Graphene Oxide from Carbon Rod Waste

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Abstract. Carbon rods extracted from Zn-C primary battery waste was used as raw material for graphene oxide (GO) synthesis. The synthesis used a modified Hummers method by providing potassium permanganate-sulfuric acid as the oxidizing agent. XRD analysis confirms a significant change between the graphite waste pattern and the produced graphene oxide pattern. A major peak at 2θ 27° which present in the graphite waste pattern is disappeared after it converts to the product, as well as a broad peak under 25° referring the presence of amorphous carbon. A broad peak at low angle of 12.02° dominantly present in the prepared GO pattern as a characteristic peak of GO. Meanwhile, some small peaks at 2θ of 17.76°, 28.58°, and 37.28° confirming the presence of manganese oxide which was used as oxidizing agent. A sharp peak at 1700 – 1500 cm⁻¹ in the FT-IR spectrum indicates the presence of –C=O group, and at 1600 cm⁻¹ refers to –C=C group. It confirms that this research has produced the targeted GO. Even though, the purity is need to be enhanced by removing the rest of oxidizing agent that still exist in the material.

1. Introduction
Graphene has the excellent mechanical, electrical, thermal, and optical properties. It can be produced by micro-mechanical exfoliation of highly ordered pyrolytic graphite, epitaxial growth, chemical vapor deposition, and the reduction of graphene oxide (GO). GO itself can be produced from graphite as raw material which is inexpensive. GO also can easily produce a stable aqueous colloid for large scale graphene production or reduced GO (rGO) by a simple solution process [1]. Graphene oxide contains a range of reactive oxygen functional groups allowing this GO to be a good candidate for some applications through chemical functionalizations [2]. GO is formed by oxidizing graphite by a strong oxidation agent to exfoliate the flakes of graphitic stack into mono-and few layer sheets [3].

Hummer’s method is known to successfully produce GO from graphite by mixing it with potassium permanganate (KMnO₄) and concentrated sulfuric acid (H₂SO₄)[4]. However, the products may show strong variance, depending not only on the particular oxidants used, but also on the graphite source and reaction conditions [2]. Therefore, this research used a graphite extracted from Zn-C primary battery waste. It is known that waste batteries increase year by year due to high demand on the portable electronic devices. More than 80 % of batteries sold in Europe are a primary battery, in which the large majority of primary batteries are alkaline and zinc carbon batteries [5]. Many of the components of these batteries could be recycled, avoiding the release of hazardous substances to the environment. These will contribute to the improvement of environment quality. Zinc carbon battery is

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a primary or disposable battery in which a carbon rod is inserted into electrolyte mixture and serve as a cathode. The carbon rod is a good electronic conductor with inert properties. An effort to reuse those carbon rod waste became another reason to use it as a raw material for graphene oxide synthesis or other well synthesized carbonaceous materials.

2. Experimental
The graphene oxide was synthesized by pouring a 69 mL of high concentrate sulfuric acid in a three necks bottle and the bottle was dipped into an ice bath and adjusted the temperature at around 0 – 3°C. The 1.5 g of graphite powder was poured into the sulfuric acid solution, and followed by 6 g of Kalium permanganate powder under stirred condition. The temperature must be kept under 15 °C. After the mixture became homogeneous, the stirring then to be continued for 1 hour under 35 °C. a 100 mL of distilled water was then poured into the mixture. The reaction released heat due to the exothermic process. Therefore, the temperature must be kept under 100 °C for 30 minutes under stirred condition. After 30 minutes, the mixture was poured into 300 mL of distilled water. The oxidation reaction was terminated by add 10 mL of hydrogen peroxide 10% until the mixture turn into yellow suspension.

The suspension was leached with HCl 5% to remove the sulphate ions, and then continued by centrifugation and water leaching. The precipitate as resulted by centrifugation was dried at 60 °C in the oven. After dry, the powder was collected to be characterized. X-ray diffraction (Bruker D8 X-ray diffraction, Cu Kα source at λ of 1.5406 Å) analyzed the diffraction pattern of the prepared materials at 2θ = 10-80°. The diffraction pattern then compared with the diffraction pattern of graphene oxide. X-ray Fluorescent analysis (Bruker S2 Ranger) was conducted for elemental analysis. Meanwhile, the change in the functional group at before and after the reaction was tracked by doing FTIR analysis (Prestige-21 Shimadzu, 4 cm⁻¹ of resolution) at the wave number range of 4000- 400 cm⁻¹.

3. Result and Discussion
The XRD pattern of the waste graphite as raw material is described in Figure 1, in comparison with the diffraction of the standard graphite ICSD/#76767, and also with the diffraction pattern of the product of reaction.
Figure 1 shows a significant molecular change between the graphite waste pattern and the product of synthesis. The major peak in graphite waste is at $2\theta = 27^\circ$. Meanwhile, when the graphite waste pattern is compared to the standard graphite diffraction ICSD #76767, the major peak is similar, at $2\theta = 27^\circ$, with some small peaks at 20 of 42°, 44°, 50°, 55°, 60°, and 77°. Meanwhile, a broad peak at 20 below 25° indicates the presence of amorphous carbon [6]. A peak at 20 21.45° also present in the graphite waste diffraction which is not present in the standard graphite diffraction. This peak indicates the presence of impurities. The indication is silica, which was present when the graphite waste powder crushed with other reagent in a porcelain mortar. The peaks itself are in agreement with Si standard diffraction ICSD#81382 (Figure 2). The diffraction pattern of the prepared material is compared to the diffraction pattern of graphene oxide found by other researchers in Figure 2[7],[8]. The graphene oxide by Chen [7] shows a characteristic peak at 20 of 14.6°. Meanwhile, the graphene oxide pattern by other researcher shows a peak at 20 12.02°. Those patterns are also in agreement with a standard diffraction found in a graphite when an oxygen functionality is introduced into the graphite, i.e., a peak present at around 2010.3° [9].

Some peaks at larger 2theta might be some impurities as it was confirmed by Figure 6, by comparing the XRD pattern with standard diffraction of MnO2, SiO2. Peaks at 20 17.76°, 28.58° and 37.28° are match well with MnO2 standard diffraction ICSD#73363. Manganese dioxide might be produced from the remaining oxidation reaction. Meanwhile, silica is the oxide contains in the graphite waste.

Figure 3. XRD patterns of the prepared GO (a) in comparison with GO XRD pattern (b)(c)
Some peaks at larger 2theta might be some impurities as it was confirmed by Figure 6, by comparing the XRD pattern with standard diffraction of MnO$_2$, SiO$_2$. Peaks at 20 17.76°, 28.58° dan 37.28° are match well with MnO$_2$ standard diffraction ICSD#73363. Manganese dioxide might be produced from the remaining oxidation reaction. Meanwhile, silica is the oxide contains in the graphite waste. XRF analysis also confirms the presence of MnO$_2$ in the prepared GO, among other minerals that may also exist in the material. Even though, their characteristic peaks do not appear in the diffraction pattern, probably due to their amorphous phase. The XRF result is depicted in Table 2. Due to XRF instrument measure the wavelength of individual fluorescence emission after X-ray radiation, therefore only a specific weight element that able to emit X-ray radiation as a fluorescence light. Carbon, C, is a light element that does not emit such fluorescence light.

Table 1. Elemental content in the prepared GO as analyzed by XRF

| Formula | Z | Content (%) |
|---------|---|-------------|
| MnO     | 25 | 62.08       |
| Na$_2$O | 11 | 14.34       |
| SO$_3$  | 16 | 5.36        |
| K$_2$O  | 19 | 4.27        |
| SiO$_2$ | 14 | 3.63        |
| MgO     | 12 | 2.69        |
| CaO     | 20 | 2.09        |
| Al$_2$O$_3$ | 13 | 1.58       |
| Trace element | 3.96 |

Figure 4. The XRF spectrum of the prepared material
FTIR analysis spectrum as described in Figure 8, shows some vibrational changes. The graphite waste shows a sharp peak at 3500 – 3250 cm⁻¹ indicating the presence of OH vibration. The OH vibration might coming from the adsorbed H₂O molecules. FTIR spectrum of the prepared GO shows a broad peak at 3000 cm⁻¹ indicating that the OH vibration is not only from the adsorbed H₂O molecules, but also from the specific OH groups contained in the GO, as it can be seen in Figure 10 the presence of OH group in a GO compound. Graphite waste does not provide a peak at 1700 – 1500 cm⁻¹ as it is provided by GO compound. The peak confirms the presence of carbonil, C=O vibration as a functional group in a GO. The C=C peak is also detected at a round 1600 cm⁻¹. Meanwhile, the presence of Mn is confirmed by a sharp peak at around 500 cm⁻¹, as the characteristic peak also appear in the FTIR spectrum of dispersed Mn in acetone [10].

4. Conclusion
Analysis of the prepared material indicates the production of graphene oxide (GO), even though the material still consist some impurities dominated by Mn that possibly remains from the oxidation agent. Therefore, the effort to purify the graphite waste as raw material is required for this GO synthesis, as well as the requirement to purify the prepared GO after production.

Aknowledmengement
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