



REDUCTION OF GRAPHENE OXIDE TO GRAPHENE BY USING GAMMA IRRADIATION

(Penurunan Grafin Oksida kepada Grafin Menggunakan Sinar Gama)

Shamellia Sharin, Irman Abdul Rahman*, Ainee Fatimah Ahmad, Hur Munawar Kabir Mohd, Faizal Mohamed, Shahidan Radiman, Muhamad Samudi Yasir, Sukiman Sarmani, Muhammad Taqiyuddin Mawardi Ayob

*School of Applied Physics,
Faculty of Science and Technology,
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia*

**Corresponding author: irman@ukm.edu.my*

Received: 9 December 2014; Accepted: 16 October 2015

Abstract

This research aims to gauge the ability of gamma radiation to induce the reduction of graphene oxide to graphene. Graphene oxide powders were dispersed into a mixture of alcohol and deionized water, and the mixture was then irradiated with a ^{60}Co source using a GammaCell 220 Excel irradiator at absorbed doses of 0, 5, 15, 20 and 35 kGy. According to characterization using Fourier Transformed Infrared Spectroscopy (FTIR), it can be seen that almost every oxygen-containing functional group has been removed after irradiation of the graphene oxide mixture. Reduction of graphene oxide was also proven from the characterization using UV-Vis Spectroscopy, in which the wavelength of graphene oxide at 237 nm was red-shifted to 277 nm after being irradiated and the peak at 292 nm, (indicating the carboxyl group) disappears in the UV-Vis spectrum of reduced graphene oxide. Morphology of graphene oxide also changed from a smooth and flat surface to crumpled. The ratio of carbon/oxygen in the graphene oxide was lower than the carbon/oxygen of reduced graphene oxide. At the end of the experiment, it can be deduced that graphene oxide underwent reduction, characterized before and after irradiation using Emission Scanned Electron Microscopy and Energy Dispersive X-ray, Fourier Transformed Infrared Spectroscopy and UV-Vis Spectroscopy. Therefore, we postulate that the irradiation technique that induces reduction, can be used to obtain reduced graphene oxide from graphene oxide.

Keywords: graphene, graphene oxide, gamma radiation, FTIR, FESEM-EDX, UV-Vis

Abstrak

Kajian ini dijalankan untuk menguji kebolehan sinar gama untuk mengaruh penurunan daripada grafin oksida kepada grafin. Serbuk grafin oksida yang dilarutkan dalam campuran alkohol dan air ternyah ion disinarkan dengan punca sinaran ^{60}Co menggunakan penyinar GammaCell 220 Excel pada dos serapan 0, 5, 15, 20 dan 35 kGy. Berdasarkan pencirian yang dibuat menggunakan Spektroskopi Infra Merah Transformasi Fourier (FT-IR), didapati hampir kesemua kumpulan berfungsi yang mempunyai ikatan dengan oksigen berjaya disingkirkan selepas campuran grafin oksida disinarkan. Penurunan grafin oksida turut dibuktikan melalui pencirian Spektroskopi Penyerapan Ultralembayung-cahaya Nampak, yang mana panjang gelombang grafin oksida iaitu pada 237 nm beralih kepada 277 nm selepas disinarkan dengan sinar gama dan puncak pada 292 nm mewakili kumpulan berfungsi karboksil hilang pada spektrum grafin oksida terturun. Morfologi grafin oksida bertukar daripada rata dan licin kepada berkedut. Nisbah karbon/oksigen bagi grafin oksida adalah lebih rendah berbanding dengan grafin oksida terturun. Pada akhir kajian ini, didapati grafin oksida berjaya diturunkan setelah membuat analisa daripada pencirian Mikroskopi Imbasan Elektron Pancaran Medan dan Penyerakan Tenaga Sinar-X, Spektroskopi Infra Merah Transformasi Fourier dan Spektroskopi Penyerapan Ultralembayung-cahaya Nampak sebelum dan selepas grafin oksida disinarkan. Ini menunjukkan teknik penyinaran boleh digunakan bagi menurunkan grafin oksida kepada grafin oksida terturun.

Kata kunci: grafen, grafen oksida, sinar gama, FTIR, FESEM-EDX, UV-Vis

Introduction

As a remarkable material having great physical and chemical properties, graphene has generated tremendous interest all over the world. Graphene, discovered by Novoselov and Geim [1] possesses superior electronic conductivity, good thermal stability, remarkable structural flexibility and high specific surface area [2]. Graphene oxide (GO), though similar to graphene in the sense that it is also a two-dimensional nanomaterial, differs by having a carbon backbone decorated with hydroxyl and epoxide groups on the basal planes and carboxyl and carbonyl groups along the edges [3]. These unique nanostructure holds great promise for potential applications in fields such as in nanoelectronics, sensors, nanocomposites, batteries, supercapacitors, and hydrogen storage [4].

There are various challenges in producing graphene from graphene oxide (GO). The physical route, which involves processes such as mechanical exfoliation, epitaxial growth and vapour deposition, is time consuming and produces graphene sheets with inherent physical defects. The chemical method, which is the more preferred by chemist, is convenient in casting graphene into various structures or to integrate with other materials to prepare novel nanocomposites, produces graphene sheets with even more defects, plus the added dangers of utilizing chemicals such as hydrazine, sodiumborohydride and hydroquinone [5,6,7], which are poisonous and explosive. Solvothermal methods require high temperatures above 100 °C, even at high pressures [8].

Although each of these methods has its own merits, an ionizing radiation induced reduction of graphene oxide promises to be a rapid and facile way of producing graphene, while avoiding the use of harsh chemicals and high temperature approaches. In this study, we demonstrate the irradiation technique using gamma radiation to reduce graphene oxide. The objective of this study is to determine the optimum gamma radiation exposure to reduce graphene oxide to graphene within the range of 0 kGy to 35 kGy.

Materials and Methods

Research Materials

Graphene oxide nanopowder was purchased from Reade Advanced Material, while other chemical reagents were purchased from Sigma-Aldrich Co. All chemicals were used as received without further purification.

Sample Preparation

An amount 0.1 g of graphene oxide nanopowder was dispersed in 50 ml deionized water using an ultrasonicator for 60 minutes. Next, various type of alcohols (methanol, ethanol and isopropanol) were added into the mixture separately (the volume ratio of deionized water to alcohol was 1:1). The mixtures were then exposed to gamma radiation from a ⁶⁰Co source in the range of 0 kGy – 35 kGy. The irradiated mixture was then dried for 24 hours at 60°C. Reduced graphene oxide was obtained.

Irradiation Setup

The mixture of graphene oxide, deionized water and alcohols were irradiated with a ⁶⁰Co source at ambient temperature using a GammaCell 220 Excel irradiator at a dose rate of 4.20kGy/h. The mixtures were irradiated with 5, 15, 20, and 35 kGy gamma radiation, with 0 kGy as a control. Time required to irradiate each sample was determined with the following equation 1 below;

$$\text{Time} = \frac{\text{Dose}}{\text{Dose Rate}} \quad (1)$$

Sample Analysis

The reduction of graphene oxide to graphene was determined through the removal of oxygen atoms that were attached to the thin layer of carbon atoms. Analysis of FTIR, UV-Vis, FESEM and EDX confirm the chemical composition formed after irradiation.

Results and Discussion

Graphene oxide powder was dispersed in alcohol/water solution and underwent gamma irradiation at 0 kGy, 5 kGy, 15 kGy, 20 kGy and 35 kGy. Due to the presence of oxygen functionalities, graphene oxide is said to be hydrophilic

and tend to disperse well in water and other organic solvents. When graphene oxide powder was dispersed in ethanol/water solution and irradiated at 35 kGy, it did not produce a homogenous suspension even after long sonication process as it was being reduced [5]. This reduction process was proven through other characterization techniques, which are FTIR, UV-Vis, FESEM and EDX.

Graphene oxide that was dispersed into various alcohols, and irradiated at 0 kGy, 5 kGy, 15 kGy, 20 kGy and 35 kGy were all tested for FTIR analysis. It is noted that almost all samples did not display significant changes to their chemical bonding except for the sample that was dispersed in ethanol/water and irradiated at 35 kGy. The comparison between the FTIR spectrum of graphene oxide and reduced graphene oxide obtained from the 35 kGy gamma irradiation is shown in Figure 1.

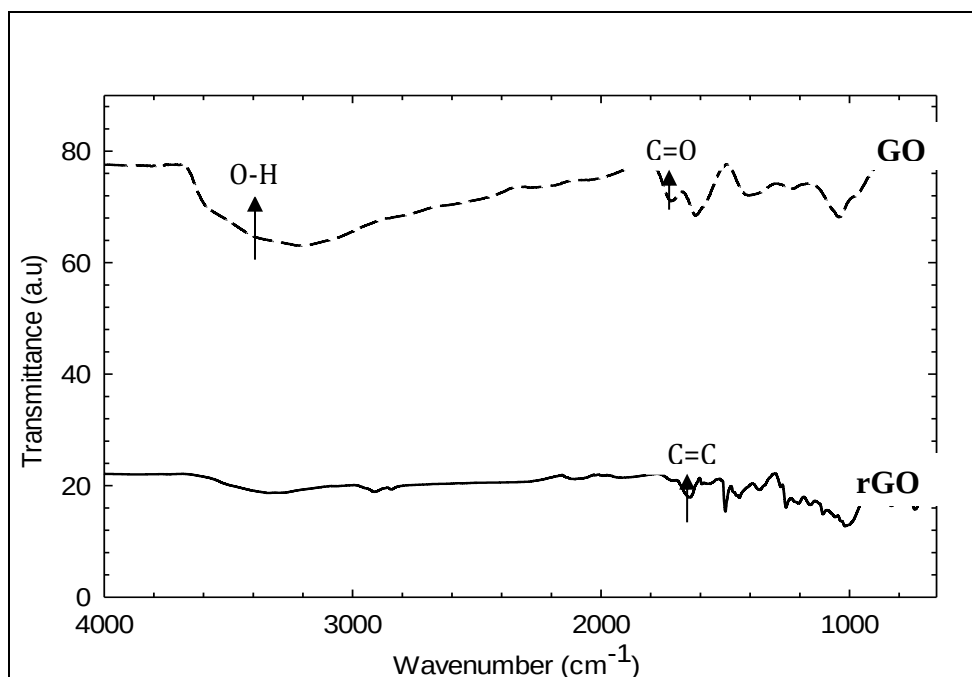


Figure 1. Comparison of Graphene Oxide and Graphene FTIR Spectrum

The spectrum of graphene oxide shows that there is a presence of an abundant oxygen containing functional groups attached to the sample. These include the O-H bond from alcohol functional group at peak 3201.64 cm^{-1} , carboxyl group at peak 1718.77 cm^{-1} and C-O bond from alkoxy group at peak 1042.93 cm^{-1} . After irradiation, the chemical bonds are reconstructed, withdrawing oxygen from the sheets. It shows in the FTIR spectra that deoxygenation happens when intensity of O-H bonds at wavelength 3338.75 cm^{-1} decreases after irradiation. Furthermore, decarboxylation effect can also be seen from the FTIR spectra. The peak at 1718.77 cm^{-1} from the graphene oxide spectrum, indicating the carboxyl group, disappeared in the spectrum of reduced graphene oxide. New chemical bonds in GO sheets are reformed after irradiation as functional group alkene, C=C at wavelength 1642.93 cm^{-1} appeared in the spectrum of reduced graphene oxide as well as 3 peaks that can be seen in the wavelength range of $1400\text{--}1070\text{ cm}^{-1}$ showing that aromatic C=C is formed.

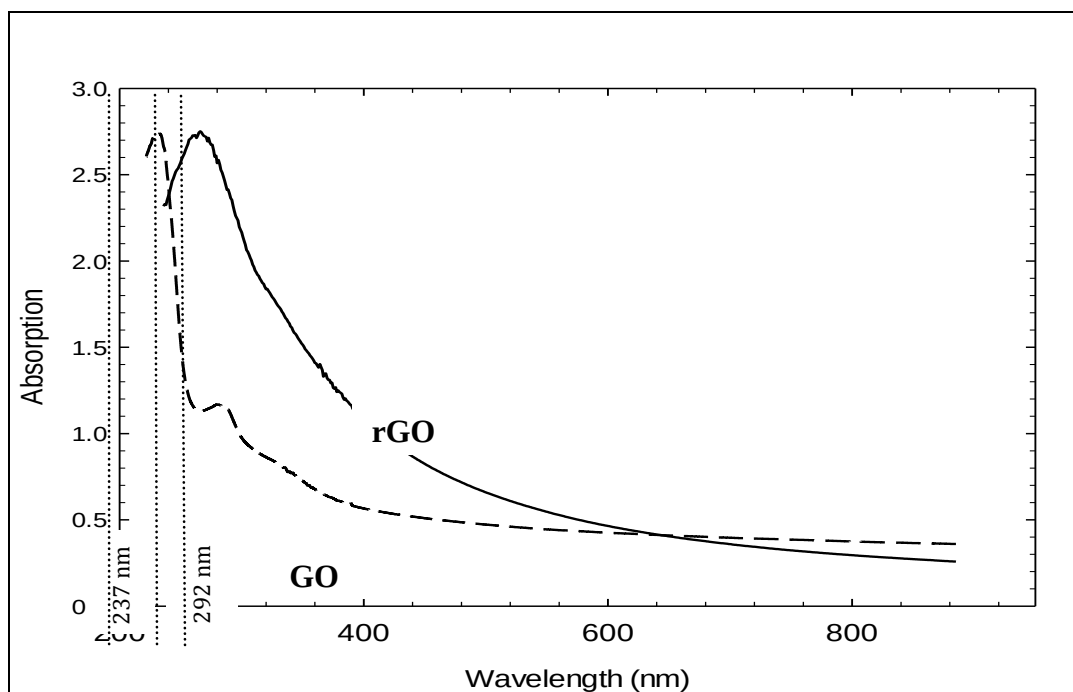


Figure 2. UV Vis Spectrum for Graphene Oxide and Graphene

UV-Vis spectra of GO (Figure 2) before and after irradiation at 35 kGy, shows that there are two absorption peak which appears at 292 nm and 237 nm. The absorption peak at 292 nm which indicates $n \rightarrow \pi^*$ transitions of C=O bonds, only appears at the spectrum of graphene oxide and the absorption peak at 237 nm ($\pi \rightarrow \pi^*$ transitions of aromatic C-C bonds) is red-shifted to 277 nm after gamma irradiation which is consistent with the characters of reduced graphene oxide [9], confirming the reduction process that occurred.

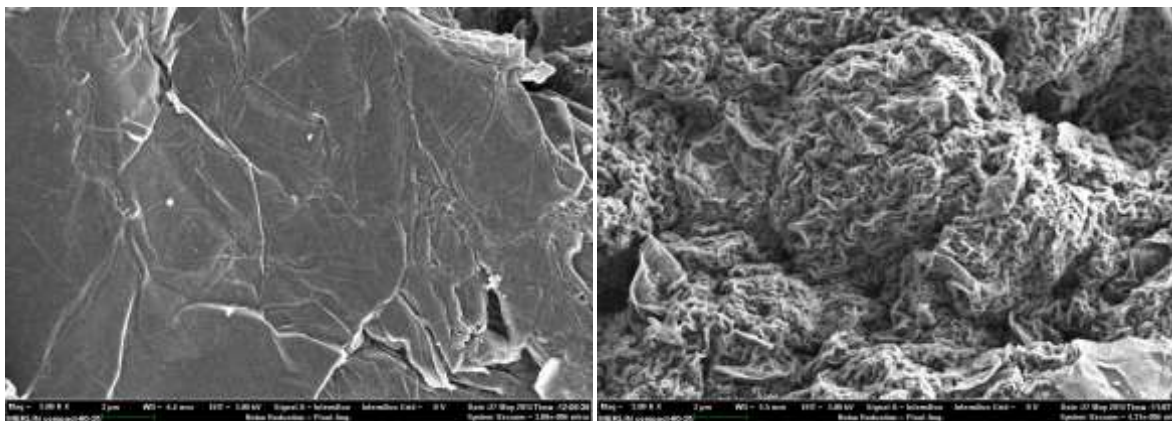


Figure 3. Morphology of Graphene Oxide (left) and Graphene (right)

The morphology of graphene oxide before and after irradiation was analyzed using FESEM as shown in Figure 3. Results obtained show that graphene oxide have flat and smooth surface. After it underwent gamma irradiation, the

morphology of the product obtained changed from flat and smooth to wrinkled and crumpled. This may be due to the formation and reconstruction of new chemical bonds on the single layered carbon as reported by Song et al. [10]. The lattice defect is also contributed by the formation of alkyl group attached to the reduced graphene oxide.

The reduction process that took place was also proved by the elemental composition analysis using EDX. Results obtained show that the atomic weight of carbon in graphene oxide is much lower than in the reduced graphene oxide by 20% while the atomic weight of oxygen in graphene oxide is greater than in the reduced graphene oxide by 20%. Spectrum below shows the increment of carbon and the significant drop of oxygen in the sample. The carbon/oxygen ratio of graphene oxide increases after irradiation from 2.69 to 5.68 proving that reduced graphene oxide is successfully produced. Based on all results mentioned earlier, we conclude that gamma irradiation induces reduction of graphene oxide to reduced graphene oxide.

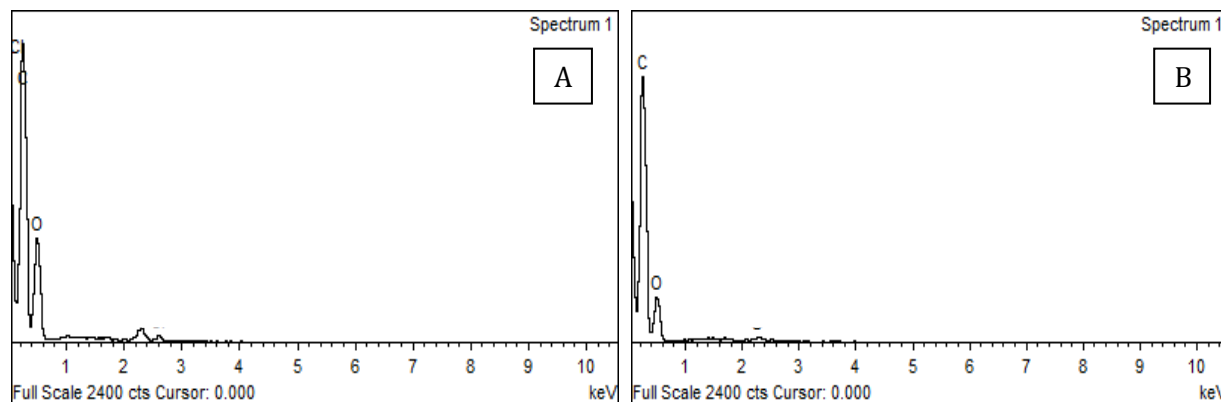


Figure 4. Elemental Composition of Graphene Oxide (A) and Reduced Graphene Oxide (B)

Table 1. EDX Analysis of Graphene Oxide and Reduced Graphene Oxide

Sample	Element			
	Carbon		Oxygen	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
Graphene Oxide	58.58	66.84	41.41	33.16
Reduced Graphene Oxide	76.32	81.00	23.68	19.00

The radiolysis of water was believed is the main mechanism that induced the reduction process. Based on the radiation chemistry of water, gamma irradiation can decompose water molecules into eight products which are $\cdot\text{H}$, $\cdot\text{OH}$, OH^- , e_{aq}^- , H_2 , H_2O_2 , H_3O^+ and H_2O . Hydrated electron (e_{aq}^-) is the major reducing species among the products of water radiolysis, while hydroxyl radical, $\cdot\text{OH}$ is the major oxidizing species produced [11]. In order to perform reduction, the oxidative radical must be eliminated. In this study, ethanol was added to eliminate the hydroxyl radical as radical scavengers, hence creating a reductive medium. Hydrated electron helps in the reduction process as it interacts with hydroxyl and carboxyl group attached to graphene oxide, eliminating oxygen thus forming reduced graphene oxide.

Conclusion

Graphene oxide underwent reduction by gamma irradiation in the mixture of alcohol and deionized water forming reduced graphene oxide. The optimum exposure dose to produce reduced graphene oxide was 35 kGy, while the best solvent used among the alcohols was ethanol that helped in creating the reductive medium. The reduction

process induced by gamma irradiation was proven by performing characterization before and after irradiation using FTIR, UV-Vis, FESEM and EDX. According to the characterization made by FTIR, there were no significant changes to the chemical structure of graphene oxide that were irradiated at 0 kGy, 5 kGy, 15 kGy, 20 kGy except for 35 kGy where decarboxylation occurred. Almost every oxygen-containing functional group was successfully eliminated and new chemical bonds were formed and reconstructed causing the flat and smooth surface of graphene oxide to crumpled. This was caused by the reconstruction of multiple new carbon bonding on a single layer of carbon after the irradiation, leading to a lattice defects. EDX analysis shows that the carbon/oxygen ratio of graphene oxide was lower than the reduced graphene oxide formed proving that reduction process took place. In conclusion, irradiation technique can be used to perform reduction process to obtain reduced graphene oxide without using hazardous chemicals, high pressure and temperature.

Acknowledgement

The authors would like to acknowledge funding from UKM in this work through research grants FRGS/1/2014/SG06/UKM/02/3, DLP-2013-037 and ERGS/1/2012/STG02/UKM/02/1. We would also like to thank the Centre of Research Instrumentation (CRIM) UKM for extending their facilities to us.

References

1. Novoselov, K.S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang Y., Dubonos, S. V., Grigorieva, I. V., Firsov, A. A. (2004). Electric field effect in atomically thin carbon films. *Science* 306(5696): 666-669.
2. Lee, C., Wei, X., Kysar, J. W., Hone, J. (2008). Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science* 321 (5887): 385-388.
3. Yang, K., Liang, S., Zou, L., Huang, L., Park, C., Zhu, L., Fang, J., Fu, Q. and Wang, H. (2012). Intercalating oleylamines in graphite oxide. *Langmuir* 28(5): 2904-2908.
4. Geim, A.L., Novoselov, K.S. (2007). The rise of grapheme. *Nature Materials* 6(3): 183-191.
5. Stonkovich, S., Dikin, D. A., Piner, R. D., Kohlhaas K. A., Kleinhammes, A., Jia, Y., Wu, Y., Nguyen, S.T. and Ruoff, R. S. (2007). Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* 45(7): 1558-1565.
6. Si, Y. and Samulski, E.T. (2008). Synthesis of water soluble graphene. *Nano Letters* 8(6): 1679-1682.
7. Wang, G., Yang, J., Park, J., Gou, X., Wang, B., Liu, H. and Yao, J. (2008). Facile synthesis and characterization of graphene nanosheets. *Journal American Chemical Society* 131: 9910-9911.
8. Nethravathi, C. and Rajamathi, M. (2008). Chemically modified graphene sheets produced by solvothermal reduction of colloidal dispersions of graphite oxide. *Carbon* 46(14): 1994-1998.
9. Luo D., Zhang G., Liu J. and Sun X. (2011). Evaluation Criteria for Reduced Graphene Oxide. *Journal Physics Chemistry* 115: 11327-11335
10. Song P., Zhang X., Sun M., Cui X. and Lin. Y. (2012). Synthesis of graphene nanosheets via oxalic acid-induced chemical reduction of exfoliated graphite oxide. *RSC Advances* 2: 1168-1173.
11. Khan K. A. (1981). The Radiation Chemistry of Water. *Journal Physics Chemistry*: 105-110.