder. Then, NMP was poured on the graphite flakes in a beaker. The mixture was then exfoliated by bath sonication for 3 hours. A controlled centrifugation process was used for the separation of flakes in LPE. After exfoliation process prepared dispersion was first centrifuged at 4000 rpm for 45 minutes. Larger flakes were tending to sediment at the bottom of the centrifuge tube. Supernatant of graphene in NMP was decanted from the sediment by take away of top ~ 80 % of the dispersion by pipette without disturbing the sedimentation. Separated supernatant dispersion was then preserved into the other tube for characterization. Then 16 ml of NMP was added into the sedimentation and re-dispersed by a mild sonication of 15 minutes and centrifuged with 3000 rpm for 45 minutes. Supernatant of graphene in NMP was decanted again from sediment by take away of top ~ 80 % of the dispersion. This procedure was further repeated for three times, centrifuging the re-dispersed sediment at 2000, 1000 and 500 rpm, after every time separating the supernatant.

After 500 rpm centrifugation, the procedure was stopped as it has been found 500 rpm for 45 minutes to be the minimum required [15] to remove un-exfoliated graphitic crystal. Centrifugation with 500 rpm is sufficient to remove all the graphitic crystallites from the dispersed flakes [15]. Each of the supernatant suspension was the products. Then the dispersed concentration of the suspension was measured by absorbance analysis. Same procedure was repeated for the solvent DMF with maintaining all the parameters and conditions same. During the experiment water level was maintained carefully at the exact position in the water bath sonicator. Two separate standard curves were produced by preparing the known suspension in NMP and DMF solvents. The Beer's law ($A = \alpha C_G l$) provides a linear relationship between an absorbance of light and the properties of a material through which light is passing. Absorption coefficients, α are identified [5, 8, 9] using the Beer's law with the web-length (λ) 660 nm. The value of absorption coefficients were varied for different solvents [8, 15].

3. Results and Discussion

3.1. FESEM

Typical FESEM images of exfoliated Graphene flakes are presented in Figure 1. Images were taken on the sample prepared from supernatant Graphene suspension separated by final centrifugation speed (500 rpm). Figure 1(a) and 1(b) are showing the representative samples in solvents NMP and DMF respectively for the centrifugation speed of 500 rpm. FESEM analyses of the exfoliated Graphene samples revealed the presence of few layers of Gr flakes stacking. It can be seen that most of the exfoliated flakes are very thin and Graphene layers are stacked one over another in an ordered manner [16].

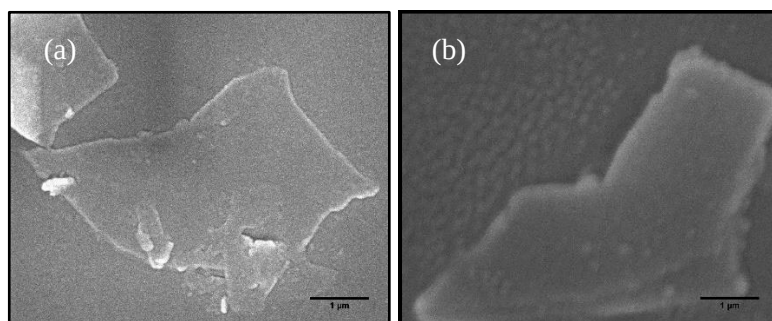


Figure 1. Representative FESEM images of exfoliated Graphene flakes of 500 rpm samples by solvent: (a) NMP and (b) DMF.

3.2. Raman Spectroscopy of Exfoliated Graphene

Representatives of Raman spectrum measured on the precursor graphite powder and samples of exfoliated Gr in DMF and NMP solvents for final centrifuge speed 500 rpm are shown in Figure 2.

The spectrum for the starting precursor powder is presented for the comparison purpose. Three characteristic peaks in the Raman spectra of graphitic carbon materials appear. In the measured Raman spectrum on precursor Graphite powder (PGP), G-band peak is found at $\sim 1578.73 \text{ cm}^{-1}$, 2D-band at $\sim 2648.96 \text{ cm}^{-1}$ and D-band at $\sim 1311 \text{ cm}^{-1}$. G band peak position for exfoliated Gr samples by NMP and DMF (supernatant of 500 rpm centrifugation) are shifted to $\sim 1583.64 \text{ cm}^{-1}$ and $\sim 1582.59 \text{ cm}^{-1}$ respectively. It reveals the transformation of Gr from the graphite flakes by LPE. Increases in Raman shift (cm^{-1}) of G-band peak from the precursor graphite is the indication of the conversion of graphite to Gr sheets [17]. The sharp G-band peak appeared at around 1583 cm^{-1} in the spectrum of Gr, for the in-plane vibrational of sp^2 hybridized carbon atoms that comprise of the Gr sheet [17].

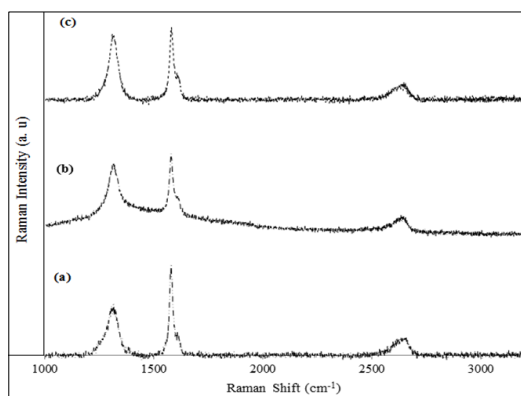


Figure 2. Raman spectra of (a) graphite powder (LPE precursor), exfoliated Graphene samples of 500 rpm centrifuge in solvent: (b) DMF and (c) NMP.

3.3. Physical Appearance of Exfoliated Graphene Suspensions

Digital photographs of supernatant graphene suspensions separated by varying centrifugation speeds (rpm) are shown in Figure 3. Although very slight levels of aggregation and sedimentation occurred within 30 days of centrifugation, the dispersions remain of high quality at least five months after preparation. Exfoliated Graphene suspensions in NMP are shown in Figure 3(a), 3(b), 3(c), 3(d) and 3(e) for the centrifugation speed of 4000, 3000, 2000, 1000 and 500 rpm respectively. Similarly exfoliated Graphene suspensions in DMF are shown in Figure 3(f), 3(g), 3(h), 3(i) and 3(j) for the same centrifugation speeds (rpm) respectively.

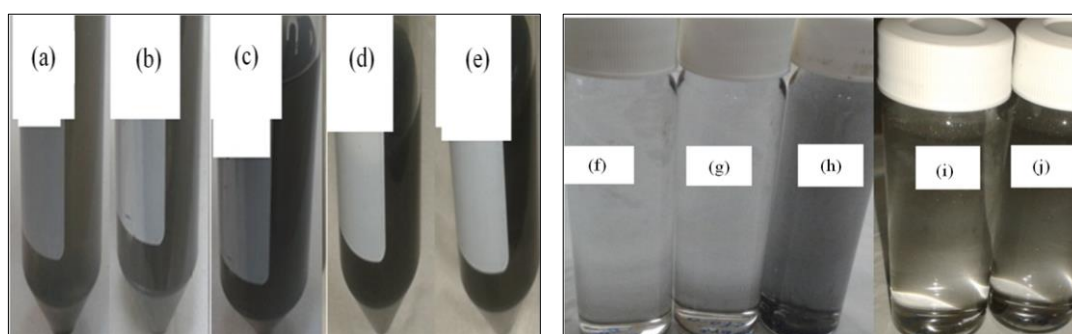


Figure 3. Dispersions of exfoliated graphene in NMP (a-e) and DMF (f-j) for the varying centrifuge speed from 4000 to 500 rpm respectively.

3.4. Concentration Estimation of Exfoliated Gr Suspension

Standard curves of the suspensions in NMP and DMF solvents are shown in Figure 4. Absorbance per cell length, (A/l) is obtained from these generated standard curves. In Figure 4a and 4b; the values of α is estimated 983.9 and $126.49 \text{ ml mg}^{-1} \text{ m}^{-1}$ for suspensions in NMP and DMF solvents respectively. Degree of correlations (R^2) between concentration, C_{Gr} and A/l are found 0.9984 and 0.9846 for NMP

and DMF suspensions respectively which are close to the unity. It indicates that instrument reading follow the Beer's law in readily with ideal case.

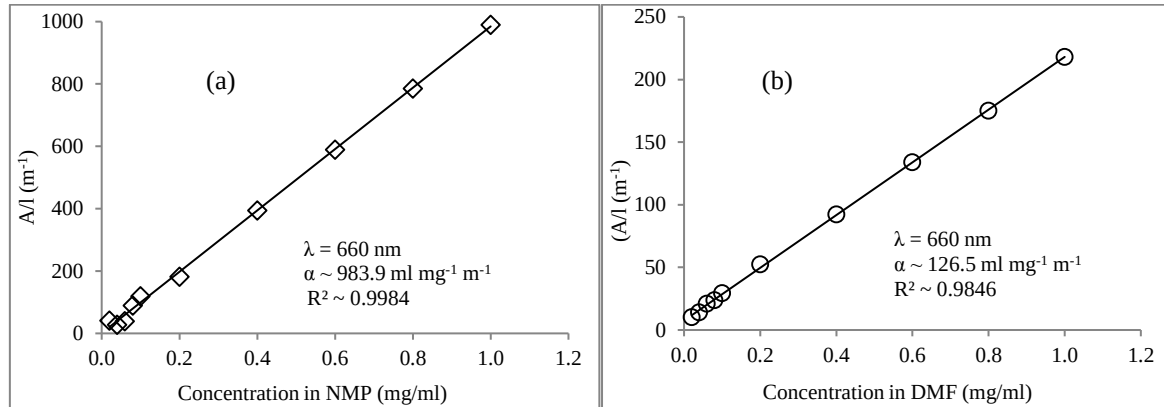


Figure 4. Standard curves of absorbance ($\lambda = 660$ nm) per cell length, A/l (m^{-1}) verses concentration in two different solvents: (a) NMP and (b) DMF.

After sonication assisted exfoliation, graphene concentration, C_{Gr} of separated supernatant suspensions for varying centrifugation rates are estimated by the calculated value of absorbance per cell length, A/l (m^{-1}) of standard graphs once absorption coefficients, α is identified. C_{Gr} of supernatant graphene dispersions in NMP and DMF solvents verses centrifugation rate are plotted in Figure 5a and 5b respectively. Corresponding A/l (m^{-1}) is shown in the right axis of both graphs. It is seen that C_{Gr} is decreased monotonically with increasing centrifuge rate. It is agrees with work reported by Lotya et al., 2009 [9] and Khan, et al., 2010 [15]. The y-axis error bars represent the standard deviation calculated from measurements.

Concentration, C_{Gr} of 4000 rpm centrifuge supernatant solution (graphene suspension) in NMP (Figure 5a) is obtained 0.230 mg/ml. C_{Gr} of the collected supernatant suspensions of successively lower centrifugation speed of 3000, 2000, 1000 and 500 rpm are obtained 0.244, 0.268, 0.290 and 0.316 mg/ml respectively. While, C_{Gr} of exfoliated graphene suspensions (in figure 5b) in DMF are obtained 0.191, 0.222, 0.241, 0.260 and 0.313 mg/ml for the centrifugation rate 4000, 3000, 2000, 1000 and 500 rpm respectively.

Repeated exfoliation was conducted by maintaining exactly same procedure except for the different solvent DMF in lieu of using the solvent NMP. It is noted that C_{Gr} in NMP is higher than that of in DMF. Exfoliation of graphite is relying on the surface energy of solvents [8]. Where surface energy of solvents converted to enthalpy of mixing (per unit volume). For graphite, the surface energy is defined as the energy per unit area required to overcome the van der Waals forces when peeling two sheets apart [5, 8]. Surface energy of NMP solvent is perfectly matched [5, 8, 9] that of graphite were optimum exfoliation occurs. DMF surface energy is a bit lower than NMP resulting of higher exfoliation in NMP for the same sonication time from the same graphite precursor.

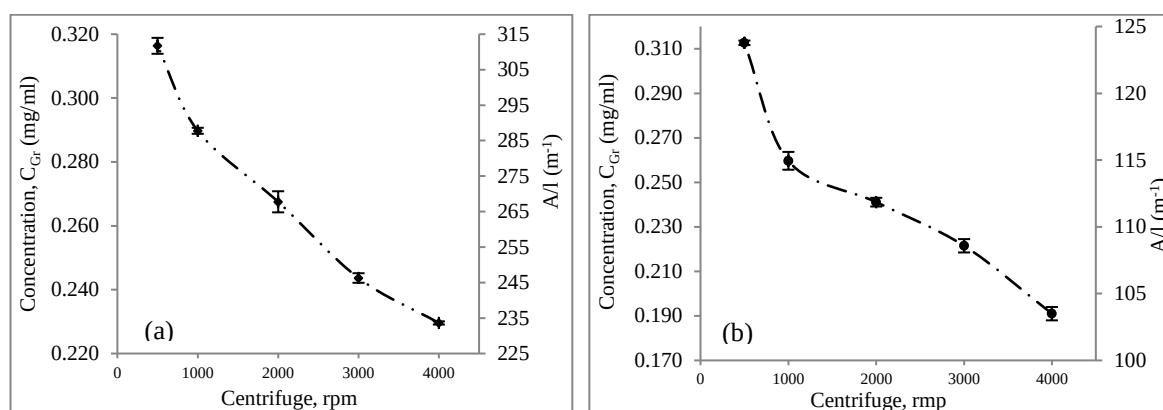


Figure 5. Exfoliated graphene concentrations as a function of centrifugation speed, rpm: (a) NMP and (b) DMF

4. Conclusions

Graphene flakes have been effectively fabricated using sonication assisted LPE separately in two different solvent NMP and DMF. Separate suspensions of exfoliated graphene were obtained using a systematic centrifugation scheme. FESEM analyses of the exfoliated Graphene samples revealed the presence of few layers of Graphene flakes stacking. Analysis of the Raman spectrum of the samples it was revealed that the precursor graphite flakes was converted to Graphene sheets. From the investigation of concentration of exfoliated Graphene suspensions, it is seen that the concentrations in lower centrifugation speed (rpm) is successively increased in both of the organic solvents NMP and DMF. In NMP concentrations of supernatant Graphene suspensions are obtained 0.230, 0.244, 0.268, 0.290 and 0.316 mg/ml for the successively lower centrifugation speed of 4000, 3000, 2000, 1000 and 500 rpm respectively. While in DMF, these are obtained 0.191, 0.222, 0.241, 0.260 and 0.313 mg/ml for same centrifugation rate (rpm) respectively. It is also perceived that, for the same centrifugation speed (rpm) concentration of Graphene suspension was higher in NMP than that of in DMF.

5. Acknowledgments

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