

Study of Morphological, Optical and Electrical Properties of Graphene Oxide Thin Film Relative to the Reaction Time of Synthesis

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Abstract—In this work, graphene oxide (GO) was synthesized by treating graphite powder with potassium permanganate (KMnO₄) and a mixture of concentrated sulphuric acid (H₂SO₄)/phosphoric acid (H₃PO₄) at various reaction time. The GO thin film is coated on a glass substrate by using drop casting method. The morphological, optical and electrical properties of GO thin film were carried out by using scanning electron microscopy (SEM), UV-Vis spectroscopy (UV-Vis), Fourier Transform Infrared Spectroscopy (FTIR), and current-voltage (I-V) characteristic. The morphological study of GO shows that more oxygen functional groups were observed as the reaction time increases from 24h to 96h and is justified from the optical properties of GO thin films. The optical and morphological properties of GO thin film affects the electrical properties as the resistivity increase from 9.33 x 10⁶Ω.cm to 26.15 x 10⁶Ω.cm. Morphological and optical data confirms that 48h is the optimized reaction time having a resistivity of 12.30 x 10⁶Ω.cm.

Index Terms—Graphene Oxide; Reaction Time; Synthesis; Thin Film.

I. INTRODUCTION

Carbon-based nano-materials have undergone an explosion of interest due to their unique combination of chemical and physical properties [1]. Unusual and exotic properties make the graphene, graphene oxide (GO), reduced graphene oxide (rGO) appeared as the hot topic among all the carbon-based [2]. In every field of technology [3], carbon-based nanomaterials have shown their importance including in energy sources [4]. Graphene oxide (GO) consists of a 2D network of sp² and sp³ bonded atoms, while graphene sheet consist 100% sp² hybridized carbon atoms [5]. Furthermore, GO is a wide band gap two dimensional (2D) material with graphene sheets occupied by epoxy and hydroxyl groups at its basal plane, and carboxylic acid groups at the edges call as graphene oxide (GO) [6]. In certain aspects, GO is comparable to graphene with oxygen moieties and holds a remarkable position independent of graphene in the research field [7].

Graphene oxide (GO) is the result of the oxidizing graphite powder with oxidation agents which function as adding oxygenated functionalities to the graphite structure and exfoliate the layers [8]. There are various methods used for its synthesis which are Brodie's [9], Staudenmaier [10], Hoffman [11], Hummer's [12], Modified Hummer's and Improved Methods. In this work, graphene oxide was prepared by an improved method in order to obtain greater

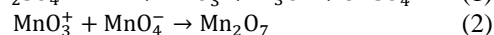
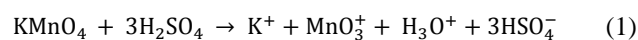
yield, and environmentally friendly method [13]. Graphene oxide was prepared by easy, cost-effective and convenient method via treating graphite powder with potassium permanganate (KMnO₄) and a mixture 9:1 mixture of concentrated H₂SO₄/H₃PO₄.

GO thin film is made up from deposition process which is process deposited the GO solution on the substrate to form a thin film by using spin coating, drop casting [14] and spray pyrolysis [15]. By using drop casting to deposit thin film, it can avoid wastage of solution during deposition and it is the simplest method. More recently with intense scientific investigations, GO thin film can be used as electron-accepting material in organic solar cells due to its unique structural [16], electronic properties [17], active electrochemical materials [18], cellular imaging and drug delivery applications [19]-[20].

Synthesis condition also influences the properties of graphene oxide including the reaction time, reaction temperature, stirring speed and synthetic route [21]. Reaction time is the condition that was explored in this study. Properties of GO are highly associated with its morphological, optical, electrical properties which are strongly dependent upon the synthesis condition. Graphene oxide was characterized by UV-Visible spectroscopy, FT-IR spectroscopy, Scanning Electron Microscopy and I-V characteristic.

II. EXPERIMENTAL METHOD

Graphene oxide (GO) was prepared by the oxidation of natural graphite powder using improved method as shown in Figure 1. Firstly, 0.75g of graphite powder was added to 4.5g of potassium permanganate (KMnO₄). Then the mixture of sulphuric acid (H₂SO₄)/ phosphoric acid (H₃PO₄) (90 ml: 10 ml) was slowly added. Equation (1) and (2) took place in the reaction between potassium permanganate (KMnO₄) and sulphuric acid (H₃PO₄) which produce diamanganese heptoxide (Mn₂O₇) to oxidize the graphite [21].



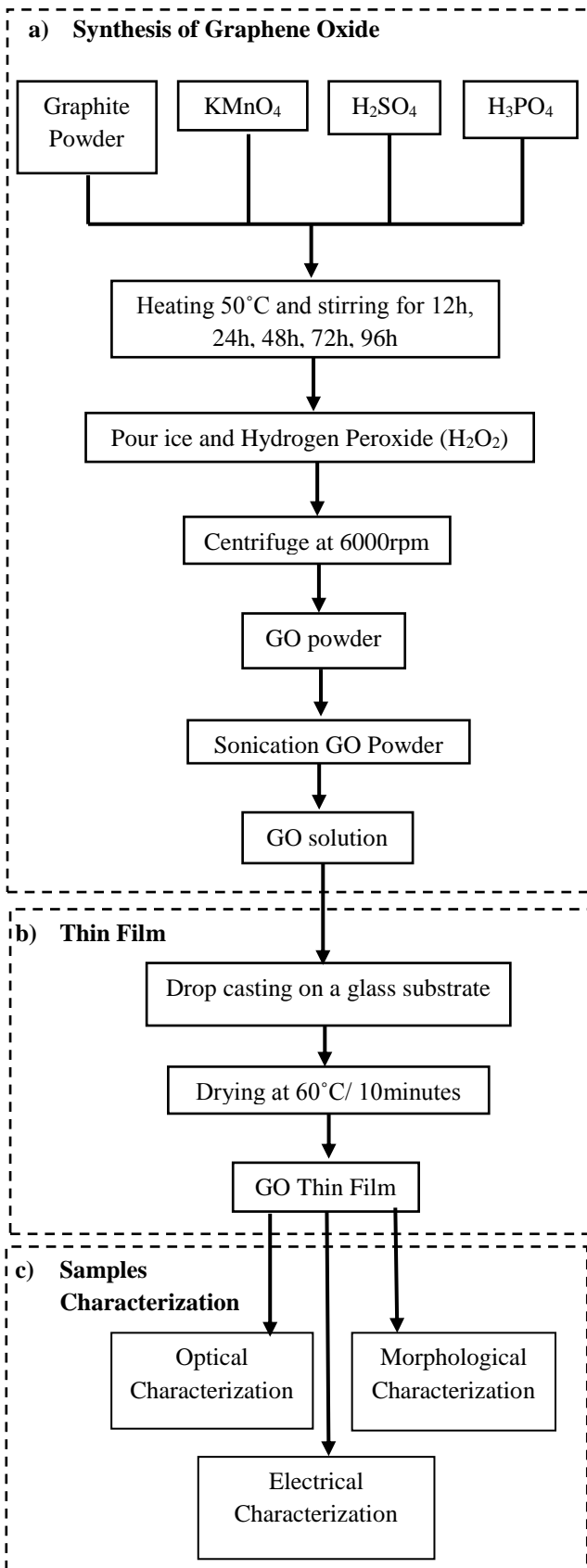


Figure 1: Flow Chart of Overall Process

The reaction temperature was maintained at 50°C and stirred for 12h (GO1), 24h (GO2), 48h (GO3), 72h (GO4) and 96h (GO5). The colour of the mixture changed from dark purplish green to light purple. The reaction mixture was cooled to room temperature and poured into ice. Then 0.75ml of hydrogen peroxide (H₂O₂) was added to stop the reaction.

It resulted in a colour change of the suspension to dark yellow and a production of graphene oxide (GO). The washing process was carried out using simple decantation of supernatant via a centrifugation technique at 6000rpm for 10minutes. The suspension was repeatedly washed with HCL and deionized water which results in the formation of graphene oxide (GO) and GO was dried at 60°C for 2h. Next, 10 mg of graphene oxide powder was dispersed in 5ml of distilled water and was sonicated until no visible particle can be seen while glass substrates were ultrasonically cleaned in acetone, isopropanol, ethanol and distilled water for 10 minutes each. The substrates were dried using air blow. Drop casting method was used in deposition process and graphene oxide solution was drop on a glass substrate and dried it for 10 minutes at 60.

UV-Visible spectroscopy was used to detect the conjugation network and absorption of GO. UV-Vis absorption spectrum was carried out in the range of 200nm to 800nm using UV-1800 Shimadzu. The Fourier Transform Infrared (FTIR) were recorded from 400 to 4000 cm⁻¹ (with a resolution of 2 cm⁻¹ and 4 averaged scans) on a Shimadzu IRAffinity-1. The morphology and structure of GO were investigated through scanning electron microscope (SEM). SEM characterization was carried out using TM3030 Hitachi. Keithley Source meter 2450 was employed to characterize the electrical properties of GO.

III. RESULTS AND DISCUSSION

A. Morphological Properties

Figure 2 displayed the SEM images of graphene oxide (GO) at different reaction time from 12h to 96h. Fig. 2(a) shows the SEM image for 12 hours reaction time of GO. The absence of crumple structure revealed that the graphite is not completely oxidized.

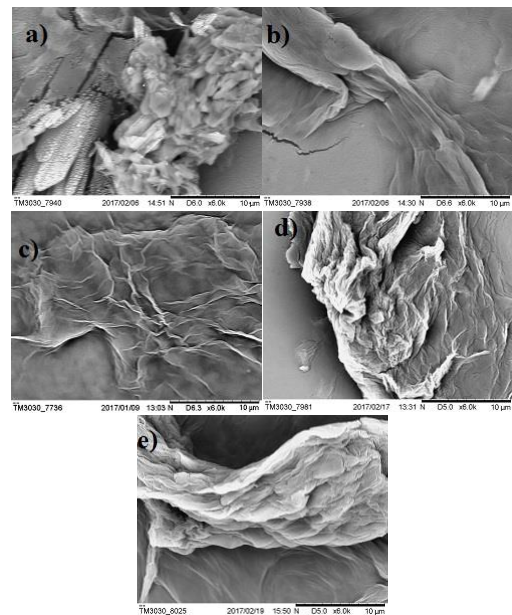


Figure 2: SEM image of graphene oxide (GO) at different reaction time (a) 12h (b) 24h (c) 48h (d) 72h (e) 96h.

In fact, graphene oxide is produced from the reaction of graphite powder with strong oxidizers agent [8] and the graphite will exfoliate whenever it is fully oxidized by oxidizer agent. As shown in Figure 2(b) the crumpled structure is starting to begin that show the exfoliation of

graphite to become graphene oxide while in Figure 2(c) the graphite is fully exfoliated, that can be justified by existing crumpled and rippled structure that results in deformation upon the exfoliation and restacking process [22]. As seen from Figure 2(d) and (e), there is a crumple and ripple structure appeared and the result shows that the graphite was exfoliated. Furthermore, the GO is over oxidation due to the presence more functional groups [23] and can be proved by UV-Vis result (Figure 3) for 72h and 96h.

B. Optical Properties

Figure 3 shows the optical properties of as-deposited GO thin films at different reaction time. The absorption peak was at 223nm for 12h, 226.5nm for 24h, 48h and 72h and 226 nm for 96h. These peaks correspond to π to π^* transition for the C=C bonding [24].

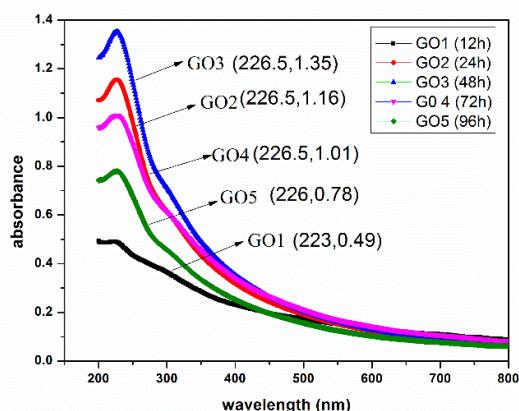


Figure 3: UV-visible of graphene oxide (GO) at different reaction time.

A similar shoulder was also observed around 300nm for all five samples which are attributed to n to π^* transition of the carbonyl groups (C=O) [13]. As depicted in Fig. 3, the peak intensity of GO increased with increasing reaction time from 12h to 48h. This suggests that enough time is required for higher degree of oxidation. However, the absorption peak intensity decreased, as the reaction time further increased from 48h to 96h. This may be due to over-oxidation [25].

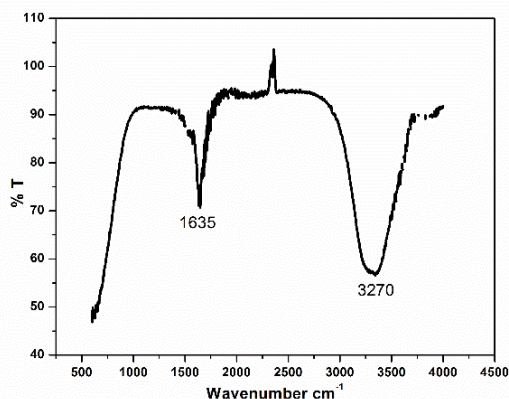


Figure 4: FTIR spectra of graphene oxide (GO).

FTIR spectroscopy is to characterize the presence of different functional group in graphene oxide including oxygen containing functional groups. FTIR spectra of the GO shown in Figure 4, to ensure the successful oxidation of

graphite. The presence of different types of oxygen functional groups in GO was confirmed by its FTIR spectrum.

FTIR spectrum was recorded and the spectrum of the GO obtained confirmed the successful oxidation of the graphite. A broad peak between 3600cm^{-1} and 2900cm^{-1} in the IR spectrum of GO due to the carboxyl O-H stretching mode [26]-[28]. The absorption peaks corresponding to O-H stretching (3270cm^{-1}) which is superimposed on the OH stretching of carboxylic acid, due to the presence of absorbed water molecules and alcohol groups [26]. The peak located at 1635cm^{-1} was associated with aromatic C=C bonds.

C. Electrical Properties

Figure 5 shows the electrical properties of as-deposited GO thin films. The samples were tested and the results were taken in the range between 0V to 5V. The I-V characteristics show that there is a decrease in current values for GO2 to GO5 from $7.98 \times 10^{-7}\text{A}$ to $2.90 \times 10^{-7}\text{A}$ respectively, whereas for 12h the value for current was $5.85 \times 10^{-7}\text{A}$ and the graph shown that the current value of GO1 is lower than GO3, this may be due to the incompletely exfoliated graphite [29] as shown according to the SEM image (Figure 2(a)).

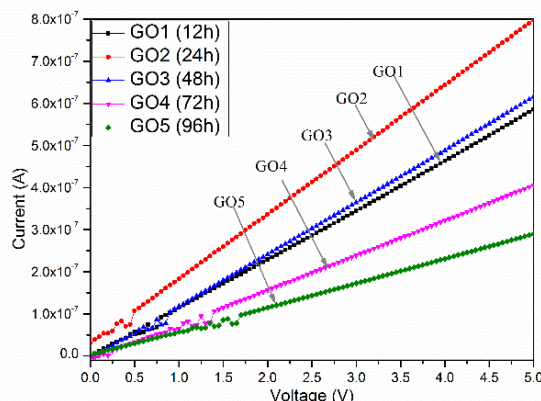


Figure 5: Current-Voltage Characteristic of graphene oxide (GO).

The decreasing trend from GO2 to GO5 is due to the oxidation level that occurs based on the reaction time of graphene oxide. The oxidation level of graphene oxide was affected by the reaction time; it can be shown in Figure 3 which show over oxidation is affected by the longer reaction time [25]. Table 1 shows that the resistivity of graphene oxide increases from GO2 to GO5, this is due to the presence of more oxygen functional groups that resulted at longer reaction time [29] as shown in Figure 2.

As seen in Table 1, the resistivity of GO1 is higher than GO3 is due to the incomplete oxidation during the synthesis of graphene oxide [29]. This incomplete oxidation is caused by the reaction time that needed to exfoliate the graphite and become graphene oxide.

Table 1

Effect of reaction time on electrical properties of graphene oxide (GO).

Label	Resistance (M Ω)	Resistivity (10 ⁶ Ω .cm)
GO1	8.64	12.96
GO2	6.22	9.33
GO3	8.20	12.30
GO4	12.38	18.57
GO5	17.43	26.15

Enough time is required to exfoliate the graphite. Thus 12h is not enough time to make the graphite become graphene

oxide and the resistivity is higher compared to GO2 and GO3. This work shows the improvement in electrical properties as compared to the reported literature [30] and the value of resistance for GO was $>10^{12} \Omega$.

IV. CONCLUSION

GO thin films having different reaction time were deposited on a glass substrate by using drop casting technique. It was notified that increasing in the reaction time affects the properties of GO thin films. The resistivity becomes lower when the longer reaction time was taken. In addition, 48h is the good reaction time for the synthesis of graphene oxide due to the absorption that can be seen in UV-Visible Spectroscopy. Moreover, the scanning electron microscopy shows that 48h reaction time resulted in the full oxidation by appeared crumpled and wrinkled structure. Although, the resistivity for 48h reaction time is higher than 24h reaction time but the UV-Visible spectroscopy and scanning electron microscopy characterization supports that 48h reaction time shown higher absorbance and full oxidation. In addition, the graphene oxide formation also confirmed through Fourier Transform Infrared Spectroscopy.

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