Effect of Graphene Oxide with Controlled Stirring Time

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In this study, the effect of graphene oxide (GO) with controlled stirring time was investigated. Five different samples with different stirring time of GO were used at 2 h, 4 h, 6 h, 8 h, and 10 h. The synthesization of GO was conducted using hummers' method by adding graphite, hydroxide sulphuric, permanganate potassium, sodium nitrate, and hydroxide phosphorus. Hydroxide phosphorus was used as main peripheral material to increase the hydrophilic properties in GO performance. Characterization was carried out via XRD, FTIR and contact angle measurement. Results show that the appearance XRD peaks at range between 1,590 cm^{-1} until 1,750 cm^{-1} with increase stirring time. However, the lowest contact angle measurement of graphene oxide with high hydrophilicity effect was obviously shown by sample 3.

1. Introduction

Graphene oxide (GO) is one of the most recent remarkable materials that actively used in most crucial applications owing to the expanded structural diversity that able to improved overall material properties. Generally, GO has a similar structure layered to graphite, only the different is the plane of carbon atoms in GO has bonding with oxygen. GO is heavily ornamented by oxygen-containing groups, which this carbon not only expand the interlayer distance but also make the hydrophilicity of atomic-thick layers (Bykkam et al., 2013). GO has been known to disperse very well in water subsequently its first discovery over a century ago. Hence, GO has been routinely defined as hydrophilic in the literature (Kim et al., 2010). This has made this GO property to be easily dispersed in water or in other organic solvents. In fact , this strong hydrophilicity property also suitable for various applications ranging from energy storage or conversion and environment protection, including hydrogen storage materials, photo-catalyst for water splitting, removal of air pollutants as well as water purification and water separation process (Bykkam et al., 2013). In particular, its derivative GO have brought new opportunities for membrane based water treatment (An et al., 2016).

Especially, effect of GO shows the great characterisation toward membrane technology nowadays. The properties of hydrophilicity in GO create the big impact in membrane activities to solve the wastewater problem. The previous study by Harun et al. (2013) revealed that, the increasing hydrophilic property can minimize the fouling problem is often used in polymer membrane fabrication. Therefore, the addition of small amount of additive (graphene oxide) into some techniques can lead to excellent significant changes of membranes performance and characteristics (Harun et al., 2013). Other previous study that used graphite as inorganic additive, polymer additive, carbon nanotube or nano-particles also prove that the properties of membrane such as permeability and resistance of fouling increased by adding these additive (Harun et al., 2013). Recent reviews by Jambunathan (2004) reported that, characteristics of GO are hydrophilic, cheap to

produce in bulk quantities, easy to process and dispersible in a variety of solvents which as in water, NMP, DMSO, acetone, methanol and many more (Jambunathan, 2004).

Basically, the application of GO is for monolayer, bilayer and few layers from 3 to 10 layers, GO-derived graphene based on the materials (Zhu et al., 2010). GO can be synthesized or oxidized from the graphene structure. However, graphene itself possessed a remarkable properties and structure which has made this material is very expensive. The other reason is, graphene are hard to be incorporated and distributed homogeneously into various matrices for applications (Li et al., 2014). An extensive works and studies have been conducted previously showed that graphene can be originated and synthesized from low cost materials i.e. graphite using exfoliation and milling technique to get one layer of graphene by using a simple hummers' method. Marcano et al. 2010 mentioned that the greatest common approach to graphite exfoliation is the use of strong oxidizing agents to yield GO, a non-conductive hydrophilic carbon material (Marcano et al., 2010). Improvement of hummers' method in synthesizing GO have been conducted by several researcher such as Brodie by adding the portion of potassium chlorate to a slurry of graphite in fuming nitric acid (Shahriary and Athawale, 2014). Other researcher by Hummers reported that the method most commonly used to achieve the GO easily, the graphite is oxidized by treatment with $KMnO_4$ and $NaNO_3$ in concentrated H_2SO_4 (Marcano et al., 2010).

Although, preparation of GO can be easily by chemical synthetic procedures. Recent studies by Hu et al. (2013) mention that the preparation of GO is always tremendously poly-disperse and its transverse size is typically microns or larger, and tend to persuade aggregation, which limits its direct use in associated application (Hu et al., 2013). Further, improvement of hummers' method involves the used stirring time which is more eco-friendly technique and easy to produce within a short duration of times. By controlling stirring times particles size and homogeneity of GO will be improved (Hu et al., 2013). Further work by Hu et al. (2013) also revealed that particle size and geometry of GO obviously effected by the duration and velocity of stirring times Intense study by Tian et al. (2010), also has proven that homogeneity of GO in term of its particles size and its distribution also strongly influenced by the stirring times (Hu et al., 2013). In fact, detail investigation of GO characteristic after synthesizing at different stirring times also show that hydrophilicity property is increased with increasing stirring times. This strong effect of Hydrophilicity property definitely can create more advantages of GO application to build new materials for future challenge applications and globalization.

2. Experimental

2.1 Materials

Synthesisation of graphene oxide (GO) via hummers' method was prepared. Graphite is main resource to synthesize the GO. The chemical materials will be used in this method are sulphuric acid (H_2SO_4) and phosphorus acid (H_3PO_4) were used as solution to mixed graphite and sodium nitrate ($NaNO_3$), potassium permanganate $KMnO_4$ was reacted as oxidizing agent, hydrogen peroxide H_2O_2 and deionized water (Meng and Park, 2012).

2.2 Experimental Procedure

Synthesisation of graphene oxide (GO) was conducted using by hummers' method. The preparation of GO powder was synthesized at different stirring time (2 h, 4 h, 6 h, 8 h and 10 h). The main material was graphite and other materials which are sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), sulphuric acid (H_2SO_4), and phosphorus acid (H_3PO_4). The initial steps of this technique was mixing process of 5 g graphite and 2.5 g of $NaNO_3$ into the 108 mL of H_2SO_4 and 12 mL of H_3PO_4 that immersed into the ice bath. Next, the suspension was stirred at 500 rpm for 10 min. Then, followed by addition of 15 g of $KMnO_4$ in a mixture with slowly condition. During the stirring process, the temperature must below 5 °C. The suspension was continued stirred until the temperature reached to 40 °C. At 98 °C, the temperature of the mixture was adjusted so that it became constant for 60 min. After that, 140 mL of deionized water was continuously added in the suspension. After that, the colour of the suspension will be changed from purple to brown. 5 min before stir completed, added 15 g of H_2O_2 in the suspension. The mixtures were transferred into 2,000 mL flask of distilled water and mixed together. Finally, the suspension was dried in the furnace for one day (Shahriary and Athawale, 2014).

3. Results and Discussion

3.1 X-Ray Diffraction (XRD)

Graphene oxide (GO) was synthesized from the natural graphite powder using hummers' method. GO powder was prepared and then was characterized using XRD machine. Synthesization of GO was carried out at different stirring time (2 h, 4 h, 6 h, 8 h, and 10 h) and follow up by the characterization step using XRD Bruker

D8 Advance. The natural graphite powder and synthesized GO were presented by XRD pattern respectively. Based on the Figure 1 the sharp peak of natural graphite was produced at 26.6 °, this is in agreement with the work conducted by Meng et al. (2012).
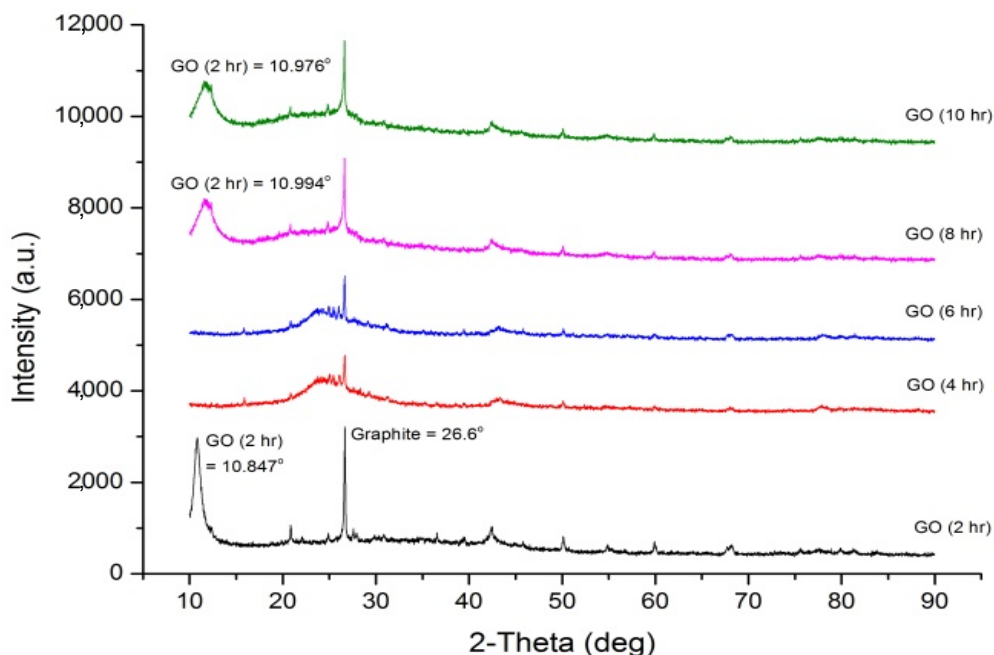

Figure 1: XRD pattern of the synthesization of graphite and GO (2 h, 4 h, 6 h, 8 h, and 10 h)

Figure 1 was shown the sharply peak for GO for 2 h was recorded at 10.847 °. The development of GO had been seen the peaks slowly appeared at GO (8 h) and GO (6 h) as increasing the stirring duration. A strong effect of stirring time towards the formation of GO powder was proved. Figure 1 also shows the graph peak for GO (4 h) and GO (6 h) powder. The peak of GO was not appeared on the graph because of some defects was detected during the preparation of GO (4 h and 6 h) powder.

3.2 Contact angle measurement test

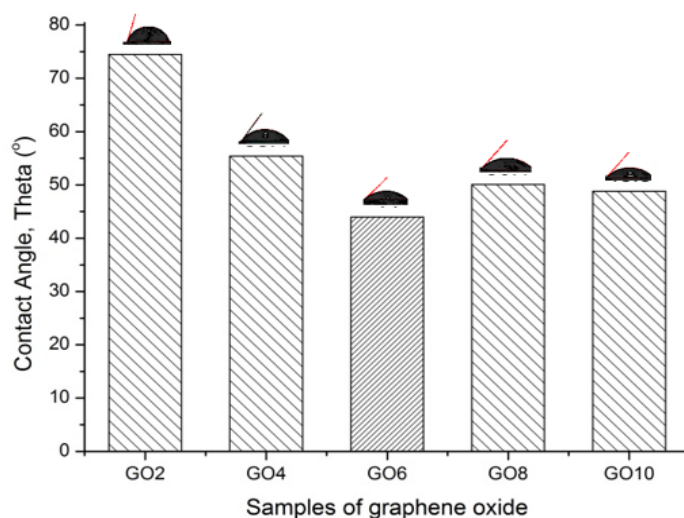Figure 2 shows the contact angle value at different synthesisation time of graphene oxide (GO).

Figure 2: Contact angle analysis of different time synthesis of GO flat sheets

Contact angle measurement is ability to identify the hydrophilic properties in membrane performances. Basically, the sample performances have two categories which it called as hydrophilic and hydrophobic properties. The samples surface is considered as a hydrophobic property if the degree of wetting is more than 90 ^{o} and smaller than 90 ^{o} is considered as hydrophilic properties. In this study, water contact angle was measured through the sessile drops method using goniometric technique (Rosa and Pinho, 1997). Water was injected on the membrane surface and the tangent of water drop was measured automatically.

The contact angle of sample 1 GO (2 h synthesized) flat sheet show the highest value indicating the weakest the hydrophilic sample. However, the value of water contact angle decreased with the time synthesized of GO was increased. The lowest of water contact angle value with 44.0 ^{o} is given by sample 3 of GO (6 h synthesized) flat sheet indicating the strongest hydrophilic sample. In fact, the value of contact angle slightly increased at sample 4 could be due to agglomeration effect as particle becoming smaller (Li et al., 2014).

3.3 Fourier transform infrared spectroscopy (FTIR)

Based on the FTIR spectrum of GO at Figure 3, Figure 4 and Figure 5, a sharp peak was obviously seen. This strong sharp peak at range between 2,500 cm^{-1} until 3,645 cm^{-1} indicates the existence of O-H stretching bonding was developed in GO powder as similar peak was reported by Rezaee et al. (2015). Meanwhile the of graphene oxide peak was determined at range between 1,590 cm^{-1} until 1,750 cm^{-1} as shown in all figures. The slow growth existence of GO spectrum is absolutely showed the transition of graphite to oxidized form of GO as similar reported by Ganesh et al. (2013).
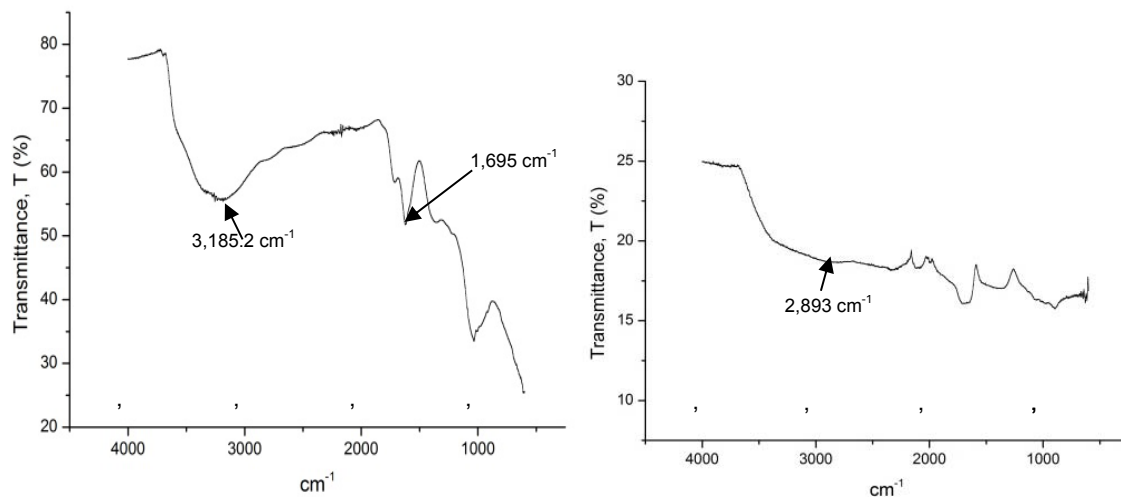

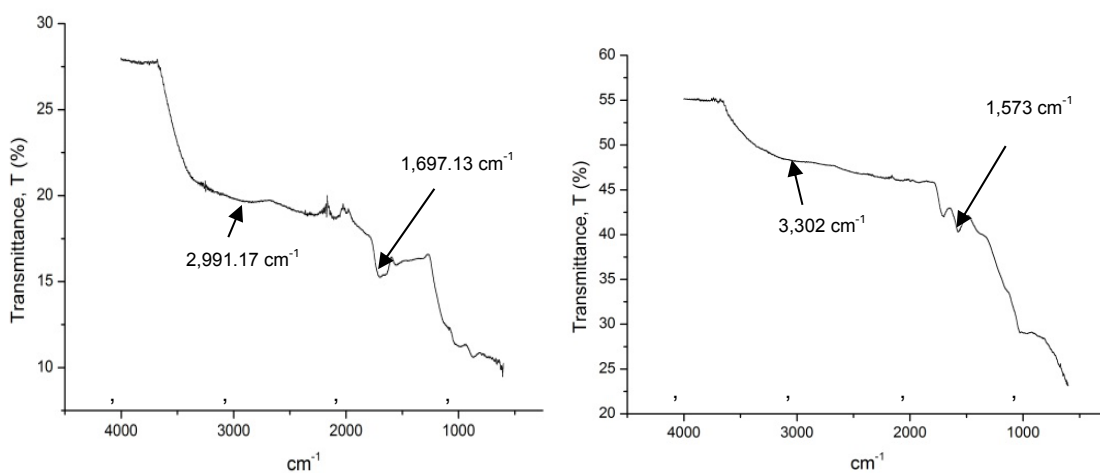
Figure 3: FTIR peak value of GO (2 h) and GO (4 h) powder

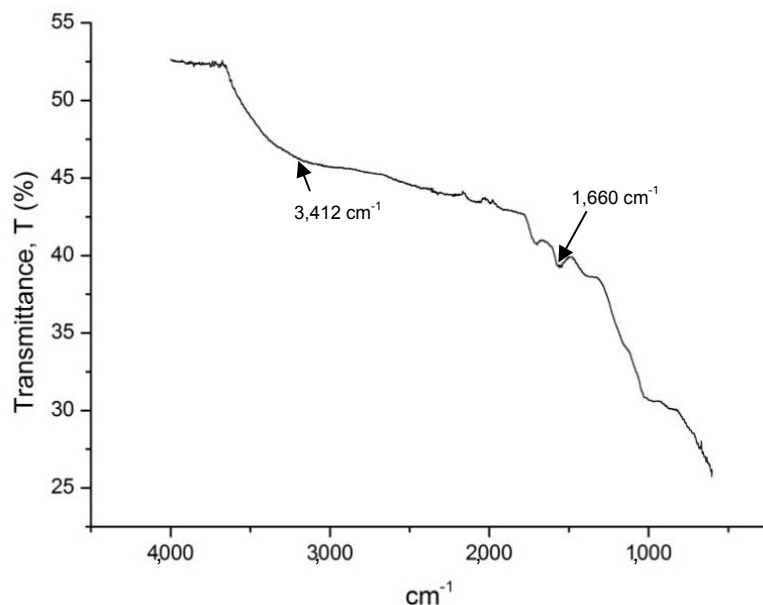

Figure 4: FTIR peak value of GO (6 h) and GO (8 h) powder

Figure 5: FTIR peak value of GO (10 h) powder

These figures demonstrated the effectiveness of synthesising the GO through the hummers' method. The effect of stirring time was investigated by varying the stirring time from 2 h, 4 h, 6 h, 8 h and 10 h.

4. Conclusion

As a conclusion, the synthetisation of graphene oxide can be carried out by adding graphite, hydroxide sulphuric, permanganate potassium, sodium nitrate, and hydroxide phosphorus. The synthetisation of graphene oxide (GO) via hummers' method using different stirring time from 2 h, 4 h, 6 h, 8 h and 10 h was completed in order to investigate the effect of different stirring time. Whereas, the effect of GO with stirring time was accomplished which the result was shown at XRD test, contact angle measurement test and FTIR spectrum test. From the XRD test, the sharp peak values were shown at sample GO for 2 h (10.847 $^{\circ}$). Refer to contact angle graph of GO flat sheet, the strong hydrophilic effect toward GO for 6 h. However, the chemical bonding of O-H was showed at sharp peak between 2,500 cm^{-1} until 3,645 cm^{-1} indicate existence of O-H stretching bonding in GO powder as similar peak reported by Rezaee et al. (2015). A conjugated peak of GO was determined between 1,590 cm^{-1} until 1,750 cm^{-1} in Figure 3 until Figure 5 was corresponding to the GO bonding.

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