



Full Length Article

Hydrogen cold plasma for the effective reduction of graphene oxide

Victor K. Abdelkader-Fernández^a, Manuel Melguizo^b, María Domingo-García^a,
F. Javier López-Garzón^a, Manuel Pérez-Mendoza^{a,*}

^a Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

^b Departamento de Química Inorgánica y Orgánica, Facultad de Ciencias Experimentales, Universidad de Jaén, 23071 Jaén, Spain



ARTICLE INFO

Keywords:

Graphene oxide reduction
Hydrogen cold plasma
Reduced graphene oxide

ABSTRACT

We report the reduction of GO by hydrogen cold plasma as an effective alternative to the usual chemical (with harsh reducing agents) or physical (through high-temperature treatments) methods. The hydrogen plasma is generated through microwave radiation and the reduction is performed barely above room temperature, avoiding structural degradation of the graphene oxide. Three commercial GOs, with several oxygen and sulfur contents, have been used in this study. As a consequence of the exposure to the hydrogen plasma, the oxygen content is decreased in large extent while sulfur is scarcely removed. Thus a two-stage methodology consisting of a simple water treatment under reflux conditions of GO (to remove sulfur) and further treatment with H₂ plasma is proposed. The combination of both steps allows the total elimination of sulfur while achieving very high degrees of reduction, lowering the initial oxygen content by more than 60%. These degrees of reduction are comparable to those obtained when the reduction is carried out by using the standard procedure with NaBH₄ on the same materials. The reduction with hydrogen plasma clearly shows advantages over the conventional reduction procedures due to its simplicity: no chemicals or high temperatures are needed, and the procedure is very fast.

1. Introduction

The reduction of graphene oxide (GO) is currently a topic of great scientific interest due to the enormous expectation raised by graphene derivatives [1,2]. Originally, the aim of this process has been to obtain pure graphene sheets by the reduction of GO. Many efforts have been done to obtain graphene-like materials from GO reduction processes with similar characteristics to those of the pristine graphene obtained from mechanical exfoliation. In spite of these efforts, the preparation of high-quality graphene in large amounts by reduction of GO is still a goal to be reached. Nevertheless, the material obtained by reduction of GO, usually referred as reduced graphene oxide (rGO), is a product with certain amount of heteroatoms remaining, and it is of wide interest by itself, as it can have a wider range of applications than GO or even pure graphene. The great importance of rGO to enlarge the application possibilities of graphene derivatives have been well documented, as it can offer improved solutions in comparison to other carbon nanomaterials. It has been, for example, reported its application in many electric and electronic devices, as catalyst and for optical and photovoltaic components among others [3–5]. Similarly, intense research is being developed for its use in water purification and sea water

desalination [6–10].

The structure of graphene and GO are closely related. While graphene consists of a single layer of sp² carbon atoms arranged in a hexagonal pattern, the GO has a similar structure but the layers are decorated with oxygen-containing groups, so that many of the carbon atoms have sp³ hybridization instead. The structure of GO depends on the experimental conditions of its preparation. Therefore, it is variable but it can be generally described as a 2D-network of sp³ carbon atoms bound to oxygen-containing groups, with regions formed by sp²-clusters. Moreover, GO is a non-stoichiometric solid whose structure is still a subject of controversy. Among the proposed structural models of GO, these of Lerft-Klinowsky and Dékány seem to be the most accepted nowadays [11,12].

There are several reduction strategies of GO, which include physical and chemical procedures [2,5,13–19]. Among the former, thermal annealing at several temperatures at atmospheric pressure in inert or reducing atmospheres, or under vacuum, has been reported. The processes are in general highly efficient but they are energy and time-consuming, usually needing very high temperatures. Moreover, oxygen is evolved as CO and CO₂, i.e., the elimination of carbon atoms is also produced, which results in many structural defects. The reduction by

* Corresponding author.

E-mail address: mjperezm@ugr.es (M. Pérez-Mendoza).

microwave and the photo reduction by laser or x-rays have been also reported [20–24]. The chemical processes are typical redox reactions in which GO is the oxidant and it is able to react with several reducing agents. Thus a large amount of chemicals, from harsh and aggressive reactants (as for example, hydrazine or hydroiodic acid) to more environmental friendly reagents (like vitamin C) [1,25,26] have been used as reducing agents [13]. A modification of the chemical reduction is the solvothermal reaction by using either water or organic solvents [13]. Moreover, reduction procedures in several consecutive steps have also been developed in order to improve the results obtained by the above methods. Extensive comments about these processes can be found in the literature [1,2,17,27].

This paper reports the reduction of GO by treatment with microwave hydrogen cold plasma. The electron species in cold plasmas are at much higher temperature than heavy species like ions and atoms, so that they are also known as non-equilibrium plasmas. Usually the electrons are at temperatures as high as $\approx 10^4$ K while the energies of the ions and neutral particles are barely above room temperature. Due to these characteristics these plasmas are highly reactive and currently are being used for functionalization of material surfaces [28–31]. Moreover, the use of cold plasmas for the modification of surfaces (reduction of GO in this case) has the advantage that tend not to damage the materials subjected to the treatment. In addition, the treatments are very fast (they do not need more than 5–10 min), and they are clean, as they need minimum amounts of reactants and no solvents are used. In this work, the only reactant which is used is hydrogen and the largest time of treatment is ten minutes. Thus, the advantage of this procedure compared to the already commented physical and chemical methods is evident.

2. Experimental

Three commercial GO samples which have been manufactured by Graphenano (GO_{GN}), NanoAmor (GO_{NA}) and AppliedNano (GO_{AN}) have been used. The treatments with hydrogen cold plasma were carried out using a device from Europlasma (Europlasma Junior Advanced SS). The equipment produces plasma by using a 2.45 GHz microwave source. The GO samples, once in the device chamber, were outgassed to a residual pressure of 50 mTorr before the treatments. Prior to the treatment, hydrogen was flowed during 5 min (15 mL min^{-1}) up to a stable pressure of ≈ 400 mTorr. The source power was set to 500 and 700 w and three times of treatment (1, 5 and 10 min) were used. The samples so obtained are labeled GO_{XX}-pH2-t[w], where the subscript xx stand for the commercial origin of the sample (GN, NA or AN), pH2 for the plasma treatment, t is the time of plasma treatment and w is the microwave power. For reasons that will be explained in the results and discussion section some samples where previously treated with boiled water for 1 h. In the label of these samples H₂O is inserted after GO_{XX}. For instance, the sample labeled GO_{GN}-H₂O-pH₂-5[700] refers to GO from Graphenano after being treated with boiling water and hydrogen plasma for 5 min with a power of 700 w.

Reduction with NaBH₄ was also carried out in order to compare the results of the plasma treatment with this “standard” reduction procedure. For this purpose around 60 mg of GO were suspended in 200 mL of 0.25 M aqueous solution of NaBH₄. The mixture was stirred for 2 h and the temperature was set at 50 °C. Then the solid in suspension was collected by filtration in a sintered glass funnel (porosity 4), repeatedly washed with hot (50 °C) distilled water and finally dried under vacuum (20 mbar) at 50 °C.

The samples were characterized by x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, Attenuated Total Reflectance-Infrared spectroscopy (ATR-IR) and thermal programmed desorption (TPD). The chemical surface composition (at.%) of the samples was obtained from the survey XPS spectra. The spectra were obtained in a Kratos Axis Ultra-DLD spectrometer. Monochromatic AlK_α radiation in the constant analyzer energy mode with pass energies of 160 and 20 eV

for the survey and high resolution spectra, respectively, was used. The deconvolutions of the high resolution spectra have been carried out by using CASA XPS software so that the chemical environments of the surface atoms were analyzed.

The Raman spectra were obtained in a spectrometer (Renishaw, DM LM model) equipped with an adapted confocal microscope (LEIKA) and a 514 nm Ar-ion laser source. The Fourier transform infrared (FTIR) spectroscopy allowed the analysis of the functional groups in the samples. An ATR-IR spectrometer Bruker Tensor 27 with an ATR accessory “dura SamplIR” and a control software “OPUS 5.0” were used.

Thermal programmed desorption (TPD) allowed us to study the thermal stability of the heteroatoms covalently attached to the GO surface. For this purpose, the samples were previously conditioned in helium flow (50 mL min^{-1}) at 120 °C for two hours and then they were heat treated at 10 °C min^{-1} up to 900 °C. The evolved gases were analyzed with a quadrupole mass spectrometer Omnistar mod GSD 320.

3. Results and discussion

The atom percentages of the original GO_{GN} obtained from the survey XPS spectrum (c.f Fig. S1 in supplementary information, SI) are 67.1, 29.1, 3.1 and 0.7 at.% of C, O, S and N, respectively (Table 1). The deconvolution (Fig. 1a) of the C 1s high resolution spectra show the most abundant oxygen containing group of the C 1s spectrum is that at 286.8 eV, which is assigned to C-O of epoxide and alcohol, although it can also be assigned to C sp³ and C2-SO₂ (sulfonyl). The assignment of this component to –SO₂ functions covalently bonded to C atoms from the graphene oxide skeleton is based on data derived from the water treatment of GO_{GN} (described below). The less abundant components appear at 288.1 and 288.9 eV. The former is due to C=O and C–SO₂OH (sulfonic groups) and the latter to COO[–] groups. The deconvolution of the O 1s (Fig. S2 in SI) shows that the component at 532.1 eV, due to C=O, sulfonic and sulfonyl groups, is predominant. Nevertheless, it is plausible to think that the signal of this component must come mainly from sulfonic and sulfonyl groups as the content of C=O groups is not large, as we have just commented on the basis of the C1s spectrum [13,32,33]. The O 1s spectrum also contains a component at 533.1 eV due to C–O groups and a very small component at 535.1 eV due to COO[–] and H₂O. The deconvolution of the S 2p spectrum (Fig. S2 in SI) shows the two components (1/2 and 3/2) due to spin-orbit coupling of the sulfur containing groups. The ATR-FTIR spectrum (Fig. S3 in SI) also supports the above comments on the oxygen containing groups and on the presence of sulfur derivatives.

As commented above, we have tried to reduce the original GO_{GN} with hydrogen cold plasma. It is known the main species in hydrogen cold plasma are, among others, H, H⁺, H[–], electrons and radiation [34]. Thus it is expected the reducing character of the species present in this plasma can be able to remove oxygen. We have studied the effect of the time of treatment (between 1 and 10 min) and of the source power (500 and 700 w). The composition of the samples after the plasma treatment is shown in Table 1. Several conclusions can be drawn from

Table 1
Composition of GO_{GN} and samples after the different treatments.

Sample	C (%)	O (%)	S (%)	N (%)
GO _{GN}	67.1	29.1	3.1	0.7
GO _{GN} -pH2-1[500]	69.5	27.3	2.8	0.4
GO _{GN} -pH2-5[500]	71.9	23.8	2.8	1.5
GO _{GN} -pH2-10[500]	67.8	25.1	3.9	3.2
GO _{GN} -pH2-1[700]	68.4	28.9	2.7	
GO _{GN} -pH2-5[700]	72.6	23.5	2.6	1.3
GO _{GN} -pH2-10[700]	68.6	26.4	2.8	2.2
GO _{GN}	67.1	29.1	3.1	0.7
GO _{GN} -H ₂ O	78.1	21.9	0.0	0.3
GO _{GN} -H ₂ O-pH ₂ -5[700]	87.3	12.7	0.0	1.3

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