



Reduction of Sonication-Assisted Graphene Oxide via Chemical and Thermal Treatments

Nurul Fattin Diana Junaidi¹, Nur Hidayati Othman^{1*}, Ili Nadia Ismail¹, Nur Hashimah Alias¹, Munawar Zaman Shahrudin, Husna Hayati Jarni¹, Mohammad Fiqri Zainuddin¹, Nik Raikhan Nik Him¹, Wan Fazlida Hanim Abdullah²

¹ Faculty of Chemical Engineering, Universiti Teknologi MARA, Shah Alam, 40450, Selangor, Malaysia

² Faculty of Electrical Engineering, Universiti Teknologi MARA, Shah Alam, 40450, Selangor, Malaysia

*Corresponding author E-mail: nurhidayati0955@salam.uitm.edu.my

Abstract

Graphene has sparked an intense interest in the energy field over the recent years due to its excellent mechanical, electrical, thermal and optical properties. There are several ways to produce graphene, however, large-scale production of this material is still an issue and subjected to intense research effort. In this work, graphene oxide (GO) was first synthesized using sonication-assisted oxidation of graphite followed by reduction process. The reduced graphene oxides (rGOs) are then produced using two routes; chemical L-ascorbic acid (AA) reduction and thermal reduction (T). The sonication process facilitates the washing step and reduces the time required to produce rGOs. The chemical and structural properties of the rGOs were comparatively investigated using XRD, FTIR, BET and FESEM. Results showed that both chemical and thermal methods were effective in removing oxygen-containing functional groups in GO and restore the electrical conductivity of the obtained rGO. rGO-T700 had the highest electrical conductivity (56.39 S/m) in comparison to rGO-T300 (15.87 S/m) and rGO-T500 (35.6 S/m) that were obtained using thermal reduction method. The rGO-AA, which used L-ascorbic acid as a reductant possessed an electrical conductivity of 46.87 S/m. Although this value was slightly lower as compared to rGO-T700, it still demonstrated the potential of using environmentally friendly ascorbic acid for rGO synthesis compared to thermal reduction. The elimination of high temperature reduction could significantly save the production cost and it is believed that further optimization of reduction process parameters might enhance the conductivity of rGO-AA.

Keywords: Reduced graphene oxide (rGOs); graphene oxide (GO); chemical reduction; thermal reduction; conductivity.

1. Introduction

Graphene is a two-dimensional (2D) material and an allotrope (form) of carbon consisting of a single layer of carbon atoms arranged in a hexagonal lattice. The interest on graphene has grown substantially since it was first isolated from three-dimensional graphite and extracted as a single sheet (a monolayer of atoms) using a technique called micromechanical cleavage by Novoselov et al. [1] in 2004. Graphene is known to have superior properties such as high thermal conductivity at room temperature, high transparency (97.7% transmittance in the visible spectrum), high electrical conductivity, high Young's modulus and high specific surface area (2630 m²/g) [2]. All these extraordinary properties makes graphene suitable for various applications, including energy storage[3][4], catalysis[5] and adsorbent[6].

Separation of thin layers of graphene (a 2D material) from a 3D layered bulk graphite is known to significantly increases the electrochemical properties of graphene and the technique used during the graphene production can greatly affect the purity, thickness and size of graphene [7]. There are various processes that can be used to exfoliate the chunks of graphite into the layers of graphene such as mechanical exfoliation, CVD-growth on metals, chemical process and thermal treatment.

In general, there are two routes to synthesize graphene i.e. top-down approach and bottom-up approach (Fig.1). A bottom-up approach is defined as a process in which the starting material is in a smaller entity and later brought up to a larger entity. The example of bottom-up approach for graphene synthesis is by using chemical vapour deposition (CVD). The bottom-up approach is more advantageous than the top-down approach because it has a better chance of producing less defects, more homogenous chemical composition, and better short- and long-range ordering of graphene. Conversely, a top-down approach is when the process starts with bulk or micro structures and the reduction of size was carried out through several methods. It is also implied that the nanostructures are synthesized by removing the planes or layers (building blocks) from the substrate to form the desired nanostructure. Typically, the top-down approach provides better control for graphene synthesis [2]. Top-down approach includes mechanical and chemical exfoliation of the graphite.

Graphite oxide is a compound of carbon, oxygen, and hydrogen in variable ratios which usually obtained by treating graphite with strong oxidizer. It can be considered as a highly oxidized form of graphite with a higher inter-layer spacing due to the presence of a large number of oxygen functionalities. On the other hand, graphene oxide (GO) is known as the exfoliated form of graphite oxide, comprising monolayers or few stacked layers. It is also a heavily oxygenated compound with the presence of many oxygen-containing functional group such as epoxide, hydroxyl, car-

bonyl and carboxyl groups on its basal plane, thus, improving the GO hydrophilicity for better interfacial interaction with polar polymer matrices [8]. As a result, GO can be easily dispersed in several polar solvents like ethylene glycol, dimethylformamide, N-methylpyrrolidone, and tetrahydrofuran. However, the incorporation of this oxygen-functional group also leads to deterioration of electrical conductivity of GO making it less preferable for the development of conductive polymer-based composites.

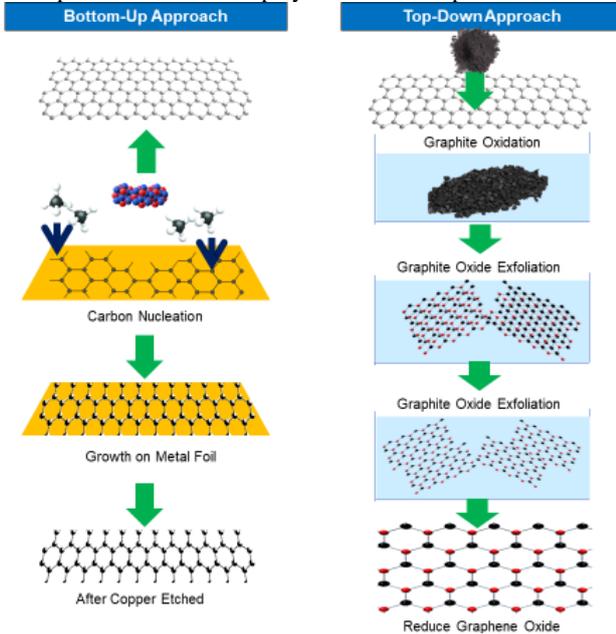


Fig. 1: Routes for graphene synthesis

As GO is an electrical insulator, it needs to be reduced into reduced graphene oxide (rGO) first to be used as a conductive nanomaterial. The reduction process is considered as an extremely vital process as it has a large impact on the quality of the rGO produced which will determine how close the final structure of rGO is compared to pristine graphene. The reduction of GO can be carried out using chemical, mechanical, thermal or electrochemical means. Thermal reduction is considered as a simpler and non-chemical process. Besides, it has potential in significantly lowering the cost of mass-produced graphene. High reduction level and conductivity could be achieved through rapid temperature increase, causing oxygen-containing functional groups attached on carbon plane to decompose into gases that create huge pressure between the stacked layers. During the thermal reduction of GO, some of the partially oxidized sp^3 carbon atoms become fully oxidized to carbonaceous gases such as CO_2 and the rest is reduced to the sp^2 graphene product. Botas et al. [9] carried out graphene oxide reduction and found that the thermal reduction of GO (TRGO) produced a wrinkled structure, with a C/O ratio of 10:1, and is electrically conducting, suggesting the effective reduction of GO. However, temperature control is very important to obtain high quality of graphene.

Among those reduction methods available, solution-based chemical reduction of GO is one of the most preferred methods because of low-cost and bulk-scale production. Chemical reduction of GO sheets can be carried out using several reducing agents such as hydrazine hydrate, sodium hydride, sodium borohydride and ascorbic acid. The use of hydrazine hydrate to prepare graphene was first reported by Stankovich et al. [10] and he found that the reduced graphene oxide (rGO) shows aggregated sheets and crumpled structure as rGO becomes less hydrophilic due to the removal of oxygen atoms. This irreversible agglomerates occur through van der Waals interaction, which can affect the unique properties of individual sheet and cause difficulty for further processing [11]. Although hydrazine reduction is found to produce high conductivity of rGO [12], the use of hydrazine as reducing

agent is not preferred due to its toxicity and contamination to the resulting materials [13]. Recently, the use of L-Ascorbic acid (L-AA) or widely known as vitamin C has been investigated as a new approach for effectively reducing GO under mild conditions [14]. L-AA is a non-toxic reducing agent and has been widely used in living things. Besides, the reduction using L-AA can be made not only in water, but also in some common organic solvents, such as N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP).

In this work, the effects of graphene oxide reduction methods (chemical and thermal) towards the crystal structure, morphology and electrical conductivity properties of rGO were investigated by using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and I-V test.

2. Materials and Methods

2.1. Materials

Purified graphite powder (MW=12.01 g/mol, Merck), 30% hydrogen peroxide (R&M Chemicals), 37% hydrochloric acid (Merck), potassium permanganate (MW=158.03 g/mol, R&M Chemicals), 98% sulphuric acid (R&M Chemicals), L-Ascorbic acid (Sigma Aldrich), sodium chloride crystal (MW=58.44 g/mol, J.T.Baker), N,N-Dimethyl-acetamide (MW=87.12 g/mol, Merck) were used for the synthesis and reduction of GO. All the chemicals were analytical grade and used as received without further purification. Distilled water was used during dilution and washing processes.

2.2. Synthesis of Graphene Oxide (GO) using Sonication

GO was synthesized using modified Hummer's method with sonication. 5 g of graphite powder and 250 mL of concentrated sulphuric acid were first added into a 1000 mL beaker that was maintained at a low temperature ($<10^\circ C$) in ice bath condition and stirred for an hour. Then, 30g of potassium permanganate was added to the mixture at a 5 minutes interval within two hours to prevent the temperature from exceeding $15^\circ C$. The mixture was continuously stirred for another 2 hours. After 2 hours, the ice bath was removed and the mixture was kept to stir for another 20 hours at room temperature. At this step, the mixture was observed to be a brown color paste. The mixture was then heated to $70^\circ C$ under stirring conditions. Consecutively, 100 mL of distilled water was slowly added to the mixture and stirred for ten minutes. The distilled water has to be added gradually to avoid drastic increment of temperature. Then, the mixture was sonicated using ultrasonic for about 30 minutes. The ultrasonic step was introduced to fasten up and improve the oxidation process. Next, the temperature was increased and maintained at $90^\circ C$ in order to increase the oxidation degree of GO and continuously stirred for 1 hour. Then, the mixture was diluted with 100 mL of distilled water and stirred for another hour. Subsequently, the mixture was sonicated again for another 30 minutes and after that, the mixture was further treated with 30mL hydrogen peroxide to stop the reaction and cooled to room temperature. Then, the mixture was sonicated for two hours followed by repeated washing with diluted hydrochloric acid to remove residue and chemical ions as well as neutralizing the pH. Prior to drying, the mixture was centrifuged at 10,000 rpm at $4^\circ C$ condition for 10 minutes. Then, the dark brown gel was poured into a glass petri dish and dried in the oven at $60^\circ C$ for 24 hours. Fig. 2 illustrates the steps involved in the synthesis of GO.

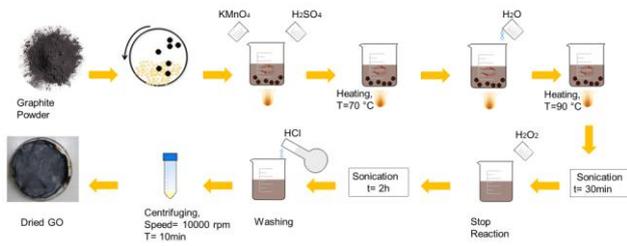


Fig. 2: Representation of the GO synthesis procedures

2.3 Chemical Reduction of GO using L-Ascorbic Acid (AA)

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

2.4 Thermal Reduction of GO

Thermal reduction of GO was carried out in vacuum furnace (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 allowed to cool at room temperature. During the heating process, the film was secured tightly to ensure oxidation does not happen.

2.5 Characterizations

X-Ray Diffraction (XRD) analysis was used to determine the orientation of single crystal and measured average spacing between layers or row of atoms. The analysis was carried out at 40 kV and 40 mA and a scan rate of 2 min⁻¹ in the 2θ range of 5 to 60 using Rigaku D/MAX 2550 XRD with Cu-Kα radiation.

The functional groups of graphite and GO were characterized using Fourier Transform Infrared Spectroscopy (FTIR, Perkin Elmer) in the range of 500-4000 cm⁻¹. The morphology of graphene oxide was studied using scanning electron microscopy (SEM, Hitachi, Japan). The samples were coated with gold prior to the analysis to improve the quality of the analysis.

Analysis of I-V test with single measurement was carried out for r-GO to measure the conductivity value of each sample. The test was carried out on the rGO film. The conductivity was then calculated from the relation of resistance and resistivity as shown in Eq. 1-3 [42].

$$\sigma = \frac{1}{\rho} \quad (1)$$

$$\rho = R \times \frac{A_s}{L} \quad (2)$$

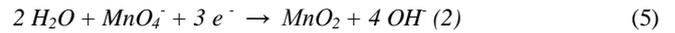
$$R = \frac{V}{I} \quad (3)$$

where σ is conductivity, ρ is resistivity, R is resistance, A_s is cross sectional area, L is length of sample, V is voltage and I is current.

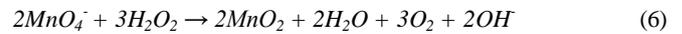
3. Results and Discussions

3.1. Preparation of GO

During the synthesis of GO, the color of solution was observed to change from blackish to greenish brown when KMnO₄ was added to the mixture of graphite and H₂SO₄. This is due to the oxidation of KMnO₄ in which some of the manganese (MnO₄⁻) is reduced to manganate ion (MnO₄²⁻) producing green color and manganese dioxide (MnO₂) producing brown color as shown in Eq 4 and 5, respectively.



After the hydrogen peroxide (H₂O₂) was added to the mixture to stop the reaction, vigorous bubbling can be seen and the color of solution changed from greenish black to brownish yellow as shown in Fig. 3(a). This indicates the reaction of H₂O₂ with KMnO₄ produces oxygen and water vapor as shown in Eq. 6. The reaction is spontaneous and exothermic [5].



During the washing stage, a centrifuge was used due to the high viscosity of 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 inter-particle adhesion forces. When sonication is carried out, the temperature of solution increases and the heat provides extra energy for molecules separation, resulting in the reduction of attractive forces between molecules. As a result of using the centrifuge, a faster and clearer separation can be achieved as shown in Fig. 3(b).

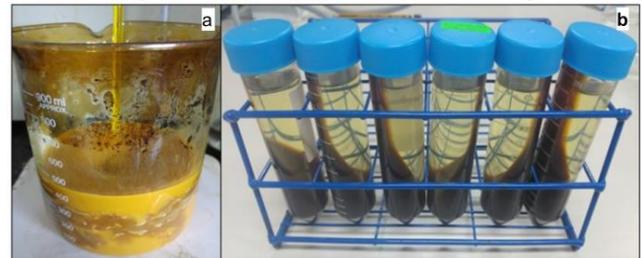


Fig. 3: Photograph of a) GO solution after addition of H₂O₂ and b) GO suspension after centrifugation

The gel-like GO obtained after the centrifuge process was dried in an oven to obtain GO before being reduced using ascorbic acid and thermal treatment at various temperatures (300 °C, 500 °C and 700 °C). Fig. 4 shows the photographs of GO and r-GO film as well as the r-GO suspensions with DMAc prepared in this work. In Fig. 4(d), the rGO produced were then dissolved in DMAc to investigate on the solubility properties of rGO. It can be seen that rGO produced from ascorbic acid (AA) has lower rate of solubility as it was not completely dissolved in DMAc as compared to rGO produced by thermal reduction method. As for the effects of thermal annealing, it was found that T300 dissolved faster, indicating that the solubility rate of T300 was much higher as compared to T500 and T700. This can be explained by the structure of rGO obtained. GO reduced by chemical reduction often shows higher oxygen removable rate compared to thermal reduction as proven by Stankovich et. al.[15]. As a result, less hydrophilic rGO was produced due to significantly lesser oxygenated alkyl group in the structure. Similarly, with thermal reduction, when the removal of oxygen alkyl that occurred was incomplete at lower temperature (T300), more hydrophilic graphene was obtained. Therefore, T300 can easily dissolved in solvent as compared to T700 where a complete removal of oxygen-

ated alkyl group occurred resulting in less solubility graphene [16].

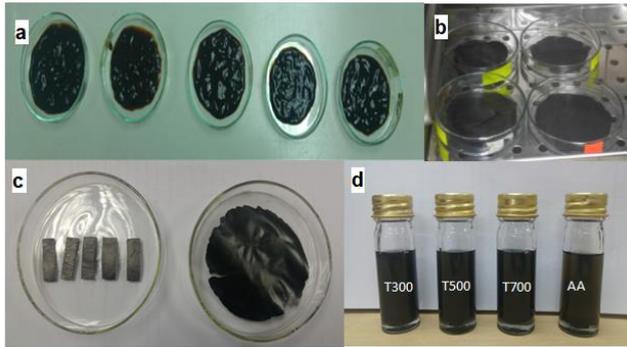


Fig. 4: Photograph of a) gel-like GO; b) dried GO; c) left: rGO film, right: GO film and d) rGO dissolved in DMAc, from left: thermal reduction at 300°C (T300), 500°C (T500), 700°C (T700) and ascorbic acid (AA)

3.2. Characterization of GO and r-GOs

Graphite, GO and r-GO powders were characterized using FTIR, XRD and TGA to observe structural and chemical changes of graphite after experiencing oxidation and reduction process. Fig. 5 compares the FTIR spectra of graphite, GO and the reduction GO products (AA, T300, T500 and T700). Graphite powder was observed not to show any peaks in the spectrum due to the sole atom of carbon in graphite powder. Graphite is known to contains layers of carbon covalently bonded with each other. On the other hand, GO shows several characteristic peaks as it is laced with oxygen-containing groups such as hydroxyl, O-H (3200 cm^{-1}), carbonyl, C=O (1730 cm^{-1}), aromatic C=C (1600 cm^{-1}), carboxy C-O (1414 cm^{-1}), epoxy C-O (1300 cm^{-1}), and C-O (1100 cm^{-1}). It can be clearly seen that the peaks for oxygen functional groups were substantially weakened and almost disappeared with the application of chemicals and thermal reduction treatments. As the temperature of reduction increases, the peaks widened and shifted to higher wave numbers (it moved from 1725 cm^{-1} to 1744 cm^{-1}). These observations indicate both intra- or/and intermolecular anhydride and ester formation. In general, anhydrides are formed between two adjacent carboxyl groups and cause two well-defined absorbance peaks at $\sim 1775\text{ cm}^{-1}$ and at $\sim 1835\text{ cm}^{-1}$ (the band at 1775 cm^{-1} , overlapped by the initial CO stretching, causes the peak shift to higher wavenumbers). In addition, newly formed esters between a hydroxyl and a neighboring carboxyl group, may also cause the carbonyl peak shift to higher wave numbers (in general, ester carbonyl bonds stretch at higher wave numbers than acids, aldehydes and ketones).

XRD analysis was carried out to observe the crystallite structure of rGO and to confirm the reduction of GO to rGO occurred. Fig. 6 compares the XRD spectra of graphite, GO and r-GO prepared using ascorbic acid and thermal treatments. The XRD of graphite shows a characteristic peak at $2\theta = \sim 26^\circ$ and after the oxidation process, the peak disappeared and a new peak was observed at a lower angle of $2\theta = \sim 8.5^\circ$. In comparison to the graphite, a very wide peak is observed for GO which clearly indicates the damage of the regular and highly crystalline pattern of graphite during the oxidation. When GO was reduced, the peak at 2θ disappeared and a new broad peak appeared at $2\theta = 26.68^\circ$ due to the decrease of intercalated oxygen functionalities. However, it can be seen that the value shifted to a lower degree due to the compression on the lattice space during the reduction process. The shifting of XRD peaks are mainly associated with strain which led to stress in lattice. A peak that shift to a lower angle indicates that expansion of d-spacing in the out-of-plane direction took place, which also means that the lattice is under compression. On the other hand, compression will cause the degree to be shifted towards a higher angle. This result is expected since the GO that was used is ex-

panded GO. The angle of which GO absorb the most rays will be slightly lower than the graphite.

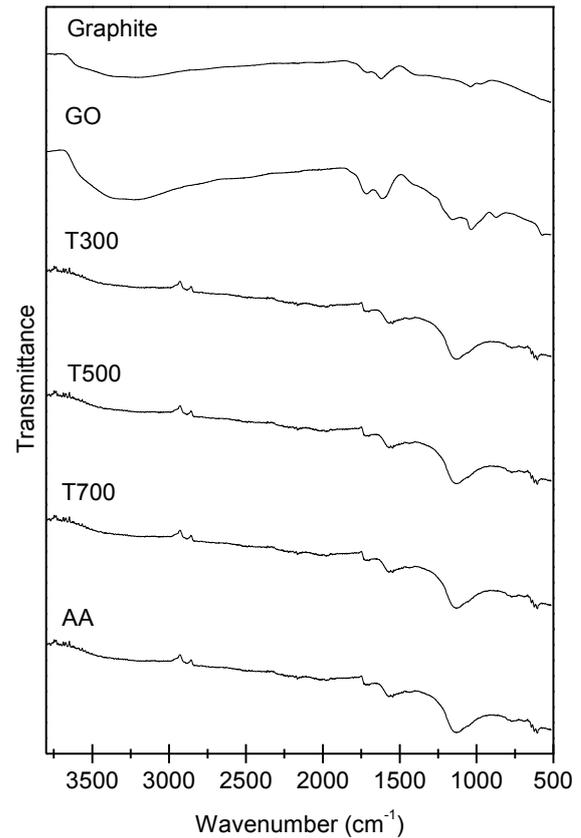


Fig. 5: FTIR spectra of graphite, GO and rGO after chemical and thermal reduction

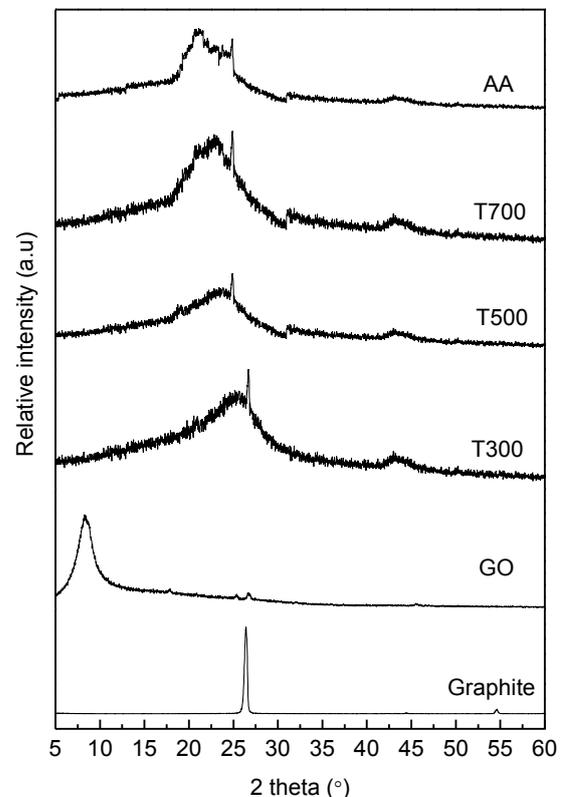


Fig. 6: X-Ray Diffraction analysis spectra of graphite, GO, T300, T500, T700, AA rGOs

3.3 Morphology analysis

Fig. 7 shows the FESEM images of graphite, GO and rGOs. It can be seen that graphite consists of thick layer of carbon as it contains stacks of graphene layers. After the oxidation and exfoliation process, a distinct layer of GO was observed indicating a significant gap between each layer owing to the oxygen alkyl group attached to the structure. Besides, the use of ultrasonic during the synthesis of GO was found to help in increasing the gap between each layer. After the reduction of GO, all rGOs samples were observed to exhibit typical graphene-like morphology; smooth surface with wrinkled and folded sheet-like surface[17]. The layer arrangement of GO had also disappeared. The surface morphology of T300 appeared smoother and less wrinkled and as compared to the one subjected to higher temperature of thermal treatment. During the thermal treatment, graphene oxide will react with air and decompose into volatile products (e.g. residual H₂O, CO₂, CO or other small gas molecules) that are trapped within GO layers due to the limited nature of diffusion, creating the observed “blisters”. However, as the reduction temperature was increased to 700 °C, the surface morphology appears rougher with slight “blistered”.

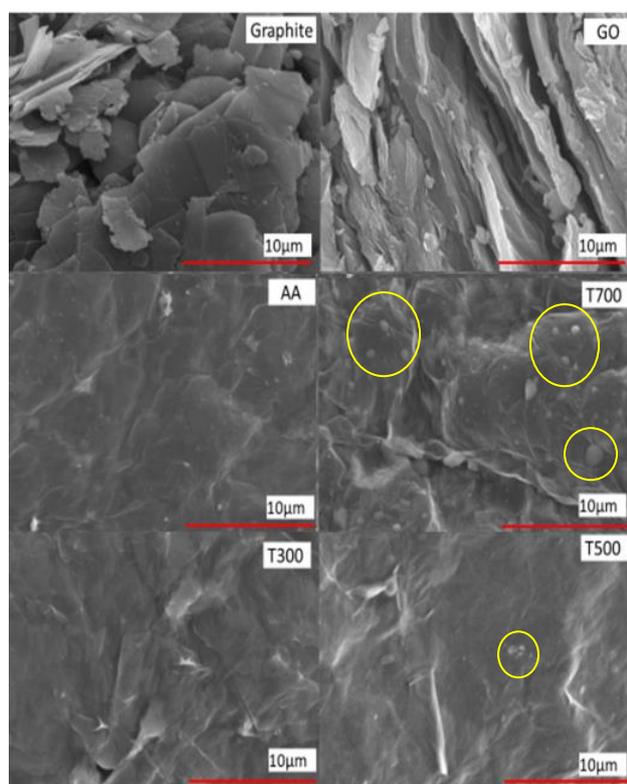


Fig. 7: FESEM images of graphite, GO and rGO produced from chemical reduction (AA) and rGO produced from thermal reduction at 300°C (T300), 500°C (T500) and 700°C (T700)

3.4. Conductivity Study of r-GOs

Electrical conductivity can be a direct indicator of the reduction degree and defect repair degree. In order to determine the extent to which the reduction methods of exfoliated GO can restore the electrical properties of the graphitic network, the electrical conductivities of rGO films were investigated using DC current vs. voltage test at room-temperature. Prior to the conductivity study, the rGO films were formed by vacuum filtration method. Fig. 7 shows the graph of current vs. voltage for each of the r-GO samples produced using various reduction method. It can be seen that the resistance ($R=I/V$) slope decreases with the thermal treatment temperatures.

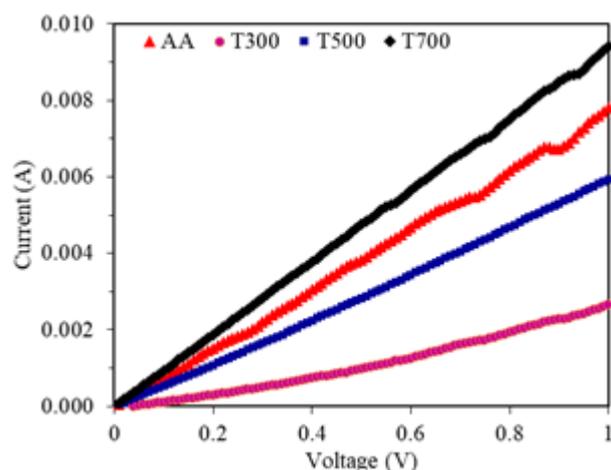


Fig. 7. Current vs. voltage graph of reduction method (a) ascorbic acid, (b) thermal treatment 300 °C (T300), (c) 500 °C (T500), (d) 700 °C (T700)

Table 1 tabulates the conductivity of rGOs prepared in this study. The highest conductivity value was observed for r-GO film reduced by thermal treatment at 700 °C (T700) followed by the one that is reduced by ascorbic acid (AA). Interestingly, the conductivity of rGO-AA was found to be at par with the one that underwent thermal reduction at 700 °C. The value of conductivity of rGO that subjected to thermal treatment at 300 °C was found to be the lowest at 15.87 S/m.

Table 1: Comparison of rGO conductivities prepared using various method

Sample	Conductivity (S/m)
AA	46.87
TT300	15.87
TT500	35.60
TT700	56.39

The results obtained in this work is consistent with study by Wang et al. [18] in which he found that the increase of reduction temperature will cause the conductivity of the graphene film to be increased. This can be explained by deoxygenation of GO. For instance, the critical dissociation temperature (T_c) of hydroxyl groups attached to the edges of GO is 650 °C and will be fully removed above 650 °C [18]. Pei et al. [16] 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 to remove full deoxygenation of GO solely by thermal annealing is rather difficult even at temperature as high as 1200 °C. The success ability of exfoliation is different between 200 to 1200 °C depends on time consumption during process and pressure exerted between graphene sheet during heating of graphene oxide. Huge pressure is created when rapid temperature increases due to decomposition of oxygen functional groups between graphene sheets to form CO and CO₂ gas. The obtained conductivity in this work was slightly lower as compared to other reported work [18]. However, this value can still be improved in the future by optimizing the concentration of L-AA and reaction time. On the other hand, for thermal reduction future work can be carried out in inert or vacuum condition in order to eliminate the residual oxygen in the air as etching of oxygen increased rapidly at high temperatures.

4. Conclusions

From this preliminary work, rGO was successfully prepared using chemical and thermal treatments. In general, thermal treatment at low temperature produced low conductivity of rGO. However, as the annealing temperature increased to 700 °C, the conductivity of rGO obtained (T700=56.4 S/m) was observed to be at par to the one reduced using ascorbic acid (46.87 S/m). It was found that the use of ascorbic acid in this work leads to the removal of oxygen

under mild and green conditions and at the same time minimize the defects caused during the reduction. However, by using thermal treatment at high temperature, the rGO prepared have some defects because of the fast reduction. By understanding the different characteristics of rGO produced by each route, it can be helpful in tailoring the characteristics of graphene materials for diverse applications and to develop a green and efficient method for the mass production of high quality graphene.

Acknowledgement

The authors would like to acknowledge Universiti Teknologi MARA and Ministry of Higher Education (MOHE) Malaysia for LESTARI (Grant no. 600-RMI/DANA 5/3/LESTARI (79/2015) and FRGS (Grant no. 600-IRMI/FRGS 5/3 (087/2017) research funding.

References

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, "Electric field effect in atomically thin carbon films," *Science* (80-.), 2004.
- [2] C. Soldano, A. Mahmood, and E. Dujardin, "Production, properties and potential of graphene," *Carbon*. 2010.
- [3] H. J. Choi, S. M. Jung, J. M. Seo, D. W. Chang, L. Dai, and J. B. Baek, "Graphene for energy conversion and storage in fuel cells and supercapacitors," *Nano Energy*. 2012.
- [4] P. Dhiman, F. Yavari, X. Mi, H. Gullapalli, Y. Shi, P. M. Ajayan, and N. Koratkar, "Harvesting energy from water flow over graphene," *Nano Lett.*, vol. 11, no. 8, pp. 3123–3127, 2011.
- [5] B. F. MacHado and P. Serp, "Graphene-based materials for catalysis," *Catalysis Science and Technology*. 2012.
- [6] S. Gadipelli and Z. X. Guo, "Graphene-based materials: Synthesis and gas sorption, storage and separation," *Progress in Materials Science*. 2015.
- [7] M. Acik and Y. J. Chabal, "A Review on Thermal Exfoliation of graphene oxide," *J. Mater. Sci. Res.*, 2012.
- [8] J. R. Potts, D. R. Dreyer, C. W. Bielawski, and R. S. Ruoff, "Graphene-based polymer nanocomposites," *Polymer (Guildf)*, 2011.
- [9] C. Botas, P. Álvarez, C. Blanco, R. Santamaría, M. Granda, M. D. Gutiérrez, F. Rodríguez-Reinoso, and R. Menéndez, "Critical temperatures in the synthesis of graphene-like materials by thermal exfoliation-reduction of graphite oxide," *Carbon N. Y.*, 2013.
- [10] S. Stankovich, R. D. Piner, X. Chen, N. Wu, S. T. Nguyen, and R. S. Ruoff, "Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate)," *J. Mater. Chem.*, 2006.
- [11] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. B. T. Nguyen, and R. S. Ruoff, "Graphene-based composite materials," *Nature*, 2006.
- [12] M. J. Fernández-Merino, L. Guardia, J. I. Paredes, S. Villar-Rodil, P. Solís-Fernández, A. Martínez-Alonso, and J. M. D. Tascón, "Vitamin C is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions," *J. Phys. Chem. C*, 2010.
- [13] Y. Shang, D. Zhang, Y. Liu, and C. Guo, "Preliminary comparison of different reduction methods of graphene oxide," *Bull. Mater. Sci. Indian Acad. Sci.*, 2015.
- [14] J. Zhang, H. Yang, G. Shen, P. Cheng, J. Zhang, and S. Guo, "Reduction of graphene oxide via L-ascorbic acid," *Chem. Commun. (Camb)*, 2010.
- [15] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. B. T. Nguyen, and R. S. Ruoff, "Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide," *Carbon N. Y.*, vol. 45, no. 7, pp. 1558–1565, 2007.
- [16] S. Pei and H. M. Cheng, "The reduction of graphene oxide," *Carbon N. Y.*, vol. 50, no. 9, pp. 3210–3228, 2012.
- [17] J. Lilloja, E. Kibena-Pöldsepp, M. Merisalu, P. Rauwel, L. Matisen, A. Niilisk, E. Cardoso, G. Maia, V. Sammelselg, and K. Tammeveski, "An Oxygen Reduction Study of Graphene-Based Nanomaterials of Different Origin," *Catalysts*, 2016.
- [18] X. Wang, L. Zhi, and K. Müllen, "Transparent, conductive graphene electrodes for dye-sensitized solar cells," *Nano Lett.*, vol. 8, no. 1, pp. 323–327, 2008.