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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.

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

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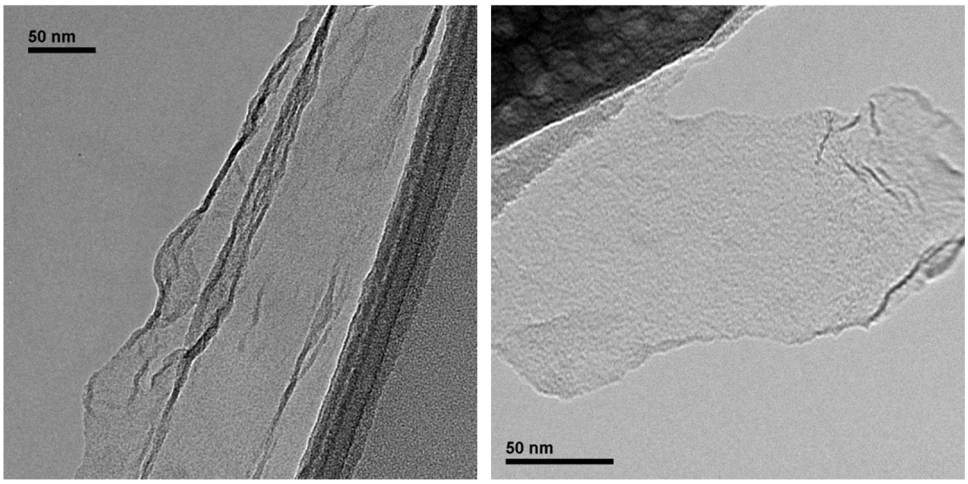

Fig. 1. TEM images of the GONR (left) and RGONR (right) materials.

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 h, followed by mild centrifugation at 4500 rpm for 60 min, leading to a brown-colored dispersion of exfoliated GO with

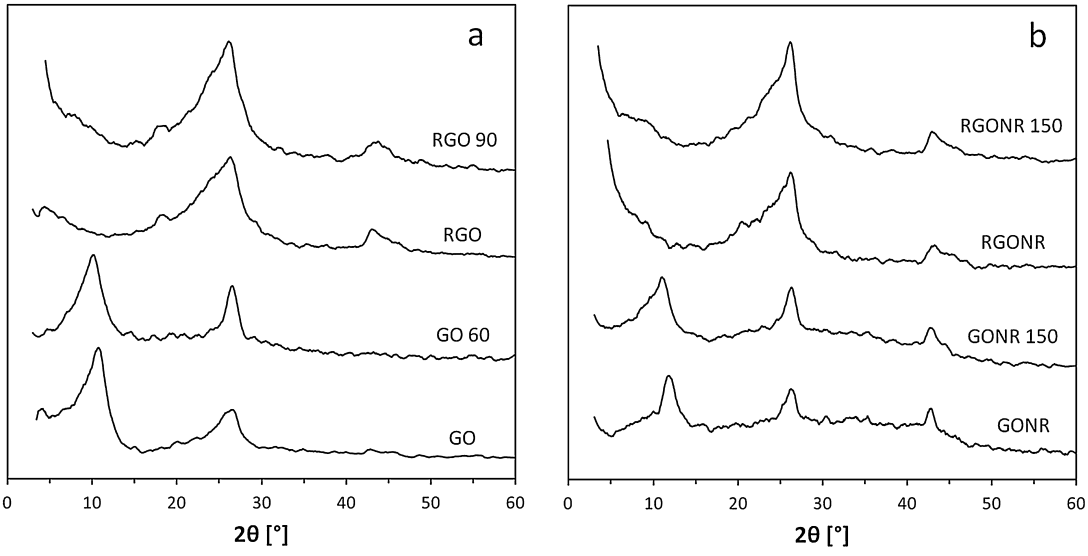

Fig. 2. XRD patterns of non-irradiated and selected samples irradiated at 60, 90 or 150 kGy: (a) GO and RGO, (b) GONR and RGONR.