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INFLUENCES OF SOLVENT TYPES ON THE FORMATION OF GRAPHENE IN THE ELECTROCHEMICAL EXFOLIATION METHOD

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Abstract. The aim of this study was to evaluate the effect of different solvents in sonication process on the formation of graphene from the electrochemical exfoliation of graphite. In short, graphite rod was exfoliated by electrochemical process with ammonium sulfate as salt-electrolyte. The exfoliated powder then sonicated under two different solvents, which are Dimethylformamide (DMF) and aqueous solution to form graphene. It was found that similar structure of graphene was obtained from both types of solvent. However, the amount of graphene produced was different due to the differences in graphene stability. Graphene is more stable in DMF solvents compared to the aqueous solution. The aqueous solution can allow the reversible reaction that can reform graphite oxide from graphene due to the existence of hydroxyl component in the aqueous solution.

Keywords: graphene, graphite, electrochemical exfoliation, solvent, sonication

1. Introduction

Graphene is a two-dimensional block of carbon allotropes originating from every other dimension [1]. Further, this material has several distinctive properties, including extremely strength, high thermal, electrical conductivity, transparency, and flexibility [2]. Based on those excellence properties, this material has a high potential be applied in various applications, such as electronic devices, supercapacitors, batteries, composites, flexible transparent displays, sensors [2] and corrosion inhibitor [3].

There are two methods for synthesizing graphene, namely top-down and bottom-up methods [2]. Several methods in the top-down method are micromechanical cleavage, exfoliation of graphite oxide, electrochemical exfoliation, exfoliation of graphite intercalation compounds (GICs), solvent-based exfoliation, arc discharge, and unzipping carbon nanotubes. Bottom-up methods include epitaxial growth on silicon carbide, chemical vapor deposition, and miscellaneous methods. The processes using the top down method have more advantages compared with that using bottom up method. Specifically, the processes using the top down process allow for the obtainment of large size and unmodified graphene, inexpensive and scalable synthesis procedure, a single step functionalization and exfoliation, and the production of graphene with high electrical conductivity [4]. Among the top down process, the electrochemical exfoliation method is one of the most popular methods for the production of graphene because of its simplicity, short-time process, and potentiality in producing high

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quality of grapheme [5]. An example of this technique was reported by Liu et al. [6] which produced graphene flakes using this method added with an ultrasound sonication process. The results showed that the final product synthesized by the sonication had largely bi-layer graphene flakes, in which the result is thinner in layers compared with the process without sonication. Although the reports in the synthesis of graphene using the electrochemical exfoliation are well-documented, there is no report on the investigation of solvent types on the successful formation of graphene.

Here, this study evaluated the synthesis of graphene using an electrochemical exfoliation process under various types of solvents during sonication process. The selection of solvents during this sonication process is important in the graphene synthesis because it will affect the product of graphene, including the long-term dispersing stability of graphene. Two different solvents were used, namely Dimethylformamide (DMF) and aqueous solution. These solvents were selected based on Paredes et al. [7], stating that these are the best solvent for providing and diluting graphene oxide (GO). However, their study concerned only on GO (not in graphene).

The finding of DMF and aqueous solution effects on the graphene synthesis would be good for providing information that can contribute in the industrial world or engineering application. Specifically, DMF and aqueous solution are able to disperse graphene without additional surfactant. Thus, when we understand this solvent parameter, we can estimate and predict the way for minimizing the amount of surfactant and stabilizing agent. The surfactant and stabilizing agent are sometimes undesirable for most applications.

In short of the experimental procedure, graphene was synthesized from graphite rods using the electrochemical exfoliation method. To support the synthesis process, a sonication process was added to decipher the graphene layer, whereas the centrifugation process was to remove large agglomerates.

In addition, this study focused on understanding the effect of solvent types on the formation of graphene. Thus, this study did not concern on the number of layers in the graphene. Indeed, the present method allowed the formation of multilayer of graphene (MG) and graphene oxide (MGO) from both solvents. This is probably because of the limitation in the processing time used in the electrochemical exfoliation as well as sonication process.

2. Experimental method

Synthesis of graphene via electrochemical exfoliation. Graphite rods with a purity of 95% and a dimension of diameter and length of 0.40 and 10 cm were used as an anode and a cathode electrode. Prior to being used, both graphite materials were immersed into 300 mL ammonium sulfate solution (0.1 M; R&M chemicals, UK). The electrochemical exfoliation process was carried out for 5 hours with a 10 V. This process consumed three graphite rods in the anode site. During the process, a black product is gradually formed, which indicated that exfoliation of graphite is in progress. Then, electrolyte was filtrated using a vacuum filtration. The residue was dried, and the dried residue was a black powder. The dried black powder was dissolved in a 300 mL of specific solvent (i.e., N,N-Dymethylformamide (DMF; R&M Chemicals, UK) or aqueous solution). The amount of dried black powder was fixed at 2 wt%, in which this is due to the fact that graphite fine powder is well-suspended in the concentration range of 1-2% during the sonication process [8]. Indeed, concentration of 2% was selected to get maximum yield of graphene. The dissolved black powder was sonicated for 3 hours, and the result was filtered using a vacuum filtration. The final product was a black filtrate. Detailed information for the synthesis process was shown in Fig. 1.

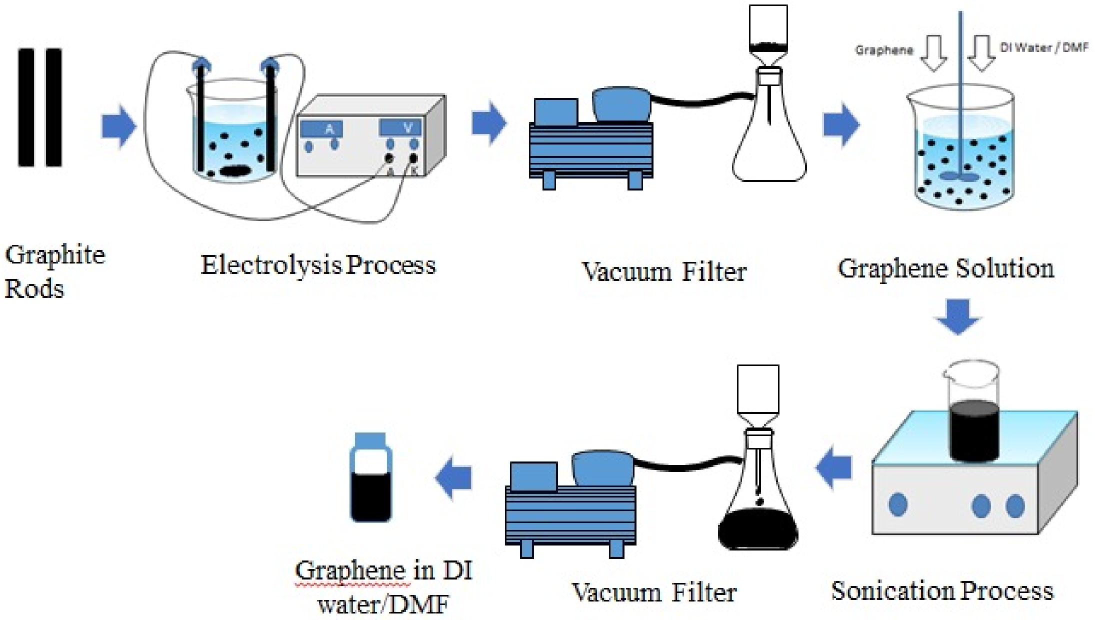


Fig. 1. Steps of graphene synthesis by electrochemical exfoliation method followed by sonication process

Characterizations. Chemical properties of the product were investigated using a Fourier Transform Infrared (FTIR, Nicolet iS50 FT-IR) in the range of 400-4000 cm^{-1}. A Raman Spectroscope (Raman, Horiba LabRam HR Evolution) was used to analyze the chemical composition and characteristics of the products at 514 nm. A Transmission Electron Microscope (TEM, FP 5022/12 Tecnai G2 20 Twin) was used for the analysis of the morphology of graphene. Analysis of the effect of solvents on the products produced was also done by a UV-Vis spectroscope (UV/VIS Spectrometer, Lambda 1050 PerkinElmer), where the solution before and after centrifugation were investigated.

3. Results and discussion

The FTIR analysis (presented in Fig. 2) shows that the process using various solvents can allow the formation of graphene from graphite. Detailed analyses are in the following.

In the case of process with aqueous solution, there are two peaks at the wavelengths of 3331 and 1636 cm^{-1}, which indicated the vibration of the -OH group and the aromatic C = C group. The -OH group is from the water molecule.

In the sonication process with DMF, there are peaks at wavelengths of 1254, 1096, 1062, and 660 cm^{-1}, which were due to the vibrations of C-N groups. The peak at wavelength of 1651 cm^{-1} was also found, corresponding to the vibration of C = O group. This result was in a good agreement with the results reported by Tatariants et al. [9]; this is due to the existence of DMF. In addition, peaks at wavelengths of 1496, 1438, and 1411 cm^{-1} were due to a vibration of the C = C aromatic group [10]. The C = C aromatic group was also found in sample produced using the aqueous solution, in which this is due to the possible formation of graphene or graphene oxide.

The results of the Raman Spectroscopy analysis (see Fig. 3) showed that the use of different solvents did not have impacts on the chemical components of the product. Three types of chemical compositions were obtained, namely multilayer graphene (MLG 1 and 2) and graphene oxide (GO). In the three Raman spectras, there are two main peaks, namely G and 2D peaks. The G peak is located at 1580 cm^{-1} and peak 2D at 2700 cm^{-1}, which arises due to the optical vibrations in the center of the E_{2g} degeneration zone and second-order zone on the phonon boundary. In addition, there is a secondary peak, namely the D peak located at

1350 cm^{-1}. This peak arises in defected graphene, indicating the existence of carbon impurities (as the main impurities component) that are released from imperfect exfoliation process [11].

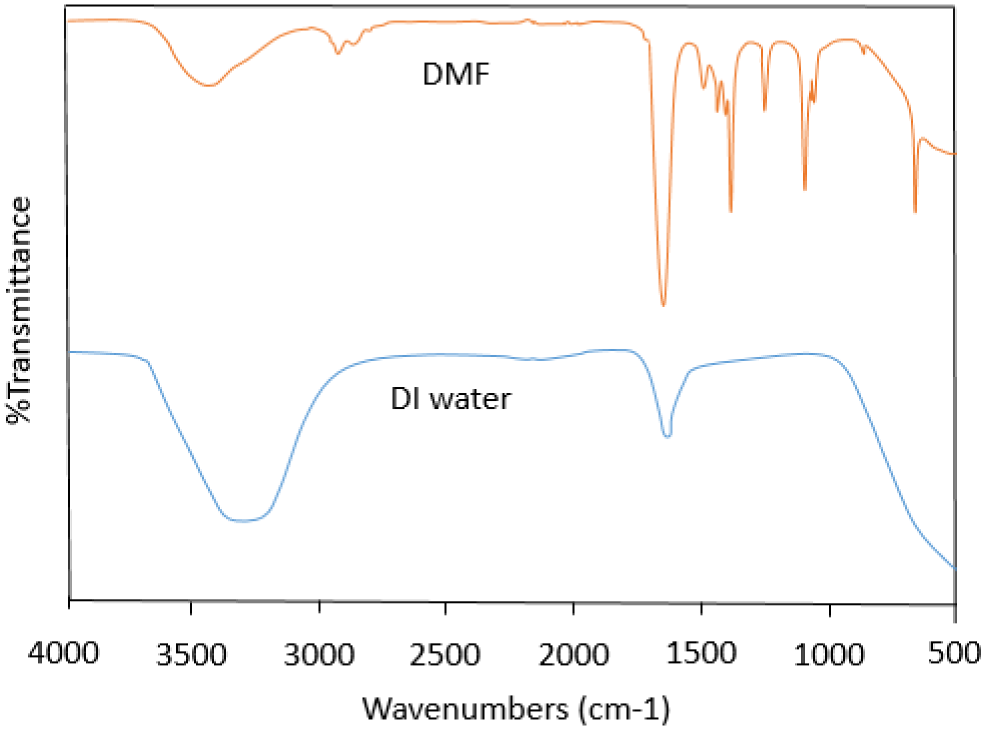


Fig. 2. The FTIR analysis results of graphene after the sonication process using DMF and aqueous solution

The Raman Spectra can be used as a reference in determining the quality and number of graphene layers based on 2D shape, width, and peak position [1]. MLG 1 and 2 indicated from G peak is higher than 2D peak. The both spectras from MLG 1 and MLG 2 are in accordance with the results of the study by Niilisk et al. [12] that the higher the 2D peak intensity, the more the number of layers in MLG. Therefore, MLG 2 has more layers than MLG 1. Actually, the specific analysis of single layer graphene can be done, by justification through Raman Spectroscopy analysis to show sharp single 2D peaks with higher intensity than G [1]. However, this study is for comparing the aqueous solution and DMF only; thus, we did not concern this specific peaks in our results.

The results of TEM analysis of the both sample produced with different solvents are shown in Fig. 4. Different morphologies were obtained, but they are almost the same. Their morphologies are rolls and wavy sheets forms. The rolls and wavy sheets are an intrinsic characteristics of grapheme [13-15]. The analysis showed dark and transparent areas. The dark areas can occur due to the existence of a number of graphene sheets, oxygen groups from graphene oxide, graphite, and impurities attached to the surface of the products. The transparent areas are the parts of thin layers from graphene. The more transparent has correlations to the thinner sheets or fewer groups of oxygen [16].

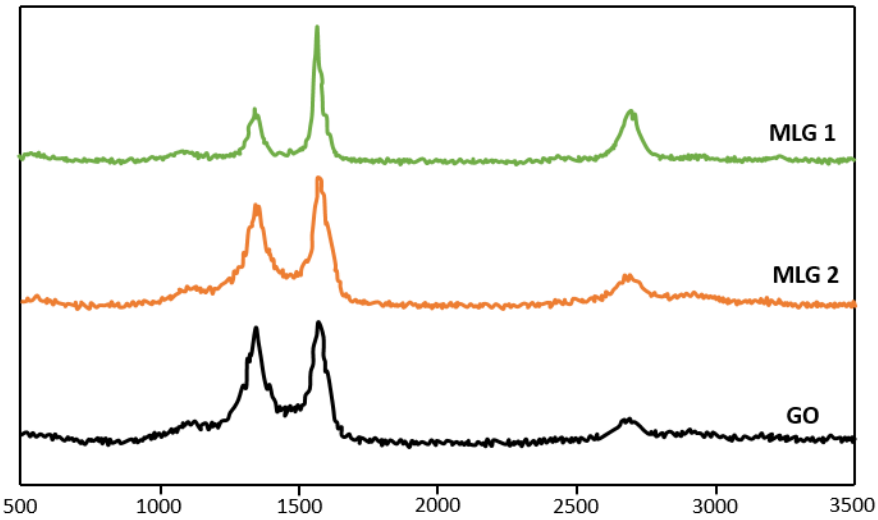


Fig. 3. The results of the Raman Spectroscopy analysis of compounds contained in the product

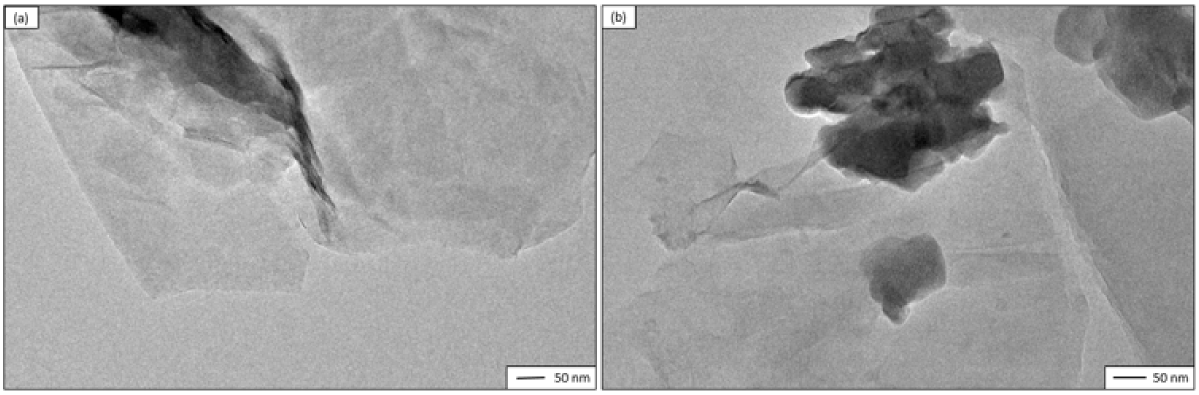
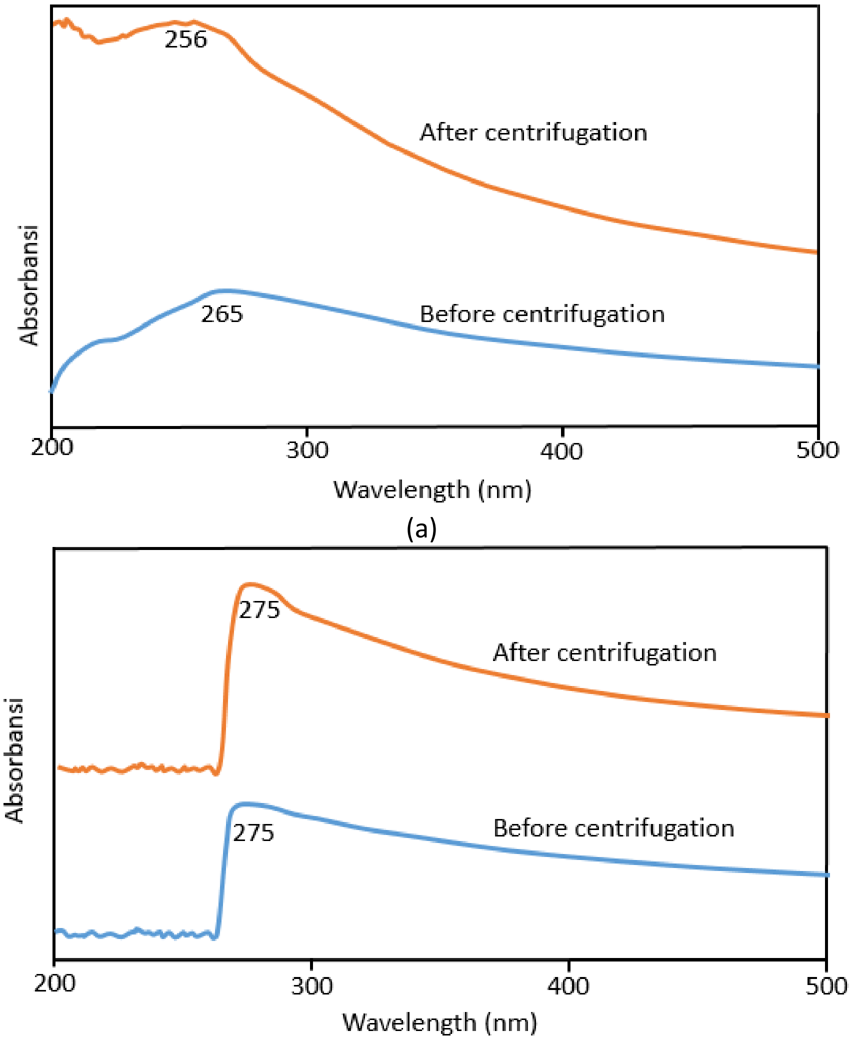


Fig. 4. The results of TEM analysis of graphene with sonication process using DMF (a) and aqueous solution (b)

Figure 5 shows the results of UV-Vis spectrophotometry before and after the centrifugation process. In the use of DMF, a peak did not change at 275 nm, which is an absorption area of graphene [17]. In the use of aqueous solution, the absorption changed from 265 to 256 nm, in which these represented the graphene absorption area [18-19]. There is no peak change in DMF solvents, confirming that graphene in DMF is more stable than that in aqueous solution.

Aqueous solution can allow the reversible reaction that can reform graphite oxide from graphene. This is due to the existence of hydroxyl components in the aqueous Solutions. In the case of DMF, this type of solvent has better effects on producing more graphene in the final product. No reversible reaction is formed in DMF process. As a consequence, this solvent is also able to produce high quality single layer graphenes compared to aqueous solution. However, since this study focused on understanding the effect of solvent types on the formation of graphene, we did not concern on the number of layers in the graphene. Indeed, the present method allowed the formation of multilayer of graphene and graphene oxide from both solvents. We believe that the main reason is due to the limitation in the processing time used in the electrochemical exfoliation as well as sonication process.



(a)

(b)

Fig. 5. The results of UV-Visible spectrophotometry analysis of graphene with sonication process using aqueous solution (a) and DMF (b) solvents before and after centrifugation

4. Conclusion

The electrochemical exfoliation process of graphite has successfully led the production of multilayer graphene (MLG) product with layers of 1-6 and graphene oxide (GO). The results indicated that both types of solvents can promote the formation of graphene from graphite. Similar structure of graphene was obtained. However, the amount of graphene produced was different, in which this is due to the differences in graphene stability.

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