A Study of Dispersion Behavior of Graphene Oxide in Organic Solvents

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Abstract: Graphene has attracted the scientific interest in recent years due to its unique physical and chemical properties. The two-dimensional graphene is a new material with many emerging applications, and studying its chemical and physical properties is an important goal. In this study, graphene oxide was prepared by modified Hummer's method and the surface morphology of GO is examined using FESEM. The prepared GO powder was dispersed in three different solvents, namely, Water, N,N-dimethylformamide (DMF), and Dimethyl sulfoxide (DMSO). Ultrasonic bath was used to prepare the dispersion of GO in solvents and the effect of different sonication time on the dispersion behavior of GO was observed. UV-Vis was used to measure the absorbance of GO in the solvents. Homogeneous dispersion was found in solvent with longer sonication time, however, only DMF and Water showed stable dispersion after 1 week which indicated that DMF and Water can be used for dispersion formation and further processing of graphene.

***Keywords*: DMF. DMSO, Graphene Oxide, Dispersion, Water**

I. INTRODUCTION

Graphene (G) is a two-dimensional (2D) carbon nanomaterial which is made up of a single layer of carbon atoms that are chemically bonded in a crystalline hexagonal arrangement [1-3]. Graphene has high mechanical strength (>1060 Gpa), high thermal conductivity (~3000 W/m K), high electron mobility (15000 $cm^2/V\ s$) and high specific surface area (2600 m^2/g) [4]. Due to its outstanding properties, graphene are able to attract an exceptional amount of interest for potential applications such as supercapacitors, biosensors, photovoltaic, and touch panels [5].

However, graphene also suffers from some important drawbacks. It is a poor electric conductor due to the presence of oxides. Even though the oxides can be removed by reduction, the major problem is that reduction process are not able to remove the many structural defects introduced by the oxidation process. These will disrupt the band structure and completely degrade the electronic properties that make graphene unique [17]. The preparation and processing process of graphene sheets has been a challenge because of its hydrophobic properties and is prone to form aggregation which restrains graphene from exhibiting outstanding properties [18-19].

There are several ways that have been developed for the preparation of graphene, which includes, micromechanical exfoliation, epitaxial growth, ultrasonic exfoliation of graphite, chemical vapor deposition (CVD), as well as the chemical reduction of GO. [5-7,12].

Both the micromechanical exfoliation and CVD methods are known for the fabrication methods of less defective graphene films [5]. In the micromechanical method, the natural graphite is exfoliated repeatedly and this method is clearly impractical for a large-scale production because the graphene sheets produced has a very low yield [12]. Even though CVD method is widely used to prepare graphene, but the graphene obtained from this method exhibits very low solubility in organic solvents due to the addition of stabilizer as the exfoliation liquid medium [5].

Recent studies have shown that the chemical reduction method of GO is able to produce a large quantities of reduced graphene oxide (rGO) at low cost [6,12]. This technique uses the help of reducing agent such as hydrazine, $NaBH_4$, hydroquinone, ethylenediamine, or even more environmentally friendly reducing agent, like bovine serum albumin, reducing sugars, green tea, and wild carrot root [12].

Graphene oxide (GO) is consists of two-dimensional oxidized graphene sheets and is made up of an abundant layers of oxygen-containing groups, such as epoxide, hydroxyl, and carboxylic groups [3.8-9]. Based on the Lerf-Klinowski model, the basal planes of the GO is made up of epoxide and hydroxyl groups, whereas the carbonyl and carboxylic groups is attached at the edges of the GO [7,10]. The presence of this oxygen-containing groups is one of the advantages of GO compared to other form of graphene. These oxygen-containing groups will play an important role for interacting with gas molecules [11], DNA [15], and enzyme [16].

Due to the presence of oxygen-containing groups also, GO has the ability to disperse easily in organic solvents [4,7] and aqueous medium [14], provided that the organic solvents used are suitable. Such dispersions are very useful as they facilitate both materials processing and fundamental characterization. For example, they have been used to deposit individual sheets for spectroscopic analysis, prepare polymer-graphene composites, and develop graphene thin films [17].

Different organic solvents used for the dispersion purposes will form different long-term stability and thickness of single layer GO. Some examples of organic solvents that is good at dispersing of graphene are NMP, DMSO, THF, and ethylene glycol [11,17]. These organic solvents are able to form a single layer of GO sheet just as similar as the single layer of GO when dispersed in water [11]. According to Johnson et al, the dispersibility of graphene and its derivative is inversely proportional to its physical properties whereby the dispersibility follows the trend GO > rGO > G [17]. Organic solvents used for the dispersion purposes should have the suitable Hansen solubility parameter, normally range in between 13 to 29 in order to have a good dispersion of GO [6]. Hansen solubility is defined as the sum of the polarity cohesion parameter (δ_p) and the hydrogen bonding cohesion parameter (δ_h) [6].

There are many different ways to obtain graphene dispersion. Initially, a graphene dispersion was obtained by the attachment of the surfactant stabilizer or polymers on the sheets[18]. Li et al showed that dispersion of graphene can be obtained by controlling the reduction of GO dispersion and maintaining the pH level [18]. Yan et al demonstrated that graphene dispersion can be achieved via microwave in a mixture of N,N-dimethylaxetamide and water [18].

However, with the advances of new technology, dispersion of graphene can be achieved through ultrasonic irradiation due to its cavitation and vibration effect [18]. A good dispersion can be achieved by introducing a sufficient amount of electrostatic or steric repulsion which act as an energy barrier and consequently the Brownian motion will help to maintain the dispersion [12]. The modification of graphene either by covalently or non-covalently, as well as solvent selection can help in maintaining a good dispersion [17]. There are certain criteria that need to be attained in order to identify whether the graphene dispersion is useful or otherwise, including concentration of graphene, solvent used, and the time taken for the graphene to remain dispersed [17].

In this study, graphene oxide was dispersed in various organic solvents, namely, Dimethyl formamide (DMF), Dimethyl sulfoxide (DMSO), and Water. The dispersion of GO in the organic solvents is prepared and sonicated at different period of time (1 h and 2h) to observe the effect of time taken for sonication on the dispersion of graphene oxide.

II. METHODOLOGY

A. *Materials and Preparation*

The graphene oxide (GO) powder (1g) was prepared by modified Hummer's method from graphite powder (12.01 MW) supplied by COMAK. The GO dispersion was prepared in two batches. For the preparation of graphene oxide dispersions in different solvents, the dried product was first ground with pestle and mortar then added into the solvent. The solution was stirred for 15 minutes and then sonicated in an ultrasonic bath XUBA 1, Fisher Scientific with a frequency of 40 kHz. The first batch of the GO dispersion was sonicated for 1 hr whereas the second batch of the dispersion was sonicated for 2 hrs. To allow direct comparisons between the dispersing behavior of different solvents, same amount of graphene oxide powder (~5 mg) was added to a fixed volume of solvent (~10 mL) which results in a total concentration of 0.5 mg mL^{-1} for all solvents. Graphene oxide dispersions were tested in two organic solvents namely, DMSO (99.9 % pure), from Merck, Germany and DMF (99.9% pure), from R&M Chemicals. Graphene oxide dispersion in water was also made under the same conditions as those used in organic solvents to be served as a reference because water is the common solvent for the preparation of graphene oxide dispersions.

B. *Characterization*

Prepared graphene oxide dispersions were characterized by UV-Vis absorption spectroscopy. The surface morphology of the prepared GO was examined by Field Emission Scanning Electron Microscope (FESEM).

C. *UV-Vis Spectroscopy*

UV-Vis absorption spectroscopy was performed on a SECOMAM UviLine 9400. The absorbance of the GO dispersions were measured at different wavelength: 200nm, 400nm, 600nm, 800nm, and 1000nm.

III. RESULTS AND DISCUSSION

A. *Graphene Oxide Dispersion*

In order to study the dispersion behaviors of graphene oxide dispersions, the as-prepared graphene oxide (GO) materials have been dispersed in water and two other organic solvents namely DMF and DMSO with the aid of ultrasonication. The dispersions were observed right after sonication and were left for 1 week to settle. Figure 1 and 2 shows the pictures of all the dispersions immediately after sonication for 1 hr and 2 hr respectively. By observation, we can see that the dispersion of GO in the solvent are well-dispersed after being sonicated for 2 hr. This can be seen through the color difference of the dispersions itself. From Figure 1, the dispersion of GO in water were incomplete as there were still quite a lot of GO precipitate at the bottom of the dispersion. However, in DMF and DMSO, there were very little GO precipitated at the bottom of the dispersion. As for that, we have extended the period of sonication to 2 hrs to see if there were any difference in the degree of dispersion. Figure 2 shows the dispersions of GO in all three solvents for a sonication period of 2 hrs. From the figure, it was observed that GO has been well-dispersed in all three solvents. Darker dispersion was seen in all three solvents after being sonicated for 2 hrs and there were no visible precipitate in all three solvents.

After sonication for 1 hr:

Water DMF DMSO

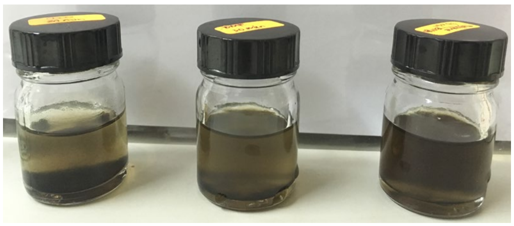

Fig 1: Graphene oxide dispersions in water, DMF, and DMSO immediately after sonication for 1 hr.

After sonication for 2 hrs:

Water DMF DMSO

Fig 2: Graphene oxide dispersions in water, DMF, and DMSO immediately after sonication for 2 hr.

In order to examine the long-term stability, all suspensions were left undisturbed for one week. Figure 3 shows the dispersions that were left for a week after sonicated for 1 hr whereas Figure 4 shows the dispersions that were left for a week after sonicated for 2 hr. In Figure 3, it was seen that all three solvents yielded somewhat larger amount of precipitate after a week. On the other hand, in Figure 4, we have found that DMF had formed homogeneous and sustainable dispersions as in water whereas there was still small amount of GO precipitate found in DMSO after a week. Johnson et al stated that long sonication times are generally undesirable as it can reduce sheet size and introduces defects which undermine graphene's properties [16], which we can relate with the condition of dispersion in DMSO.

Herein, we suggested that the DMF is a good solvent for dispersion preparation of GO because it has a long term stability, provided that the sonication time is made at least 2 hr and DMSO, however possess a comparatively smaller dispersing ability.

After 1 week (sonication period of 1 hr):

Water DMF DMSO

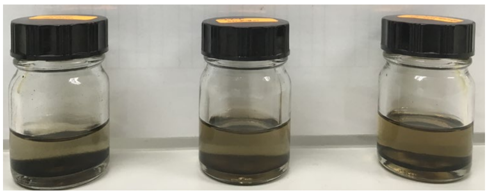

Fig 3: Graphene oxide dispersions in water, DMF, and DMSO after 1 week (Sonication time: 1 hr)

After 1 week (sonication period of 2 hr):

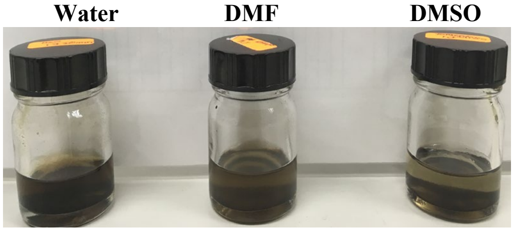

Fig 4: Graphene oxide dispersions in water, DMF, and DMSO after 1 week (Sonication time: 2 hr)

The structure and surface morphology of graphene oxide can be observed by using field emission scanning electron microscope (FESEM). FESEM images give qualitative insight into the interlinked three-dimensional graphene sheets, as illustrated in Figure 5. This was synthesized using graphite flakes.

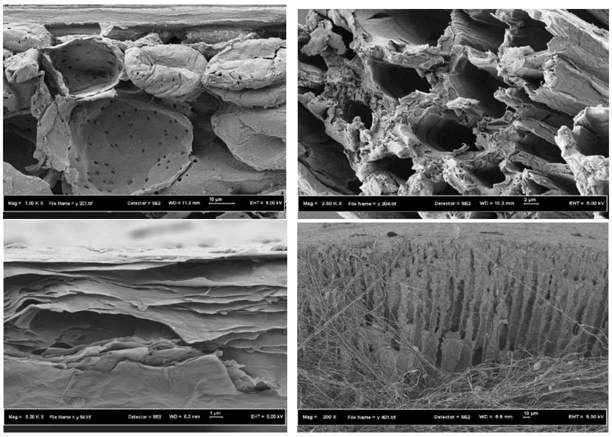

Fig 5: FESEM images of graphene oxide cross section surfaces

B. *Characterization*

UV-vis absorption spectroscopy was employed to gain further insight into the capability of the solvents to disperse graphene oxide. Using the 1 week left suspension, the dispersibility of GO in each solvent was examined from the relationship between the absorbance (A) and the wavelength (nm) of the UV-vis spectrum. Figure 6 and 7 shows UV-vis absorption spectra for the dispersion of GO in water, DMF, ad DMSO by means of bath ultrasonication for 1 hr and 2 hr respectively. The spectra were plotted in the wavelength of 200 to 800 nm.

According to Paredes et al, the UV-vis spectrum of graphene oxide exhibits two characteristic features that can be used as a means of identification: a maximum at 231 nm, corresponding to $\pi \rightarrow \pi^*$ transitions of aromatic C-C bonds, and a shoulder at ~300 nm, which can be attributed to $n \rightarrow \pi^*$ transitions of C=O bonds in which both are bathochromically shifted by conjugation.

From Figure 6 below, we can see that all the solvents were able to disperse GO within the period of 1 hr but with a slightly small absorbance when compared with the absorbance recorded in Figure 7.

Based on both graph, we can say that DMF was a good solvent for the preparation of dispersion of GO. The reason to this phenomena was because after sonicated for 2 hr, GO dispersion in DMF was still able to read a positive reading, however, in DMSO, the reading recorded was of negative values which is why there were no data appeared in Figure 7 for DMSO. From both graph also, water shows the highest absorption intensity and we can say that water has the best dispersing ability. Through this study, it was indicated that graphene oxide dispersions with long-term stability could be prepared in DMF, other than using the usual dispersion solvent which is water.

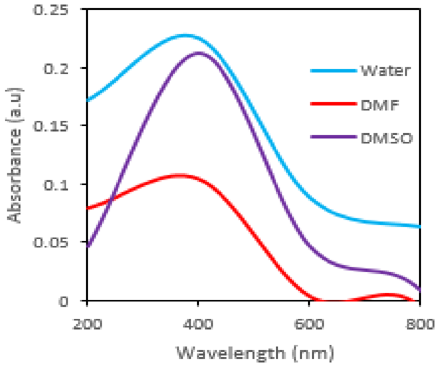

Fig 6: UV-vis absorption spectra of graphene oxide dispersed in different solvent and left for one week (1 hr sonication time)

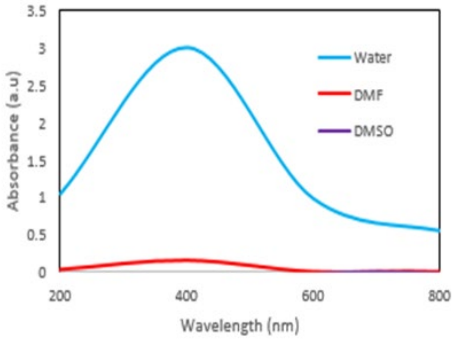

Fig 7: UV-vis absorption spectra of graphene oxide dispersed in different solvent and left for one week (2 hr sonication time)

IV. CONCLUSION

We have studied the dispersion ability of graphene in Water, DMF, and DMSO. From this research, we identified that DMF can be one of the organic solvents used to form dispersions with long-term stability. The ability of DMSO to disperse graphene oxide decreases as the sonication time increases. The dispersion stability of GO in organic solvent was compared according to the length of sonication period. Most of the dispersions were short lived right after sonication but only water and DMF yielded a stable dispersion after a week. Therefore, we have concluded that DMF can be used as an alternative for dispersing preparation instead of using the common solvent which is Water.

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References

[1] Rattana, T., Chaiyakun, S., Witit-Anun, N., Nuntawong, N., Chindaudom, P., Oaew, S., … Limsuwan, P. (2012). Preparation and characterization of graphene oxide nanosheets. *Procedia Engineering*, *32*, 759–764. https://doi.org/10.1016/j.proeng.2012.02.009

[2] Bykkam, S., & Rao, K. (2013). Synthesis and characterization of graphene oxide and its antimicrobial activity against Klebsiella and Staphylococus. *International Journal of Advanced Biotechnology and Research*, *4*(1), 142–146. Retrieved from http://www.bipublication.com/files/IJABR-V4I1-2013-20.pdf

[3] Zhang, Y., Wu, C., Guo, S., & Zhang, J. (2013). Interactions of graphene and graphene oxide with proteins and peptides, *2*(1), 27–45. https://doi.org/10.1515/ntrev-2012-0078

[4] Kim, D. H., Yun, Y. S., & Jin, H. (2012). Difference of dispersion behavior between graphene oxide and oxidized carbon nanotubes in polar organic solvents. *Current Applied Physics*, *12*(3), 637–642. https://doi.org/10.1016/j.cap.2011.09.015

[5] Konios, D., Stylianakis, M. M., Stratakis, E., & Kymakis, E. (2014). Journal of Colloid and Interface Science Dispersion behaviour of graphene oxide and reduced graphene oxide. *JOURNAL OF COLLOID AND INTERFACE SCIENCE*, *430*, 108–112. https://doi.org/10.1016/j.jcis.2014.05.033

[6] Jang, J., Pham, V. H., Hur, S. H., & Chung, J. S. (2014). Journal of Colloid and Interface Science Dispersibility of reduced alkylamine-functionalized graphene oxides in organic solvents. *JOURNAL OF COLLOID AND INTERFACE SCIENCE*, *424*, 62–66. https://doi.org/10.1016/j.jcis.2014.03.018

[7] Kashyap, S., Mishra, S., & Behera, S. K. (2014). Aqueous Colloidal Stability of Graphene Oxide and Chemically Converted Graphene, *2014*.

[8] Pavlidis, I. V., Patila, M., Bornscheuer, U. T., Gournis, D., & Stamatis, H. (2014). Graphene-based nanobiocatalytic systems: Recent advances and future prospects. *Trends in Biotechnology*, *32*(6), 312–320. https://doi.org/10.1016/j.tibtech.2014.04.004

[9] Zhang, J., Zhang, J., Zhang, F., Yang, H., Huang, X., Liu, H., & Guo, S. (2010). Graphene oxide as a matrix for enzyme immobilization. *Langmuir*, *26*(9), 6083–6085. https://doi.org/10.1021/la904014z

[10] Stankovich, S., Dikin, D. A., Piner, R. D., Kohlhaas, K. A., Kleinhammes, A., Jia, Y., & Wu, Y. (2007). Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, *45*, 1558–1565. https://doi.org/10.1016/j.carbon.2007.02.034

[11] Zaaba, N. I., Foo, K. L., Hashim, U., Tan, S. J., Liu, W., & Voon, C. H. (2017). Synthesis of Graphene Oxide using Modified Hummers Method : Solvent Influence. *Procedia Engineering*, *184*, 469–477. https://doi.org/10.1016/j.proeng.2017.04.118

[12] Ji, X., Song, Y., Han, J., Ge, L., Zhao, X., Xu, C., … Qiu, H. (2017). Journal of Colloid and Interface Science Preparation of a stable aqueous suspension of reduced graphene oxide by a green method for applications in biomaterials, *497*, 317–324. https://doi.org/10.1016/j.jcis.2016.09.049

[13] Muazim, K., & Hussain, Z. (2017). Graphene oxide — A platform towards theranostics. *Materials Science & Engineering C*, *76*, 1274–1288. https://doi.org/10.1016/j.msec.2017.02.121

[14] Tang, L., Li, D., & Li, J. (2013). Graphene Oxide / DNA Duplex − Based Logic Gate and Sensor Mediated by RecA-ssDNA Nucleoprotein Filaments, 5–7.

[15] Zhang, G., Ma, J., Wang, J., Li, Y., Zhang, G., Zhang, F., & Fan, X. (2014). Lipase immobilized on graphene oxide as reusable biocatalyst. *Industrial and Engineering Chemistry Research*, *53*(51), 19878–19883. https://doi.org/10.1021/ie503596j

[16] Johnson, D. W., Dobson, B. P., & Coleman, K. S. (2015). Current Opinion in Colloid & Interface Science A manufacturing perspective on graphene dispersions. *Current Opinion in Colloid & Interface Science*, *20*(5–6), 367–382. https://doi.org/10.1016/j.cocis.2015.11.004

[17] Lotya, M., King, P. J., Khan, U., De, S., & Coleman, J. N. (2010). High-Concentration, Surfactant- Stabilized Graphene Dispersions, *4*(6), 3155–3162.

[18] Park, S., An, J., Jung, I., Piner, R. D., An, S. J., Li, X., … Ruoff, R. S. (2009). Colloidal Suspensions of Highly Reduced Graphene Oxide in a Wide Variety of Organic Solvents 2009, 1–5.

[19] Zhang, W., He, W., & Jing, X. (2010). Preparation of a Stable Graphene Dispersion with High Concentration by Ultrasound, 10368–10373.

[20]