



# The Effect of Different Radiation Sources on Graphene Oxide Reduction and Scale-Up

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## 1. Introduction

Graphene is one of the crystalline forms of carbon, consisting of a monolayer of carbons with sp<sup>2</sup> hybridization arranged in a hexagonal structure that has a large specific surface area, excellent electrical and thermal conductivities, high mechanical strength, and chemical stability [1]. The reduction mechanism is based on the generation of active free radicals through water radiolysis. The reducing species, hydrogen radicals (H•) and solvated electrons (e<sup>-</sup><sub>aq</sub>), are produced by ionizing radiation and promote the partial reduction of graphene oxide and the formation of metallic nanoparticles [2]. The main objective of this work is to scale up the reduction of graphene oxide by gamma radiation for applications in different research fields and compare the used methods for reducing GO through ionizing radiation. Specific objectives include synthesizing graphene oxide, characterizing graphene oxide, studying the dose and methods for reducing graphene oxide by ionizing radiation, and characterizing reduced graphene oxide.

## 2. Methodology

### Reagents

Powdered graphite 99.99%, sodium nitrate (NaNO<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) 30%, isopropanol (C<sub>3</sub>H<sub>7</sub>OH), all marketed by the brand Merck; potassium permanganate (KMnO<sub>4</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), from the brand Sigma-Aldrich, and ethanol (C<sub>2</sub>H<sub>5</sub>OH) from Labsynth.

### Equipment

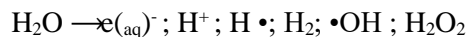
For the synthesis of graphene oxide (GO), the following equipment was used: Hitachi CR 20B ultracentrifuge, Excelsa Fanem 206 BL benchtop centrifuge, Unique ultrasonic cell disruptor, Sanders Soniclean 2 ultrasonic washer, Fisatom heating mantle and magnetic stirrer hotplate, and Shimadzu AUY220 analytical balance. The Cobalt-60 Multipurpose Irradiator from CETER/IPEN/CNEN-SP. According to the International Atomic Energy Agency (IAEA), this facility belongs to category IV, and according to the National Nuclear Energy Commission (CNEN), it is included in group 1.

## Graphene Oxide Synthesis

Graphene oxide was synthesized from graphite using the modified Hummers method [3]. In a flask, 3 g of graphite, 3 g of NaNO<sub>3</sub>, and 140 mL of H<sub>2</sub>SO<sub>4</sub> were added, and the mixture was kept under stirring in an ice bath. Then, 18 g of KMnO<sub>4</sub> was added while maintaining the temperature at 10°C. After this period, the mixture was stirred for about 2 hours at room temperature and then adjusted to 35°C, and the system remained under stirring for another 1 hour. Subsequently, 240 mL of deionized water was slowly added, and the temperature was maintained at 90°C under stirring for 1 hour, followed by the addition of another 300 mL of deionized water. Finally, 10 mL of H<sub>2</sub>O<sub>2</sub> (30%) was added under stirring at room temperature. The graphene oxide was successively washed with sodium hydroxide and hydrochloric acid solutions (1 mol.L<sup>-1</sup>) and centrifuged at 13000 RPM until reaching pH 6. For the graphene oxide exfoliation process, the aqueous mixture was kept in an ultrasonic probe and then lyophilized.

## Graphene Oxide radiation

In all methods used to reduce graphene oxide, the principle for reduction is the same, where upon interaction with water (radiolysis process), hydrogen (H•) and hydroxyl (•OH) free radicals are produced.



The product responsible for reducing graphene oxide is the H• ion, which, upon reacting with carboxylic acid groups, reduces them to carbonyls and ketones groups. The presence of alcohol (isopropanol or ethanol) captures the •OH species, disfavoring the reduction of carbonyls into alcohol.

In the experiments conducted throughout the project, the samples received doses of 25 kGy (7 kGy/h) and 40 kGy (10 kGy/h) from the cobalt-60 multipurpose irradiator, with graphene oxide sample concentrations 1 g/L.

## Co<sup>60</sup> Multipurpose Irradiator

The multipurpose irradiator was used for the scale-up experiment in graphene oxide reduction because it allows for the use of a larger amount of material compared to electron beam and gamma cell. The samples were separated into a 1 L container of GO with a concentration of 1 g/L and 4 vials of 20 ml each with the same concentration.

## 3. Results and Discussion

### Graphene Oxide

Graphene oxide is produced through a process involving graphite oxidation using potent oxidants in an acidic medium. This generates graphite oxide, which is a form with incorporated oxygen atoms. This incorporation alters the material's structure, increasing the distance between layers compared to graphite, allowing graphite oxide to be exfoliated to obtain graphene oxide.

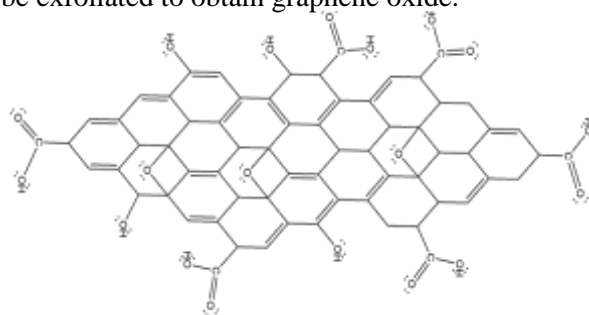


Figure 1: Author-drawn molecular structure of graphene oxide in ChemDraw.

Although graphene oxide possesses several attractive characteristics for technological applications, such as a wide surface area and oxygenated groups for functionalization, the production process creates a significant amount of defects in the carbon structure. These defects have a negative impact on crucial properties such as heat and electron transfer through the material. A common approach to mitigate this issue is the partial reduction of graphene oxide, converting it into reduced graphene oxide (rGO). This reduction aims to partially reverse the effects of oxidation without compromising desired characteristics such as the availability of functional groups [4].

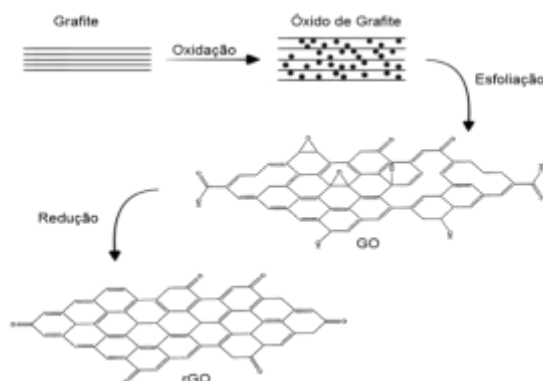


Figure 2: Summary of the synthesis, exfoliation, and reduction of graphene oxide.

## Characterizations

### Raman Spectroscopy

Raman spectroscopy allows us to analyze the G bands ( $1580\text{ cm}^{-1}$ ) corresponding to  $sp^2$  carbon hybridizations in relation to the D band ( $1350\text{ cm}^{-1}$ ) related to defects and disorder, where an increase relative to GO indicates reduction. Thus, spectra were obtained for the experiments with 25 kGy and 40 kGy.

### X-ray Diffraction (XRD)

X-ray diffraction is a technique that uses radiation to interact with a sample, and from the diffraction caused by atomic planes in relation to the angle of incidence of the beam, it is possible to determine the crystalline structure of the analyzed sample. According to the consulted literature [5], the peak at approximately  $2\theta$  of  $24^\circ$  in the Fig. 3 and Fig. 4 indicates that graphene oxide reduction occurred during the radiation process.

The Fig. 3 below belongs to the experiment conducted with the multipurpose irradiator. The spectra of the samples that received a dose of 25 kGy did not show a peak at  $2\theta$ , but rather the peak at  $1\theta$ , which is characteristic of graphene oxide, indicating that there was no reduction in the 1 L container and in the vial tubes.

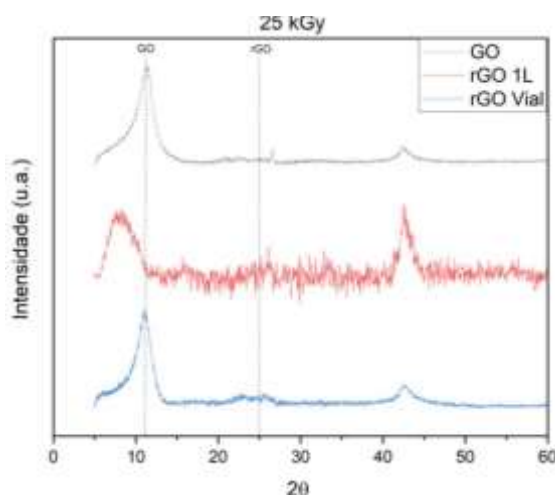


Figure 3: XRD of 25 kGy graphene oxide.

However, in the experiment with a dose of 40 kGy, the presence of both characteristic peaks of GO and rGO was observed for the 1 L sample. However, in the vial tube sample, only the peak at approximately  $2.5\theta$  of rGO was observed, indicating partial reduction.

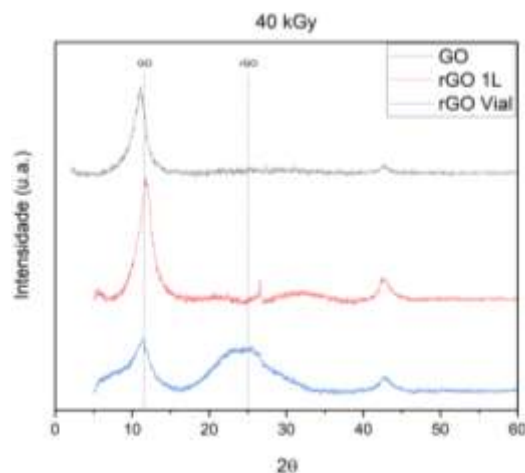


Figure 4: XRD of 25 kGy graphene oxide.

### Thermogravimetry (TGA)

Thermogravimetric analysis corroborates with the results obtained from Raman and XRD analyses. The technique is based on collecting data on heat flow and mass variation simultaneously and aims to visualize the percentage of reduction by radiation of graphene oxide concerning the irradiated sample to confirm reduction.

The reduction of graphene oxide by ionizing radiation is a beneficial alternative as it does not use organic solvents, toxic reagents, generates by-products, and occurs at ambient temperature and pressure.

## 4. Conclusions

In this work, it was observed that there was no reduction of graphene oxide for 1 L volumes. Although the characterizations showed reduction just for the 20 mL vials in 40 kGy. Further studies should be conducted to prove the real efficiency of this process in large scale. Future work will be based on increasing the nitrogen exposure time to which the samples will be subjected, exploring different concentrations, increasing the dose rate, or even using higher doses.

## Acknowledgements

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