

Graphene Synthesis by Electrochemical Reduction of Graphene Oxide and Its Characterizations

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ABSTRACT

Graphene is one of the nanoscale materials that has attracted many researchers to continue in-depth study on its unique properties where both the graphene oxide (GO) and electrochemical reduced graphene oxide (ERGO) are the derivatives of graphene. GO and ERGO can be further modified chemically for many types of application such as sensor and water filter membrane. However, to restore the electrical property of graphene, GO should be reduced to ERGO. There are several types of reduction methods which are fast to produce good quality and high yield of graphene material. However, those methods use toxic chemicals to reduce GO which can bring negative impact to both human and environment. Therefore, an electrochemical approach can be carried out to solve this issue. This study presents the electrochemical synthesis of GO and electrochemical reduction of ERGO. All characterizations were conducted by using Fourier transform infrared (FTIR) spectroscopy, X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

Keywords: Graphene oxide, reduced graphene oxide, scanning electron microscopy.

1. INTRODUCTION

Graphene has a one-atom-thick layer, also described as a two-dimensional (2D) nanocrystalline structure consisting of a flat single layer of carbon species that organized in honeycomb lattice. It is also regarded as a basic building block against all sp² graphitic materials such as graphite sheets, fullerenes and carbon nanotubes. Due to the two-dimensional structure, graphene has some unique properties that differ from other carbon materials such as exceptional electronic properties, high specific surface area [1], electron transport capability [2] and high thermal conductivity [3][4].

Graphene is the most focused material as compared with other several of carbon species because its properties are unique and good [5][6]. For large scale synthesis, the mechanical exfoliation technique showed as the ineffective method thus, this method is not suitable for large scale synthesis of graphene because an important factor graphene synthesis is the scalabilities. The use of a strong oxidizing agent becomes one of the popular approaches to synthesize

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graphene oxide (GO) [7]. However, the use of toxic chemicals pollutes the environment. Therefore, GO can easily be synthesized from graphite rod using electrochemical exfoliation in low cost, safe and green production. Generally, GO have a similarity with graphite oxide in term of basic unit of honeycomb lattice except the sizes and thickness of GO are smaller and thinner than graphite oxide [8][9].

The formation of high-quality 2D graphene layers is the first and utmost key step, as the presence of remaining defects will influence the electronic properties of graphene heavily. Mechanical cleavage of graphite was the 1st approach which led to the invention of graphene sheets[10][5]. However, the low production efficiency of this method causes it inappropriate for large-scale application. Besides, ultra-thin epitaxial graphene layers which synthesized on a single-crystal silicon carbide by vacuum graphitization also limited to low productivity. This method permits the production of a patterned graphene structure, which is required for electronic applications[11][12],[13].

To synthesize the graphene in the bulk amount, one of step is needed to use graphite oxide as raw material. The methods that are commonly used are electrochemical reduction, chemical reduction, thermal reduction and photocatalytic reduction. The presence of defect at the sp^2 carbon network are resulted from the existence of oxygen functional groups at basal plane and edges which make GO become an insulator [14]. The removal of oxygen functional groups from GO [15] is needed to ensure that the π -network is recovered which directly improved the electrical conductivity of reduced GO. Though, the electrical conductivity of reduced GO was not as good as pure graphene due to the remaining defects [16]. Thus, the GO can be reduced by using electrochemical reduction method. Based on some reported articles, the technique of electrochemical reduction of GO is very straightforward, rapid and environmental friendly to reduce GO to graphene materials in a large-scale amount [17][18].

In this research, GO sheets were prepared by electrochemical exfoliation method before undergo reduction process. Different reaction voltages of exfoliation and reduction were used to investigate the effects on the synthesis of GO and electrochemical reduction graphene oxide (ERGO) respectively. This study shows some benefits to provides new possibility toward a green synthesis of GO and ERGO as an alternative to protect our environment from chemicals pollution.

2. MATERIALS AND METHODS

In this study, the raw materials such as graphite rod and copper foil were used as anode and cathode respectively. In addition, the chemical reagents such as Aluminium Sulphate (Al_2SO_4), Sulphuric acid (H_2SO_4) and Sodium Sulphate (Na_2SO_4) were used as electrolytes. To synthesize ERGO, the GO samples which produced using Sulphuric acid (H_2SO_4) and Sodium Sulphate (Na_2SO_4) were used. All the chemicals and raw materials were purchased from Sigma Aldrich, Malaysia.

In the work, the electrochemical exfoliation method was used to synthesize GO. Firstly, 96.657g of Na_2SO_4 was mixed with distilled water and stirred for several minutes until the compound was dissolved completely. 150ml of the prepared Na_2SO_4 was measured and added into a beaker. Graphite rod and copper foil were immersed in the electrolytes with a distance between them. A potential of +3V was initially applied for 5 mins. The experiment was continued by increasing

the potential to +6V and maintained for 5 mins. The same procedure was carried out by increasing potential value with interval of +3V until +15V. The exfoliated GO sheets in electrolytes were filtered by using filter paper. Then, the wet black samples and filter papers were dried at room temperature before samples were scrapped for further drying in crucible in oven at 80 °C for 24 hours. Last, the dried black powder was stored in plastic bag for characterizations. The same procedure was repeated for another three types of electrolytes: Al_2SO_4 and H_2SO_4 .

The ERGO was prepared by using electrochemical reduction method after electrochemical exfoliation was completed. The electrochemical reduction method was carried out by connecting the graphite rod as cathode whereas copper foil as anode. Both electrodes were immersed into black GO solution. Power supply was controlled at 3 V for 5 mins of reduction time. After that, it was increased to 6 V with interval of 3 V until 15 V for 5 mins in every subsequence voltage. The same procedure was repeated for another GO solution which prepared using H_2SO_4 as electrolytes. Furthermore, the ERGO solution was filtered by using filter paper. The process was continued until all solution was dropped into beaker from filter paper. The wet filter paper with ERGO was dried at room temperature before it was scrapped for next drying step in crucible in oven at 80°C for 24 hours. The dried ERGO powder was stored into plastic bag for characterizations. The same above procedure was repeated for another ERGO sample.

3. RESULTS AND DISCUSSION

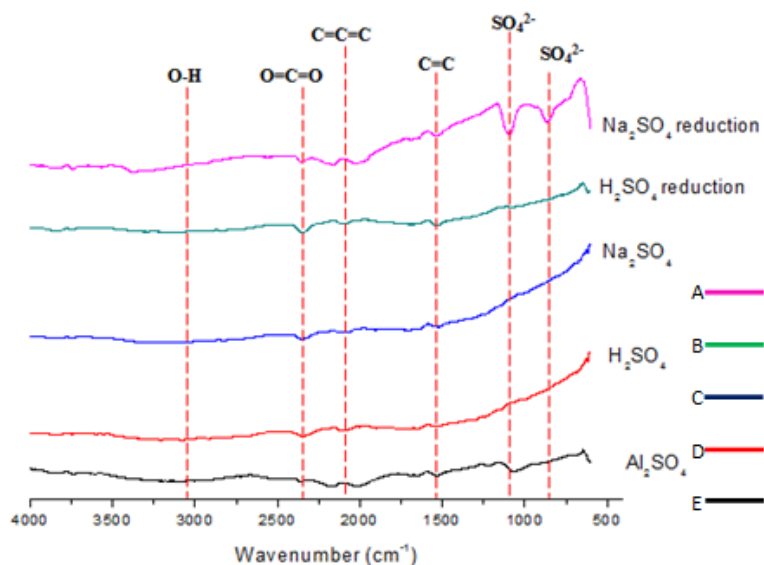


FIGURE 1. FTIR spectra of GO and ERGO.

Fourier transform infrared (FTIR) spectroscopy was used to affirm the successful synthesis of GO and reduction of GO to ERGO. The FTIR spectra of GO and ERGO was shown in Figure 1. In the spectra of GO, the intense peak can be seen at the wavelength of 3100 cm^{-1} , corresponded to the O-H bond (alcohol group). In addition, O=C=O (carbon dioxide), C=C stretching (cyclic alkene group) and C=C=C appeared at wavelength of 2100, 1590 and 2349 cm^{-1} respectively.

Furthermore, SO_4^{2-} bands (inorganic ion) appeared at wavelength of 867 and 1098 cm^{-1} . The existence of oxygen containing functional groups such as alcohol demonstrated that GO sheets were synthesized successfully in the electrochemical exfoliation using electrolytes such as Al_2SO_4 , Na_2SO_4 and H_2SO_4 (C, D and E) [19].

Based on the result of ERGO spectrum [20,21], the peak at 3100 cm^{-1} shows less intensity as compared with GO as seen in Figure 1, indicating the amount of oxygen containing functional groups were reduced successfully in electrochemical reduction [22,23]. The intensities of the peaks at 3100 cm^{-1} for both A and C spectrums were compared where the latter is lower than the former. This is because the oxygen containing functional groups were removed partially during the electrochemical reduction [24].

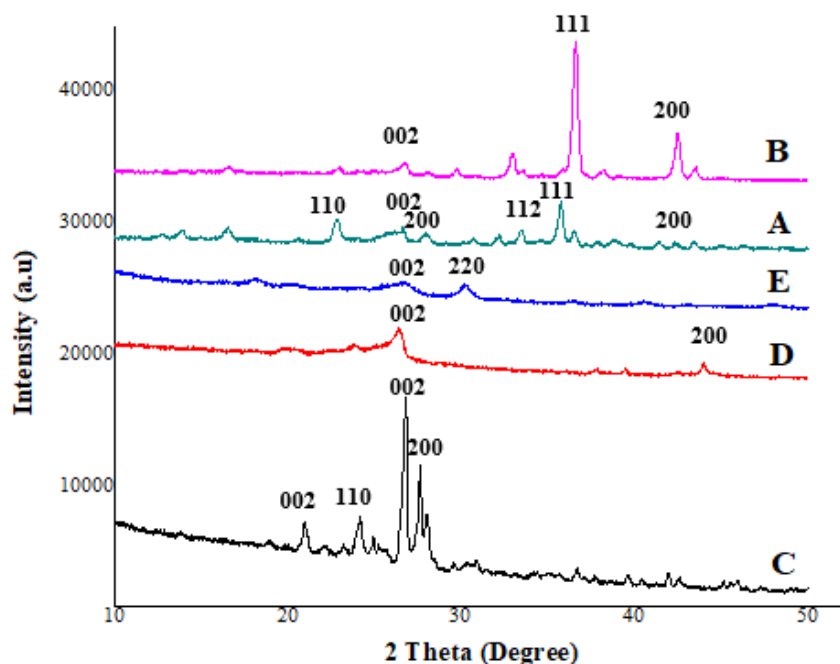


FIGURE 2. XRD spectra of GO and ERGO.

The XRD spectra of GO and ERGO were studied. A sharp and intense peak of graphite appeared at approximately $26.6\text{-}28^\circ$ (002) with an interlayer spacing of 0.335 nm [22,25] for sample C whereas low intensities of peak were observed for samples A, B, D and E (JCPDF card No. :46-1240). The presence of peak at 10° was not seen due to very low amount of GO. However, the existence of oxygen containing functional groups at 3100cm^{-1} was proven in the FTIR spectra (Figure 2). In addition, a small diffraction peak in sample E at 30.9° with (220) plane was observed due to the presence of Aluminium Sulphate, $(\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O})$ [26] (JCPDS Card number 01-077-0066). After the exfoliated GO was electrochemically reduced, the diffraction peaks of ERGO for samples A and B were found between $2\theta = 24\text{-}26.6^\circ$ (002) which are similar with the results of C, D and E. However, the GO peaks in samples A and B were not obvious appeared as well due to very low quantity of GO.

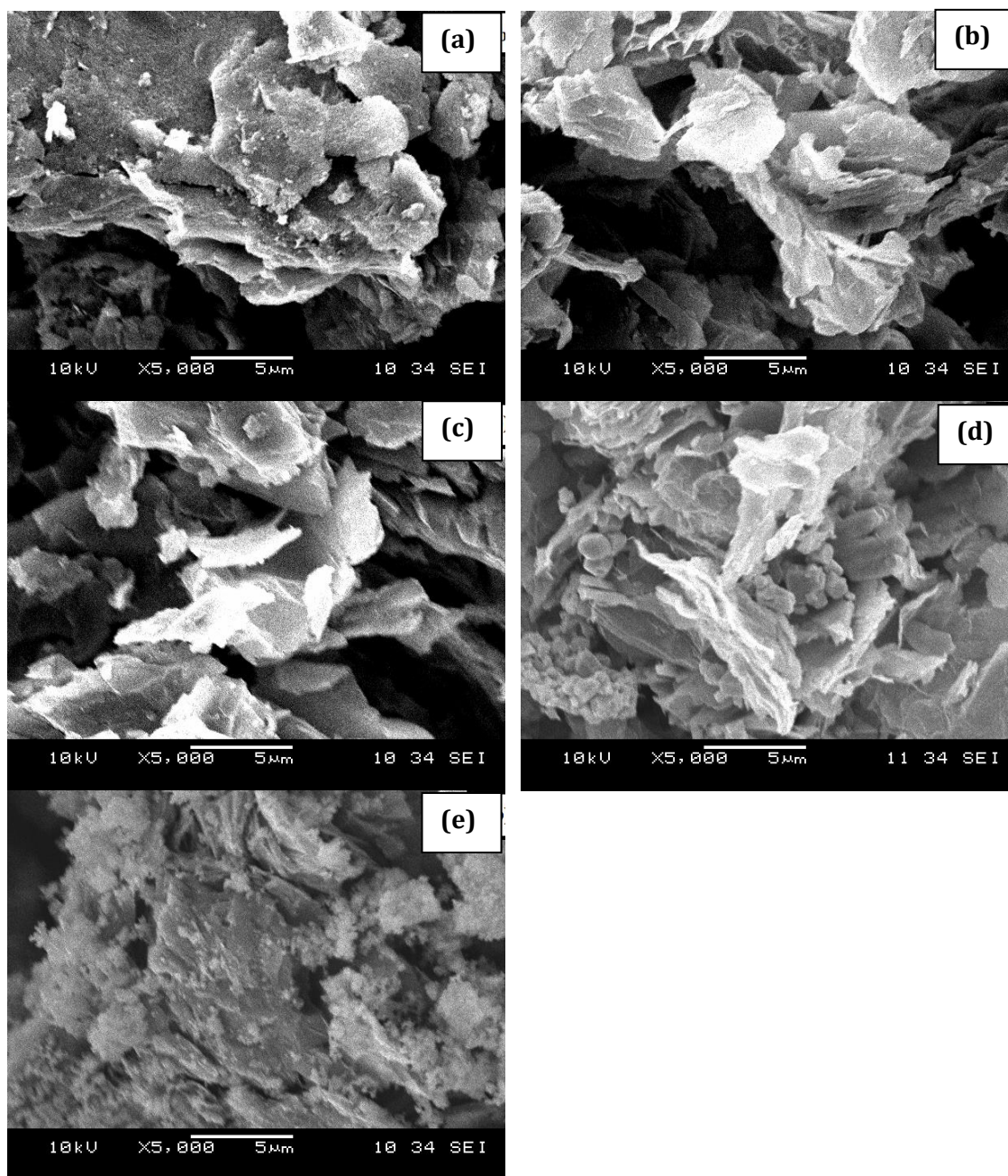


FIGURE 3. SEM images of GO (a, b, c) and ERGO (d, e).

SEM microscopy was conducted to investigate the morphologies of samples. In Figure 3(a), a soft carpet-like structure was appeared. It shows that the electrochemical exfoliation process was successful with intercalation of water molecules and oxygen functional groups which could expanded the distances between GO sheets [27][28]. In contrast, in Fig. 3(b), GO sheets

showed the higher degree of exfoliation by using H_2SO_4 as electrolyte where the surface of GO sheets became coarser and flurry at magnification of 5kX. This morphology was due to the use of high voltage which caused faster intercalation of large size SO_4^{2-} into the graphite rod. On the other hand, thin GO sheets with high defect level were formed because H_2SO_4 is a strong oxidation of acid and oxidized further the GO sheets [28]. Figure 4.9 shows the SEM micrographs of GO prepared by using Na_2SO_4 as an electrolyte. In Fig. 3(c), GO sheets have wrinkle and flaky structures. Besides, it is noticed that the surface of GO sheets became course and furry when look closer by increasing the magnification to 5kX. This morphology was formed could be caused by the presence of remaining water molecules which trapped between GO layers and attachment to oxygen-containing functional groups at the GO sheets [29]. Therefore, the morphology shows almost similar structure with GO sheets as shown in Fig. 3(b), indicating both H_2SO_4 and Na_2SO_4 demonstrated the quite similar exfoliation rate on graphite rod.

When the magnification was increased to 5kX (Figure 3(d)), some parts showed similar morphologies with GO's structure such as course and furry surface. This indicates that the ERGO sample was not reduced completely due to insufficient time of reduction. On the other hand, in Fig. 3(e), the micrographs of ERGO sheets have a porous sponge-like structure and overlapped each other's. It could be caused by the presence of strong interaction between ERGO sheets after the oxygen-containing functional groups were removed partially. In addition, it is also implies that the normal plane of graphene has been rebuilt partly after the reduction of GO and ERGO [30].

4. CONCLUSION

In conclusion, the synthesis GO and ERGO were successfully achieved. FTIR analysis shows the oxygen functional groups were significantly declined when GO was reduced to ERGO. In XRD analysis, GO and ERGO displays their unique characteristics at $26.6-28^\circ$ and 43° respectively. SEM micrographs of GO and ERGO show the different morphologies between them. Finally, the objective of this research to study the formation of graphene by electrochemical reduction of graphene oxide has been achieved. Therefore, some unique features of GO and ERGO can open up the opportunity to satisfy the needs in various applications.

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