

Vitamin C is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions

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Abstract

The preparation of solution-processable graphene from graphite oxide typically involves a hydrazine reduction step, but the use of such a reagent in the large-scale implementation of this approach is not desirable due to its high toxicity. Here, we compare the deoxygenation efficiency of graphene oxide suspensions by different reductants (sodium borohydride, pyrogallol and vitamin C, in addition to hydrazine), as well as by heating the suspensions under alkaline conditions. In almost all cases, the degree of reduction attainable and the subsequent restoration of relevant properties (e.g., electrical conductivity) lag significantly behind those achieved with hydrazine. Only vitamin C is found to yield highly reduced suspensions in a way comparable to those provided by hydrazine. Stable suspensions of vitamin C-reduced graphene oxide can be prepared not only in water, but also in common organic solvents, such as *N,N*-dimethylformamide (DMF) or *N*-methyl-2-pyrrolidone (NMP). These results open the perspective of replacing hydrazine in the reduction of graphene oxide suspensions by an innocuous and safe reductant of similar efficacy, thus facilitating the use of graphene-based materials for large-scale applications.

Keywords: Graphite oxide; Solution-processable graphene; Deoxygenation; Reductant

1. Introduction

Owing to its remarkable physical properties and to the perspective of important applications, graphene has emerged in recent years as the subject of intense research efforts.¹⁻³ Although such efforts were originally driven and are still largely motivated by the prospect of graphene as a key component in future nanoelectronic devices,^{1,2,4} other potential applications of this two-dimensional material are also being actively pursued, including its use in composite materials,^{5,6} gas sensors,^{7,8} solar cells,⁹ supercapacitors¹⁰ or drug delivery.¹¹

Central to the success of graphene in practical uses is the availability of production methods that can deliver large quantities of the material at low cost. In this regard, the approach that first led to the isolation of graphene (i.e. micromechanical cleavage of graphite)⁴ is a low-yield, low-throughput process and therefore not likely to be industrially scalable, which has made the search for alternative preparation techniques a priority. At present, there are three main routes towards graphene with potential for mass production: 1) processing of graphite and graphite derivatives (mostly graphite oxide) in the liquid phase by chemical methods to afford colloidal suspensions,^{12,13} 2) epitaxial growth via high temperature treatment of silicon carbide,^{14,15} and 3) chemical vapor deposition (CVD) of hydrocarbons on transition metal substrates such as nickel or copper.^{16,17} Even though the epitaxial growth and CVD techniques are particularly promising in terms of providing the large-area, high quality graphene wafers required for applications in electronics,¹⁸ the colloidal route, and especially the one based on graphite oxide, is currently considered the most attractive option for many other prospective uses of graphene. The main advantages of this route are its cost-effectiveness, massive scalability, versatility for chemical functionalization and easy processability into paper-like materials, coatings, composites, etc.^{12,13}

The production of colloidal suspensions of graphene from graphite oxide typically involves exfoliation of the latter in a suitable solvent (usually water, but also some polar organic solvents),¹⁹ followed by chemical reduction of the dispersed single-layer sheets (graphene oxide sheets) with hydrazine.^{12,13,20,21} When the reduction is carried out under controlled conditions, the resulting deoxygenated graphene oxide sheets form stable suspensions without the need of surfactants or any other stabilizers, which is an added advantage.^{12,20,21} Unfortunately, hydrazine is a highly toxic and potentially explosive chemical,²² and therefore its use should be avoided in the large-scale implementation of this approach. In the search for alternatives to hydrazine, two relevant factors should be taken into account in addition to environmental and safety issues. First, the process should be at least as effective as hydrazine in the deoxygenation of graphene oxide. Second, for the sake of further processability, the reduced material should remain dispersed as single-layer sheets in aqueous and organic media, i.e. it should not precipitate after reduction.

We have carried out an exhaustive comparison of the performance of several different reducing agents towards deoxygenation of graphene oxide suspensions, which has not been previously reported in the literature. Most significantly, we find that the efficiency of hydrazine in the reduction of graphene oxide is only matched by vitamin C (ascorbic acid), a natural antioxidant essential for many metabolic functions in living organisms and widely employed as a food additive.²³ Reduction with vitamin C can be made not only in water, but also in some common organic solvents, such as *N,N*-dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP). These findings, together with the non-toxicity of this natural product, suggest that vitamin C represents an ideal substitute for hydrazine in the large-scale production of solution-processable graphene.

2. Experimental

Graphite oxide was prepared in the form of both a thick slurry and a fine dry powder as previously reported,^{19,24} starting from natural graphite powder (Fluka 50870) and using the Hummers method.²⁵ To prepare suspensions of graphene oxide sheets in a given solvent (usually water, but also DMF and NMP), the graphite oxide slurry or dry powder was bath-sonicated (JP Selecta Ultrasons system, 40 kHz) in the solvent for 1 h and then centrifuged (Eppendorf 5424 microcentrifuge) at 10000g for 10 min to remove unexfoliated material, the supernatant being the final graphene oxide dispersion. The concentration of the dispersions was determined through UV-vis absorption spectroscopy using a double-beam Helios α spectrophotometer, from Thermo Spectronic, and following a procedure described elsewhere.²⁴

To study the performance of different reducing agents towards the deoxygenation of graphene oxide, dispersions of the latter at a concentration of 0.1 mg mL^{-1} were reacted at 95 °C with the following reductants: hydrazine monohydrate, sodium borohydride, pyrogallol and vitamin C. When the solvent used was water, the pH of the dispersions was adjusted to ~9-10 with 25% ammonia solution (~2 μL per mL of dispersion) to promote the colloidal stability of the graphene oxide sheets through electrostatic repulsion. For comparison purposes, deoxygenation of the sheets was also carried out in the absence of any reducing agent simply by heating the dispersions at 95 °C under basic conditions,²⁶ which were attained via the addition of either ammonia (25% solution) or potassium hydroxide. In all cases, the reactions were accomplished at different molar concentrations of reducing agent or base in the dispersions, so as to assess its effect on the reduction level of graphene oxide and to establish the optimal amounts required. The progress of reaction as a function of time was monitored through UV-vis absorption spectroscopy. To this end, 0.5 mL aliquots of dispersion were taken

from the reaction vial every 15 min and their UV-vis spectra recorded. It is well known that the position of the absorption peak of graphene oxide dispersions gradually redshifts from a value of 231 nm as reduction proceeds,¹² so such position was routinely used as a quick, convenient probe of the reduction degree achieved with the reductants or bases. Further characterization of the reduced products with different techniques confirmed a generally good correlation between the extent of deoxygenation of the graphene oxide sheets and the absorption peak position.

The reduced dispersions were processed into free-standing, paper-like films via filtration through Anodisc membranes (47 mm in diameter and 0.2 μm pore size, from Whatman) and characterized by thermogravimetric analysis (TGA), attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and also by measurement of their electrical conductivity. TGA was accomplished by means of an SDT Q600 thermobalance (TA Instruments) under Ar gas flow (100 mL min⁻¹) at a heating rate of 10 °C min⁻¹, using Pt crucibles. ATR-FTIR spectra were recorded in a Nicolet 8700 spectrometer (Thermo Scientific) using diamond as ATR crystal. For XPS measurements, a SPECS apparatus working under 10⁻⁷ Pa with a monochromatic Al K α X-ray source (100 W) was employed. The surface charging effect observed for the nonconductive, unreduced graphene oxide sample was corrected by the use of an electron flood gun operating at 0.4 eV and 0.10 mA.¹⁹ Surface composition (atomic %) of the samples was determined from their survey spectra by considering the integrated intensities of the main XPS peaks of the elements that were found. The electrical conductivity of the graphene films was determined through measurement of their resistance with a Fluke 45 digital multimeter.²⁷ To this end, the films were cut into rectangular strips about 6×25 mm² large and their thickness was estimated via scanning electron microscopy. To evaluate the dispersion state of the

sheets in the suspensions after reaction with the different reductants or bases, atomic force microscopy (AFM) was carried out. Samples for AFM were prepared by drop-casting the suspensions onto preheated ($\sim 50\text{-}60\text{ }^{\circ}\text{C}$) freshly cleaved highly oriented pyrolytic graphite (HOPG) substrates, which were subsequently rinsed with Milli-Q water. Imaging was accomplished under ambient conditions ($\sim 22\text{-}24\text{ }^{\circ}\text{C}$, RH $\sim 40\%$) with a Nanoscope IIIa Multimode apparatus (Veeco Instruments) in the tapping mode of operation and using rectangular Si cantilevers with spring constant of $\sim 40\text{ N m}^{-1}$ and resonance frequency between 250 and 300 kHz.

3. Results and discussion

Table 1 summarizes the results of the reaction of 0.1 mg mL^{-1} aqueous graphene oxide dispersions with different molar concentrations of bases (ammonia and potassium hydroxide) and reductants (sodium borohydride, pyrogallol, vitamin C and hydrazine monohydrate). The progress of reaction was monitored as a function of time by measuring the position of the UV-vis absorption peak of the dispersions. Such peak is located at 231 nm for the unreduced dispersion, but gradually red-shifts as deoxygenation takes place and electronic conjugation is restored.¹² For a given reductant or base at a given molar concentration, the reaction was considered to be completed when the observed red-shifting became arrested. The final position of the absorption peak upon reaction completion and the time required to reach that position are listed in Table 1, together with the acronyms that will be used to refer to the corresponding samples. The performance of hydrazine monohydrate was used as a reference to establish the suitability of the other reducing agents and bases towards deoxygenation of the graphene oxide dispersions. Indeed, the reported optimal ratio for reduction with such reagent (2.0 mM for 0.1 mg mL^{-1} dispersions)¹² was taken as a

starting point in the case of the other three reductants. Reduction with the two bases was observed to be much less effective, so higher molar concentrations were typically employed for ammonia and potassium hydroxide.

To a first approximation, the overall efficiency of a given reductant or base was estimated from the maximum red-shift that can be attained when its molar concentration is increased (Table 1). For example, in the case of pyrogallol the absorption peak can be red-shifted up to a value of 266 nm regardless of the amount of reagent used above a certain level (samples P2-P4). By contrast, a value of 268 nm is reached with hydrazine monohydrate, suggesting that this reductant is somewhat more efficient than pyrogallol. Based on such assessment, the performance of the reductants and bases can be classified into three groups. The first includes the two bases (ammonia and potassium hydroxide), which would provide a relatively limited reduction degree (absorption peaks located slightly below 260 nm). The second group is formed by sodium borohydride and pyrogallol, with absorption peaks at 263-266 nm. The third group is constituted by the most efficient reductants (hydrazine monohydrate and vitamin C), with absorbance peaking at 268 nm upon reaction completion. We note that all the reduced suspensions described in Table 1 displayed long-term stability, i.e. they were stable for at least several weeks, except sample K4, which precipitated during reduction, and samples B4 and B5, which precipitated within a few days (B4) and several minutes (B5) after reduction.

TGA, ATR-FTIR spectroscopy and XPS analysis of the reduced suspensions processed into paper-like films provided further evidence of the basic differences in the extent of reduction that can be achieved with the reductants and bases. Fig. 1 shows the thermogravimetric (TG) and differential thermogravimetric (DTG) plots of unreduced graphene oxide (a), as well as those of several characteristic reduced samples: N1 (b),

B3 (c), P3 (d), V4 (e) and H4 (f). Consistent with previous reports,^{19,28,29} the main mass loss for unreduced graphene oxide (~30%, Fig. 1a) takes place around 200 °C, which is attributed to the decomposition of the most labile oxygen functionalities present in the material. The slow, steady mass loss (~20%) observed in the whole temperature range above 300 °C can be ascribed to desorption of more stable oxygen functional groups. Removal of adsorbed water accounts for the mass loss (~15%) measured below 100 °C. Hydrazine appears to be rather efficient in removing the labile functionalities, as the abrupt mass loss at about 200 °C characteristic of unreduced graphene oxide is no longer present after reaction with this reductant (e.g. sample H4, Fig. 1f). By contrast, such functionalities can only be partially eliminated when reduction is carried out just by heating the dispersions under alkaline conditions. This is exemplified in Fig. 1b for sample N1, which exhibits a mass loss of ~15% around 200 °C. Reduction with sodium borohydride and pyrogallol lowers the mass loss at this temperature (e.g., ~5-10% for samples B3 and P3 in Fig. 1c and d, respectively), but the rate of mass loss is still significantly larger than that measured at higher temperatures (see DTG plots in Fig. 1c and d). As noticed in Fig. 1e, only vitamin C matches the efficiency of hydrazine monohydrate in the elimination of the labile functional groups. However, in agreement with previous reports,²⁸ there is still a significant mass loss for all the reduced samples in the temperature range above 300 °C (~10-15%), suggesting that even the apparently strongest reductants (hydrazine and vitamin C) cannot remove the most stable functionalities.²⁸

Representative ATR-FTIR spectra of the different reduced samples are shown in Fig. 2. For unreduced graphene oxide (Fig. 2a), the following features are observed: a broad, intense band at 3000-3500 cm⁻¹ (O-H stretching vibrations) and narrower bands at about 1720 cm⁻¹ (C=O stretching vibrations from carbonyl and carboxyl groups),

1620 cm^{-1} (C=C stretching, skeletal vibrations from unoxidized graphitic domains), 1400 cm^{-1} (O-H bending vibrations from hydroxyl groups), 1300-1350 cm^{-1} (C-OH stretching vibrations), 1220 cm^{-1} (breathing vibrations from epoxy groups) and 980 cm^{-1} (attributed to vibrations from epoxy, ether or peroxide groups).^{20,30-34} For all the reduced materials (Fig. 2b-f), the intensities of the bands associated to oxygen functional groups strongly decrease in relation to those of unreduced graphene oxide. However, the decrease is most significant when reduction is carried out with hydrazine and vitamin C (Fig. 2e and f) and relatively limited when performed only under alkaline conditions without any reducing agent (e.g. Fig. 2b), reduction with sodium borohydride and pyrogallol lying somewhere in between. In particular, for sample N1 (Fig. 2b) the intensity of the bands assigned to epoxy groups (~ 1220 and 980 cm^{-1}) is not very different to that observed for unreduced graphene oxide (Fig. 2a). By contrast, the decrease appears to be much more significant for bands related to hydroxyl groups ($3000\text{-}3500$ and $\sim 1350 \text{ cm}^{-1}$), which suggests that reduction under alkaline conditions without reductant removes preferentially hydroxyl groups over epoxides. In the case of reduction with hydrazine and vitamin C, we observe a much more exhaustive decrease of both the hydroxyl and epoxy regions of the spectra. Nevertheless, the elimination of these bands is not complete, as becomes evident when comparing the spectra of samples V4 and H4 (Fig. 2e and f, respectively) with that of pristine graphite (Fig. 2g). In particular, the persistence of the band at about $1300\text{-}1350 \text{ cm}^{-1}$ would seem to imply that a certain fraction of hydroxyl functionalities remain even in the most reduced dispersions.

Fig. 3 shows the high resolution C1s X-ray photoelectron spectra of unreduced graphene oxide (a), several representative reduced samples (b-f) and the starting pristine graphite (g). As previously reported,¹⁹ the C1s band of the unreduced material is

characterized by the presence of two maxima separated by ~2 eV. Peak fitting of this band yields three components, located at 284.6 (fwhm = 1.4 eV), 286.6 (fwhm = 1.2 eV) and 287.9 eV (fwhm = 2.0 eV), as illustrated in Fig. 3a. The component at 284.6 eV is assigned to carbons in unoxidized, aromatic sp^2 structures, whereas the one at 286.6 eV can be attributed to carbons in hydroxyl and epoxy groups (C-O bonds) and also possibly to C-C bonds in defected structures. The defect C-C component would be located at ~285.5 eV, but for unreduced graphene oxide (Fig. 3a) it was not possible to clearly discriminate it from the C-O component at 286.6 eV. The 287.9 eV component can be ascribed to carbons in C=O structures, i.e. carbonyl groups.

Following all reductions, a narrowing of the graphitic component at 284.6 eV can be noticed (fwhm values of 0.8-1.1 eV, compared to 1.4 eV for unreduced graphene oxide), which is indicative of the development of a more homogenous chemical environment and/or ordered structure. However, the most significant change upon reduction is the decrease in the relative contribution of the higher binding energy components of the C1s envelope, reflecting a smaller proportion of oxidized carbons in the samples. In agreement with the TGA and UV-vis and ATR-FTIR spectroscopy results, the relative decline of the higher binding energy components is much larger for dispersions reduced with vitamin C and hydrazine (Fig. 3e and f, respectively), intermediate for dispersions reduced with sodium borohydride and pyrogallol (Fig. 3c and d, respectively) and less apparent when deoxygenation is carried out just by heating under alkaline conditions without reductant, i.e. in the case of ammonia (Fig. 3b) and potassium hydroxide (spectra not shown, but very similar to that of Fig. 3b). For those samples that could be sufficiently reduced, i.e. for samples reacted with pyrogallol, vitamin C and hydrazine (Fig. 3d, e and f, respectively), peak fitting of the C1s band allowed discrimination of the defect C-C component (285.5 eV) from the C-O component (286.6 eV). By contrast,

such discrimination was not possible with the comparatively limited reduction provided by ammonia, potassium hydroxide and sodium borohydride (e.g., Fig. 3b and c), yielding the three same components as those obtained for unreduced graphene oxide (Fig. 3a). For the highly reduced samples (vitamin C and hydrazine), the shape of the C1s envelope does not change appreciably with the amount of reductant used once the position of the UV-vis absorption peak reaches the value of 268 nm (Table 1), confirming that reduction was completed. However, as can be noticed by comparing the spectra of these samples (Fig. 3e and f) with that of the starting pristine graphite (Fig. 3g), the highly reduced materials still contain a certain amount of oxygen functionalities (higher binding energy components) that apparently cannot be removed under the used reaction conditions. Such result is consistent with that obtained by TGA and ATR-FTIR spectroscopy, and also with previous reports on the reduction of graphene oxide with hydrazine,¹² supporting the idea that chemical reduction under the present conditions has an intrinsic limit, which is not well understood at present. The presence of residual oxygen even on the most reduced materials is also apparent from the O/C atomic ratios derived from the XPS data: 0.43 for unreduced graphene oxide, ~0.08 for samples reduced with vitamin C and hydrazine, ~0.18 for reduction with pyrogallol, and ~0.20-0.30 for reduction with ammonia, potassium hydroxide and sodium borohydride.

The electrical conductivity is considered a highly sensitive indicator of the extent to which electronic conjugation is restored after deoxygenation of graphene oxide. Electrical conductivity was measured on free-standing paper-like films prepared by vacuum filtration and air-drying of the different reduced suspensions. The data obtained for several representative samples are presented in Table 2. Consistent with the results discussed above, restoration of the π -conjugated structure is most effective using hydrazine and vitamin C (conductivity values between 2690 and 9960 S m⁻¹),

intermediate for reduction with pyrogallol (488 S m^{-1}), and relatively inefficient with ammonia, potassium hydroxide and sodium borohydride ($0.02\text{-}1.55 \text{ S m}^{-1}$). Up to now, only hydrazine reduction could provide conductivity values as large as $5000\text{-}10000 \text{ S m}^{-1}$ for as-prepared films of reduced graphene oxide (the conductivity can still be improved to some degree, but only after an additional thermal annealing step of the films).³⁵ The present results show that, as opposed to other reductants, vitamin C can rival hydrazine in this regard.

In addition to constituting a highly efficient reductant for graphene oxide, vitamin C has the advantage of its non-toxicity. In marked contrast to hydrazine, there are virtually no risks to the human health or to the environment associated with the use of this chemical, which is indeed an essential component of a healthy diet in humans.²³ Besides, vitamin C-reduced graphene oxide suspensions can be prepared not only in water, but also in some common organic solvents, such as DMF and NMP, which should facilitate the further manipulation and processing of this material for practical applications. The aqueous and organic suspensions display long-term stability, showing no signs of precipitation at least for several weeks (Fig. 4), and are constituted by individual, single-layer sheets, just as in the case of unreduced and hydrazine-reduced graphene oxide suspensions. As evidenced by the AFM images of Fig. 5 for unreduced and chemically reduced aqueous suspensions, the large majority of the dispersed objects have an apparent thickness of $\sim 1 \text{ nm}$, which are attributed to single-layer sheets.^{5,12,19,24,28} Only less than 5% of the dispersed objects were ascribed to thicker sheets (mainly two and three layers). Similar conclusions were obtained for the organic suspensions. The combination of all the above-mentioned qualities makes vitamin C reduction a strong candidate to replace hydrazine in the large-scale preparation of solution-processable graphene from graphite oxide. Other reductants, such as pyrogallol

or the relatively common sodium borohydride, lag behind vitamin C in reduction efficiency, and also present some toxicity. Heating the graphene oxide suspensions under alkaline conditions would in principle be a very attractive route towards solution-processable graphene,²⁶ but the results of this work suggest that deoxygenation in this case is rather poor, which seriously affects the properties of the reduced products (e.g., electrical conductivity).

During the last year, several green approaches to the deoxygenation of graphene oxide suspensions that circumvent the use of hydrazine have been documented in the literature. These include electrochemical, hydrothermal and microwave-assisted solvothermal reduction methods.³⁶⁻³⁸ The performance of such methods in relation to hydrazine reduction has not been thoroughly investigated, but a general comparison of some relevant features of the resulting graphenes can be made based on the published data. Table S1 in the Supporting Information compares such parameters as UV-vis absorption peak position, O/C atomic ratio, stability in solvents and electrical conductivity of graphenes prepared through different green approaches. Weighing up the available data, vitamin C reduction appears as one of the most attractive routes towards deoxygenation of graphene oxide suspensions.

Finally, as is the case with most of the deoxygenation approaches of graphene oxide documented so far, the reduction mechanism of this material by vitamin C and the reason why complete reduction does not appear to be possible under the employed conditions are currently unclear. Reduction probably involves hydride transfer from the 5-membered ring of the vitamin C molecule to either the epoxy or hydroxyl groups of graphene oxide, yielding water molecules.²³ This point is currently the focus of additional experimental and theoretical modelling work in our group.

4. Conclusions

A comparison of the deoxygenation efficiency of graphene oxide suspensions by different reductants, as well as by simply heating the suspensions under alkaline conditions, has been made, revealing that only vitamin C can compete with the widely employed, but highly toxic hydrazine in terms of reducing ability. Using vitamin C, stable suspensions of highly reduced graphene oxide can be prepared not only in water, but also in some common organic solvents, such as DMF and NMP. These findings are significant, because an innocuous and effective reagent that can replace hydrazine in the large-scale preparation of solution-processable graphene from graphite oxide has now been identified. Another potential advantage of using vitamin C is that such reductant is only composed of carbon, oxygen and hydrogen, thus minimizing the risk of introducing heteroatoms in the reduced products that were not present beforehand.

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Supporting Information Available: Table S1. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Table 1. UV-vis absorption peak position of 0.1 mg mL⁻¹ aqueous graphene oxide suspensions after completion of deoxygenation with different concentrations of reductants (sodium borohydride, pyrogallol, vitamin C, hydrazine) and bases (ammonia, potassium hydroxide), with indication of the sample acronyms used throughout the text.

Reductant or base	Sample acronym	Concentration of reductant or base (mM)	Absorption peak position (nm)	Time to reaction completion (min)
None (unreduced graphene oxide)	GO	-	231 ± 2	-
Ammonia	N1	26	257 ± 2	240
	N2	51	260 ± 2	240
	N3	103	256 ± 2	240
	N4	206	257 ± 2	240
Potassium hydroxide	K1	0.8	252 ± 2	240
	K2	4	258 ± 2	180
	K3	20	258 ± 2	120
	K4	100	251 ± 2	60
Sodium borohydride	B1	0.5	251 ± 2	180
	B2	2	246 ± 2	45
	B3	8	253 ± 2	45
	B4	10	263 ± 2	15
	B5	31	266 ± 2	15
Pyrogallol	P1	0.3	262 ± 2	120
	P2	0.5	266 ± 2	60
	P3	1	266 ± 2	60
	P4	2	266 ± 2	60
Vitamin C	V1	0.3	263 ± 2	240
	V2	0.5	268 ± 2	180
	V3	1	268 ± 2	30
	V4	2	268 ± 2	15
Hydrazine monohydrate	H1	1	268 ± 2	15
	H2	2	268 ± 2	15
	H3	10	268 ± 2	15
	H4	219	268 ± 2	15

Table 2. Electrical conductivities of free-standing paper-like films prepared from different deoxygenated samples. The sample acronyms are defined in Table 1.

Sample acronym	Electrical conductivity (S/m)
N1	0.05
N4	0.32
K1	0.02
K3	0.19
B3	1.55
B4	0.26
P3	488
V2	2690
V4	7700
H1	4160
H4	9960

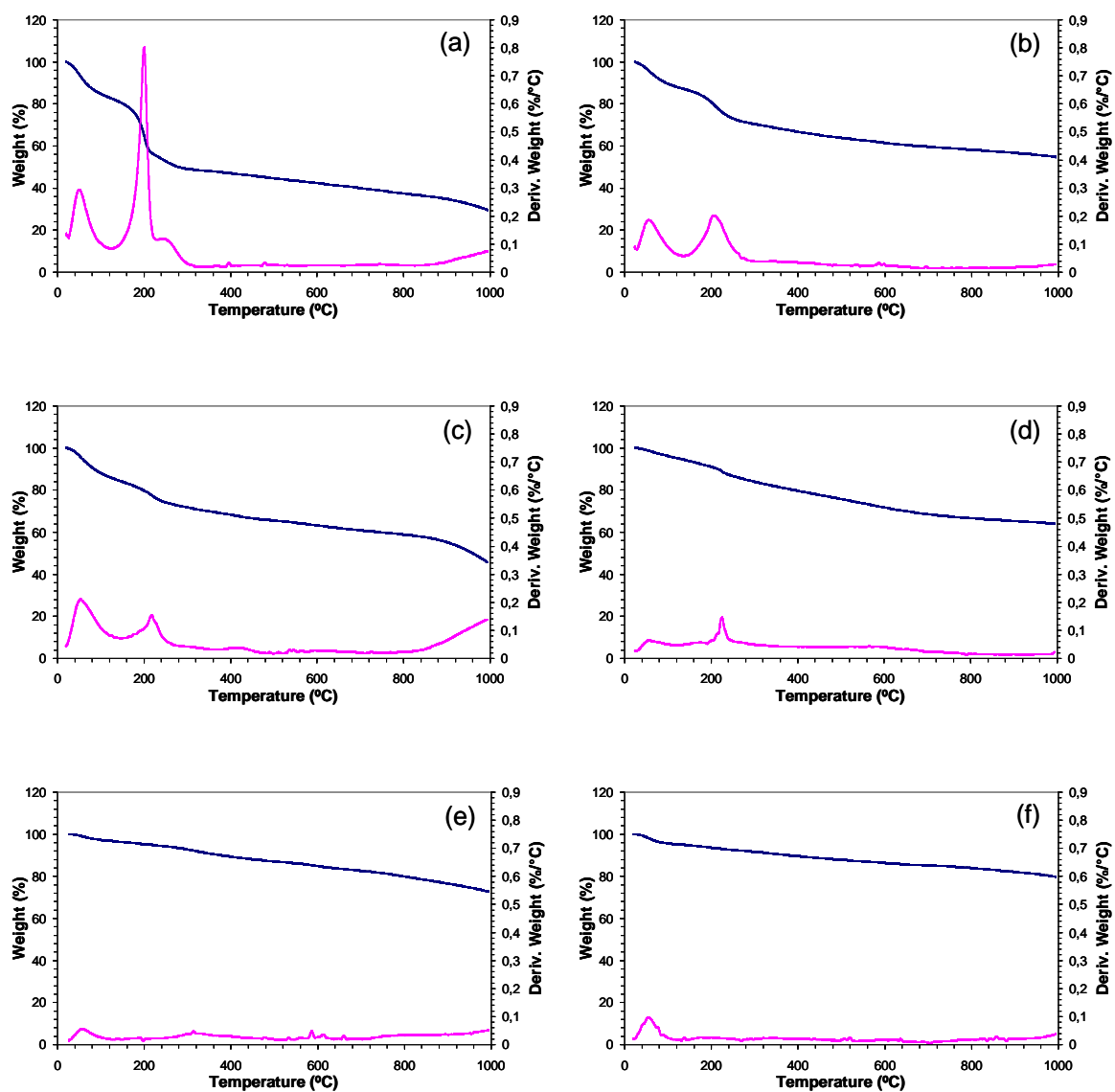


Figure 1. TG (blue) and DTG (red) plots of unreduced graphene oxide (a) and deoxygenated samples N1 (b), B3 (c), P3 (d), V4 (e) and H4 (f). The acronyms of the deoxygenated samples are defined in Table 1.

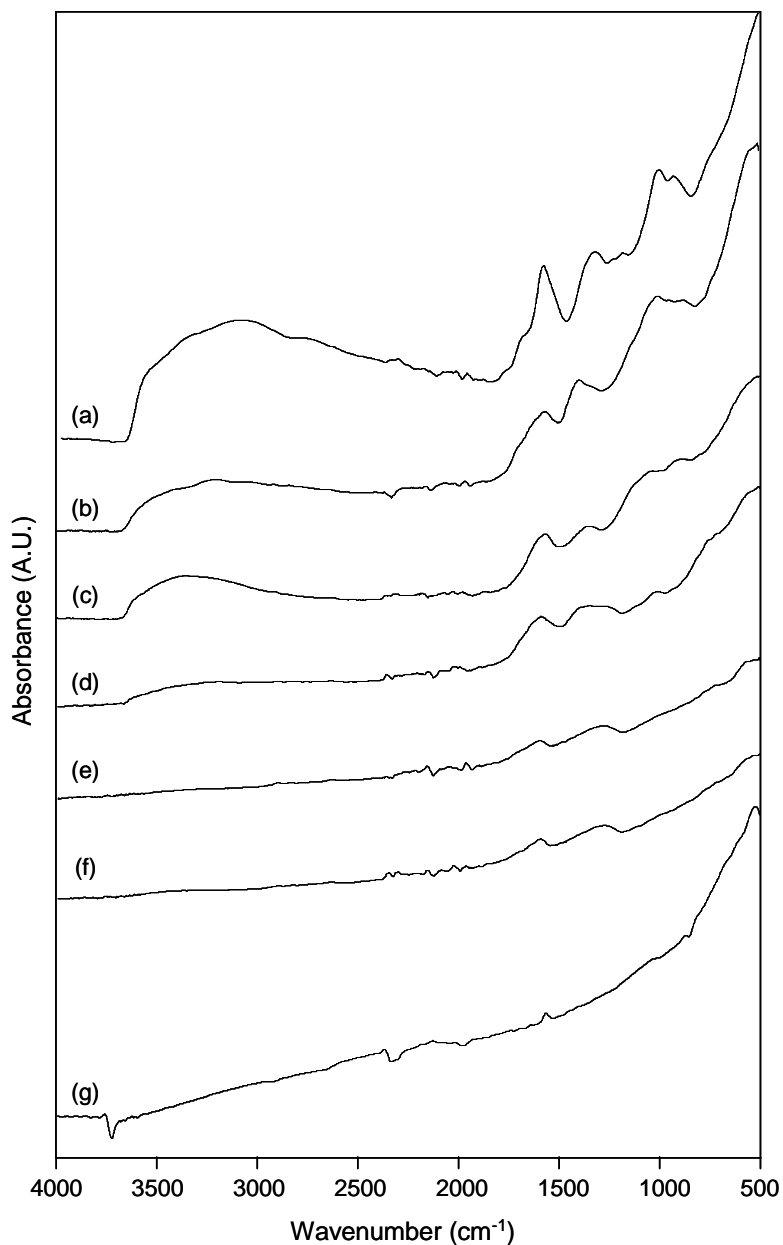


Figure 2. ATR-FTIR spectra of unreduced graphene oxide (a), deoxygenated samples N1 (b), B4 (c), P3 (d), V4 (e) and H4 (f), and pristine graphite (g). The acronyms for the deoxygenated samples are defined in Table 1.

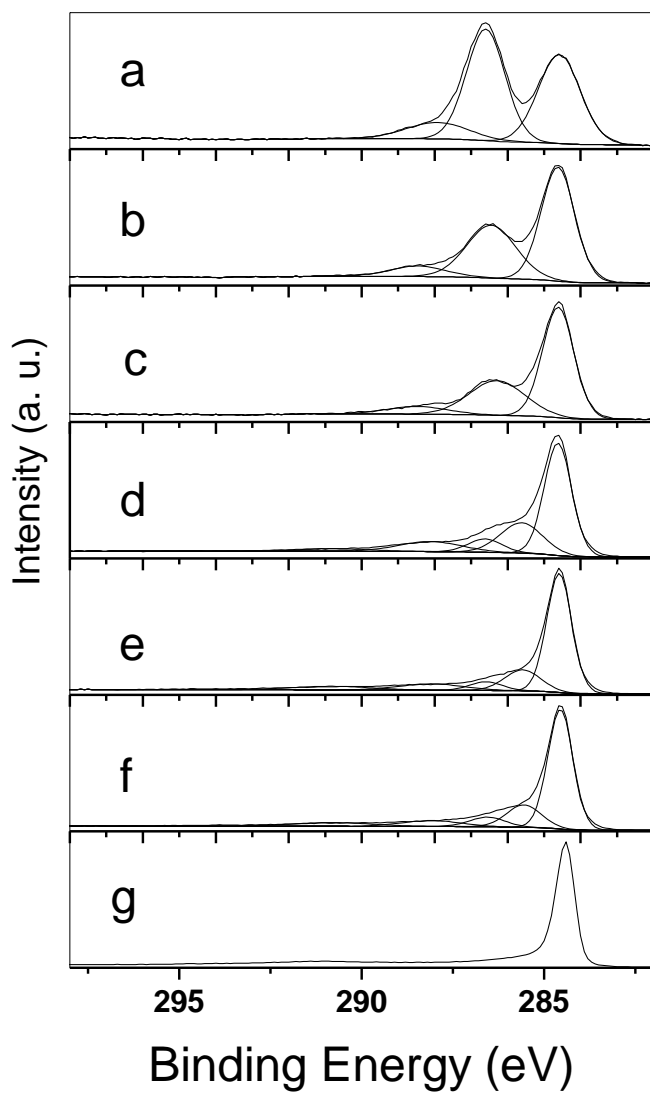


Figure 3. High resolution C1s X-ray photoelectron spectra for unreduced graphene oxide (a), deoxygenated samples N1 (b), B4 (c), P3 (d), V4 (e) and H4 (f), and pristine graphite (g). The acronyms for the deoxygenated samples are defined in Table 1.

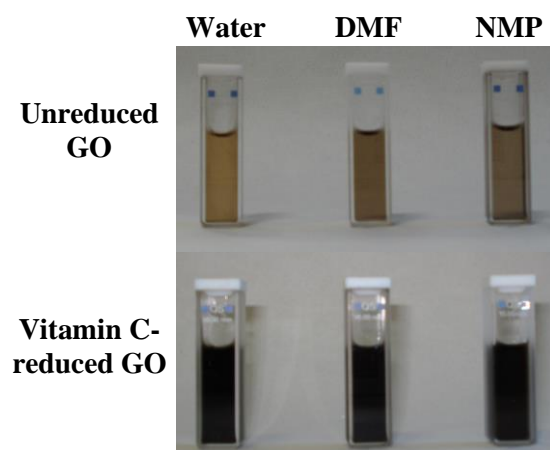


Figure 4. Digital pictures of unreduced graphene oxide suspensions in water, DMF and NMP (top), together with their deoxygenated counterparts 4 weeks after reduction with vitamin C (bottom).

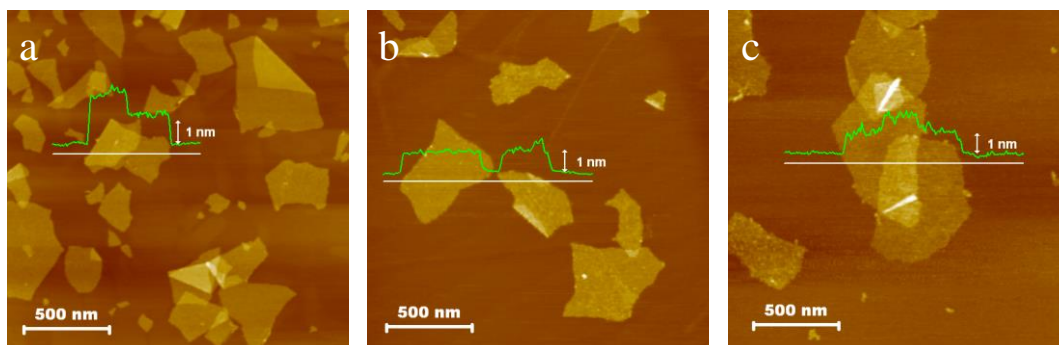


Figure 5. Representative AFM images of unreduced (a), hydrazine-reduced (b) and vitamin C-reduced (c) graphene oxide sheets deposited onto HOPG substrates from their corresponding suspensions. Lines profiles are superimposed onto each image, showing that single-layer sheets are obtained in all cases.

Supporting Information for

Vitamin C is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions

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Table S1. Comparison of several characteristics of graphene sheets produced by deoxygenation of graphene oxide suspensions through different green approaches and hydrazine. The figures between parentheses in the “O/C ratio” column correspond to the starting graphite oxides.

Method	UV-vis peak	O/C ratio	Stability in solvents	Electrical conductivity	Ref.
Electrochemical reduction	Unknown	Unknown	Reduced material obtained as a precipitate in water	3500 S/m	1
Hydrothermal dehydration	254 nm	0.15 (0.36)	Stable in water	Unknown	2
MW-assisted solvothermal reduction	Unknown	0.09 (0.43)	Stable in tetraethylene glycol and water. Precipitates in DMF, ethanol, 1-butanol	Unknown	3
Vitamin C reduction	268 nm	0.08 (0.43)	Stable in water, DMF, NMP	Up to 7700 S/m	Present work
Hydrazine reduction	268 nm	0.08 (0.43)	Stable in water, DMF, NMP	Up to 9960 S/m	Present work

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Table of Contents Graphic

