

Flexible Conductive Graphene Paper Obtained by Direct and Gentle Annealing of Graphene Oxide Paper

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ABSTRACT

We report the fabrication of flexible conductive graphene paper through a direct and gentle annealing process of graphene oxide paper. Thermal treatments at 700 °C under argon or hydrogen atmosphere directly applied to parent graphene oxide paper lead to a significant removal of disruptive oxygen-containing functional groups, and to a considerable recovery of the sp^2 network structure. Detailed comparison of chemical and combined chemical-thermal treatments by scanning electronic microscopy (SEM), Raman, X-photoelectron spectroscopy (XPS) and conductivity measurements underline the high efficiency of the direct annealing process. The resulting highly reduced graphene oxide paper exhibits electrical conductivities as high as 8100 S/m representing an increase of 5 orders of magnitude with respect to the parent graphene oxide paper,

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which significantly outperforms the results of chemical treatments. Moreover, our direct and gentle thermal reduction allows maintaining the structural integrity and mechanical flexibility of the parent graphene oxide paper thus overcoming problems of brittleness typically encountered in annealing processes. Our approach sets the base for an easy, cost-effective and environmentally friendly fabrication route for flexible conducting graphene paper of great application potential as flexible electrodes in various fields of technology.

1. Introduction

There is currently a great demand for the development of new inexpensive, flexible, robust, light-weight and environmentally friendly paper-like materials. Here especially carbon-based paper materials have raised great interest for various types of applications such as electrochemical energy storage devices [1-3], catalyst supports and fuel cells [4-6], sensors and actuators [7-10], chemical filters and membranes [11-12], and structural composites [13-14], to name only a few. A promising building block of intriguing actual scientific and technological interest is graphene, best described as a two-dimensional single-atom thick sheet of sp^2 hybridized carbon atoms arranged in a honeycomb lattice with outstanding electronic, mechanical, thermal and chemical properties [15-16]. Recently individual water soluble graphene oxide (GO) sheets [17] – heavily oxygenated graphene sheets bearing epoxy and hydroxyl functional groups on their basal planes, in addition to carbonyl and carboxyl groups located at the sheet edges – were assembled by a flow-directed vacuum filtration process into an interlocking-tile arrangement yielding free-standing and highly flexible GO paper [18]. While the presence of oxygen moieties provides GO sheets their hydrophilic character and imparts

versatile high volume processing possibilities from stable aqueous suspensions into GO paper and other macroscopic assemblies [19], they also heavily disrupt the conjugated sp^2 network of the basal plane of the individual graphene sheets and drastically degrade their electric properties. However, the electrical conductivity of GO sheets is typically enhanced by removal of the oxygen functional groups by chemical reduction processes [17], resulting in reduced graphene oxide (RGO) sheets, consisting of graphene domains, defects and residual oxygen-containing groups. Only few works describe strategies of how to obtain conducting RGO paper. Two different approaches are reported, namely the direct production of conducting RGO paper and the post-reduction of pre-fabricated GO paper. Direct fabrication of RGO paper as described by Li et al. [20] and Chen et al. [21] involves the chemical reduction of individual GO sheets in aqueous dispersion by hydrazine hydrate [17] into RGO sheets followed by flow directed vacuum filtration. This yields flexible free-standing RGO paper with conductivities as high as 7200 S/m [20]. Despite these favorable characteristics water dispersibility of RGO sheets, a pre-requisite for paper fabrication, only can be achieved in a very narrow window of reduction conditions outside of which irreversible agglomeration and precipitation of RGO sheets takes place making processing from liquid phase into homogeneous paper materials impossible [20]. Alternatively, few works are dedicated to post-reduction processes applied to parent GO paper. These are based on chemical [22-23], combined chemical-thermal [23], or pure thermal processes [21]. Chemical and chemical-thermal processes typically employ hydrazine as reducing agent, either in aqueous solution filtered through the GO paper [23] or as vapor to which the GO paper is exposed [22]. When followed by a subsequent thermal annealing step at temperature of around 300 °C modest improvements of electrical conductivity are found, however on cost of the flexibility of the treated paper [23-24]. Direct thermal

reduction treatments as alternative to chemical processes only were successfully employed for deposited thin GO films [25-26]. Becerril et al. [26] showed that high temperature annealing at 1000 °C under vacuum for 3 hours significantly can enhance film conductivities by several orders of magnitude, assuming even better results when done under inert atmosphere. However, when such a strategy was applied to GO paper Chen et al. [21] report a delicate trade-off between restoring electrical conductivity and maintaining mechanical integrity and flexibility of the papers, which become seriously deteriorated above temperatures of 200 °C.

In this article we report on a gentle annealing processes directly applied to parent GO paper and carried out at 700 °C under argon or hydrogen atmosphere. Detailed comparison with chemical and combined chemical-thermal treatments analyzed by scanning electronic microscopy (SEM), RAMAN, X-photoelectron spectroscopy (XPS) and conductivity measurements consistently underline the high efficiency of these direct reduction processes in what concerns the removal of functional oxygen groups and the restoration of the sp²-network. Consequently, graphene paper (i.e. highly reduced graphene oxide (HRGO) paper), is obtained exhibiting electrical conductivities as high as $8 \cdot 10^3$ S/m, which represents an increase by 5 orders of magnitude with respect to the parent GO paper and significantly outperforms results of chemical treatments. Moreover, the direct annealing process does not alter the structural integrity and mechanical flexibility of the parent GO paper thus contrasting the typical problems of brittleness mentioned in literature [21, 23]. These findings set an attractive base for an easy, cost-effective and environmentally-friendly fabrication route for flexible conducting graphene paper being of great interest for flexible electrode applications in various fields.

2. Experimental

2.1 *Preparation of solutions of exfoliated graphene oxide sheets*

Graphite oxide was prepared using Hummers' method from graphite powder (Sigma- Aldrich) by oxidation with NaNO_3 , H_2SO_4 and KMnO_4 in an ice bath as reported elsewhere [27]. A suspension of graphene oxide (GO) sheets was obtained by sonication of the prepared graphite oxide powder in distilled water (1 mg/mL) for 2 hours, followed by mild centrifugation at 4500 rpm for 60 min to remove non-exfoliated materials, according to an experimental procedure described recently [20] leading to a brown-coloured solution of exfoliated GO sheets with a final concentration of 0.45 mg/mL, as determined from the residual weight of a freeze-dried aliquot.

2.2 *Preparation of graphene oxide and graphene paper*

Free-standing flexible GO-paper is prepared by vacuum assisted flow-filtration of 180 mL of the 0.45 mg/mL aqueous solution of GO-sheets using a Nylon membrane. Paper samples were rinsed with water and dried before being peeled-off. The thickness of the paper samples is about 6 – 10 μm . Different reductive techniques were applied to freestanding GO-paper to obtain corresponding graphene (i.e. highly reduced graphene oxide (HRGO)) paper.

- i) Exposure of GO-paper to vapors of hydrazine monohydrate ($\text{NH}_2\cdot\text{NH}_2\cdot\text{H}_2\text{O}$) at room temperature overnight.
- ii) Exposure of GO paper to vapors of hydrazine monohydrate ($\text{NH}_2\cdot\text{NH}_2\cdot\text{H}_2\text{O}$) at room temperature overnight followed by a 700 °C thermal annealing under an argon flow of 50 mL/min at atmospheric pressure for 30 minutes.

iii) 700 °C thermal annealing of GO paper under an Argon flow of 50 mL/min at atmospheric pressure for 30 minutes.

iv) 700 °C thermal annealing of GO paper under a hydrogen flow of 50 mL/min at atmospheric pressure for 30 minutes.

2.3 Characterization of the paper materials

X-ray diffraction of all the prepared paper materials was performed on a Bruker D8 Advance diffractometer using a Cu tube as X-ray source ($\lambda_{\text{Cu K}\alpha} = 1.54 \text{ \AA}$) a tube voltage of 40 kV, and a current of 40 mA. The morphology of the paper samples was characterized by scanning electronic microscopy using a Hitachi S-3400N microscope. Raman spectroscopy was performed using a Horiba Jobin-Yvon HRLAB HR 800 UV apparatus (excitation laser $\lambda = 514 \text{ nm}$) on the prepared papers. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCAPlus Omicron spectrometer using a monochromatized Mg X-ray source (1253.6 eV) on the prepared paper materials to probe their different electronic structures. Electrical conductivity of the prepared papers samples was measured in a co-lineal four-point probes method [28] using a Keithley 2000 System SourceMeter current source.

3. Results and discussion

3.1 Morphology and structure of graphene paper

All the obtained graphene (i.e. HRGO) paper are free-standing and flexible indicating that the individual sheets within the paper form continuous networks providing good structural and mechanical integrity, even after a thermal reduction (it is worthwhile mentioning here the need for working under an oxygen-free atmosphere during the

thermal treatment to maintain the structural and mechanical integrity. A weight loss of 80% at 700°C is observed in the thermogravimetric analysis of GO paper under air (see Supplementary Information) revealing that upon an experiment in air at 700°C the structural and mechanical integrity of the paper otherwise would not be maintained). Photographs of obtained paper samples are shown in Figure 1. A darkening of the paper after an effective reduction treatment is observed suggesting a restoration of the π -electron system in the GO sheets, as reported elsewhere [29].

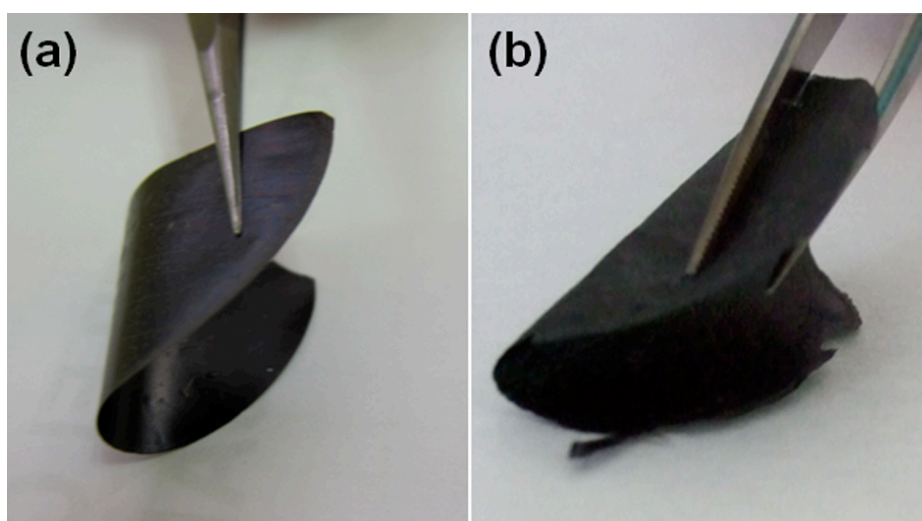


Figure 1. Photographs of free-standing paper samples: (a) GO paper; (b) HRGO paper.

The morphology of the prepared GO and graphene paper was observed by SEM and is displayed in Figure 2. From these images, a layered structure for the GO paper (Figure 1a) is observed showing the presence of individual, well-defined sheets with an overall thickness of the paper between 6 and 10 μm . None of the applied treatments seem to alter the appearance of the reduced paper (Fig. 2b-h), while the thickness appears in general slightly decreased, confirmed by the reduced interlayer spacing revealed by XRD diffraction, due to the removal of oxygen-containing functional groups and molecules of water intercalated in the spacing between the GO sheets upon reduction.

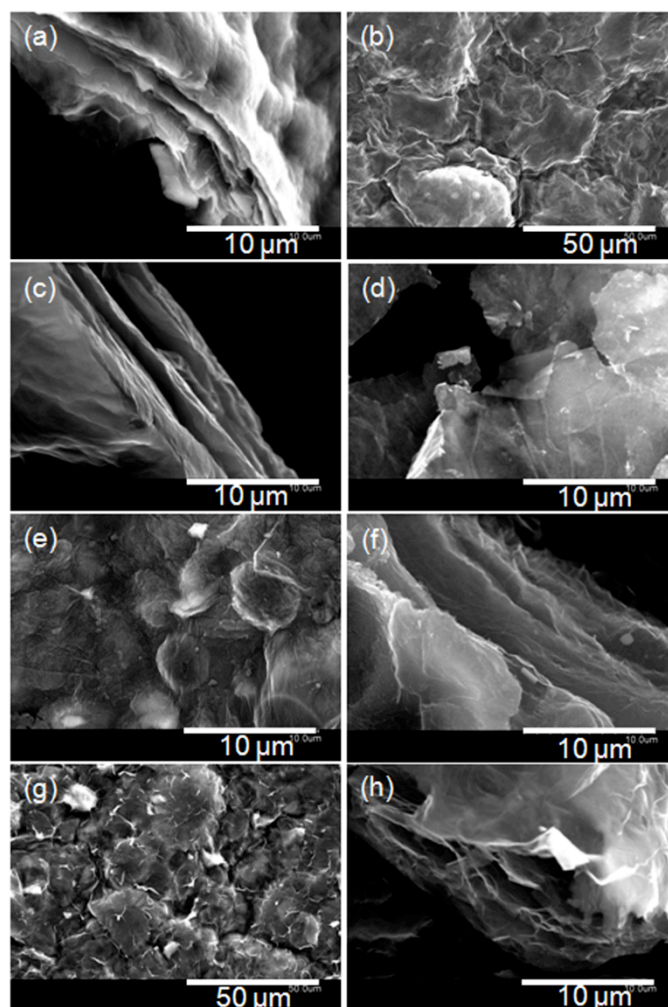


Figure 2. SEM images of paper samples: (a) GO; (b, c) hydrazine-HRGO; (d) (hydrazine+Ar)-HRGO; (e, f) Ar-HRGO; (g, h) H₂-HRGO.

XRD diffractions of prepared paper materials, as well as of the starting bulk graphite and graphite oxide powders are depicted in Figure 3. The XRD pattern of graphite oxide powder presents a diffraction peak at $2\Theta = 10.72^\circ$, indicating a higher interlayer spacing (0.84 nm) than that typical of the starting bulk graphite ($2\Theta = 27^\circ$, corresponding to 0.34 nm) due to the presence of functional groups attached to the GO sheet surfaces and molecules of water coming from the harsh oxidation applied [30]. This is probed by the thermogravimetric analysis of the GO powder in an Ar flow (see Supplementary Information). The weight loss of $\sim 10\%$ appearing at 100°C is attributed to the

elimination of interlamellar water, while the 15% weight loss observed at around 200°C is related to the removal of oxygen from graphene oxide sheets by evolution of CO and CO₂ [31]. As expected, the GO paper obtained by filtration of an aqueous solution of GO sheets exfoliated from graphite oxide presents similar diffraction peaks as the original graphite oxide powder. An up-shift and increased intensity in the diffraction peak is observed for the GO paper though with respect to the graphite oxide powder, pointing to a decreased interlayer distance likely due to the “packing effect” derived from the vacuum filtration. In case of HRGO paper the interlayer distance is decreased back to 0.35 nm ($2\theta = \sim 26^\circ$), revealing a de-intercalation and removal of oxygen-containing functional groups and molecules of water from the interlayer spacing of the GO paper upon reduction without reaching the interlayer spacing typical of the starting bulk graphite. No obvious differences in width are observed for the XRD peak when comparing the differently reduced HRGO paper, suggesting a similar stacking thickness of graphene layers independently of the reductive method employed.

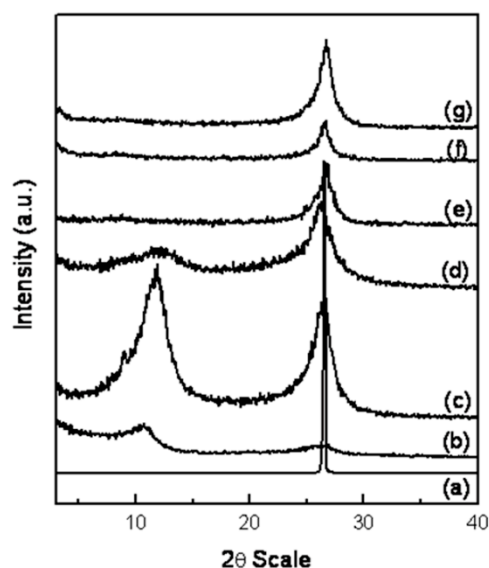


Figure 3. XRD patterns of: (a) bulk graphite, (b) graphite oxide powder, and paper samples: (c) GO; (d) hydrazine-HRGO; (e) (hydrazine + Ar)-HRGO; (f) Ar-HRGO; (g) H₂-HRGO.

In addition to this de-intercalation of water molecules from the interlayer spacing, during reduction the GO paper is expected to undergo structural changes due to the loss of oxygen. The carbon atoms in the basal plane may also rearrange during annealing due to the available thermal energy. Such loss of oxygen and the corresponding structural changes can be monitored by XPS and Raman spectroscopy.

The increased at. % of C corresponding to the relative content of carbon not bound to oxygen or nitrogen (~ 284.5 eV) and the increased C/O atomic ratio observed in the reduced papers constitute important evidences of the removal of oxygen-containing functional groups of the GO-paper upon reduction. The removal of oxygen constitutes an important step in the reduction, as sp^2 clusters in GO are isolated by oxygen atoms and a reduction by removal of O leads to greater connectivity among the existing graphitic domains by formation of new sp^2 clusters [32], which can be followed by

Raman spectroscopy. The well-known G-band (at 1585 cm^{-1}) and the 2D-band (at 2700 cm^{-1}) are characteristic of the sp^2 -hybridized carbon-carbon bonds in graphene [33-34]. The 2D-band located at $\sim 2700\text{ cm}^{-1}$ is the second-order Raman feature of the D-band and originates from a double-resonance process [35]. The presence of the D-band (at 1350 cm^{-1}) indicates the presence of structural imperfections induced by the attachment of oxygen functional groups on the carbon basal plane [34]. Both $I(2D)/I(G)$ and $I(G)/I(D)$ ratios are widely used to provide structural information of the GO with different degree of reduction. High $I(2D)/I(G)$ ratios, as well as increased intensity and decreased width of the 2D-band, are commonly employed to indicate the restoration of sp^2 -hybridized carbon-carbon bonds in graphitic structures[36], while a low $I(G)/I(D)$ is related to the presence of disorder carbon and/or functionalities attached to the graphene sheets. Raman spectra of the GO and the reduced papers were performed and are shown in Figure 4. The values of the $I(2D)/I(G)$ and $I(G)/I(D)$ ratios were calculated and are compiled in Table 1.

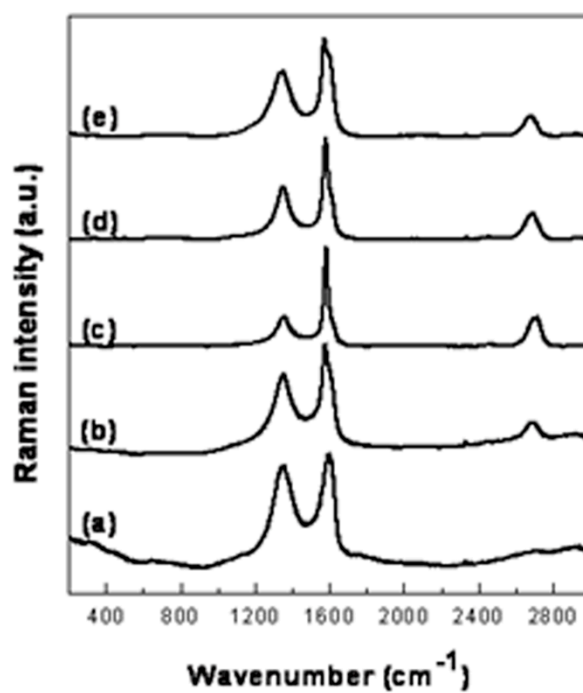


Figure 4. Raman spectra of paper samples: (a) GO; (b) hydrazine-HRGO; (c) (hydrazine + Ar)-HRGO; (d) Ar-HRGO; (e) H₂-HRGO.

Table 1 - I(G)/I(D) and I(2D)/I(G) ratios for GO and HRGO paper samples

Paper	I(G)/I(D)	I(2D)/I(G)
GO	1.092	0.0397
hydrazine-HRGO	1.40	0.183
(hydrazine + Ar)-HRGO	3.20	0.302
Ar-HRGO	1.918	0.260
H ₂ -HRGO	1.39	0.196

High resolution XPS scans from the carbon region (C1s) were performed on the studied paper materials. The most prominent components were deconvoluted with the help of a fitting program and the obtained spectra are shown in Figure 5. Deconvolution of C1s in the GO-paper (Figure 5a) revealed the presence of a strong peak at ~ 284.8 eV, corresponding to large amounts of sp^3 carbon (C-C), with contributions of C-O (~ 286.3 eV), C=O (~ 287.8 eV) and carboxyl (O-C=O)/lactone/ester (~ 289.6 eV) groups. Percolation amongst the sp^2 clusters is mitigated by these structural defects due to the presence of residual oxygen, which appears as a result of the harsh oxidation and destruction of the sp^2 network structure within the chemical transformation of graphite into graphite oxide using Hummers' method. The presence of such a high number of structural defects in the GO paper is confirmed by the low values for I(G)/I(D) and I(2D)/I(G) revealed by Raman spectroscopy (Figure 4a).

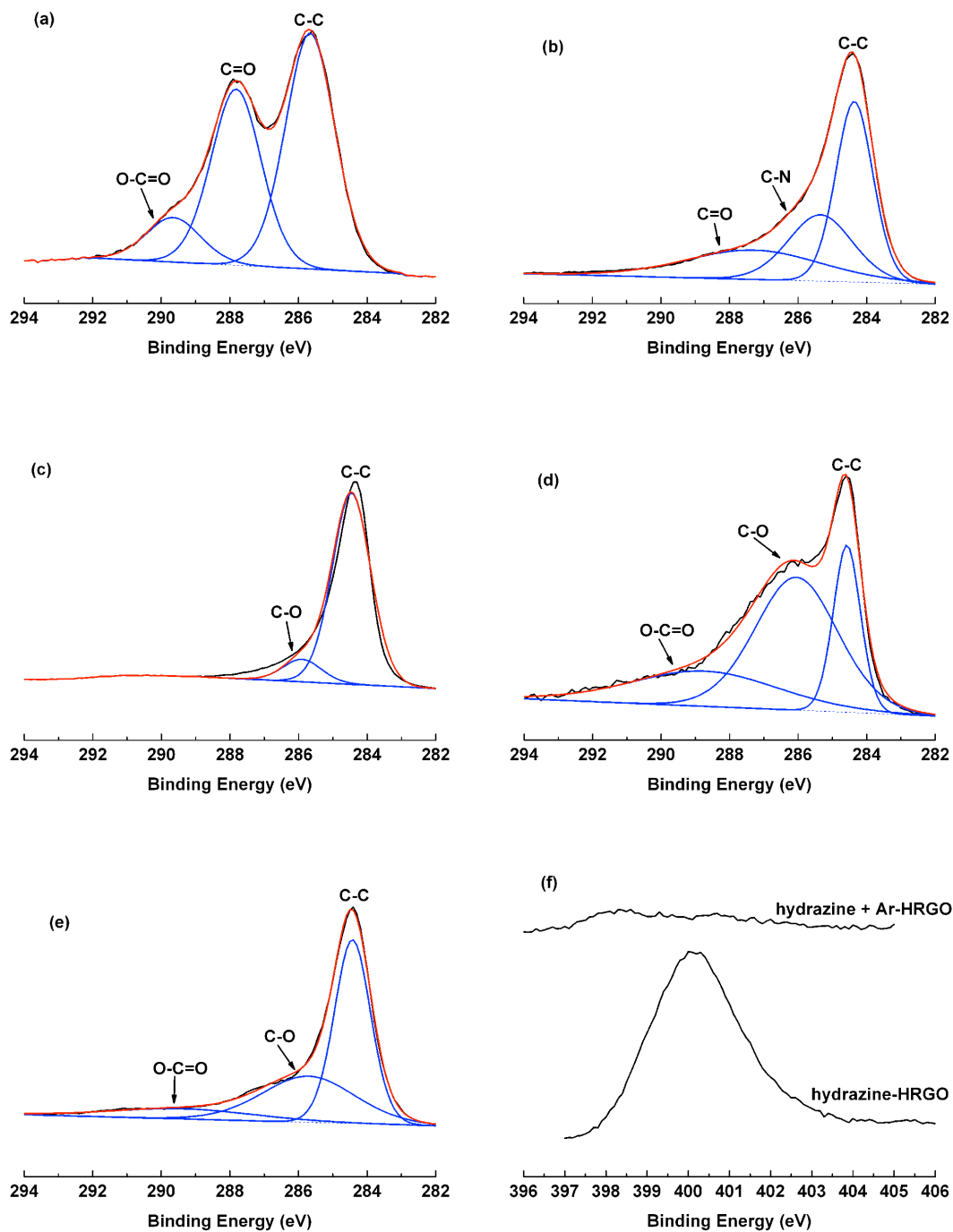


Figure 5. High-resolution XPS analysis (C1s) of paper samples: (a) GO; (b) hydrazine-HRGO; (c) (hydrazine + Ar)-HRGO; (d) Ar-HRGO; (e) H₂-HRGO. (f) High-resolution XPS analysis (N1s) of the hydrazine-HRGO and (hydrazine + Ar)-HRGO paper.

The quantified at. % of the elements C, O and N found in the surface composition of the studied papers and the calculated C/O and C/N atomic ratios are determined by XPS and compiled in Table 2. These values show that the exposure to hydrazine vapors reduces considerably the oxygen content of the GO paper, from 22.23 % in the starting GO paper to 10.76 %, showing a high efficiency of this chemical treatment in what concerns the removal of oxygen-containing functionalities. As XPS shows (Figure 5b) exposure to vapors of hydrazine removes completely the carboxyl (O-C=O) and (C-O) groups and reduce considerably the amount of carbonyl (C=O) groups from the GO paper. The C-C bonds become dominant as shown by the one single peak at ~284.3 eV, with a small tail in the higher binding energy region, which can be deconvoluted into two weak peaks at ~285.3 eV and ~287.3 eV, corresponding to small amounts of C-N and C=O species, respectively.

Table 2 – XPS analysis of C, O, N content and calculated C/O and C/N ratios for GO and HRGO paper samples

Paper	C (at. %)	O (at. %)	N (at. %)	C/O	C/N
GO	76.91	22.23	0.85	3.46	0.011
hydrazine-HRGO	85.94	10.76	3.29	8	0.038
(hydrazine + Ar)-HRGO	87.12	12.49	0.38	7	0.0043
Ar-HRGO	54.55	44.88	0.56	1.2	0.010
H ₂ -HRGO	96.1	3.407	0.48	28.57	0.0049

Upon removal of oxygen-containing functional groups from the GO paper by exposure to hydrazine vapors multiple reactions may occur simultaneously: hydrazine can react with epoxides to open their rings and form hydrazino alcohols [37], amine groups can react with carboxylic acid groups through the amidation process [17], hydrazine can react with anhydrides and lactones to form hydrazides and with quinones to yield hydrazones [38]. During these de-oxygenation reactions, the reorganization of unsaturated carbon as well as the incorporation/adsorption of N atoms into/on the carbon network originating from the reducing reagent $N_2H_4 \cdot H_2O$ is thought to occur spontaneously [17, 39].

The use of hydrazine vapors results in a significant removal of the oxygen-containing groups. This treatment introduces however a 3.297 at. % of N in the paper as undesired sub-product. This incorporation of nitrogen coming from the vapors of hydrazine is confirmed by XPS analysis of the nitrogen region (N1s) revealing an easily achieved nitrogen-doping effect in the graphene sheets. Figure 5f compares the high resolution XPS of the N1s region for both the hydrazine and the (hydrazine + Ar) treated GO paper. A nitride-like peak located at 395.7 eV appears in the hydrazine vapors treated GO paper, which should be ascribed to adsorbed N_2H_4 . Similar nitrogenated carbon signals in hydrazine treated GO have been previously observed by Stankovich et al. [17] from their analysis of GO reduced in hydrazine solutions, which they attribute to a partial reduction of carbonyl functionalities to hydrazone groups [17, 39].

A further thermal annealing under argon at 700 °C applied to the hydrazine treated GO paper (Figure 5c) not only removes the remaining C=O content, but also reduces notably the undesired introduced nitrogen content from 3.29 at. % to 0.38 at. % likely through desorption of nitrogen. Apparently large part of nitrogen does not form covalent

bounds in addition to the partial reduction of carbonyl functionalities proposed by Stankovich [17, 39].

The use of hydrazine vapors alone seems unable to restore the sp^2 carbon sites, making a further annealing step essential not only to remove the introduced sub-products but also to achieve a higher degree of restoration of the sp^2 carbon-carbon bonds leading to higher reduction degrees than those observed by chemical reductions. A thermal treatment in an argon environment is not sufficient though to further reduce the oxygen content of the hydrazine treated paper (10.76 %). The thermogravimetric analysis of the hydrazine treated paper was performed in Ar (see Supplementary Information). In addition to the observed weight loss of 5% corresponding to the removal of molecules of water remaining after the treatment with hydrazine, the lack of an essential weight loss at around 200°C reveals the absence of oxygen functionalities from the hydrazine treated paper, which points to the treatment with vapors of hydrazine as the main responsible of the removal of the oxygenated functionalities of the paper, in agreement with the XPS results. Similarly, a thermal treatment under argon applied directly to the GO paper does not decrease the oxygen content either, but it is increased up to 44.88 %, clearly evidencing its low efficiency in removing oxygen containing functional groups under the applied conditions. When this thermal treatment under argon is applied directly to a GO paper ~20 % of the carbon content of the paper is removed, so that the final C/O ratio decreases from 3.46 in the GO-paper to 1.21. The deconvolution of C1s of the GO paper after direct annealing under argon atmosphere (Figure 5d) reveals that the number of O-C=O and C=O groups are considerably reduced, on cost of an increased amount of C-O, likely through a transformation of C=O groups into C-O, with no final loss of oxygen though. The thermogravimetric analysis of the GO paper in an Ar atmosphere (see Supplementary Information) shows a weight loss of ~10 % at

around 100 °C corresponding to the content of molecules of water intercalated between the layers in the GO paper followed by a second weight loss of 20 % at around 200°C, attributed to the removal of oxygen containing functionalities, i.e. C=O and O-C=O according to XPS analysis.

We attribute the removal of carbon without any loss of oxygen observed in the Ar treated GO paper to a high efficiency in improving the growth of graphene nanodomains through a rearrangement of the carbon atoms, which becomes the dominant process rather than the removal of chemical functional groups in the creation of large sp^2 domain sizes upon annealing applied to both hydrazine treated- and starting GO paper.

This reorganization of carbon atoms leading to a high degree of sp^2 restoration and an enhancement of the domain size of nanographitic structures is confirmed by the high values of $I(G)/I(D)$ and $I(2D)/I(G)$ observed for the Raman spectra of the (hydrazine + Ar)- and (Ar)-treated paper (Figures 4c,d). Our (hydrazine + Ar)-treatment, which combines both a chemical and a thermal reduction method renders the highest $I(G)/I(D)$ and $I(2D)/I(G)$ values, 3.20 and 0.302 respectively, evidencing that a high efficiency for restoring the sp^2 carbon network of GO is strongly related to a thermal treatment where the available thermal energy can rearrange the atoms of carbon of the graphene oxide during annealing.

The high-resolution C1s region for the GO paper thermally treated under hydrogen, shown in Figure 5e, reveals that the observed reduction of oxygen content is due to a complete removal of C=O and almost complete removal of O-C=O groups, in combination with a considerable reduction of the amount of C-O groups. These XPS results are supported by the thermogravimetric analysis of GO paper in a hydrogen atmosphere (see Supporting Information) showing a weight loss of 10 % corresponding

to intercalated molecules of water, and a weight loss of ~20 % at around 200°C, related to the removal of oxygen functionalities, i.e. C-O and O-C=O groups. A thermal treatment in hydrogen seems even more effective than an exposure to hydrazine vapors in what concerns the removal of oxygen moieties of the paper materials. Although it is thought that the reduction mechanism should be similar to that described for hydrazine, we propose here that the reduction mechanism for the thermal treatment in hydrogen atmosphere is based on the removal of the oxygen containing functional moieties (mainly -OH) in the presence of both heat and hydrogen. Here, hydrogen may react with -OH groups present in the GO paper to form water vapor decreasing the amount of oxygen in the paper. The applied temperature further assists the formation of an enhanced number of sp² carbon nanodomains, as revealed by Raman spectroscopy.

Advantageously, in contrast to the chemical treatment, no sub-products are introduced in the paper and, even more, the highest C/O ratio (28.57) for all the HRGO paper studied here are achieved. A comparison with highest C/O values found in literature (14.1) on reduced GO-films obtained by UHV annealing at 900 °C [25] once more underlines the efficiency of the hydrogen annealing process (please note that, to the best of our knowledge, no C/O values are reported in literature for reduced GO paper).

In addition to the removal of oxygen-containing functional groups revealed by XPS, Raman results have shown that a thermal treatment in hydrogen restores efficiently the carbon sp² network of the GO paper, increasing the size of the sp² clusters, shown as well by the Raman spectrum of the H₂ treated paper (Figure 4e), showing I(G)/I(D) and I(2D)/I(G) values higher than those typical of the starting GO paper.

We show here that upon thermal treatments in argon and hydrogen environments higher reduction degrees of GO paper than those obtained by a chemical reduction alone are

achieved. Both the removal of oxygen-containing functionalities of the GO paper and the degree of carbon sp^2 restoration through a transformation of sp^3 carbon into sp^2 carbon produced by the thermal energy lead to a considerable enlargement of the domain size of nano-graphenic structures and thus to a higher recovery degree of the electrical properties of the papers than those achieved by chemical means. In this sense, as thermal treatments are proved to lead both to a superior removal of oxygen containing functional groups and to a higher degree of restoration of the sp^2 network than the chemically reduced materials, we propose here the term “highly reduced graphene oxide” for the materials presented here to point out that the thermal treatments reported here go one step further than the widely employed chemical methods in the reduction of graphene oxide materials.

3.2 Restoration of the carbon sp^2 network and electrical properties of the graphene paper

We correlate the effects of the structural changes and the increased sp^2 bonding obtained upon these reduction processes with the recovery of the electrical properties of GO paper. Conductivities of the prepared papers were measured in a co-linear four-point probes method [28] and the obtained values are compiled in Table 3.

Table 3 – Electrical conductivities for GO and HRGO paper samples

Paper	Electrical conductivity (S/m)
GO	$8.5 \cdot 10^{-2}$
hydrazine-HRGO	$1.7 \cdot 10^2$
(hydrazine + Ar)-HRGO	$3.9 \cdot 10^3$
Ar-HRGO	$8.1 \cdot 10^3$
H ₂ -HRGO	$5.0 \cdot 10^3$

GO materials are suggested to contain large sp^2 domain sizes that are interrupted by sp^3 bonds due to the presence of oxygen, showing thus a very low electrical conductivity ($8.5 \cdot 10^{-2}$ S/m). An exposure to vapors of hydrazine makes the paper electrically active increasing its conductivity in four orders of magnitude reaching $1.7 \cdot 10^2$ S/m likely due to the removal of oxygen-containing functional groups from the GO paper enhancing the connectivity among the graphitic domains by formation of new sp^2 clusters.

Higher values of electrical conductivities are observed for the thermally treated papers, i.e. for the (hydrazine + Ar), argon and hydrogen treated papers, reaching values as high as $3.9 \cdot 10^3$, $8.1 \cdot 10^3$ and $5.0 \cdot 10^3$ S/m, respectively, improving the conductivity of the GO paper up to five orders of magnitude and enhancing as well the conductivity of the chemically treated papers by one order of magnitude. These values demonstrate that the thermal treatments restore much better sp^2 carbon domains and the electrical properties of GO papers than the chemical reductions providing higher reduction degrees, in agreement with XPS and Raman spectroscopy.

In general, we explain the recovery of the electrical properties of the papers in terms of an effective restoration of the sp^2 carbon network ensured by a reduction of the GO paper, resulting in an increase of the charge carrier transport in individual graphene sheets. GO-materials are thought to contain sp^2 clusters isolated by oxygen atoms, which impede the electronic mobility. As the material is progressively reduced, interactions among the clusters increase. Reduction by removal of oxygen leads to greater connectivity among the graphitic domains by formation of new sp^2 clusters, in addition to an increase in structural defects via evolution of CO and/or CO₂ species (specially from epoxy groups) [32]. The presence of residual oxygen significantly hampers the carrier transport among the graphitic domains. C. Mattevi et al. reported that transport at the initial stages of reduction is dominated by hopping or tunneling amongst the sp^2 clusters [32]. At latter stages of reduction the original sp^2 clusters are connected by newly formed smaller sp^2 domains so that transport by percolation can occur.

Two important effects need to be considered in the global restoration of the carbon sp^2 network and enhancement of the conductivity of the prepared graphene paper:

i) The removal of oxygen-containing groups from GO paper occurring mainly through a chemical reduction (i.e. hydrazine monohydrate vapors or H₂), which represents the origin of a new sp^2 cluster in the basal plane of the paper. In case of the thermal treatment in Ar the appearance of new sp^2 clusters is produced by the applied thermal energy, providing a nucleation point for the restoration of the carbon sp^2 network. The creation of these new sp^2 clusters in this case is however considerably less numerous compared to the use of a reducing agent, explaining the less efficient removal of oxygen moieties observed upon this treatment.

ii) The recovery of sp^2 carbon to carbon bonds of the graphitic structure of the sheets forming and connecting new sp^2 clusters in the papers through a thermal treatment. We have probed here that although a chemical reductive treatment removes quite efficiently the oxygen-containing groups, it is not sufficient to achieve a complete reorganization of the atoms of carbon towards new sp^2 carbon to carbon nanodomains. In this sense, a thermal treatment under Ar, although highly efficient in restoring the sp^2 carbon system, has been shown to be less efficient in removing oxygen-functionalities from the GO paper. The thermal treatment in H_2 however constitutes at the same time a thermal annealing and a chemical reduction leading to both an efficient removal of oxygen-functionalities and an efficient restoration of the sp^2 carbon network. This observation is supported by an increased C/O value obtained using H_2 and a decreased value upon a treatment under an Ar atmosphere, revealing a considerably superior removal of oxygen containing functionalities upon a treatment under H_2 compared to the one using Ar. Nevertheless, both treatments lead to a reorganization and restoration of sp^3 into sp^2 carbons as can be explained by the decreased C/O values observed for the Ar treated paper. In order to achieve a good degree of both effects (removal of oxygen-containing functionalities of the GO paper and a higher degree of sp^2 carbon restoration through a transformation of carbon sp^3 into carbon sp^2) the thermal treatment in Ar should be preceded by a chemical treatment, i.e. a treatment with vapors of hydrazine. A thermal treatment emerges here thus as an important improvement for obtaining higher reorganization degrees of sp^2 carbon to carbon bonds of GO paper and efficiently reduced GO paper.

We here have demonstrated that direct and thermal treatments of GO paper lead to higher degree of sp^2 carbon clusters formation, as revealed by the optimal values obtained for C/O, I(2D)/I(G) and I(G)/I(D) ratios, and significantly improved electrical

conductivity in comparison to chemically reduced GO paper. The excellent structural and mechanical integrities of the resulting graphene (i.e. HRGO) paper, even when obtained by thermal treatments are contrasting observations of decreased mechanical strengths of GO paper upon annealing processes [21, 24], possibly due to the application of gentle and controlled annealing conditions. It should be underlined that combining a short thermal treatment performed at a lower temperature than those used in conventional annealing steps, and carried out under an oxygen-free atmosphere seems to be essential to maintain structural integrity of the papers and avoid their thermal degradation.

4. Conclusion

Flexible conductive graphene paper can be obtained through direct and gentle annealing of parent GO paper. Thermal treatments under argon or hydrogen atmosphere are shown to be highly efficient methods to improve the reduction of GO paper, leading to a significant removal of oxygen-containing functional groups and to an efficient recovery of the sp^2 network structure. The resulting graphene (i.e. HRGO) paper exhibits electrical conductivities up to $8 \cdot 10^3$ S/m, 5 orders of magnitude higher than the original GO paper, significantly outperforming the results of chemical treatments. Moreover, our direct thermal reduction treatment allows maintaining the structural integrity and mechanical flexibility of the parent GO paper. Our approach suggests an easy, cost-effective and environmentally friendly fabrication route for flexible conducting graphene paper of great application potential as flexible electrodes in fields, such as energy storage/harvest (supercapacitors, batteries) and sensors.

Acknowledgments

This research was supported by Spanish Ministry of Science and Innovation (MICINN) under project MAT2010-15026 and the Government of Aragon (DGA) under Project DGA-T66 CNN. CV acknowledges MICINN for her post-doc contract under Juan de la Cierva Programme, J. D. N. thanks CSIC for his JAE PhD grant.

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Figure captions

Figure 1. Photographs of free-standing paper samples: (a) GO-paper; (b) HRGO-paper.

Figure 2. SEM images of paper samples: (a) GO; (b, c) hydrazine-HRGO; (d) (hydrazine+Ar)-HRGO; (e, f) Ar-HRGO; (g, h) H₂-HRGO.

Figure 3. XRD patterns of: (a) bulk graphite, (b) graphite oxide powder and paper samples (c) GO; (d) hydrazine-HRGO; (e) (hydrazine + Ar)-HRGO; (f) Ar-HRGO; (g) H₂-HRGO.

Figure 4. Raman spectra of paper samples: (a) GO; (b) hydrazine-HRGO; (c) (hydrazine + Ar)-HRGO; (d) Ar-HRGO; (e) H₂-HRGO.

Figure 5. High-resolution XPS analysis (C1s) of paper samples: (a) GO; (b) hydrazine-HRGO; (c) (hydrazine + Ar)-HRGO; (d) Ar-HRGO; (e) H₂-HRGO. (f) High-resolution XPS analysis (N1s) of the hydrazine-HRGO and (hydrazine + Ar)-HRGO paper.

Table captions

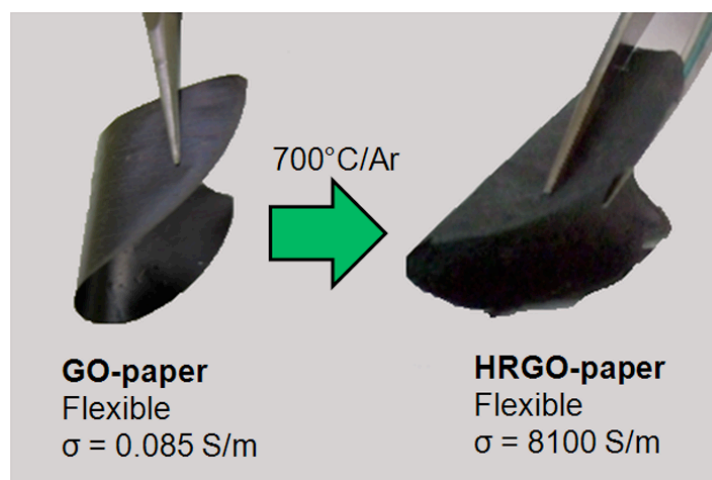
Table 1. I(G)/I(D) and I(2D)/I(G) ratios for GO and HRGO paper samples

Table 2. XPS analysis of C, O, N content and calculated C/O and C/N ratios for GO and HRGO paper samples

Table 3. Electrical conductivities for GO and HRGO paper samples

GRAPHICAL ABSTRACT

Flexible conductive graphene paper is obtained by direct and gentle annealing of graphene oxide paper at 700 °C under argon atmosphere. Conductivity increases by 5 orders of magnitude up to 8100 S/m while the structural integrity and mechanical flexibility of the paper are maintained.



Research highlights

- Graphene paper is prepared by gentle annealing of graphene oxide paper.
- Thermal treatments remove oxygen-containing functional groups from the paper.
- Direct annealing processes efficiently recover the sp^2 network structure.
- The electrical conductivity of the paper is enhanced up to 8100 S/m.
- The structural integrity and mechanical flexibility of the paper are maintained.

Supporting information

Flexible Conductive Graphene Paper Obtained by Direct and Gentle Annealing of Graphene Oxide Paper

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1. TGA of the GO paper under air

The thermogravimetric analysis of GO paper under air is shown in Figure S1. It can be observed the loss of molecules of water at 100°C, followed by a weight loss of 15% around 200°C corresponding to the removal of oxygen containing functionalities, in agreement with our XPS observations. The weight loss observed above 350°C has been attributed to sublimation or burning of damaged graphitic regions [1]. At 700°C a weight loss of 80% is observed, revealing that upon a thermal treatment under air the structural and mechanical integrity of the GO paper is affected.

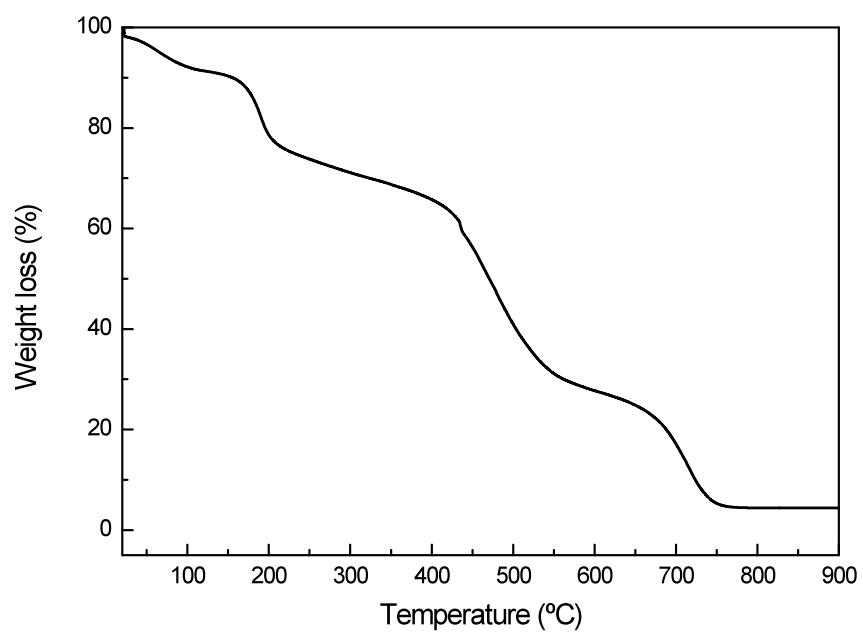


Figure S1. Thermogravimetric analysis of the GO paper under air.

2. TGAs performed under Ar and H₂

Thermogravimetric analysis simulating the experimental reduction conditions were performed and are depicted in Figure S2.

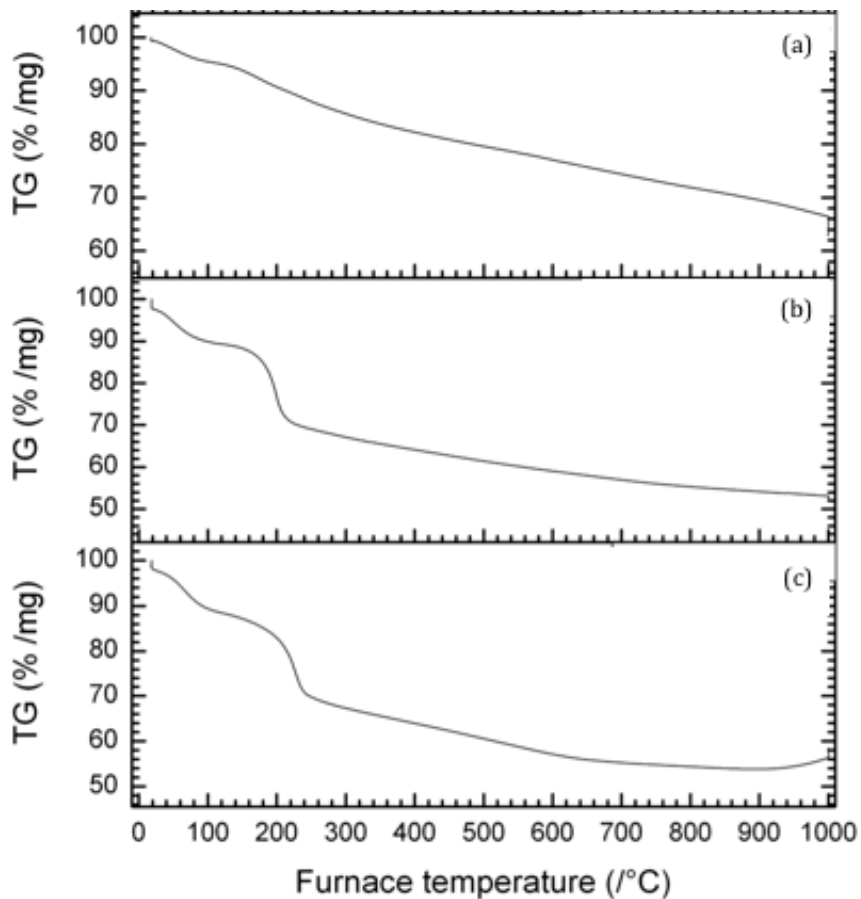


Figure S2. Thermogravimetric analysis of: (a) hydrazine treated paper under Ar; (b) GO paper under Ar; (c) GO paper under H₂.

The thermogravimetric analysis of the hydrazine treated paper in Ar (Figure S2a) shows the weight loss upon the annealing in Ar applied to the hydrazine treated paper. In addition to a weight loss of 5% corresponding to the removal of molecules of water still remaining after the treatment with hydrazine a slight weight loss is observed at around 200°C, revealing that the

treatment with vapors of hydrazine is the responsible of the removal of the majority oxygen-containing functionalities, in agreement with our XPS results.

The thermogravimetric analysis of the GO paper in an Ar atmosphere (Figure S2b) shows a weight loss of ~10% corresponding to the content of molecules of water intercalated between the layers in the GO paper followed by another weight loss of 20% at around 200°C corresponding to the removal of oxygen-containing functional groups.

The thermogravimetric analysis of the GO paper in a H₂ atmosphere (Figure S2c) shows a weight loss of 10% corresponding to intercalated molecules of water and a weight loss of ~20% at around 200°C, related to the removal of C-O and O-C=O groups in agreement with our XPS results.

3. References

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