Preparation of Reduced Graphene Oxide Film by Chemical and Thermal Reduction Method Targeted for Energy Harvesting

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***ABSTRACT*—Graphene has sparked an intense interest in the energy field over the recent few years. A water flow over graphene has been proved that it can generate energy approximately ~175W/m^2 due to the actively charged ions present in the water. In order to harvest the energy, a good quality of graphene film with high electrical conductivity is desired. In this work, two techniques were used to prepare reduced graphene oxide film. Characterization by X-Ray Diffractometer and Fourier Transform Infrared Spectrocopy, as well as electrical tests were done on the film to measure the ability of reduced graphene film to harvest energy. Thermal reduction at 700°C has shown the highest conductivity when compared to reduction done at 300°C and reduction by ascorbic acid. The conductivity obtained from thermal reduction at 700°C is relatively higher at 56.39 S/m followed by reduction with ascorbic acid at 46.87 S/m. Referring to the results obtained, it is proven that the conductivity increases significantly when the temperature increase, thus for that reason, the reduced graphene oxide by thermal reduction at higher temperature was suggested for energy harvesting purposes.**

***KEYWORDS*— Reduced graphene oxide, chemical and thermal reduction, conductivity, energy harvesting**

I. INTRODUCTION

Energy production and storage are both critical research domains where increasing demands for the improved performance of energy devices and the requirement for greener energy resources constitute immense research interest. Carbon nanomaterials especially carbon nanotubes (CNTs) have been widely demonstrated to be capable of producing a voltage when being immersed in flowing water or polar liquids. Many researchers have been improvising since the nanotube electron drag in flowing ionic liquids was proposed in 2001, but none of them can provide satisfied explanation for all the observed phenomena and most importantly only microvolt level could be harvested. However recently in 2010, an exciting research was reported that a 30 × 16 μm^2 sized graphene surface surrounded by four patterned electrodes (Ti/Au, 3/30 nm, connected with gold wires by silver epoxy) can generate a peak voltage ~25 mV and power ~85 nW in flowing solution of 0.6 M HCl at ~1 cm/s, while only ~0.8 mV can be induced in aligned multiwalled CNTs in the same solution.[1] The flow-induced voltage in graphene was explained by a net drift velocity of Cl− ions adsorbing/desorbing or hopping on graphene on the basis of a force-field molecular dynamics simulation, which showed no adsorbing or hoping of hydronium ions on the graphene.

Graphene has incurred intense interest since its freestanding form was isolated in 2004, and with the vast array of unique and highly desirable electrochemical properties it offers, comes the most promising prospects when implementation within areas of energy research is sought. Graphene is a two dimensional (2D) crystal that is stable under ambient conditions; it has a special electronic structure which gives it unusual electronic properties. As a new material, the uses of graphene are very attractive since many interesting properties, mechanical, thermal and electrical have been reported to confirm the wonder of graphene to traditional materials. Graphene nowadays is produced from graphite oxide. Graphite oxide was first reported over 150 years ago but today graphite oxide also received a lot of research interest due to its role as a precursor for the cost-effective and mass production of graphene-based materials. Graphite oxide has a similar layered structure to graphite, but the plane of carbon atoms in graphite oxide is packed with oxygen-containing groups, which not only expand the interlayer distance but also make the atomic-thick layers hydrophilic. As a result, these oxidized layers can be exfoliated in water under moderate ultrasonication. If the exfoliated sheets contain only one or few layers of carbon atoms like graphene, these sheets are named graphene oxide (GO). The most attractive property of GO is that it can be reduced to graphene-like sheets by removing the oxygen-containing groups.

There are several techniques in removing the oxygen containing groups. Technique of synthesizing graphene affect greatly on the desired purity, thickness, size and etc. Basically there are two different approaches to preparing graphene. The method can be divided into two categories that are top-down approach and bottom-up approach. A bottom-up approach is defined as a process in which the starting material is a smaller entity and later brought up to larger entity. Bottom-up approach is mostly known as natural in that all system in nature is in bottom-up approach. The example of bottom-up approach is chemical vapour deposition. Conversely, a top-down approach is when the structure is made from a bigger piece as the starting steps of the process or in other words, top-down approach is a self-structuring process whereby it is called a nano-fabrication. The process starts with bulk or micro structures and the decrease in size through several methods. It is also implies that the nanostructures are synthesized by removing the plane or layer which is present on the substrate to form the desired nanostructure. Typically, top-down approach provides better control.[2] Top-down approach are mechanical and chemical exfoliation of starting material either graphite or GO. The techniques of chemical and thermal reduction are categorized into this approach.

Thermal reduction was usually used to exfoliate graphite oxide to achieve graphene. The mechanism of exfoliation is mainly the sudden expansion of CO or CO_2 gases evolved into the spaces between graphene sheets during rapid heating of the graphite oxide. The rapid temperature increase makes the oxygen containing functional groups attached on carbon plane decompose into gases that create huge pressure between the stacked layers. Studies shows that thermal annealing at 1100°C in flow of Ar/H_2 would gave a conductivity of 72,700 S/m.[3] On the other hand, chemical reduction of graphene oxide is usually the most common way to obtain graphene. Reduction by chemical reagents is based on their chemical reactions with GO. Usually, the reduction can be realized at room temperature or by moderate heating. As a result, the requirement for equipment and environment is not as critical as that of thermal annealing treatment, which makes chemical reduction a cheaper and easily available way for the mass production of graphene compared with thermal reduction. Reduction by ascorbic acid has been reported to have conductivity of 7,700 S/m.[4]

Consequently graphene has been utilised beneficially as a promising alternate electrode material in many applications for enhancing specific technological fields and particularly the issues surrounding energy storage and generation – graphene is at the centre of future prospects where its unique attributes have begun to be utilised with astonishing outcomes when contrasted to current devices, that until now have dominated the field. Thus the utilisation of graphene in future applications with technological advances within energy related fields holds great promise, where revolutionary performance is expected to surpass the current achievement whilst at the same time proving to be a greener and more energy efficient alternative.

In this work, the effects of graphene oxide reduction methods i.e. thermal and chemical were investigated with an aim to obtain the highest conductivity reduced graphene oxide film targeted for energy harvesting.

II. MATERIALS AND METHODOLOGY

A. Materials

Purified graphite powder (MW=12.01g/mol, Merck), 30% hydrogen peroxide (R&M Chemicals), 37% hydrochloric acid (Merck), potassium permanganate (MW=158.03g/mol, R&M Chemicals), 95-98% sulphuric acid (R&M Chemicals), ascorbic acid (Dae-Jung), sodium chloride crystal (MW=58.44g/mol, J. T. Baker), N,N-Dimethyl-acetamide (MW=87.12g/mol, Merck). All the chemicals were analytical grade and used as received without further purification. Distilled water was used for dilution and washing. Seawater and river water were for harvesting energy testing.

B. Synthesis of Graphene Oxide (GO)

GO was synthesized using Modified Hummer's method with exfoliation by sonication. 5g of graphite powder and 250mL concentrated sulphuric acid were added into beaker in ice bath condition (<10°C). The solution was stirred for an hour. 30g of potassium permanganate was then added to the mixture in interval within two hours (<15°C) and continued stirred for another two hours. Removed ice bath and stirred for 20 hours at room temperature. Mixture was then heated to 70°C for 2 hours. Then, 100 mL of distilled water was added gradually to the mixture followed by 30 minutes sonication. Temperature was then increased to 90°C and continuously stirred for another 1 hour. The mixture was then dilution with 100 mL of distilled water and stirred for one hour, followed by 30 minutes sonication. In order to stop the reaction, the mixture was further treated with 30mL hydrogen peroxide and cooled to room temperature followed by 2 hours sonication. The mixture was then repeated washing by centrifuging at 10,000 rpm with 4°C condition for ~30 minutes with diluted hydrochloric acid of 1M to remove residue as well as chemical ions and followed by distilled water to neutralize the pH. Lastly, the dark brown gel was poured into glass petri dish and dried in oven at 60°C for 24 hours.

C. Chemical Reduction of Graphene Oxide (GO)

The GO film obtained from previous section was reduced to reduced graphene oxide (r-GO) by ascorbic acid. Ascorbic acid (1mg/L) was prepared by diluting 100 mg of ascorbic acid powder in 100mL distilled water. Reduction was done at 95°C for 1 hour with 100mg GO film. After an hour, the resulted r-GO film was washed with distilled water for several times and dried in oven.

D. Thermal Reduction of Graphene Oxide (GO)

Thermal reduction of GO was done in vacuum furnace (MODEL: VT Furnace) at three different temperatures i.e. 300°C, 500°C and 700°C. The synthesized GO was reduced in furnace for 5 minutes and let cooled to room temperature. During heating process, the film was make sure to be enclosed tightly to ensure oxidation does not happen.

E. Characterization of the Samples

Fourier Transform Infrared (FTIR) spectroscopy (MODEL: Perkin Elmer, Spectrum One) and X-Ray Diffractometer (XRD) (MODEL: Rigoku) analysis were carried out on the graphite powder, GO film and r-GO film to verify the film obtained was according to specification. XRD patterns were analyzed at 40kV and 40mA in the range of 2θ=5°-60° with a speed angle of 2°/min. Additional analysis of I-V test with single measurement was done on r-GO to obtain the conductivity value of each of the samples for later comparison. The conductivity was calculated from the relation of resistance and resistivity as shown in Eq. 1, Eq. 2 and Eq. 3 respectively.

$$Conductivity, \sigma = \frac{1}{Resistivity, \rho} \quad (4)$$

$$Resistivity, \rho = Resistant, R \ x \ \frac{Cross\ Sectional\ Area, A_S}{Length\ of\ Sample, \ell} \quad (5)$$

$$Resistant, R = \frac{Voltage, V}{Current, I} \quad (6)$$

III. RESULTS AND DISCUSSION

3.1 Preparation of GO

Color changes were observed during synthesis of GO, from blackish to greenish brown when $KMnO_4$ was added to the mixture of graphite and H_2SO_4. This is due to the oxidation of $KMnO_4$ wherein some of the manganese (MnO_4^-) is reduced to manganate ion (MnO_4^{2-}) as shown in below Eq. 1 producing green color while manganese dioxide (MnO_2) in Eq. 2 producing brown color.

$$MnO_4^- + e^- \rightarrow MnO_4^{2-} \quad (1)$$

$$2\,H_2O + MnO_4^- + 3\,e^- \rightarrow MnO_2 + 4\,OH^- \quad (2)$$

When the hydrogen peroxide (H_2O_2) was added to the mixture to stop the reaction, vigorous bubble can be seen and the color change from brownish to gold as shown in Fig. 1. The reaction of H_2O_2 with $KMnO_4$ produces oxygen gas and water vapor as shown in Eq. 4.3. The reaction is spontaneous and exothermic.[5]

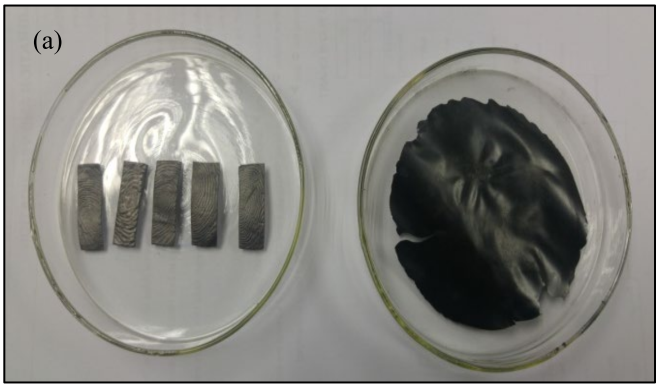
$$2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 2H_2O + 3O_2 + 2OH^- \quad (3)$$

Fig. 1 GO solution after addition of H_2O_2

During washing stage, centrifuge was needed due to high viscosity of the solution after sonication, making it difficult to be filtered after washing. The viscosity of the solution increases after each sonication processes due to the weakening of interparticle adhesion forces. When sonication was done, the temperature increases and the heat energy provide extra energy to separate the molecules, resulting in the reduction of attractive forces between molecules.[6] As a result of using centrifuge, clear separation can be seen after each rotation as shown in Fig. 2.

Fig. 2 GO suspension after centrifugation

The gel like GO obtained after centrifuged was dried in oven to get the GO film and proceed with reduction by ascorbic acid and thermal treatment at 300°C, 500°C and 700°C. Fig. 3 shows the photographs of GO and r-GO film as well as the r-GO suspensions with DMAc.



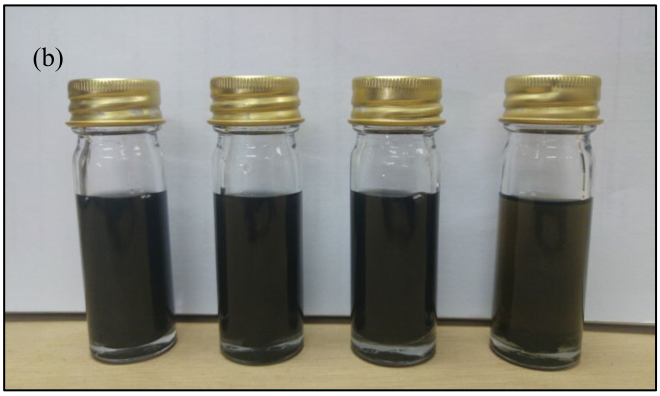


Fig. 3 Photographs of GO and rGO Samples (a) From left: rGO film after thermal reduction at 700°C. Right: GO film after drying in oven at 60°C for 24 hours. (b) rGO dissolved in DMAc, from left: thermal reduction at 300°C, 500°C, 700°C and ascorbic acid

3.2 Characterization of GO and r-GO

Samples of graphite powder, GO and r-GO film were then characterized by several instruments to show the comparison between each samples when there is structure change. Fig. 4 shows the Fourier Transform Infrared spectra comparison of the three samples.

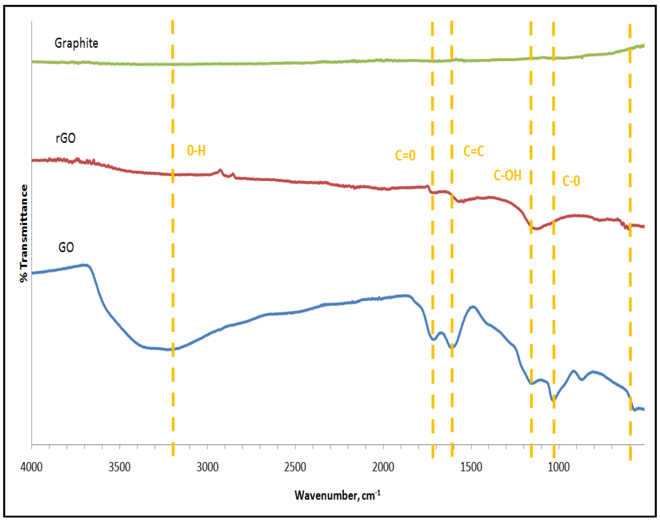


Fig. 4 FTIR Spectrum of Graphite, GO and rGO

From Fig. 4, graphite powder does not show any peaks in the spectrum due to the sole atom of carbon in graphite powder. Graphite contains layers of carbon covalently bonded with each others. On the other hand, GO shows many peaks in the spectrum. Since GO is an oxidized form of graphene, it is laced with oxygen-containing groups such as alcohol, carboxylic acid, ketone and epoxide. Hence, the reason of peaks at 3200cm^{-1}, 1600cm^{-1}, 1300cm^{-1} and 1100cm^{-1} indicating O-H, C=O, C=C, C-OH and C–O. Quite similarly with r-GO spectrum, the peaks of GO was noticeable at r-GO spectrum. Theoretically, graphene should exhibit spectrum similar to the graphite spectrum because of the sole atom of covalent bonded carbon in the structure. However, due to reduction from GO, there were still some oxygen-containing groups noticed in the spectrum might be due to incomplete reduction of GO, hence, the peaks observed were alike GO spectrum.

Similarly with studies by Karimzadeh et. al. [7], in his work the spectrum of graphene oxide exhibits the presence of O–H (3400 cm^{-1}), C=O (1730 cm^{-1}), C=C (1624 cm^{-1}), C–OH (1368 cm^{-1}), epoxide groups (1230 cm^{-1}) and C–O (1064 cm^{-1}). After the graphene oxide is reduced by laser beam irradiation, all the characteristic absorption bands of oxygen-containing groups (O–H, C=O, and C–O) are substantially weakened and almost eliminated. The similarity of his work with this paper can be seen in Fig. 5.

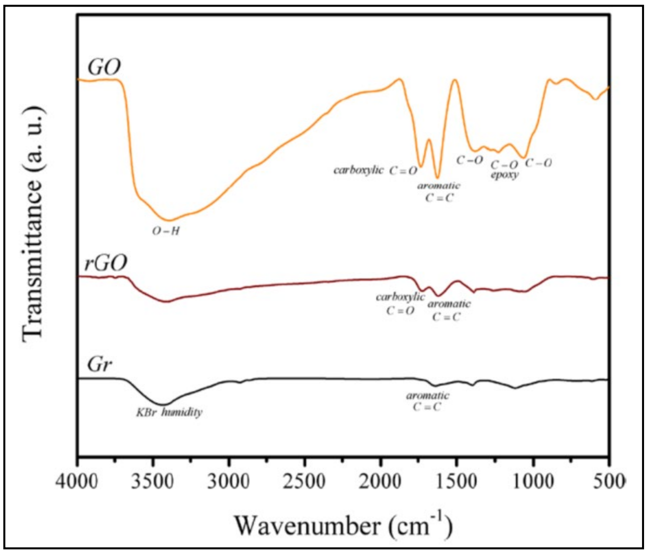


Fig. 5 FTIR Spectrum of Graphene, Fresh Graphene Oxide and rGO [7]

In addition to FTIR, XRD was carried out to check on the crystallization angle of the structure. Fig. 6 compares the X-Ray Diffraction spectra of graphite, GO and r-GO prepared using various technique. The XRD of graphite should portray a peak at 2θ = ~26° whereas GO should have a peak at 2θ = ~10° while r-GO at 2θ = 24~°.[8][9][10][11] In Fig. 6, graphite shows a characteristic peak at 2θ = 26.42°. After the introduction of oxygen functionalities, the peak shifts to 2θ = 8.26°. When GO was reduced, no peak at 2θ = 10.3° was observed and a new broad peak appears at 2θ = 26.68° due to the decrease of intercalated oxygen functionalities. However, it can be seen that the value was observed to have slightly shifted to lower degree. The shifting might be due to compression on the lattice space when sonication done intervally during synthesis process. Shift of XRD peaks are mainly associated with strain which leads to stress in lattice. A peak shift to lower angle indicates that expansion of d-spacing in the out-of-plane direction is took place which means that lattice under the compression. On the other hand, compression will caused the degree to be shifted towards higher angle. This result is expected since the GO that was used is expanded GO. The angle of which GO absorb the most rays will be slightly lower than the normal GO.

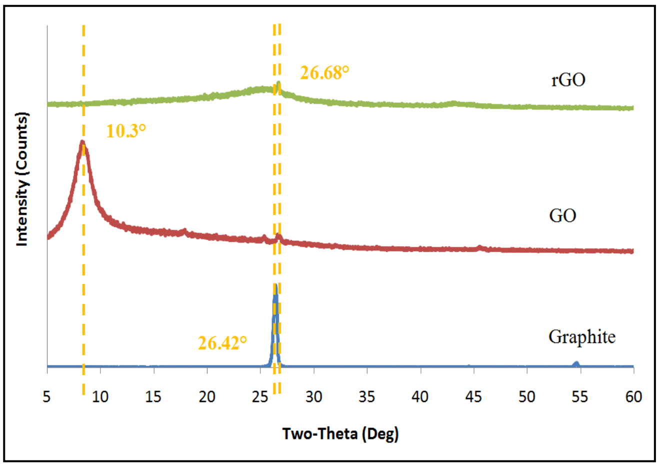


Fig. 6 X-Ray Diffraction Analysis Spectra of (a) Graphite, (b) GO, (c) r-GO

3.3 Conductivity Study of r-GO

In order to investigate the ability of r-GO film to harvest energy, DC current vs. voltage test was done to get the conductivity of the r-GO film. Fig. 7 shows the graph of current vs. voltage for each of the r-GO samples produced from different method of reduction. The highest value as seen from the graph is from r-GO film reduced by thermal treatment at 700°C and followed by chemical reduction by using ascorbic acid. Referring to the graphs of current versus voltage, it is visible that the slope or Resistance, (R=I/V) for different temperature decreasing when the temperature increase. For instance, at 300°C the slope calculated was 377.16Ω, 500°C is 168.23Ω and 700°C is 106.20Ω. Data in Fig. 7 was extracted and conductivity was calculated using conductivity and resistivity relation as explained in methodology. The results from the calculation were tabulated into Table 1.

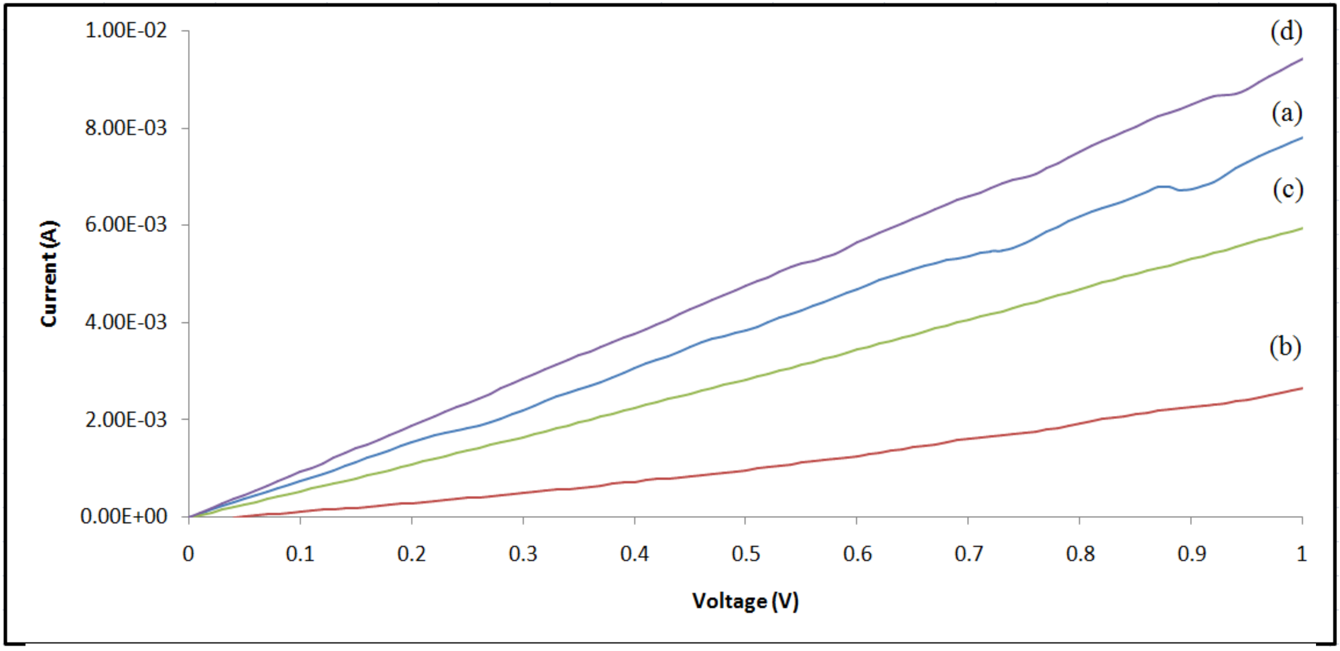


Fig. 7 Current Vs. Voltage Graph of Reduction Method (a)Ascorbic Acid, (b) Thermal Treatment 300°C, (c) 500°C, (d) 700°C

Table 1 Current vs. Voltage Data

Sample	Abbreviation	Voltage (V)	Current (A)	Resistance (Ω)	Resistivity (Ω.m)	Conductivity (S/m)
Ascorbic Acid	a	1	0.0078	128.03	0.0213	46.87
Thermal Treatment 300°C	b	1	0.0027	377.16	0.0629	15.87
Thermal Treatment 500°C	c	1	0.0059	168.23	0.0281	35.60
Thermal Treatment 700°C	d	1	0.0094	106.20	0.0177	56.39

From Table 1, it can be seen that the value of the conductivity was affected by the temperature. This is consistent with study by Wang et. al. [12] in which he found that the increase of temperature will cause the conductivity of the graphene film to also be increased. The reason behind this might be explained by deoxygenation of GO. For instant, the critical dissociation temperature (T_c) of hydroxyl groups attached to the edges of GO is 650°C and only above this temperature can hydroxyl groups be fully removed.[13] Pei et. al. [14] has also pointed out that based on experimental data, a large number of functional groups can be removed by moderate heating above 200°C with enough time, but in order to remove full deoxygenation of GO solely by thermal annealing is rather difficult even at temperature as high as 1200°C. Pei also reported that only at temperature above 1760°C, almost all the functional group will be removed.

When comparing the conductivity between the two techniques i.e. thermal treatment and ascorbic acid, the value of conductivity as for reduction using ascorbic acid is unchanging whereas reduction by thermal treatment can be manipulated by varying the temperature as it is known that the conductivity is affected by temperature. However, the obtained conductivity was not as expected. Typical value of conductivity by graphene has been reported to be as low as 7,700 S/m to as high as 72,700 S/m [15] with a power harvested from ~0.6M HCl to be ~85nW.[16] In contrast with the obtained results, the measured conductivity is drastically low compared to reported reference. Therefore, it is highly likely that the produced rGO film will harvest too little energy from water flow and produces weak power that might not be sufficient to power a simple circuit.

This can be somehow explained, the method used in producing rGO which is thermal reduction was done in vacuum or atmosphere condition, in which it has been noted in some research that thermal reduction at vacuum condition or at atmosphere will result in defects on the graphene film in terms of its electronic properties. Solution has been proposed by Wu et. al [17] and Su et. al. [18] whereby Wu uses arc-discharge treatment to exfoliate graphite oxide to graphene and Su carried out thermal annealing of 1100°C with a flow of Argon/Hydrogen gas. Both of them have reported to have a conductivity of 200,000S/m and 131,400S/m respectively. The lacked of instrument in the facility was the main obstacle in proceeding with this project. Therefore, in future work, it is recommended that in producing rGO film by thermal treatment, the reduction must be done in inert condition in order to eliminate the residual oxygen in the air, since the etching of oxygen increased rapidly at high temperatures. On the other hand, a suggestion on chemical reduction is by using hydrohalic acid such as hydroiodic acid to produced highly conductive rGO films for the purpose of harvesting energy.

IV. CONCLUSION

In conclusion, the conductivity obtained from thermal reduction at 700°C is relatively higher at 56.39 S/m followed by reduction with ascorbic acid at 46.87 S/m. Based on the results obtained, it is proven that the conductivity increases when the temperature increases significantly. However, for the harvesting energy purposes, the conductivity measured was not on par with the current research of energy harvesting by graphene. Hence, it is recommended that for energy harvesting purpose, a good quality of reduced graphene oxide with high conductivity should be produced by thermal reduction at higher temperature in Argon/Hydrogen flow in which the inert gases are used to consume the residual oxygen in the atmosphere.

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