Artemisia herba-alba Asso eco-friendly reduced few-layered graphene oxide nanosheets: structural investigations and physical properties

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ABSTRACT

Nowadays graphene is universally known as a promising material. Hence, the development of eco-friendly synthesis methods for this material is of great importance. This study reports on the bio-synthesis of graphene by a green chemistry process using Artemisia herba-alba Asso (AHAA) natural extract. Moreover, this work reports on the physical properties, including surface/interface and optical and electrical properties of the obtained graphene sheets. UV–VIS, Raman, XPS spectroscopies and TEM microscopy investigations confirmed the reduction, and the conversion of graphene oxide to few-layered reduced graphene oxide as well as the efficiency of this plant extract compared with several natural extracts and chemical agents. Furthermore, it was found that the optical and electrical properties of graphene can be modulated and controlled via this eco-friendly cost-effective process. Hence, AHAA can be an effective chelating agent to produce graphene sheets.

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Introduction

Nanotechnology provides a new platform for innovation in all fields of research, particularly within the context of meeting the challenges involved in the move toward greener and more eco-friendly processes. Recent developments in nanoscience have already played an important role in reducing the formation and emission of certain pollutants. Furthermore, other developments in the field of nanotechnology have led to an upsurge in the commercial uptake of several types of manufactured nanoparticles. These nanoparticles and nanomaterials have been applied in various fields, such as in electronics, sensors, and even in the biomedical space, due to the immense range of useful and diverse properties that are intrinsic to certain nanoparticles.

Nanoparticles can be grouped into different types, such as carbon-based nanomaterials, metal nanoparticles, dendrimers and nanocomposites (1–4). Carbon-based nanomaterials are well known for their innumerable applications in all fields of science and technology. One of the most incredible carbon-based nanomaterials in recent years is graphene, due to its amazing properties.
Owing to its unique physical and chemical properties, this material is set to revolutionize the twenty-first century for its wide practical uses, such as in nanoelectronics, (5, 6), sensors, (7, 8), capacitors, (9–11), solar cells, (12–14), fuel cells, (15, 16), Li ion batteries, (17–19), photocatalysis, (20, 21), electrocatalysis, (22, 23), drug delivery (24, 25) and plasmonics (26, 27). Given this exceptional level of utility, there is a clear need to prioritize processes that are amenable to the large-scale synthesis of high-quality graphene, at low cost and with easy processing methods. So far, several techniques have been used to synthesize graphene, which mainly include mechanical or ultrasonic exfoliation (28); chemical vapor deposition (CVD)/plasma enhanced CVD (PECVD) (29, 30); epitaxial growth (31); electric arc discharge (32); chemical intercalation (33) or the thermal/chemical reduction of graphene oxide (GO) (34–36), where various carbon sources were used to synthesize this material. Among these cited methods, the chemical reduction of GO is recognized as a versatile and suitable method for the preparation of graphene in bulk quantities at a low cost.

In general, graphene synthesis via chemical methods mainly involves two steps: (1) the oxidation of graphite into graphite oxide and (2) the reduction of GO into graphene. The reduction process is an essential step, however, many of the reductants used to reduce GO, such as hydrazine (37, 38), hydrazine hydrate (39, 40), sodium borohydride (NaBH₄) (41), metal hydrides (42, 43) hydroquinone, amino acids, sodium borohydride and sodium hydroxide are either strongly acidic or highly toxic. Moreover, the by-products of these reductants are not environmentally benign, thus making bulk production of graphene difficult and not suitable for further applications, particularly in the biomedical field. An additional obstacle that presents itself when chemically reduced graphene oxide (rGO) is produced is the poor quality of the process. This is because the rGO tends to form irreversible aggregations, which result from strong van der Waals attractive forces between the graphene planes, unless a modification step (both covalent and non-covalent) is included in the process (44, 45, 46). Recently, efforts have been made toward addressing the above-mentioned problems by using natural products instead of toxic-reducing agents.

A number of plant extracts are currently being investigated to assess the potential role that they could play in the development of ‘green’ processes to support the large-scale synthesis of certain nanoparticles. Recent research in this field has reported the use of different plant leaf extracts for synthesizing silver nanoparticles, such as Gloriosa superba L. (47), Citrus limon L. (48), Carob (49) and Tephrosia purpurea L. (50). On the other hand, the synthesis of gold nanoparticles was reported using a tea leaf extract (51), Pelargonium graveolens (PeG) (52), Punica granatum (PuG) (53), Salvia officinalis (SO) (54) and Morinda citrifolia roots extracts (55). Different nanoparticles derived from silver, nickel, cobalt, zinc, copper and indium oxide have also been synthesized using plants extracts of Brassica juncea L. (Indian mustard), Medicago sativa L. (Alfalfa), Helianthus annuus L. (Sunflower) and Aloe barbadensis (56, 57). Furthermore, our present research team has also synthesized many nanomaterials using eco-friendly processes (58–65).

Recently, new and more eco-friendly reducing agents for GO have been reported for the substitution of hydrazine, such as ascorbic acid (vitamin C) (66–68), alkyl amines (69–72), reducing sugars (43, 73), wild carrot root (74), metal nanoparticles (75, 76) and powders (77, 78), phytoextracts (79), green tea (80), baker’s yeast (81), supercritical alcohols (82) and amino acids (67, 83).

Beyond the role of plant extracts in green chemistry processes, it is noted that the health and cosmetic industries have long relied on natural plant extracts, particularly for their beneficial antioxidant effects, which serve to promote health and general well-being. One of the well-known plants that fall in this category is Artemisia, a large and diverse genus of hardy herbaceous plants and shrubs, numbering between 200 and 400 species. Plants of the Artemisia genus, further belong to the daisy family Asteraceae, which are widely known for the powerful chemical constituents that make-up their essential oils. Artemisia herba-alba Asso (AHAA) (white wormwood (English); armoise blanche (French); shieh (Arabic)) is a perennial shrub in this genus that grows commonly on the dry steppes of the Mediterranean regions in northern Africa (Saharan Maghreb), western Asia (Arabian Peninsula) and southwestern Europe (84). Typically, AHAA grows to a height of about 30–40 cm, and can be identified by a characteristic smell of thymol, and is very leafy with tomentose young branches (85). In herbal medicine, AHAA is used as an antiseptic and also as an antispasmodic agent. The therapeutic uses of AHAA are likely a consequence of the diverse chemical composition of the essential oils found within the plant that are dominated by molecules containing hydroxyl groups (86).

Given that polyphenols from some plants such as green tea were successfully used to reduce GO to graphene nanosheets (87–88), the current study was initiated to propose a green and facile method for the chemical reduction of GO using AHAA as the reducing and capping agent. In general, to reduce 0.5 g of few layered graphene oxide (FLGO) dispersed in aqueous solution we have used 1 g of AHAA leaves. It is important to mention that the price of these leaves is US $/Kg.

The reduction of GO was successfully performed with a simple procedure. To understand the mechanism of
the reduction process and the transformation of GO to rGO, the main physical properties of the prepared materials were characterized by various characterization techniques, including, UV–VIS, Raman, TEM, XPS, PL and I–V systems.

Materials and methods

AHAA leaves were carefully taken from selected shrubs located in East Morocco. Green tea was purchased from Sultan Ltd., Morocco. Hibiscus subdariffa (SD) was purchased from ElNasr LTD., Sudan. The sample of wholegrain sorghum (Sorghum bicolor L. Moench (FM)) was kindly supplied by Prof. B. Ndimba, of the Agricultural Research Council, Stellenbosch, South Africa. Tartaric acid and bismuth sulfate were purchased from PnP, South Africa, while the rest of chemicals were purchased from Sigma-Aldrich.

The absorption spectra were recorded at room temperature using a Cary UV–visible-near-infrared spectrometer. Raman scattering spectra were recorded using an excitation wavelength of 514 nm. TEM images were captured using a FEI/Tecnai F20 Cryo TWIN FEGTEM, while the elemental composition was investigated using Energy Dispersive X-ray (EDX). XPS measurements were obtained using AXIS SUPRA XPS SYSTEM, and photoluminescence measurements were realized using Fluorolog-3. Finally, conductivity was measured with a Picoammeter/Voltage Source-Keithley Model 6487 system.

Synthesis of few-layered graphene oxide (FLGO)

FLGO was synthesized using a modified Hummers method which involved the exfoliation of graphite in the presence of strong acids and oxidants (89). The oxidative treatment involved the use of potassium permanganate (KMnO4) in concentrated sulfuric acid (H2SO4) (30). Natural flake graphite powder (2.0 g) was weighed and placed in a round bottom flask. 46 mL of concentrated sulfuric acid was added and the mixture was cooled in an ice bath. 6.0 g of potassium permanganate (KMnO4) was gradually added over a period of 30 min with continuous stirring. The mixture was stirred at 35°C for 2 h, then 92 mL of distilled water was slowly added to the mixture, and the temperature was maintained below 100°C for 15 min. Finally, 280 mL of 30% hydrogen peroxide (H2O2) solution was added to the mixture. The product was finally filtered with 500 mL of 10% hydrochloric acid (HCl) solution to remove metal ions and then thoroughly washed with distilled water. A dark brown solution of FLGO was obtained.

Preparation of the AHAA and other natural plant extracts

High-quality dried AHAA leafs were weighed and cleaned extensively with deionized cold H2O (15°C). Following a drying phase under sunny conditions at ambient temperature (26°C), the samples were ground to a fine powder. An estimated 4 g of AHAA leaf powder was then mixed with 100 mL of deionized H2O at 35°C for 2 h. The duration of 2 h was considered to ensure the maximum extraction of the bioactive compounds from the ground AHAA leaves. The brown-yellowish solution was filtered twice to eliminate residual solids (if any). The natural extract has a pH of 4.6 at room temperature. Water-soluble extracts of Hibiscus subdariffa leaves and Sorghum bicolor (powdered wholegrains) were prepared by mixing these samples with normal deionized water for 24 h. A green tea extract was also prepared by steeping green tea leaves in deionized water for 30 min at 50°C. Hydrazine hydrate, Tartaric acid and bismuth sulfate solutions were also prepared and used in a dropwise manner.

The reduction of GO

The resultant extracts/solutions were separately added in a dropwise manner to a FLGO solution, which was prepared using a modified Hummer’s method, and the reaction was left to run for 24 h. To separate AHAA from the obtained sheets, the solution was centrifuged and subsequently washed with deionized water several times.

A comparison was then made of the potency of each of the reducing agents or extracts in terms of their capacity to reduce the solution of FLGO to FLrGO, using UV–VIS absorption.

Results and discussion

UV–VIS spectroscopy

UV–VIS absorbance spectra are displayed in Figure 1. The non-reduced form of GO is characterized by two principal absorption peaks: a peak at 270 nm attributed to \( \pi \rightarrow \pi^* \) transitions of C–C and a band of \( n \rightarrow \pi^* \) transition of C–O band at 300 nm. Another characteristic is the brownish yellow color, which changes to a distinctive black color, when it has been reduced. This color change therefore provides a clear visual demonstration of the occurrence of reduction in our experiments. Furthermore, the transformation of FLGO in our samples was confirmed by the disappearance of the C–C band, cantered at ∼231 nm; and its displacement to 273 nm, which is likely indicative of the decrease in the
Figure 1. UV-VIS absorbance of graphene oxide reduced with: Green tea ‘GT’, *Hibiscus subdariffa* ‘SD’, *Sorghum bicolor* ‘FM’, *Artemisia herba-alba Asso* ‘AHAA’, hydrazine hydrate ‘H–H’, Tartaric acid ‘T–A’, and bismuth sulfite ‘BS’.

Figure 2. Raman spectra of FLGO and AHAA FLrGO.
concentration of carboxyl groups. The underlying mechanism responsible for these observed changes is likely attributable to a revived state of electronic conjugation within the reduced graphene sheets, due to the reduction process.

Compared to the other natural extracts (i.e. Green tea ‘GT’, Hibiscus subdariffla ‘SD’, Sorghum bicolor ‘FM’), Artemisia herba-alba Asso ‘AHAA’ was more effective as a reducing agent, as demonstrated by the shift of the C−C band from its original position to ~270 nm as well as the disappearance of the C−O band. In comparison to the chemical-reducing agents (hydrazine hydrate ‘H−H’, Tartaric acid ‘T−A’, and bismuth sulfate ‘BS’), AHAA displayed similar reducing capabilities, thus confirming its status as a powerful natural source of antioxidants.

**Raman spectroscopy**

Raman spectroscopy was used to monitor structural changes during the reduction processes. As shown in Figure 2, the oxygen-containing functional groups attached to the basal plane of graphene during oxidation of graphite form GO-induced structural defects and significantly intensified the D band in the Raman spectrum of GO. Moreover, the D peak of GO which is located at 1349 cm\(^{-1}\) and at 1351 cm\(^{-1}\) for rGO streams from a defect-induced breathing mode of sp\(^2\) rings (90). The G peak at around 1603 cm\(^{-1}\) for GO and rGO is due to the first-order scattering of the E\(_{2g}\) phonon of sp\(^2\) C atoms (90). On the other hand, the changes in relative intensity of the main D and G peaks can clearly indicate the reduction process of GO to rGO (91). The intensity of the D band is related to the size of the inplane sp\(^2\) domains (92). It is clearly shown in Figure 2 that the intensity of the D peak is higher than that of G peak in rGO indicating formation of more sp\(^2\) domains (93). The relative intensity ratio of both peaks D and G (I\(_D\)/I\(_G\)) is an estimation of the disorder level in graphene and is inversely proportional to the average size of the sp\(^2\) clusters (91, 94). As it is seen in Figure 2, the I\(_D\)/I\(_G\) intensity ratio for FLrGO is higher than that for FLGO (I\(_D\)/I\(_G\)(FLrGO) = 1.049 and I\(_D\)/I\(_G\)(FLGO) = 0.98). This confirmed that the number of sp\(^2\) cluster was increased and suggested that new graphitic domains are formed (90) showing good reduction efficiency by using our new reduction technique.

The presence of the 2D band, which is referred as the overtone of the D band, in both Raman spectra of FLGO and FLrGO are composed of three principal peaks. The presence of these peaks serves to confirm the presence of layered graphene. The 2D FLGO band centered around 2707 cm\(^{-1}\) after graphite oxidation and exfoliation indicates that few layers of GO have been formed, and further that these layers have all been oxidized. In the case of FLrGO, this band was slightly blue-shifted to 2668 cm\(^{-1}\). Raman results confirmed the reduction of FLGO to FLrGO.

**TEM microscopy**

The HRTEM image (Figure 3) revealed the presence of wide and flat graphene sheets that did not feature any folds along their length. Straight and nearly atomically smooth edges were discerned without signs of any roughness or parallel lines characteristic of graphite sheets.

In our FLrGO sample it was rare to observe parallel lines, which are indicative of a double-layered or multilayered structure. The HRTEM images also serve to confirm that the graphene sheets are fully exfoliated and thus the final product is composed of few layers. The mean average of the inter-fringe distance was determined from 20 sites of the HRTEM image and was found to be 0.35 nm.

The HRTEM images also reveal the typical large flake structure of graphene sheets. The transparency of these flakes confirms the successful exfoliation and reduction of the graphene sheets. Furthermore, HRTEM has also revealed that each flake is composed of a few individual graphene sheets.

**EDX analysis**

EDX analysis was done on different areas of the graphene sheets. From the EDX spectrum (Figure 4) oxygen atoms and other chemical residues were not found in high quantities, whereas the percentage of carbon atoms was higher than 90%, thus confirming the quality and high purity of the obtained FLrGO. The presence of other elements can be observed from the remaining AHAA extract which played the role of a capping agent and inhibits nanosheet aggregation.

| Table 1. XPS Cs1 Binding energies of FLGO, FLrGO and annealed FLrGO. |
|-----------------|-----------------|-----------------|-----------------|
| Binding energy origins | FLGO | FLrGO | ANN-FLrGO |
| C−C: 284.5 | 284.5 | 284.5 | 284.5 |
| C−C: 285 | 285.25 | 285.1 | 285.1 |
| C−O:285, C−O:285.6 | 285.8 | 285.8 |
| CN:286.4, C−O−C:286.5 | 286.5 | 286.5 | 286.5 |
| C = O:287.4 | 287.5 | 287.5 | 287.3 |
| Carboxy:C288.3 | 288.66 | 288.5 | 288.2 |
| CDOH, COD: 289.1 | 289.75 | 289.5 | 289.0 |
| Pi−Pi* satellite & shake-up features | 290.6 | 290.1 |
| Plasmon loss feature | 291.13 | | |


XPS spectroscopy

To analyze the structure of the studied materials and the effect of annealing, X-ray photoelectron spectroscopy (XPS) was employed. The study was based on the curve-fitted C1s of GO, FLrGO and the annealed FLrGO film. The annealing was for 10 h at 200°C (Figure 5).

Immediate observations from C1s high-resolution scan showed a clear shift in the XPS bands toward lower binding energy.

The deconvolution of the obtained spectra showed many broad components to account for the overlapping C1s features. It informs the probable origin of the peaks with their binding energies, as described in Table 1. In all samples, the presence of the sp² graphite component at 284.5 eV and the C = C at 285.1–285.25 eV is easily observable. Moreover, most of components listed in Table 1 are assigned to the different functional groups (e.g. carbonyl, epoxy and hydroxyl groups) present in the surface of graphene layers.

Figure 3. HRTEM of AHAA FLrGO.

Figure 4. EDX graph of AHAA FLrGO.
The deconvolution of C1s XPS spectra of FLGO indicates a weak C–C band and a remarkable degree of oxidation due to the presence of the mentioned functional groups.

From the obtained intensities, it can be observed that the $I_{C_C}/I_{O}$ ratio of FLrGO is much higher than $I_{C_C}/I_{O}$ ratio of FLGO; this ratio became higher in the case of annealed FLrGO. In addition, the atomic ratio of carbon to oxygen in FLGO, FLrGO and Ann-FLrGO was found to be 2.4, 2.8 and 3.1, respectively. These results suggest significant removal of oxygen functional groups but the reduction of FLGO using AHAA is not complete which can be explained by the remaining of some functional groups, as was confirmed by XPS.

**Fluorescence**

To understand the effect of reduction in the photoluminescence (PL) of GO, the origins of emissions should be discussed. Commonly, GO/rGO thin films emit near-UV blue light, red and near-infrared emissions (95, 96, 97) and green PL emissions (98). The green PL emission is originally from thoroughly exfoliated suspensions due to the presence of isolated sp² clusters within the carbon–oxygen sp³ matrix leading to the localization of e–h pairs, facilitating a radiative recombination of small cluster (95). Clusters of several conjugated repeating units yield band gaps consistent with blue emission. Red emission, however, is generated from poorly dispersed suspensions containing multi-layered and aggregated flakes (96, 97).

The corresponding FLGO PL spectra (Figure 6) excited at different wavelengths show a broadband emission that covers the visible range and peaks at around 590 nm. It is clearly shown that after reduction the PL intensity was drastically decreased. The PL characteristics of graphene derivatives and its dependence on the reduction of GO indicates that it originates from the recombination of electron–hole (e–h) pairs, localized within small sp² carbon clusters embedded within a sp³ matrix and agglomeration phenomena (95).

Significantly, the results obtained show that the modulation of emissions can be possible by controlling the dose of the reducing agent which is AHAA in the case of this study.

**I-V characteristics**

GO is often described as an electrical insulator, due to the disruption of its sp² bonding networks. In order to recover the honeycomb hexagonal lattice, and with it the associated electrical conductivity, it is necessary to remove all the oxygen-containing groups (i.e. to reduce FLGO to conductive reduced graphene oxide (FLrGO)). In our study, the I-V characteristics were measured on three different sites of each sample. The obtained
results show that FLGO was efficiently reduced by AHAA and the sp² carbon networks restored, leading to higher conductivity and mobility of FLrGO (Figure 7).

The higher electrical conductivity of FLrGO was obtained after annealing because there was a small amount of carbonyl pairs that remains in GO after the reduction, which can participate in the coupling reaction suggesting the recovery of p-conjugated system in the graphene sheets. However, more functional groups are removed after temperature annealing, leading to the graphene networks becoming more continuous. Furthermore, the decrease in the layer-to-layer distance and improvement in stacking order has likely contributed to layer-to-layer hopping, which ultimately enhances electrical conductivity in the obtained FLrGO. In addition, the quantum nonlinear behavior and fluctuations were observed in our prepared films. Similar results were obtained by Jang et al. (99) from fibers of rGO nanoribbons. This can be caused by the large scattering of the effective individual sheet resistance which is likely due to the combined effect of fluctuations in the degree of reduction of individual graphene sheets, variations in the sheet thickness (number of layers), and inaccuracies caused by non-negligible and varying contact resistance at the metal contact pads which cannot be excluded in a 2-probe measurement (100).

Thus, it may be proposed that the synthesized graphene presented in our method, may be used to improve the electrical conductivity of its potential composites, leading to a more flexible and toxic free graphene-based transparent conductive film (TCF). Moreover, the graphene-based TCFs are far more flexible than traditional indium-doped tin oxide films, and cost effective, thus leading to interesting future prospects for TCFs in bendable electronic and optoelectronic devices.

Conclusion

In this work, and to the best of our knowledge, we have demonstrated that our method of FLrGO synthesis using AHAA, which makes no use of substrates, no toxic/hazardous agents or energy input, can be an important means
of facilitating the production of high-quality and high-purity graphene sheets on a commercial scale, to improve cost efficiencies and high throughput processing. To investigate the quality of the obtained sheets, their physical properties including surface/interface and optical and electrical properties were studied using UV–VIS, Raman, XPS spectroscopies and TEM microscopy which confirmed the reduction and the conversion of GO to few-layered rGO.

This approach also opens the door to many well-established green eco-friendly techniques that could be used to cast graphene sheets into various structures or to integrate graphene with other materials to form nanocomposites.

Finally, this work also demonstrates how the properties of the graphene sheets can be controlled for better efficiency of optoelectronic applications.

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