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Improvement Synthesis of Graphene Oxide Yield in Two Steps of Intercalation and Oxidation of Flexible Graphite Foil by Electrochemical Exfoliation

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ABSTRACT

Synthesis of high quality and quantity of graphene by cost-effective methods are highly desirable for various application. In electrochemical exfoliation, graphite foil has been used as carbon source for the synthesis of high yield of graphene flakes. Electrochemical exfoliation is one of the faster and cheaper method to synthesize graphene sheets. In this work, five different types of concentration of sulphuric acid were used for electrochemical exfoliation. The electrochemical cell design where graphite foil as anode and copper foil as cathode which were connected to DC power supply of 5V. To examine the morphology scanning electron microscope (SEM) was employed in which the sheet structures with large lateral dimension and thin graphene flakes. Furthermore, X-ray diffraction (XRD) revealed that exfoliated graphene samples showed a significant peak at about 2θ = 26º corresponded to graphite.

Keywords: Graphene oxide, scanning electron microscope, electrochemical exfoliation

1. INTRODUCTION

University of Manchester was the first to conduct the popular exfoliation method using High Directed Pyrolytic Graphite (HOPG) that generates to form high quality graphene. Scientists and engineers have been studying different graphene production techniques for almost two decades due to its limitation in yield, uniformity and reproductivity. Chemically exfoliated graphene has lately gained appeal utilizing Hummers' approach due to the advantages of low-cost production and solution operation [1,2]. Different of electrolytes have been expressed for electrochemical exfoliation such as HBr, HCL, HNO_3 and H_2SO_4 but sulphuric acid is good enough with the HOPG exfoliation technologies.

The sixth element in an electronic ground state and in periodic table is carbon. Monolayer graphene had known because of carbon atoms share sp^2 electrons with nearest carbon atoms and form honeycomb structure which is in planar shape. Moreover, graphene is a promising substance in a general application and made of a single layer C-C bonded in honeycomb structure. Some of the popular applications are electrical devices [3], energy conversion and transportation [4] and advanced composites [5]. In addition, graphene also has a good intrinsic carrier mobility $(\sim 200\ 000 cm^2/V.s)^2$, vast thermal conductivity $(\sim 5000\ W\ m^{-1}K^{-1})$, elasticity, a great surface area of (2630 m^2/g) and an outstanding mechanical property in Young's modulus $\sim 1.0\ TPa$ with an intrinsic strength of $\sim 130\ GPa$ [5,6]. One of promising substances that can replace indium tin oxide (ITO) is graphene which for widely applications in electric devices [7] and graphene also a visible translucent material which only block 2.3% of visible light.

In this research, electrochemical exfoliation method gained very much attention in producing graphene sheets because of fast exfoliation mechanism, cheap, easy and rapid exfoliation process. However, Hummers' method can be used to synthesize graphene sheets but this method using high amount and concentration of hazardous chemicals. Moreover, Hummers' method is expensive in cost and complicated to be carried out. The electrolyte that has been used in this research is sulphuric acid because the acid displays ideal exfoliation efficiency compared to other chemicals. Five different types of concentration of dilute sulphuric acid been used in the exfoliation of graphite foil. The two steps of electrochemical exfoliation are pre-intercalation of graphite and exfoliation, and oxidation graphite intercalation compound takes place in second step.

2. EXPERIMENTAL

Electrochemical exfoliation is the method which took place in this research to synthesize graphene sheets. Various parameters were taken into consideration for all conducted experiments.

2.1. Materials

The graphite foil of 2 cm x 4 cm (bought it from Sigma Aldrich Malaysia) was used as anode whereas copper foil of 4 cm x 4 cm (bought it from Sigma Aldrich Malaysia) was employed as cathode. Five different concentrations of electrolytes were prepared from concentrated sulphuric acid (98 wt.%, H_2SO_4) (bought it from Sigma Aldrich Malaysia): 0.1 M, 0.2 M, 0.3 M, 0.4 M and 0.5 M. In addition, concentrated sulphuric acid was used for pre-intercalation of graphite foil.

2.2. Preparation of electrolytes

As seen in Table 1, the required volume of H_2SO_4 was calculated to prepare different electrolyte concentrations of 0.1, 0.2, 0.3, 0.4 and 0.5 M. Then, the required amount of H_2SO_4 was diluted to 1000 mL with distilled water in a 1000 mL volumetric flask. Figure 1 shows the diluted H_2SO_4 solutions for the electrochemical exfoliation of graphite.

Figure 1 The diluted electrolytes were kept in the volumetric flasks; a) 0.1 M H_2SO_4 b) 0.2 M H_2SO_4 c) 0.3 M H_2SO_4 d) 0.4 M H_2SO_4 e) 0.5 M H_2SO_4.

Table 1 Various types of electrolytes and anode configurations of experimental details of electrochemical exfoliation.

No.	Type of electrolyte	Anode	Duration (minutes)
1	0.1 M of sulphuric acid H_2SO_4 diluted solutions	Graphite Foil	40
2	0.2 M of sulphuric acid H_2SO_4 diluted solutions	Graphite Foil	40
3	0.3 M of sulphuric acid H_2SO_4 diluted solutions	Graphite Foil	40
4	0.4 M of sulphuric acid H_2SO_4 diluted solutions	Graphite Foil	40
5	0.5 M of sulphuric acid H_2SO_4 diluted solutions	Graphite Foil	40

2.3. Experimental set-up

A 50 ml of concentrated sulphuric acid was poured into a 250 ml beaker. The rectangular size (2 cm x 4 cm) of graphite foil was clipped to the anode whereas the cooper foil was clipped to the cathode and followed by immersing both anode and cathode into the concentrated sulphuric acid. Both the anode and cathode were connected to a portable DC power supply as shown in Figure 2. In the experiment, the half surface of graphite anode was exposed to the 50 ml of concentrated sulphuric acid H_2SO_4. Firstly, both the graphite anode and copper foil (cathode) were immersed in the concentrated sulphuric acid H_2SO_4 for 20 minutes with 1.6 V to conduct the pre-intercalation of graphite anode in the first step. In the second step, exfoliation and oxidation were carried out. 100 ml of 0.1 M solution was poured into 250 ml beaker. Then, both anode and cathode were transferred into the 0.1 M solution from the previous concentrated sulphuric acid. The exfoliation time allocated for the graphite was 40 minutes with 5.0 V since the small surface area was exposed to the electrolyte. After 40 minutes, the expanded graphite was exfoliated into tiny black pieces which suspended in the solution. This experiment was repeated using the rest of the electrolytes from 0.2 to 0.5M (Table 1). A sufficient amount of graphene can be obtained within that period of time.

Figure 2 Experimental set-up for electrochemical pre-intercalation of graphite anode; a) copper foil (cathode)(black), b) graphite foil (anode)(red), c) concentrated sulphuric acid H_2SO_4 and d) DC power supply.

The exfoliated and oxidized graphene was filtered using filter paper as displayed in Figure 3. Then, the black samples were left to dry temporarily at the filter paper before collected into crucible. The gravity or natural convection oven was utilized to dry all samples for 24 hours at 100 °C. The dried black samples were collected from the crucibles and secured it into a small plastic bag in the form of powder. Finally, the powder of graphene is subjected for SEM, XRD and FTIR characterizations.

Figure 3 The process of filtration of black solution by using filter paper and black samples were collected in crucibles for drying in oven.

3. RESULTS AND DISCUSSIONS

A few methods such as XRD and SEM were used to analyze the properties of all the graphene samples. These approaches were used to investigate the impact of various concentrations of diluted sulphuric acid on the shape and presence of oxygen functional groups in exfoliated graphene sheets.

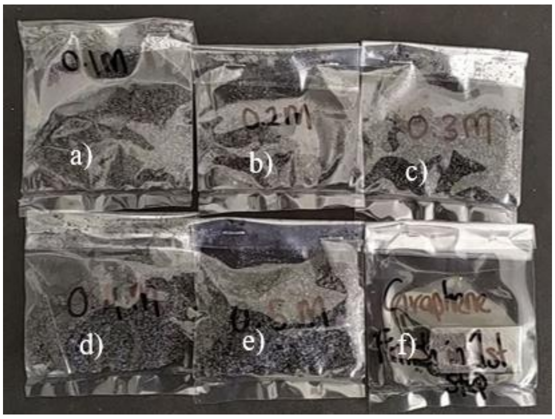

Figure 4 Images of dried graphene flakes: a) 0.1 M b) 0.2 M c) 0.3 M d) 0.4 M e) 0.5 M and f) GIC sample.

3.1. X-ray diffraction (XRD)

In Figure 5, shows sharp XRD patterns peak of all samples at approximately 2θ = 26º, which is close to the diffraction peak of a normal graphite crystalline reported by Guo et al. [8]. Sample A (0.1 M) exhibited a moderate sharp peak at 26.5º in the direction of (002) and an interlayer spacing of 0.3376 nm, which matched the graphite reference pattern (JCPDS no. 00-041-1487). The carbon peak (002) appears due to sulphuric acid exhibits ideal electrochemical exfoliation efficiency of graphite. Among all the samples, one of them exhibits the best crystalline graphite quality due to the high strength of the peak.

Furthermore, sample B (0.2 M) exhibited a comparable peak at 26.87º in the direction of (002) with an interlayer spacing of 0.2553 nm, which corresponded to the graphite reference pattern (JCPDS no. 00-056-0159). Sample B, on the other hand, has the sharpest and highest intense peak as compared to samples A, C, D, and E. Furthermore, a diffraction peak at 26.75º was observed for sample C (0.3 M), which was attributed to the (002) diffraction plane of a graphitic structure with an interlayer spacing of 0.3355 nm (JCPDS no. 01-089-7213). This is the broadest and smallest peak of sample C as compared with other samples. In addition, a graphite peak was observed at 27.3º in sample D (0.4 M). Meanwhile, the diffraction pattern of sample E (0.5 M) revealed a second smaller intensity peak as compared with other samples at 26.9º, with an interlayer of 0.3348 nm (JCPDS no. 00-025-0284). According to the literature, the occurrence of a sharp diffraction peak at 10º suggests the presence of GO because of the existence of oxygen functional groups after graphite oxidation by electrolytes [9]. All the samples tend to have a very low intensity diffraction peak near 10º. The low intensity is due to the insufficient amount of GO phase presented in samples. The low volume of GO may be clarified as follows: during the extended electrochemical exfoliation of graphite at a high voltage of 5 V, the electrolytes were heated. Therefore, a certain amount of the functional groups was removed because of the heating to the sulphuric acid that leads to a low GO level in the samples.

Pei et al. (2018) [10] demonstrated the exfoliation of graphite foil in two steps and found that highly oxidized GO (C/O < 2) was formed successfully when H_2SO_4 with concentration between 40wt.% to 60wt.% of was used as electrolyte. The lowest C/O ratio of 1.5-1.8 was noticed at 50wt.% of H_2SO_4. On the other hand, very low oxidized samples were synthesized by H_2SO_4 with below and above 40-60 wt.%. As compared with highly oxidized GO synthesized by Pei et al. (2018), all H2SO4 that used in this experiment have concentration below this concentration range of 40-60 wt.%. Thus, the GO peak was hardly to be detected by XRD equipment due to the very low amount of GO in all samples.

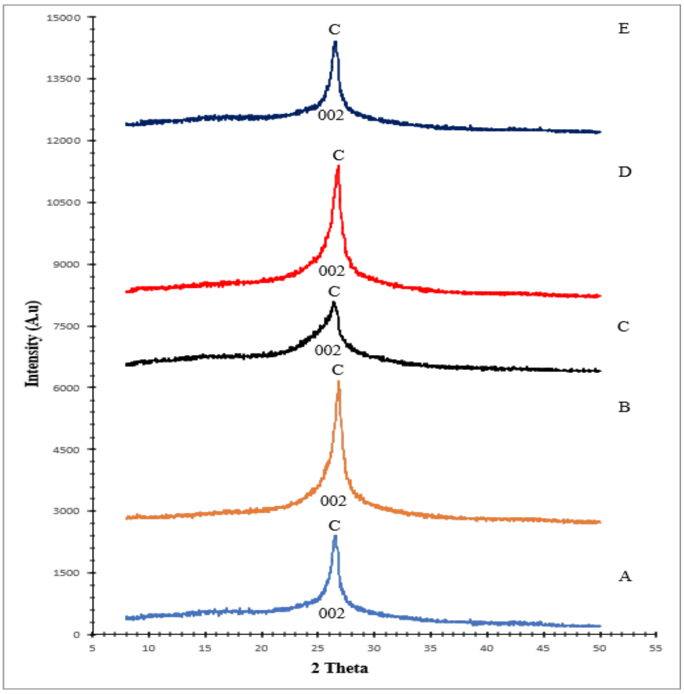

Figure 5 XRD diffraction pattern of the exfoliated graphene samples using different concentrations of diluted sulphuric acid.

3.2. Scanning electron microscopy (SEM)

In way of comparison to the other graphene samples as shown in figure 6, SEM photographs of all samples revealed edge-corrugated sheet structures with large lateral dimension and thin graphene flakes. Thinner structures indicate less stacked graphene flakes, which is typically preferred. The irregular structures and crumpled nanosheets of all samples (A-E) may be attributed to the fact that various parameters were used during the experiment. The graphite precursor was intercalated by anions (SO_4^{2-}), during the electrochemical exfoliation phase, following by the expansion and dissociation of the graphite precursor into graphene flakes after applying a medium voltage of 5V. Furthermore, similar experimental procedures were used to generate samples (A-E), with the exception that various concentrations of dilute sulphuric acid were used for electrochemical exfoliation.

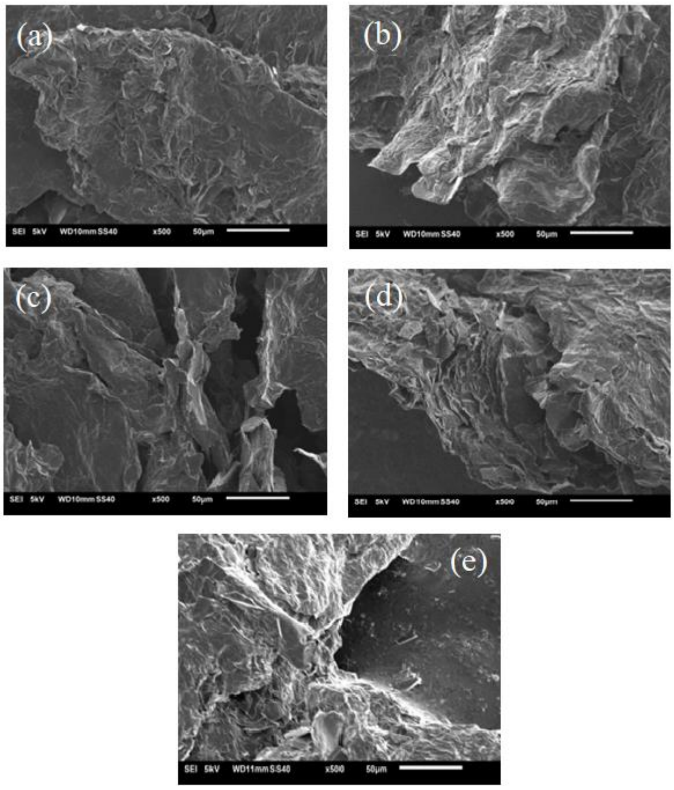

Figure 6 SEM imaging of graphene flakes samples (a) (0.1 M of dilute sulphuric acid), (b) (0.2 M of dilute sulphuric acid), (c) (0.3 M of dilute sulphuric acid), (d) (0.4 M of dilute sulphuric acid) and (e) (0.5 M of dilute sulphuric acid) Left images: x100 magnification and Right images: x500 magnifications.

4. CONCLUSION

XRD revealed the presence of crystalline graphite at approximately 2θ=26º along the distance of (002) in all the samples. Sample B (0.2 M diluted sulphuric acid) showed highly crystalline graphite because it had the most extreme peak at 26º as comparison to the others. In addition, sample D (0.4 M diluted sulphuric acid) had the second highest diffraction peak amplitude. Furthermore, the intensities of diffraction noises at approximately 10º, which corresponded to the presence of GO in all samples A-E, were very mild, owing to the removal of oxygen functional groups by high temperature during electrochemical exfoliation. From the aspect of morphologies, all the samples revealed edge-corrugated sheet structures with large lateral dimensions and thin graphene flakes while thinner structure indicates less stacked graphene flakes, which is typically preferred.

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