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Synthesis of Few Layers Graphene Sheets from Graphite Rod via Electrochemical Exfoliation

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ABSTRACT

Graphene has many excellent properties in mechanical strength, electrical conductivity, optical transparency and thermal conductivity. The basic unit of graphene is made of hexagonal ring of carbon shape. The production of graphene in large amounts can be done using conventional ways such as chemical vapour deposition (CVD). However, the cost production is very high due to high reaction temperature. Therefore, electrochemical exfoliation could become a promising method in future because of its simple, low cost and large-scale production. Electrochemical method is performed in the manner by connecting the graphite rod to the positive terminal (anode) while the copper sheet is connected to the negative terminal (cathode) and both of were immersed into electrolyte with a distance between them. Then, due to the potential difference, the exfoliation of graphite into graphene sheets occurs. X-Ray Diffraction revealed that high amount of exfoliated graphene sheets was synthesized successfully where the peak was seen at approximately 26.60°. Fourier Transform Infrared confirmed the synthesized of graphene oxide (GO) sheets (by using H_2SO_4 as electrolyte) shows the higher intensity of O-H band because of strongest oxidation behaviour of H_2SO_4 acid among all electrolytes used in experiment. Besides. SEM images show that the morphologies of the exfoliated graphene sheets have stacked, flaky-like, wrinkled and crumpled structures.

Keywords: Graphene oxide, X-Ray Diffraction, Fourier Transform Infrared Spectroscopy, Scanning Electron Microscope

1. INTRODUCTION

Since 2004, the amount of academic publications associated with graphene has been increased substantially. In 2013, there are various methods of graphene production with pros and cons to synthesize several forms of graphene (monolayer, multi-layer etc.) for several applications. Solar cell is one of the applications of graphene. Recently, solar cell technology had platinum-based electrodes that leads to two problems due to insufficient of platinum available on earth and thus, the price of platinum increases. Since graphene is an outstanding conductor, it is great benefit for the design of a graphene electrode to substitute platinum to reduce the cost production and weight without affects the efficiency [1].

Graphene is an allotrope of carbon with a two-dimensional (2D) and is often stated as a wonderful material due to its remarkable properties. It has very good electrical, thermal, mechanical and optical properties to make it as one of the preferable materials for various applications such as transparent conductive electrodes, highly efficient solar cells, water

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systems and enhanced gas sensors. Therefore, the production of graphene is expected highly increased in coming years due to the high demand in various application [2]. Graphene oxide (GO) has a layer structure similar with graphene, but GO is grafted with oxygen-containing groups, which not only increase the interlayer space but also make the GO becomes hydrophilic.

Many different synthesis methods of graphene sheets have been reported such as chemical route [3], micromechanical cleavage [4], mechanical methods [5], chemical vapor deposition (CVD) [6, 7] and epitaxial growth [8]. However, some of the techniques involve the use of hazardous compounds [9] and high flammable gases [10] to synthesize low quality and quantity of graphene. Therefore, the disadvantages related with conventional methods increase the challenges in the synthesis of high-quality graphene. Electrochemical exfoliation demonstrate as a better option to synthesize graphene because of its convenience and reliability [11, 12]. In addition, the electrochemical route requires simple and low cost since pencil core can be used as graphite rod.

In this study, we demonstrated the facile and low-cost synthesis of graphene sheets using electrochemical exfoliation of graphite rod without the use of harmful chemicals. The experimental set-up consists of counter electrode and working electrodes (e.g, graphite rod) where both electrodes were immersed in an electrolyte. The counter and working electrodes were connected to the power source. Then, due to the potential difference between the two electrodes, the exfoliation of graphite layers into graphene sheets happens until the graphite rod is consumed into graphene sheets. Besides, the results of characterization techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were discussed in this paper.

2. MATERIALS AND METHODS

This research is focus on the electrochemical exfoliation of graphite rod, filtration of the samples and characterization of the samples. The raw materials used was graphite rod. The chemical reagents that used to synthesize GO were copper (II) sulfate pentahydrate ($CuSO_4.5H_2O$) (Sigma-Aldrich; 98%), sodium sulfate-10-hydrate ($Na_2SO_4.10H_2O$) (Sigma-Aldrich; 99%) and sulfuric acid (H_2SO_4) (Sigma-Aldrich; 98%).

In the work, electrochemical exfoliation was performed using potentiostatic technique with two electrodes configuration. The graphite rod electrode with 2.0 mm diameter and 120 mm length was connected to the positive terminal (anode). The copper sheet was connected to the negative terminal (cathode). Both of anode and cathode electrodes were immersed into electrolyte with a distance between them and due to the potential difference between the two electrodes, the exfoliation of graphite layers into graphene sheets occurs. Furthermore, the electrolytes used in the electrochemical exfoliation consisted of three types of solutions: copper (II) sulfate pentahydrate ($CuSO_4.5H_2O$), sodium sulfate-10-hydrate ($Na_2SO_4.10H_2O$) and sulfuric acid (H_2SO_4) solution. First, the copper (II) sulfate pentahydrate solution was prepared by dissolving an amount of 0.0500 kg of $CuSO_4.5H_2O$ into 1000 ml distilled water to produce 0.2 M concentration of electrolyte. Meanwhile, a 0.0967 kg of $Na_2SO_4.10H_2O$ was used to prepare 0.2 M of sodium sulfate-10-hydrate solution in 1000 ml of distilled water. In addition, sulfuric acid solution was prepared by mixing 10 ml of 50 M of high concentrated sulphuric acid, with 1000 ml distilled water in a volumetric flask.

In order to get excellent exfoliation of carbonaceous material, the sample must first be intercalated, expanded and then separated into graphene. The exfoliation parameters were conducted using potential of 3V, 6V, 9V, 12V and 15V to synthesize five samples using different electrolytes. The electrochemical exfoliation process was prolonged for a relatively around 5 minutes for each voltage to encourage oxidation reactions. Filtration technique was used to filter suspended small particles (graphene) and big particles from an electrolyte after exfoliation process was finished. The mixture of exfoliation product and solution (electrolyte) were poured slowly into the filter paper to allow the filtration to proceed and avoid clogging of the filter by the solid particle. The liquid in the beaker was called as filtrate while the solid particle that remained on the filter paper was called as residue. After finished the filtration process, the filter paper was removed carefully from the beaker and allowed the excess liquid to dry at room temperature. The same process was repeated for all samples. When the residue was completely dried, the residue was scraped out from the filter paper and followed by drying in an oven at 80°C for 24 hours. Finally, the dried samples were stored in plastic bag with silica gel to prevent absorption of moisture.

3. RESULTS AND DISCUSSION

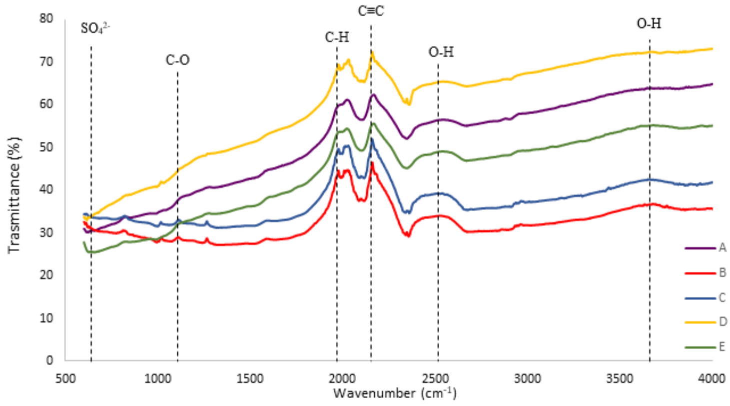

Figure 1. FTIR spectra of exfoliated graphene sheets using different types of electrolytes.

Table 1. The exfoliation parameters and types of electrolytes used to synthesize GO sheets.

Legends	**Electrolytes**	**Voltages (V)**	**Duration (minutes)**
A	Copper (II) sulfate pentahydrate ($CuSO_4.5H_2O$)	3, 6, 9, 12 and 15	5 minutes for each voltage
B	Sodium sulfate-10-hydrate ($Na_2SO_4.10H_2O$)	3, 6, 9, 12 and 15	5 minutes for each voltage
C	Sulfuric acid (H_2SO_4)	3, 6, 9, 12 and 15	5 minutes for each voltage
D	Sodium sulfate-10-hydrate ($Na_2SO_4.10H_2O$)	15	25 minutes
E	Sulfuric acid (H_2SO_4)	15	25 minutes

FTIR spectroscopy was used to identify the chemical compounds and functional groups present in the graphene sample. Figure 1 shows the IR spectra of exfoliated graphene sheets by using different types of electrolytes. In Table 1, each sample was represented by A, B, C, D and E. There are different electrolytes, voltages and duration were used to synthesize the samples.

In Figure 1, the absorption peak at approximately 3588 cm^{-1} was attributed to the O-H stretching vibration of the alcohol group. It can be observed that GO sheets synthesized by using H_2SO_4 showed the higher intensity of O-H band because of highest efficiency in exfoliation by using strongest oxidation behaviour of H_2SO_4 acid among all electrolytes used in experiment [11]. In addition, the peak appeared at 2541 cm^{-1} was due to the stretching vibration of O-H bond which corresponded to the functional group of carboxylic acid. Besides, the absorption peak at 2227 cm^{-1} was allocated to C≡C stretching of alkyne group. The peak of C≡C stretching has the highest peak, indicating strongest intensity as compared with other peaks. Furthermore, a distinct peak at 2000 cm^{-1} was also appeared, which could be referred to the bending of C-H bond. Moreover, the peak showed up at approximately 1100 cm^{-1} can be corresponded to the C-O stretching vibration from the functional group of secondary alcohol.

Finally, a peak at 664 cm^{-1} was also detected, implying the presence of a SO_4^{2-} bond of inorganic ion. The SO_4^{2-} ions are expected to be absorbed on the surface of exfoliated graphene [11]. The presence of functional groups such as alcohol, carboxylic acid, alkyne, aromatic compound and inorganic ions in all samples could facilitated the intercalation of anions and expanded the interlayer spacing between graphite layers for further exfoliation into graphene sheets [11].

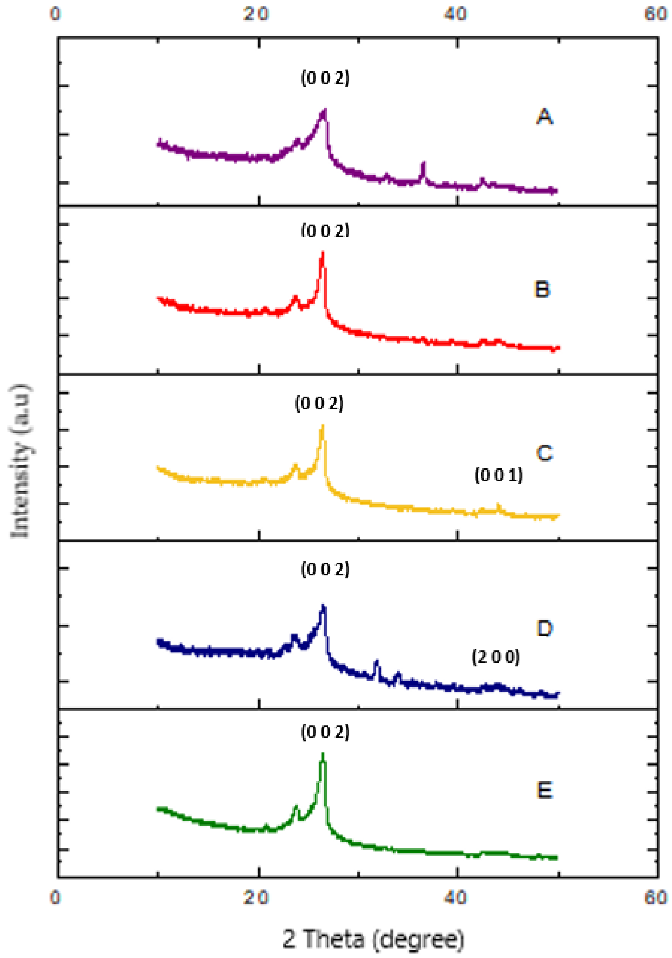

Figure 2. XRD spectra of exfoliated graphene sheets using different type of electrolytes.

XRD was used for the purpose to determine crystal structures, atomic spacing and number of sheets in an exfoliated graphene. XRD measurement was carried out by using a scan range of 2θ = 10° to 50°. The data was obtained in the step-scan mode using steps of 0.034° with a counting time of 2s at each step. In Figure 2, XRD spectra have been labelled with A, B, C, D and E that represent the XRD spectrum of exfoliated graphene sheets synthesized by using (A) $CuSO_4.5H_2O$, (B) $Na_2SO_4.10H_2O$, (C) H_2SO_4, (D) $Na_2SO_4.10H_2O$ (15 V, 25 minutes) and (E) H_2SO_4 (15 V, 25 minutes). Different types of electrolytes, voltages and duration were used to synthesize the samples.

In Figure 2, the exfoliated graphene sheets show the characteristic of a sharp and strong peak at approximately 26.60° which corresponded to (0 0 2) peak with an interlayer spacing (d value) of 0.334 nm (JCPDF No. 46-1240) [13]. It can be observed that graphene sheets synthesized by using H_2SO_4 showed the sharp diffraction peak at (0 0 2) plane as compared to other electrolytes in this experiment.

In addition, it can be observed that graphene sheets synthesized by using H_2SO_4 showed the diffraction peak at approximately 44.12º which corresponded to (0 0 1) plane was due to the incomplete oxidation of graphite rod [14]. Also, a noticeable peak can be seen for graphene sheets synthesized by using $Na_2SO_4.10H_2O$ corresponded to (2 0 0) position (JCPDF No.81-0577).

In XRD results, the crystallization degree was strongly associated to the values of applied voltage. The graphene sheets synthesized using sulfuric acid, H_2SO_4 displayed the most intense peak, indicating the presence of crystalline structure. However, the graphene sheets synthesized using $CuSO_4.5H_2O$ and $Na_2SO_4.10H_2O$ demonstrated lower crystallinity as compared to H_2SO_4 acid. Therefore, it is a great benefit by using electrochemical exfoliation method to form high amount of exfoliated graphene sheets in few minutes especially sulfuric acid was used. However, a small amount of GO sheets only was produced due to the oxidation of graphene sheets take very long time for oxygen containing functional groups to be attached on graphene structure. As reported by Hidayah et al. [15], 72 hours were required in the improved Hummers' method to prepare graphene oxide with high amount of oxygen containing functional groups.

SEM is one of the non-destructive tests to examine the morphologies of graphene samples. SEM images were taken at magnification of 1000X and 5000X for every sample with accelerating voltage of 10kV.

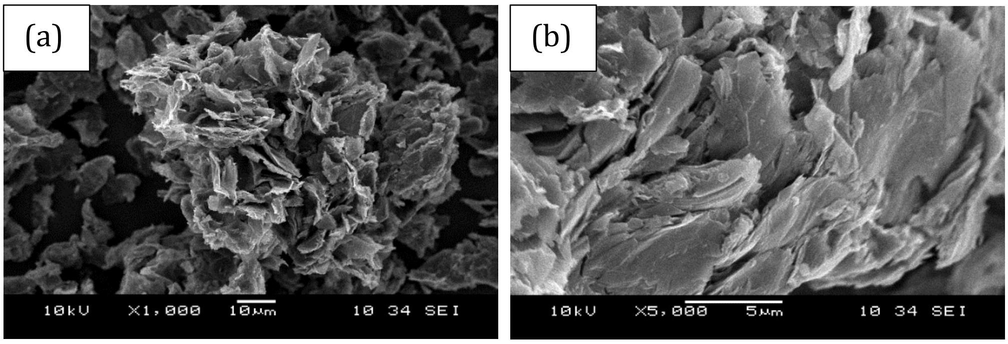

Figure 3. SEM micrographs of graphene sample at magnification of (a) 1000X and (b) 5000X.

Figure 3 displays the SEM micrographs of exfoliated graphene using copper (II) sulfate pentahydrate as an electrolyte. Figure 3 (a) and (b) show the stacked, wrinkled and crumpled texture of graphene structure. This was resulted from the exfoliation of graphite rod to form graphene layers during electrochemical exfoliation process. In exfoliation process, the anions of

SO_4^{2-} which carried negative charge from the copper (II) sulfate electrolyte hit the contact surface of graphite rod which is positively charge. Therefore, the anions intercalated into graphite rod, expanded and exfoliated thick graphite layers into graphene sheets. Moreover, the anion also hit the graphite rod with random direction which contributed to the exfoliation in different ways to synthesize irregular shapes of graphene layers as shown in Figure 3 (a) and (b).

Furthermore, graphene sheets were also oxidized to GO. This is because FTIR analysis indicated the presence of O-H bond which resulted of the oxidation of graphene to GO. However, small amount of oxidation only was occurred when copper (II) sulfate was used as electrolyte due to copper (II) sulfate was a weak oxidizing agent.

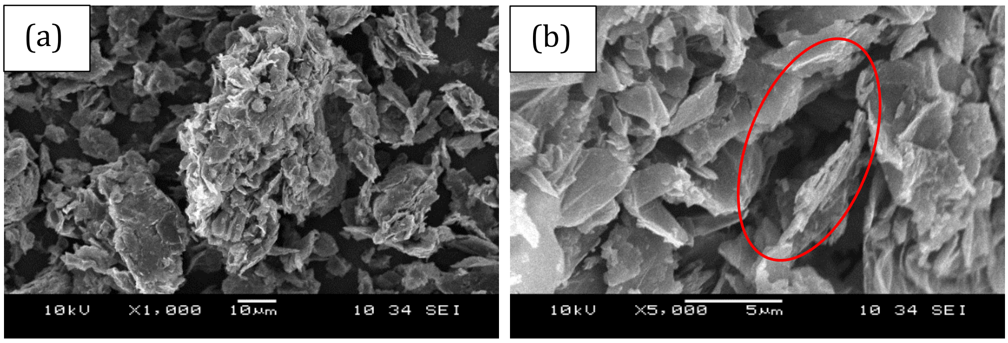

Figure 4. SEM micrographs of graphene sample at magnification of (a) 1000X and (b) 5000X.

Figure 4 shows the exfoliated graphene sheets using sodium sulfate-10-hydrate as an electrolyte. Figure 4 (a) show the SEM micrograph with the magnification of 1000X and it is clearly displays that the exfoliated graphene sheets have flaky-like structure. The flaky surface of graphene was due to the anions collided the surface of graphite rod randomly and then, they were inserted into the space between the layers of the graphene sheets. However, Figure 4 (b) shows a big hole was seen (marked with red circle) to demonstrate the effect of collision by anions.

In addition, FTIR analysis also revealed that graphene sheets were oxidized to form GO. From the FTIR analysis, there are several functional groups such as O-H and SO_4^{2-} induced the oxidation of graphene into GO. However, very low amount of GO sheets only was produced due to the formation of oxygen gas was faster than the formation of oxygen containing functional groups on graphene structure. Therefore, reactive OH, O and OOH from water electrolysis was consumed mainly for formation of oxygen molecules rather than formation of covalently bonded oxygen containing functional groups [16]. This also explains the presence of high amount of bubble gas during the electrochemical exfoliation.

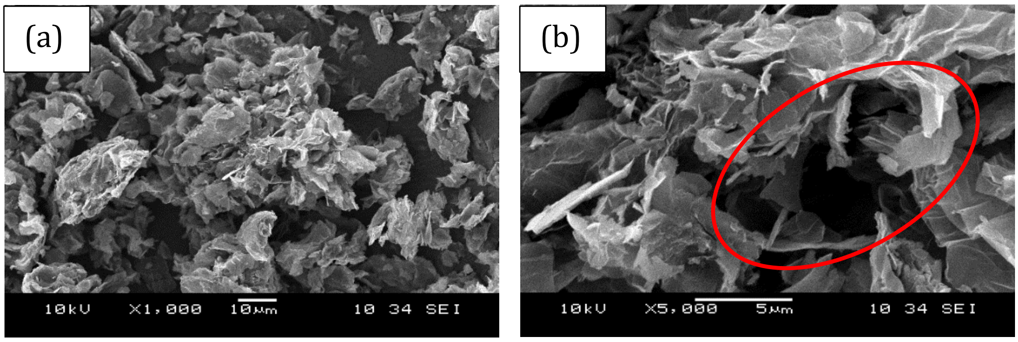

Figure 5. SEM micrographs of graphene sample at magnification of (a) 1000X and (b) 5000X.

Figure 5 shows the SEM images of exfoliated graphene using sulfuric acid as an electrolyte. In Figure 5 (a), the graphene sheets were seen in rough and flaky morphology. The reason was due to highest exfoliation efficiency by using strongest oxidation behaviour of sulfuric acid as compared with other electrolytes such as copper (II) sulfate pentahydrate and sodium sulfate-10-hydrate. Figure 5 (b) shows the higher magnification of SEM micrograph of graphene with layered-flakes structure. A big pore was observed in Figure 5 (b) which may be resulted from the bulky anions of SO_4^{2-} crashed the surface of graphite rod. Therefore, the bulky anions intercalated, expanded and exfoliated the tiny space between graphite layers into graphene sheets.

Additionally, FTIR analysis also exposed that graphene sheet synthesized by using sulfuric acid showed the higher intensity of O-H band due to the strong oxidizing agent of sulfuric acid among all electrolytes used in experiment. The presence of the functional groups such as alcohol, carboxylic acid and inorganic ions could facilitated the intercalation of anions and expansion the interlayer spacing between graphite layers for further exfoliation into graphene sheets.

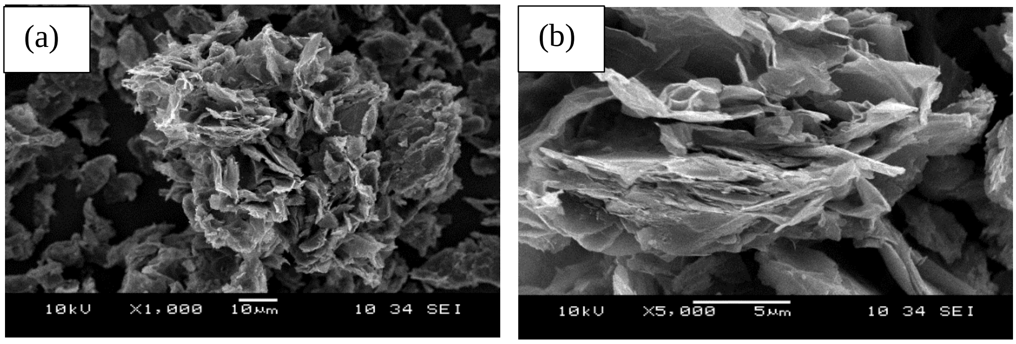

Figure 6. SEM micrographs of graphene sample at magnification of (a) 1000X and (b) 5000X.

Figure 6 shows the exfoliated of graphene sheets using sodium sulfate-10-hydrate as an electrolyte at highest voltage of 15 V for 25 minutes. Figure 6 (a) show the SEM micrograph with the magnification of 1000X. In these figures, it is clearly displays that the graphene appeared in flaky-like form. However, Figure 6 (b) shows the graphene layers were opened widely as compared with the samples in Figure 4 due to the higher voltage of 15V was applied to exfoliate graphite rod. With high voltage of 15 V, larger amount of bulky anions from the electrolyte such as OH^- and $SO_4{}^{2-}$ were driven to strike the surface of graphite rod which acted as anode at higher impact. Thus, the edge sheets of the graphite rod were expanded significantly in faster rate which enable the intercalation of bulky anions into the space between the layers of the graphene and lead to the fast exfoliation of graphene layers.

Furthermore, upon the electrochemical process was conducted at 15 V for 25 minutes, the compounds of CO_2 and O_2 also were formed as the electrolysis by-products [16]. Consequently, the presence of gaseous bubbles at surface of graphite rod was clearly seen and the quantity of bubbles was increased with increasing of the exfoliation time. Therefore, the presence of gaseous bubbles also induced the expansion and exfoliation of graphite layers to graphene sheets.

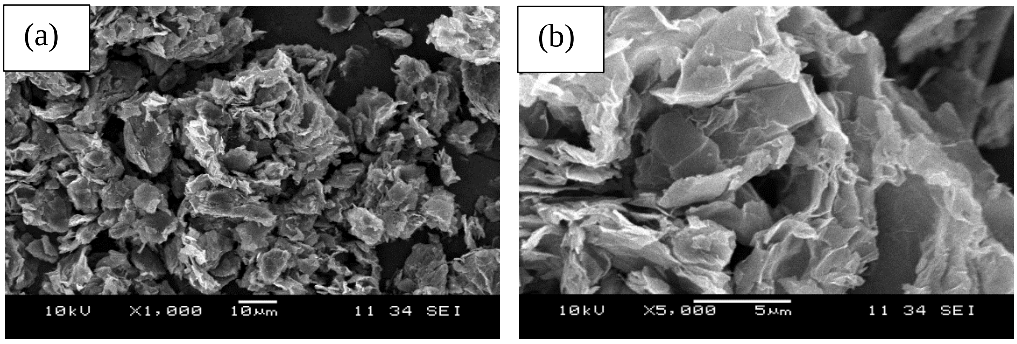

Figure 7. SEM micrographs of graphene sample at magnification of (a) 1000X and (b) 5000X.

Figure 7 shows the SEM images of exfoliated graphene using sulfuric acid at highest voltage of 15 V for 25 minutes. In Figure 7 (a), the morphology of graphene was seen in wrinkled and flaky structures. Moreover, Figure 7 (b) shows the higher magnification of SEM micrograph of graphene with various pore sizes, showing the serious crash effect by anions at high voltage than the sample as seen in Figure 5. For comparison, the voltage of 15V attracted more anions to graphite rod and increased the exfoliation rate at the same time. Thus, the edge sheets of the graphite rod were opened up which facilitate the intercalation of bulky anions into the space between the layers of the graphite, followed by expansion and exfoliation into graphene sheets.

Besides, the compounds of CO_2 and O_2 gaseous which formed as the electrolysis by-products during the electrochemical process [17] were clearly seen during electrochemical process and it was more bubbles were formed with increasing of the exfoliation time. Therefore, the presence of strong gaseous bubbles induced the opening layer by layer of graphene and enhance the effectiveness in exfoliation of graphene layers.

4. CONCLUSION

In this research, the synthesis of GO sheets by using electrochemical exfoliation method of different electrolytes was successfully conducted. The result of FTIR shows the light oxidation degree of graphene sheets by using strong oxidation agent of sulfuric acid. In addition, the XRD analysis also supported that graphene sheets were synthesized where the sharp diffraction peak at (0 0 2) plane was noticed. SEM images reveal that the morphologies of the exfoliated graphene sheets consist of a pile of graphene sheets, flaky-like structure, wrinkled and crumpled texture. Overall, it was found that H_2SO_4 electrolyte show the highest efficiency in exfoliation process as compared with $CuSO_4$ and Na_2SO_4 electrolytes.

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