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Exfoliation of Graphite into Graphene Oxide and Reduction by Plant Extract to Synthesize Graphene

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ABSTRACT

Graphene oxide (GO) is a demand material in industrial field for many applications such as electronic devices, capacitor and sensor. This is due to its unique structures and excellent properties. The GO sheets were exfoliated from graphite rod in electrochemical exfoliation. To reduce GO, an electrochemical reduction of GO using green tea was carried out in this research. The conventional chemical reduction method consumed highly toxic and strongly hazardous chemicals such as hydrazine to reduce GO to reduced GO (RGO). Therefore, a green synthesis method was proposed by using green tea leaves extract as the reducing agent to synthesize RGO. Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) results show that low amount of oxygen-containing functional groups was remained after green tea reduction due to weak reduction capability by green tea. In addition, EDX indicates that oxygen content of GO was decreased from 23.23 to 16.89 Mass% after green tea reduction.

Keywords: *Graphene oxide, reduced graphene oxide, electrochemical exfoliation, green tea*

1. INTRODUCTION

Carbon is one of the important elements to support life of living objects and other non-living materials. All carbon-based materials have large different structures and properties because of the carbon bond adaptability. As a result, the research of graphene has attracted many scientists to investigate the excellent properties [1]. Lavoisier had found the uniqueness of carbon since he had shown that it was the basic for diamond and graphite [2]. Since then, more scientists had interest about explaining the properties of more allotropes of carbon that able to adopt in many structures ranging from diamond and graphite (3D) to graphene (2D), nanotubes (1D) or fullerenes (0D) [3-5].

As a result, graphene has been explored for application in the devices and materials by the technologists and materials scientists. Graphene is an individual layer or the basic structural element of graphite. Graphene is known as "the mother of all graphitic forms of carbon" [6]. It is a flat monolayer of carbon atom arranged in two-dimensional honeycomb lattice. The thickness of graphene is only one atomic thick sheet of sp^2-bonded carbon atom that contains hexagonal carbon aromatic structure [7]. The thickness is about 0.334 nm flat sheets and can be considered as thick as one atom size [8].

Graphene properties are unique as it is the lightest weight, thinnest and very strongest material ever measured [7]. It has very strong C-C bond and its length is equal to ~1.42 Å but weak bonding between layers [9]. Graphene with two-dimensional nanosheets is essential for various applications such as electronic devices, energy storage devices and sensors due to its chemical stability, high surface area, excellent in thermal and electrical conductivity and possess excellent mechanical properties [10-12].

In this paper, we demonstrate the synthesis of GO and followed by the reduction of GO to a mixture of reduced GO and graphene. The electrochemical exfoliation of graphite was conducted to prepare GO. For reduction of GO, green tea extract was used to avoid any strong and harmful chemical reduction which contaminated the environment. All samples were subjected to the characterization techniques of Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscope (SEM) and Energy Dispersive X-Ray Analysis (EDX).

2. MATERIALS AND METHODS

The synthesis of GO and RGO were mainly used graphite rod and green tea extract respectively. Besides, several chemicals that were used as electrolytes in the project were sulfuric acid (H_2SO_4), aluminium sulphate ($Al_2(SO_4)_3$) and sodium sulphate (Na_2SO_4).

Graphite rod was taken from the pencil core as the working electrode whereas copper foil was used as the counter electrode. H_2SO_4, $Al_2(SO_4)_3$ and Na_2SO_4 solution were used as the electrolyte solution. For the preparation of electrolytes solution, 96.66 g of Na_2SO_4 and 133.28 g of $Al_2(SO_4)_3$ were dissolved into distilled water in two beakers separately before filled into two 1000 mL of volumetric flask to prepare 0.2 M solution. Next, 10 mL of the 0.5 M H_2SO_4 was diluted with distilled water in a 1000

mL of volumetric flask. Graphite rod was exfoliated with the electrolytes by using the electrochemical exfoliation technique with potential of 3.0 V, 6.0 V, 9.0 V, 12.0 V and 15.0 V. Every voltage was kept constant for 5 minutes.

In the reduction of GO, green tea leaves extract was obtained by soaking the commercial tea bag into 250 mL of boiled water. The GO solutions which were obtained from the electrochemical exfoliation were then mixed with the green tea leaves extract by using magnetic stirrer at room temperature for 12 hours. After that, samples were filtered by using filter paper and dried at room temperature until partially dried before samples were scraped from the filter paper for further drying in oven at 80°C for 24 hours. Finally, the obtained products were kept inside the sealed plastic bag.

3. RESULTS AND DISCUSSION

3.1. FTIR

In connection with FTIR plot, Figure 1 above shows the results of the FTIR for five samples. A_1 and A_2 represent the FTIR spectrum of GO sheets synthesized by using Al_2SO_4 and H_2SO_4 whereas B_1, B_2 and B_3 represent the FTIR spectrum of RGO sheets prepared by reducing the GO samples synthesized by using Al_2SO_4, H_2SO_4 and Na_2SO_4 as the electrolytes respectively. FTIR was used to identify the type of oxygen-containing functional groups and bonding configurations in GO and RGO. After treated graphite rod with different types of oxidizing agents in electrochemical exfoliation, GO sheets displayed different positions of characteristic peaks. The oxygenated GO sheets exhibited a series of different characteristic peak range from 600 until 4000 cm^{-1}.

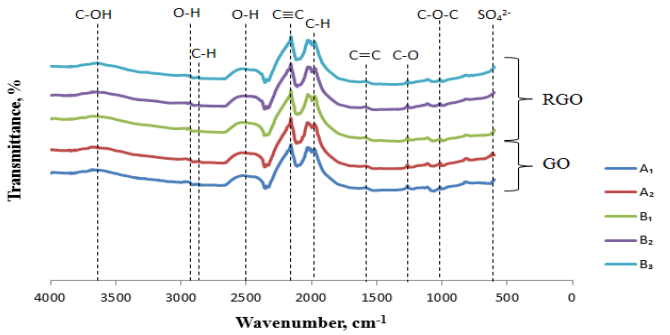

Figure 1 FTIR spectra for GO sheets (A_1 and A_2) and RGO sheets (B_1, B_2 and B_3).

Figure 1 above shows the peak position of GO and RGO with their characteristic infrared bands of oxygen-containing compounds. These included the infrared bands at 667 cm^{-1}, 1068 cm^{-1}, 1341 cm^{-1}, 1648 cm^{-1}, 2000 cm^{-1}, 2124 cm^{-1}, 2500 cm^{-1}, 2994 cm^{-1}, 2924 cm^{-1} and 3716 cm^{-1}. These wavenumbers were attributed to the functional groups of inorganic ion, ether, epoxy, alkane, aromatic compound, alkyne, carboxylic acid, alkane and alcohol and phenol respectively. To differ the results, characteristic peaks of GO such as O-H band became weaker in intensity for RGO. This indicates the successful removal of oxygen-containing functional groups from RGO by using green tea reduction [7]. The oxygen-containing functional group will not completely be removed by reduction since it is difficult to get the pristine graphene by using green tea due to the weak reduction capability as compared to chemical reduction agent such as hydrazine hydrate [13].

3.2. XRD

XRD was used to reveal the peak position and the interlayer spacing of GO and RGO. This characterization was used to examine the degree of oxidation of graphite using $Al_2(SO_4)_3$, H_2SO_4 and Na_2SO_4. Besides, the analysis of XRD is also important to determine the successful reduction of GO using green tea extracts. Figure 2 shown XRD patterns of graphite at 2θ of 26°-27° corresponding to the formation of graphene sheets with interlayer spacing 0.3346 nm along the (002) orientation for all samples. The oxygen-containing functional groups were formed in low amount at graphene sheets due to the short exfoliation time. Hence, it was difficult to observe the diffraction peak at 2θ of approximately 10° in the exfoliated samples.

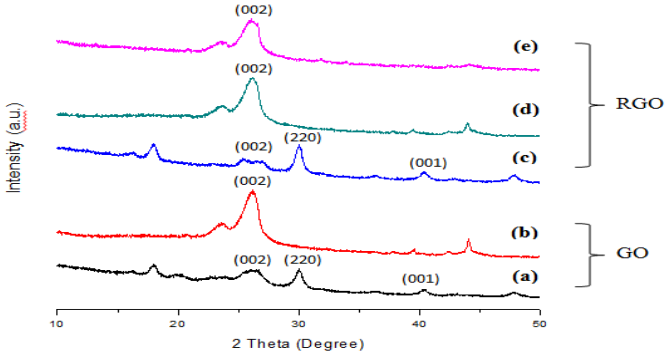

Figure 2 XRD patterns of synthesis GO sheets (a-b) and RGO sheets (c-e).

In samples (a) and (c), the presence of peak at 41° (001) was noticed due to the partially oxidized graphite materials [13]. Furthermore, a peak at 30° was seen because of the presence of characteristic peak of (220) corresponding to $Al_2(SO_4)_3$ due to residue of electrolyte in exfoliation [14]. In RGO, samples (d) and (e) show sharp peak due to the restacking of graphene sheets by Van der Waals forces [7, 13] while in GO, the sharp peak of sample (b) was due to incomplete oxidation of bulky exfoliated graphite layers since the reaction time for oxidation was not enough to allow the oxygen functional groups to be attached between the layers.

3.3. SEM

SEM and Energy dispersive x-ray spectroscopy (EDX) were used to study the morphology and elemental composition of samples. Figure 3 (a) and (b) above show the SEM images of GO after oxidizing with Al_2SO_4 and H_2SO_4 respectively. In Figure 3 (a), GO sheets were opened randomly due to the effect of exfoliation by anions. The presences of oxygen-containing functional groups and anions become the spacer between the layers and increased the *d*-spacing [15]. Next, the GO sheets as shown in Figure 3 (b) had flaky structure and some areas showed the presence of stacked and partially exfoliated graphene layers. This occurred due to electrolyte of H_2SO_4 was an excellent oxidizing agent in exfoliation [16].

Figure 3 (c), (d) and (e) show the SEM images after reducing GO into RGO by using green tea extract as the reducing agent. Green tea extract was stirred together with GO solution for 12 hours. In Figure 3 (c), RGO showed rough and irregular shape structure while thin and wavy wrinkled structure were observed in Figure 3 (d). Moreover, in Figure 3 (e), the RGO

sample displayed thin and wrinkled structure which nearly same with flower-like shape. The results indicate that the morphology of GO was not seen after the reduction by green tea.

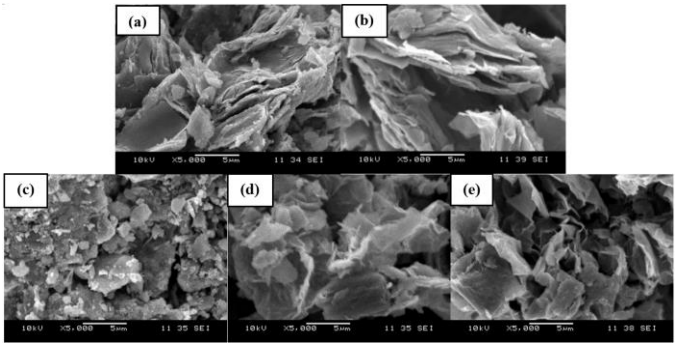

Figure 3 SEM images of (a) GO (Al_2SO_4), (b) GO (H_2SO_4), (c) RGO (Al_2SO_4), (d) RGO (H_2SO_4) and (e) RGO (Na_2SO_4) at magnification of 5kX respectively.

3.4. EDX

Analysis EDX of GO and RGO which prepared by using H_2SO_4 solution were shown in Figure 4 (a) and (b) respectively. EDX spectra of GO showed elements of carbon (C), oxygen (O) and sulphur (S) which indicates the oxidation occurred during the electrochemical exfoliation. Although the analysis of GO shows low percentage of O (Table 1) but oxidation still occurs even partially. Next, in analysis EDX of RGO, Table 2 shows lower count percentage of O was noticed in RGO than GO, indicating the successful removal of oxygen-containing functional group by using green tea extract as the reducing agent. The existence of element S was a result of acid H_2SO_4 which is used in the oxidation of graphite.

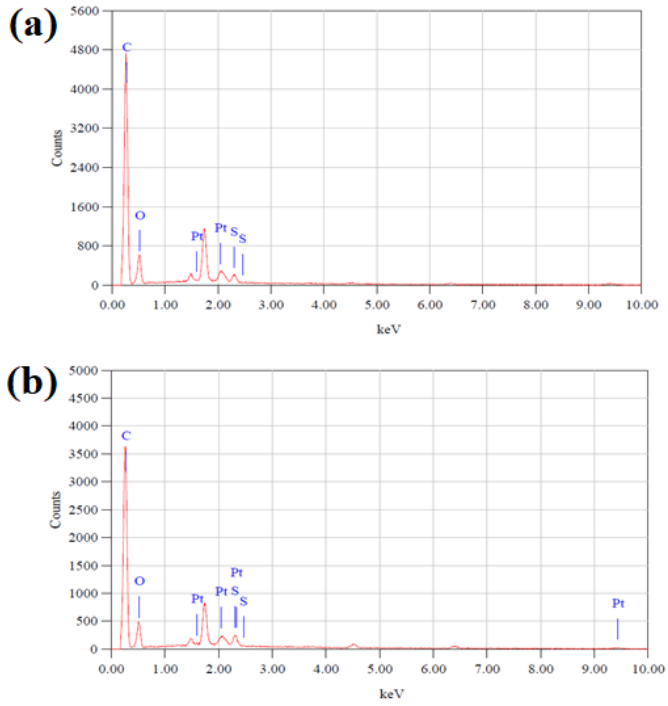

Figure 4 EDX profile of (a) GO and (b) RGO.

Table 1 EDX elemental microanalysis of GO where H_2SO_4 was used as the electrolyte.

Element	keV	Mass%
C	0.277	70.50
O	0.525	23.23
S	2.307	1.37
Pt	2.048	4.90

Table 2 EDX elemental microanalysis of RGO after reduced the GO which prepared by using H_2SO_4 as the electrolyte.

Element	keV	Mass%
C	0.277	65.37
O	0.525	16.89
S	2.307	1.30

4. CONCLUSION

The synthesis of GO and RGO was successfully conducted by using electrochemical exfoliation method and reduction using green tea extract respectively. Both products were examined by several characterizations such as FTIR, XRD and SEM. The FTIR spectra show the presences of OH bands which proved the successful oxidation of graphite rod using H_2SO_4 as the electrolyte. The OH band in RGO samples became weaker in intensity which proved that the reduction of GO by using green tea extract were successfully. All samples showed XRD pattern of graphite at 2θ of 26°-27° (002) corresponded to the formation of graphene sheets. In addition, the synthesized of GO and RGO sheets displayed different morphologies by SEM analysis and the EDX spectra also validated the successful reduction of GO to RGO. This study demonstrated green synthesis method of GO and RGO which provide an alternative route to reduce the use of toxic chemicals to preserve our environment.

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REFERENCES

[1] P.R. Wallace, "The band theory of graphite," *Phys. Rev.*, vol. 71, pp. 622–634, 1947.

[2] A.L. Lavoisier, "Traité élémentaire de chimie," Paris, 1789.

[3] K.S. Novoselov *et al.*, "Electric field effect in atomically thin carbon films," *Science*, vol. 306, no. 5696, pp. 666–669, 2004.

[4] S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, vol. 354, no. 6348, pp. 56–58, 1991.

[5] H.W. Kroto *et al.*, "C60: buckminsterfullerene," *Nature*, vol. 318, no. 6042, pp. 162–163, 1985.

[6] D.G. Papageorgiou *et al.*, "Mechanical properties of graphene and graphene-based," *Prog. Mater. Sci.*, pp. 75–127, 2017.

[7] A.A. Moosa *et al.*, "Green Reduction of Graphene Oxide Using Tea Leaves," *Nanoscience Nanotechnol.*, pp. 38–47, 2017.

[8] S. Ren *et al.*, "Preparations, properties and applications of graphene in functional," *Ceram. Int.*, pp. 11940–11955, 2018.

[9] N.A. Abdel Ghany *et al.*, "Revolution of Graphene for different applications: State-of-the-art. Surfaces and Interfaces," pp. 93–106, 2017.

[10] A.K. Geim, "Graphene: status and prospects," *Science*, vol. 324, no. 5934, pp. 1530–1534, 2009.

[11] K.L. Yap and W.W. Liu, "Exfoliation of charcoal by electrochemical method to synthesize few layers graphene sheets," pp. 012019–012026, 2020.

[12] S. S. Bhullar and W. W. Liu, "The effect of different electrolytes on the synthesis of graphene sheets by electrochemical exfoliation," *pp. 020262-020269*, 2021.

[13] S. I. Djelloul, "ZnO/ZnAl2O4 Nanocomposite Films Studied by X-Ray Diffraction, FTIR, and X-Ray Photoelectron Spectroscopy," *J. Spectroscopy*, pp. 1-9, 2015.

[14] L. C. Khamirul Amin Matori, "Phase Transformations of α-Alumina Made from Waste Aluminum via a Precipitation Technique," *Int. J. Mol. Sci.*, pp. 16812-16821, 2012.

[15] Z.-S. Khaled Parvez, "Exfoliation of Graphite into Graphene in Aqueous Solutions," *J. Am. Chem. Soc.*, pp. 1-25, 2014.

[16] T. T. M. Nguyen, Y.-N. Kwon, and C. Lee, "Journal of Industrial and Engineering Chemistry," pp. 282-288, 2015.