

Preliminary study of green synthesis and characterization of graphene-based materials for photovoltaic application

Nur Ezyanie Binti Safie¹, Mohd Asyadi Azam^{1,*}

¹Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia

*Corresponding e-mail: asyadi@utem.edu.my

Keywords: Green synthesis; graphene-based materials

ABSTRACT – Graphene oxide (GO) and reduced graphene oxide (rGO) are known to have superior properties and become favourable materials in photovoltaic application due to its tunable bandgap which make them suitable materials to be incorporated as charges transport material. Inspire by the vision of finding a green and straightforward method to synthesis these graphene-based materials; this work aims to conduct functionalization of GO under the mild condition to produce rGO using lemon extract as the source of a natural reducing agent. Raman analysis is conducted in order to identify the qualities of rGO production.

1. INTRODUCTION

Graphene, a single-layered carbon arranged in a honeycomb structure, has attracted massive scientific interest due to its fascinating electronic, mechanical, and thermal properties, especially in the field of photovoltaic. However, since pristine graphene generally has zero bandgaps [1], the application of graphene is limited in thin-film solar cells such as perovskite solar cells leads to the introduction of graphene-based materials such as graphene oxide (GO) and reduced graphene oxide (rGO). The bandgap of graphene-based materials is tunable depending on the surface functionalization [2], make it favourable materials to be incorporated into the photovoltaic devices. On the other hand, one of the critical challenges in the synthesis of bulk-quantity graphene sheets in industrial is to overcome the intense, cohesive van der Waals energy of the p-stacked layers in graphite. On the contrary, large amounts of graphene-based materials are quickly produced via the oxidation of graphite.

To date, chemical reduction of GO has become the most widely used method for the preparation of graphene-like product, known as reduced graphene oxide (rGO) due to its cost-effectiveness and bulk productivity. However, this method usually involves highly toxic chemicals, such as hydrazine, hydroquinone, and sodium borohydride, which known to harm both human health and the environment. Therefore, it is highly desired to develop and introduce less- or non-toxic reducing agents into the procedure to replace these chemicals, especially with concern for the mass production of high-quality rGO. Thus, this work conducted the GO reduction using lemon extract as the reducing agent to produce rGO with higher qualities to

facilitate the bulk production of graphene-based materials.

2. EXPERIMENTAL

2.1 Synthesis of GO

In this work, GO was synthesized from graphite powder via a modified Hummer's method [3]. Briefly, 0.5 g graphite powders were stirred in an ice-water bath with the addition of 25 ml H₂SO₄ until the temperature reduced to 10°C. 1.5 g of KMnO₄ was gradually added while maintaining the temperature under 10°C before alternately stirred the suspension at room temperature for 25 min followed by 5 min sonication in an ultrasonic bath for 12 times. Then, slowly added 100 ml of distilled water to quench the reaction and continue with sonication for 2 h to produce a graphite oxide solution which later will be dividing into two equal parts (One part was further processed for preparation of rGO as described below). Next, for the GO exfoliation process, 10 ml of H₂O₂ was added gradually into one part of the graphite oxide solution until gas evolution ceased. The suspension was washed with 1M HCl acid solution and distilled water for several times until reach pH 7 and filtered to get the precipitate. The final precipitates were dried in the oven at 60°C to get GO.

2.2 Synthesis of rGO

1M NaOH solution was added into one part of the exfoliated graphite oxide solution until reached pH 13. Then, the suspension was sonicated for 1 h before added 100 ml of lemon extract at room temperature. The reduction takes place at 95°C for 1 h. The resultant black precipitates were filtered and further washed with a 1M HCl acid solution and distilled water to neutral pH. Finally, the filtrate was dried in the oven at 60°C to get rGO.

3. DISCUSSION

The Raman spectrum in Figure 1 shows two dominant bands for graphene-based materials which their position and shape provide information on their properties. The G band is the primary mode that represents the planar configuration of sp² bonded carbons in graphene-based materials. Pristine graphite shows a sharp G peak, centred at 1558 cm⁻¹ due to the first-order scattering of E_{2g} mode [4], while for GO and rGO, these peaks are centred at 1569 and 1572 cm⁻¹,

respectively. On the other hand, the D band represents the 'disorder' band or the 'defect band' that shows defects caused by breaking in the symmetry of the infinite carbon honeycomb-shaped lattice. The peak is centred at 1340, 1334, and 1341 cm^{-1} for graphite, GO, and rGO. After the conversion of graphite to GO, the D and G peaks broaden and raise in their intensity due to the introduction of oxygen functional groups into the graphitic chain. Besides, the G band also widens and exhibits a shift to higher wavenumber, which is from 1558 to 1569 cm^{-1} . The change in position of G band to higher wavenumber during oxidation of graphite indicates the presence of double bonds. However, the G peak in rGO also shifted towards higher wavenumber (1572 cm^{-1}), indicates rGO obtained in this work might not successfully restore the graphitic structure.

The integrated intensity ratio of the D and G bands (I_D/I_G) of graphite, GO, and rGO were found to be 0.14, 1.59, and 0.05, respectively. The I_D/I_G ratio is responsible for evaluating the average size of the sp^2 cluster in the graphene materials. In this work, GO obtains the higher I_D/I_G ratio compared to pristine graphite, which confirms the graphite oxidation to have occurred. GO is not consisting of a purely sp^2 structure but a highly disordered structure with a significant sp^3 content. Thus, contrary to the standard sp^2 materials, the decrease of defects in GO would produce an increase of the D/G ratio because there would be more sp^2 C atoms surrounding the defects. On the other hand, after the chemical reduction of GO to rGO, the I_D/I_G ratio decreased, indicates a considerable recovery of the conjugated graphitic framework upon defunctionalization of epoxide, hydroxyl, and other oxygen-containing functional groups during the exfoliation process. The peak positions and I_D/I_G ratios of graphite, GO, and rGO are summarized in Table 1 and 2.

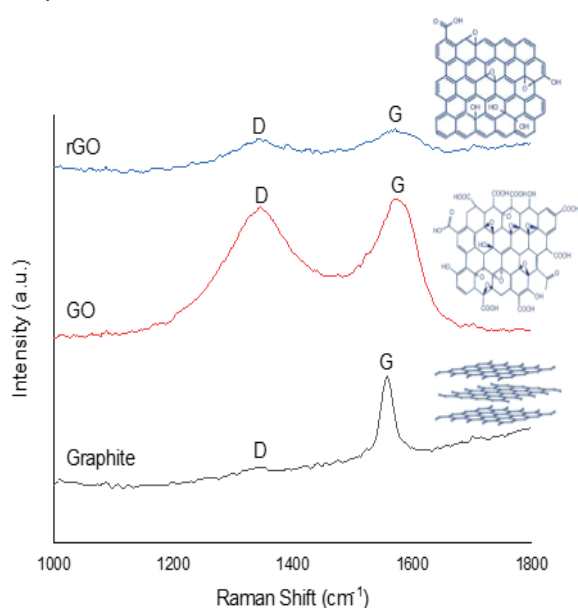


Figure 1 Raman spectra of the graphite, GO, and rGO

Table 1 Position of the D and G bands in the Raman spectra of the graphite, graphene oxide (GO), and reduced graphene oxide (rGO)

Materials	Peak Position (cm^{-1})	
	D band	G band
Graphite	1340	1558
GO	1334	1569
rGO	1342	1572

Table 2 I_D/I_G ratio of the graphite, graphene oxide (GO), and reduced graphene oxide (rGO)

Materials	Calculated Integrated Intensity (cm^{-1})		I_D/I_G ratio
	D band	G band	
Graphite	5755	41948	0.14
GO	305925	192526	1.59
rGO	18978	293926	0.05

4. SUMMARY

In this work, GO was successfully prepared from the oxidation of graphite with broadening and sharp intensity from Raman analysis that indicates the disordered structure due to the introduction of the oxygen functional group to the graphite structure. Besides, The lemon extract can effectively facilitate the deoxygenation of GO and simultaneously promote the formation of rGO with reduction of I_D/I_G ratio as compared to the I_D/I_G ratio calculated for GO. However, rGO obtained from the reduction of GO did not show sharp intensity in D and G bands of Raman analysis, this might have happened because of the high pH condition during the reduction process that limits the quality of the reduction process. Hence, it is desirable to lower the pH in reduction procedures for high qualities rGO in future work.

ACKNOWLEDGEMENT

Authors are grateful to Universiti Teknikal Malaysia Melaka for the facilities support and UTeM Zamalah Scheme for PhD support of NE Safie.

REFERENCES

- [1] R.M. dos Santos, L.E de Sousa, D.S. Galvão, L.A. Ribeiro, *Scientific reports*, vol. 10, no. 1, pp. 1-8. 2020.
- [2] M. Junaid, M.H. Khir, G. Witjaksono, N. Tansu, M.S. Saheed, P. Kumar, Z. Ullah, A. Yar, F. Usman, *Molecules*, vol. 25, no. 16, pp. 3646, 2020.
- [3] A. Alkhouzaam, H. Qiblawey, M. Khraisheh, M. Atieh, M. Al-Ghouti, *Ceramics International*, vol. 46, no. 15, pp. 23997-24007, 2020.
- [4] M. Karakoti, R. Jangra, S. Pandey, P.S. Dhapola, S. Dhali, S. Mahendia, P.K. Singh, N.G. Sahoo, *International Journal of Applied Ceramic Technology*, vol. 17, no. 4, pp. 1899-1908, 2020.