Bio-reduction of graphene oxide using grenade peels and gas sensing application

Khaoula Kacem [a,b], Sami Ameur [b,c] Juan Casanova-Chafer [d], Mohamed Faouzi Nsib [a,b], Eduard Llobet [d]

[a] Higher School of Sciences and Technology of Hammam Sousse, University of Sousse, Tunisia.

[b] Laboratory of nanomaterials and microsystems for Health, Environnement and Energy (NANOMISENE. LR16CRMN01) CRMN, Technopole Sousse, Tunisia.

[c] High Agronomic Institute of Chott Meriem, University of Sousse, Tunisia.

[d] Universitat Rovira i Virgili, MINOS, Avda. Països Catalans, 26, 43007, Tarragona, Spain.

Abstract: This work presents a straightforward, inexpensive, and eco-friendly approach for the reduction of graphene oxide (GO) using a nontoxic reducing agent from grenade peels bio-extract. The graphene oxide was prepared by a modified Hummers' method from natural graphite and subsequently reduced using grenade peels bio-extract. The prepared GO and rGO were characterized by several techniques such as UV-Vis, FTIR, Raman, XRD, and FESEM. The results obtained reveal the successful graphene bio-reduction using grenade peels due to the removal of a significant content of oxygen functional groups and the partial restoration of sp^2 carbon structures, resulting in rGO. The bio-reduced GO material was also tested for the detection of NO_2 gas, showing interesting performance as a candidate material for gas sensing applications.

Key words: graphene, rGO, bio-reduction, NO_2, gas sensor.

1. Introduction

Pristine graphene consists of a single sheet of sp^2 hybridized carbon atoms arranged in a two-dimensional honeycomb lattice [1–5]. Owing to its excellent and unique properties such as high specific surface area (2630 m^2g^{-1}), excellent thermal conductivity (~5000 $Wm^{-1}K^{-1}$), and high electron mobility (2×10^5 $cm^2V^{-1}s^{-1}$) [6–11], graphene has become an attractive nanomaterial for the scientific community in the last decade. Indeed, these unique properties allow graphene implementation into a wide range of applications like electronics, sensors, biomedical, supercapacitors for energy storage, fuel cells, or solar cells [12–15]. High-quality graphene can be produced in large quantities using chemical vapor deposition (CVD) [16]. However, several methods have been also used to produce graphene from pristine graphite such as the scotch tape method [17] or thermal exfoliation [18]. Alternatively, graphene oxide (GO) is widely obtained via the modified Hummers' method, which consists of exfoliating and oxidizing graphite. This method leads to the introduction of oxygen functional groups on the sheets, which makes GO an electrical insulator [19]. Moreover, in contrast to pristine graphene, the presence of oxygen functional groups in GO flakes enables their dispersion/ suspension in aqueous solutions, which highly enhances processability and eases their integration in electronic devices.

Additionally, it is reported that one of the most effective methods for obtaining graphene-like structures (i.e., keeping or restoring the sp^2 hybridized carbon) is the chemical reduction of graphene oxide (GO) [20]. The reduction of GO has the advantage of producing reduced graphene oxide (rGO) at a large scale with high quality and at a low cost in a short time [21]. Thereby, the reduction of GO is an effective strategy to remove oxygen groups and partially re-establish the electrical conductivity of graphene [22]. However, reducing GO usually presents a significant drawback as the use of hazardous chemical agents such as hydrazine, sodium borohydride, and hydroquinone [23]. These reducing agents are toxic and could have harmful effects on the environment if not properly disposed of. For this reason, it is necessary to develop environmentally friendly alternatives to reduce GO. Particularly, the bio-reduction approach seems to be a promising way to reach this goal. Indeed, the use of various types of green reducing agents have been reported as algal extract [22], lemon extract [24], eucalyptus leaf extract [25], allium cepa (onion) [26], and Kaffir lime peels [27]. Nevertheless, the present work develops a new bio-reducing agent extracted from grenade peels to reduce GO effectively and inexpensively.

The bio-reduction reaction was also studied and the obtained rGO product was characterized with several techniques. Not limited to this, the synthesized nanomaterial was implemented in gas sensing devices to detect toxic gases. Specifically, low concentrations of NO_2 were detected in a few minutes, which have significant interest for ambient monitoring applications. Indeed, graphene-based nanomaterials have been attracting large research interest for pollutant monitoring due to some intrinsic properties. For instance, their capability to work at room temperature or moderate temperatures, high sensitivity to detect trace levels of NO_2, or wide versatility due to their 2D configuration to be functionalized or decorated with other nanomaterials and creating nanohybrids [28, 29]. Nevertheless, to the best of our knowledge, grenade peels were not tested before in such reduction reaction and nanotechnology application.

2. Materials and Methods

2.1. Preparation of Graphene Oxide (GO)

GO was synthesized from natural graphite powder using the modified Hummers' method [30]. Thus, 2 g of graphite and 1.25 g of sodium nitrate ($NaNO_3$) were added to 23 ml of concentrated sulfuric acid (H_2SO_4) under magnetic stirring for 20 minutes in an ice-water bath. Then, about 7.5 g of potassium permanganate ($KMnO_4$) were carefully added and stirring was continued for 2 hours. Subsequently, the mixture was removed from the ice bath and stirred again at T = 30 °C for 30 minutes. After that, 120 ml of distilled water were slowly added and the temperature of the reaction mixture was suddenly increased, obtaining a brown suspension. After 15 minutes of stirring at 90 °C, 350 ml of distilled water were added to the mixture and the heating was turned off. The suspension was further treated by adding H_2O_2 (30 %) until the color of the solution became green. The solution was filtered and washed with distilled water to remove OH^- ions and then dried overnight. The obtained powder was dispersed in an appropriate amount of distilled water and maintained in an ultrasonic bath for 1 hour. Finally, after filtration and drying, a powder of exfoliated graphene oxide was obtained.

2.2. Reduction of GO by grenade peel phytoextract

First, 5 g of grenade peels were dried, powdered, and then dispersed in 500 ml of distilled water at T = 80 °C under magnetic stirring. The bio-extract was subsequently obtained through filtration. The bio-reduction of GO was carried out by adding 2 g of GO to 400 ml of peel phytoextract and stirred at T = 80 °C for 20 hours. The resulting suspension was washed, filtered, and dried overnight. Finally, a reduced graphene oxide (rGO) powder was obtained.

2.3. Material Characterization

The reduction of GO was monitored over time using UV-Visible spectroscopy (UV-Vis, Biochrom Libra S22) within a wavelength range of 200-400 nm. Then, Fourier Transform Infra-Red (FTIR, Perkin Elmer UATR two) was used to study the presence of oxygen functional groups within the wavelength range of 4000-400 cm^{-1}. Besides, Raman spectroscopy was used to determine the quality of the prepared samples at wavelength 1000-3250 cm^{-1}. Furthermore, X-Ray Diffraction (XRD) was used to evaluate the crystallinity of GO and rGO. The morphological structure was studied employing Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss AG - ULTRA 55).

2.4. Sensing Device Fabrication and Measurement

The synthesized rGO and GO nanomaterials were dispersed in ethanol through an ultrasonic bath and deposited by airbrush onto interdigitated electrodes (IDE). Specifically, the platinum IDE were screen-printed over an alumina substrate, with a heater printed at the backside. Subsequently, the samples were placed in an airtight Teflon test chamber.

The gas sensing tests were carried out by stabilizing the sensors under synthetic dry air for 15 min and then exposing them for 5 min to NO_2 diluted with synthetic air to apply different concentrations. The resistance values of the sensors were measured using an Agilent HP 34972A multimeter.

The response of the sensors was defined as:

$$\Delta R/R_0\ (\%) = [(R-R_0)/R_0] \times 100, \qquad [31]$$

Where R_0 is the resistance under dry air and R is the last resistance value obtained under each exposure to NO_2.

3. Results

3.1. UV-Visible Spectroscopy

The reduction of GO was monitored and confirmed by recording UV-Visible absorption spectra as a function of reaction time. Initially, the spectrum of GO (**Figure 1a**) shows two absorption peaks; the first at 232 nm is attributed to π-π^* transitions of aromatic C=C bonds and the second at 284 nm is due to n-π^* transitions of C=O bonds [25]. After 20 hours of the reduction reaction, the aromatic C=C peak was observed to redshift until 265 nm. This finding confirms the removal of most oxygen-containing functional groups in the GO allowing the change of carbon from sp^3 to sp^2 hybridization, and subsequently the decrease of the gap π-π^* to finally enable the restoration of the electronic conjugation characterizing the graphene network [32]. Furthermore, it was observed that upon reduction, the color of GO suspension changed from yellowish-brown to dark black, which is considered as a confirmation for the formation of reduced graphene oxide (rGO) [33].

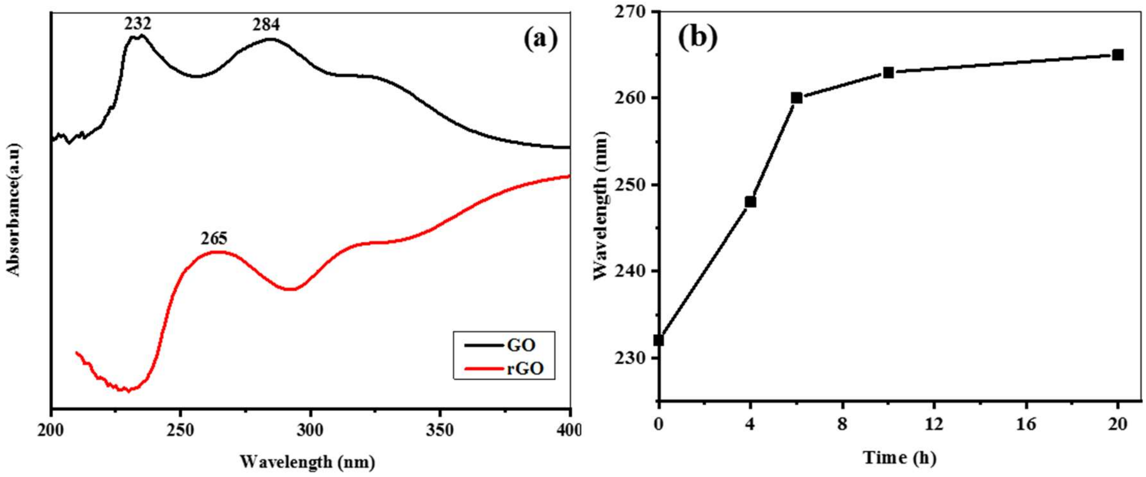


Figure 1. (**a**) UV-Vis spectra of GO (t = 0) and rGO (t = 20h)**.** (**b**) Variation of λ_{max} of the C=C absorption peak during the reduction reaction of GO using grenade peels at T = 80 °C.

Further analyses were performed to obtain more information about the bio-reduction kinetics of GO. Specifically, the evolution of the C=C absorption peak and its corresponding red-shift were assessed (**Figure 1b**). The wavelength (λ_{max}) of the absorption peak was recorded after 4, 6, 10, and 20 hours. Accordingly, it can be noticed the kinetic bio-reduction of GO with grenade peels shows two phases. The first one comprises the initial 10 h, in which the λ_{max} value of the π-π^* absorption peak was significantly increased, ranging from 232 to 260 nm. Conversely, after these 10 hours, λ_{max} remains almost stable, ranging from 260 to 265 nm, achieved after 20 hours of bio-reduction. This result shows the potential of grenade peels to reduce GO faster than other reducing agents. For instance, Wang et al. [33] obtained rGO using alanine as a reducing agent after 24 hours.

3.2. FTIR Analysis

The functional groups present in the as developed samples were identified using FTIR analysis (**Figure 2**). The GO spectrum shows the presence of several peaks related to oxygen-containing groups such as a broad peak at around 3250 cm^{-1} due to the hydroxyl group (OH), C=O (carboxylic) stretching vibration peak at 1715 cm^{-1}, O-H deformation peak at 1398 cm^{-1}, C-O (epoxy) stretching peak at 1176 cm^{-1} and the C-O (alkoxy) stretching peak at 1040 cm^{-1} [34]. Moreover, a peak corresponding to the C=C stretching mode of the aromatic ring [35] was observed at 1617 cm^{-1}. This peak could result from the sp^2 unoxidized graphite domains [36].

After reduction with the grenade peels, the broad peak corresponding to the hydroxyl group disappeared, while peaks related to the carboxylic, hydroxyl, epoxy, and alkoxy groups decreased their intensity in comparison to the GO spectrum. These results reveal that oxygen-containing functional groups were partially removed [23]. Furthermore, the peak attributed to the C=C stretching vibration was shifted from 1617 cm^{-1} to 1567 cm^{-1} which can be explained by the partial reduction of GO [37].

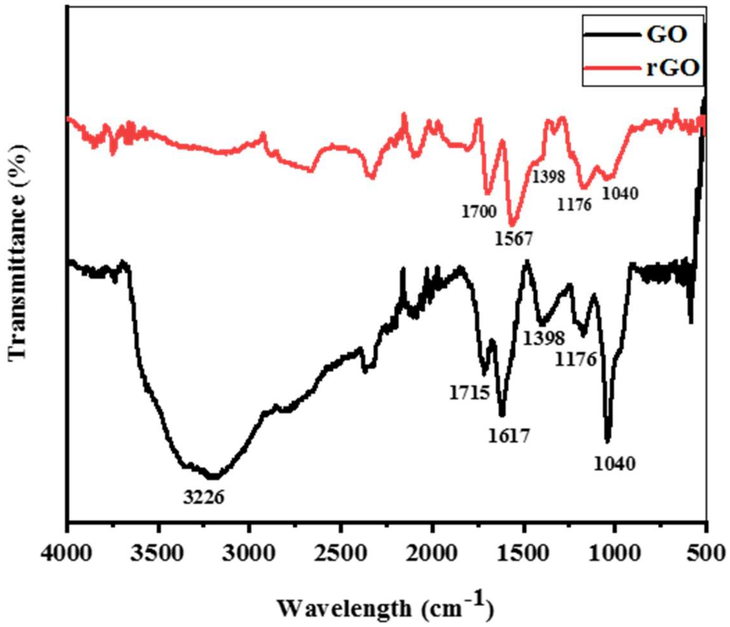


Figure 2. FTIR spectra of GO and rGO.

3.3. Raman Spectroscopy

Raman spectroscopy can provide structural information, being widely employed to analyze carbon-based nanomaterials, including graphene and its derivatives. **Figure 3** shows Raman spectra of the prepared GO and rGO. The spectrum of GO shows two fundamental vibration bands; the D vibration band at 1353 cm^{-1}, which is formed from a breathing mode of j-point photons of A_{1g} symmetry, and the G vibration band at 1603 cm^{-1} due to the first-order scattering of E_{2g} phonons by sp^2 carbon [38]. After reduction, the D band was broadened and shifted to 1356 cm^{-1}, whereas the G band was shifted to a lower region, 1595 cm^{-1}. Furthermore, the intensity ratio of the D and G bands (I_D/I_G) was increased from 0.9 for GO to 1.12 for rGO due to the partial restoration of the sp^2 network during the reduction process [39].

It is worth noting that additional information can be obtained from the Raman spectrum of graphene. Specifically, the 2D band enables the determination of the graphene layers (monolayer, double layer, or multilayer) as it is highly sensitive to the stacking of graphene sheets [40]. According to Figure 4, the 2D band appeared at 2702 cm^{-1} for GO and was shifted towards a higher value for rGO (2711 cm^{-1}). This shift is attributed to the decrease of oxygen-containing functional groups leading to the rGO stacking [23]. The location of the 2D band confirms a multilayer structure for both, GO and rGO since monolayer graphene is normally observed at 2679 cm^{-1} [19].

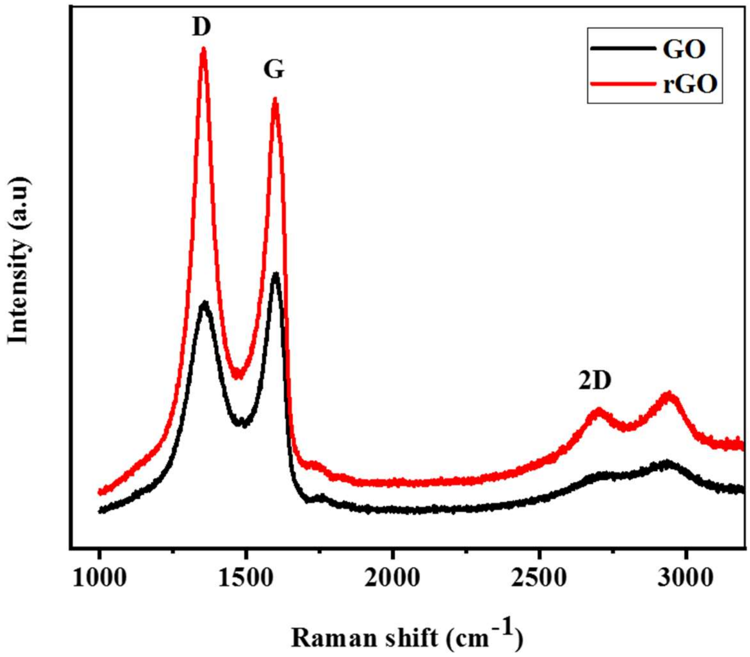


Figure 3. Raman spectra of GO and rGO.

3.4. XRD Analysis

XRD patterns of GO and rGO also confirm the structural formation of GO and the partial removal of the oxygen-containing groups after the bio-reduction process (**Figure 4**). For GO, the appearance of the (002) diffraction peak at 2θ = 11.1° indicates that the oxidation of graphite by the modified Hummers' method has occurred successfully, leading to the formation of GO [41, 42]. After the bio-reduction with grenade peels, the (002) peak of GO disappeared in the XRD pattern of rGO and a broad peak (001) was observed at 2θ = 25.3°. This shift reveals the lowering of the inter-planar distance between graphene sheets due to the removal of entrapped oxygen-containing functional groups [43]. As a result, an efficient removal of oxygen groups during the bio-reduction process was achieved. Besides, a less intense peak was observed at 2θ = 42° for both GO and rGO implying the existence of graphene plane (001) [23].

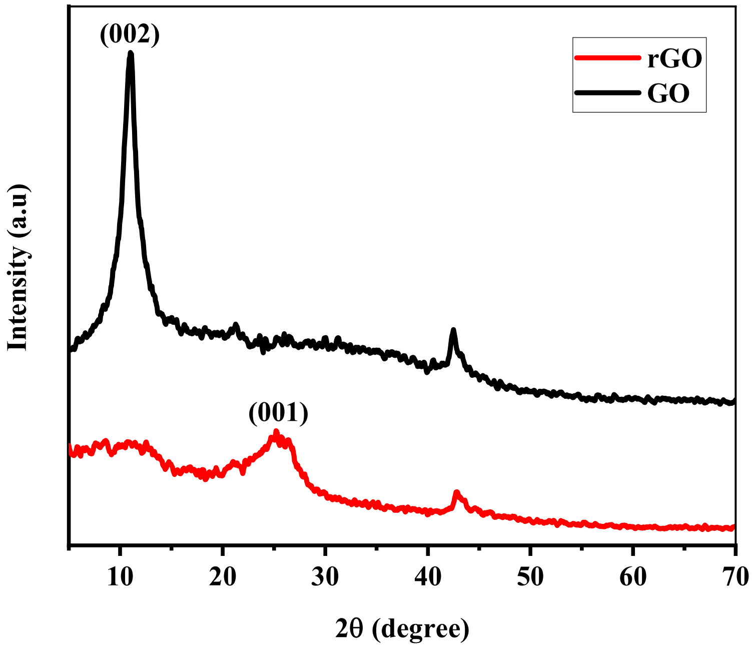


Figure 4. XRD patterns of GO and rGO.

3.5. FESEM Analysis

The morphological structure of both GO and rGO was observed using a Field Emission Scanning Electron Microscopy (FESEM). The image of GO (**Figure 5a**) shows layers of graphene as thin wrinkled and folded sheets. The presence of folding is due to the oxidation of graphite, allowing the existence of oxygen-containing functional groups. In contrast, the rGO sample (**Figure 5b**) presents partially folded individual sheets along with less aggregation, proving the successful reduction of GO by grenade peels phytoextract.

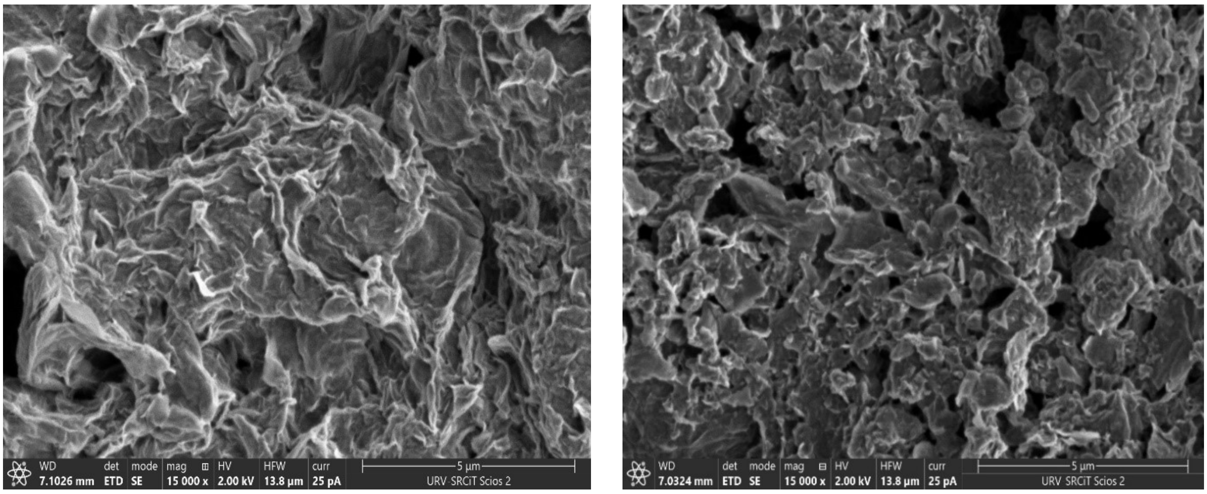
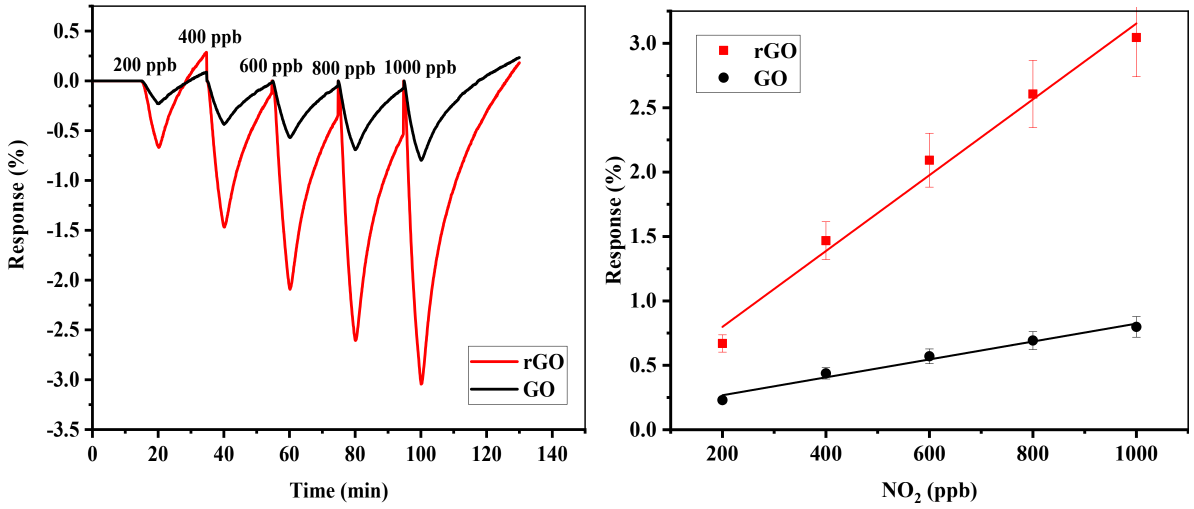


Figure 5. FESEM images of GO (**a**) and rGO (**b**).

3.6. Gas Sensing Application

The chemical synthesis of graphene oxide using the Hummers' method followed by a bio-reduction step is an effective strategy to produce large amounts of graphene, allowing its potential use in industrial applications. Particularly, the bio-reduced graphene oxide (rGO) using grenade peels was tested for the detection of nitrogen dioxide (NO_2), which is a well-known harmful pollutant gas. The obtained results were compared to those found using non-reduced GO.

GO and rGO sensors were tested for the detection of NO_2 by applying different concentrations (200, 400, 600, 800, and 1000 ppb) at room temperature and 100°C. However, both samples show slight resistance changes at room temperature, which are not enough to effectively distinguish them from the noise levels, unlike at 100 °C where clear sensing responses were obtained (**Figure 6a**). When increasing the operating temperature, a thermally activated process is induced, leading to greater adsorption of gas species owing to more intense gas-surface interaction [44]. As a result, higher charge transfer occurs at 100 ºC, enlarging the resistance changes, and thereby reducing the signal-to-noise ratio. **Figure 6b** presents the calibration curves corresponding to NO_2 sensing by the prepared GO and rGO. It is noteworthy that rGO exhibits higher responses than GO. In addition, since the device sensitivity is given by the slope of the calibration curve, **Figure 6b** shows that rGO based sensor is more sensitive to NO_2 (up to 4-fold) than their GO counterpart (**Table 1**).



(a) (b)

Figure 6. GO and rGO sensors responses when detecting NO_2 at 100°C from 200 to 1000 ppb (**a**) and associated calibration curves (**b**).

Table 1. Sensor sensitivity ($10^{-2} \times ppm^{-1}$).

Test gas	GO	rGO
NO_2	69.5	294

4. Discussion

Both nanomaterials, GO and rGO show an increase in their conductivity upon exposure to NO_2, which is an electron-withdrawing gas [45]. The reason is the higher concentration of majority carriers (holes) in p-type carbon-based nanomaterial when interacting with NO_2, showing clear electrical responses [46]. Nevertheless, the bio-reduced GO sample exhibits significantly higher sensing responses than the GO-based device despite the lower presence of sp^3 carbon configuration and oxygen groups, which usually tend to show higher interactions with gas species [47]. Therefore, other parameters should have a significant effect on the sensing performance. For instance, **Figure 5** revealed remarkable morphological differences between both samples. In that sense, rGO showed lower agglomeration than GO, leading to theoretically higher surface area available to interact with NO_2. In addition, surface porosity has probably a significant effect on the electrical responses obtained for rGO. These findings confirm the efficiency of grenade peels as reducing agents of GO, which makes the green synthesized rGO a potential candidate for gas sensors. **Table 2** depicts the sensitivity comparison to NO_2 gas of the sensor based on reduced GO with grenade peels with other previously reported in the literature. It can be observed an outstanding sensing performance for the synthesized rGO grenade peels under similar experimental conditions (i.e., operating temperature or flow rate) than other works previously published.

Table 2. Comparison of NO_2 sensing performance for reduced GO with grenade peels and other previous works reporting similar approaches. (*Sensitivity Coefficient*: value estimated considering the response (%)/ unit of concentration (ppm)).

Material-based sensor	Temperature (°C)	Sensitivity coefficient	Type of device	References
Graphene	150	1.44	Resistor	[31]
rGO by thermal reduction	100	0.004	Resistor	[48]
L-Glu rGO	150	0.12	Resistor	[46]
rGO caffeic acid	RT	0.33	FET	[49]
rGO grenade peels	100	3.04	Resistor	This work

5. Conclusions

A straightforward, inexpensive, and eco-friendly approach for the reduction of graphene oxide (GO) using a nontoxic reducing agent from grenade peels bio-extract was developed. The bio-reduction reaction was carried out at 80 °C and during the initial 10 h, a 34.8% of oxygen removal was achieved. After this time, a stabilization phase was observed, being the oxygen content almost unchanged. As a result of the bio-reduction applied, partial restoration of the sp^2 carbon structure was demonstrated. In addition, the synthesized GO and rGO were extensively characterized through several techniques, revealing their multilayer structure. These results show the potential of grenade peels to reduce GO faster than other reducing agents previously tested. But not limited to this, the nanomaterial developed was effectively implemented in a gas sensing device for detecting NO_2 at the sub-ppm level. Indeed, the bio-reduced GO developed in this work showed an outstanding sensing performance, paving the way towards eco-friendly and low-cost sensing devices. Furthermore, considering the high versatility of graphene nanocomposites to be decorated or functionalized with other types of compounds, it would be possible to perform further modifications over the bio-reduced GO developed for improving some sensing parameters as selectivity or response times.

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