Electrochemical Exfoliation of Pencil Graphite Core by Salt Electrolyte

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Abstract. Exfoliation of pencil graphite core throughout electrolysis process is considered as one of the simple and friendly method to synthesis graphene from graphite. In this research, sodium sulphate (Na₂SO₄) was used as an electrolyte to investigate the effect on pencil graphite core with different grades for exfoliation process. Pencil graphite core was applied as both anode and cathode electrodes and exposed in 0.1 mol of Na₂SO₄ solution and followed with sonication in DMF solution. The morphology of exfoliated graphite was characterized by FESEM and TEM image. It was found that higher pencil grade produced more exfoliated powder as compared to lower grade pencil, and morphology investigation revealed that the exfoliated powder can produced graphene in nanoplatelet forms.

1. Introduction

Recently, synthesis of graphene had become one of popular topic in material science due to its excellent mechanical and thermal properties, as well as electric performance for future advanced technology application[1]. The existence of graphene oxide (GO) and reduced graphene oxide (rGO) brought up a great deal in future graphene applications such as corrosion inhibitor, conductive ink, solar cells, lithium ion batteries, marine application and many more[2–4].

Various techniques have been studied and implemented are among the famous one to produce graphene[5–9]. Four major techniques as epitaxial growth, mechanical cleavage, chemical method and chemical vapor deposition (CVD) [10]. The failure of mechanical cleavage of the past has resulted in a new method of methodology in graphene synthesis [11]. Similarly with epitaxial growth and CVD also contributed greatly to high quality graphene production[12][13]. CVD is also used to transfer graphene into other substrate for device applications[14,15]. It has become a necessity in industrial applications to produce large amounts of graphene[16]. Furthermore, the method for generating large-
scale graphene is the decomposition of the chemical method. Unfortunately, those methods bring its own disadvantages. Cleavage exfoliation produce less and low quantity of graphene, epitaxial growth gives intermittent effect, CVD process required an expensive cost and difficult to transfer graphene and lastly, chemical method involved harmful effect[17–21]. In other hand, a new and simple process has been introduced recently as a safe and friendly process to produce graphene. In this process, a salt solution can be used as an electrolyte, and within a simple and fast process, graphene can be synthesized [22].

Furthermore, commercially available pencil leads are commonly available as hetero-structured graphite materials[23]. Moreover, pencil graphite core is an intercalated compound with clay particles (majorly silica and a few metal oxides) in conductive graphite[24–26]. However, such pencil graphite are further categorized on the ratio of graphite and clay from 9h to 9b, where h and b stand or hardness (amount of clay) and darkness (amount of graphite), respectively[24–28]. For instance, the higher grade of pencil represents higher contain of graphite percentage[28]. In this work, electrolysis process is applied to synthesis graphene from pencil core by using salt electrolyte. The effect of pencil grade is investigated in the production of exfoliated graphite powder.

2. Experimental Procedure

2.1 Sample preparation
A commercially available pencil (Stein, Germany) from different types of grades; B, 3B and 6B was used. Figure 1 shows an image of pencil purchased and the pencil core which were separated from its wood holder. This pencil graphite core was installed as anode and cathode electrode for electrochemical processes. The length for every graphite pencil cores were same but its diameter was different as shown in Table 1.

![Figure 1](image_url)
Table 1. Dimension size of pencil core

| Pencil Grade | Diameter (mm) | Area of Pencil Graphite Core (mm\(^2\)) | Length of Immersion (mm) |
|--------------|---------------|----------------------------------------|--------------------------|
| B            | 2             | 56.56                                  | 90                       |
| 3B           | 2.5           | 70.70                                  | 90                       |
| 6B           | 3.6           | 112.86                                 | 90                       |

2.2 Exfoliation process
The two electrodes were immersed inside 0.1 M of Na\(_2\)SO\(_4\) solution. 10 V of bias voltage is supplied and the exfoliation process was run for 1 hour. The experiment setup shown in Figure 2. The exfoliated products that floated on top of the electrolyte were taken out and dried by vacuum filtration. The powder was sonicated di-methylformamide (DMF) for 2 hours. After that, the sonicated solution is filtered again by vacuum filtration.

![Figure 2. Electrochemical exfoliation process.](image)

2.3 Characterization
The morphology of the powder was investigated by using field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The FeSEM model type is JSM-7800F. In FESEM, the powder was put barely on carbon tape without any platinum or gold coating but in TEM, the powder is sonicated again in ethanol for 2 hours and placed on copper grid.

3. Results and Discussion

3.1 Powder obtained
Figure 3 shows the image of dried powder after sonication process using vacuum filtration. After finished exfoliation, the weight of before and after sonication of powder obtained has been taken as shown in Table 2.
Figure 3. Exfoliated powder is dried up.

Table 2. Weight of powder before and after sonification.

| Pencil Grade | Weight Of Powder in Gram (Before Sonification) | Weight Of Powder in Gram (After Sonification) | W/A (mg/mm²) |
|--------------|-----------------------------------------------|-----------------------------------------------|--------------|
| B            | 0.0501 mg                                      | 0.0300 mg                                      | 8.86 x 10⁻⁴  |
| 3B           | 0.0872 mg                                      | 0.0762 mg                                      | 12.33 x 10⁻⁴ |
| 6B           | 0.1624 mg                                      | 0.1052 mg                                      | 14.39 x 10⁻⁴ |

The Figure 4 shows graph of weight of pencil graphite powder against pencil grade. It shows the quantity of powder produced by 6B pencil grade is much higher compared to the B and 3B pencil grade. Therefore, it proved that the higher the pencil grade, the bigger the weight of powder exfoliated. It is because of the higher grade of pencil represents higher contain of graphite percentage[28]. Instead of that, the research was further investigated on higher pencil grade which is 6B pencil graphite core for characterization on FeSEM and study the effect on different concentration of Na₂SO₄ electrolyte.

Figure 4. Graph of powder obtained from electrochemical process after and before sonification with deionized water.
3.2 Concentration of \( \text{Na}_2\text{SO}_4 \) on 6B pencil rod

After tabulated the weight obtained from exfoliation of pencil graphite core, it shows 6B is heaviest weight obtained. Therefore, study the effect on 6B grade pencil core in different types of concentration is investigated. Table 3 shows the data tabulation of the results. It proved higher concentration of electrolyte can affected the exfoliation process. This data shows the result of half an hour of electrochemical process only.

Table 3. Result obtained through electrolysis of three different pencil graphite core of 6B in half an hour

| Concentration \( \text{Na}_2\text{SO}_4 \) | Weight of Powder (g) |
|------------------------------------------|----------------------|
| 0.1 mol                                  | 0.0132               |
| 1 mol                                    | 0.5373               |

Effect on \( \text{Na}_2\text{SO}_4 \) with different concentration shows 1 mol has increased the weight of graphite powder compared to 0.1 mol of concentration. This is due to sulphate ion inside the electrolyte brought a great performance in exfoliating graphite powder from the pencil rod. The higher the concentration, the higher the amount of sulphate ion inside the electrolyte.

3.3 Characterization of GNP and sonicated pencil graphite powder

The morphologies of the purchased GNP (from Sigma Aldrich) and sonificated pencil graphite core were investigated using FeSEM. The FeSEM images of GNP and pencil graphite powder (synthesized 1 M of \( \text{Na}_2\text{SO}_4 \)) are shown in Figure 5 (a) and (b) respectively. The purchased of GNP were much thinner and like flakes in shape compared to sonificated pencil graphite powder. Eventhough sonificated pencil graphite powder shows like flakes shape similar as GNP but the layer size is much thicker a bit and still in group formation. It still resulted in graphite powder. Therefore, sonificated pencil graphite powder need be more improvement by using different types of electrolyte and need to have longer sonification process as reviewed by U.R. Farooqui et al.[29]

![Figure 5. (a) Purchased GNP and (b) 6B pencil graphite core image after sonification with dmf.](image-url)
The morphology of pencil graphite core is continued in TEM image as shown in Figure 6. The image had been zoom for 200 nm magnification and proved that sonicated 6B pencil graphite had similar image of graphene layer. The image shown layers of potential graphene obtained.

![TEM image of 6B pencil graphite core powder image after sonification with DMF.](image)

**Figure 6.** TEM image of 6B pencil graphite core powder image after sonification with DMF.

4. **Conclusion**
A simple and cost-effective approach to synthesize graphene from pencil graphite core was successfully conducted by applying electrolysis process with Na$_2$SO$_4$ salt electrolyte. The higher the pencil grade, the more powder of graphite can be obtained. According to FESEM and TEM results, a combination of electrolysis and sonication has successfully graphene in platelet forms.

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