

Effects of Synthesis Method on Electrical Properties of Graphene

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Abstract. The aim of this study is to achieve the highest reduction capability and complete reductions of oxygen from graphene oxide (GO) by using different type of chemical methods. The modification of Hummer's method has been proposed to produce GO, and hydrazine hydrate has been utilized in the GO's reduction process into graphene. There are two types of chemical method are used to synthesize graphene; 1) Sina's method and 2) Sasha's method. Both GO and graphene were then characterized using X-Ray Powder Diffraction (XRD) and Fourier Transform Infrared Spectrometry (FT-IR). The graph patterns obtained from XRD showed that the values of graphene and GO are within their reliable ranges, FT-IR identified the comparison functional group between GO and graphene. Graphene was verified to experience the reduction process due to absent of functional group consist of oxygen has detected. Electrochemical impedance spectrometry (EIS) was then conducted to test the ability of conducting electricity of two batches (each weighted 1.6g) of graphene synthesized using different methods (Sina's method and Sasha's method). Sasha's method was proven to have lower conductivity value compare to Sina's method, with value of $6.2\text{E}+02$ S/m and $8.1\text{E}+02$ S/m respectively. These values show that both methods produced good graphene; however, by using Sina's method, the graphene produced has better electrical properties.

1. Introduction

Graphene oxide (GO) consists of oxygenated graphene sheets with oxygen-containing functional groups on their basal planes and edges. Thus, GO shows excellent hydrophilicity, strong chemical activity, and uniformity of dispersion in water, making it more easily to be handled and deposited on membrane. A successful use of GO ceramic hollow fiber composite membrane has been recently reported for dehydration of dimethyl carbonate and high water flux is obtained [6]. It is also reported that membranes made with pure GO exhibited a lot of special properties for separation due to their 2D channels, hydrophilic surface as well as the defects on GO sheets [7]. In this work, the graphene oxide membrane was synthesized and deposited onto the alumina hollow fibre substrate using a vacuum assisted technique. The performance of the membrane to treat oily wastewater was then investigated. Graphene, a one-atom thick planar sheet of sp^2 bonded carbon atoms packed in a honeycomb lattice, is considered to be the mother of all graphitic materials like fullerenes, carbon nanotubes, and graphite [1]. Graphene also has been known for its ability to conduct an electricity and good mechanical



properties[2-4]. It also known for its zero band gap properties that lead to good conductivity properties for graphene.

This study is conducted to synthesis graphene oxide by using modified Hummer's method [3][4]. This modified method is used as it is simpler and less harm to environment. After that it will be followed by an experiment that to carry out reduction of graphene oxide to synthesis graphene with different type of chemical method based on Sina's method [3] and Sasha's method [4]. Both methods using hydrazine hydrate as reducing agent which is the most widely used reducing agent as a way of control to reduce GO [5]. Preparation of graphene via chemical is found approximately around 70 years before, where this method is being widely used at the moment. Transformation of graphene oxide to graphene can be observed clearly through colour change of the mixture from brown (graphene oxide) to black (graphene) [3][6]. Next, characterization analysis was conducted to investigate which method could synthesis a good graphene.

2. Experimental

2.1 Preparation of Graphene Oxide (GO)

Graphene Oxide was prepared from graphite flake (Sigma Aldrich) using modified Hummers method [3][4][7]. 5 g of graphite flake (Sigma Aldrich) was added with 2.5 g sodium nitrate (NaNO_3) into 1000ml beaker. 200ml of sulfuric acid (H_2SO_4) was then added into solution. Solution was stirred for 1 hour. 30g of potassium permanganate (KMnO_4) was added slowly within 2 hours at temperature was maintained below 15°C . The solution was keep on stirred at room temperature for 12 hours after that. Solution was heated till 70°C for 2 hours before added 100ml of distilled water slowly. Temperature was increased up to 90°C then and stirred for 1 hour. 100ml of water was added again slowly before 30ml of hydrogen peroxide (H_2O_2) was added. GO solution then washed with acidic hydrochloric acid (36%, Merck). GO solution centrifuged by 1000 rpm in 30 minutes and dried in oven at 70°C to gain GO in (solid) thin film form.

2.2 Reduction of Graphene Oxide using Sina's Method

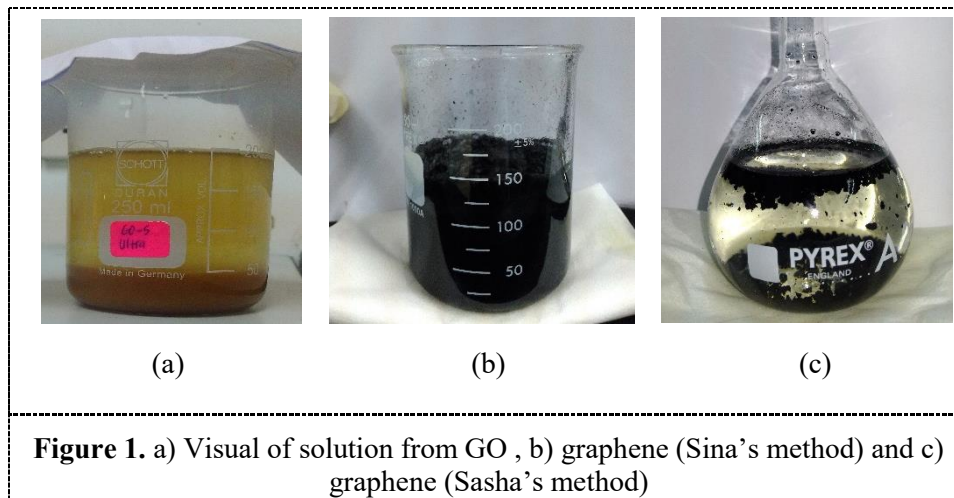
GO solution was prepared by dissolving 10 mL of hydrazine hydrate (80%, Merck) in 100 mL of distilled water. The solution then was added slowly into GO solution at room temperature. Reduction process then conducted at 95°C for 1 hour. Resultant of black precipitate was filtered by cellulose filter paper. 1M of hydrochloric acid (36%, Merck) used to wash filtered precipitate for neutralized the pH value. Those precipitate was dried in the oven for about 3 hours with temperature at 70°C to obtain graphene powder.

2.3 Reduction of Graphene Oxide using Sasha's Method

100 mg GO powder was added into 250 mL round bottom flask. 100 mL of distilled water then was added to dissolve GO powder into GO solution. GO solution then was sonicated using ultrasonic bath cleaner for 45 minutes (till the dispersion is clear). 1 mL of 32.01 mmol hydrazine hydrate (80%, Merck) was prepared and added into the solution. Solution was left in 100°C of oil bath for 24 hours. Precipitate from the solution was filtered to isolate it. 100 mL of distilled water and 100 mL was used to wash precipitate for three times. Precipitate was dried in oven for 3 hours with 70°C to obtain graphene powder.

2.4 Characterization Test

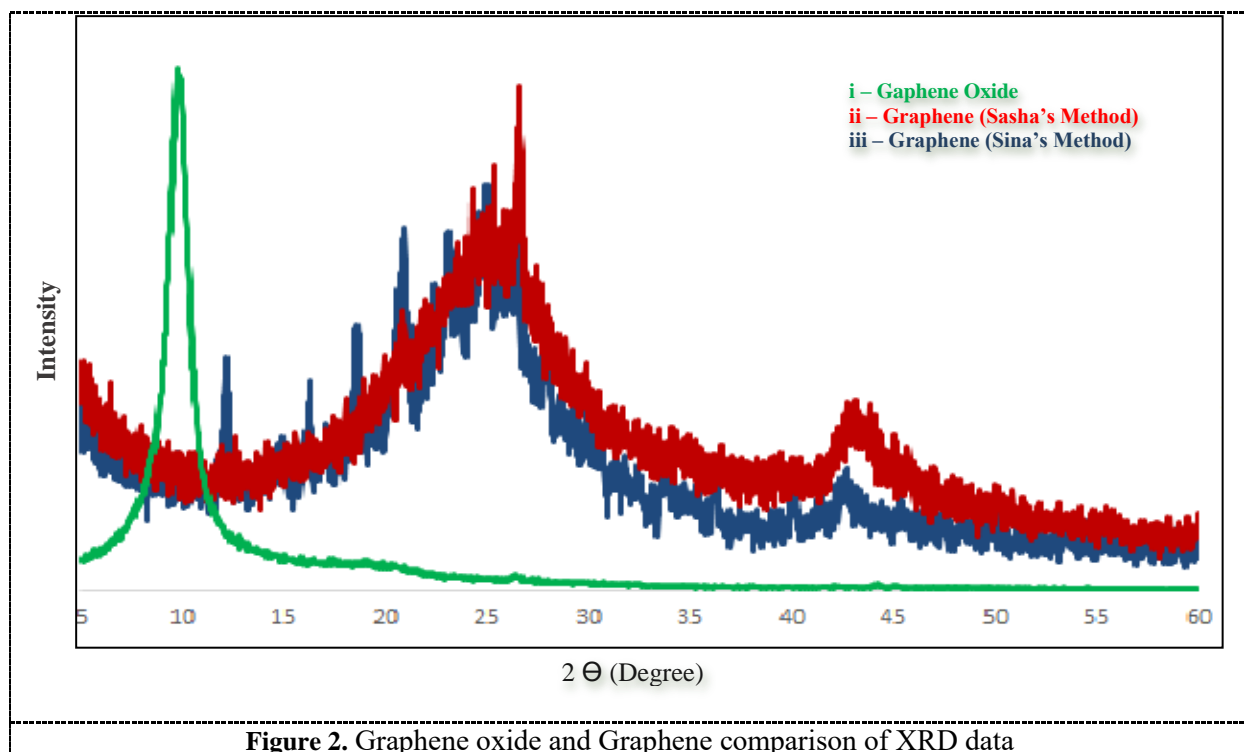
This characterization test is conducted to identify properties for each GO and graphene synthesis. XRD test is conducted using (XRD Sigma 3-18K), with range angle from 5° till 60° , at 2 minute for each angle. Functional group data for each material was gained from Fourier transform infrared (FT-IR) study on the GO and graphene powder by (FTIR Spectrum One). FT-IR was performed over the wave number range of $4000\text{--}500\text{ cm}^{-1}$ for each sample. Electrochemical impedance spectrometry (EIS, HIOKI 1) was conducted at room temperature then to measure conductivity for each GO and graphene. The test was implemented $V = 1.00\text{ V}$ with auto range and normal speed as it perimeter.



3. Results and Discussions

3.1 XRD Analysis

Graph pattern for each GO, graphene (Sina) and graphene (Sasha) is analyze to identify each (d-spacing) and peak value for 2° (degree). XRD pattern of GO and graphene by Sina's and Sasha's method are presented in Figure 2. It clearly showed that typical broad peak position for GO was $2^\circ = 9.76^\circ$ (d-spacing $\sim .0905$ nm). Compared with GO, both graphene shifted to higher 2° angles; ii - 26.58° (d-spacing ~ 0.335 nm) and iii - 24.88° (d-spacing 0.358 nm). It was convinced that there was a decrease in the average interlayer spacing of both graphene based on d-spacing values [5]. Furthermore, from the broaden peak of graphene and lower d-spacing compare to GO, it showed (sp^2 carbon) reestablished during reduction due to removal of oxygen-containing functional groups and the stacking of graphene layers. This proved formation of few layer graphene [8].



3.2 FTIR Analysis

Figure 3 represent FT – IR spectroscopy of the GO and graphene samples. From the FT – IR spectra of GO it showed that the absorption bands corresponding to C – H deformation vibration at 2886.42 and 2864.58 cm^{-1} (carbogen). The C=O (carboxyl and carbonyl) form at vibration of 1719 cm^{-1} and followed by remaining sp^2 skeletal vibration C=C at 1626 cm^{-1} . After GO undergo reduction process, characteristic absorption has been decreased. It showed =C – H character due to a new absorption band at 1625 cm^{-1} and also C – H at absorption band 1540 cm^{-1} . Another stretching vibration happens at 1440 cm^{-1} that showed character of C=C which is related to graphite structure of graphene [8].

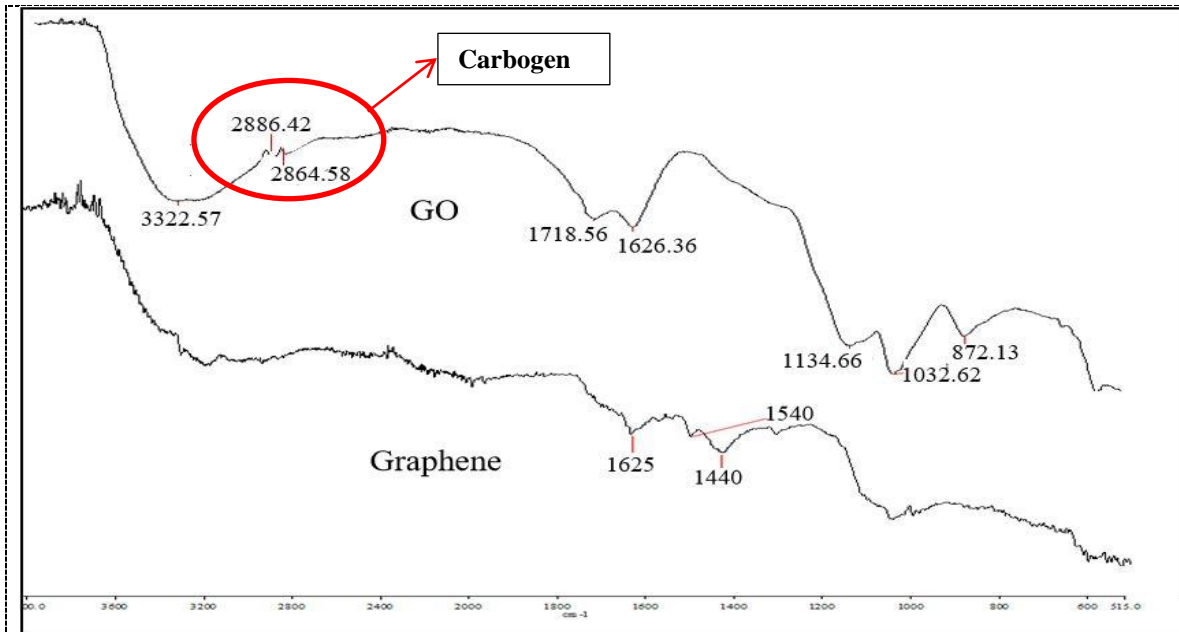


Figure 3. Graphene oxide and Graphene comparison on FTIR graph EIS Analysis

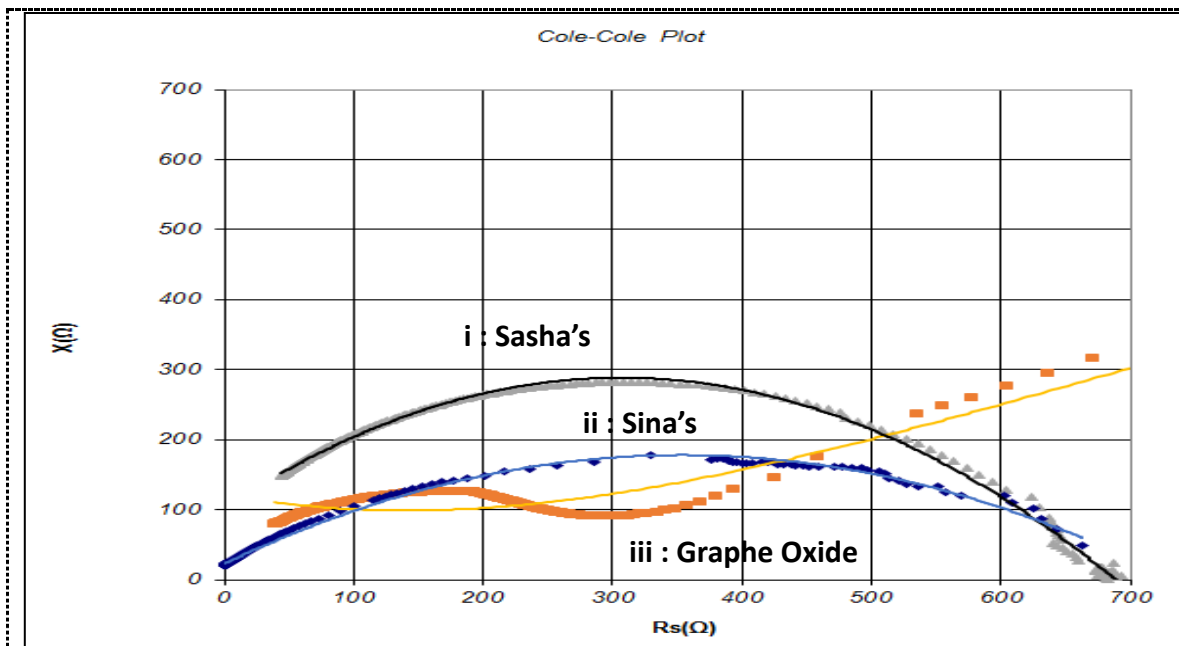


Figure 4. EIS data comparison for GO and Graphene

From Figure 4 above, it showed three pattern of graph produced from EIS test. From that graph it has labelled as (i), (ii) and (iii), where it showed graph pattern of graphene (Sasha's method), graphene (Sina's method) and GO respectively. From the calculation based on the result acquired, it has

indicated that conductivity value for (i) is approximately $6.2\text{E}+02$ S/cm then followed by (ii) graph that indicate value of $5.7\text{E}+02$ S/cm. From these data, it showed graphene that synthesis by Sasha method (i) is better than Sina method (ii) as it produces higher conductivity value. While for (iii) which is GO there is approximately $2.9\text{E}+02$ S/cm for its conductivity value, where it can be concluded as low a conductivity. However, by using a constant weight of 0.16 g for each graphene, it showed result of $8.1\text{E}+02$ S/cm for graphene synthesis by Sina's method. Data was tabulate in Table 1 below to simplify understanding for conductivity value for each material.

Table 1. Conductivity and Resistivity Data for Graphene .

Material	Conductivity [S/cm]	Resistivity [Ω]
Graphene Oxide	$2.9\text{E}+02$	$3.4\text{E}-03$
Graphene (Sina's Method at 0.09g)	$5.7\text{E}+02$	$1.8\text{E}-03$
Graphene (Sina's Method at 0.07g)	$2.5\text{E}+02$	$4.1\text{E}-03$
Total Graphene (Sina's Method at 1.6g)	$8.1\text{E}+02$	$1.2\text{E}-03$
Graphene (Sasha's Method 1.6g)	$6.2\text{E}+02$	$1.6\text{E}-03$

4. Conclusions

As conclusion chemical method has been proved able to achieve highest reduction capability even not a complete reduction of oxygen from GO. Chemical method using hydrazine hydrate as reducing agent for graphene synthesis is split into (a) Sina Abdolhosseinzadeh and (b) S. Stankovich. All the data of comparison has been proved as the characteristic test taken as for GO is reliable compare to [1-10].

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