

Caffeine as a source for nitrogen doped graphene, and its functionalization with silver nanowires in-situ

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Abstract. In this work, we report the use of caffeine as an alternative source of nitrogen to successfully dope graphene (quaternary 400.6 eV and pyridinic at 398 eV according XPS), as well as the growth of silver nanowires (in-situ) in the surface of nitrogen doped graphene (NG) sheets. We used the improved graphene oxide method (IGO), chemical reduction of graphene oxide (GOx), and impregnation with caffeine as source of nitrogen for doping and subsequently, silver nanowires (NW) grow in the surface by the reduction of silver salts in the presence of NG, achieving a numerous of growth of NW in the graphene sheets. As supporting experimental evidence, the samples were analyzed using conventional characterization techniques: SEM-EDX, XRD, FT-IR, micro RAMAN, TEM, and XPS.

Keywords: caffeine; nitrogen-doping; graphene; nanowires; functionalization; pyridinic; monolayer; synthesis; carbon nanostructures; nanomaterials

1. Introduction

Graphene is a two-dimensional material that consists only of carbon atoms. The arrangement is composed by a packed covalently bonded honeycomb lattice. Since the report of the synthesis of graphene in 2004, developed by Geim and Novoselov (2007), the scientific community has developed a series of studies about the fascinating, superlative and unique properties of this material such as high electrical conductivity (Wu *et al.* 2009, Shin *et al.* 2009), quantum hall effect at room temperatures (Kane and Mele 2005, Novoselov *et al.* 2007, Castro *et al.* 2009), high surface area (Liu *et al.* 2010, Ning *et al.* 2011), charge transfer (Schedin *et al.* 2007, Kong *et al.* 2010), atomic interactions with molecules (Schedin *et al.* 2007, Su *et al.* 2009, Lazar *et al.* 2013), high thermal conductivity (Balandin *et al.* 2008, Pop *et al.* 2012, Sadeghi *et al.* 2012), and high transmittance (Zhu *et al.* 2014). This nanomaterial can be considered as the constructor block or a unit base to build other carbon allotropes such as zero dimensional fullerene, a one dimensional structure known as carbon nanotube, or a tridimensional graphitic structure (Rao *et al.*

2009), each of them with specific properties and applications. Aside from the superlative properties of the intrinsic graphene which means it is only composed by carbon atoms or with the changes of properties attributed to the defects in the basal plane as free links, properties of graphene can also be modified by the inclusion of other elements in their carbon basal structure plane. Hence, the main focus of the present work is to be able to find an easy route to dope graphene with nitrogen atoms. The doping with foreign atoms in other carbon allotropes such as in fullerenes (Martin *et al.* 1992, Li *et al.* 2013), and carbon nanotubes (Terrones *et al.* 2008), shows that the incorporation of different atoms in the hexagonal carbon lattice results in a change of physical and chemical properties of the nanostructure, as reported with nitrogen (Leela *et al.* 2010, Shao *et al.* 2010, Sheng *et al.* 2011), phosphorous and boron (Jo *et al.* 2015, Lin *et al.* 2016), or hetero-doping (Audiffred *et al.* 2013). So far there are three known doping types for this which have been reported by different research groups: (i) pyridinic doping (Zamudio *et al.* 2006); (ii) graphitic or substitutional doping; and (iii) pyrrolic doping (Luo *et al.* 2011). Each one has a certain quantity of atoms that can be included in the carbon hexagonal network by some experimental techniques and nitrogen sources. One of the most important modifications in doping is the change of electronic properties. When graphene is doped, the new properties depend of the kind of

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atom and type of doping (Pearson 2010, Vinayan *et al.* 2013). Regarding the study of the doping in graphene sheets, XPS is one of the most useful tools for the characterization and to determine the type of doping (Luo *et al.* 2011, Podila *et al.* 2012, Tison *et al.* 2015). In the present manuscript, we have selected the nitrogen atom as a doping element in order to promote sites in the sheet with reactivity as reported by (Wang *et al.* 2010, Geng *et al.* 2011). One goal in this work is the N insertion in the hexagonal network of atoms during the impregnation process with caffeine, and the subsequent thermal annealing in argon atmosphere, as reported in single wall nanotubes by Filippo *et al.* (2017). Another important issue is the fact that the nitrogen atom in the sheet induces structural defects in the honeycomb lattice that, in a certain percentage concentration, modifies the crystallinity of the material, and subsequently new intrinsic properties arise in the graphene (Wang *et al.* 2010, 2012).

The nitrogen doped graphene has different physical-chemical properties in comparison with intrinsic graphene, due to the charge distribution being influenced by the nitrogen dopant and the doping type (graphitic, pyridinic or pyrrolic). Furthermore, insertion of a foreign atom in the 2D network favors the generation of activated sites to promote cluster nucleation for the growth of nanostructures, or the use of it as template for anchoring different elements or molecules in order to produce hybrid or functional nanomaterials (Shao *et al.* 2010, Wang *et al.* 2012, Sun *et al.* 2012). As for the synthesis, there are two main routes to fabricate doped graphene: Direct Doping Synthesis or bottom-up synthesis such as CVD (chemical vapor deposition) that involves high temperatures, a hydrocarbon source, inert atmosphere and high quality copper substrates (Leela *et al.* 2010), and MBE (molecular beam epitaxy) which involves ultra-high vacuum and a hydrocarbon source. The sheet quality is very high but the yield of product is very poor and its cost is high. Another method is Plasma treatment that involves strong magnetic fields for ion implantation. This method has a low rate of production and it is a little less expensive compared to the MBE technique. It is important to note that, most of the time, these methods need special and costly infrastructure. There are other synthesis methods known as Doping Post Treatment or Top-Down methods and the most used are: Arc-discharge which employs two electrodes, a controlled atmosphere and high electrical currents; and Ball Milling, which employs high energy to grind up graphite and mix it with the doping source in order to promote the atom bonding in the defects of graphene sheets. Another important method that is cheap and friendly for the synthesis of nitrogen doped graphene is the Hydrothermal Method or Wet-Chemical Method. With this we can obtain high yield but it involves autoclave reactors and in most of cases, dangerous doping sources (Leela *et al.* 2010, Sun *et al.* 2012). There are other methods that can use urea, ammonia and hydrazine (Geng *et al.* 2011, Wang *et al.* 2009, Long *et al.* 2010, Wu *et al.* 2012), and caffeine for N doping in single wall carbon nanotubes in a CVD experimental setup (Filippo *et al.* 2017). In our case, the goal for NG is the use of a combination of wet chemical

method using caffeine to impregnate nitrogen into the graphene sheets, and also the use of a low temperature heat treatment over a relatively short time. We used the IGO method (Marcano *et al.* 2010) to synthesis graphene oxide, then we dissolved the nitrogen source (caffeine) in order to GOx impregnate via a hydrothermal method. Then at a temperature (600°C), heat treatment was conducted in a reductive atmosphere (Ar-H 50%). Subsequently, after doping with nitrogen, we carried out the synthesis of silver nanoparticles, and we found that nanowires grew on the surface of NG, meanwhile spherical nanoparticles grew up in the reduce graphene. These experiments for the surface functionalization were carried out using an ethylene glycol reflux and silver salts (Caswell *et al.* 2003, Nair *et al.* 2018, Ji *et al.* 2018), using the NG as a support matrix. It is important to mention that some interesting applications for this material (NWNG) are focused on its use as electrodes for energy storage or catalysis.

2. Experimental section

Graphene oxide GOx, reduced graphene RG impregnated with caffeine, nitrogen doped graphene NG and silver nanowires functionalized nitrogen doped graphene NWNG were synthesized as follows:

2.1 Materials

The materials used in this study were purchased from Sigma Aldrich as reagent grade and used as is, graphite flakes CAS 7782-42-5, H₂SO₄ CAS 7664-93-9, H₃PO₄ CAS 7664-38-2, KMnO₄ CAS 7722-64-7, AgNO₃ CAS 7761-88-8, C₈H₁₀N₄O₂ CAS 58-08-2, PVP wt30k CAS 9003-39-8, 30% H₂O₂, and distilled water.

2.2 GOx synthesis

For the synthesis of graphene oxide, we carried out a method as described by Marcano *et al.* (2010). Our first stage product was a dark brown slurry containing 3%-6% in solids.

2.3 Caffeine GOx impregnation and chemical reduction

A hydrothermal experiment was carried out in order to dissolve 1,3,7 trimethylxanthine (caffeine) and impregnate the entire GOx surface, as follows. 150 mg of GOx was added in flask ball with 150 ml distilled H₂O. The solution was mixed at 600 rpm for 30 min and ultrasonic dispersion (40 kHz/150 W) was applied at the same time in order to keep a homogeneous amber colloidal solution. Using a hot stirrer plate, the temperature was increased to 90°C while stirring at 300-400 rpm. Then the solution was added to in the following order: caffeine 15 mg, ethylene glycol 15 ml and reducing agent NH₄OH 15 ml. The reaction was kept in a reflux mode for 90 min before finally, the solution turned black. After the impregnation processes with caffeine, the reduced graphene RG was filtered and dried in oven at 70-80°C for 4 hours.

2.4 Nitrogen doping

NG was obtained as follows. The RG impregnated with caffeine was annealed at 650°C for 30 min under a reductive atmosphere composed by a mixture of gases in equal proportions Ar/H 50-50, in a quartz tube reactor.

2.5 NG Silver NW functionalization NWNG

In a three necked flask, 150 mg NG was added to 150 ml ethylene glycol in a reflux setup. The solution was heated at 150°C and was stirred at 800-1000 rpm. After this process 50 ml ethylene glycol solution with polyvinylpyrrolidone (PVP) with a concentration of 0.6 M, and AgNO₃ with a concentration 0.1 M, were simultaneously dripped into the main solution and kept in reflux and mixing for 180 min. The final product was filtered and dried in a convection oven at 90°C for 3 hours.

2.6 Characterization

The characterization was carried out with the following techniques: X-Ray Diffraction (XRD) in a Bruker D8 Advance diffractometer. The vibrational characteristics of the samples were analyzed in a HORIBA Xplora Plus Raman spectrometer using a 0.5 mW-1 mW 785 nm laser. Morphological and chemical composition characteristics were determined with the following electron microscopes: scanning electron microscope JEOL 6610LV equipped with EDS Oxford. Transmission electron microscopes (TEM/STEM) JEOL 2100 200 kv LaB₆ with EDS Oxford. Functional groups were determined using a Thermo Scientific i550 Nicolet ATR/FTIR spectrometer for powders. X-ray photoelectron spectroscopy XPS was used to analyze the type of the nitrogen doped graphene.

3. Results and discussion

3.1 Morphology of GOx and NG

SEM micrographs of the pristine material (graphite flakes) show that the lateral size of the samples was 1 mm size and 20 μm of average thickness (see Figs. 1(a) and (b)), that is equal to 60,000 stacked sheets of single layers. The FTIR spectra in Fig. 1(c) shows there are the following functional groups in GOx: C-O at 1037 cm^{-1} , OH at 1308 cm^{-1} , C=C at 1621 cm^{-1} , OH at 1673 cm^{-1} , and COOH at 2518 cm^{-1} . All of them promote changes in the interlayer distance that results in a facile route for exfoliation to obtain GOx single layers due the decrease of attraction forces (energy) between neighboring planes. TEM micrographs, Fig. 1(d), shows a large thin sheet of GOx composed by very thin continuous layers. The micro RAMAN spectra in Fig. 2(a) compares graphite, GOx and NG. For graphite the spectrum shows the typical G band at 1574 cm^{-1} , it is a first order vibration of the layers. Meanwhile for GOx and NG, the spectrum shows two characteristic peaks, the G band at 1597 cm^{-1} and the D band at 1350 cm^{-1} , that confirms the change in the surface of basal planes due the oxidation and functional groups attached for GOx, and the doping. In the

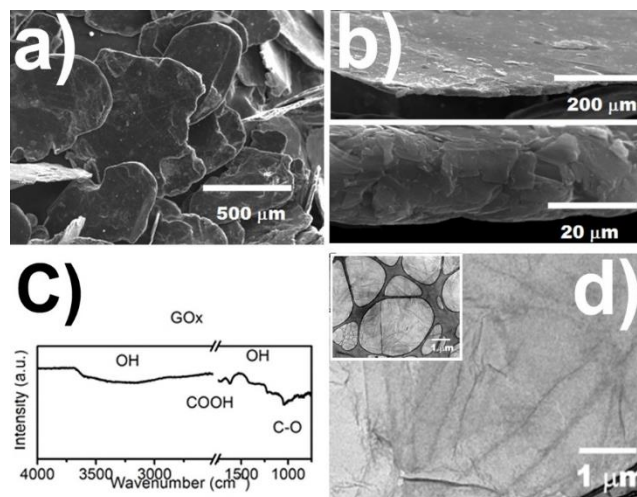


Fig. 1 SEM micrographs of pristine graphite and subsequent GOx (a) low magnification graphite flakes; (b) cross view of a graphite flake; (c) FTIR of GOx showing its functional groups; (d) TEM image that shows the morphology of GOx sheets before caffeine impregnation

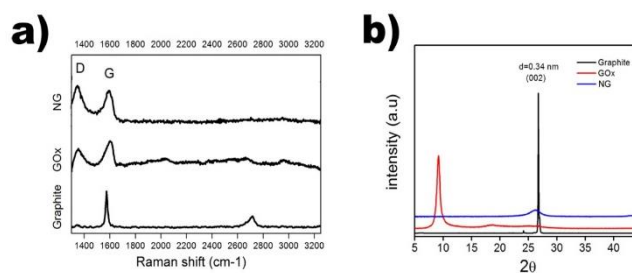


Fig. 2 Pristine Graphite, subsequent GOx and Graphene after doping (a) the RAMAN spectra for GOx showing D band and G band that are the result of the change of atom positions due the intercalation, and subsequent treatment for reduction and doping; (b) XRD of Graphite, GOx and NG; the main peak of GOx is the shift due the increment of interlayer distance in plane (002), from 0.34 nm to 1.2 nm due the oxygen and functional groups intercalation

XRD analysis, Fig. 2(b) shows a comparison between pristine graphite, GOx and NG. In the graphite the main peak of intensity at $2\theta = 26.1^\circ$ corresponds to the planes [002], with an interlayer distance $d = 0.34$ nm, meanwhile for GOx, the main peak is at $2\theta = 10^\circ$, that corresponds to the interlayer distance $d = 1.2$ nm. This peak shift is due the oxygen and functional groups intercalation in the graphite interlayers (OH and COOH groups) as a result of the treatments with strong acid agents. For NG, a peak with a very low intensity at $2\theta = 26.1^\circ$ corresponds to the planes [002], with an interlayer distance $d = 0.34$ nm, due the rearrangement of the sheets due to the heat treatment.

3.1.1 Characterization of nitrogen doped graphene (NG)

The study of the obtained material was carried out as

follows: the NG morphology was analyzed by SEM. Fig. 3(a) shows large sheets, some of them apparently free from agglomerates. An important result is that there are no other particles or crystals over the surface of the sheets, and the morphology is similar to the GOx which means that the change in the graphene sheets is at the atomic level in the hexagonal honeycomb structure due the intercalation of nitrogen atoms. TEM characterization shows isolated slim sheets with a structure and morphology similar to GOx sheets. According to the EDX chemical analyses, the nitrogen detected in the sample is 9.3 wt.% (Fig. 3(b)). This indicates that we have a large percentage of doping using caffeine as a nitrogen source, and our results correspond to that reported by Filippo *et al.* (2017). At this point it is important to mention that this method involves an easy experimental set-up and a low toxic nitrogen source. According to Rao *et al.* (2014) there are several methods to produce nitrogen doped graphene that involve an expensive experimental setup, such as CVD, ball milling, plasma enhanced CVD, and Arc-discharge, and these also involve

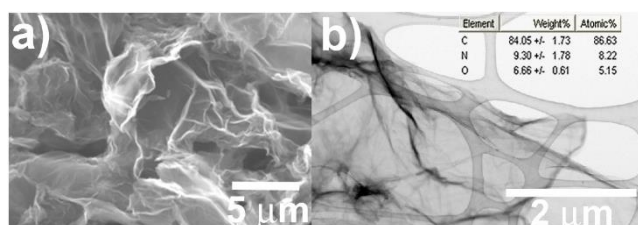


Fig. 3 Surface morphology of nitrogen doped graphene: (a) SEM micrograph of the morphology of nitrogen doped graphene sheets; (b) HRTEM micrograph and EDX quantification shows the content of nitrogen: 9.3 wt.% in the region of analysis

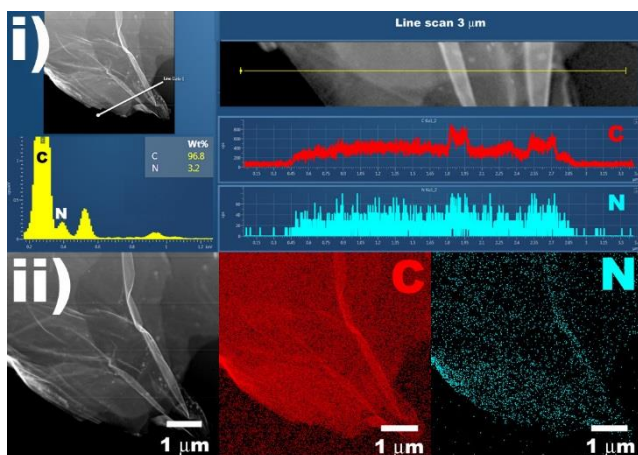


Fig. 4 Elemental mapping and EDX line scan that shows the content of a nitrogen doped graphene: (i) EDX line scan of NG with content 3.2%, carbon is colored red and nitrogen is colored aqua; (ii) Two dimensional elemental EDX mapping of NG: note that the elemental distribution of the elements are homogeneous: carbon distribution is colored red, meanwhile homogeneous nitrogen distribution is indicated in color aqua

dangerous chemicals, reagents and gases, such as ammonia, or large periods of synthesis at high temperatures (Rao *et al.* 2014). Using scanning transmission electron microscopy (STEM) at 200 kV in bright field mode over an isolated single layer (Fig. 4(i)) and EDX line-scan analysis, we found the elemental distribution as follows: carbon (red line) and nitrogen (blue aqua line) that are presented in a separates frames, both graphs are in the same path that indicates a homogeneous distribution of carbon and nitrogen. Meanwhile in Fig. 4(ii), an EDX analysis over the surface of the sheet, we made an elemental mapping presented in individual frames for each element. Carbon distribution in color red is present in the entire graphene sheet and nitrogen distribution, presented in color aqua-blue, is present homogeneously over all the graphene sheet.

As part of complementary characterization techniques, and regarding Fig. 4, the nature or type of nitrogen doping, the binding energy between neighboring atoms is unique for each material and the properties can change if this binding is modified experimentally. In this case we analyzed via high resolution X-ray photoelectron spectroscopy (XPS); the result binding in each stage was shown in Fig. 4. We divided the spectra into regions of energy to analyze the type of each one. We analyzed and compared the results with an XPS reference database and other authors. The main spectra shows peaks around 284 eV that correspond to the binding energy C-C (sp^2) at 284.5 eV for all carbon samples (graphite, GOx and NG). Additionally for GOx, the spectra shows a wide peak around 286 eV that corresponds to bindings C-OH/C-O-C at (286.3, 286.7)eV, respectively, and around 288 eV the bindings C=O/O-C=O (288, 289)eV, respectively. In Fig. 5(a), the binding C-O is present only in the GOx sample around 532 eV as shown in Fig. 5(b); the goal of nitrogen doping and its type was found in the XPS spectra around 400eV. The two main peaks of energy correspond to pyridine doping type (GN-p) at 398.9 eV and quaternary or substitutional doping type (GN-q) at 400.6 eV (Fig. 5(c)). The results are consistent with those reported by other authors (Leela *et al.* 2010, Geng *et al.* 2011, Wang *et al.* 2012, Jiang *et al.* 2014). Fig. 5(d) shows the models of the obtained system at each stage: graphite is the pristine system, GOx is the result of acid treatment for oxidation and functional groups intercalation, and NG with the different types of nitrogen doping obtained with the use of caffeine as the source of nitrogen.

3.1.2 Silver NW functionalization

The second part of our study it is related to the analysis of the silver nucleation in the whole graphene sheet. After nitrogen doping, the silver nanowires functionalization on graphene was analyzed via SEM, TEM-STEM and EDX mappings, in order to determine the shape and distribution of silver nanowires and nanoparticles on the nitrogen doped graphene sheet. It is important to mention that we conducted a previous silver nanoparticles functionalization experiment with two types of graphene with the same conditions: the first one was reduced graphene and the second one was GN (nitrogen doped graphene) in order to analyze the surface reactivity of both types of graphene. The results were characterized with TEM. We found that with the nitrogen doped graphene the average silver

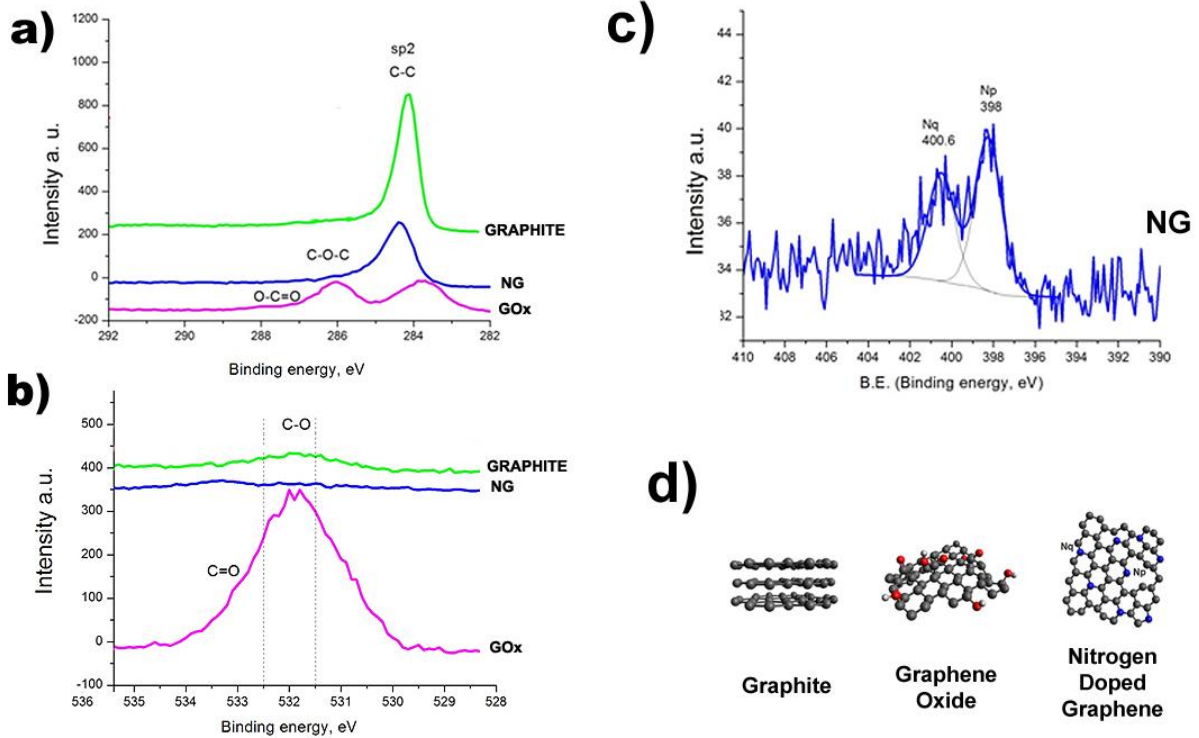


Fig. 5 XPS spectra: (a) binding energy for C-C sp^2 around 284 eV for NG and graphite; for GOx the bonding has drifted to the right; (b) C-O bonding only is present in GOx; (c) XPS in the range 390 eV to 410 eV clearly shows two peaks that correspond to quaternary doping or substitutional in 400.6 eV and pyridinic at 398 eV; (d) models for Graphite, GOx and NG

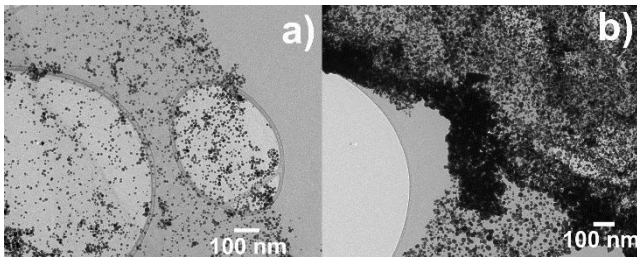


Fig. 6 TEM micrographs of growth comparison: (a) reduced graphene with Ag nanoparticles (b) NG with Ag nanoparticles; both samples were produced under the same experimental conditions. The difference in nanoparticle density (large number of nanoparticles) could be the result of the nitrogen dopant acting as nucleation sites on the graphene surface

nanoparticles nucleation was larger than that of the reduced graphene, because of its reactivity, meaning that the nitrogen atoms act as active sites on the graphene surface. According to the TEM micrographs (Figs. 6(a) and (b)), most of the GN surface was covered with silver nanoparticles, and the average size and width range was 20-40 nm in a spherical shape. Meanwhile, for reduced graphene, the average size and wide range was 10-20 nm, also in a spherical shape.

On the other hand, SEM micrographs (see Figs. 7(a) to (b)) show that the growth of silver nanowires is all over the surface of the sheet of nitrogen doped graphene. Nair *et al.* (2018) grew silver nanowires between graphene sheets

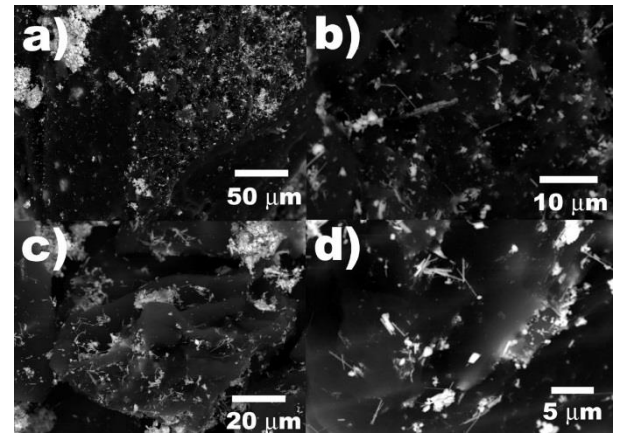


Fig. 7 SEM micrographs show silver nanowires in the surface of the sheets, we present four random regions of the sample

while Ji *et al.* (2018) produced nitrogen-doped graphene wrapped around silver nanowires, meanwhile we growth in the sheets (anchoring); we found that the average length of silver nanowires obtained in the surface of NG was 1 to 2 μm and 20-50 nm of width, meaning that the aspect ratio width/length is in the range of (20,50). Regarding the elemental composition or chemical analysis of the obtained silver nanowires, STEM EDX mapping (see Fig. 8) shows the distribution of silver nanowires and nanoparticles over nitrogen dope graphene sheet, carbon in a blue aqua frame, nitrogen in a red frame and silver in a yellow frame.

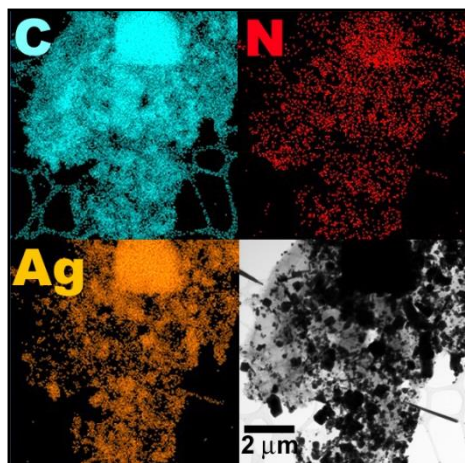


Fig. 8 In the frame on the left side we show an EDX elemental mapping of NG decorated with Ag nanowires and nanoparticles distribution: Carbon in a blue aqua frame, nitrogen in red frame and silver in yellow frame. At the right side a TEM micrograph of silver nanowire over the graphene

4. Conclusions

As demonstrated, this proposed experimental method of synthesis of nitrogen doped graphene was carried out using caffeine as an alternative nitrogen source, and its nanowire's functionalization is a useful and easy method to grow in-situ. We determined that the surface of NG is more reactive due to the content of nitrogen, which promotes the nucleation of silver nanowires and nanoparticles in the active sites over all the surface. According to these results it is possible to use the new method to produce NG and make hybrid materials with silver NW to produce functionalized graphene for applications in electrodes, or circuits interconnected by silver nanowires which can be used in electronics and other novel applications.

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