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INVESTIGATION OF EXTRACTION YIELDS OF EXFOLIATED GRAPHENE IN DEIONIZED WATER FROM ORGANIC SOLVENTS

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ABSTRACT

Organic solvent is suitable for the exfoliation of graphene. However, for the end application of exfoliated graphene it needs to extract and re-disperse to the required media. Extraction of exfoliated graphene from organic solvents to a polar solvent is a crucial challenge in graphene synthesis. The principal objective of this study is to examine the concentration yields of exfoliated graphene extraction and make a comparison of the estimated percentage concentrations of graphene in between organic solvents and deionized water (DW). Exfoliated graphene from the solvents N-Methyl-2-Pyrrolidone (NMP) and N, N-dimethylformamide (DMF) were taken. The extraction of exfoliated graphene was conducted by membrane filter using a vacuum filtration system. Concentration of exfoliated graphene solvents were estimated using Beer's law by preparing separate standard graphs. It is seen that concentrations of exfoliated graphene in DW from both NMP and DMF solvents for all the centrifugation was reduced. These reductions were found to be varied from ~ 21 to 25.5%. Morphology analysis using TEM and FESEM images reveals that the few layers of graphene staked in the sonication assisted liquid phase exfoliated (LPE) graphene in both of NMP and DMF solvents. Very minor levels of aggregation occurred and very slight sedimentation appeared after centrifugation of 30 days.

Keywords: Concentration; Extraction; Graphene; Re-dispersion; Solvents

1. INTRODUCTION

A one atom thick graphene sheet of ultra-thin carbon film with two-dimensional planer's geometry was first discovered by Novoselov et al. (2004). Various chemicals and natural resources (Supriadi et al., 2017) have been used as precursor materials for the fabrication of graphene. This carbon based material has a vast application in nanofluids (Ahlatli et al., 2016). Various types of graphene have been processed using various methods, such as chemical vapor growth (Hu et al., 2012), molecular building blocks by annealing of SiC substrates (Palma &

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Samorì, 2011), bottom-up growth through the wet ball-milling method (Leon et al., 2011), and burning Mg metal in solid CO_2 (dry ice) (Arifutzzaman et al., 2015). Due to their initial setup and very low final yielding limits, their wide implication of graphene fabrication (Ciesielski & Samorì, 2014), in this case green chemistry, could be a viable approach (Kusrini et al., 2015).

Commercially obtainable microcrystalline graphite flakes can be exfoliated into distinct graphene flakes by an interaction in a solvent (Kotov et al., 1996). To exfoliate the graphite flakes into separate layers, two different mechanical forces are required (Arao et al., 2016). One is normal force which changes the interlayer space, and the other is the lateral shared force which slides away from the sheets. Applying the shear force across the flake's of graphite surfaces causes the exfoliation graphite into the separate graphene layers (Yang & Liu, 2014). This chemical or liquid exfoliation method possesses very modest and straight forward one-step processes to exfoliate graphene in the liquid solvents which is most widely used technique to produce graphene (O'Neill et al., 2011; Khan et al., 2012). The surface energy of the organic solvents NMP (40 m Jm^{-2}) or DMF (37 m Jm^{-2}) (Hernandez et al., 2008) perfectly matches the graphite (Zacharia et al., 2004) and fulfils the requirement for a successful exfoliation to graphene sheets (Compton et al., 2010). Sedimentation based centrifugation is used to separate the graphene (O'Neill et al., 2011). In this approach, a higher centrifugation rate (rpm) gives lower concentrations of the graphene (Khan et al., 2012).

An organic solvent is necessary for the exfoliation of graphite to get separate graphene sheets. However, for further application purposes, it may need to extract the graphene from the solvent produced and re-dispersed in to a required solvent. For example, organic solvents will be influenced highly on the thermal and electrical transport properties (Behabtu et al., 2010). Sometimes, it could have a high impact on the device performance. However, solvents with low boiling points, such as water, will be preferable because they are incompatible for exfoliation and very suitable for the end application, such as the preparation of the heat transfer of nanofluids (Ciesielski & Samorì, 2014).

Irin et al. (2015) analyzed the different techniques for removing solvents from graphene dispersion. They found that vacuum filtration was the most suitable way compared to the other techniques, such as dialysis and spray drying, to separate the graphene from the organic solvent dispersion, and re-disperse to other suitable media. After vacuum filtration, graphene flakes prevail with an ordered multi-layered film on the filter paper (Dikin et al., 2007). Due to the application of constant suction force by a vacuum pump to the graphene sheets at the interface of solid and liquid, sheets are placed parallel to the membrane filter (Yang et al., 2011). Repulsive force amongst the solvent and exfoliated graphene was sufficient in preventing the graphene sheets from the re-staking together before they touch the filters surface (Yang et al., 2011). For these reasons, most of the graphene sheets tend to prevail horizontally on the membrane filter surface during the suction by vacuum pump (Cheng & Li, 2013). Importantly, it was confirmed by Yang et al. (2011) that the chemically transformed graphene sheets never return to their graphite form farther in the created wet film on the membrane filter. Although, literature has found few reports on the analysis of graphene yields in different base liquids, and based on knowledge, there is no systematic investigation reporting on the analysis of extraction yields of exfoliated graphene from the exfoliating organic solvents into DW. Therefore, the objective of this research is to conduct a systematic investigation on the extracted exfoliate graphene concentration yields, and make a comparison among the percentage variation of concentration yields into two different organic solvents with DW.

2. MATERIALS AND METHODS

Graphene flakes used in this study were synthesized using an easy and effective LPE technique in two different organic solvents: NMP and DMF. The exfoliation of graphene using two different organic solvents have been shown elsewhere by Arifutzzaman et al. (2019).

2.1. Extraction and Re-dispersion of Graphene

For the removal of exfoliated graphene from organic solvents and re-dispersion into DW a filtration unit was prepared with a polyvinylidene fluoride (PVDF) membrane filter of ≤ 0.22 µm. A suction (vacuum) pump was attached to the filtration unit. The filtration process was conducted by taking a segment of the exfoliated Gr samples separately from both NMP and DMF to get un-interrupted suction from the stacking of very thick layers of graphene on the filters surface. Before filtration, ethanol was added with the taken exfoliated graphene dispersion in organic solvents (NMP and DMF) to avoid the risk of tearing the membrane filters, as use of only NMP or DMF could destroy the membrane filter during suction due to their corrosive effect. This whole process was conducted at room temperature.

About 30 ml of ethanol was added into the 20 ml NMP sample and stirred for about 60 seconds by a glass rod. Then, it was carefully poured into a cylindrical filter funnel. NMP and ethanol liquid mixture was collected in the suction flask through continuous suction by using a vacuum pump. Graphene flakes were simply placed horizontally on top of each other making multiple layers on the filters surface. Then, the filter cake emerged immediately into around 25 ml of DW in the centrifuge tube. After that, a tube was put on a vortexer for about 3-4 minutes. Most of the graphene flakes separated from the membrane filter and re-dispersed into the DW. To peel out the remaining graphene flakes from the filter surface, a mild (for about 5 min) sonication was conducted. Finally, a homogeneous dispersion of graphene flakes was obtained in the DW. A similar procedure was followed for all the samples to get exfoliated graphene dispersion in DW for both solvents, NMP and DMF. Figure 1 illustrates the schematic diagram of the re-dispersion process of exfoliated graphene in DW from organic solvents.

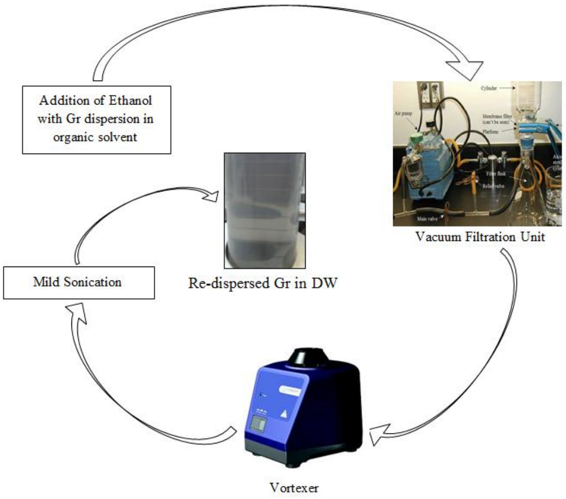

Figure 1 Schematic illustration of the re-dispersion process of exfoliated graphene form organic solvents into DW

2.2. Microscopy Analysis of Exfoliated Graphene

The flakes morphology of sonication assisted exfoliated graphene were inspected using a Hitachi Transmission Electron Microscopy (TEM) system of 60 kV. Graphene flakes were also characterized by field Emission Scanning Electron Microscopy (FESEM) (Model JEOL JSM-6700F). Few drops of exfoliated graphene suspension in solvents were dripped onto the copper stub sample holder of FESEM and dried by air flow. A gold coat was made on the samples using a sputter coating technique before taking the images.

3. RESULTS AND DISCUSSION

3.1. Characterization

3.1.1. Morphology of exfoliated graphene

Figure 2 displays the TEM and FESEM pictures of the representative graphene samples. Morphology of the exfoliated graphene from solvent NMP is shown in Figures 2a and 2b, and DMF in Figures 2c and 2d, respectively. Analysis revealed the existence of a few layers of graphene in the flakes. It can be seen that most of the graphene flakes are very skinny and transparent when gathered one above another in an orderly way (Vadukumpully et al., 2019). Graphene flakes in a base fluid are far from straight or completely flat, where the basal plane of the graphene flakes prevailed as non-flat sheets in the dispersion (Cheng & Li, 2013). It is speculated that the flake size is similar for both graphene from NMP and DMF solvents for the same exfoliation condition with the same precursor graphite powder.

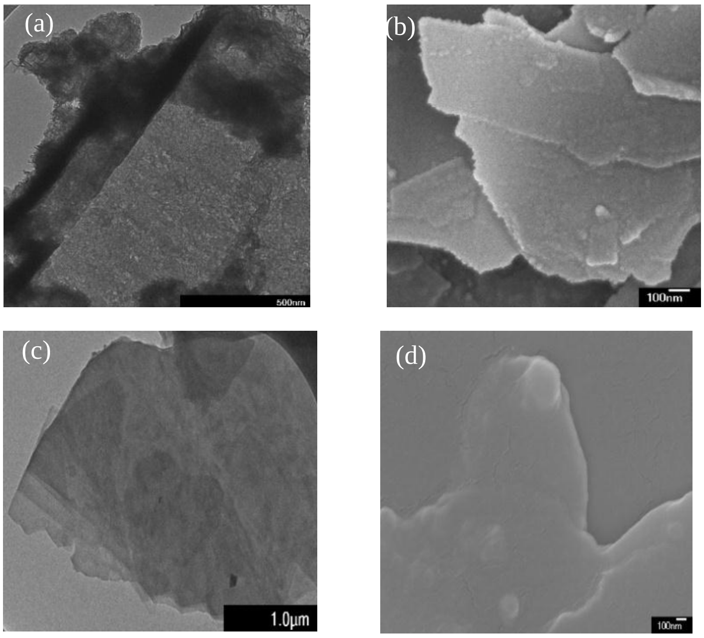

Figure 2 Representative TEM and FESEM pictures of exfoliated flakes of graphene in: NMP (a and b) and DMF (c and d)

3.1.2. Appearance of graphene dispersions

Digital photos of graphene dispersions in organic solvents NMP and DMF for the varying centrifuge rate (rpm) are exposed separately in Figure 3. Very minor levels of aggregation occurred and a very slight sedimentation appeared after centrifugation of 30 days of preparation.

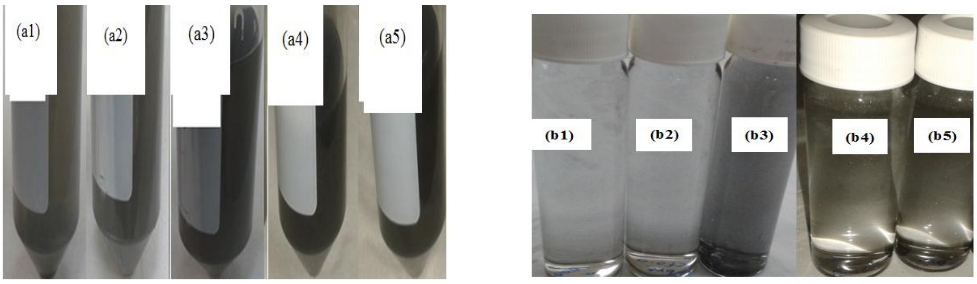

Figure 3 Graphene dispersions in NMP (a:1-5) and DMF (b:1-5) for the centrifugation speed of 4000 to 500 rpm correspondingly

Obtained graphene dispersions endured in high quality for about five months from the day of preparation. Graphene suspensions in NMP are presented in Figure 3(a:1-5) for the successively increasing centrifuge speed of 4000, 3000, 2000, 1000 and 500 rpm. Likewise, graphene suspensions in DMF are displayed in Figure 3(b:1-5) for the same rpm correspondingly.

3.1.3. Estimation of concentration yields of graphene

Two separate standard graphs were formed; the first by preparing the known suspensions in organic solvents NMP (Figure 4a) and DMF (Figure 4b) for the measurements of exfoliated graphene concentrations. The second standard graph was created by preparing the known suspensions in DW as shown in Figure 4c. Standard graph in Figure 4c is used for the estimation of graphene concentration in DW after extraction from the organic solvents NMP and DMF separately.

Absorbance per cell length (A/l) was attained from the created standard curves shown in Figure 4. Where the absorption coefficient, α, is identified (Hernandez et al., 2008; Khan et al., 2010; Ciesielski & Samorì, 2014; Liu et al., 2017) using the Lambert-Beer Law ($A= \alpha C_{Gl}$) with the wavelength (λ) of 660 nm. The obtained coefficients of absorption are varied for the changed solvents (Niyogi et al., 2006; Hernandez et al., 2008; Khan et al., 2010; Mehrali et al., 2014). From the generated standard curve in Figures 4a–4c, the values of the absorption coefficient (α) were assessed as 983.9, 126.49 and 1.25 ml mg^{-1} m^{-1} for suspension in solvents NMP, DMF and DW, respectively. The degree of the correlation (R^2) among the concentration (C_{Gr}) and A/l were obtained as 0.9984, 0.9846 and 0.9995 for NMP, DMF and DW solutions which were closer to one. It directs that apparatus reading ideally follows the Beer Law.

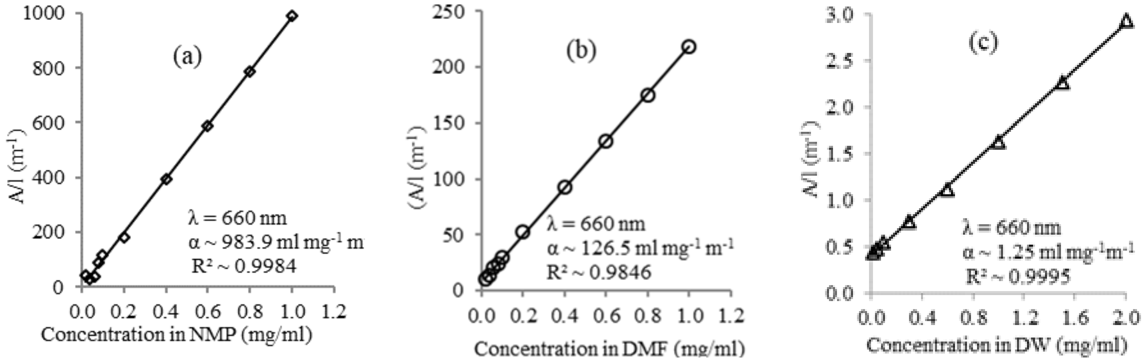

Figure 4 Standard graphs of absorbance (λ = 660 nm) per cell length as a function of concentration in organic solvents: (a) NMP; (b) DMF; and (c) pure DW

Exfoliated graphene concentration (C_{Gr}) of the extracted supernatant of the suspensions was estimated for the varying centrifugation rates (rpm) using the obtained value of A/l (m^{-1}). Value of A/l was obtained from the created standard graphs with the aid of attained coefficients of absorption, α. Extracted graphene from the organic solvents NMP and DMF were suspended in pure DW.

Figures 5a–5b shows the supernatant C_{Gr} of graphene dispersion in solvents NMP and DMF as a function of their respective centrifugation rate (rpm). Extracted C_{Gr} in DW from the corresponding solvents are also fitted in Figures 5a and 5b, respectively. C_{Gr} is reduced terribly with rising centrifugation rate (rpm). It aligns with the results obtained by Khan et al. (2010), Lotya et al. (2010) and Khan et al. (2012).

Concentration of C_{Gr} supernatant graphene suspension in NMP at 4000 rpm centrifugation (Figure 5a) was found to be 0.230 mg/ml. Extracted supernatant C_{Gr} of the graphene suspensions of sequentially reduced centrifugation rate of 3000, 2000, 1000 and 500 rpm were attained as 0.244, 0.268, 0.290 and 0.316 mg/ml correspondingly. Repetitive exfoliation was conducted by maintaining the same protocol by varying the solvent DMF instead of applying NMP as a solvent. C_{Gr} was also found to have decreased with the increasing centrifuge speed (Figure 5b). C_{Gr} of graphene suspensions in DMF were found to be 0.191, 0.222, 0.241, 0.260 and 0.313 mg/ml for the centrifuge rates of 4000, 3000, 2000, 1000 and 500 rpm, respectively. In both graphs, extracted graphene concentrations in DW were found to be lower than the concentration in organic solvents NMP and DMF. It was perceived for all the samples with the centrifugation rate of 4000, 3000, 2000, 1000 and 500 rpm. The error bars with the y-axis denote the standard deviation estimated from the measurements.

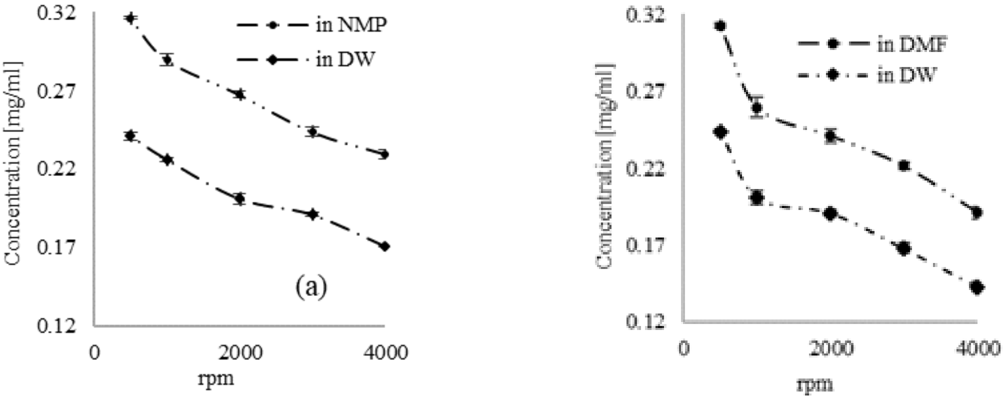

Figure 5 Extracted graphene concentrations in DW verses centrifugation rate (rpm) with the comparison of: (a) NMP; and (b) DMF

Percentage reduction of graphene concentration due to the extraction from organic solvents (exfoliated) to DW are presented in Figure 6. This plot is presented for both organic solvents NMP and DMF for the five different centrifuge rates of 500, 1000, 2000, 3000 and 4000 rpm. Percentage concentration reductions of exfoliated graphene are estimated using the correlation $((C_o-C_f)/C_o)\times100\%$. Where, C_o is the exfoliated graphene concentration in organic solvents after exfoliation, C_f is the concentration of graphene in DW after extraction from organic solvents. The percentage reduction of concentration is expressed as, $\eta = ((C_o-C_f)/C_o)\times100\%$. The y-axis error bars in the bar graphs are the standard deviation with the repeated concentration measurements for the samples. All standard deviations are found to be ±0.001.

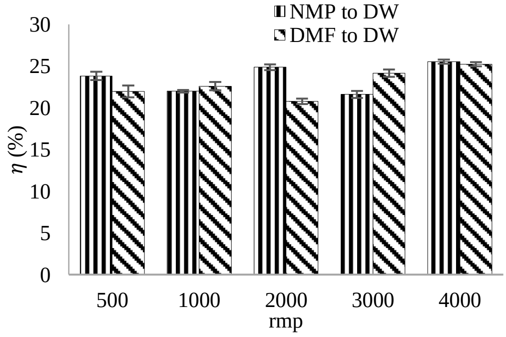

Figure 6 Percentage reduction of extracted exfoliated graphene concentration in DW from organic solvents.

It is seen that the concentrations of exfoliated graphene in DW from both solvents NMP and DMF for all the centrifugation was reduced. These reductions were found to be varied from ~21 to 25.5%. After vacuum filtration, Graphene flakes prevail with an ordered multi-layered film on the filter paper (Dikin et al., 2007). Due to the application of constant suction force by a vacuum pump to the graphene sheets in the solid and liquid interface, sheets were placed parallel to the membrane filter (Yang et al., 2011). Due to the repulsive force among the graphene sheets (Yang et al., 2011), they tend to prevail horizontally on the membrane filter surface during the suction by vacuum pump (Chen et al., 2008). Thus, all the graphene sheets did not disperse into the DW from the filter paper. Although chemically transformed graphene sheets never return to their graphite structure farther in the filtrated wet film on the membrane filter (Chen et al., 2008).

4. CONCLUSION

Exfoliated graphene was effectively extracted from two different organic solvents, NMP and DMF, and re-dispersed into DW using a vacuum filtration process. From the investigation, it can be seen that concentrations of exfoliated graphene in DW from both solvents for all the centrifugation was found to be reduced. These reductions were found to be varied from ~21 to 25.5%. Morphology analysis using TEM and FESEM images reveals that, the few layers of graphene in the exfoliated graphene in both of solvents. Very minor levels of aggregation occurred and very slight sedimentation appeared after centrifugation of 30 days.

5. ACKNOWLEDGEMENT

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