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Nitrogen Radiofrequency Plasma Treatment of Graphene

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The incorporation of nitrogen (N) atoms into a graphitic network such as graphene (Gr) remains a major challenge. However, even if the insertion mechanisms are not yet fully understood, it is certain that the modification of the electrical properties of Gr is possible according to the configuration adopted. Several simulations work, notably using DFT, have shown that the incorporation of N in Gr can induce an increase in the electrical conductivity and N acts as an electron donor; this increase is linked to the amount of N, the sp^2/sp^3 carbon configuration, and the nature of C–N bonding. Nitrogen radio-

frequency (RF) plasma has been used to incorporate N into Gr materials. The RF plasma method shows the possibility to incorporate N-graphitic nitrogen into Gr after a pre-treatment with nitric acid. X-ray photoelectron spectroscopy and Raman spectrometry were used to quantify the functionalized groups. The modifications of the graphene surface chemistry along the amount of N inside the Gr change the chemical environment of N. This method, enabling the incorporation of N inside Gr matrix, opens up a route to a broad range of applications.

Introduction

Graphene (Gr) and its variants are materials theorized in 1947 by Philip R. Wallace. These materials seemed to be only a fantasy due to their thermal agitation,^[1] since 2D materials were considered to be unstable at room temperature. However, in 2004, Geim and Novoselov^[1] achieved what seemed impossible by isolating a mono-atomic layer of carbon by mechanical exfoliation of a graphite crystal. The great attraction of scientists for this 2D material comes from the sp^2 hybridization of carbon atoms^[2] generating the non-bonding p_z orbital directed perpendicular to the graphitic plane. The formation of the π – π^* bonds involving p_z orbitals are at the origin of the amazing electronic properties of graphene.^[3,4] Therefore, Gr has a singular band structure with the behaviour of a zero-gap

semiconductor. These Gr particularities are the origin of the exceptional electrical ($200\,000\text{ cm}^2/\text{Vs}$,^[5,6]), thermal (5600 W/mK ^[7]), and mechanical properties (1 TPa Young's modulus and 130 GPa tensile strength^[8]). For these properties, Gr has been used as a reinforcement in different kinds of composite materials such polymers, metals, and ceramics.

Due to its excellent thermal (thermal conductivity (TC) close to 400 W/mK) and electrical (electrical conductivity (EC) close $58.5\cdot 10^6\text{ S/m}$, and electron mobility of $33\text{ cm}^2/\text{Vs}$) properties, copper (Cu) is often used for heat sinks and electrical conductors (electric industries).^[9] In electronic industries, different forms of carbon (carbon fibre, graphite flake and diamond powder) are added to Cu to improve the TC of Cu and lower its thermal expansion coefficient. For the electric industries, the increase of the EC for metals like Cu and aluminium is a major challenge. Carbon nanotubes (CNT) and Gr are the only materials which show ECs higher than that of Cu.^[5,6,10]

In composite materials (polymer, ceramic or metal based), the transfer of properties between the matrix (M) and the reinforcement (R) is mostly linked to the properties of the M–R interfacial zone involving chemical bonds between M and R. For a non-reactive system (absence of chemical bonds between M and R) like Cu–Gr, the surface treatment of R is one option to switch from a non-reactive system to a reactive one.^[11]

The most common surface treatment of carbon species like CNTs or Gr is the covalent functionalization. Different acids such as nitric, hydrochloric, and orthophosphoric acids can be used to graft oxygen groups on the surface of CNTs or Gr as can be found in the well-known Hummer method.^[12] However, the main limitation of this method is the degradation of the graphitic network due to the rupture of C–C bonds to form C–O, C=O, and O–C–O bonds. Softer techniques like radio-frequency (RF) plasma (power $< 30\text{ W}$) have also been used. This technique is not very conventional but some works linked to Gr surface modifications can be found in the literature.^[13] X. Li

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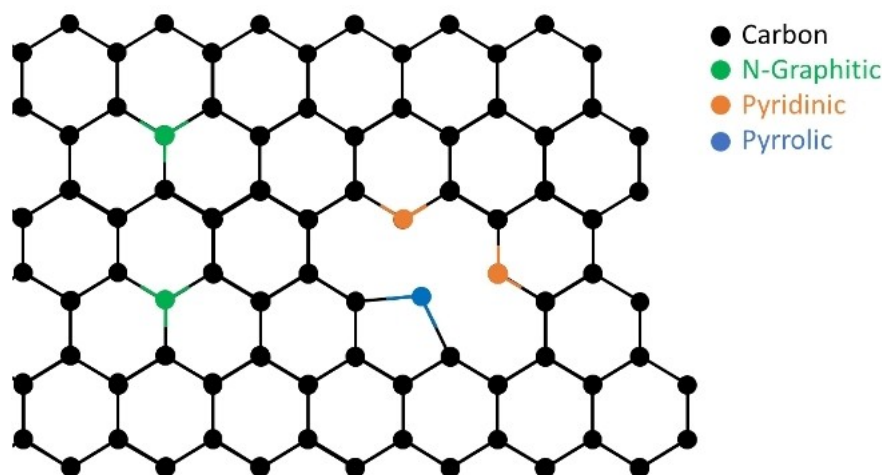


Figure 1. Various configurations of N doping in Gr network.

et al.^[14] compared N₂ and NH₃ RF plasma treatment of Gr. The authors observed that N atoms configurations should be quite different, modifying its electronic properties.

Within the graphitic network, different nitrogen configurations can be obtained which can lead to p- (by increasing the hole density) or n-doping (by increasing the electron density).^[15, 16] Actually, depending on the configuration of N, the electronic density near the Fermi level is different. With a majority of N-graphitic (green atom Figure 1), a simple substitution of a nitrogen atom for a carbon atom leads to an increase of +0.64 e (electron) per nitrogen atom. Otherwise, with N-pyridinic and pyrrolic configurations (orange and blue atoms Figure 1), the presence of one or two holes in the graphitic network can be detected, leading to a decrease in the electron density of −0.4e per nitrogen atom (according to DFT calculations^[17]).

In this work, we developed an original surface treatment of Gr to incorporate nitrogen atoms in the N-graphitic configuration for improving the intrinsic EC of Gr. Another objective of this study was to investigate the interface properties between a metal such as Cu and Gr through the creation of chemical bonds in between. Experimental conditions of N-RF plasma doped Gr were optimized. The control of the surface modification was followed by Raman and X-ray photoelectron spectroscopies. The N-doped Gr was used for the fabrication of Cu/Gr composite materials for the investigation of EC and mechanical properties.

Results and discussion

Acid treatments

MLG is known for its chemical inertness. Therefore, a modification of its surface chemistry is necessary, with a functionalization step to allow the insertion of nitrogen atoms. In this study, nitric and orthophosphoric acids (HN and HP, respectively) were used. The functionalization was carried out in a reflux heating setup at 90 °C, under magnetic agitation during different times

ranging from 30 to 150 min. XPS and Raman analyses were performed to characterize the surface chemistry of the MLG after the acid treatments.

The XPS survey spectra and the semi-quantitative analysis are respectively presented in Figure 2 and Table 1, shows that, in the case of the HN treatment, no insertion of oxygen or other elements (even nitrogen) were observed. However, in the case of HP treatment, a high amount of oxygen (11.5 at.%) and phosphorus (3.0 at.%) are incorporated after 30 min of treatment. The presence of oxygen groups on the surface of the MLG, after functionalization, is an advantage for improving its reactivity.

However, the presence or absence of additional chemical groups does not imply that the Gr carbon network has undergone a significant chemical modification. For this reason, XPS analysis of the high-resolution spectrum of the C_{1s} was carried out to follow the evolution of the chemical bonding involving carbon (%C_{sp2}, %C_{sp3}). Full spectra and high-resolution spectra obtained were fitted using the AVANTAGE software provided by ThermoFischer Scientific®. Scofield sensitivity factors were used for quantification.^[18,19]

For the deconvolution of XPS spectra, the commonly accepted C_{sp2} was placed at 284.4 eV. The C_{sp3} was then

Table 1. Evolution of the atomic percentage present in different MLGs after various HN and HP treatment times.

Acid	Time (min)	C (%)	O (%)	P (%)
Initial		98.4	1.6	/
HN	30	98.5	1.5	/
	150	98.5	1.5	/
HP	30	85.5	11.5	3.0
	60	76.0	18.6	5.4
	90	78.6	16.7	4.6
	120	79.0	16.5	4.5
	150	77.2	17.8	5.0

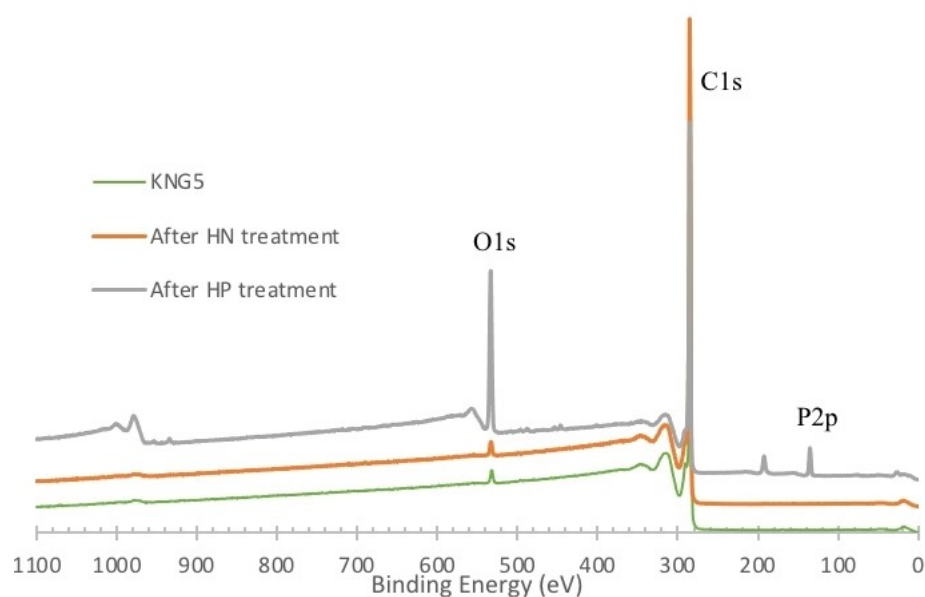


Figure 2. XPS survey spectra of initial Gr and after HN and HP treatments.

positioned at a binding energy of 0.6 eV higher compared to the C_{sp2} .^[18] The following contributions were assigned, making sure to have 1 eV difference between each of them. The peak analysis and quantification to the initial MLG are presented in Figure 3.

In the case of the HN treatment, it can be seen, through the evolution of the at.% C_{sp2} and the ratio of C_{sp2}/C_{sp3} , that the amount of sp^2 hybridized carbon increased (Table 2). This increase is not due to a “restoration” of the graphitic network of the MLG, but rather due to elimination of surface carbon

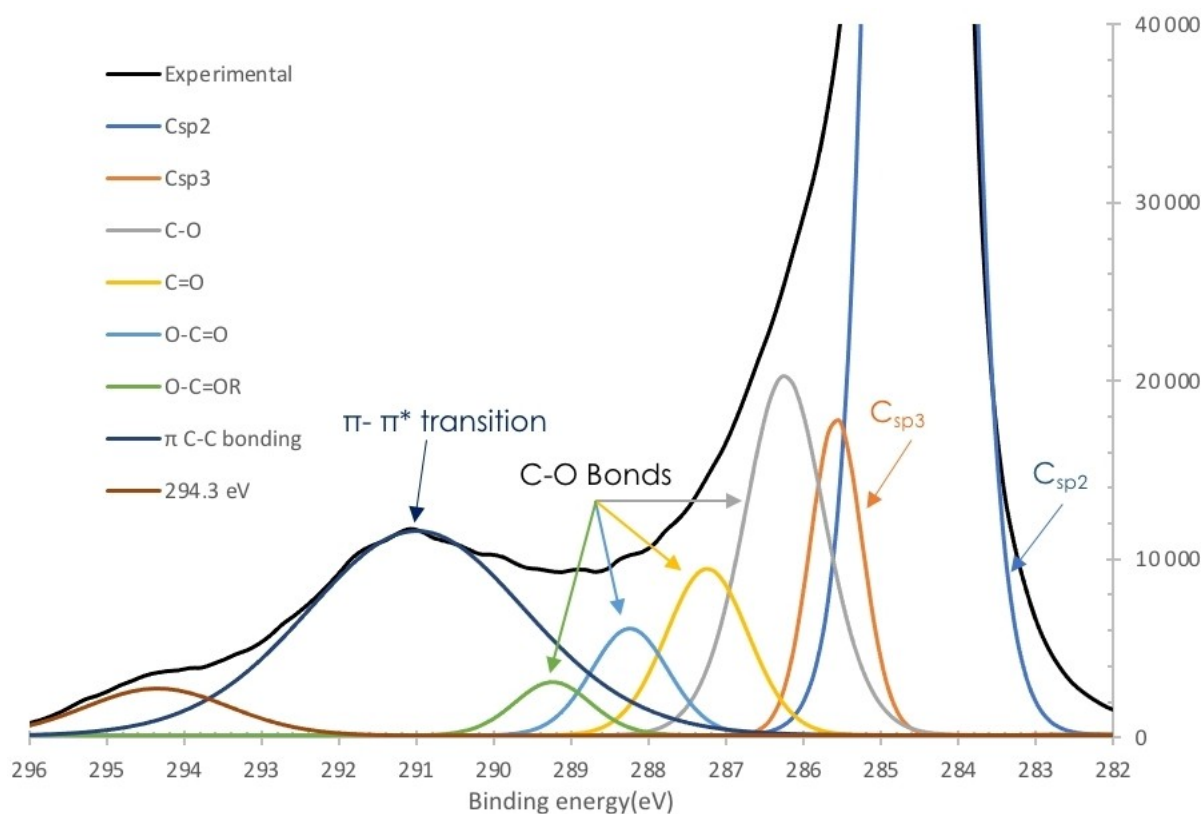


Figure 3. Deconvolution of a high-resolution C1s peak of MLG.

Table 2. Evolution of C_{1s} contributions after different HN and HP treatment times (thanks to the addition of the C–O bonding contribution/percentage to reach 100%).

Acid	Time (min)	Chemical environment (at.%)			
		C_{sp2}	C_{sp3}	C_{sp2}/C_{sp3}	π bond
Initial		69.0	6.7	10.3	9.3
HN	30	70.5	5.3	13.4	8.6
	150	73.0	4.5	15.1	7.6
HP	30	74.0	4.2	17.8	6.5
	60	71.7	6.9	10.3	6.5
	90	73.1	5.2	13.9	6.7
	120	73.6	4.5	16.4	6.9
	150	72.6	6.8	10.7	5.9

contamination (C_{sp3} or amorphous C). Knowing that the XPS analysis in depth does not exceed a few atomic layers, the quantity of C_{sp2} analysed increases by eliminating the surface carbon contamination.

In the case of the HP treatment, the proportion of sp^2 hybridized carbon increases sharply during the first 30 min of the treatment, with a stabilization thereafter (Table 2). We also observed a strong decrease in the proportion of π – π conjugated bonds (greater than that after nitric acid treatment), indicating a deterioration of the graphitic network. This increase can be explained by the removal of surface carbonaceous contamination (C_{sp3} or amorphous C). This increase in the proportion of C_{sp2} overlaps with an increase in the quantity of oxygen, showing that it also contributes to eliminating the contamination. With the increase of the treatment time, an oscillation (decrease then increase) of the C_{sp2}/C_{sp3} ratio was also observed. This could be explained that, with the increase of the treatment time (60 min), the insertion of oxygen generates degradation of the network. Beyond one hour of the treatment, however, the sp^2/sp^3 carbon layer (i.e., a sheet of our MLG) ends up being eliminated. The signal analysed corresponds to the second layer of the graphitic network, which is less deteriorated. We can also notice a peak at 294.3 eV; unfortunately, we could not identify the source of this contribution.

To analyse the potential degradation of the C network induced by the acidic treatments, Raman spectroscopy analyses were also performed. Commonly, the ratio between the D (corresponding to a vibrational mode of the aromatic cycles of sp^2 carbons, which can occur in case of deterioration) and the G bands (corresponding to in-plane vibrations involving sp^2 carbons) was used to quantify defects in the MLG. The I_D/I_G ratio suggests that the intensity of the G band is independent of the presence of defects. However, the work by J. Maultzsch et al.^[22] has shown that this is not always the case. Therefore, it is necessary to normalize the first-order signals by the second-order signal (which is insensitive to the defects) to better reflect the defects. That is why the ratio I_D/I_{2D} has been proposed to be considered because the intensity of the 2D band is not sensitive to the defects.

Therefore, the I_D/I_{2D} ratio was investigated (instead of the I_D/I_G ratio) to ensure a better sensitivity to the defect evolution.^[20]

The results of these analyses and Raman spectra are presented in Table 3 and Figure 4. After HN the treatment, the MLG shows a decrease of the intensity of the D band, like the defect ratio (I_D/I_{2D}). The same as before, due to the removal of the surface contamination, the MLG exhibits a less damaged graphitic network. This result is consistent with the results obtained by the XPS analysis. In the case of the HP treatment, a higher value of the defect ratio was observed than with the 30 min HN treatment, due to the insertion of oxygen and phosphorous (even if the contamination has been removed) atoms. An increase followed by a decrease in the defect ratio was then induced by the successive degradation of the graphene layers.

In view of the results obtained, low treatment times (30 min) were kept. First of all, this surface treatment allows an elimination of the carbon contamination with both acids, but also a sufficient oxygen grafting (11.5 at.%) in the case of the HP treatment. This difference in surface chemistry is very important because it can lead to various N-graphitic, N-Pyridinic and N-Pyrrolic bonding's (Figure 1) after N-doping by the RF plasma treatment.

Nitrogen doping

For the nitrogen doping of the MLG, several treatments were performed with the variation of two parameters. First, five samples were prepared by varying the treatment times under the nitrogen RF-plasma for 10 s, 1, 2, 10, and 60 min. Two other samples were produced with a treatment time of 60 min and pre-treated with nitric and orthophosphoric acids as previously described.

Surface analysis (XPS)

Table 4 shows the atomic composition of the MLG, based on the XPS analysis and quantification, after different processing times. For the non-pretreated MLG, independent of the treatment time, N is present only with a trace amount, below the detection limit of the XPS analysis. There are two possible explanations for the absence of nitrogen in the material. Firstly,

Table 3. Evolution of the I_D/I_{2D} ratio after the HN and HP treatments.

Acid	Time (min)	I_D/I_{2D}
Initial		0.55
HN	30	0.26
	150	0.33
HP	30	0.50
	60	0.74
	90	0.22
	120	0.38
	150	0.24

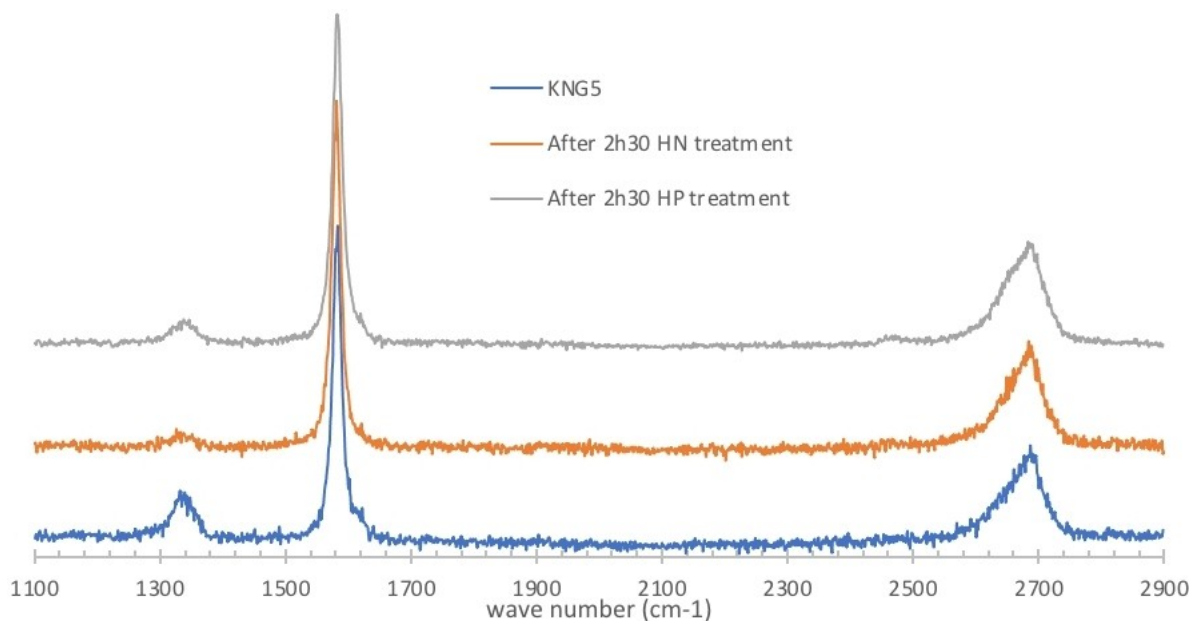


Figure 4. Raman spectroscopy of graphene KNG5 and after HN/HP treatment of 2 h30.

Table 4. Evolution of the composition in atomic percentage of different MLGs after N₂ RF-plasma treatments.

Pre-treatment	RF-plasma treatment time	%C	%O	%N
Initial		98.4	1.6	0
/	10 s	97.3	2.6	0.1
	1 min	98.7	1.2	0.1
	2 min	98.3	1.6	0.1
	10 min	97.9	2.0	0.1
	60 min	97.6	2.3	0.1
HN 30 min	0	98.5	1.5	0
	60 min	96.3	3.4	0.3
HP 30 min	0	85.5	11.5	0
	60 min	88.5	11.3	0.2

it may be due to the no chemical reactivity of graphene's surface, and we use low-power plasma to limit material degradation. Secondly, the presence of the carbon contamination can also limit the insertion of nitrogen, so it needs to be eliminated (as seen previously). The oxygen content slightly increases with the treatment time. The oxidation of the MLG is due to the oxygen partial pressure present inside the reaction chamber.

As seen previously, to increase the MLG surface reactivity, 30 min functionalization pre-treatments were performed using HN and HP. XPS analyses carried out upstream showed that this treatment allows the elimination of carbon contamination presented on the surface of the MLG, and the incorporation of oxygen (only for HP treatment).

To maximize the incorporate of nitrogen in the N-graphitic configuration, 1 h RF-plasma treatment was applied to the MLG. XPS analysis of the survey highlights the presence of a nitrogen

quantity of 0.3 and 0.2 at.% with HN and HP, respectively (Table 4). With this amount of nitrogen, the major N atom configuration can be determined by deconvolution of the N_{1s} high-resolution peak. It is possible to correlate a binding energy to a chemical environment. The different nitrogen environments are N-pyridinic, N-pyrrolic, N-graphitic, and N–O at the binding energies of 398.4, 399.3, 400.5, and 401.8 eV, respectively.^[21] Figure 5 represents the deconvolution of the high-resolution N_{1s} peaks of the pre-treated MLG with a RF-plasma processing time of 1 h.

For the MLG pretreated with HP, the deconvolution shows three major contributions where the major one is found at 401.1 eV. At this binding energy, nitrogen binds mainly to oxygen atoms with a formation of amine function. A pre-treatment with HP is therefore not the most suitable way for the targeted application.

For the MLG pretreated with HN, the main configuration adopted by nitrogen is the N-graphitic bonding (binding energy close to 400.4 eV). This configuration is more favourable to improve the density of the load carriers for an improved MLG.

Characterisation of structural defects (Raman spectroscopy)

Raman analyses were carried out to determine if functionalization and RF-plasma treatments could induce defects in the network. Table 5 shows the results obtained.

N₂ plasma treatments do not seem to cause additional defects in the graphitic network after the acidic pre-treatment. This result is consistent with the fact that a very small quantity of nitrogen was inserted and therefore very little change was made to the graphitic network. The decrease in the I_D/I_{2D} Raman ratio, after the nitric acid treatment, is consistent with the XPS analyses. Indeed, the removal of carbon contamination leads to

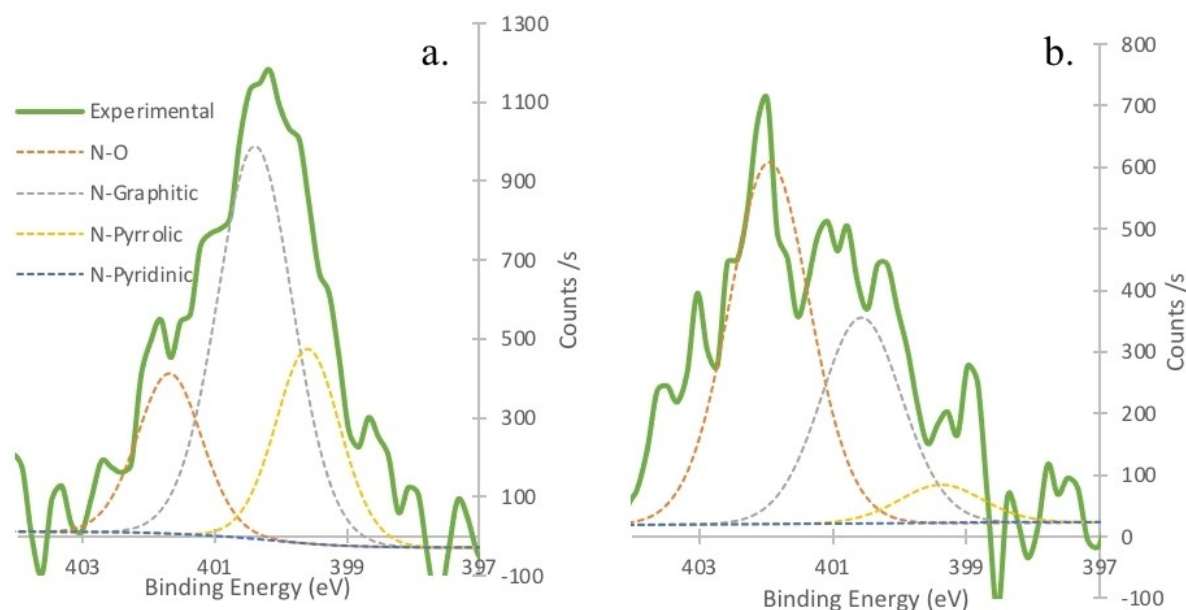


Figure 5. N1s high-resolution spectra after surface treatment of the MLG pretreated with: a) HN and b) HP treatments.

Table 5. Evolution of the I_D/I_{2D} ratio after various treatments.	
Treatment	I_D/I_{2D}
Initial	0.55
HP	0.50
HP + Plasma	0.47
HN	0.26
HN + Plasma	0.24

a decrease in the proportion of sp^3 or amorphous carbon and thus the reduced I_D/I_{2D} ratio.

Conclusions

A method of grafting nitrogen into the MLG graphitic network has been developed using a low-energy nitrogen RF-plasma without causing major graphene deterioration. However, the inertness of this material does not allow a direct insertion of nitrogen more than a trace amount. Two pretreatments using nitric and orthophosphoric acids were carried out. The orthophosphoric acid treatment allows the removal of carbon contamination on the graphene surface and the incorporation of a large amount of oxygen. This induces the insertion of nitrogen due to the presence of a large amount of oxygen, which is not favourable for the desired properties. Indeed, the nitrogen configuration leads to a decrease in the density of the charge carrier at the Fermi level. However, in the case of the treatment using nitric acid, only surface contamination is eliminated with no grafting of any chemical groups, which permits the insertion of nitrogen atoms in the N-graphitic configuration, leading to the increased the density of the charge carriers in the MLG. The surface-treated graphene is

promising as a reinforcement in a metal matrix composite such as Cu, to be used to improve the electrical properties, in particular by reducing electrical resistivity.

Experimental Section

Raw materials

Dendritic Cu powder with an average length of 50 μm and a diameter of 10 μm was purchased from ECKART. This powder was used as received without further treatment. Multilayer Gr powder (MLG) with a lateral size of 5–10 μm and an average thickness of 2–3 nm, i.e., 3–9 atomic layers, were bought from KNANO company. This MLG was prepared with a chemical exfoliation method.

RF-Plasma N-doped Gr

RF-plasma treatment using nitrogen as a precursor gas, is currently employed for etching and polymerization processes in micro-electronics and material science. Nitrogen was used as the gas a dopant to limit the formation of toxic substances such as cyanuric acid, which can be obtained using ammonia. As these substances cannot be filtered, this precursor will not be used. Nitrogen gas is also more suitable for nitrogen substitution, forming better configuration (as N-graphitic) to improve the electrical properties. In the treatment, about 20 mg of the MLG powder was placed in the centre of the enclosure on a flame-retardant paper. In a vacuum of 100 mTorr, nitrogen was introduced into the chamber with a controlled pressure difference, before and after introduction (150, 300 and 600 mTorr in this study), several treatment times are used, ranging from 10 seconds to 60 minutes. The plasma was then generated by applying a potential difference between two plates via an 80 W RF generator. The use of low-power RF generator is to minimize damage to the MLG. This allows a treatment close to room temperature (close to 25 °C). The uniformity of the treatment is verified through the utilization of three zones for XPS analysis.

Material characterization

Surface analyses were carried out using X-ray Photoelectron Spectroscopy (XPS) with a Thermo Scientific K-Alpha with an Al K α X-ray source and a spot size between 30 to 400 μm . Horiba XploraTM PLUS Raman Spectrometer was also used with a laser wavelength of 633 nm which is the more appropriate for Gr analysis.

Data and materials availability

All data needed to support the conclusions in the paper and the datasets generated during the current study are available from the corresponding author on reasonable requests.

Author Contributions

The work was completed through contributions of all authors. All authors have given approval to the final version of the manuscript. The individual contributions are: supervision and conceptualization: Jean-François Silvain, Nathalie Caillault, Florence Delange; manuscript writing: Jean-François Silvain, Yongfeng Lu/Antoine Bident; material elaboration and characterizations: Antoine Bident, Christine Labrugere, Guillaume Aubert, Cyril Aymonier, Etienne Durand, Alain Demourgues

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Conflict of Interests

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords: Graphene · Nitrogen · Plasma chemistry · Surface analysis

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