Dispersion Behavior of Graphene Oxide in Organic Solvents (Alcohol)

NurulSyahibah Binti Che Man and Dr Fauziah Binti Marpani.

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract—**Graphene is considered unique material promising for a range of new practical application for electronic, mechanical and electrochemical. In this work, the graphene oxide (GO) was prepared by modified Hummer's method. The Scanning Electron Microscope (SEM) images demonstrate ultrathin and the successful GO sheet exfoliated from graphite containing ordered stacking graphene layers. The dispersion behavior of graphene oxide (GO) has been investigated in a wide range of organic solvent. Here in this report, the dispersion of GO has been investigated in three different solvents namely Water, Methanol and Ethanol. The method used for dispersion is ultrasonication. The effect of sonication time on dispersion behavior was also investigated. GO dispersion in water at 2hr sonication had formed homogeneous and sustainable dispersions compare to the other two solvent, methanol and ethanol. Estimation of the capability of the solvent to disperse the GO used UV-vis adsorption spectroscopy and the spectra are plotted in the wavelength range from 200 to 1000 nm. A stable dispersion remained only in water after 1 week. GO dispersion in methanol and ethanol settled after few times of sonication.**

Keywords— Graphene Oxide, Methanol, Ethanol, Dispersion Sonication, precipitate.

I. INTRODUCTION

Graphene has unique 2D surface with flat hexagonal structure. Its 2D surface make it as unique host of electronic properties which not seen in other thicker carbon films or carbon monostructure.[11]. Graphene is an atom with a thin layer of sp^2-bonded carbon atoms, stacked in a two-dimensional (2D) honey comb lattice, forming the basic building block of carbon allotropes of any dimensionality.[18]. It is discovered in 2004, graphene has been remarkable properties attracted a tremendous attention worldwide from the fundamental, applied science and also electrochemical community. Graphene known as the thinnest materials and become the strongest ever measured for thermal conductivity and stiffness. Besides, grapheme has the right proportional between brittleness and ductility and also it's permeable to gases. [11].

With the fascinating strength and unique properties, such as electronic characteristic, exceptional thermal conductivity ~5 × $10^3 Wm^{-1} K^{-1}$, superior mechanical strength properties at (>1060 GPa), high surface area (theoretically 2630 m2/g for the single layer of graphene) and high electron transport capabilities of over 200,000 $cm^2 V^{-1}s^{-1}$ at electron densities of ~2 × $10^{11} cm^{-2}$ make graphene become wide potential application. [5, 7-8, 10]. Thus, graphene is excellently used in electronic, mechanical, optical and thermal properties. [3].

However, still has a lack of scalable synthetic routes to produce graphene in the quantities required for industrial applications. But, nowadays there are emerging number of methods for fabricating the graphene There are several methods that has been established to fabricate graphene such as chemical vapor deposition (CVD) , liquid exfoliation of graphite, micromechanical cleavage, graphitization of silicon carbide, reduction of graphene oxide, electrochemical exfoliation of graphite and ball milling processing of graphite.[8,11].

According to (He. P et. al) , graphene dispersions in various solvents are often required for the preparation of macroscopic graphene-based materials, such as coatings, films, tapes and composites.[1-3, 5] There are several criteria must be met for a graphene dispersion to be useful such as the graphene must disperse at the useful concentration and solvent for the appropriate application. Thus, the dispersion will remain stable and reasonable at period of time. [3, 5].

However, the dispersion of graphene become a challenging due to strong intersheet van der Waals attractions (π−π stacking), leading to aggregate or precipitate. [5]. Current strategies to solve these challenges are by separating the application of graphene based on it physical and chemical properties. The physical properties of graphene might be exploited in a more controlled manner or even modulated by engineering its structure at the atomic and molecular level. [10-11]. For the chemical properties, it is expected to stimulate the development of several new applications in many different fields such as composites, super capacitors, batteries, fuel cells, inks, flexible touch screen displays, intelligent coatings, sensors, photonics and optoelectronic devices. [4, 8, 11].

Also, the capability of graphene in aqueous solution and most organic solvent resulted a poor dispersion. [17]. Thus, it makes the process of using graphene in other potential application system is extremely hard. The recent progress in making stable dispersions allows the production of graphene on a more preparative scale, opening the way to solution/ dispersion chemistry through the ideal alternative which is exfoliated grapheme oxide (GO). Graphene oxides can be synthesize in large quantities from the inexpensive graphite powder. [10, 12]

Graphene oxide (GO) also known as graphitic consists of a single-layer of graphite oxide with a compound of carbon, oxygen, and hydrogen in variable ratios. [1-2]. It can be obtained by treating graphite oxidation with the present of strong acid and oxidant in the chemical treatment. [1-3] GO is prepared from natural graphite containing abundant surfaces of an oxygen-containing functional group such as epoxide, hydroxyl and carboxylic group. [15-17]. In addition, GO is more favourable as it has large surface area and a low-cost solid substrate. Another advantage of GO is the surface of functional groups provide the empty space of reaction site for linking the external species such as small molecules, polymers and bio macromolecules. [17].

GO more soluble in water compared to graphene and easily undergo chemical modification. Thus, it is can be disperse and stable in water and suitable organic solvent. GO is a good biocompatibility which has unique conjugated structure.The dispersion of graphene oxide in organic solvents has been accomplished via covalent functionalization of the graphene oxide sheets with different molecules and polymers but the presence of such stabilizers is not desirable for most applications. [8, 10]

According to (Chan. D et. al), the present of oxygenated group in GO can strongly affect its electronic, mechanical and electrochemical properties as the covalent oxygenated functional groups in GO limit the direct application of GO electrical material or devices. However, these functional groups also can provides the good advantages and applications as the first polar of GO render the strong "hydrophilic" which is water love. It is mean that GO good dispersibility in water and other solvent. [10-12].

The dispersion of GO in organic solvent have been investigated. By referring to He.P et.al, the Good solvents (e.g., benzyl benzoate, N-methyl-2-pyrrolidone (NMP) and Dimethyl sulfoxide (DMSO)) are basically organic agents with high boiling points (>150 °C) and are very hard to remove in subsequent applications. [5]. Besides that, N, N-dimithylformide (DMF) and Ethylene Glycol also contributed as a good solvent for GO dispersibility. [3].

The dispersion approaches of GO is the direct dispersion by continuous sonication. [10]. Long period of sonication time able to improve graphene concentration s, reduce the size of graphene layers, and increase the number of defects. This fact can be attributed to the formation of oxidizing radicals, such as peroxyl radicals, in air-sonicated solutions. [11].

In this work, the dispersion behavior of GO tested in water and two organic solvent (alcohol) Methanol and Ethanol. To investigate the stability dispersion of alcohol towards the GO and also the relationship of period of time sonication. 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

The graphene oxide prepared from the modified Hummer's Method containig Sodium Nitrate, $NaNO_3$ (84.99 g/mol, SYSTERM), Potassium permanganate (158.05 g/mol, R&M Chemicals), Sulphuric acid (95-98%, R&M Chemicals), Hydrogen Peroxide, Deionized water, Ice bath and Hydrochloric acid (37%,R&M Chemicals). For GO dispersion the organic solvent involved is water, methanol and ethanol.

B. Preparation of Graphene Oxide (GO)

GO preparation start the dilution of the hydrochloric acid at percentage of 37%. The dilution required 160ml HCl mixed with 1840ml distilled water. By Modified Hummer's Method, the synthesis of GO start with 5g of graphite powder and 2.5g of NaNO3 (84.99 g/mol) were added into 1000ml beaker in low temperature (ice bath). Later, 200ml of concentrated H2SO4 (98.08 g/mol) were added into the mixture and the mixture were stirred for 1 hour. Next, 30g $KMnO_4$ (158.04 g/mol) were slowly added into the mixture within 2 hours and the mixture was continued stirred for another 2 hours and the temperature was ensure to be below 15℃.

Synthesis of GO continued by ice bath removing and the mixture was kept stirred for another 20 hours at room temperature. Then the mixture was heated to 70℃ and stirred for 2 hours. After that, the water slowly added into the mixture about 100ml and again, the mixture was heated to 90℃ and kept stirred for another 1 hour.

To stop the reaction 30ml of H_2O_2 was added into the mixture. The resulting mixture was repeatedly washed by HCl and distilled water several time and the mixture was centrifuged at 25℃, 10000 rpm for 25 minutes. Lastly, the gel like solution was dried in the oven for 24 hours at 60-70℃ to formed GO sheet. The graphene oxide (GO) powder (1g) was prepared by modified Hummer's method from graphite powder (99% pure). A general characterization of the graphite oxide product was carried out by Scanning Electron Microscope (SEM).

C. Dispersion of Graphene Oxide

For the Go dispersion in different solvent, the dried GO (5mg) added into 10ml of water, methanol and ethanol to allow direct comparison of different solvent been used. The mixture stirred about 15 minutes each and sonicated in an ultrasonic bath cleaner for 1 hour. The steps repeat for sample sonicated at 2 hours to determine the dispersion behavior and stability. In all of the solvents, the water content was below 0.1%. Because the common solvent for the preparation of graphite oxide dispersions is water, aqueous dispersions of our as-prepared graphite oxide material were also made under exactly the same conditions. [10].

D. Characterization

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

III. RESULTS AND DISCUSSION

A. Characterization of Graphene Oxide

The morphology of both samples were determined by SEM. Fig. 2 shows the structure of GO on the device at 500 X magnification. The working distance is range from 10 to 1 µm at high vacuum mode with 5.00 kV.

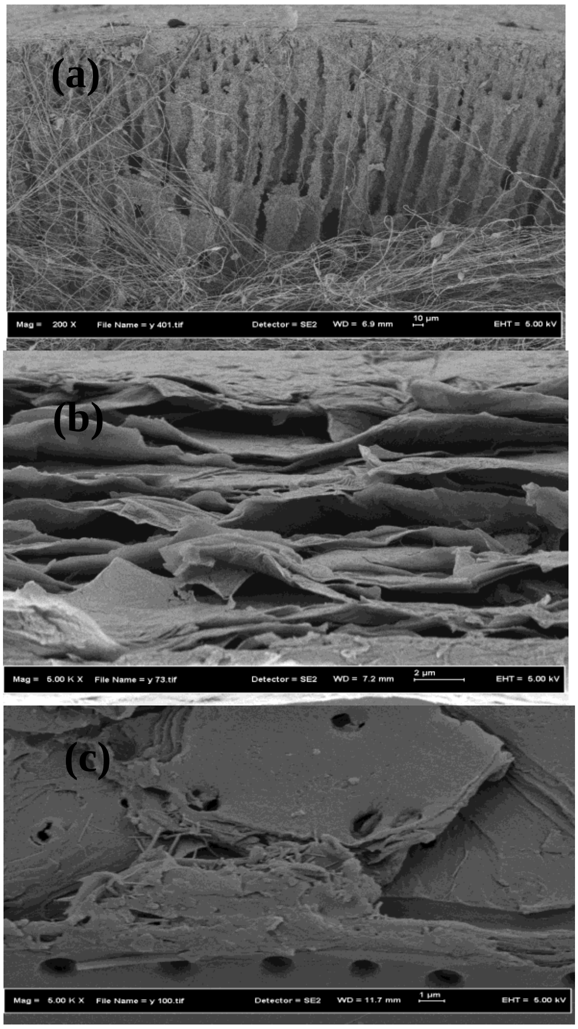

Fig 1: SEM image of graphene oxide (GO) at different size of microsphere range; (a) 10 µm (b) 2 µm and (c) 1 µm

In the presence of an oxidizing agent, synthesis of graphene oxide was achieved by placing graphite in concentrated acid. Hummer's method demonstrated a less hazardous and more efficient method for graphite oxidation [20]. Individual sheets of GO can be viewed as graphene decorated with oxygen functional groups on both sides of the plane and around the edges as described by Lerf et al [19].

Figure 1, indicate that the graphene oxide consist of randomly aggregated, thin, crumpled sheets closely associated with each other and forming a wrinkled nanosheets with an irregular shape. This confirms that the GO sheet had been successfully exfoliated from graphite containing ordered stacking graphene layers. Figure 1 (b) shows that, the thin and an onion layer [20] of GO with large surface area indicate the tremendous potential applications of graphene for improving mechanical, electrical, thermal, and gas barrier properties of polymers. In figure 1 (c) there are pores on the surface are helps in providing are good adsorption. GO is the surface of functional groups provide the empty space of reaction site for linking the external species such as small molecules, polymers and bio macromolecules [17]. It is increase the possibility to immobilize enzyme on the surface of GO as GO is a good biocompatibility which has unique conjugated structure.

B. Graphene Oxide Dispersion

From the experimental section explained that, the as-prepared grahene oxide material was dispersed in water and another two alcohol solvent, methanol and ethanol. Alcohol is a homologous series in which the compounds contain a functional group called the hydroxyl group (-OH). The hydroxyl group is also responsible for imparting certain chemical properties to the compound.

The dispersion were then allowed to be settle for one week. This experiment conducted via the aid of bath ultrasonication at different period of time (1hr and 2 hr). The result and observation taken at the right after the sonication and after one week.

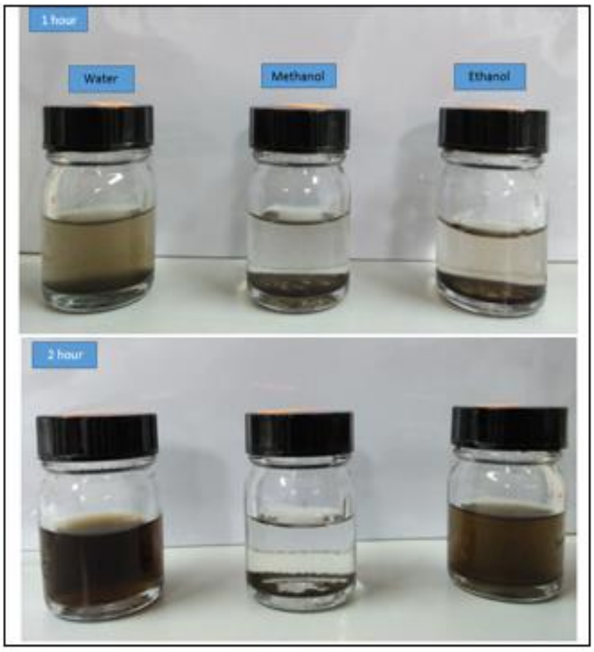

Fig 2: Graphene oxide dispersions in water, DMF, and DMSO immediately after sonication for 1 hour and 2 hour

Figure 2 and 3 show the behavior of GO dispersion in water, methanol and water. Based on the figure, the observation can be made by comparing the color of each samples. The longer the samples undergo the sonication phase the more GO will be dispersed in the solvent which make it more stable. As we can see from figure 2, after 1hr sonication the dispersion of GO in water were incomplete as there were still GO precipitate at the bottom of the dispersion. But, after we extended the time of sonication to 2hr the dispersion of GO in water were complete as all GO dispersed in the water.

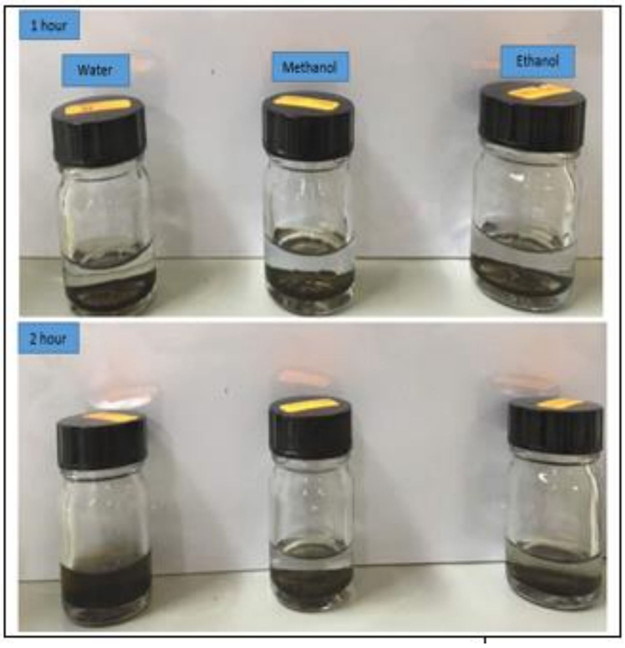

Fig 3: Graphene oxide dispersions in water, DMF, and DMSO 1 week after sonication for 1 hour and 2 hour.

However, in methanol almost no GO being dispersed. As the sonication time increased, all of GO precipitate remain at the bottom of the bottles. In Ethanol, at 1hr a little of GO dispersed in the solvent and as the sonication time increased to 2hr the solution become more darker. But, GO still not completely dispersed in Ethanol as there were GO precipitate at the bottom of the bottle. Maybe, if we increase the sonication time of GO in ethanol, the dispersion will be complete.

In order to determine the long-term stability of the GO dispersion in these three different solvents, the sample left for one week. Figure 3 shows the dispersion of GO after one week. At 1h sonication, there large amount of precipitate was seen develop after one week, thus we conclude that the GO material could not be sufficiently exfoliated at 1hr sonication period. GO dispersion in water at 2hr sonication had formed homogeneous and sustainable dispersions compare to the other two solvent, methanol and ethanol.

Thus, based on the observation shows that GO dispersion in methanol and ethanol is not stable as clearly seen the clear supernatant and the GO precipitate at the bottom of the bottles. By referring to the introduction, stated that the good solvent for GO dispersion basically organic agents with high boiling points (>150 °C). Thus, the statement is accepted as the methanol and ethanol is not stable and not able to performed good dispersion as it has low boiling point than 150°C (methanol, 64.7°C and ethanol, 78.4°C).

Due to ionization of carboxyl groups, which are primarily present at the edges of sheet, GO can be electrostatically stabilized to form a colloidal suspension in water and alcohols. However, the stability of these three solvent ranked as shown below due to its solubility as dispersibility in GO:

Methanol < Ethanol < Water

For further estimation of the capability of the solvent to disperse the GO, UV-vis adsorption spectroscopy was employed to gain the further insight into capability of the solvent to disperse GO. 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. The spectra are plotted in the wavelength range from 200 to 1000 nm.

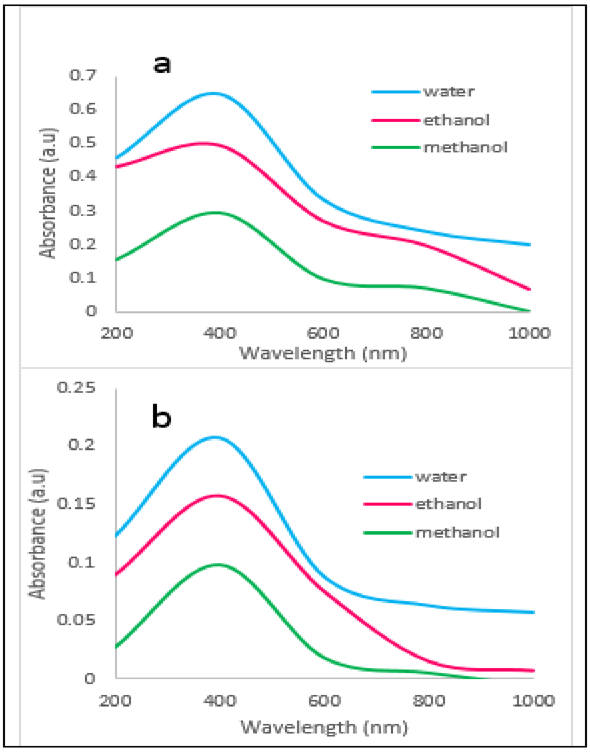

Fig 4: UV-vis absorption spectra of graphene oxide dispersed in different solvent (a) immediately after sonication and (b) left for one week (1 hour sonication time).

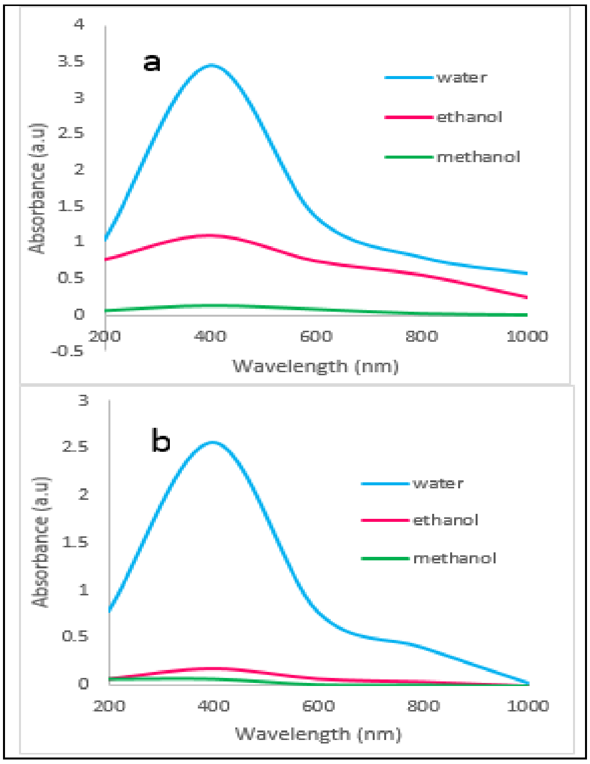

Fig 5: UV-vis absorption spectra of graphene oxide dispersed in different solvent (a) immediately after sonication and (b) left for one week (2 hour sonication time).

Figure 4 and 5 shows UV-vis absorption spectra for the dispersion of GO in water, methanol, and ethanol by bath ultrasonication for 1 hr and 2 hr respectively. Clearly shows that water is the good solvent for GO dispersion as it obtained the highest absorption intensity and we can say that water has the best dispersing ability. Meanwhile, the methanol and ethanol show the least absorbance.

From both graph shows in Figure 4 and 5 there is the decrement of absorbance for all solvent used for dispersion. Figure 4 (a) the highest reading is water at 0.647 a.u but after one week figure 4 (a) the result decreased to 0.208 a.u which mean that the GO has settle down. Same goes to Figure 5, the GO has settle down and the absorbance read by UV-vis reduced. Based on the graph, it is show that the best wavelength to test GO dispersion is at 400nm as the reading is higher at that wavelength. Thus, it can be conclude that, ethanol and methanol (alcohol) is not a good choice for GO dispersion as both of these alcohols do not stable for long –term period.

IV. CONCLUSION

The dispersion behavior of GO in water, methanol and ethanol was compared. We have identified that alcohol is not the organic solvent that can perform GO dispersion with long-term stability. Only water had formed homogeneous and sustainable dispersions compare to the other two solvents. The result of GO dispersion obtained at 2h sonication data and observation is the best compared to 1hr sonication. This because, as the sonication time increased, GO in water is completely dispersed. The longer the time of sonication, the least the amount of GO precipitate remain at the bottom of the bottle.

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