



Morphological and structural properties in graphene oxides and reduced graphene oxides

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Abstract

In this work, graphite powder was used as initial material to obtain graphene oxides (GO). We propose the reduction of graphene oxides, by physical-chemical method, which consists in a thermo and chemical reduction in the presence of $NaBH_4$ to obtain reduced graphene oxides (RGO). Furthermore, the presence of functional groups and the nanocrystal size were determined by Visive, FTIR and Raman spectroscopy in both samples, GO and RGO. Thereby, we observe that the use of physical-chemical method to obtain RGO produces a significant defects decrease, shown by the D band of the Raman spectrum which practically disappear after this reduction. In addition to this, a morphological study made by AFM have shown relative flats surfaces in the nano-graphene samples obtained by the presented technique.

Keywords: Graphene oxides, reduced graphene oxide, chemical-thermal reduction, defects, Micro-Raman Spectroscopy, Atomic Force Microscopy (AFM).

Propiedades morfológicas y estructurales en óxidos de grafeno y óxidos de grafeno reducido.

Resumen

En este trabajo, se utilizó polvo de grafito como material inicial para obtener óxidos de grafeno (GO). Proponemos la reducción de los óxidos de grafeno, por un método físico-químico, que consiste en una reducción térmica y química en presencia de $NaBH_4$ para obtener óxidos de grafeno reducidos (RGO). Además, la presencia de grupos funcionales y el tamaño de los nanocristales se determinaron por el método de Visive, FTIR y espectroscopia Raman en ambas muestras, GO y RGO. De este modo, observamos que el uso del método físico-químico para obtener RGO produce una disminución significativa de defectos, como lo demuestra la banda D del espectro Raman que prácticamente desaparece después de esta reducción. Además de esto, un estudio morfológico realizado por AFM ha mostrado superficies planas relativas en las muestras de nano-grafeno obtenidas por la técnica presentada.

Palabras clave: Óxidos de grafeno, óxido de grafeno reducido, reducción termoquímica, defectos, espectroscopia Micro-Raman, microscopía de fuerza atómica (AFM).

Introduction

Graphene is a pseudo two-dimensional material formed by the union of carbon atoms with sp^2 hybridization, as similar as the structure of a “bee hive”, which has superior properties when compared to its allotropes, polymorphous compounds (CNTs, fullerenes, diamond, graphite, and others) as mechanicals, electronics, optical and electronic transport, as a big superficial area, high thermal conductivity and high transparency [1]. Regarding to those

several properties, it has been showing its importance for potential applications in the development of super capacitors, fuel cells, biosensors, electrodes, catalytic supports, and conductor films, for its application in transistors development [2]. After its discovery in 2004 by Novoselov and others, the investigations of new synthesis routes in this material have been intensified. The most cited techniques are micro-mechanical exfoliation, chemical exfoliation and chemical vapor deposition (CVD), thanks to its predisposition in the graphene obtaining process on industrial

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scale [3]. To obtain graphene oxide (GO) through chemical exfoliation, we can mention the centralization in the oxy-functionalization of the scales of graphene which are set in graphite through a strong oxidative process. In that process, it is possible to change the graphite's scale polarity in an aqueous medium thanks to a polar colloidal dispersion, in which an inter-plane rupture between graphene sheets may occur. It conforms into graphite in a controlled way, obtaining a stable colloidal suspension [4].

Nowadays, one of the most cited ways for obtaining

GO is the Hummers-Offeman's method, in which the inter-plane rupture occurs thanks to an intercalation of sulfate and bi-sulfate groups, noted in graphite's oxidation stage with the presence of concentrated H_2SO_4 . This process is enhanced by the presence of $NaNO_3$ and $KMnO_4$ in different stages and with rigid temperature control [5]. Further studies have been demonstrating that the use of an ultrasound device increases the percentage of disperse material in this route [6].

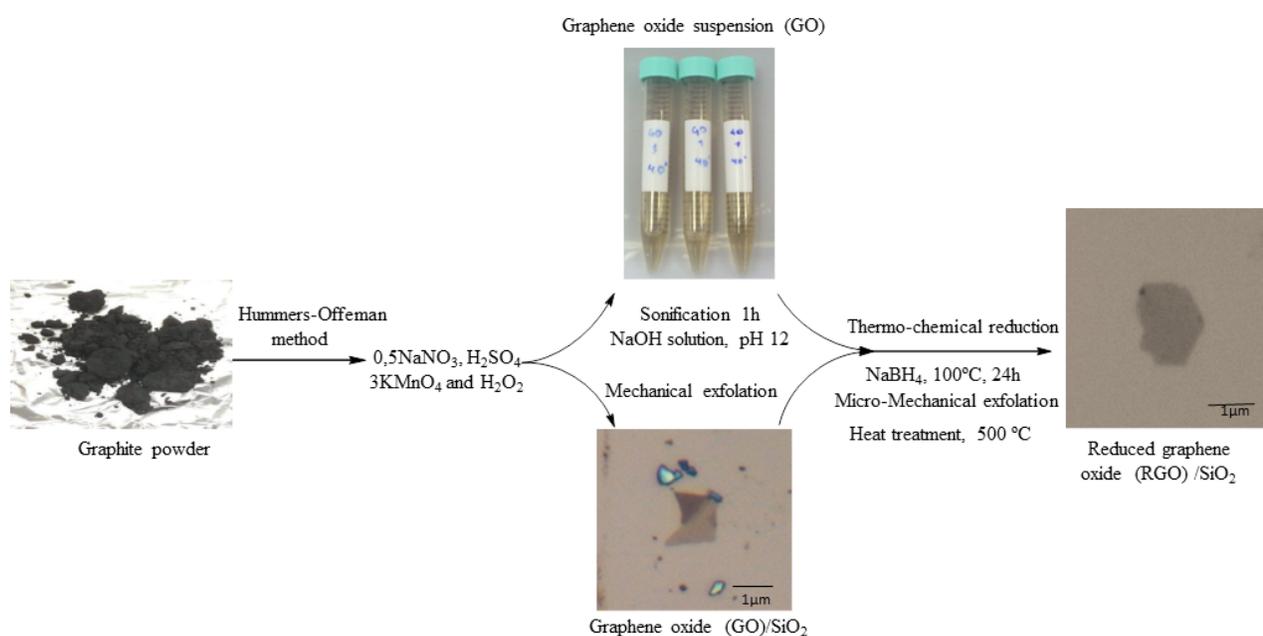


Figure 1: Synthesis of GO and RGO sheets. Graphite powder were chemical treatment by Hummers Offeman method to obtained graphene oxide as an aqueous suspension and isolated sheets supporting on Si/SiO₂-300 nm substrate. In this study, we focused our attention on supported GO sheets that were reduced by $NaBH_4$ 150 mM aqueous solution, mechanical exfoliated and heat treatment at $500^\circ C$ to obtained RGO with a regular topology.

As mentioned before, the chemical exfoliation is centered in the alteration of structural and electronic properties of the original graphene scales; which is mostly generated by ruptures inside and outside in the planes, by the use of the ultrasound device or by other dispersion technique, which can be chemical or physical, to cause the oxy-functionalization on the graphene sheets [7]. Many techniques have been proposed, which allow the partial restitution for electronic properties, through GO reduction by chemical agents as NaH_4B , N_2H_4 , ascorbic acid, and the use of surfactants or organic polymers, as glucose and gelatin; the ones which have the function to repair structural properties [8]. Instead of the common sense, modification on graphene grade can give to it new properties and expand the studies on it and its applications. That is the reason why the ruptures of the mono-layer

graphene are used to obtain sheets of graphene which are needs for develop biosensors [9]. On the other hand, Kaner et. al. reports the obtainment of GO/ RGO in micro-scales for developing super capacitors [10]. Kamat et. al., describe the 'advantages of the functionalization rate in RGO', which one were obtained through reduction using UV radiation, in the development of photo-catalysts which uses RGO/TiO₂ as raw material [11].

There is a broad knowledge about the relations between the syntheses in chemical and physical routes of GO and RGO. Indeed, it is uncommon to find literature about its physical-chemical properties and it is even harder to find studies about the possible chemical routes for its obtainment. It is important to highlight that the N_2H_4 reduction mechanism is the most reported currently, despite the existence of a big variety of reduction agents and

techniques, as $NaBH_4$ and thermal reduction which in this work we can see than the use these hybrid techniques results in a better chemical exfoliation and reduction of defect incorporated with the oxidation process. Keeping this introduction in mind, we present a structural study of GO functionalization rate and one structural analysis of RGO micro-scales.

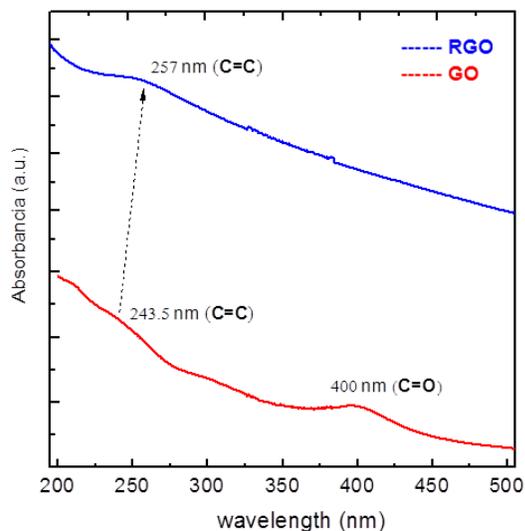


Figure 2: UV-visible spectrum of graphite oxide (GO) and reduced graphene oxide (RGO) suspensions. The shifting from 243.5 to 257 nm after the reduction process can be explained as the partial recovery of the C=C groups and it is related to the elimination of the second absorption band at 400 nm, corresponding to the double bonding of the C=O group.

Experimental Procedure

Through Hummers-Offeman modified process, 1.0 g of graphite powder, used to elaborate electrodes, with 99.5% of purity (Tecnofil S.A., Peru). By following the recipe of the literature of this amount was obtained 0.68 g of GO [12], [13], [14], [15]. Graphite powder was mixed with $NaNO_3$ (pp. $\geq 99\%$, Sigma Aldrich), after reacting with H_2SO_4 concentrated (pp. 98%, MERCK) under low and constant agitation. After this, the sample was homogenized and $KMnO_4$ (pp. 97%, MERCK) and H_2O Milli-Q (18.2 M Ω .cm) were slowly added with the temperature fixed between 95-98°C. The obtained liquid was dark brown and reacted with H_2O_2 (30% wt, MERCK) in constant agitation, we obtained one final light brown liquid, which was centrifuged a 5000 RPM by 45 minutes and it was washed in double sessions with bi-distilled water, HCl 30% and with ethanol, after it was dried at room temperature. The resulting material is called acidic graphite oxide. This material solid was dispersed in NaOH (pH between 10 and 12), by ultrasound during 60 min-

utes. Lately, the liquid was centrifuged a 10000 RPM during 5 minutes so that the material, which was exfoliated by the ultrasound, was eliminated, finally obtaining a colloidal suspension of stable GO. On this stage, the hybrid reduction process was set in two stages: The first is a chemical reduction in which 30 ml of GO colloidal suspension (0.3 mg/ml) reacts with 20 ml of a $NaBH_4$ (pp. $\geq 99\%$, Sigma Aldrich) solution in a concentration of 150 mM, sufferings constant agitation and the temperature between 98-100°C for 24 hours. After this, the RGO solid material, pre-reduced was filtered and dried at room temperature [16], [17], [18]. The second stage, in which solid RGO pre-reduced is sustained above Si/SiO₂-300 nm substrates, through the Nitto Tape technique and thermally treated in a furnace at 500°C [1], [19], [20]. All these procedures mentioned above are shown summary form in Figure 1. With the initial characterization, we analyzed the GO and RGO colloidal suspensions through UV-visible spectroscopy. We used one Perkin Elmer spectrometer, model lambda 25 in a 200 to 500 nm rage for this study. On the other side, we realized one analysis of the functional groups which was presented in the solid samples and in the GO and RGO through an FTIR-ATR spectrometer, using a range from 500 to 4000 cm^{-1} in wave number with the aim of study the functional groups present due to oxidation and reduction process. A comparative study was made in the graphite pure, GO and RGO through of the D and G bands; using a micro-Raman spectrometer T64000, Horiba Jobin-Yvon with the $\lambda_{laser} = 532$ nm. Finally, a morphological study in GO and RGO were made, using an atomic force microscope 5500 Agilent Technologies in tapping mode, which has allowed us observed the thickness, length and uniformity in the samples before and after the reduction process.

Results and Discussion

Figure 2, we did an analysis in UV-visible spectra in GO and RGO samples in the colloidal suspensions. This has been reported by Robert Vajtai, explaining the elimination of this band is characterized by the recuperation of a π conjugated system, but it is even more related with the reduction of -COOH group presents in the border of graphite oxides [21], [22]. Against what is reported by Pei et al., for the ones the reduction realized by $NaBH_4$ is highly effective on C=O groups (about 400 nm) and less effective in carboxyl groups (-COOH) and epoxy (C-O-C), because this is yet a debate theme [23]. Considering that the GO and RGO structural characteristics are different in the percentage of carbon present and in graphite, as in the route of synthesis used for oxidation and reduction. In this way, it is necessary to have a description of the functionalization rate of graphite in its conversion to GO and estimate the restitution rate of the π conjugated sys-

tem, through the reduction of GO as can be observed in Figure 3. In GO there is a change in hybridization state from sp^2 to sp^3 in carbon atoms which forms the π conjugated system in graphene sheets, this happens with the formation of $C=O$, $-COOH$, $C-O-C$, $(-O-)$ and $C-OH$ that can be found in the edges of GO. Because of these changes on hybridization states would change the percentage of π bonds and it would decrease the number of electronic states in Fermi level, in which causes a restriction on conductivity of GO [24].

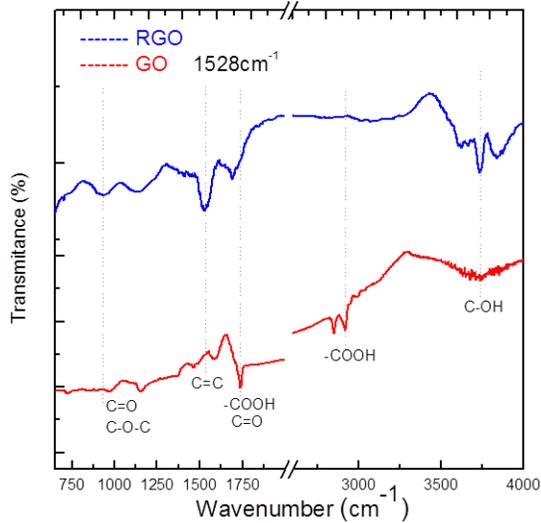


Figure 3: FTIR-ATR spectrum of graphene oxide (GO) and reduced graphene oxide (RGO). The main chemical groups formed during the oxidation stage (Graphite GO) were the epoxy ($-O-$), carboxyl ($-COOH$) and hydroxyl ($-OH$) groups. Some of these staying as part of the RGO structure after the reduction stage, mainly the carboxyl $C-OH$ and epoxy ($C-O-C$) groups indicate that thermal-chemical reduction was a partial restoration of sp^2 hybridization state on graphene structure.

In Figure 3, the FTIR spectra are shown with the vibrational modes which are characteristics of GO and RGO structures. The band located between 900 and 1100 cm^{-1} is associated with stress modes present in the following groups: $C=O$ and $C-O-C$, $-COOH$ and $C-OH$, they are present in GO and in minor proportion in graphite. Anyway, the two last bands between 1100 to 1250 cm^{-1} and 1300 to 1400 cm^{-1} are equally related to the existence of the vibrational modes in ether ($C-O-C$), carbonyl ($C=O$) and epoxy ($-O-$) [25]. Characteristic vibrational modes of some known functional groups as $C=C$ in 1550 to 1650 cm^{-1} , the groups $-COOH$ and $C=O$ exist between 1650 to 1800 cm^{-1} , as well as between 2800 to 3000 cm^{-1} and the groups $C-OH$ and $H-O-H$ from 3200 cm^{-1} to 3750 cm^{-1} . Besides the existence of ketones and carboxyl between 1700 to 1900 cm^{-1} , as the existence of a stretch the “stretching” existent in $C=C$ groups in the planes on the carbon net represented by an absorption band between

1550 to 1650 cm^{-1} which indicate an increase of sp^2 bonds in the RGO in compared with the GO. On the other hand, it has one absorption band between 3200 to 3750 cm^{-1} corresponding to hydroxyl groups OH , exists in $-COOH$ or in water molecules that can be interleaved between the mono layers of GO, which indicates a certain degree of hygroscopic in GO.

In figure 4, through Raman spectroscopy it is possible to quantify the formation of defects in the graphite powder \rightarrow GO transition, which were caused by the oxidation process and by the regeneration of the sp^2 system in the $GO \rightarrow RGO$ transition after the chemical-thermal reduction process. Because of it, the existence of a D vibrational mode in the graphite structure is forbidden and it only occurs when there are defects, it is possible to infer the disorder rate existent in the graphene sheets after the oxidation process. The Raman spectrum GO shows a considerable increment on the D vibrational mode, and it is caused by the formation of defects in the functionalization process of the carbon atoms and considering the results obtained in FTIR analysis of this process occurs on the carbon atoms existent in the borders forming epoxy, carboxyl and ether or on the intern network generating hydroxyl. However, we observe the replacement in the intensity of the D band after the reduction process of GO to RGO, with which we can verify the recovery of π conjugated system. Given that the G band is related with the presence of $C(sp^2)$ atoms, it is possible to conduct to an analysis of the displacement in its position $POS(G)$. We observed the decrease of $POS(G)$ in the first transition ($GC \rightarrow GrO$) from 1591 cm^{-1} to 1587 cm^{-1} and in the second transition ($GrO \rightarrow rMGO$), from 1587 cm^{-1} to 1581 cm^{-1} , this one has been reported as a transition from nanocrystalline graphite to amorphous carbon with a change in the maximum hybridization kind for 20% of sp^2 to sp^3 . However, a relation between the rate of defects formation can be given through the relation of the D and G band Intensity ($I(D)/I(G)$) and the nanocrystalline size as was found by Pimenta et. al. and it presents the following relation [30]:

$$L_a(nm) = \frac{560}{E_l^4} \left(\frac{I(D)}{I(G)} \right)^{-1} \quad (1)$$

Where L_a is the size of nano-crystal and E_l is the laser excitation energy, used in Raman analysis in eV. Considering that in this study we have used a laser with wave number equal to 532 nm ($E_l = 2.33$ eV). However, using the equation 1 as we can notice in the Table 1, L_a goes from 177 nm to 19 nm in the transition graphite powder GO and an increment in the size of the crystal for the second transition from 20 nm to 72 nm, GO and RGO.

The first case can be explained by a decrease on the value of, as a consequence of the sub process of chemical interaction. After this, a second behavior can be given from a des-functionalization process of the oxy-

generated groups after the chemical-thermal reduction process, which would reduce the shallow charge that allows us to keep apart the RGO sheets, given to it the capacity to stack again. This last process is confirmed with an increment on the dimensions of the supported sheets of GO and RGO observed through atomic force microscopy (AFM). It was observed sheets of GO with dimensions ranging from 1.3 μm to 1.8 μm (Figure 5 b1, b2). Comparing to RGO sheets whose dimensions ranges from 0.6 to 0.9 μm (Figure 5 a1, a2). On the other hand, we observed a big topological improvement on RMGO sheets obtained after the hybrid chemical-thermal reduction process, as a decrease in its thickness from 30 nm to 15 nm indicating that it was formed approximately 10 to 15 sheets of graphene, according to profilometric analysis (Figure 5 a3 y b3).

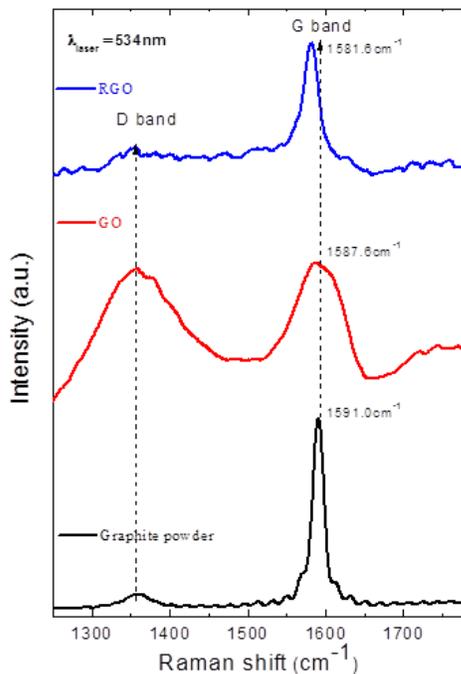


Figure 4: Raman spectrum of graphite, GO and RGO sheets. The oxidation stage of Graphite to GO presents a negative shift of POS(G), as well an increasing of I(D) band intensity that meaning a change of hybridization from C(sp²) to C(sp³) in certain regions of the graphene crystals. This interchange was

Samples	POS(D) cm ⁻¹	I(D) (au)	POS(G) cm ⁻¹	I(G) (au)	$\frac{I(D)}{I(G)}$	L_a (nm)
Graphite	1362.8	05.84	1591.0	53.97	0.11	177.6
GO	1357.3	13.01	1587.6	13.23	0.98	19.6
RGO	1356.3	0.97	1581.6	01.75	0.56	72.1

Table 1: Parameters determined from the Raman spectrums to the graphite, GO and RGO. Using the D and G bands in these systems was determined the position (POS(D) and POS(G)), intensity (I(D) and I(G)), the intensity ratio ($I(D)/I(G)$) and the size crystalline L_a .

partially restored during the reduction stage of GO to RGO showed from a displacement of the POS(G) of 10 cm⁻¹ as well as considerable reduction of I(D) band intensity in relation to I(G) band.

Conclusions

As part of the synthesis process, it is important to highlight that the oxidation process is oriented by the functionalization of carbon atoms located on the edges, oxidizing them to carboxyl, ether and carbonyl groups. However, the chemical reduction by NaBH_4 has shown, in a similar manner to oxidation, to be a selective process because it restores the sp² hybridization in carbon atoms which are functionalized in GO. Certainly, this reducer agent has showed to have the capacity to restore the π conjugated system, since the initial system had a fraction of defects GO and after the chemical-thermal reduction process the fraction of defects RGO, after this we can conclude that the reduction of the superficial defects was equal to 0.42 according to the analysis made with Raman spectroscopy. Anyway, we report that for the transition Graphite powder GO, a decrease in the POS(G) related with the diminution in the number of C (sp²), which is observed in the Raman and FTIR spectrums.

Furthermore, we observe a diminution in size of the crystals (L_a) that exists initially on GC, from 177.6 nm to 19.6 nm which is caused by the ruptures on the nets of carbon, as consequence of intercalation process and the ultra sound has provided the transition stage. Anyway, after the chemical-thermal reduction process we observed an increase on size of the crystal (L_a), what indicates a partial enlargement of the scales of RGO. On this analysis the functionalization grade is confirmed through atomic force microscopy, AFM. Principally is highlight the dimensions of the sheets of RGO equals to 0.6 to 0.9 μm , that indicates a sectioning on the initial sheets of graphite, not only in the inter-plane direction but in plane ruptures too; this increases the proportion of shallow defects and it raises difficulties the restore of π system on the final product. Anyway the profilometric analysis of the thickness of this sheets of CMG, showing us that after the process of chemical-thermal reduction they have a thickness of 10-15 nm, that would indicate the existence of 10 to 15 sheets of graphene in its structure.

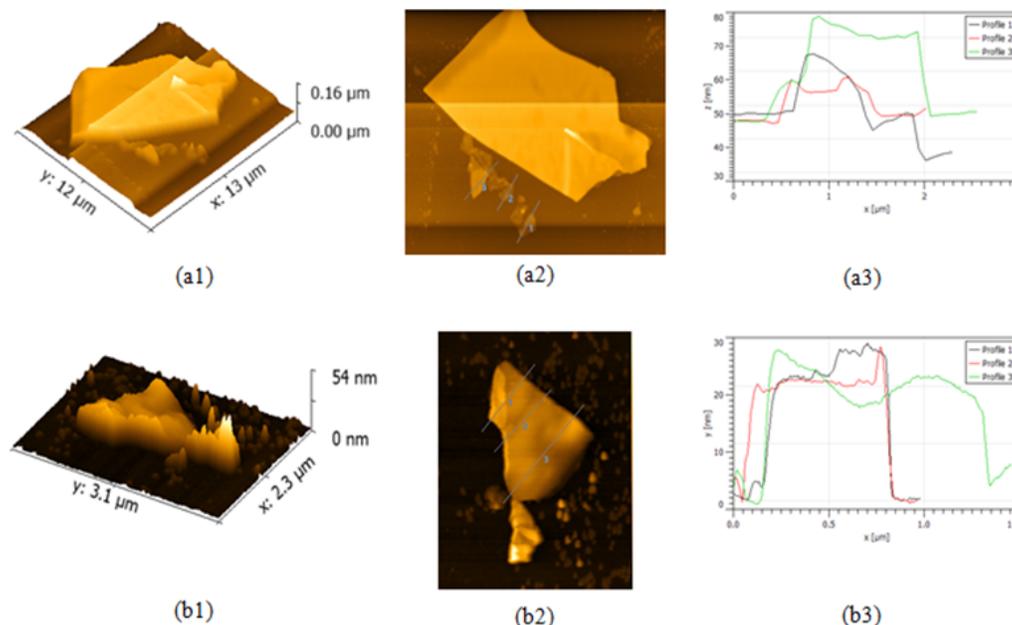


Figure 5: AFM pictures of Graphene Oxide, GO (a1, a2) and Reduced Graphene Oxide, RGO (b1, b2) sheets supported onto Si/SiO₂-300 nm substrate, also of their 3D and 2D views. (a3, b3) Profilometric analysis shows an irregular topology for GO, profiles 1 (black) and 2 (red); in contrast to RGO sheets topology that looked more regular than GO sheets. Moreover, these last one show a less thickness than GO samples with a value equal to 10-15 nm that could indicate the presence of 10 to 15 of RGO monolayers.

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