Environmental-friendly synthesis of reduced graphene oxide (rGO) using gamma irradiation

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Abstract. Graphene has drawn much attentions in recent years, mainly due to its excellences in their strength and thermal/electrical conductivity with various possible applications. However, some common graphene synthesis methods involve in using/producing poisonous chemicals and other production drawbacks, leading to attempts to adopt more efficient and more environmental-friendly synthesis methods. This work reported preliminary results in developing a method for graphene synthesis using gamma irradiation on graphene oxide (GO) with the accumulated doses of 14, 21, 28, 35, and 42 kGy, respectively. The results showed that gamma irradiation could successfully initiate the reduction of GO in water-ethanol mixture to reduced graphene oxide (rGO) with different efficiencies, which were confirmed by using SEM, SEM-EDS, UV-Vis spectroscopy, and FT-IR spectroscopy. In particular, SEM-EDS showed that irradiating GO with 35-kGy gamma dose led to the highest reduction of oxygen in GO as seen by the highest ratios of carbon and oxygen (C:O) content in rGO that increased by ~20% compared with the value from GO.

1. Introduction
Graphene, a one-atom-thick two-dimensional layer of carbon arranged in a honeycomb (hexagonal) network shown in figure 1, has gained much attentions from industries and academic researchers in recent years, mainly due to its excellences in electrical and thermal conductivities, high mechanical strength, good biocompatibility, large theoretical specific surface area, and good optical transmittance [1-2]. These preferable properties have led to the utilization of graphene in various fields including applications in medicine (tissue engineering, drug delivery, and contrast agents in bio-imaging [3–5]), electronics (transistors, transparent conducting electrodes, and optoelectronics [6-8]), light processing (optical modulator and ultraviolet lens [9-10]), and energy (solar cells, fuel cells, and supercapacitor [11-13]).
To synthesize graphene for actual uses, several methods have been introduced and utilized with mixing advantages and drawbacks. For instance, the very first method to obtain graphene sheets was to exfoliate graphite mechanically (cleaving). In spite of being a low-cost method, graphene sheets obtained are usually in the sizes of several micron levels and also having irregular shapes, making them unsuitable for applications that require structurally coherent graphene sheets or graphene flakes with a unique azimuthal orientation [14]. Other methods that are also widely used include chemical exfoliation [15], chemical synthesis [16], thermal chemical vapor deposition (CVD) [17], unzipping nanotube [18], and microwave synthesis [19]. Among the mentioned methods, chemical synthesis and thermal CVD methods are presently the most common techniques use in graphene synthesis due to their relatively high-qualitied graphene sheets obtained with only a few layers thick, making them a better candidate for applications that require specific azimuthal orientation and larger graphene sizes. Nonetheless, these two methods also have disadvantages, for example, reducing agents such as hydrazine, sodium borohydride, and hydroquinone used in chemical synthesis are known to be highly poisonous and explosive, hence, raising safety concerns for both producers and users.

In order to introduce safer and more environmental-friendly methods for graphene synthesis, gamma (γ) irradiation could be used to initiate the reduction of graphene oxide (GO) to reduced graphene oxide (rGO), of which rGO has important properties similar to graphene (the chemical structures of GO and rGO are shown in figure 2a and figure 2b, respectively). Moreover, in addition to being safer method, gamma irradiation also generates higher uniform reducing agents in the solution, is able to get absorbed regardless of light-absorbing solutes and products, and is more cost effective than chemical synthesis and CVD methods. In principle, GO is normally dispersed in water-ethanol mixture before being gamma irradiated due to its highest efficiency in synthesizing rGO compared with dispersing in pure water or other water-alcohol mixtures [2]. The mechanism to obtain rGO from GO using gamma irradiation involves the water molecules undergo radiolysis (decomposition) after gamma interaction, forming several oxidative and reductive species such as H-, \( \cdot \)OH, OH⁻, \( e_{eq} \), H₂, H₂O₂, H₃O⁺, and H₂O. Then, ethanol, which is mixed with water, would scavenge the \( \cdot \)OH radicals (oxidative radicals must be eliminated), forming water and alcohol radicals (R•). These R• would then act as a reducing medium for chemical reaction to occur after gamma irradiation that would result in the reduction of GO to rGO. The equations that show the mentioned mechanisms are shown in (1.1) and (1.2).

\[
\begin{align*}
\text{H}_2\text{O} & \xrightarrow{\text{gamma irradiation}} e^{-}_{eq} + H\cdot + \cdot \text{OH} \\
\text{RH} + \cdot \text{OH}(\cdot \text{H}) & \rightarrow \text{H}_2\text{O(H}_2) + \text{R}•
\end{align*}
\]

where RH represents an ethanol molecule.
Figure 2. Chemical structures of (a) graphene oxide (GO) and (b) reduced graphene oxide (rGO).

Due to high potential of using gamma irradiation for a safe and environmental-friendly graphene synthesis, this work carried out a preliminary study aimed to synthesize rGO using gamma irradiation with the accumulated doses of 14, 21, 28, 35, and 42 kGy (dose rate 2.9 kGy/h) on GO dispersed in water-ethanol mixtures, in which GO was prepared from nano-sized graphite. Testing methods used for rGO characterization in this work included Scanning Electron Microscopy (SEM) and Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SEM-EDS), UV-Vis spectroscopy, and Fourier-Transform Infrared Spectroscopy (FT-IR). Thorough details on GO preparation from graphite, procedures and conditions to synthesize rGO using gamma irradiation, results of rGO characterization from different accumulated doses, and discussion on all results are included in this report.

2. Materials and methods

2.1 Chemicals and reagents

Nano-sized graphite powder was purchased from Richest Group Co., Ltd. (China). NaNO₃, H₂SO₄, HCl, KMnO₄, and 30% H₂O₂ were purchased from Gammago Co., Ltd. (Thailand) and ethanol was purchased from Chemipan Co., Ltd. (Thailand). All chemicals were of analytical grades and used as received. Note that all aqueous solutions were prepared in deionized water unless noted otherwise. The SEM image of nano-sized graphite powder used in this work is shown in figure 3.

Figure 3. SEM image of nano-sized graphite powder used in this work.
2.2 GO synthesis

GO was synthesized from nano-sized graphite powder using the modified Hummer’s method [20-21], in which 1 g of graphite powder was mixed with 0.5 g of NaNO₃ and 23 mL of H₂SO₄ in 1000-mL flask. The solution was continuously stirred for 1 hour, then, 3 g of KMnO₄ was added to the solution and continued to be stirred for another 1 hour. Note that, during the mixing and stirring processes, the temperature of the solution was kept at 15-20°C to prevent overheating and explosion. Next, 500 mL of deionized water was gradually added to the solution, while the temperature was slowly increased to 35°C, of which vigorous stirring was continued for another 1 hour. In order to remove KMnO₄ and other impurities, 5 mL of 30% H₂O₂ was added to the solution, then the suspension was sonicated and washed using HCl and deionized water to remove residual ions of SO₄²⁻. The resulting suspension of GO was then filtered/dried and ground into fine powder. The images of the suspension of GO during sonication and after filtration/dry are shown in figure 4a and figure 4b, respectively.

![Figure 4. Images of GO (a) during sonication and (b) after filtration and drying.](image)

2.3 Gamma irradiation and rGO synthesis

5 mg of GO powder obtained from Section 2.2 was dispersed in 10-mL water-ethanol (1:1) mixture using an ultrasonic bath for 1 hour. The dispersion was then transferred into a glass bottle and the dissolved oxygen was removed by bubbling with nitrogen gas for 10 minutes. Then, the samples were irradiated with gamma (the accumulated doses of 14, 21, 28, 35, and 42 kGy, respectively). Note that a ⁶⁰Co source with the dose rate of 2.9 kGy/h at the Thailand Institute of Nuclear Technology (TINT) was used as a gamma source for this work. After the gamma irradiation was completed, the samples were washed with deionized water and oven-dried at 70°C until constant weights were achieved before being characterized.

2.4 rGO characterization techniques

Magnified images of GO and rGO powder were taken using SEM (Quanta 450 FEI, the Netherlands) at a 10-kV accelerating voltage with back-scattered electrons (BSE). In addition, the percentages of carbon and oxygen (C:O) contents of GO and rGO (for all accumulated doses) samples in terms of weight and atomic ratios were measured using SEM-EDS. Ultraviolet-Visible (UV-Vis) spectra of GO and rGO (for all accumulated doses) samples were collected using a UV-Vis spectrophotometer (Biochrom Libra S32, UK) within the wavelength region of 200-600 nm. Fourier-Transform Infrared (FT-IR) spectra of GO and rGO (at the accumulated dose of 28 kGy) were recorded using a FT-IR spectrophotometer (Bruker: Model Vertex70, USA) within the wavenumber region of 400-4000 cm⁻¹.
3. Results and discussion

3.1 SEM and SEM-EDS studies

As shown in figure 5, the morphology of GO in figure 5a is flatter and smoother than the one from rGO shown in figure 5b, which presents more wrinkles and crumples. This change in the morphology between GO and rGO could be due to the formation and reconstruction of new chemical bonds on the single-layered carbon [20,22].

When considering percentages of carbon and oxygen (C:O) contents of GO and rGO (for all accumulated doses) samples using SEM-EDS shown in Table 1, the results clearly showed that gamma irradiation led to the increases in C:O contents for all irradiation doses with the highest value at 35 kGy (68.9:31.1 by % weight content and 74.8:25.2 by % atomic content, which increased by ~20% compared with the values from non-irradiated GO). The increase in C:O implied that rGO was successfully produced using gamma irradiation. It should be noted that the value of C:O decreased once the gamma irradiation dose was further increased from 35 kGy to 42 kGy. This could be due to the fact that, at too high gamma doses, gamma irradiation induced oxidation on the rGO, resulting in the increases of hydroxyl/carbonyl groups and oxygens in rGO.

![Figure 5. SEM images of (a) GO and (b) rGO after 28-kGy gamma irradiation.](image)

| Gamma dose (kGy) | Percentage By weight content | Percentage By atomic content |
|------------------|-----------------------------|-----------------------------|
|                  | Carbon (C)                  | Oxygen (O)                  | Carbon (C) | Oxygen (O) |
| Non-irradiation  | 49.1                        | 50.9                        | 56.2       | 43.8       |
| 14               | 55.7                        | 44.3                        | 62.6       | 37.4       |
| 21               | 51.9                        | 48.1                        | 59.0       | 40.1       |
| 28               | 51.3                        | 48.7                        | 58.4       | 41.6       |
| 35               | 68.9                        | 31.1                        | 74.8       | 25.2       |
| 42               | 52.9                        | 47.1                        | 59.9       | 40.1       |

However, in order to improve the accuracy of the elemental composition of the specimens, other characterization techniques besides SEM-EDS such as X-ray photoelectron spectroscopy (XPS) that could characterize the specimens in wider areas of interest, as well as be able to measure the composition in the parts per thousand (ppt) range, could be used.
3.2 UV-Vis spectroscopy
As shown in figure 6, the UV-Vis spectra show that GO has the maximum absorption peak at ~230 nm, which is corresponding to $\pi-\pi^*$ transition of C–C bonds and shoulder peaks at ~300 nm, which is corresponding to n–$\pi^*$ transition of aromatic C–C bonds [2]. However, once GO samples were irradiated with gamma rays for all accumulated doses, the spectra show significant decreases in the intensity with a red shift of ~2–3 nm. These changes implied that partial reduction of GO to rGO and the restoration of C=C occurred [21], as well as the electronic conjugation within graphene sheets was restored, leading to the increase in $\pi$-electron concentration and structural ordering that consistent with the restoration of $sp^2$ carbon and the arrangement of atoms [23].

![Figure 6. UV-Vis spectra of GO and rGO obtained from different doses of gamma irradiation.](image)

3.3 FT-IR spectroscopy
As shown in figure 7, the FT-IR spectra of GO and rGO obtained from 28-kGy gamma irradiation show that both samples contained oxygen-containing functional groups as seen by the peaks at 1400 cm$^{-1}$/3300 cm$^{-1}$ (O–H bond from alcohol functional group) and 1043 cm$^{-1}$ (C–O bond from alkoxy group). However, after gamma irradiation, rGO had slightly higher peak intensity at 1643 cm$^{-1}$, which corresponds to C=C, than GO, implying the reduction of GO occurred with the re-creation of aromatic C=C bonds. Note that some peaks which represent oxygen-containing functional group also increased after gamma irradiation, probably due to the imperfect removal of dissolved oxygen during the nitrogen bubbling process. It should be noted that, for other gamma irradiation doses, similar patterns and intensities of IR bands with only slight differences compared with the results of a 28-kGy irradiated rGO sample were also observed.
4. Conclusions
Due to the needs to develop safer and more environmental-friendly methods for graphene synthesis, gamma rays was used to irradiate GO samples prepared from nano-sized graphite powder in order to initiate the reduction of GO to rGO. The results showed that gamma irradiation at the accumulated doses of 14, 21, 28, 35, and 42 kGy could successfully produce rGO with different efficiencies. The characterization methods used in this work included SEM, SEM-EDS, UV-Vis spectroscopy, and FT-IR spectroscopy, of which SEM-EDS indicated the highest reduction efficiency in the gamma dose of 35 kGy as seen by the highest ratios of C:O, which was higher than the value of non-irradiated GO by also 20%. The overall results implied that the rGO could be successfully synthesized using gamma irradiation, presenting high potential to adopt this method as safer and more environmental-friendly techniques for actual uses.

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References
[1] Stankovich S, et al. 2006 Graphene-based composite materials Nature. 442 282–6
[2] Shahriary L, et al. 2015 Synthesis of graphene using gamma radiations. Bull. Mater. Sci. 38 739–45
[3] Shin S R, et al. 2016 Graphene-based materials for tissue engineering Adv. Drug Deliv. Rev. 105 255–74
[4] Liu J, et al. 2013 Graphene and graphene oxide as new nanocarriers for drug delivery applications Acta Biomater. 9 9243–57
[5] Zhang M, et al. 2018 Ultrasound graphene oxide based T1 MRI contrast agent for in vitro and in vivo labeling of human mesenchymal stem cells Nanomed-nanotechnol. 14 2475–83
[6] Yankowitz M, et al. 2018 Dynamic band-structure tuning of graphene moire superlattices with pressure Nature. 557 404–8
[7] Xu Y, et al. 2016 Graphene as transparent electrodes: fabrication and new emerging applications Small. 12 1400–19
[8] Bonaccorso F, et al. 2010 Graphene photonics and optoelectronics Nat. Photonics. 4 611–22
[9] Liu M, et al. 2011 A graphene-based broadband optical modulator Nature. 474 64–7

Figure 7. FT-IR spectra of GO and rGO obtained from 28-kGy gamma irradiation.
[10] Liu W, et al. 2018 Graphene-enabled electrically controlled terahertz meta-lens Photonics Res. 6 703–8
[11] Yin Z, et al. 2014 Graphene-based materials for solar cell applications Adv. Energy Mater. 4 1300574
[12] Antolini E. 2012 Graphene as a new carbon support for low-temperature fuel cell catalysts Appl. Catal. B. 123–124 52–68
[13] Manjakkal L, et al. Flexible self-charging supercapacitor based on graphene-Ag-3D graphene foam electrodes Nano Energy. 51 604–12
[14] Avouris P, et al. 2012 Graphene: synthesis and applications Mater. Today. 15 86–97
[15] Vicullis L M, et al. 2003 A chemical route to carbon nanoscrolls Science 299 1361
[16] Park S, et al. 2009 Chemical methods for the production of graphenes Nat. Nanotechnol. 4 217–24
[17] Reina A, et al. 2009 Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition Nano Lett. 9 30–5
[18] Jiao L Y, et al. 2010 Facile synthesis of high-quality graphene nanoribbons Nat. Nanotechnol. 5 321–5
[19] Xin G Q, et al. 2010 A graphene sheet exfoliated with microwave irradiation and interlinked by carbon nanotubes for high-performance transparent flexible electrodes Nanotechnol. 21 40
[20] Sharin S, et al. 2015 Reduction of graphene oxide to graphene by using gamma irradiation Malays. J. Anal. Sci. 19 1223–8
[21] Tuyen L A, et al. 2016 The effect of gamma-irradiation on graphene oxide in a monoglyceride/ethanol solution Nucl. Sci. Technol. 6 48–53
[22] Song P, et al. 2012 Synthesis of graphene nanosheets via oxalic acid-induced chemical reduction of exfoliated graphite oxide RSC Advances. 2 1168–73
[23] Gurunathan S, et al. 2012 Oxidative stress-mediated antibacterial activity of graphene oxide and reduced graphene oxide in Pseudomonas aeruginosa Int. J. Nanomedicine. 7 5901–14