The effect of voltage bias on the yield and electrical properties of Exfoliated Graphene synthesized via electrochemical method

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Abstract. Graphene has been gaining immense attention from scientists over the world for its exceptional properties, which makes it promising for several applications such as energy storage, electronic devices, and biomedicine. Graphene synthesis via the electrochemical exfoliation route offers a cheap, simple, eco-friendly, and scalable process for industrial purposes. In this work, the effect of voltage bias during electrochemical exfoliation on the electrical properties and yield of the obtained exfoliated graphene (EG) was studied. Graphite sheet as raw material was pre-treated by immersing it into H₂SO₄/H₂O₂ mixture before the electrochemical process. By applying the optimum voltage of 10 V, the electrochemical method was able to produce EG with yield as high as 40.95% in a relatively shorter time. Moreover, EG also demonstrated the highest electrical conductivity of 25.45 S/cm.

1. Introduction

Graphene is a two-dimensional material that composes other carbon allotropes such as graphite, carbon nanotube, and fullerene. This material consists of sp²-hybridized carbon atoms bonded in a hexagonal honeycomb lattice that forms a single thin layer [1]. Thanks to the exceptional properties of graphene, such as superior electrical conductivity, wide surface area, high modulus Young, and high transparency, graphene can be utilized in various applications [1]. The high transparency, exceptional elasticity, and excellent electrical conductivity properties, make graphene suitable for flexible and transparent electronic devices, such as foldable smartphones and displays [2]. Meanwhile, its large surface area and high electrical conductivity are essential for battery and supercapacitor applications, as it can provide active sites for ionic or charge storage and transport [3]. Whereas, in the medicinal and healthcare area, the functionalized graphene can be utilized as a biosensor and drug delivery material [4].

The quality and quantity of graphene are influenced by the synthesis method. Several methods are widely engaged to synthesize graphene such as micromechanical cleavage, chemical vapor deposition (CVD), epitaxial growth, reduction of graphene oxide, liquid-phase exfoliation, and electrochemical exfoliation. Micromechanical exfoliation is the first introduced method for isolating graphene from bulk graphite. This method could obtain high quality of graphene, but the yield is very low, which makes it
only suitable for research necessity [5]. Meanwhile, CVD and epitaxial growth can also produce good quality graphene, however high cost for substrate preparation and the subsequent process hinder their application for mass production [6]. Large scale production graphene can be obtained via the reduction of graphene oxide. However, highly defected graphene is often yielded from the incomplete restoration of sp2-hybridized carbon atoms after the reduction of oxygen functionalities [7]. Liquid phase exfoliation is an alternative method for synthesizing low defected graphene with the low cost through sonication or shearing of bulk graphite in an appropriate solvent. Nevertheless, the obtained graphene has a wide range of sizes and thickness that leads to an inhomogeneous product of graphene [8].

On the other hand, electrochemical exfoliation offers several advantages such as cheap, simple equipment preparation, and eco-friendly route to synthesize graphene [9]. This method also permits the tunability of graphene properties through the optimization of several parameters, such as voltage bias, electrolyte concentration, graphite precursor, and exfoliation time [10]. Hofmann et al. reported that the magnitude of the applied potential and duration of electrochemical exfoliation could affect the size, thickness, and functionalization of exfoliated graphene [11]. In other literature, the higher voltage bias was reported to produce a mixture of graphene and graphene oxide products. Whereas the application of lower bias tends to produce graphene only in the range of 2.5 – 6 V. It was also reported that the applied voltage also influences the average number of graphene layers in the sample [12]. Zhang et al also investigated the effect of voltage bias on the yield of graphene produced by electrochemical exfoliation using a graphite rod as the precursor and molten salt as the electrolyte. They reported that the yield of graphene increased with the decreasing of the applied potential [13]. Therefore, it can be concluded that the voltage bias is one of the critical parameters that should be optimized to obtain graphene with the desired quality and quantity.

In our previous work, the pre-treatment of graphite precursor into H2SO4/H2O2 mixture was found to be able to increase the electrical conductivity of the obtained exfoliated graphene [14]. Herein, the effect of applied voltage bias during electrochemical exfoliation of the pre-treated graphite sheet was studied. This study was conducted by considering two parameters, i.e., electrical conductivity and yield of the obtained exfoliated graphene (EG).

2. Methods
Prior to pre-treatment, the H2SO4/H2O2 solution with the volume fraction of 95:5 was freshly prepared by mixing the required amount of H2SO4 98% (Smartlab Indonesia) and H2O2 50% (Bratachem). A raw graphite sheet (Hi-tech Carbon, Ltd.) was immersed in the H2SO4/H2O2 95:5 solution and subsequently subjected to an electrochemical exfoliation by applying variety positive biased voltages of 5 V, 10 V, and 15 V. During the process, a platinum wire was set as a counter electrode and ammonium sulfate (Pure Analysis, Merck) 0.1 M was employed as the electrolyte. The electrochemical exfoliation was conducted until the current cannot be measured any longer (I = 0 A). The electrochemical exfoliation product was washed by DI water and ethanol until pH ~ 7, then followed by drying at 60 °C for 3 hours. After that, the dried samples were dispersed in 1 mg/mL and were subjected to ultrasonic treatment (68 W). Centrifugation of the resulted dispersion was conducted 1000 rpm for 20 minutes to remove the unwanted un-exfoliated product. The top parts of the dispersion or supernatant were then dried at 80 °C for subsequent characterization.

The yield was calculated using equation (1) by comparing the weight of the dried supernatant with the total weight of the dried supernatant and the precipitate of EG dispersion after centrifugation, which was considered as an exfoliated and unexfoliated product, respectively [13]:

\[
Yield = \frac{{\text{mass of supernatant}}}{{\text{mass of supernatant} + \text{mass of precipitate}}} \times 100\%
\]  

(1)

The four-point probe method was used to measure the electrical conductivity of samples in the pelleted form, which connected to DC source (R6240A, Advantest) and multimeter (2100 Series: 6½-digit USB multimeter, Keithley). Meanwhile, the morphology of the samples was observed using Scanning Electron Microscope (SEM, SU3500, Hitachi) at 15 kV.
3. Results and Discussion

Figure 1 exhibits the images of the raw graphite sheet before and after pre-treatment with the H$_2$SO$_4$/H$_2$O$_2$ mixture, which shows a thin and smooth graphite sheet before pre-treatment underwent expansion after 5 min of pre-treatment process. The expansion could be caused by oxygen gas development during the H$_2$SO$_4$/H$_2$O$_2$ intercalation into graphite interlayer, which may facilitate the entrance of water molecules or electrolyte ions in the following electrochemical exfoliation process.

![Graphite sheet images (a) before and (b) after pre-treatment in H$_2$SO$_4$/H$_2$O$_2$ mixture.](image)

By applying positive voltage into the graphite sheet, the nucleophilic water molecules will be attracted to graphite edges and form oxygen functionalization. Water molecules is then oxidized into O$_2$ gases that will give force to induce exfoliation of graphite layers [7,15]. Table 1 shows the exfoliation time required when different voltage bias was applied. From the table, higher potential accelerates the rate of exfoliation process, which results in the reduction of required time for completing the exfoliation process.

| Voltage Bias (V) | Exfoliation Time (min) |
|------------------|------------------------|
| 5                | 358                    |
| 10               | 170                    |
| 15               | 90                     |

Yield and electrical conductivity are two of several important parameters that should be considered to assess the quality of the exfoliation process of graphite sheet for large scale production. Figure 2 shows the yield and electrical conductivity of the EG obtained after the electrochemical exfoliation process employing different voltage bias. As can be seen from Figure 2, the highest yield of 40.95% was obtained during the electrochemical exfoliation applying 10 V bias, whereas the low yield of EG had resulted when lower voltage bias (5 V) was used. It seems that at lower voltage bias, the current density was not enough for inducing the exfoliation process. However, the application of higher voltage bias (15 V) also seems to cause the lower yield produced during electrochemical exfoliation. The higher voltage developed the harsh electrochemical exfoliation which caused the pre-treated graphite sheets to fall apart easily into large un-exfoliated EG fragments, thus lowering the yield of exfoliation [16].
The result of electrical conductivity measurement also suggested that 10 V is the optimum voltage bias that should be applied during electrochemical exfoliation of the pre-treated graphite sheets. By applying 10 V of voltage bias, the process could produce EG with the highest electrical conductivity value of 25.45 S/cm. On the other hand, when 15 V bias was applied, the electrical conductivity decreases significantly. As reported previously, the higher voltage bias increases the rate of nucleophilic reaction causing the formation of higher oxygen functionalities [12]. It is widely known that the higher oxygen content inhibits electron transport in EG caused by the transformation of highly conductive sp²-hybridized carbon atom bonds to lower conductive sp³–hybridized carbons [17]. At lower voltage bias (5 V), however, the electrical conductivity of the produced EG was also lower than the sample produced at 10 V. This phenomenon is allegedly caused by the increases the time required for the overall electrochemical process, as the prolonged exposure of graphite electrode to electrolyte may cause the higher chance of oxygen functionalities formation [18].

Figure 3 demonstrates the SEM images of graphite sheet and EG obtained after electrochemical exfoliation at the optimum voltage bias, i.e., 10 V. While graphite sheet shows thick and smooth morphology (Figure 3 (a)), the obtained EG reveals a thinner morphology (Figure 3 (b)) indicating that the delamination of graphite sheet has been successfully carried out. This study demonstrated that employing the optimum voltage bias during electrochemical exfoliation is useful to produce a high yield of thin layer EG with excellent electrical conductivity. Thus, the EG produced using this method can be applied in several devices which require high surface area and excellent electrical conductivity such as battery and supercapacitor.
Figure 3. SEM image of (a) Graphite sheet, (b) EG obtained after electrochemical exfoliation by applying 10 V voltage bias.

4. Conclusion
The effect of voltage bias on the yield and electrical properties of EG of the pre-treated graphite has been studied. The optimum voltage bias is 10 V, with the yield and electrical conductivity of 40.95% and 25.45 S/cm, respectively. Graphite sheet has been successfully delaminated into fewer layers, as confirmed by SEM characterization. This study is beneficial to produce a high-quality EG with scalable quantity for various applications, including for the energy storage devices.

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