The effect of gamma-irradiation on few-layered graphene materials

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Abstract

The effect of γ -irradiation on the structure and composition of chemically synthesized few-layered graphene materials was studied. Fully oxidized graphene oxide and graphene nanoribbons, as well as their respective chemically post-reduced forms, were treated under γ -irradiation in an air-sealed environment. Three different irradiation doses of 60, 90 and 150 kGy were applied. Structure and composition of the irradiated materials were analyzed by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The XRD patterns were not affected by γ -irradiation, and small changes were observed in the FTIR and TGA results. However, significant modifications were detected by Raman spectroscopy and XPS, particularly in the Raman G/D band intensity ratios and in the C 1s XPS profiles. Comparatively, the changes in Raman and XPS spectra after γ -irradiation were even greater than those occurring during the chemical reduction of graphene oxides. Our results indicate that the graphene carbon lattice was strongly affected by γ -irradiation, but the materials experienced small variations in their oxygen content.

Keywords: Graphene oxide; graphene nanoribbons; reduced graphene oxide; gamma rays; carbon lattice defects.

1. Introduction

The scientific interest in the interaction between γ -rays and carbon nanostructures is focused on two directions: 1) the use of carbon nanomaterials as additives for improving the properties of polymeric matrices under γ -irradiation, and 2) the use of γ -rays for tuning the physicochemical properties of carbon materials at the nanoscale.

Gamma irradiation is utilized for the sterilization of single-use medical products (syringes, surgical gloves, gowns, orthopedical implants, surgical kits, sutures and trays), labware, packaging, cosmetics, etc. [1]. In these products, the addition of nanostructured fillers could be sometimes interesting for reinforcing the polymeric biomaterials. Our research group has previously studied the beneficial effects of carbon nanotubes as additives for polypropylene [2] and medical grade ultra high molecular weight polyethylene (UHMWPE) [3-5]. In both cases, γ -irradiation provides the polymer chain crosslinking, which ultimately improves the wear resistance against metallic materials. In a UHMWPE matrix, carbon nanotubes act as radical scavengers, protecting the polymer against degradation under γ -irradiation [2-6]. The positive effect of carbon nanotubes under γ -irradiation has been associated to structural changes in the nanotubes. Thus, some structural effects of γ -irradiation could be expected on other nanostructured fillers including graphene.

In the last years, irradiation with γ -rays is being studied as a clean easy method for modifying the nanostructure and properties of carbon materials, and for promoting chemical reactions on their surfaces. The consequences of γ -irradiation strongly depend on the irradiation conditions, the materials type and the irradiation medium. A large number of examples showing different (or even contradictory) results after irradiating under different conditions can be found in the literature [7]. The specific surface area increased during irradiation for activated carbons prepared from lignite [8], while it decreased for an activated carbon cloth produced from viscose rayon [9]. Irradiation decreased the diameter of multi-walled carbon nanotubes (MWCNTs), increased their specific surface area and modified their oxygen functional groups [10]. Additionally, the graphitization of MWCNTs improved with doses of 100 kGy, while a higher dose of 150 kGy induced structural damage [10]. In another report, it was shown that both the

total dose and the irradiation rate determined structural modifications in graphite flakes and MWCNTs during γ -ray treatments in an air sealed atmosphere [11].

Regarding the topic of graphene, γ -irradiation in different liquid media has been successfully utilized for the reduction of graphene oxide and for the synthesis of graphene composites. The mechanisms of those reactions are based on the generation of active radicals through the solvent radiolysis. Graphene oxide was reduced during γ -irradiation in ethanol/water under an inert atmosphere, while the reduction reaction did not occur in pure water or under an oxygen atmosphere [12]. Graphene oxide has been also reduced by γ -irradiation in N,N-dimethylformamide [13]. Covalently functionalized graphene has been prepared by γ -irradiation of graphite oxide in styrene [14]. Graphene nanosheets decorated with metal nanoparticles have been prepared by the simultaneous reduction of graphene oxide and metal ions under γ -irradiation in an aqueous solution of an ionic liquid [15] or in the presence of ethylene glycol [16].

In the present article, we report the effect of γ -irradiation on two different graphene materials under an air sealed environment. The first type of graphene is produced by chemical methods from graphite. The second type consists on graphene nanoribbons (GNRs) that are produced by longitudinally unzipping MWCNTs. The effect of γ -irradiation is studied in both the oxidized and the chemically post-reduced forms of the graphene materials. We evaluate possible structural and compositional modifications by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The consequences of γ -irradiation are compared with changes taking place during the chemical reduction of graphene oxides. The nanomaterials are studied in their powder form, in which they may be utilized as additives for improving the response of polymeric matrices under γ -irradiation. That is the reason why we utilized γ -irradiation conditions identical to those required for the sterilization of medical products or the induction of polymer crosslinking.

2. Experimental

Graphite oxide was prepared using a modified Hummer's method from graphite powder (Sigma-Aldrich) by oxidation with NaNO_3 , H_2SO_4 and KMnO_4 in an ice bath as reported elsewhere [17]. A suspension of graphene oxide (GO) was obtained by sonication of the prepared graphite oxide powder in distilled water (1 mg/mL) for 2 hours, followed by mild centrifugation at 4500 rpm for 60 min, leading to a brown-

coloured dispersion of exfoliated GO with a final concentration of 0.3 mg/mL [18]. GO powder was obtained by freeze-drying the GO dispersion.

Reduced graphene oxide (RGO) was prepared by adding an excess of hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) to the GO dispersion (6 $\mu\text{L}/\text{mL}$ GO dispersion) and refluxing for 5 hours. Filtration through a polycarbonate membrane filter of 3 μm pore size, followed by washing with 200 mL of distilled water and vacuum drying at 80°C for 48 h afforded the powder-like RGO material.

Graphene oxide nanoribbons (GONRs) were prepared by the oxidation of MWCNTs in a $\text{KMnO}_4/\text{H}_2\text{SO}_4$ mixture [19, 20]. In a typical experiment, 150 mg of arc-discharge MWCNTs were dispersed in 150 ml of concentrated H_2SO_4 by bath sonication. The dispersion was heated to 65°C and then 750 mg of KMnO_4 were added. The mixture was allowed to react for 120 min; after cooling down to room temperature, it was poured in a beaker containing 400 ml of ice and 10 ml of H_2O_2 . The precipitate was vacuum-filtered through a 3 μm polycarbonate membrane (ISOPORE), washed with 0.1M HCl and rinsed with ultrapure water until neutral pH. The GONR material was chemically reduced with N_2H_4 following the protocol described in the literature [19]. An aqueous dispersion of the GONR material (0.2 mg/ml) was mixed with 1% NH_3 and 1% N_2H_4 for two hours at 95°C. The resulting reduced suspension (RGONR) was flocculated with HCl, filtered through a 1.2 μm pore diameter polycarbonate membrane, and washed. Figure 1 shows transmission electron microscopy (TEM) images of these GONR and RGONR samples, taken in a JEOL microscope model 2000 FXII at an acceleration potential of 200 kV. The nanoribbons have lengths of several hundreds of nanometers and widths of ~ 100 nm, in agreement with previous atomic force microscopy measurements [21]. It can be seen that each nanoribbon is formed by various stacked sheets, which may exhibit folds.

Gamma irradiation was performed on powder samples in a Co^{60} irradiator (Aragogamma, Spain) in an air atmosphere at room temperature. The average dose rate was 3 kGy/h and it was applied in steps of 30 kGy until the required total dose (60, 90 or 150 kGy) was achieved. During irradiation, glass vials experienced a color transformation, from colorless to dark yellow. This color change has been previously associated with a softening of the Si-O bond [22].

XRD was performed in a Bruker AXS D8 Advance diffractometer using $\text{CuK}\alpha$ radiation. For FTIR (Bruker Vertex 70 spectrometer) measurements, small amounts of the powder samples were mixed with spectroscopic KBr and pressed to form pellets.

TGA was carried out in a Setaram balance, model Setsys Evolution, under a nitrogen inert flow and a heating ramp of $10\text{ }^{\circ}\text{C min}^{-1}$. Micro Raman spectroscopy was performed in a HORIBA Jobin Yvon spectrometer (model HR 800 UV) working with a green laser at 532 nm. For each material, 3-4 representative spectra of different sample zones were considered. XPS was performed in an ESCAPlus Omicron spectrometer provided with a Mg anode (1253.6 eV) working at 150W (15mA, 10 kV). When it was required, binding energy positions were corrected by setting the aromatic carbon band at 284.5 eV. Elemental oxygen was determined using a Thermo Flash 1112 analyzer. Samples were heated to 1080°C, and the pyrolysis products were reduced to CO in a carbon black bed and analyzed by gas chromatography.

3. Results and discussion

XRD provides, among others, important information on the interlayer distance in few-layered graphene. Typical XRD patterns for non-irradiated and irradiated graphene samples are shown in Figure 2. The graphene oxide samples (GO and GONR) show similar profiles, with a diffraction peak at around $2\theta = 10.5^{\circ}$ that is associated to expanded and oxidized few-layered graphene sheets. The diffractograms also show graphite bands at 26.5° and 42.5° due to the presence of some unreacted graphite. The chemically reduced samples RGO and RGONR do not have the band at around 10.5° , indicating the effectiveness of the chemical reduction process [18]. However, the reduced materials show widened bands at 26.5° and 42.5° due to certain irregular stacking of graphene layers. No differences were detected between the γ -irradiated samples and their respective non-irradiated precursors, even for the stronger dose of 150 kGy. Irradiation did not cause changes in the crystalline structure of the materials, and no evidence of the reduction of graphene oxides under γ -irradiation was detected by XRD.

FTIR analysis provides semi-quantitative information about the chemical composition. Figure 3 includes FTIR spectra of non-irradiated samples and samples irradiated at 90 kGy. The GO material shows some relatively strong signals that correspond to defective sites in carbon materials: the band at $\sim 3425\text{ cm}^{-1}$ is usually associated to hydroxyl groups, the shoulder at $3200\text{-}3250\text{ cm}^{-1}$ to carboxyl groups, the three peaks at 2960, 2926 and 2853 cm^{-1} to aliphatic CH_2 groups, the peak at $\sim 1726\text{ cm}^{-1}$ to lactone or carboxyl groups, and signals in the region of $1000\text{-}1300\text{ cm}^{-1}$ to various types of oxygen

groups [23]. The spectra of GO and GONR are similar to each other as both are strongly oxidized materials. On the contrary, the spectra of chemically reduced samples (RGO and RGONR) show a strong decrease in the signal intensity with respect to the oxidized samples, most notably in the bands at 1726, 3150 and 1150 cm^{-1} , due to the loss of oxygen chemical groups. No significant changes are observed in FTIR spectra after γ -irradiation. For the GO material, a certain decrease in the intensity of the bands at ~ 1726 , 1586 and 1228 cm^{-1} could be related to the evolution of water or labile oxygen chemical groups during GO irradiation.

Figure 4 shows TGA experiments under an inert atmosphere. Weight losses during the heating are associated to the evolution of moisture and functional groups. For the chemically reduced samples RGO and RGONR, weight losses are clearly lower than for the oxidized samples GO and GONR, confirming the effectiveness of chemical reduction. Changes in the TGA profiles after chemical reduction can be associated to the decrease in the intensity of FTIR bands. However, weight losses for the reduced samples RGO and RGONR are still considerable, indicating that the materials contain some defective graphene. For GO and RGO materials (Figure 4.a), a difference in the weight loss profiles was observed after γ -irradiation at 60 kGy. This difference between non-irradiated and irradiated samples mostly occurs at temperatures below 200°C and could be associated to a certain decrease in the adsorption of water moisture or weakly bonded oxygen functional groups, in agreement with changes in the FTIR spectrum of GO during irradiation. In the GO material, γ -irradiation seems to retard weight losses occurring below 200°C, indicating a thermal stabilization of some adsorbed molecules or chemical groups. No differences after γ -irradiation are observed in the TGA profiles for the nanoribbon samples GONR and RGONR.

Raman spectra of non-irradiated samples and samples irradiated at 60, 90 and 150 kGy are shown in Figure 5. Spectral features include the D band at around 1340 cm^{-1} , the G band at 1560-1600 cm^{-1} and the second order 2D band at around 2680 cm^{-1} . Chemical reduction caused a decrease in the D band intensity of GO. In addition, somewhat sharper D and G bands are observed for the RGO sample. On the contrary, no substantial changes in the peak shapes are observed during the chemical reduction of GONR to RGONR. After γ -irradiation, an increase in the 2D band intensity can be observed for the GO material. Increased intensities of the 2D band are commonly cited to indicate the restoration of sp^2 -hybridized carbon bonds in graphitic structures [18, 24].

In Figure 6, variations in the Raman spectra are analyzed in terms of the G/D intensity ratio and the G- and 2D-band maximum positions. The G/D ratio decreased after irradiating with a dose of 60 kGy in the four graphene materials studied. After a more intensive γ -irradiation treatment of 90 or 150 kGy, G/D ratios approximately remained constant for the GO and GONR materials, while they increased for RGO and RGONR. A similar non-linear G/D trend has been previously reported for MWCNTs under γ -irradiation [11]. In that work, the decrease in G/D was assigned to the generation of defects in the carbon lattice through displacements or sputtering of carbon atoms, while the subsequent increase in G/D was associated to the structure restoration after a change in the defect dynamics [11]. In another article, a non-linear correlation between G/D ratios and oxygenated defect distances has been found for graphene sheets [25]. In our case, the variations in the G/D ratio with γ -irradiation can be associated to modifications in the carbon lattice, although some chemical reactions could be also included.

Figure 6.b shows changes in the Raman G-band maximum position after irradiation. In case of GO, its position is higher compared to the other materials, and shifts to higher wavenumbers with increasing γ -irradiation doses from 1578 to 1589 cm^{-1} after 150 kGy. A similar evolution with irradiation is observed for the GONR materials, in which the G band position changes from 1563 to 1568 cm^{-1} after 150 kGy. A different trend is observed for the RGO material: the G band wavelength increase after the 60 kGy dose and then decrease after doses of 90-150 kGy. For the RGONR sample, a very slight wavelength decrease was registered. An interpretation of the G band position variation in these materials is not direct, but they seem to indicate that some modifications in the carbon lattice occur during γ -irradiation. Doping, which leads to charge transfer effects, has to be considered as a possible explanation for variations in the G-band positions, and it would also produce displacements in the 2D band [26]. In our particular system under irradiation, oxygen atoms could be exchanged between the carbon lattice and the environment, and it is expected that substitution of carbon by oxygen in the graphene lattice would lead to an upshift in the G band position [27]. In order to gain more information about charge transfer effects, we also analyzed the 2D-band positions in the irradiated samples (Figure 6.c). Some variations were observed for the GO and RGO materials, while practically no changes occurred in the GNRs. Thus, it can be hypothesized that GO and RGO undergo oxygen doping more easily than GNRs. However, it has to be reminded that displacements in the G- and 2D-bands can be caused by other structural changes not necessarily associated to doping.

XPS is a powerful technique for the analysis of surface chemistry, covering a depth range of <10nm from the outer surface of carbon materials. Figure 7 shows high resolution C 1s spectra of the non-irradiated samples and samples irradiated at 60, 90 and 150 kGy. The spectra can be interpreted in terms of 3-4 band components: i) aromatic carbon at 284.5 eV, ii) C-O bonds at 286.4-286.9 eV, iii) C=O bonds at 288-289 eV, and iv) carbonates and plasmon losses at around 291 eV [28]. The non-irradiated GO and GONR materials show prominent bands at around 285 and 288.5 eV, which can be associated to oxygen functional groups and decrease after chemical reduction. Interestingly, γ -irradiation affects the C 1s spectra in a larger extent than chemical reduction. In fact, a clear effect can be observed after irradiation of the GO material (Figure 7.a). The relative intensity of the C-O and C=O bands decreases as the irradiation dose increases. According to FTIR and TGA, the loss of oxygen functional groups during irradiation is much less important than during chemical reduction. Therefore, variations in C 1s spectra after irradiation cannot be assigned only to oxygen functional groups losses, but also to a relative increase in the C=C band at around 284.5 eV. This indicates that γ -irradiation contributes to the recovery of the sp^2 character of the hexagonal carbon lattice, in agreement with the increase in the 2D Raman band intensity. For GONR (Figures 7.c), the C-O and C=O bands at around 285 and 288.5 eV first decrease after 60 kGy and then increase a little after 90 and 150 kGy. Similar trends are observed for the reduced RGO and RGONR materials, probably coming from a complex combination of structural and compositional modifications.

Figure 8 shows XPS O 1s spectra of the starting and the irradiated materials. For their interpretation, O 1s profiles are usually decomposed into 4-5 components: i) C=O groups at around 531 eV, ii) hydroxyls, ethers and C=O in esters and anhydrides at 532.4-532.8 eV, iii) C=O in esters and anhydrides at around 533.5 eV, iv) carboxylic groups at 534.2 eV, and v) oxygen from water at 535-536 eV [28]. Spectra of the oxidized materials (GO and GONR) are dominated by the band of hydroxyl groups at around 532.5 eV. On the contrary, the chemically reduced samples show contributions of at least 4 components with comparable intensities. The strong modification in O 1s spectra with chemical reduction have to be interpreted as a complex combination of effects including reduction-evolution of oxygen functional groups, water losses or changes in the surface acidity and the chemical environment. Few variations are observed in the O 1s spectra upon γ -irradiation, and they seem to occur quite randomly. This fact confirms that changes in oxygen functional groups during γ -irradiation are less

important than during chemical reduction. However, small variations in the oxygen content could occur due to different adsorption/desorption equilibriums taking place during the irradiation treatments.

Figure 9 shows O/C atomic ratios indirectly calculated from the overall XPS spectra for all the studied materials. It can be seen that the oxidized materials show much higher oxygen contents than the chemically reduced ones, in agreement with FTIR and TGA results. Oxidized materials are more sensitive to γ -irradiation. The O/C atomic ratio for GO clearly decreased with increasing irradiation doses. For GONR, the O/C ratio increased after a 60 kGy irradiation dose, and then decreased after doses of 90 or 150 kGy. Since the GO and GONR materials showed unexpected opposite trends, we compared XPS results with direct oxygen elemental analysis for the 60 kGy irradiated samples. It was confirmed that the oxygen content for GO decreased from 38.0 to 36.4 wt.% after 60 kGy, while it increased from 37.3 to 38.9 wt.% for the GONR sample. Therefore, changes in the oxygen content after 60 kGy irradiation doses were of less than 2 wt.%. Such low variations in the oxygen content are in good agreement with FTIR, TGA, and O 1s XPS profiles, which are not substantially modified by γ -irradiation. In contrast, the oxygen content for RGO and RGONR was in the range of 15.5-16.0 wt.%, demonstrating the strong effect of chemical reduction.

4. Conclusions

Irradiation in an air-sealed atmosphere caused small changes in the XRD, FTIR and TGA profiles of the studied graphene materials, indicating that small variations are induced in the graphene sheets stacking and the overall chemical composition. This fact contrasts with the strong changes caused by chemical reduction in the XRD, FTIR and TGA profiles of graphene oxides.

Important effects of γ -irradiation on graphene materials were detected by Raman spectroscopy and XPS, particularly through the variation of G/D intensity ratios and the C 1s XPS profiles. Comparatively, changes produced by γ -irradiation in the G/D intensity ratio and in the C 1s spectra are even greater than those induced by chemical reduction on graphene oxides. This fact supports the idea of the graphene carbon lattice being affected by γ -irradiation, which caused displacements of carbon atoms. As it was indicated by the overall XPS spectra, carbon lattice modifications upon γ -irradiation sometimes occurred together with small variations in the oxygen content. Changes in the oxygen content are of less than 2 wt.% for 60 kGy irradiation doses, according to

elemental analyses and in good agreement with FTIR, TGA and O 1s XPS profiles. Such small changes in the oxygen content contrast with those produced by chemical reduction on graphene oxides.

The consequences of γ -irradiation on the graphene carbon lattice are reminiscent of those previously reported for carbon nanotubes. Therefore, it can be expected that graphene materials will show an analogous behavior to carbon nanotubes when they are utilized as fillers in polymeric composites, including in their role as radical scavengers and crosslinking generators.

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Figure 1. TEM images of the GONR (left) and RGONR (right) materials.

Figure 2. XRD patterns of non-irradiated and selected samples irradiated at 60, 90 or 150 kGy: a) GO and RGO, b) GONR and RGONR.

Figure 3. FTIR spectra of non-irradiated samples and samples irradiated at 90 kGy: a) GO and RGO, b) GONR and RGONR.

Figure 4. TGA profiles (N_2 , $10^\circ C/min$) of non-irradiated samples and samples irradiated at 60 kGy: a) GO and RGO, b) GONR and RGONR.

Figure 5. Raman spectra (532 nm) of: a) GO, b) RGO, c) GONR and d) RGONR, after different γ -irradiation treatments.

Figure 6. a) G/D Raman intensity, b) G-band maximum position, and c) 2D-band maximum position for oxidized and reduced graphene materials after different irradiation treatments.

Figure 7. C 1s XPS spectrum profile for: a) GO, b) RGO, c) GONR, and d) RGONR, after different γ -irradiation treatments.

Figure 8. O 1s XPS spectrum profile for: a) GO, b) RGO, c) GONR, and d) RGONR, after different γ -irradiation treatments.

Figure 9. Oxygen contents from XPS for oxidized and reduced graphene materials after different γ -irradiation treatments.