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Abstract. In this study, Graphene has been synthesized by using electrochemical exfoliation method. Effect of sonication times (15, 30 and 45 min) at room temperature on the production of graphene was investigated. The synthesized graphene were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Atomic Force Microscopy (AFM). The crystal structure of the exfoliated graphene were analyzed using XRD. The graphene flakes exhibit a sharp peak centered at 26.5°corresponding to the (002) plane of graphene crystal. It is found that, the crystallite sizes is gradually decreased with increased in sonication time. The FTIR spectrum reveals the prominent appearance of C-O-H group which indicate that OH^- radicals exist in conjunction with exfoliated graphene sheets. Graphene flakes with average thickness of 0.2 nm to 0.8 nm were observed using AFM. The electrical conductivity results showed that 45 min sonication time produced the highest electrical conductivity ($1.38\times10^2 sm^{-1}$).

1. Introduction

A single atomic layer of sp^2 bonded carbon material, graphene which is a 2- dimensional hexagonal honeycomb like structure, has attracted significant attention [1, 2]. The planer orbitals are energetically stable and localized sigma bonds with the three nearest neighbour atoms arranged in a honeybomb lattice [3]. This material possess various intriguing properties of interest such as intrinsically super electrical conductivity ($10^6\Omega^{-1}cm^{-1}$), nearly transparent in visible light (97.7 %), high intrinsic carrier mobility (2.5×10^5 $cm^2v^{-1}s^{-1}$), high specific surface area (2630 m^2g^{-1}), excellent mechanical properties (Young's modulus > 1TPa), and high thermal conductivity (above 3000 Wmk^{-1}) [4, 5]. These excellent properties make graphene a promising material for various applications such as nano electronics, composite materials, transparent conductive films, super capacitor, printable electronics and several other fields

[6]. Graphene has an electrical conductivity greater than any other known material, and its thermal conductivity is higher than diamond [7]. Presently, the most widely used transparent conducting materials are doped metal oxide. Indium tin oxide (ITO) is nature, high surface roughness and growing cost due to shortage of indium. Many other materials have been tried earlier but without much success. Previous studies suggest that in comparison to ITO, graphene is a better material for making transparent and highly conducting electrode.

To date, several methods have been demonstrated for graphene synthesis using both top-down and bottom-up approaches. In recent years, mechanical exfoliation, chemical exfoliation, chemical synthesis and thermal chemical vapour deposition (CVD) synthesis are the most commonly used methods. The electrochemical exfoliation is another technique for exfoliating graphene [8]. Recently, electrochemical exfoliation of graphite has attracted attention due to its easy, fast and environmental friendly nature to produce high-quality graphene. The electrochemical cell is setup with a graphite anode and a metal cathode, such as platinum. Both probes are dipped into an electrolyte solution made of water and ionic liquid or a surfactant [9, 10]. Other chemicals can be added to enhance the conductivity of the electrolyte as well. The surfactant or ionic liquid intercalate the graphite anode, penetrating the layers of graphite. A voltage is applied across the robes, facilitating cleavage of graphene flakes at the anode. The electrolyte then stabilizes the graphene sheets in solution, preventing agglomeration after exfoliation [11]. In this study the synthesis of graphene by electrochemical exfoliation of method is considered. Further the effect of sonication times (15 min, 30 min and 45 min) at room temperature on the production of graphene was investigated.

2. Experimental Method

Graphite rod with diameter of 6.35 mm was supplied by Sigma-Aldrich. Sulphuric acid (H_2SO_4) supplied by Merck assay was used as electrolytes. Ethanol supplied by J.T. Baker was used as a cleaning agent. Distilled water was used in the synthesis process. In this study, a typical electrochemical synthesis of graphene, which a conventional two-electrode system was used. Exfoliation was conducted with a graphite rod which is used as a working electrode and a platinum (Pt) rod was treated as the counter electrode. The platinum electrode was placed parallel to the graphite rod at a distance of about 2 cm. The positive voltage was supplied to the graphite electrode using DC power supply. After the graphite exfoliation was completed, the graphene solution were sonicated for 15, 30, 45 min at room temperature and washed several times by distilled water using vacuum filtration. The powder was obtained after dried in a vacuum oven at 80°C.

2.1 Characterization Techniques

X-ray diffraction (using Bruker D8 X-ray scattering systems) with Ni-filtered Cu-Kα (λ = 1.54021Å) radiation source was used to identify the crystallographic structure of graphene. Fourier transform infrared spectroscopy (FTIR) was obtained by using a Perkin Elmer FTIR spectrometer (spectrum one) at room temperature with a typical wave number of 4000- 500 cm^{-1} in open air at transmittance mode. Atomic force microscopy (AFM) observation was performed using (AFM, Nano Navi SII). Direct current (DC) electrical conductivities of graphene pellets were tested at room temperature according to the ASTM D257-99 standard test method by using a Gwinstek LCR 1817 meter at a voltage of 1V and frequency of 1KHz. The resistivity and conductivity were calculated using Equations (1) and (2), respectively.

$$\sigma = \frac{1}{\rho} \tag{1}$$

$$D = \frac{0.9\lambda}{B\cos\theta} \tag{2}$$

Where σ = electrical conductivity, ρ = resistivity, D = crystallite sizes, λ = wavelength.

3. Results and discussion

The crystal structure of the graphite and exfoliated graphene were analysed by XRD. The XRD pattern of graphite powder is shown in Figure 1 (A). The purification of graphite powder has been confirmed from XRD pattern. The XRD diffraction peak at about 26° was observed and confirmed the purification of graphite flake [14]. Figure 1 (B) shows all graphene flakes exhibit a broad peak centered at 26.5° corresponding to the (002) of a graphene crystal [15]. In the present work, the average crystallite sizes are tabulated in Table 1. It was found that the crystallite sizes is gradually decreased with increased sonication time. The acoustic cavitation's energy that generated during the sonication process decrease in crystallite size of synthesized graphene [16]. The reduction of crystallite size is with increasing sonication time.

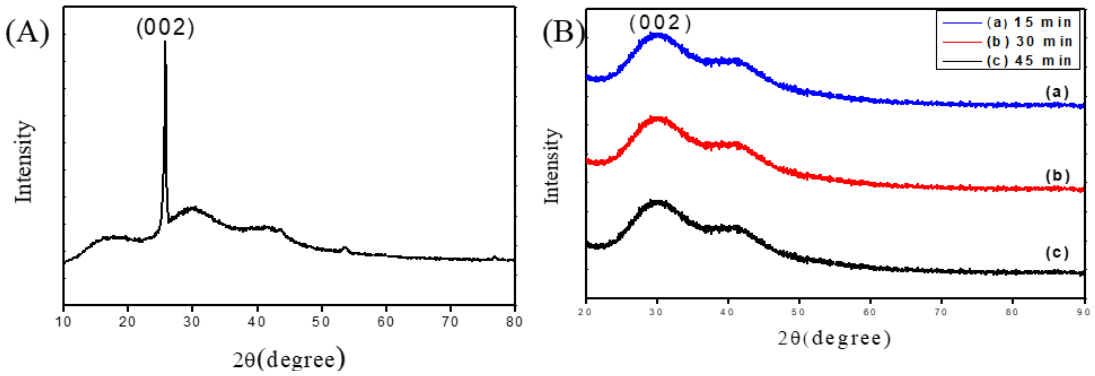

Figure 1. (A) XRD diffratogram of graphite, (B) XRD diffratogram of synthesized graphene at different sonication times (a) 15 min, (b) 30 min and (c) 45 min.

Table 1. The average crystallite size of exfoliated graphene.

No.	Sonication time (min)	Crystallite sizes (nm)
1	15	8.7
2	30	8.5
3	45	8.3

FTIR spectroscopy was carried out to investigate the surface chemical nature of graphite and exfoliated graphene. FTIR spectra of graphite and exfoliated graphene are shown in Figure 2 (a) and (b). The spectrum of graphite had broad absorption peaks at 3440 cm^{-1}, 1623 cm^{-1} and 990 cm^{-1} corresponding to O-H, C-C stretching vibration and CH deformation. Few new peaks appears after exfoliation of graphite, the peak at 1654 cm^{-1} can be attributed to C-O stretching vibration, the small peak at 1579 cm^{-1} and 1582 cm^{-1} represent C-C stretching and 1040 cm^{-1}, 1042 cm^{-1} and 1124 cm^{-1} represent C-O stretching vibration. The broad peaks at 3441 cm^{-1} and 3422 cm^{-1} show the prominent appearance of O-H group clearly shows that OH^{-1} radicals did exist in conjunction with exfoliated graphene sheets [17]. Therefore,

the FTIR peaks of the exfoliated graphene support that oxygen functional group was introduced into graphene during the exfoliation process.

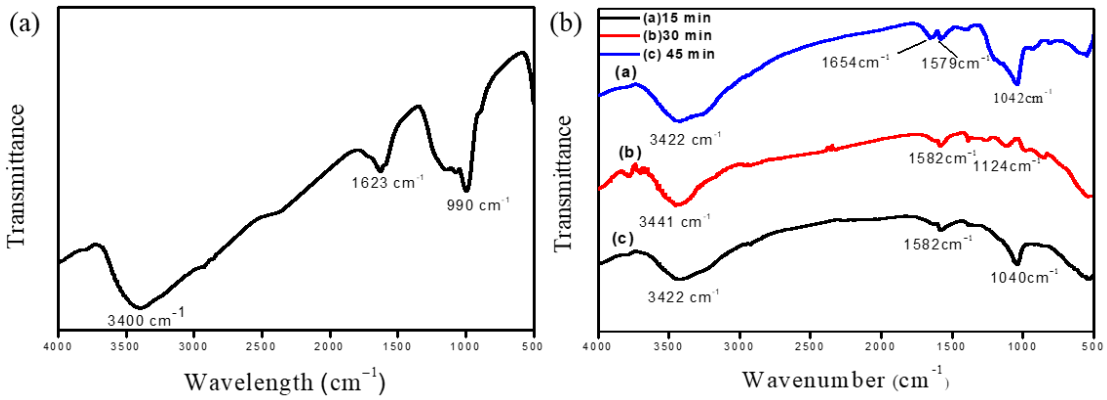

Figure 2. FTIR spectrum of (a) graphite (b) synthesized graphene at different sonication times (a) 15min, (b) 30 min and (c)

Atomic Force Microscopy (AFM) was employed to identify the thickness of the exfoliated graphene. The AFM analysis of the exfoliated graphene at different sonication times (15 min, 30 min, 45 min) are shown in Figure 3, 45 min sonication time produced graphene which is thinner than those 15 min and 30 min sonication times. Table 2 shows the thickness of graphene sheets measured by using AFM analysis.

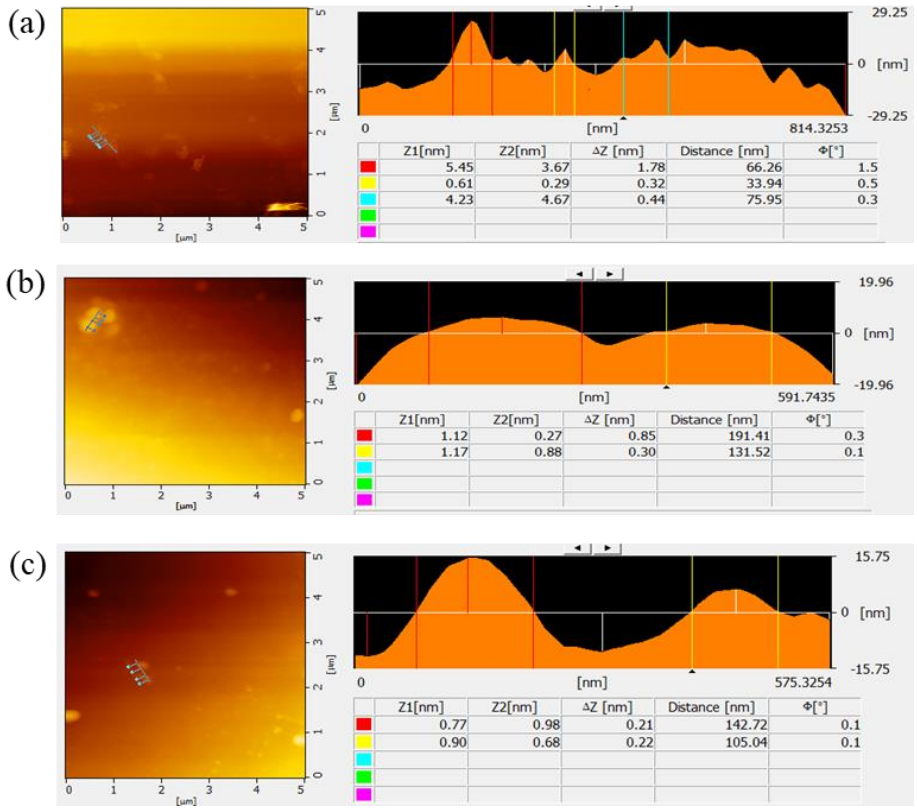

Figure 3. AFM analysis of synthesized graphene at different sonication times (a) 15 min, (b) 30 min and (c) 45 min).

Table 2. The thickness of exfoliated graphene sheets and electrical conductivity values of graphene produced by different sonication times

No.	Sonication time (min)	Thickness (ΔZ), nm	Electrical Conductivity (Sm^{-1})
1	15	0.85	1.29×10^2
2	30	0.60	1.31×10^2
3	45	0.22	1.38×10^2

The electrical conductivity of the synthesized graphene at different sonication times (15 min, 30 min, 45 min) are presented in Table 2. The synthesized graphene at 45 min sonication time showed the highest electrical conductivity. High conductivity of synthesized graphene is due to sufficient time to exfoliate the graphite.

4. Conclusions

In conclusion, characterization results of XRD, FTIR and AFM showed that sonication time of 45 min is suitable to be used to exfoliate graphene from graphite rods. As the sonication time increases, the average crystallite sizes and average thickness values are decreased. The electrical conductivity results showed that 45 min sonication time produced the highest electrical conductivity. Therefore, in this study, 45 min is considered as the maximum sonication time on the production of graphene.

Acknowledgements

The authors gratefully acknowledge ASEAN University Network for Science and Engineering Education Development Network (AUN/SEED-Net) Project and Japan International Corrperation Agency (JICA) for their financial support. And also would like to thank the Universiti Sains Malaysia (USM) for the use of their facilities.

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