

SYNTHESIS OF REDUCED GRAPHENE OXIDE BY GAMMA IRRADIATION

Raynara M. S. Jacovone, Flávio K. Tominaga, Octávio A. B. Brandão, Rafael H. L. Garcia and Solange K. Sakata*

Nuclear and Energy Research Institute, National Commission of Nuclear Energy (IPEN/ CNEN – SP)
Av. Professor Lineu Prestes, 2242
05508-000 São Paulo, SP
sksakata@ipen.br

ABSTRACT

Graphene is a 2D carbon-based nanomaterial that has a high specific surface area with remarkable physical and chemical properties. These unique properties make graphene a nanomaterial with wide electrochemical applications. However, it is not possible to functionalize graphene sheets and increase their field of application because there are no organic functions in their surface. So, an important precursor of graphene, graphene oxide (GO), then contains oxygen functional groups on the surface is been using functionalized. Partial reduction of graphene oxide leads to reduced graphene, a nanomaterial that combines both properties of graphene and graphene oxide: an excellent electrical and thermal conductivity and remaining oxygen groups that allow its functionalization. In the literature it is described many ways to produce reduced oxide graphene from graphene oxide, such as chemical reduction using hydrazine hydrate or NaBH₄ or thermal reduction using high temperatures. Here in it is described an attractive and green process to reduce graphene oxide in aqua solution using gamma radiation. Exfoliated graphene oxide (1-100mg / L) under inert medium was submitted to gamma radiation. The radiation dose ranged from 20 to 80 kGy and the product was centrifuged. The characterization was performed by X-Ray Diffraction (XRD), Infrared Spectroscopy (ATR-FTIR) and Thermogravimetric analysis (TGA). The XRD results demonstrated characteristic diffraction peaks at about 10° and 25° corresponding to GO and Graphene, respectively, indicating the rGO formation. ATR-FTIR showed the characteristic peaks of functional groups (epoxy, hydroxyl and carboxyl) for GO. After the gamma irradiation, it was noticed a reduction at the intensity of the peaks at of carboxyl/carbonyl an increase at aromatic carbon bond. TGA analysis indicated a decrease of the oxygen groups.

1. INTRODUCTION

Graphene is a single layer of carbons sp² in a honeycomb crystal lattice, with a large specific surface area, excellent electrical and thermal conductivities and high mechanical strength and chemical stability [1]. These remarkable properties make graphene a nanomaterial with applications in many areas such as electronics, producing sensors, electrodes for capacitors, batteries, solar cells [2,3]. The potential of this material can be expanded through its functionalization, which makes it a precursor for the synthesis of new materials, such as conductive nano composites [4].

However, it is not possible to functionalize graphene sheets and increase their field of application because there are no organic functions in their surface. So, an important precursor of graphene, graphene oxide (GO), contains oxygen functional groups on the surface such as hydroxyl, epoxide, carbonyl and carboxyl. These reactive sites can later be functionalized [5]. Partial reduction of graphene oxide produces reduced graphene oxide (rGO), a nanomaterial that combines both properties of graphene and graphene oxide: an excellent electrical and thermal conductivity and oxygen groups that allow its functionalization [6].

Its reported in the literature many ways to produce reduced oxide graphene from graphene oxide, such as chemical reduction using or thermal reduction, however, the traditional way

usually comprises toxic chemical reducing reagents or high temperature [7, 8]. To avoid unfeasible reaction conditions such as the use of toxic reagents, gamma radiation is considered an attractive alternative for the synthesis of the reduced graphene oxide [9,10]. It's a green synthesis that occurs in room temperature and aqueous solution.

The mechanism of reduction is based on the generation of active radicals through the water radiolysis. The reducer species, hydrogen radicals ($H\bullet$) and solvated electrons (e^-_{aq}) are produced by the gamma irradiation and promotes the partial reduction of the graphene oxide [11].

Herein it is described a green synthesis of reduced graphene oxide using gamma irradiation in water-isopropanol solution at room temperature in inert medium and the characterization.

2. MATERIALS AND METHOD

2.1 Chemicals

The following reagents were used without further purification: Graphite powder (99.99%, Merck-Millipore), sulfuric acid (98%, Aldrich), sodium nitrate and potassium permanganate (Synth), hydrogen peroxide 30% (Merck), ethyl alcohol (Synth), isopropyl alcohol (Synth), HCl (Merck) and NaOH (Merck).

2.2 Preparation of Graphene Oxide

Graphene oxide was prepared by modified Hummers method [12]. Briefly, 3g of graphite powder, 3g of $NaNO_3$ and 140 mL of H_2SO_4 were stirred in an ice bath. Then, 18g of $KMnO_4$ was gradually added and the temperature was kept at about $35^\circ C$ for one hour. In sequence, 100mL of DI water was added and the solution was stirred at $90^\circ C$. Finally, 100 mL of DI water was added to the solution, followed by 18mL of H_2O_2 (30%) turning the color of the solution from dark brown to yellow. The product was washed with DI water, NaOH (1M) and HCl (1M) until pH 7. The mixture obtained in the last step was centrifuged at 12,000 rpm for 10 minutes. GO sample was dispersed in isopropanol and exfoliated using an ultrasonicator (Sanders ultrasonic, model Soniclean 2PS, 40 kHz) and dried at room temperature for further analysis.

2.3 Preparation of Reduced Graphene Oxide

GO sample (50 mg/ml) was dispersed in water/isopropanol mixture (1:1) and exfoliated using an ultrasonicator for 30 minutes. (Sanders ultrasonic, model Soniclean 2PS, 40 kHz). Then, the sample under inert medium was submitted to gamma radiation. Samples were irradiated in the Multipurpose Gamma Irradiation Facility at CETER/IPEN/CNEN-SP, a category IV gamma irradiator by the International Atomic Energy Agency classification, in stationary mode, under the dose rate of $7.31 \text{ kGy}\cdot\text{h}^{-1}$ and the radiation dose ranged from 20 to 80 kGy.

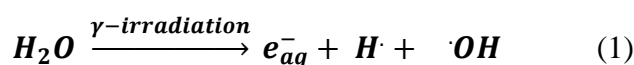
2.4 Characterization

The characterization of the GO and rGO (GO 20 kGy, 40 kGy and 80 kGy) was performed by X-Ray Diffraction (XRD), Infrared Spectroscopy (ATR-FTIR) and Thermogravimetric analysis (TGA). Thermogravimetric analysis (TGA) measurements were performed under air atmosphere with a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ under a dynamic air atmosphere of $100\text{ ml}\cdot\text{min}^{-1}$ (TA Instruments, model SDT-Q600). Spectroscopy (ATR-FTIR) was performed in a Perkin Elmer equipped, Frontier model. X-ray diffraction was performed in a Bruker D8 ADVANCE equipped with copper tube and scintillation detector, with counting times of 6 seconds per step size of 0.05° .

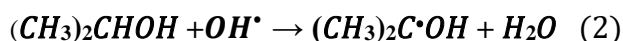
3. RESULTS AND DISCUSSION

Graphite oxide was synthesized by chemical oxidation of the graphite by the treatment with KMnO_4 and NaNO_3 in concentrated H_2SO_4 . The oxygen functional groups on basal planes and edges of the layers increase the distance between them, allowing their exfoliation to produce graphene oxide.

The reducer species $\text{H}\cdot$ radicals and solvated electrons e_{aq}^- are produced by the water radiolysis as described below (equation 1):



In radiolysis process, there are also formation of a strong oxidation species, the radical hydroxyl, $\text{OH}\cdot$. In order to avoid oxidation, isopropyl alcohol was added to the mixture to scavenger $\text{OH}\cdot$ radical (equation 2):



The graphene oxide was submitted different doses: 20, 40 e 80 kGy. All samples were made in triplicate and under same synthesis conditions.

The ATR-FTIR spectra obtained for samples are shown in figure 1. The peak at $1,726\text{ cm}^{-1}$ presents the bond of $\text{C}=\text{O}$ (carbonyl/carboxyl functional group). The peak at $1,610\text{ cm}^{-1}$ presents $\text{C}=\text{C}$ (aromatics functional group, skeletal vibrations from unoxidized graphitic domains). The peak at $1,404\text{ cm}^{-1}$ presents $\text{C}-\text{O}$ (carboxyl functional group) [13]. The FTIR showed a difference in $\text{C}=\text{C}$ bond peak at $1,610\text{ cm}^{-1}$, in which it can be observed that the GO 80 kGy peak is higher than the other GO samples indicating that the reduction process was effective. There is no peak corresponding to $\text{C}-\text{O}$ bond in the FTIR spectra of GO after gamma irradiation.

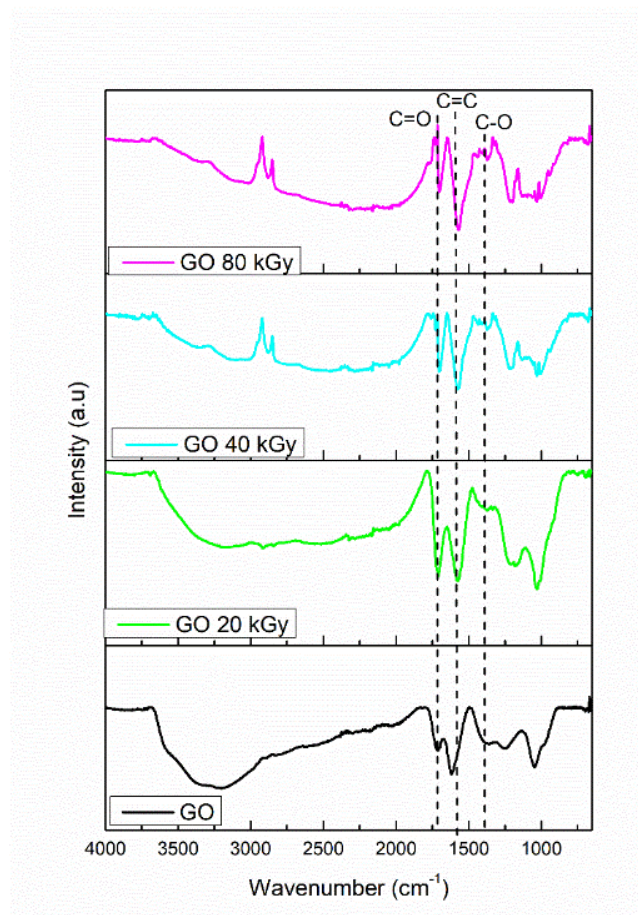


Figure 1: FTIR spectra of the GO and rGO

From the X-Ray diffraction patterns of the material before (GO) and after (GO 20, GO 40 and GO 80 kGy) irradiation procedure, it can be noticed the 2θ shift of the peak located at 11° to 23° , and concurrent decrease in intensity, demonstrating the almost complete reduction of GO to rGO [14]. Another evidence for reduction process it evaluating the distance between layers, denoted as d , in the Bragg's equation (equation 3) [15]

$$n\lambda = 2dsen\theta \quad (3)$$

The distance calculated for GO was 0,85 nm and 0,82 nm, 0,77 nm and 0,79 for GO 20 kGy to 40 kGy and GO 80 kGy respectively [14]. The decrease of the distance between layers its attributed on partial remove of the oxygen groups.

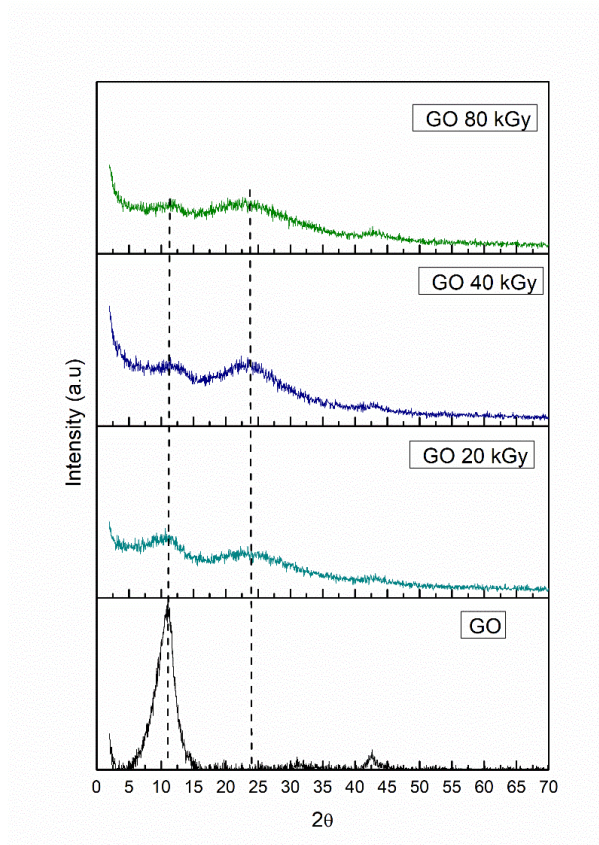


Figure 2. XRD patterns of GO before and after irradiation process.

Thermogravimetric analysis (TGA) was used to verify the reduction of the GO sheets. Figure 3 shows the thermograms GO before and after irradiation and the table 1 shows the percentual weight loss. The GO curve showed 23% mass loss near 100 ° C and it is related to the water desorption from the surface. The weight loss of water was between 6-14% for rGO samples. The gradual decrease in weight from 150 ° C to 300 ° C is due to the pyrolysis of hydroxyl, epoxide, and carboxyl groups [16] and for GO the weight loss was close to 27% while for rGO samples was, in medium, 16%, indicating than reduction process was effective. From 500 ° C to 600 ° C the mass loss was attributed to the burning of carbon backbones.

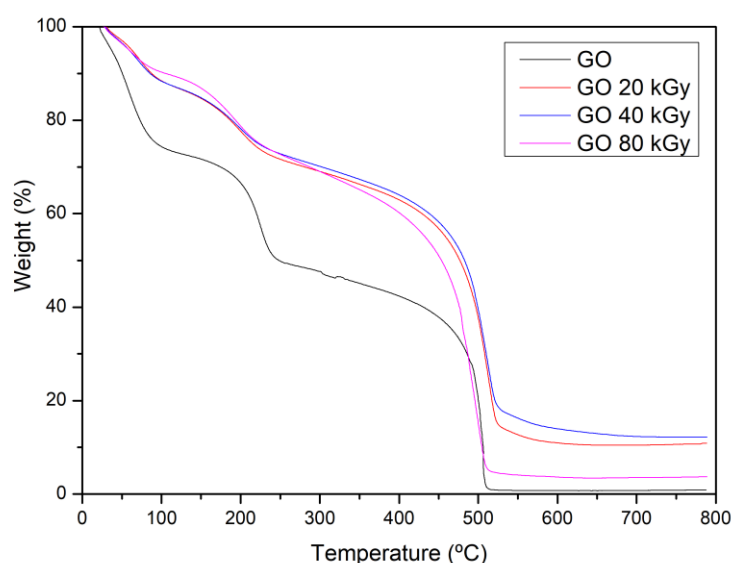


Figure 3: Thermogravimetric curves of GO and rGO (GO 20 kGy, 40 kGy, 80 kGy)

Table 1: Percentual weight loss of the GO and rGO samples.

Sample	Weight (%)		
	0-100°C	150-300°C	500°C
GO	23.3	26.9	47.5
GO – 20 kGy	11.1	16.4	58.6
GO – 40 kGy	6.3	15.1	59.4
GO – 80 kGy	13.6	16.4	65.7

4. CONCLUSION

After the gamma irradiation, it was noticed a reduction at the slight intensity of the ATR-FTIR peaks at of carboxyl/carbonyl and increase at aromatic carbon bond for all samples. TGA analysis indicated a decrease of the oxygen groups and The XRD results demonstrated shift of the peaks located at 11° to 23°, and concurrent decrease in intensity, corresponding to GO and graphene, respectively, indicating the rGO formation.

The results no demostred significant difference between radiation doses used. For future works, more characterization analysis is required

This study showed reduced graphene oxide can be synthesized by a sustainable method, that does not use toxic reagents and does not generate hazardous waste. Moreover, the process occurring at room temperature that makes it attractive.

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