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THE EFFECT OF GAMMA RADIATION ON THE STRUCTURE OF GRAPHENE OXIDE AND GRAPHENE OXIDE FUNCTIONALIZED WITH AMINO-PEG

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ABSTRACT

The functionalization of graphene oxide (GO) with polyethylene glycol (PEG) has been widely used in drug delivery systems. This nanocomposite exhibits excellent stability in the presence of high concentrations of salts and proteins and shows to be less toxic than its raw form *in vitro* and *in vivo*. However, it must be sterilized before use in the medical field and the gamma irradiation shows a promising option for this purpose. Sterilization by ionizing energy through gamma rays, generated by Cobalt-60 self-disintegration, consists in exposing the materials to short electromagnetic waves. The irradiation process provides substantial advantages when compared to thermal and chemical processes such as more precise control of the process, production of products with superior qualities, lower energy consumption and less environmental pollution. In this work the effect of gamma radiation on the structure of GO and GO functionalized com Amino-PEG (GO-PEG-NH_2) irradiated with different doses (15, 25, 35 and 50 kGy) and rate dose 7.31 $kGy.h^{-1}$ was evaluated. The analyses were performed by Fourier-transform infrared spectroscopy (FT-IR) and Raman spectroscopy. The results showed that the methods for the synthesis of GO and GO-PEG-NH_2 was effective since there was confirmation of the surface oxidation of materials and functionalization with the PEG-NH_2 and the sterilization by gamma radiation does not caused any defects on materials.

1. INTRODUCTION

Graphene oxide (GO) is one of the precursors of graphene, a flat monolayer of carbon atoms arranged in a two-dimensional (2D) network [1]. This material has been widely used in several areas in nanoscience and nanotechnology fields, especially in synthesis and characterization of new conductive composites and biomaterials [2]. The GO has a high dispersion capacity, large surface area and present functional groups capable of promoting biological interactions [3].

Despite advances in its applications in the medicine, there are some concerns about the potential biocompatibility and toxicity of graphene-based nanomaterials [4].

However, when the GO surface is chemically modified for example, functionalized with polyethylene glycol, its compatibility with the physiological environment is increased [5].
Polyethylene glycol, PEG, is widely used in biomedical applications because its excellent physicochemical and biological properties such as minimal toxicity, good solubility in water and organic solvents. In addition, the terminal hydroxyl groups of PEG can be converted into reactive primary amino groups (PEG-NH_2) increasing their biocompatibility [6].

The GO functionalized with amino-PEG (GO-PEG-NH_2) exhibits excellent stability in the presence of high salt and protein concentrations and appears to be less toxic than its raw form *in vitro* and *in vivo* [7].

For medical use, nanomaterials must be sterilized, and gamma radiation is an effective method for it, in addition this technique does not generate waste and toxic emissions. Sterilization, in the range of 10 to 30 kGy, by ionizing energy through gamma rays, generated by Cobalt-60 self-disintegration, consists in exposing the materials to short electromagnetic waves [8].
In this study was evaluated the effect of gamma radiation on the structure of GO and GO-PEGNH_2, which were irradiated with three different doses 15, 25, 35 and 50 kGy.

2. MATERIALS AND METHODS

2.1. Materials

Graphite powder with a purity of 99.99% was purchased from Sigma-Aldrich and all chemical reagents used were of analytical grade.

2.2 Equipment

Structural analysis was performed in infrared absorption spectrometry (FT-IR) brand Bruker Alpha model, and Raman spectroscopy were performed using a Renishaw inVia Reflex microscope equipped with a CCD camera (Renishaw, 600 x 400 pixels) thermally cooled and coupled to a Leica model DM2500M microscope. The lines of lasers used were 532 nm and 785 nm (diode laser, Renishaw) respectively for the GO and GO-PEG-NH_2 samples.

2.3 Statistical Analysis

The structural characterization were analyzed by spectrum profile and performed in Origin 8 software.

2.4 Synthesis of Graphene Oxide (GO)

Graphene oxide was synthesized according to Hummers method with modifications [9].

2.5 Synthesis of Amino-PEG (PEG-NH_2)

Amino-PEG (PEG-NH_2) was synthesized according to the method described by Mutter [10]. The product was purified by precipitation with ether.

2.6 Synthesis of Graphene Oxide Functionalized with Amino-PEG (GO-PEG-NH_2)

Graphene oxide functionalization was performed by amidation employing the amino-PEG (PEG-NH_2) as described by Yang et al [11].

2.7 γ – Irradiation

Samples of GO (solid) and GO-PEG-NH_2 (solution) were irradiated at the doses of 15, 25, 35 and 50 kGy and dose rate of 7.31 kGy.h^{-1}, using a ^{60}Co source.

3. RESULTS AND DISCUSSION

3.1 The Structures of GO and GO-PEGNH_2

The functionalization reaction of GO with PEG-NH_2 and N- (3-dimethylaminopropyl-N'-ethylcarbodiimide) hydrochloride (EDC) result in GO-PEG-NH_2 formation. The result of the nitrous [12] acid and ninhydrin tests [13] was positives for the presence of group amine primary in PEG-NH_2.

GO, GO-PEG-NH_2 infrared spectroscopy (FT-IR) and Raman spectroscopy as discussed below:

3.1.1 Infrared spectroscopy (FT-IR)

The FT-IR results indicated the presence of oxygenated functional groups on the surface of GO. According to Zhao et al. [14] the main bands corresponding to the hydroxyl groups (~3000 cm^{-1}) carbonyl esters (~1600 cm^{-1}), carboxylic acids (~1700 cm^{-1}), carboxyl C-O (~1300 cm^{-1}) and epoxy. (~1080 cm^{-1}). GO-PEG-NH_2 confirmed by infrared spectroscopy, bands at 1640 cm^{-1} were observed in the GO-PEG-NH_2 for carbonyls of amides by displacing in substitution for carbonyls of carboxylic acids in 1714 cm^{-1}. This result demonstrates the efficiency in the GO functionalization process.

Fig. 1 shows that there are no difference between GO spectra and GO-PEG-NH_2 before and after gamma irradiation.

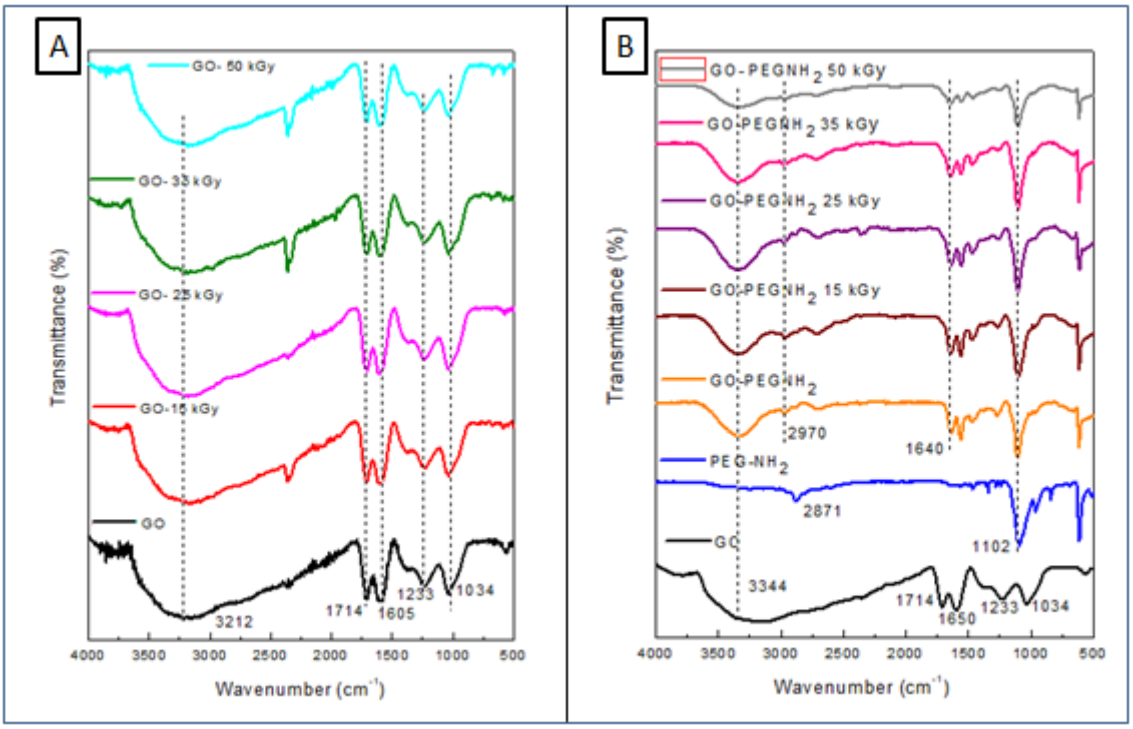

Figure 1: FT-IR spectra of (A) GO, GO gamma irradiated with 15, 25, 35 and 50 kGy and (B) GO, PEG-NH_2, GO-PEG-NH_2 , GO-PEG-NH_2 irradiated with 15, 25, 35 and 50 kGy

After irradiation with different doses, the samples of GO and GO-PEG-NH_2 showed no changes in their respective spectra as disappearance or displacements of the characteristic bands for each material.

3.1.2 Raman spectroscopy

Raman spectroscopy is a technique used to analyze the existence of defects and the extent of functionalization [15]. In this sense, it is presented as a complementary analysis to FT-IR in the evaluation of GO and GO-PEG-NH_2 structures. For both GO samples the spectra (Fig. 2) shows D band at (~1,348 $cm^{-1)}$, the G band (~1600 cm^{-1}), 2D (~2699 cm^{-1}), and D + G call at (~ 2,946 cm^{-1}), in agreement with the studies carried out by Zhao et al. [14]. The D functions are associated with the material disorder, while the G functions contributes to the graphitic organization [16].

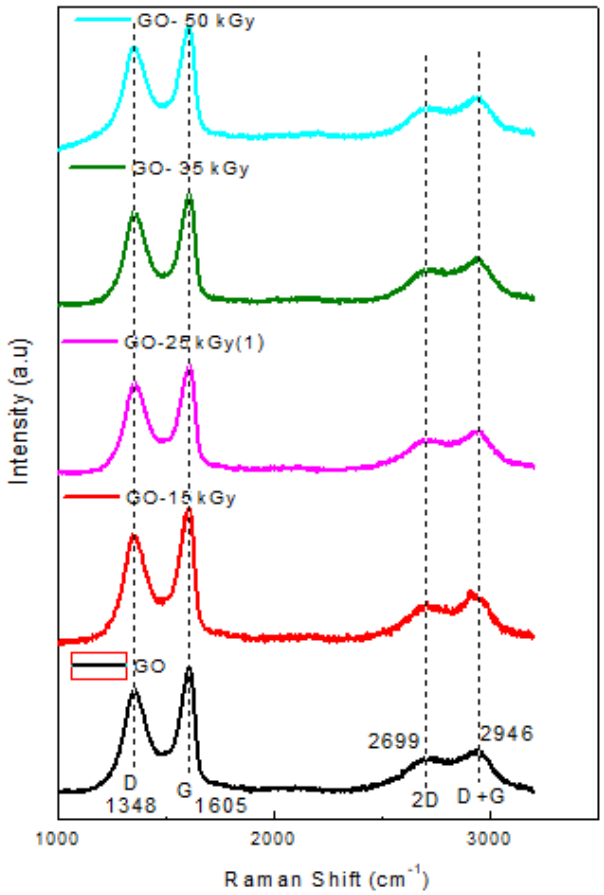

Figure 2: Raman spectra of GO, GO gamma irradiated with 15, 25, 35 and 50 kGy.

The Fig. 3 shows D and G bands of the GO, with their respective bands deconvoluted by Gaussian function.

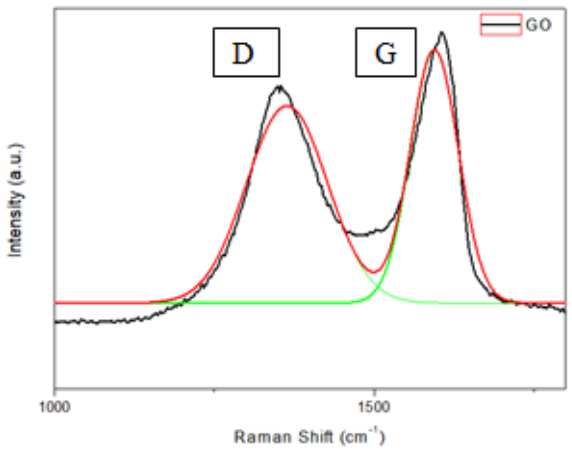

Figure 3: Raman spectra of GO and curves deconvoluted.

D and G bands of irradiated samples were deconvoluted using the Gaussian function as showed in Fig.4.

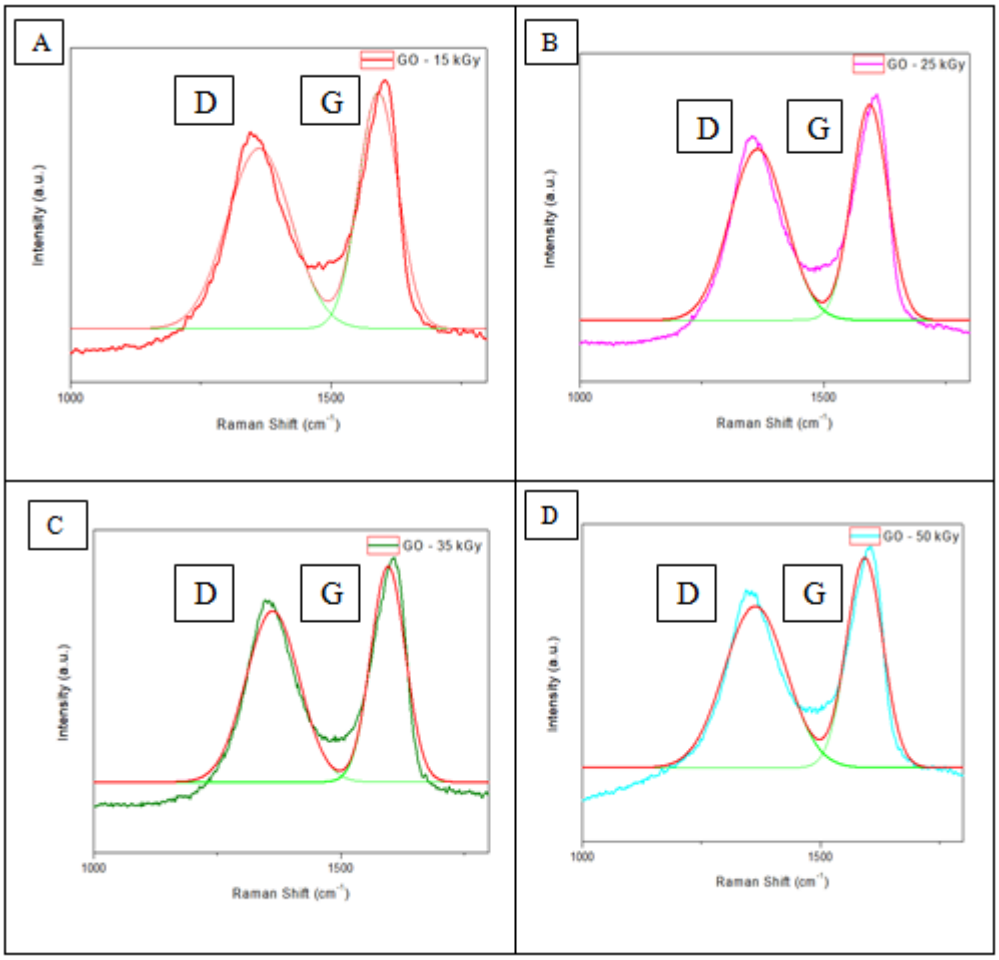

Figure 4: Raman spectra of samples GO irradiated and curves deconvoluted, (A) GO-15 kGy, (B) GO-25 kGy, (C) GO-35 kGy, (D) GO-50 kGy.

The intensity (I_{D1} / I_G) and half height (ω_{d1} / ω_g) ratios of all samples were calculated as shown in Table 1. The (I_{D1} / I_G) ration indicates the degree of the material's organization, while (ω_{d1} / ω_g) ration corresponds to amount of structural defects [17] formed as a consequence of oxygenated groups incorporated on their surface. With these data it was possible to relate the contribution of D and G bands.

Table 1: Values of (I_{D1} / I_G) and (ω_{d1} / ω_g)

	ω_{D1}/ω_G	I_{D1}/I_G
GO	1.69	1.32
GO-15 kGy	1.62	1.24
GO-25 kGy	1.52	1.23
GO-35 kGy	1.54	1.23
GO-50 kGy	1.71	1.32

In the Table 1, the results indicate that there is no difference in the GO when irradiated even at 50 kGy.

On GO-PEG-NH_2 Raman spectra (Fig.5) the following bands are observed D band at 1351 cm^{-1}, the G band at 1600 cm^{-1}, the 2D at 2688 cm^{-1} and the so-called D + G at 2933 cm^{-1} for all samples [14]. These results corroborated with FT-IR showing that the irradiation does not affect GO and GO-PEG-NH_2 structures.

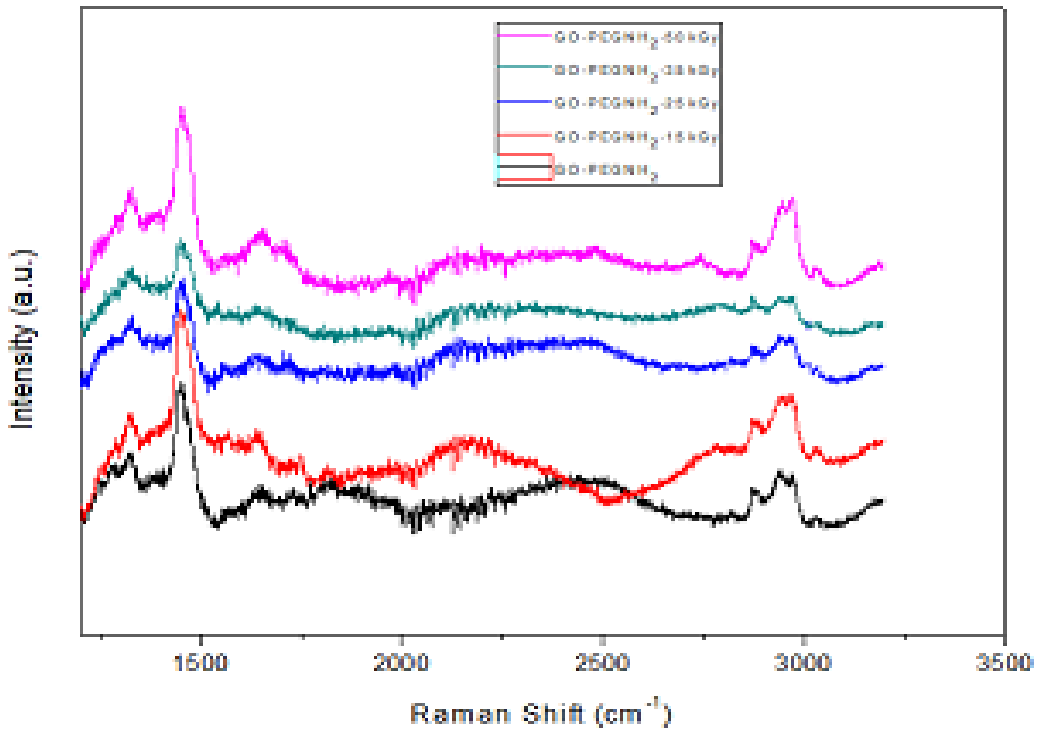

Figure 5: Raman spectra of samples GO-PEG-NH_2, GO-PEG-NH_2 irradiated with 15, 25, 35 and 50 kGy.

4. CONCLUSIONS

The methods for the synthesis of GO and GO-PEG-NH_2 proved to be effective since there was confirmation of the surface oxidation of materials and functionalization with the PEG-NH_2 group.

The sterilization by gamma radiation does not cause any structural degradation on GO and GO-PEG-NH_2.

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