The Effect of Microwave Duty Cycle on The Electrical Conductivity of Reduced Graphene Oxide (rGO)

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Abstract. Graphene is a 2D material which has attracted a lot of attention due to its various fascinating properties. The most straightforward and facile synthesis method to produce graphene is chemical exfoliation method, which is conducted by reducing the graphene oxide. In this paper, we investigated the effect of microwave duty cycles on the electrical conductivity properties of rGO. The microwave was set at a different variation of duty cycles and reduction times. The reduction process with microwave-assisted was done under nitrogen conditions. The samples were characterized using Fourier transforms infrared spectrometry (FTIR), Scanning electron microscopy (SEM), and four-point probes. The highest conductivity of 18.10 S/cm was observed from rGO samples prepared by the reduction process using hydrazine as reducing agent and treated by high microwave irradiation mode for 3 min under N₂ conditions.

1. Introduction

After the breakthrough discovery of one atom thickness graphene used mechanical exfoliation by Geim and Novoselov in 2004, the research on graphene has continued to develop. The researcher tried their best to find efficient, large-scale and inexpensive methods to produce high quality of graphene and its derivatives. Graphene material attracted attention because of its very attractive electronic, thermal, and mechanical properties. The superior properties of Graphene include the mobility of the load carriers 250000 cm²V⁻¹s⁻¹ at room temperature [1], 5000 Wm⁻¹K⁻¹ thermal conductivity [2], electrical conductivity reaches 6000 Scm⁻¹ [3], and a theoretical surface area of 2630 m²g⁻¹ [4]. Graphene is very transparent with absorbance < 2.3% against the visible light [5]. Thus, graphene has excellent potential for applications such as energy storage, catalysts, sensors and supporting materials.

In synthesis of graphene, chemical exfoliation method is one of the methods that often be used to produce graphene in large scale. There are four stages in the synthesis of rGO chemically, including (i) oxidation process by dissolving graphite in acid solution and adding KMnO₄ as an oxidizing agent, the sample obtained from this process called GO (graphite oxide), (ii) exfoliation process of graphite oxide by
sonication, (ii) reduction process by adding hydrazine hydrate as reducing agents, and (iv) heating with microwave to increase the efficiency of the reduction process.

Graphite oxide was usually synthesized using methods developed by Brodie, Staudenmaier, and Hummer. This method involves strong acids (nitric acid or sulfuric acid mixtures) and oxidizing agents (KMnO₄, KClO₃, NaNO₃) [6]. The structure and properties of GO depend on three parameters, i.e., the synthesis method, the oxidation rate, and the source of the graphite used [7]. The sample obtained by chemical exfoliation reduction process can be referred to as HRG (Highly Reduced Graphene Oxide) [8]. To adjust the nature of the device and to improve the performance of material made from HRG, more effort is required in developing the reduction process.

In this research, synthesis of reduced graphene oxide was performed using modified Marcano method assisted by microwave irradiation under nitrogen condition. The reduction process was carried out using hydrazine hydrate as the reducing agent. In the previous results, we have studied that the reduction process assisted by microwave irradiation under nitrogen condition is very effective and time-saving to produce rGO with high electrical conductivity [9]. However, future study to investigate the effect of microwave duty cycle on the electrical conductivity of rGO is highly needed. Here in this report, we focus on the influence of various microwave radiation levels (high, medium, and low) to investigate the microwave duty cycles effect on the electrical conductivity of rGO. Four-point probes measurement was used to determine its electrical conductivity. Then, FTIR and SEM measurements were used to study the bonds characteristic before and after reduction process of the prepared sample, while SEM was used to check its morphology.

2. Experimental Setup

2.1 Synthesis of graphene oxide (GO) synthesis
The GO suspensions were prepared by the modified Marcano’s method previously reported by our group [10]. Graphite powder (1 g) was dispersed into an acid mixture solution of 98% H₂SO₄ (22.5 mL) and H₃PO₄ (2.5 mL). The solution temperature was kept below ~ 5 °C. KMnO₄ (3 g) was added slowly, and oxidation temperature was maintained at 50 °C while stirring for 40 minutes. The solution was diluted with 46 mL DI water, and then 1 mL 30% H₂O₂ to terminate the oxidation process. The solution was washed with 5% HCl to remove the metal ions. DI water and ethanol were used to achieve a neutral solution. The sample was dried for 12 h at 60 °C. The graphite oxide obtained then dispersed into 134 mL ethylene glycol. The dispersing process was carried out by sonication, and subsequent exfoliation was performed by ultraturrax for 2 h.

2.2 The Reduction process of graphene oxide (rGO)
The N₂H₄ (1 mL) was added to GO solution while stirring. The reduction process of GO was completed by introducing the sample into microwave irradiation (Panasonic Microwave 2.45 MHz, 800 W) with various irradiation levels. The microwave has three irradiation levels; the low mode indicated 17% of the duty cycle, the medium indicated 80% of the duty cycle, and the high mode indicated 100% of the duty cycle. The conventional microwave was modified to flow the N₂ gas to achieve nitrogen conditions during reduction process. The reduction process was varied for 1, 2, or 3 minutes reaction times. The reduction results were filtered, and then washed using DI water and alcohol for three times, respectively. Afterward, the washed product was dried for 12 hours at 60 °C.

3. Results and Discussion
The preparation of the rGO sample start from the synthesis of GO. By using modified Marcano method, synthesis of GO was performed using acid mixture solution of sulfuric acid and phosphoric acid. Subsequently, the reduction process was conducted using hydrazine hydrate as the reducing agent and assisted by microwave irradiation under nitrogen atmosphere. This reduction process resulted in the changes in the microstructure and the physical and chemical properties of GO. The product of rGO appeared as a black precipitate from the original of brownish yellow from GO.
Most of the organic molecules will vibrate in the mid-infrared range of 4000-200 cm$^{-1}$. GO spectra has an absorption peak at 1220 cm$^{-1}$ describing the vibration from the hydroxyl group (OH) [10]. This peak is sensitive to the H bond. There is also a carbonyl group (C = O) at 1735 cm$^{-1}$, phenol (C = C) at 1622 cm$^{-1}$, and an epoxy group (C-O) at 1116 cm$^{-1}$[11]. The presence of these high-intensity peaks in GO spectrum ensures the existence of the oxygen-containing functional groups after the oxidation process was performed. The polar properties on the surface of a hydroxyl group (-OH) lead to the formation of hydrogen bonds between water molecules and graphite. In addition to the hydrophilic nature of GO, the presence of electrostatic repulsion is also one of the reasons GO is soluble in the water. Whereas GO sheets have a negative charge when dissolved in water, caused by ionization of carboxyl and phenolic hydroxyl acids present on GO sheets [12]. Figure 1 shows the FTIR spectra of rGO. After reduction process, the characteristic peak of GO (described before) do not exist in the resulting rGO. The peak at 1618 cm$^{-1}$ still exist, attributed to the aromatic C=C group.

![ATR-FTIR spectra of rGO with various microwave radiation levels (high, medium and low modes)](image)

Figure 1. ATR-FTIR spectra of rGO with various microwave radiation levels (high, medium and low modes)

The GO reduction was carried out via chemical exfoliation using hydrazine hydrate as the reducing agent and assisted by microwave irradiation. The use of microwaves in this experiment was due to the microwave radiation is more efficient than conventional heating, environmental friendly, and non-conductive heating methods [13], scalable and cost-effective to produce graphene-based materials [14]. The microwave heating reaction in the liquid phase has an inverted temperature gradient [13]. Additionally, selective absorption of waves from polar or substrate solutions so that the heating effect potential will make the process more efficient and time-saving. The heating using microwave radiation is mediated by dielectric relaxation or ionic conduction, thus warming the system more homogeneously. The difference in the ability to absorb waves from a material makes it possible to heat selectively. The FTIR spectra of rGO with various microwave irradiation levels are depicted in Figure 1. After GO was reduced, the hydroxyl and alkoxyl groups decrease significantly and even unidentified. The decrease of the hydroxyl and alkoxyl groups indicate that GO reduction process into rGO was successfully performed. The morphology of the rGO has been studied by SEM characterizations, as shown in Figure 2. The SEM results showed thin wrinkle sheets which are the intrinsic properties of graphene [15].
Four-point probe measurement was performed to determine the electrical conductivity of rGO. Carbon-based electrodes with high conductivity and stable electrochemical properties are essential for energy catalyst and storage applications [16]. As explained previously, the process of rGO fabrication was done by reducing the graphene oxide using hydrazine hydrate as a reducing agent and assisted by microwave irradiation under nitrogen conditions. We used nitrogen atmosphere conditions to avoid the unwanted reaction that might occur during reduction process. Synthesized rGO by microwave irradiation with minimum duty cycle, required 20 minutes to obtain electrical conductivity of 14.24 S/cm. For medium duty cycle with 2 minutes radiation time, the result was 9.71 S/cm of electrical conductivity. Furthermore, maximum duty cycle with 2 minutes reduction process produced rGO with 17.13 S/cm of electrical conductivity. As a summary, the electrical conductivity measurements of the samples showed that rGO conductivity increased faster when using a microwave with a maximum duty cycle (high mode) than using medium and low mode. Afterwards, in the high mode of microwave duty cycle under nitrogen condition, various irradiation times of 1, 2, and 3 minutes were performed. The electrical conductivity for rGO irradiated in 1 and 2 minutes were 11.00 S/cm and 17.13 S/cm, respectively. The highest electrical conductivity of 18.10 S/cm was achieved in 3 minutes reduction process [9]. It proves that microwave irradiation removes oxygen-containing functional groups, restore the crystallinity of the nanosheets and significantly increase the size of sp² domains [16]. This electrical conductivity result is higher than rGO produced by Marcano and Marcano’s modified methods reported by our group, previously [8,10].

4. Conclusions
The reduced graphene oxide (rGO) has been successfully synthesized using chemical exfoliation method. Based on FTIR, the result show that GO successfully transform into rGO, indicated with the reduction of oxygen-containing functional groups to a certain degree, whether used low, medium or high microwave duty cycle. The thin sheets morphology of rGO has been displayed from the results of SEM. From four-point probe results, the highest electrical conductivity obtained was 18.10 S/cm using high microwave duty cycle or high mode of microwave irradiation level. It clearly shows that microwave duty cycle has a significant effect on the rGO properties result. By using high microwave duty cycle, the time required for reduction process is faster than using low or medium microwave duty cycle, which only takes in 3 minutes.

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