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The doping of carbon nanotubes with nitrogen and their potential applications

P. Ayala [a,*], R. Arenal [b], M. Rümmeli [c], A. Rubio [d,e], T. Pichler [a]

[a] Faculty of Physics, University of Vienna, Strudlhofgasse 4, A-1090 Vienna, Austria
[b] Laboratoire d'Etude des Microstructures, ONERA-CNRS, 92322 Chtillon, France
[c] IFW-Dresden, Helmholtzstr.20, 01069 Dresden, Germany
[d] Nano-Bio Spectroscopy group and ETSF Scientific Development Centre, Dpto. Fsica de Materiales, Universidad del Pas Vasco, Centro de Fsica de Materiales CSIC-UPV/EHU-MPC and DIPC, Av. Tolosa 72, E-20018 San Sebastin, Spain
[e] Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

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ABSTRACT

This contribution provides a comprehensive overview of the experimental and theoretical topics related to the introduction of nitrogen into both single- and multi-walled carbon nanotube structures. It covers the synthesis, characterization and analysis of the potential applications of carbon nanotubes based on intrinsic changes in properties induced upon nitrogen incorporation. The reason why nitrogen-doped carbon nanotubes are the target of several investigations is explained not only from the state-of-the-art research point of view but special attention is given to present the results available in the literature weighed against the ideal materials expected for applications. A comparison with other nitrogen-doped carbon systems is also provided.

Contents

* Corresponding author: Fax: +43 1427751375.
  E-mail address: ayalap9@univie.ac.at (P. Ayala).

1.   Introduction

Carbon (C) nanotubes (NT) nowadays represent one of the most active research fields. The literature regarding the study of properties and applications of pristine C-NT has progressed enormously in the recent years and a great interest has been lately observed towards improving and controlling their properties through different functionalization methods. A modification of the crystalline nanotube properties by controllably placing defects or foreign atoms (heteroatoms) brings along tremendous technological implications [1–4], which justifies the number of experimental and theoretical investigations focused on this topic. Although some work has been done in different ways regarding endohedral doping and intercalation, the case of substitutional doping has still some difficulties to overcome.

As in other crystalline solid structures, the position of heteroatoms in the C-NT network must not exclusively be substitutional to affect the properties of the structures. In fact, the properties of nanoscopic objects depend crucially on the position of each atom [5–12]. Bearing in mind that N contains one additional electron as compared to C, novel electronic properties can be expected if N atoms directly substitute C atoms in the graphitic lattice and one could anticipate that they would generate an n-type material [13]. However, a direct substitution of the C atoms is not the only possibility to incorporate N in the nanotube assembly. Due to its size, N can also generate a defect in the tube structure keeping the heteroatoms on the walls, requiring a rearrangement of the neighboring C atoms. In this case the n-type behavior is not immediately inferred. The electronic behavior depends on the new geometry generated which involves a different wall structure, and one cannot discard that this new arrangement makes a p-type doping also feasible. Defects, direct substitution of heteroatoms and atom rearrangements are the so-called on-wall dopants. However, some atoms or molecules can also be encapsulated in the hollow core of the tubes (endohedral doping) or trapped within bundles intercalated between the outer shells of the tubes (exohedral doping), as illustrated in Fig. 1. Intercalation and endohedral doping in C-NT with atoms or molecules have exhibited peculiar changes. In fact, In all these cases, the controlled modification of the C-NT properties introducing has recently received considerable attention.

Nitrogen atoms incorporated in the C-NT structure represent for several reasons a practical and illustrative case. If a carbon single-walled nanotube (C-SWNT) is doped with a foreign N atom, its outstanding electronic properties differ drastically from an undoped C-SWNT. Even the cases of multi-walled (MW) and C-SWNTs doped with N are radically different. As compared to bulk doped carbons and also against other doped carbon layered structures, (i.e. bulk doped graphite), the electronic properties of C-NTs differ due to quantum confinement effects and the curvature of the cylinders.

This document deals extensively with the effects related to the incorporation of N in C-NTs. However, we devote part of the following sections to give a fundamental insight into the facts related of N incorporation in other carbon systems that are certainly covered in a broader context elsewhere [14–16]. The properties of doped C-NT and heteronanotubes formed of stable carbon and nitrogen-containing stoichiometries are described separately. Also a brief summary of the state-of-the-art synthesis of these materials is given, to finally conclude with the potential and already achieved applications.

Here it is important to remark that in most of the literature related to nitrogen-doped C-NTs the word *doping* is still not used in a standard way. This is related to a conceptual matter to which we will dedicate great part of Sections 2–4. To avoid confusion "SWNT" and "MWNT" will be used in this document to abbreviate single- and multi-walled nanotubes, regardless their atomic structure. The atomic composition will be identified with the atomic symbols as prefixes (i.e. C-SWNT stands for a pristine single-walled carbon nanotube).

2.   Nitrogen-containing carbon systems

The properties of carbon based structures are intrinsically linked to the type of hybridization in which the carbon atoms bond with neighboring atoms (i.e. sp^1, sp^2, sp^3). There are several review features that provide clear descriptions how different carbon materials form according to these types of hybridizations [15,17]. Historically, the studies on C systems have developed in a way that nitrogen has always been taken into account. This is clearly due to the size proximity of N in comparison to C. Almost five decades ago, analysis on solid carbon systems broke new ground through the analysis of nitrogen incorporation within bulk carbon structures, on which the first studies on thermal annealing revealed the feasibility to reach low concentrations (<0.5 at%) of N incorporation in the structure [18,19]. Later, researchers devoted to carbon based thin films, investigated the properties of such structures with various sp^2 to sp^3 carbon bonding ratios. In this context Franceschini et al. [20] were able to confirm the internal stress reduction effect by nitrogen incorporation in hard amorphous carbon thin films. Further detailed studies using X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy were also conducted on films of
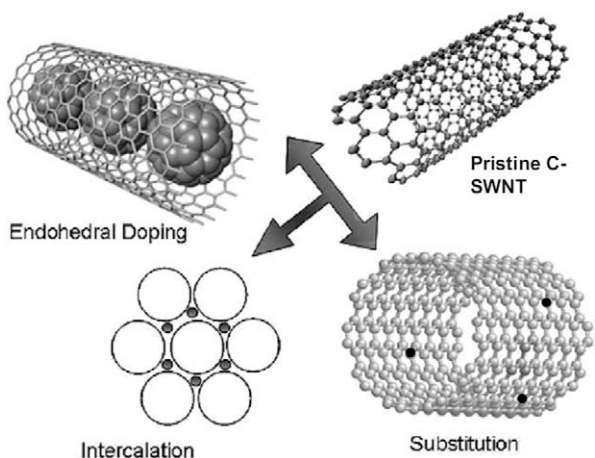
Fig. 1 – Different ways to modify nanotube electronic properties: Intercalation within C-SWNT in a bundle, formation of heteronanotubes (with substitutional atoms) and endohedral doping filling with crystals or fullerenes (so-called peapods).

these materials [21,22]. Note that these studies have been very useful to enlighten the path for the analysis of C-NTs with comparative data. Although this is very important, because C-NT are relatively new materials and thus the amount of data available on doped C-NT is limited in certain aspects, any comparison should be made very carefully. Details of such comparisons are provided later in this document.

The identification of bonding environments and assessment of dopant concentration for N-doped NTs has mainly been interpreted in terms of results on bulk doped systems. Hence, it should be borne in mind that differences particular to the molecular structure of C-NTs may exist. Studies in low nitrogen-doped highly oriented diamond films suggest that N-doping stops vacancies from aggregating to form vacancy clusters. Regarding N-doped nano-carbons Belz et al. [23] reported the doping levels of up to 4.5 at% of N within sp^2-like carbons. A more recent study by Alibart et al. [24] analyzed the semiconducting properties from these kinds of films upon N incorporation through different synthesis techniques. Many subsequent studies on N-doped bulk graphitic systems have been made and they have shown that N atoms tend to introduce disorder in the graphene planes and also, very recent theoretical studies have shown how N substitution can introduce curvature in the graphitic sheets [25]. Of course, bulk carbons differ substantially from nitrogen-doped carbon based nanostructures such as graphite, graphene, nano-ribbons [26], fullerenes [27–29], NTs and N-doped fullerides encapsulated in the NTs [30,31]. These are molecular arrangements with defined dimensions and studies on bulk systems can provide some information regarding the effects of N incorporation but they cannot be considered a pattern for comparison. Carbon NT, and in particular, C-SWNT are extremely sensitive to local nitrogen incorporation. This sensitivity opens up a whole new scope of possibilities. Not only is the quantification of N incorporated in the NT important, but so also are the bonding environments of the foreign atoms.

3. Nitrogen-containing nanotubes

The first studies analyzing the doping effects on C-NTs appeared in 1993 [32], not much later than Iijima's reports on transmission electron microscopy observations were first published [33,34]. This is just one of the many examples that inspired the investigation of nitrogen doping in C-NT.

Starting from a conceptual viewpoint: a carbon tubular nanostructure, which contains N atoms may not always be called a N-doped carbon nanotube. This is undoubtedly far from being a triviality. Substitutional doping is mainly related to the removal of C atoms from the crystalline structure of a pristine C-NT. This implies either a direct substitution of one C atom by a N one, or a multiple removal of C atoms incorporating N ones in their place, but not necessarily with the same wall configuration. This second possibility involves the elimination of C atoms from the NT walls inducing structural defects affecting the C-NT properties in distinctive manners. Indeed, N does not only act as a direct substitutional impurity. Czerw et al. [35] suggested that a second bonding environment of nitrogen would correspond to a pyridinic configuration based on tight binding and ab initio theoretical
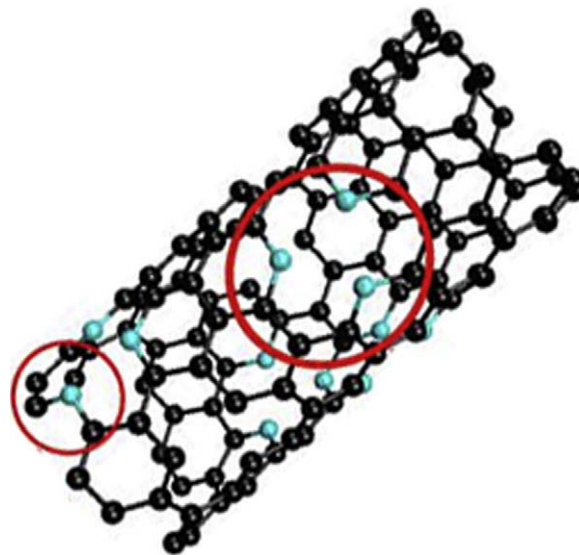
Fig. 2 – Molecular model of a C-SWNT with N on-wall doping. A direct substitution and a pyridinic bonding configuration are shown in the small and large circled areas correspondingly.

calculations. They also performed experimental studies with XPS and scanning tunneling electron microscopy (STM) performed on bamboo-like N-containing MWNT. The pyridinic configuration implies a two coordinated N upon creation of a single C atom vacancy, which is assumed responsible for the metallic behavior in those N-containing MWNT (see Fig. 2). Further theoretical studies on doped single-walled CNT structures have also been carried out but no conclusive experimental proof for this configuration has been identified at the local scale. Kang and Jeong [36] performed density functional theory calculations spotting changes on the distribution of the nitrogen atoms according to different NT chiralities. They substantiate that the pyridinic configuration proposed by Czerw et al. is energetically favorable; however, attributing it to a lone-pair state. Transport studies on single vacancies in C-NT, recently published by Rocha et al. [37] support the previous study by calculating the density of states of impurities in C-NT upon progressive removal of C atoms in the structure. Although the substitutional configuration leads to an n-type material, theoretical tight binding studies have suggested that this type of configuration can give rise to a p- or n-type structure depending on the atomic position of the N atoms [38]. Nevertheless, none of these studies have shown compelling evidence for the creation of a vacancy induced by N incorporation nor its configuration. Although bulk analysis of N-doped C-NT samples with spectroscopical techniques have shown the presence of a pyridinic configuration [38,39], as discussed later, further theoretical studies and the experimental confirmations at the local scale are still expected within this framework.

Looking deeper into the doping concept, if we consider a NT as a seamless cylinder with an inner and an outer wall, we clearly notice that there are other possibilities to dope the tube from physical and chemical points of view. Let us deal first with the case of doping of SWNT for simplicity.

In all semiconductor applications, the properties of a device depend on the control of the electronic states in the valence and conduction bands for design and optimization purposes. Doping with heteroatoms is a well established technique in Si technology to achieve this objectives. It is well known that doping with electron donors or acceptors leads to a very sensitive shift of the Fermi level considering the presence of heteroatoms in parts per million. If the electronic properties of C-SWNT depend strongly, as expected, on the substitution of heteroatoms, then the controlled synthesis of p- and n-type material should be feasible with analogue methods. In this context, the outstanding physical properties of pristine C-SWNT have been very well studied [1,2,33,40–42], but if these novel structures are to fulfill their promise in real applications within the semiconductor industry then it is mandatory to be able to control their electronic properties. One of the proposed methods is the insertion of dopants such as N as in our case of study [5,32,43]. As already mentioned, compared to carbon, nitrogen has an extra electron, and from an electronic point of view it is natural to expect an excess of donors in the N-rich areas of the C-SWNT upon doping [36,44]. This in fact occurs if N substitutes for a C atom generating an n-type semiconductor with localized states above the Fermi level.

The case of N-containing C-MWNTs is more complicated because of the number of walls involved. Although direct substitution and the pyridinic type of bonding are expected, one cannot discard the possibility of a third type of pyrrolic type of bonding environment. In this case, the wall re-arrangement leads to the formation of a five-fold type of ring [14]. This is still a matter of discussion and more conclusive studies are expected in the near future.

Recent studies of the charge transport properties on individual N-doped C-SWNTs, suggest that n-type conduction can be achieved but only when there is a high concentration of graphite-like nitrogen bonding configuration [45]. These authors suggest that the pyridine-type nitrogen bonding configuration in the honeycomb lattice is the main contributor to the electric-dipole scattering process observed in the charge transport. Furthermore, these studies confirm to a certain extent the possibility that N-doped C-SWNTs could be n- and p-type conductors as a function of the nitrogen bonding configuration (pyridine-type or high concentration of graphite-like, respectively).

4. C_xN_y heteronanotubes

As discussed above, individual N heteroatoms can substitute C atoms in the lattice or probably create defects in the tube walls. As mentioned before, from semiconductor physics the doping concept is related to a doping level in the order of parts per million. However, the cases in which higher heteroatom incorporation occurs must also be considered and in this context the concept of a C_xN_y heteronanotube must be taken into account. Keeping in mind that a C-SWNT can be pictured as a rolled-up graphene sheet, in the same manner other planar structures containing different atoms should also be able to form NT; of course, taking into account energetic considerations for the stability limits of tubular struc-

tures upon curvature of the walls. Planar heterostructures compared to graphene, which contain heteroatoms such as N or B, have been theoretically predicted. In such structures, new acceptor and donor features are observed in the local density of states of the valence and conduction bands when compared to graphene. Within this scope C_3N_4, BC_2N and BC_3 are examples structures that exhibit planar stable forms. Encouraging experimental results in the formation of tubular structures with these stoichiometries are reported in the literature [45–49]. These C_xN_y structures are better regarded as heteronanotubes rather than doped NT. This concept is particularly important when comparing the C_xN_y heteronanotube properties withe the ones of C-SWNTs doped with amounts in the order of parts per million. The dopant concentration is extremely important. At low doping levels the rigid band model can be considered. With this, the electronic density of states of a structure can be assumed from the electronic structure of the host considering that a rigid band model is applicable. In other words, for systems with low doping levels, the effect of a band structure modification by doping can be considered negligible and the band structure of the doped system can be obtained by simply shifting the Fermi level in the band structure of the pristine system towards the valence or conduction bands (one theoretical prediction of the electronic structure of a N-doped (8,0) tube is depicted in Fig. 3). The applicability of the so-called rigid band model has been successfully proven for C-SWNTs through field effect doping (p-, n-type) and intercalation with alkali metals. In the latest case, it has been proven even for considerably high doping levels (n-type) i.e. up to 10%, as well as (p-type) via Br_2, I_2, $FeCl_3$ doping [6,8–12]. For low doping levels of substitutional heteroatoms in C-SWNT, this rigid band model is appropriate since it is similar to doped Si with only a small number of dopant related defect centers. However, at higher heteroatom concentration, when heteronanotubes are formed, the story becomes more complicated and modifications in the density of states by the substitutional dopants have to be taken into account, which means that a simple rigid band shift model is no longer applicable because, in essence, novel heteronanotubes are born. BC_3-NTs and C_3N_4-NTs are good examples of heteronanotubes. The experimental data gathered on BC_3-NT reported by Fuentes et al. [49], showed the formation of a uniform energy gap of 0.4 eV for B-doped NT at very high doping. They confirmed the existence of BC_3-NTs having an acceptor like band of ~0.1 eV above the Fermi level. They observed that a BC_3 regular structure displays the pronounced vHs of a 1D band structure [49]. This underscores the relevance of the rigid band model for B-doped C-NTs with low doping whilst with higher boron incorporation, new stable structures are observed. The exact doping level, to which a rigid band model in B-containing NT is still applicable, remains an open question. Much less is reported on N-doped C-SWNT. Although the synthesis of C_3N_4-NT has been reported [46], the implications and limits of the rigid band model have still not been explored. Nevertheless, in this case one can anticipate that the band structure will exhibit completely different features [50]. The C_3N_4 stoichiometry reveals different potential configurations [51], which lead to different stacking possibilities. For this reason, also the prospects to form NTs are diverse and urgently re-
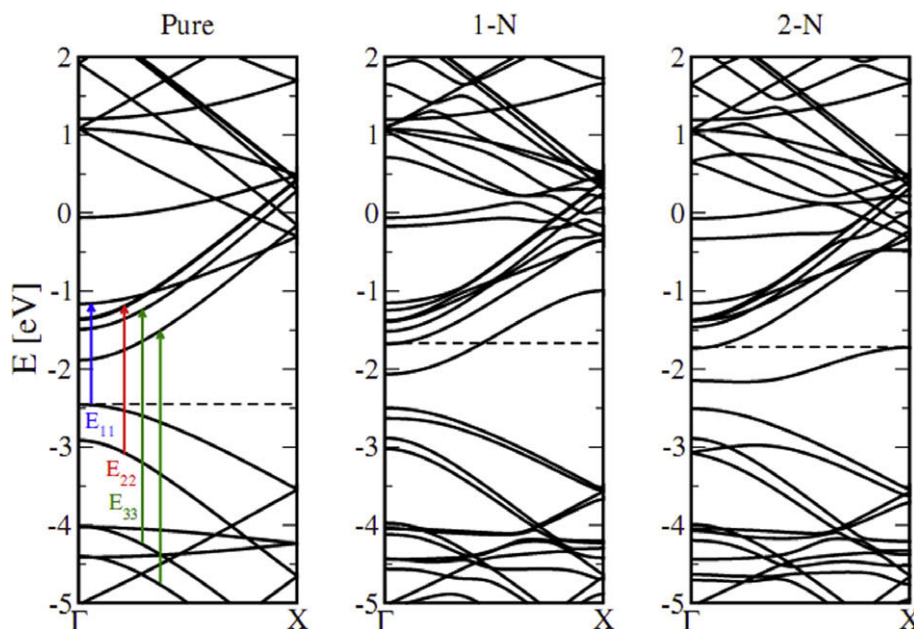
Fig. 3 – Electronic band structure of a (8,0) nitrogen-doped C-NT with one and two N substitutions (abstract/excerpt/figure) with permission from Ref. [91]. Copyright (2009) by the American Physical Society.

quire more theoretical studies. Whether it is possible to synthesize low doped C-SWNT or go to higher doping levels that allow the formation of C_xN_y-NTs (or any other stable N/C planar structure) is one of the crucial issues in this research area [52]. This involves a number of factors that include theoretical studies, synthesis processes and practical applications. Although there are very few works reported on the synthesis of C_3N_4-MWNTs [46], no experimental evidence of C_3N_4-SWNTs has been given and more theoretical studies are still expected.

5. Synthesis of nitrogen-containing nanotubes

Progress in the synthesis of CN_x-NT with the conventional methods used to produce C-NT is being made and it is now possible to produce multi-walled structures in a very controlled manner. Before any further discussion, although it might appear as a triviality, it is worth mentioning that many of the efforts devoted to the synthesis of N-containing MWNT aim at obtaining the highest record on N incorporation. However, the final objective should not only be to reach the maximum possible amount N but to keep in mind the final use of these NT as well as type of N bonding environments required for specific applications. With respect to C-MWNT and bundles of C-SWNT achieving electrochemical reactivity and porosity then, of course, high amounts of N incorporation are desirable. On the other hand, if single-walled tubes are to be integrated into semiconductor technology, then the goal is to achieve low doping. Pure C-NT are chemically inert and functionalization or surface modification is crucial to make them chemically active. Doping the tubes with foreign atoms, which are able to create superficial defects and break out the chemical inertness of pure C-NT, represents a feasible path to reactivity and implicitly towards a number of applications.

Many studies have attempted to produce N-containing NTs with the same methods to produce pristine C-NTs. However, it has been observed that the high reactivity of N requires extra experimental considerations for successful synthesis. Relatively clean and long N-containing C-MWNTs can be produced with nitrogen contents below 1% and up to 20% [53]. However, the morphology differs notoriously from pure C-MWNTs, which are tubular structures with hollow cores. Nitrogen-containing NTs, on the whole, do not exhibit a completely hollow core [54] and a strong correlation between the N incorporation and morphology of the tubes is observed and discussed in almost all related publications. The CN_x-MWNT structure is divided in hollow sections separated by one to few graphitic layers (bamboo-like structures with defined compartments or with bridging layers as shown in Fig. 4a and b).

Recent studies by Koos et al. [56] on the effect of the experimental parameters on the structure of N-Containing C-MWNTs produced by an aerosol assisted CVD method are a good illustration of the morphological structure, although the proof of nitrogen content in those samples is not studied in detail. Sen et al. [57] have also shown that according to the synthesis parameters employed, coiled structures can be produced in high yields upon nitrogen incorporation (see illustration in Fig. 4c). Furthermore, it has been clearly demonstrated that the compartments can encapsulate N_2 gas molecules or nitrogenated gaseous compounds that vary in nature according to the synthesis conditions and the precursors used [58–62]. These compounds can be easily identified with an analytical technique as shown in Fig. 5, where the XPS spectrum in the N1s region of a sample produced with acetonitrile is shown. However, there is also the possibility to intercalate gas between the walls of the CN_x-MWNT (Fig. 6) as Choi et al. proposed [63]. It has also been suggested that the nitrogen concentration and nitrogen bond-
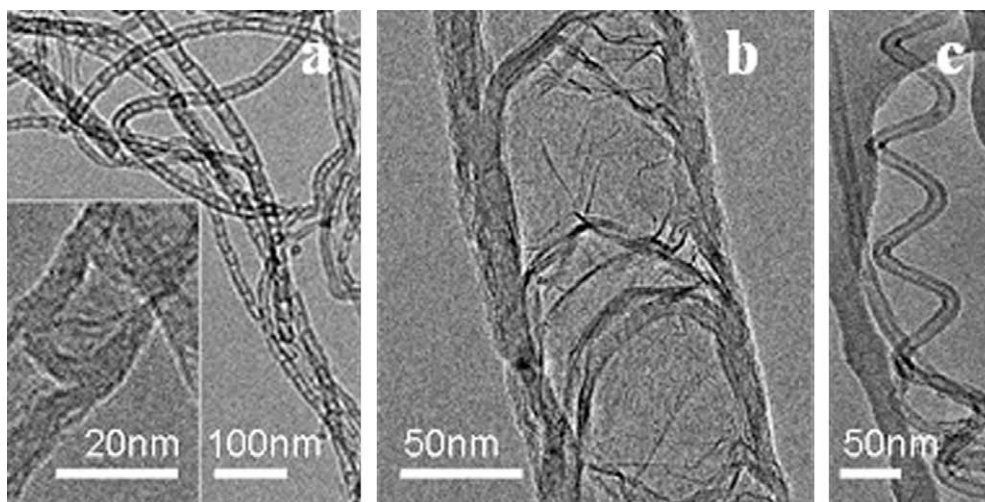
Fig. 4 – TEM micrographs of typical CN_x-NT morphologies (a) bamboo-like (compartmentalized); (b) bamboo-like (bridged); (c) helical (P. Ayala, Unpublished).
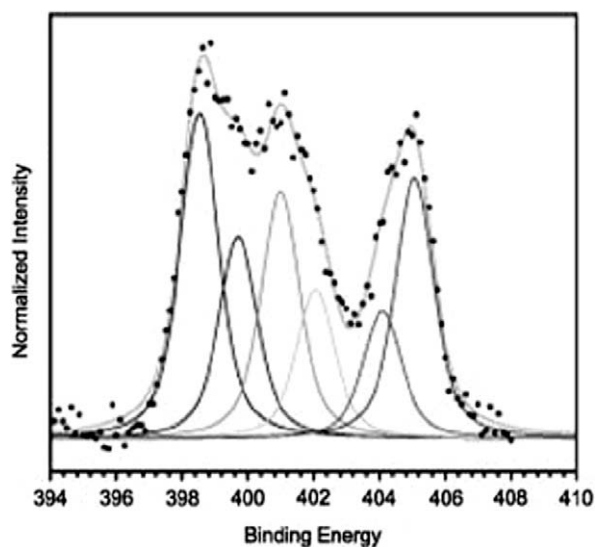

Fig. 5 – XPS Spectrum of nitrogen-doped NT synthesized using chemical vapor deposition of acetonitrile with multilayered catalysts (random example related to [55]). The lineshape analysis in the N1s region shows that the photoemission signal recorded with a monochromated Al K_α with 0.4 eV resolution can be deconvoluted in various components corresponding not only to a substitutional and pyridinic configuration, but also to other gaseous nitrogenated resulting from the synthesis conditions.
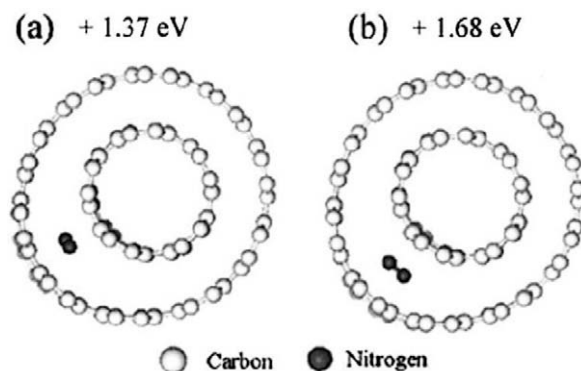

Fig. 6 – Choi et al. have suggested the intercalation of molecular N_2 in double-walled NT. The figures exhibit the intercalation with parallel and perpendicular orientation along the tube axis. Figure modified from [61] (courtesy of J. Park).

ing environments of C-NT can be controlled by changing the growth parameters [39,62,64,65]. Inspired on the applications, the research regarding synthesis the of CN_x-MWNT has increased tremendously in the last years. In particular chemical vapor deposition based methods are being exploited due to their upscaleability potential [53–57,59–72]. N-doped MWNT synthesized by these methods have shown that the incorporation of N in the CVD process requires sensitive control of the thermodynamic parameters involved in the formation process. The problem does not lie in the issue that the struc-

tures formed exhibit a bamboo type of configuration, but that the N reactivity accelerates the process leading to the formation of higher yield of defective co-products in the soot. Nevertheless, high quality multi-walled material can be synthesized. Even highly aligned material can be grown in a controlled manner [61,71], which is important for field emission applications [73]. XPS studies have suggested that high temperature annealing of CN_x-MWNT releases the N_2 encapsulated within the compartments of the bamboo structures [63]. However, further in situ studies at a local scale must still be carried out in order to determine the morphological changes upon annealing. The carbon arc discharge method is also a common way to synthesize C-NT. However, it is a technique that produces a complex mixture of components, making it difficult to scale-up in order to cover the necessities of the potential applications of these nanomaterials. Multi-walled CN_x-NT have also been successfully synthesized with this method introducing either a mixture of nitrogen/helium [74] or N_2 [75] during the arcing experiments. Alternative to

these methods, Abbas et al. succeeded in incorporating N in vertically aligned pure CNT using plasma enhanced chemical vapor deposition. They achieved a high substitutional configuration as determined by XPS and temperature dependent near edge X-ray absorption fine structure [76].

The research regarding SWNT doped with N is still in an initial stage. Few studies have been published showing the successful synthesis of C-SWNT doped with nitrogen. Although most experimental work is related to MW structures, only recently have methods for the production of high quality SW material with controlled doping and diameter distributions become available. The first reported studies with arc discharge [77] and an aerosol assisted chemical vapor deposition method [78] appeared in 2004 and 2006, respectively. Since then the very few other research papers have shown morphological improvements. More recently, CN_x-SWNT have also been synthesized via the laser vaporization technique [79,80] (see Fig. 8). However, combined synthesis and electronic properties studies on N-doped NT are still scarce. The arc discharge work by Glerup et al. [77] differed innovatively from previous experiments for CN_x-MWNTs synthesis regarding the target preparation. They proposed the introduction of nitrogen-rich precursors in the anode rods and reached doping levels up to 1 at% of N in C-SWNT in bundles (characterized by EELS). Later work reported by Krstic et al. [45] investigated the charge transport properties of individual nitrogen doped C-SWNT synthesized by the same method confirming that n-type conduction requires high substitutional N-doping. Keskar et al. [81] reported variations in the Raman spectrum of isolated CN_x-SWNTs that were grown directly on substrates with vapors of acetonitrile diluted in xylene at 750 °C. However, the changes in the Raman spectra cannot conclusively be attributed to effective doping as this was estimated from the N precursor concentration. The use of CVD methods for N-doped SWNT have also been explored. CVD studies with diluted liquid precursors was first tried in order to avoid the formation of MWCNT. In this context, Villalpando-Paez et al. [78] presented results on the synthesis of long strands of nitrogen-doped C-SWNT obtained from the pyrolysis of ferrocene/benzylamine/ethanol solutions in an argon atmosphere. In that contribution, variations on electrical conductivity were performed, although probably these changes cannot be directly related to the N concentration in the precursor as later studies [82] showed that the maximum nitrogen incorporation in such samples is 0.3 at%. Nevertheless, one cannot rule out the fact that those changes can be attributed to different bonding environments in which N is present in the samples. Further studies should be carried out in that respect. Different experiments performed with undiluted benzylamine [39], highlight the importance of low pressure conditions and slow C/N precursor feeding in order to obtain doped single or few-walled NT. These investigations revealed that the maximum amount of N incorporated in a sample from benzylamine is 0.2% in agreement with the findings reported in [38,39,82]. The N incorporates in diverse forms depending on the synthesis conditions. In the absence of N gaseous forms, sp^2 and pyridine-like configurations are present and a highest absolute value of 0.2 at% is attainable. These configurations compete with about a 1:1 constant ratio in the optimal case and the pyridinic configuration remains at
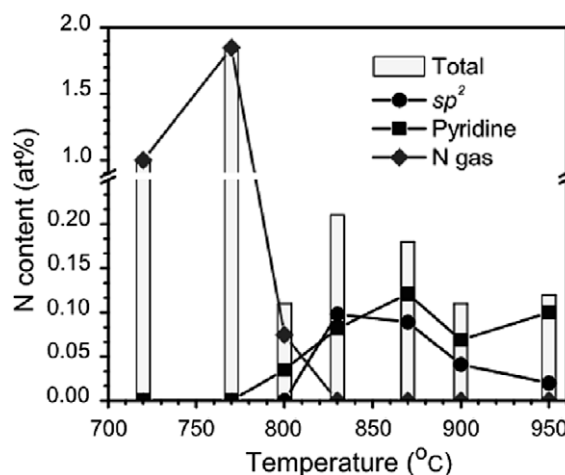
Fig. 7 – Nitrogen incorporation profile according to synthesis temperatures [39]. The gray bars corresponds to the total N content at different synthesis temperatures. The fractions of from the line shape analysis (sp^2, pyridine and N volatile species), are depicted by the symbols specified on the top right labels.

higher temperatures (see Fig. 7). Additional work with diluted feedstocks has been successful in the synthesis of double-walled nitrogen-doped NT. Kim et al. [38] employed bimetallic catalysts supported in MgO. The nitrogen content in their samples was estimated from synchrotron XPS measurements. Interestingly, from a detailed lineshape analysis assisted by theoretical calculations, they also found that the pyridine-like configuration and the substitutional doping compete in a 1:1 ratio in the optimal synthesis conditions confirming the conclusions reported in [39] for samples prepared with high-vacuum pre-synthesis conditions. The recent work from Panchakarla et al. [83] shows the formation of double-walled C-NT and they have also used XPS to characterize the N content in their samples. Although they report values around 1% for the N incorporation in the tubes, their results should be reviewed taking into account that at such doping levels a broadening of the C1s in the full width at half maximum must be considered. The obtained asymmetry suggests the presence of amorphous byproducts [39,82,84,85]. It is worth emphasizing that careful lineshape analysis of the N1s photoemission signal is necessary in order to extract correct information on the nitrogen bonding environments, particularly, given the fact that N can be present in the sample with various bonding configurations [55]. Related studies have also been recently reported by Xu et al. on commercial pristine C-SWNT doped via N_2^+ ion implantation [86]. One of the major obstacles encountered at the moment is the accurate determination of doping levels. The two natural techniques are electron energy-loss spectroscopy (EELS) and XPS. EELS can be used as a local probing method when used in a transmission electron microscope. The effectiveness of using one or the other technique is not only related to the amount of doping in the sample but also on the sensitivity and resolution of the devices associated with the photoemission cross-section or scattering cross-section of the elements in
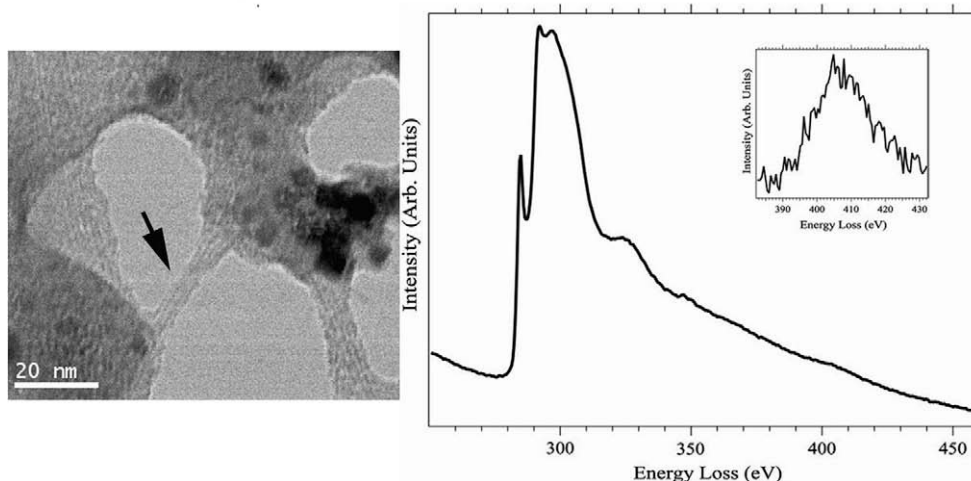
Fig. 8 – Electron energy-loss spectrum recorded on the CN$_x$-SWNT bundle shows in the bright field image (marked by an arrow). The EELS spectrum displays the C and N–K edges. The N–K edge is emphasized in the inset. This figure is modified from Fig. 2 in Lin et al. [79].

question. When working in the very low doping regime for SWNT, probing the incorporation of atoms at the local scale with TEM-EELS is a very complex task. The detection limits for atoms such as N or B doping a C structure contribute to the previously mentioned difficulties. Nevertheless, major improvements have been accomplished with this technique (especially enhanced by the use of dedicated STEMs), combining a good energy resolution (0.5 eV) and remarkable spatial resolution (below one nanometer) [85,87]. Spatially-resolved electron energy-loss spectroscopy is ideal to investigate the presence of heteroatoms within the NT at the local scale making in this way feasible the study of physical and chemical properties of materials and with improved spatial and spectral resolution. On the other hand XPS has the advantage of being a bulk probing method but it requires special attention on the sample characteristics before any measurement. It cannot be used in a straightforward manner with samples "as produced", without any previous complementary morphology characterizations. On the other hand, if experimental considerations such as the choice of material to be measured and the correct characteristics proper to the technique are taken into account, XPS represents an extremely sensitive method to for the detection of doping levels and bonding environments. Furthermore, Raman spectroscopy has been proposed as a very sensitive tool for detecting changes upon doping [88–90]. A very recent DFT study from Gerbert et al., analyzing the influence of nitrogen doping on the radial breathing (RBM) mode in C-NTs, has suggested a downshift of the RBM directly related to the exact position of the dopant within the tube wall [91]. The formation of N–N bonds is not favored for zigzag tubes. They also suggested that a symmetric position of the dopant may lead only to small downshifts of RBM frequencies. Although this topic is currently under discussion, there is still a tremendous amount of work to do in order to correlate the effect of doping on the Raman spectrum of a C-SWNT when impurities or foreign atoms are taken into account.

6.   Applications

From the beginning of this manuscript the importance of doping amounts, bonding environments, nanotube stoichiometry and doping levels have been emphasized. The type of N-containing nanotube and the amount of N incorporation should be pursued bearing in mind their later application. This section summarizes the directions to which this research is oriented focuses nowadays.

First regarding C-MWNTs with N wall doping, the defects and rugosity of the outer walls are particularly appealing. This is a way to improve the tube covalent chemistry, which once functionalized can serve to anchor groups or particles that are useful for further functionalization routes. Clear examples are the recent works on platinum particle immobilization envisaging tailored materials with high catalytic surface. Bundles of doped C-SWNT could be though for similar applications.

Achieving electrochemical reactivity and porosity of the tubes gains major importance via N incorporation because pure C-NTs are chemically inert. Hence, functionalization or surface modification is required to make them chemically active. In this context, doped tubes have superficial defects that release the chemical inertness of pure C-NTs. It is worth mentioning that if N-doped C-MWNTs are to be used taking advantage of defective sites as a mechanism for wall functionalization [92,93] reaching high doping levels is the ultimate goal. This type of functionalization method is mainly intended for chemical and biological applications that might require sidewall substitutes, or polymer wrapping [94–96].

Furthermore, this particularly high wall reactivity of N-containing NTs makes them ideal components in fast gas sensors as studied for instance by Villalpando-Paez and co-workers [97]. Under the same scope N-containing C-MWNT can be used as matrix fillers in composite materials. In this case, the improved electrical conductivity generated by the N incorporation combined with the mechanical properties of the tubes are the novel factor.

One of the most up-to-date discussions is the use of N-doped C-NTs in field emission devices, as they are expected to emit with high current densities [98–101]. In this context, Li and co-workers [102] suggested that the presence of nitrogen should significantly influence the emission properties of C-NTs, especially causing a shift in the emission to lower energies.

Although in a very preliminary stage, the use of N-doped NT in ion Li batteries has also been proposed as higher Li storage favored by the defective sites generated upon N incorporation is expected. Zhou et al. [103] performed theoretical calculations showing that the high probability of N-doped NT to be electron-rich structures leads to less efficient Li adsorption within the tubes. Further experiments as well as theoretical calculations are required in this respect. As for doping in C-SWNT, one of the major application areas is in semiconductor technology if low doping levels are attained successfully in a controlled manner. Another application for these sidewall functionalized structures is their use in sensors based on the fact that the electrical conductivity of the NT should vary and be controlled externally via the adsorption or desorption of different functional groups. This is a developing field and theoretical studies are needed to analyze these changes in conductivity. The existing theoretical work with nitrogen doped C-NT has devoted more attention to the relationship between the atomic level structures and the electronic transport properties, and some studies regarding electron–electron and electron–phonon interactions [104–106]. However, this topic requires further calculations and discussion, given that the experimental work is still limited.

In order to observe factual quantum effects in doped C-SWNT, dopants must be present within tubes of controlled diameters and should not change the mechanical properties while enhancing the electron conduction.

Graphite-like C_3N_4 should encounter potential applications for organic semiconductors and similar applications could be envisaged for C_3N_4-NTs.

7. Conclusions

If doped C-NT are to be used as building blocks in applications, it is imperative to fine tune their physical properties such as wall reactivity, mechanical performance and electronic behavior by controlling the amount of foreign atoms inserted into the tube lattices. This manuscript reviews specifically the effects of nitrogen doping in C-NT starting with an overview of the changes in the physical and chemical properties upon nitrogen incorporation. Single and multi-walled NT have been treated separately in the first sections in order to categorize heteronanotubes and doped tubes. The applications for these kinds of new structures have been introduced with nitrogen as a dopant which can be used as a functionalization agent. In this sense, most studies have employed C-MWNTs in various applications. The recently available single-walled doped samples will likely leads to novel and broad research in the field of functionalization and, in the semiconductor sector. We have drawn attention to ongoing theoretical discussions and experimental efforts. Various debates exist though. The main issue arises due to the fact

that the properties of nanoscopic objects depend critically on the position of each atom, at which level the size and quantization effects play an important role that require not only further calculations but experimental characterization with local probing methods. We have paid special attention to the techniques used to determine the actual N content in single- as well as multi-walled samples. In this context, the influence of experimental conditions to detect the doping levels in the "low doping regime" have been carefully pointed out to underscore to readers the critical need for caution when using analytical chemical composition techniques. Finally, we can summarize in a single concept: "If controlled N-doping is achieved, it presents massive promise for novel 1D nanoobjects with defined and unique properties for applications. The first steps have been made with very encouraging results and an undoubtedly interesting outcome is expected from future research in the field."

Acknowledgements

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