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SYNTHESIS OF GRAPHENE OXIDE AND CHEMICALLY REDUCED GRAPHENE NANOSHEETS

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ABSTRACT

Se desarrolló una ruta sintética para la obtención de óxido de grafeno (GO) y grafeno químicamente reducido (CRG). El proceso consta de tres etapas: (i) oxidación en fase líquida de microcristales de grafito previamente modificados a través de un tratamiento exfoliativo, (ii) conversión de óxido de grafito en nanoláminas de óxido de grafeno dispersas en agua mediante la aplicación de ultrasonido y, (iii) reducción química de óxido de grafeno en medio acuoso y su respectiva conversión en grafeno empleando hidroxilamina como agente reductor. Los resultados observados a través de técnicas espectroscópicas (difracción de rayos X, espectroscopia UV-Vis e infrarroja, dispersión dinámica de luz) y microscopía electrónica de barrido, permitieron la identificación de los materiales sintetizados y proporcionaron información acerca de sus estructuras. El procedimiento de síntesis es simplificado, eficiente y económico, por lo cual puede considerarse como una ruta importante para la producción de GO y CRG a gran escala.

Palabras clave: *Grafito, óxido de grafeno, grafeno químicamente reducido, caracterización espectroscópica, microscopia electrónica de barrido.*

ABSTRACT

In this study, a synthetic route for obtaining graphene oxide (GO) and chemically reduced graphene (CRG) was developed. The overall process involve three general stages: (i) liquid phase oxidation of microcrystals graphite previously modified by exfoliative treatment, (ii) conversion of graphite oxide in graphene oxide nanosheets dispersed in aqueous medium by ultrasound application and, (iii) chemical reduction of graphene oxide in solution to convert it in graphene, using hydroxylamine as reducing agent. Results observed through spectroscopic techniques (X-ray diffraction, UV-Vis and infrared spectroscopies, dynamic light scattering) and scanning electron microscopy, allowed the identification of the synthesized materials and know some basic aspects of its structures. The synthesis procedure proved to be simple, efficient and cost-effective, which may be considered an important route to produce bulk scale graphene oxide and chemically reduced graphene nanosheets.

Keywords: *Graphite, Graphene oxide, Chemically reduced graphene, Spectroscopic characterization, Scanning electron microscopy*

1 INTRODUCTION

Graphene is defined as a flat monolayer of carbon atoms with sp^2 hybridization tightly packed into a two-dimensional (2D) honeycomb lattice [1]. Since its discovery by K. S. Novoselov and A. K. Geim in 2004 [2], it has emerged as an exotic material of the 21st century, and attracted interest from the scientific community due to its unique electronic, thermal, optical, and mechanical properties [3]. Graphene and its derivatives (e.g. graphene oxide and chemically reduced graphene) are being studied in nearly every field of science and engineering [4-6].

Although several methodologies have been developed, bulk scale production of graphene sheets is still challenging. Among the various physical and chemical methods of preparation, the route based on reduction of graphene oxide, which is generated from oxidation of graphite has been a promising method to achieve large-scale production of graphene [7].

This paper describes the study and development of an improved methodology for the synthesis of graphene oxide and chemically reduced graphene nanosheets with excellent structural quality.

2 EXPERIMENTAL

2.1 Materials

Natural Graphite flakes were obtained from Union Carbide (SP1 grade), formic acid (98-100%) was obtained from Riedel-de Haën, potassium permanganate, sulfuric acid (98%) and hydrogen peroxide (30%) were purchased from Merck, phosphoric acid (85%, ACS grade) was obtained from Carlo Erba Reagents. All reagents were A.C.S grade.

2.2 Graphitic material preparation

Natural flake graphite (1 g) was put into a beaker. Formic acid (25 mL) and phosphoric acid (25 mL) were added into the flask. The mixture was subjected to ultrasonication (ultrasonic bath cleaner Bransonic 3510) at room temperature for 2 h to produce graphite nanoplatelets (GNPs) dispersion. The GNPs were filtered and washed with deionized water, then dried in a vacuum oven overnight taking as a reference the method described by Y. Geng *et al* [8].

2.3 Synthesis of graphene oxide

The GO was prepared according to the modified Marcano *et al* method that has been reported previously [9]. In detail, graphite nanoplatelets (0.5 g) were put into a beaker. A 9:1 mixture of concentrated H_2SO_4/H_3PO_4 was added to graphite flakes. The mixture was then heated to 50°C and stirred for 15 min. After homogenizing the mixture was added slowly $KMnO_4$ (3 g) preventing the reaction temperature exceeded 60°C. The system was maintained at 60°C under strong magnetic stirring over a period of 2 hours. After that, the mixture was cooled to room temperature and 10 mL of 30% H_2O_2 was added slowly to the dispersion. Immediately after finishing reduction, the dispersión was diluted with cold water (150mL, 5°C). The purified graphite oxide was easily dispersed in 250 mL of water by mild sonication (VCX 750 Sonics Vibra-Cell), obtaining a translucent dispersion of graphene oxide.

2.4 Synthesis of chemically reduced graphene (CRG)

To a round bottom flask of 100 mL was added 50 mL of aqueous suspension of graphene oxide (0.10 mg/mL), 25 mg of $NH_2OH.HCl$ and 1 mL of 30% NH_4OH. It measured a pH~11 and the mixture was heated in a water bath for one hour at 90°C under constant agitation (~500 rpm) using a reflux condenser; meanwhile the color of the mixture changed from yellowish brown to homogeneous black indicating the reduction took place. The as-generated CRG was separated from the reaction mixture through filtration and washed repeatedly with ultrapure water.

Materials characterization

Some structural properties of natural graphite flakes, GNPs, GO and CRG were evaluated through X-ray diffraction (XRD) using a Siemens D500 diffractometer with CuKα1 radiation (1.54059 Å) at a generator voltage of 40 kV and a 50 mA current. The scan speed was 0.02°/s in the range of 2θ: 2-70°. Some aqueous dispersion of GO samples were analyzed by dynamic light scattering (Malvern, Zetasizer Nano ZS90) for determination of particle size and zeta potential.
UV-Vis absorption analysis (200-700 nm) of aqueous dispersion of GO and CRG were performed with UV-Vis spectrophotometer (Shimadzu 2401PC). The FTIR spectra were acquired on a spectrometer (Bruker Tensor 27) between 400-4000 cm^{-1}, in transmittance mode. Samples for FTIR measurement were prepared by grinding the dried powder of GO or CRG with KBr together and then compressed into thin pellets. The size and morphology of the CRG nanoplatelets were observed by scanning electron microscopy (FEI Quanta FEG 650) working at 30 kV.

3 RESULTS AND DISCUSSION

Graphite nanoplatelets (GNPs) with a thickness in nanometer scale, which can be obtained by exfoliation of natural graphite flakes, can meet the requirement of a large specific surface area [8]. In this study, a novel technique was implemented, which involved ultrasonication of natural graphite flakes in a formic acid and phosphoric acid ($HCOOH:H_3PO_4$; 1:1 in volume) for 2 h, followed by filtration and drying.

Diffractograms of the graphite flakes and GNPs were analyzed (fig. 1). Using the Bragg and Scherrer's equations were determined the interlaminar distance and the average thickness of the crystals, respectively. This structural information is condensed in the Table 1. The inset (fig. 1) allows observing in detail the signals corresponding to the diffraction at the plane 002. For GNPs, the peak 002 is shifted to lower angles in terms of 2θ and its value is slightly higher compared to the value obtained for the graphite without exfoliation, indicating that treatment with ultrasound generated a small increase in the interlayer distance. Comparing the values d_{002} or the average number of graphene sheets can be concluded that the treatment also produced fragmentation of crystals, reducing its thickness (~20%) and increasing its effective surface area.

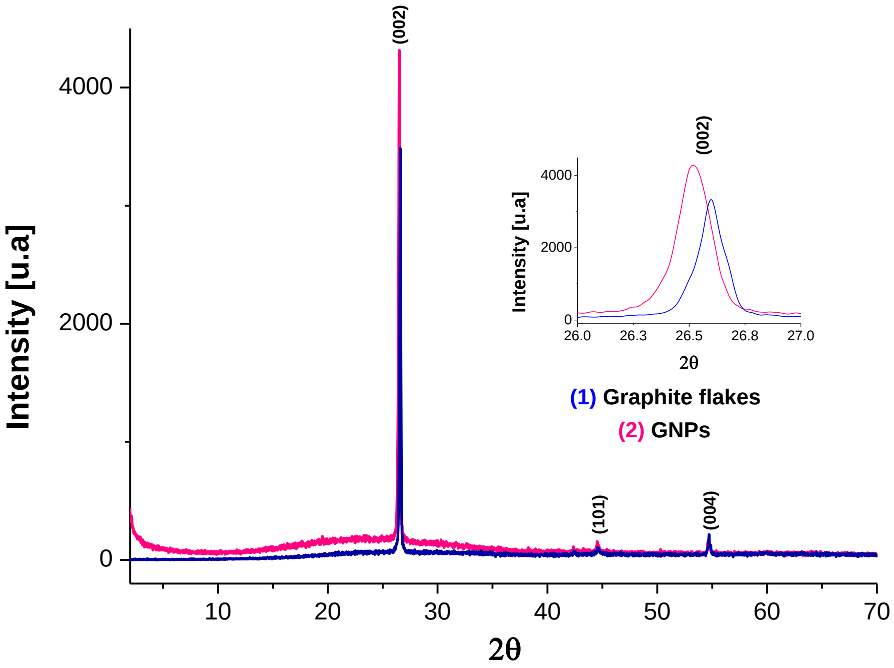

Figure 1. Diffractograms of graphite flakes (GF) and graphite nanoplatelets (GNPs)

Table 1. Structural characteristics of graphite flakes (GF), GNPs, GOs and CRG, obtained by XRD analysis.

Material	**Oxidation time [hours]**	**Diffraction 002 (2θ) [°]**	**[rad]**			**N° layers**
GF	**0**	26.60	$2.544*10^{-3}$	3.348	530	158
GNPs	**0**	26.53	$3.169*10^{-3}$	3.357	425	127
GOs	**2**	10.23	$9.857*10^{-3}$	8.638	140.1	16
	4	9.64	$9.638*10^{-3}$	9.166	143.3	15
	6	9.59	$1.095*10^{-2}$	9.215	126.2	14
	12	9.42	$3.308*10^{-2}$	9.383	41.8	4
CRG	**0**	25.63	$1.795*10^{-1}$	3.473	7.5	2

Figure 2 shows the XRD patterns of GNPs and graphite oxide at various oxidation stages. XRD analysis also allowed determining the L_c and d_{002} values of the oxidized materials (GOs) for different time periods (table 1). The 002 diffraction peak of the different graphite oxides (GOs) is shifted towards lower angles with respect to the signal of exfoliated graphite. This fact indicates that the interlaminar distance (d_{002}) is increased by the oxidation level of the graphitic material. The total conversion graphitic material to graphite oxide was achieved in a period of only 2 hours, under conditions in which the reaction took place.

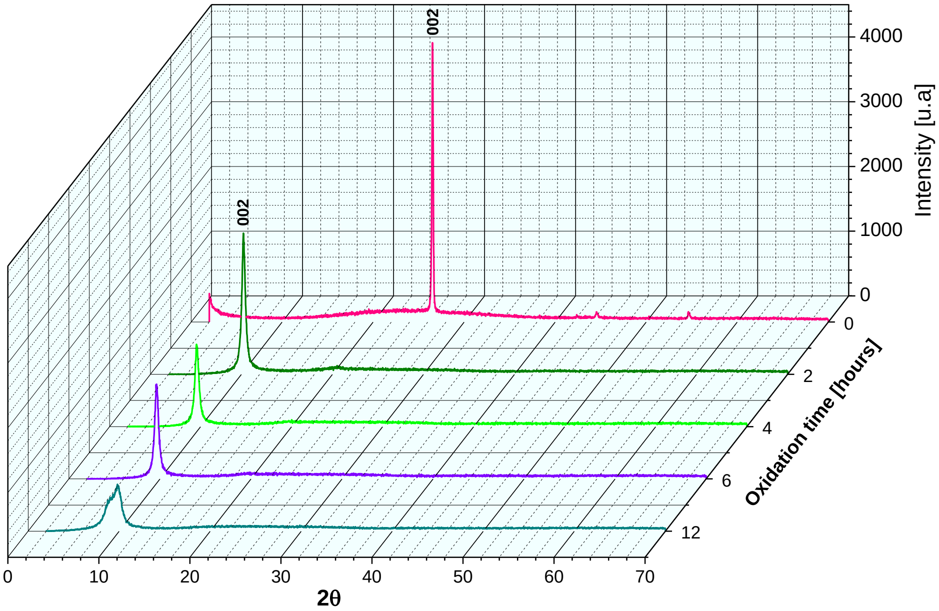

Figure 2. Diffractograms of GNPs and graphites oxides (GOs) with different oxidation levels.

There are two very important results were achieved with the ultrasound treatment: (i) graphite oxide was exfoliated efficiently over a period of 90 minutes, reaching a size distribution in the range of 100-1000 nm with an average particle diameter of 250 nm and, (ii) homogenization and stabilizing of graphene oxide in water for several weeks. For the aqueous dispersion sonicated for 90 minutes, it measured a zeta potential of -60 mV. ASTM defines colloids with zeta potentials lower than -40 mV to have “good stability” [10].

UV-Vis spectra of graphene oxide dispersions with different concentrations (0.01-0.05 mg/mL) had λ_{max} at 229 nm (fig. 3). λ_{max} is attributable to two types of electronic transitions: (i) $\pi \rightarrow \pi^*$ in the conjugated bonds C=C that remain from the original graphite structure and, (ii) $\pi \rightarrow \pi^*$ of the carbonyl groups (ketones and carboxylic acids) with α, β-unsaturations. The shoulder around 300 nm is observed and can be attributed to $\pi \rightarrow \pi^*$ transitions of the carbonyl groups [9].

The identification of the absorption bands in the IR (fig. 3) revealed that GO presents characteristic functional groups that have been reported previously in the literature [8-10]. The broad band in the range of 2500-3650 cm^{-1} corresponds to O-H stretching vibrations of hydroxyl and carboxyl groups. It is possible there embedded water molecules between the GO sheets and they contributed to the infrared absorption in this region (~ 3450 cm^{-1}).

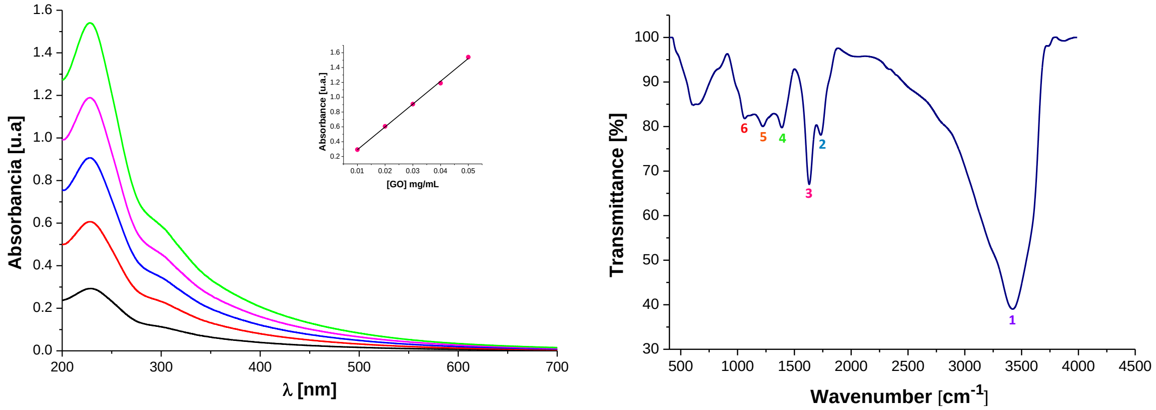

Figure 3. UV-Vis spectra of graphene oxide dispersions (left) and FTIR transmittance spectrum of graphene oxide (right).

Since the carboxyl groups are difficult to be reduced under certain conditions, the graphene sheets in aqueous solution should still be charged after reduction. It measured a zeta potential of -45 mV and an average particle size of 210 nm. These results indicate that really the CRG aqueous dispersion presented good stability without the use of stabilizing agents.

The diffractogram of graphene (fig. 4) revealed that the reduction process allowed restore the crystal structure of graphite. This was evidenced by the reappearance of the (002) and (101) diffraction signals, located in positions very close to those of graphite (table 1) [8-11].

The reduction with hydroxylamine allowed recovery the original conjugation of graphite. This was evidenced by the bathochromic shift of λ_{max} corresponding to $\pi\rightarrow\pi^*$ transitions (fig. 4). The λ_{max} absorption for GO and CRG were 229 nm and 265 nm, respectively. The shoulder located ~300 nm which was attributed to $n\rightarrow\pi^*$ transitions of the carbonyl groups in the structure of GO was not observed in the absorption spectrum of graphene. The band with λ_{max}~210 nm is due to $n\rightarrow\sigma^*$ transitions of the hydroxylamine.

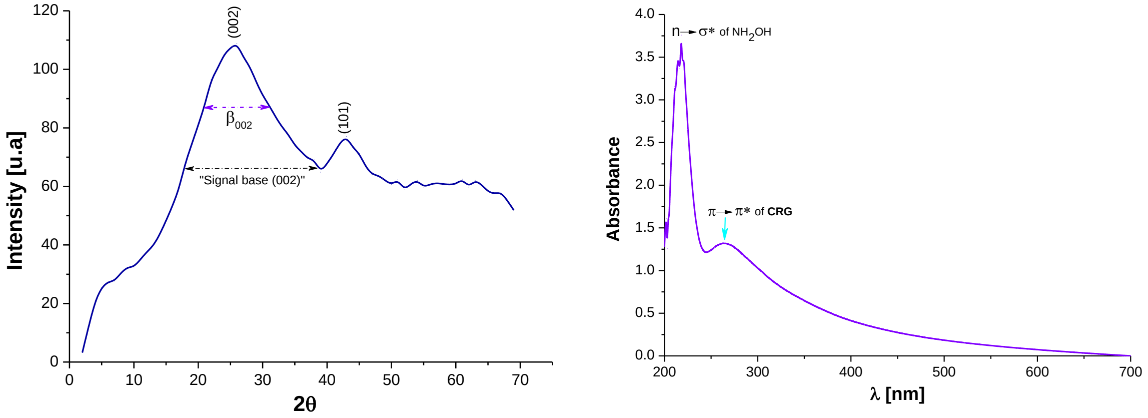

Figure 4. Diffractogram of CRG (left) and UV-Vis spectra of chemically reduced graphene in aqueous dispersion (right).

It was observed that the solid particles of CRG analyzed by SEM were obtained consists of randomly aggregated flakes with a cluttered appearance (fig. 5, left). Micrographs revealed that the material exhibits a high degree of expansion and this may relate to its large surface area [12]. High resolution micrographs (fig. 5, medium) were also obtained and they resemble those that have been published in earlier works, specifically a research where CRG was obtained by chemical reduction of GO using hydrazine how agent redactor (fig. 5, right) [13].

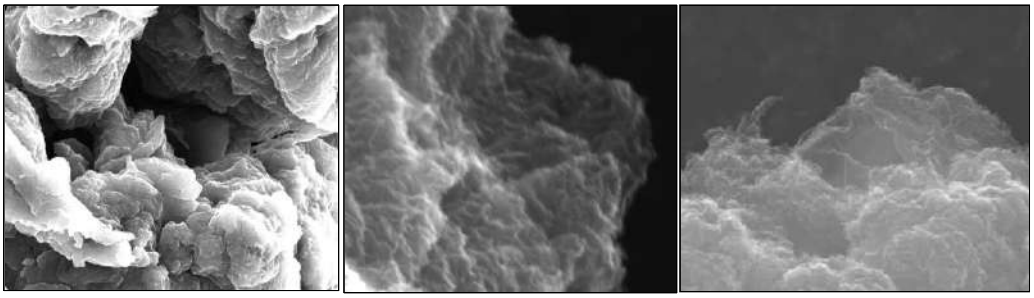

Figure 5. SEM images of agglomerate of CGR nanosheets (left and medium) and CRG sheets obtained by chemical reduction with hydrazine (right).

4 CONCLUSIONS

Exfoliative treatment applied to graphite crystals allowed improve the oxidative process. The total duration for oxidation and production of graphite oxide was significantly shortened due to the use of exfoliated graphite nanoplatelets with large surface area. The optimization of this process also contributed significantly to the simplification of the procedure employed to purify the product synthesized at this stage. The exfoliation of graphite oxide by applying ultrasound confirmed to be a fast and efficient mechanism for obtaining graphene oxide nanosheets in aqueous dispersion. Furthermore, this treatment provided a high level of stability and homogenization of exfoliated material, which was favorable for its storage and use for several weeks. The reduction of graphene oxide with hydroxylamine in aqueous solution proved to be a simple and efficient process for the production of CRG nanosheets with a high level of dispersibility at low concentrations.

Overall, the synthesis procedure implemented in this research could represent a versatile and economical alternative for the bulk production of GO and CRG nanoplatelets and its employ in a wide variety of applications.

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