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# DISSERTATION

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“Influence of purity and metallicity on gas sensing applications of single walled carbon nanotubes and their heteroatomic doping at low doping levels”

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*“Research is to see what everybody else has seen  
...and to think what nobody else has thought”*

Albert Szent-Gyorgyi



*To my family  
and beloved friends*

*for their constant support and unconditional love.*





---

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## Abstract

Single-walled carbon nanotubes are one of the most interesting and fascinating materials, which unique characteristics have transformed them into excellent candidates for a great variety of applications. The research related to single-walled carbon nanotubes has reached a fairly mature status regarding the production of clean and sorted material. This has allowed understanding their physical properties to a certain extent. However, the fast development of the field of applications started a long time before the production of ultra-pure material was achieved, i.e. material without remaining catalytic by-products or even species of dissimilar metallic character. This means that several types of established applications need to be rethought.

The specific focus of this PhD thesis is the understanding of the electronic properties of single-walled carbon nanotubes and their changes upon functionalization in different manners. Substitutional functionalization has been investigated at ultra-low amounts of doping levels in purified nanotube-material. This was done using photoemission and X-ray absorption spectroscopy, which have allowed clearly identifying the bonding environments present in such doped-tubes unambiguously. On the other hand, I have studied the on-wall functionalization of the tubes using them as sensing objects by analysing the changes in their electric response while interacting with gas molecules. In this context, most studies deal with the use of nanotube-material that is either highly defective or non-purified. It has often been proposed that the intrinsic defective sites and those created during the tube processing are responsible for the changes in their electronic response. I address this problem by studying either the physisorption or chemisorption of gas molecules from a spectroscopy point of view.

The results obtained in this thesis aim at paving the way toward controlled sensing using carbon nanotubes ruling out the effect of impurities. It aims at revealing aspects that can be applied to different applications providing an insight towards a real improvement in the design of SWCNTs with tailored functionalization.





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## Zusammenfassung

Einwandige Kohlenstoffnanoröhren sind eines der interessantesten und faszinierenden Materialien, sie sind wegen ihrer einmaligen Eigenschaften sehr vielversprechend für unzählige Einsatzgebiete. Die Produktion von reinen und sortierten Nanoröhren sind mittlerweile gut etablierte Techniken. Diese haben sehr geholfen, die Eigenschaften von Nanoröhren bis zu einem gewissen Grad zu ermitteln. Nichtsdestotrotz wurde schon in zahlreichen Anwendungsbereichen von Nanröhren gearbeitet bevor sauberes wohldefiniertes Material, ohne Metallpartikel oder einer Vermengung von halbleitenden und metallischen Nanoröhren, überhaupt erst verfügbar war. Das bedeutet nun dass auch das Potential einiger Anwendungen noch einmal eingehend untersucht werden müssen.

Die vorliegende Dissertation konzentriert sich auf die Untersuchung elektronischen Eigenschaften in ursprünglichen und auf verschiedene Art und Weise modifizierten einwandigen Kohlenstoffnanoröhren. In hochreinem Nanoröhrenmaterial wurden elektronische Modifizierungen durch ultra niedrige Konzentrationen von Elementsubstitutionen untersucht. Die lokalen Bindungen konnten mithilfe makroskopischer spektroskopischer Methoden eindeutig identifiziert werden. Des Weiteren habe ich auch die Oberflächenmodifikation der elektronischen Eigenschaften durch die Wechselwirkung mit Gasmolekülen untersucht. In den allermeisten vergleichbaren Arbeiten wurde entweder mit defektreichen oder unreinen Nanoröhren gearbeitet, zumeist wurde gefolgert dass eben solche Störstellen und Verunreinigungen die aktiven Plätze für Detektion sind. Mein Ansatz ist die Physisorption und Chemisorption von Gasmolekülen auf hochreinen Nanoröhren spektroskopisch zu untersuchen.

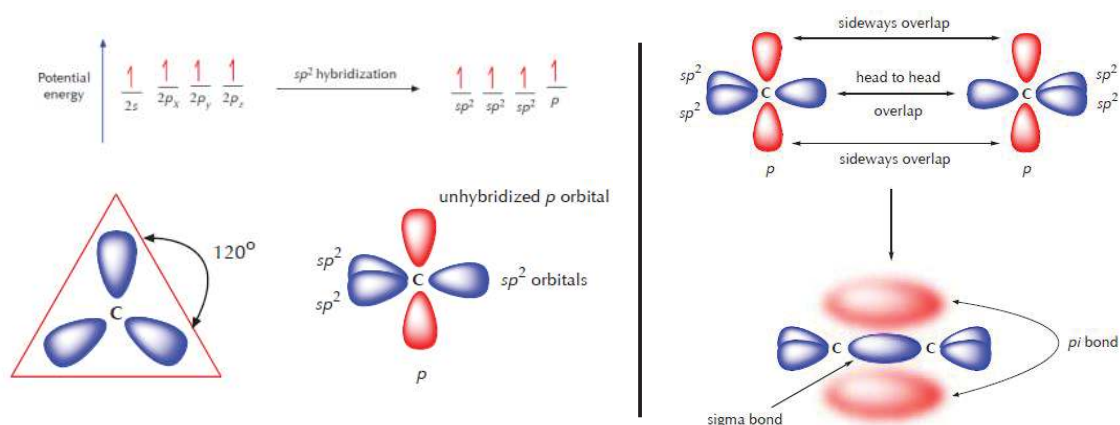
Die Ergebnisse dieser Doktorarbeit deuten darauf hin, dass die Anwendung von SWCNT als Gassensoren besser kontrolliert werden kann, indem die Effekte von Verunreinigungen ausgeschlossen werden. Die hier gefundenen Aspekte können auch auf andere Bereiche angewandt werden, was wiederum einen deutlichen Fortschritt in der Entwicklung von SWCNT mit maßgeschneiderter Funktionalisierung bedeutet.



## General Aspects

### 1.1 Carbon

Carbon is one of the most abundant element in nature and it is extremely versatile. Its electronic structure is  $1s^2 2s^2 2p^2$ , from where the  $1s$  electrons are core electrons and the other four are valence shell electrons. Core electrons do not allowed to bond as the bonding takes place only through utmost electronic levels. Giving the energy levels in elemental carbon, three different types of hybridization are possible:  $sp^1$ ,  $sp^2$  and  $sp^3$ , giving rise to all graphitic C allotropes of different dimensionality, such as fullerenes, graphite or diamond, among others.



**Figure 1.1.** Representation of the  $sp^2$  hybridization of the electron orbitals in carbon. The trigonal planar configuration of the three  $sp^2$  orbitals and the unhybridized  $p$  orbital are depicted as well as the formation of the  $\sigma$  (localized) and  $\pi$  (delocalized) bonds, as the resulting configuration of the orbital system. Illustration adapted from [www.utdallas.edu/scortes/ochem/OChem1\\_Lecture/Class\\_Materials/](http://www.utdallas.edu/scortes/ochem/OChem1_Lecture/Class_Materials/).

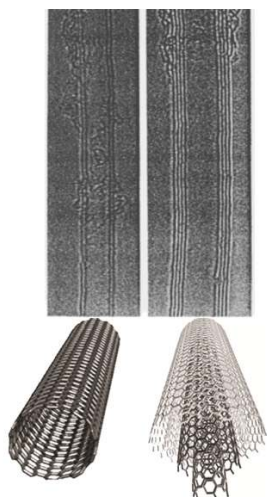
In this thesis, I am particularly interested in the study of  $sp^2$  hybridized systems, I will only briefly consider the case of graphene to understand its properties and how they are related to carbon nanotubes. As shown in Figure 1.1 for a single C atom, one  $s$  and two  $p$  orbitals create three equivalent  $sp^2$  orbitals, leaving one  $p$  orbital with its original energy and shape. Therefore, the three resulting  $sp^2$  arrange themselves in a trigonal planar configuration, at an angle of  $120^\circ$ . Additionally, the unhybridized  $p$  orbital organizes itself to be as far apart from the  $sp^2$  orbitals as possible, positioned perpendicular to the surface with both lobes coming out from the plane.

In graphene, these  $sp^2$  hybridized C atoms generate an hexagonal lattice [1]. The in-plane C-C interconnection and the bond between  $p$  orbitals are called  $\sigma$  and  $\pi$  bonds, correspondingly.

The  $\sigma$  bond is very short and strong, mainly, electrons are tightly bound in a very localized orbital. Principally, it determines the mechanical properties of the material. On the other hand, the  $\pi$  bond is relatively long and weak, being electrons relatively mobile and completely delocalized.  $\pi$  electrons govern the electronic properties and the chemical reactivity of graphene and CNTs implicitly.

## 1.2 A word on carbon nanotubes

Carbon nanotubes are seamless cylinders that can exist either in with a single wall configuration or in a multi-walled fashion where several tubes are concentrically placed one inside of the other. The first multiwalled nanotubes, reported as such, were observed during the synthesis of  $C_{60}$  fullerenes in 1991 as part of the remaining soot and shortly after their single-walled form was identified [2–4]. Although MWCNTs will not be in the focus of this thesis, it is important to keep in mind that the interlayer spacing in these structures is close to the distance between graphene layers in graphite, approximately 3.4 Å. The diameter is typically of the order of 10-20 nm and the length can be up to hundreds of microns or even centimeters [3, 5].



**Figure 1.2.** The TEM images correspond to the micrographs that Iijima first reported in 1991 and 1993. These pictures correspond to single and multi-walled nanotubes accompanied by molecular models of each specie.

Among all different kind of carbon based structures, SWCNTs have inspired the development of a new and fascinating physics. In terms of mechanical properties, nanotubes are among the strongest and most resilient materials known. They are very strong in the axial direction [6–8], where their Young's modulus is of 1.2 TPa and they have tensile strength about a hundred times higher than steel, tolerating large strains before mechanical failure [9]. Such remarkable mechanical properties are relevant for a number of potential applications and make them ideal building blocks for nanoengineering [10]. They possess high heat conductivity [11–13], large surface area and versatile electronic behaviour including high electron conductivity [14]. On the other hand, they are able to buckle in a reversible manner [15]. Particularly, the electronic properties are greatly influenced by their geometry in the axial and radial directions, which implicitly means that they depend sensitively on their diameter and chirality. SWCNTs can be metallic or semiconducting [16, 17]. This will be fully explained in the next section, where an overview of the electronic properties of SWCNTs will be given indicating their relationship with their geometrical characteristics.

### 1.3 Electronic properties of single-walled carbon nanotubes

As already mentioned, both SW- and MWCNTs are different structures and the related literature can easily be classified accordingly. The following section will simply be focused on summarizing the electronic structure of SWCNTs and their physical properties. I aim at briefly describing the properties of SWCNTs based on the graphene's structure as parent material.

The structure of SWCNTs consists of a rolled  $sp^2$  graphene sheet. One of the parameters that describe the SWCNT is the **chiral vector**. As shown in Figure 1.3, the graphene layer resembling a honeycomb lattice is rolled-up to a tubular structure to construct a nanotube. The points O and A, as well as B and B' and delimit the portion needed to construct a particular kind of nanotube. Hence, this vector defines the circumference of the nanotube connecting two crystallographically equivalent sides. The chiral vector, also called **Hamada vector** [16], is denoted by  $C_h$  and it is directly related to the real space unit vectors  $a_1$  and  $a_2$  of the hexagonal lattice.

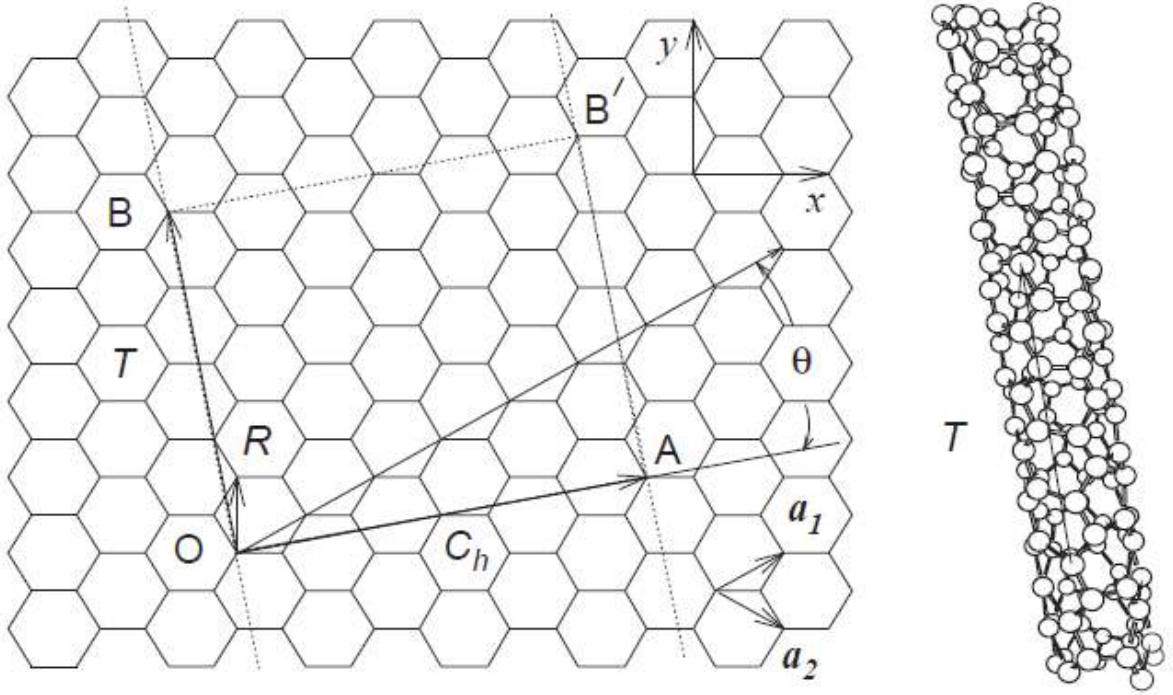
$$C_h = na_1 + ma_2 \equiv (n, m) \quad (n, m \text{ are integers, } 0 \leq |m| \leq |n|). \quad (1.1)$$

The pair of indices  $(n, m)$  of the linear combination defined in Equation 1.1 are usually used to define the chirality of the SWCNT and to identify them.

The diameter  $d$  of a SWCNTs based on the  $C_h$  is given by  $L/\pi$ , where  $L$  is the circumference of the nanotube, and  $a$ , which is the lattice constant  $a = \sqrt{3}a_0 = 2.49 \text{ \AA}$  of the honeycomb lattice and  $a_0 = 1.42 \text{ \AA}$  is the nearest-neighbor C-C distance.

$$d = L/\pi = |C_h|/\pi = a \sqrt{n^2 + m^2 + nm/\pi}, \quad (1.2)$$

Then, the chiral angle  $\theta$  is defined as the angle between the vectors  $C_h$  and  $a_1$  and gets a value in the range  $0 \leq |\theta| \leq 30^\circ$ . The expression of the chiral angle  $\theta$  as a function of the



**Figure 1.3.** Schematic representation of the honeycomb lattice that shows the possible wrapping of the graphene sheet. Thus, it depicts the formation of a (4,2) nanotube, as shown in the right side. Image adapted from [18]

integers  $(n, m)$  is

$$\cos\theta = \frac{C_h \cdot a_1}{|C_h||a_1|} = \frac{2n+m}{2\sqrt{n^2+m^2+nm}}, \quad (1.3)$$

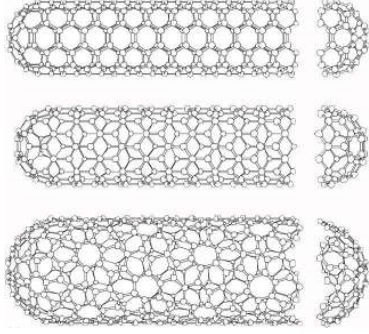
The translation vector  $\mathbf{T}$  is the smallest graphene lattice vector and specifies the translational period  $t$  along the tube axis. Thus, it is parallel to the nanotube axis and perpendicular to the chiral vector  $C_h$  in the unrolled honeycomb lattice ( $\mathbf{OB}$  in Figure 1.3).  $\mathbf{T}$  can be expressed in the terms of the basis vectors  $a_1$  and  $a_2$  from the real lattice, as:

$$T = t_1 a_1 + t_2 a_2 \equiv (t_1, t_2). \quad (1.4)$$

Based on  $C_h \cdot T = 0$ , the expressions for  $t_1$  and  $t_2$  are  $t_1 = (2m+n)/d_R$ ,  $t_2 = -(2n+m)/d_R$ , where  $d_R$  is the greatest common factor of  $(2m+n)$  and  $(2n+m)$ . The unit cell of a SWCNT is a rolled-up rectangle defined by  $C_h$  and  $\mathbf{T}$ . Thus, to determine the number of electronic and phononic bands in this 1D structures, it is needed to derive the number of hexagons per unit cell  $N$  as a function of  $(n, m)$ , as:

$$N = \frac{|C_h \times T|}{|a_1 \times a_2|} = \frac{2(n^2 + m^2 + nm)}{d_R}. \quad (1.5)$$

Therefore the number of carbon atoms in each unit cell of the carbon nanotube is  $2N$  due to each hexagon containing two carbon atoms.

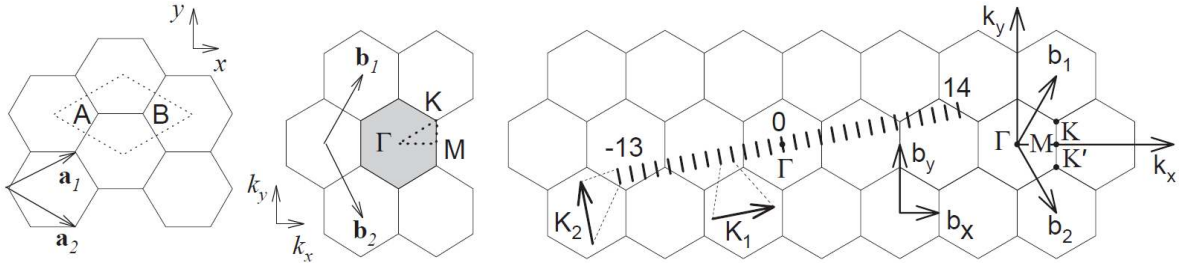


**Figure 1.4.** Exemplification of the three different types of carbon nanotubes. From top to bottom, a (5,5) "armchair", a (9,0) "zigzag" and a (10,5) "chiral" tubes are depicted [19].

Using the  $(n, m)$  indices, it is possible to classify nanotubes (Figure 1.4) as follows:

1. an **armchair nanotube** corresponds to the case of  $n = m$ , where  $\theta = 30^\circ$
2. a **zigzag nanotube** corresponds to the case where  $m = 0$  and  $\theta = 0^\circ$
3. a **chiral nanotube** defines all other chiralities.

The connection to the reciprocal lattice can be simply understood in the following manner. In Figure 1.5, the unit cell (left) and the first Brillouin zone (middle) of 2D graphite are shown, respectively. Here  $b_1$  and  $b_2$  are the reciprocal lattice vectors.



**Figure 1.5.** (Left) Hexagonal lattice of a graphene sheet in the real space. The dotted rhombus shows the sites A and B where C atoms are located in the unit cell (defined by  $a_1$  and  $a_2$ ). (middle) Shaded hexagon delineates the first Brillouin zone of a graphene layer. The reciprocal lattice vectors ( $b_1$  and  $b_2$ ) and the high symmetry points ( $\Gamma, K$  and  $M$ ) [20] are depicted. (Right) Parallel equidistant lines are determined by periodic boundary conditions along the circumference of the tube. The cutting lines for a (4,2) nanotube are shown [21].

According to the Cartesian coordinate system, the real space basis vectors can be expressed as:

$$a_1 = \left( \sqrt{3}a/2, a/2 \right) \quad a_2 = \left( \sqrt{3}a/2, -a/2 \right). \quad (1.6)$$

Correspondingly, the basis vectors of the reciprocal lattice are given by:

$$b_1 = \left( \frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a} \right) \quad b_2 = \left( \frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a} \right), \quad (1.7)$$

As clearly observed in Figure 1.5 (middle and right), the direction of the basis vectors  $b_1$  and  $b_2$  of the reciprocal lattice are rotated by  $30^\circ$  with respect to the basis vectors  $a_1$  and  $a_2$  in real space. The first Brillouin zone (shaded hexagon in Figure 1.5 (middle)) , has three high symmetry points:  $\Gamma$ ,  $K$ , and  $M$ , which are defined as the centre, the corner, and the centre of the edge, respectively, which is of particular importance to set the energy dispersion relation of this system.

Considering the definition of  $C_h$  and  $T$ , the analogous reciprocal lattice vectors are  $K_1$ , corresponding to  $C_h$  in the circumferential direction and  $K_2$ , corresponding to  $T$  along the nanotube axis. The direct relation between both spaces can be done by using the expression  $R_i \cdot K_j = 2\pi\delta_{ij}$ , with  $R_i$  and  $K_j$  being the lattice vectors in the real and reciprocal space, respectively.

By definition, only  $K_2$  can get continuous values, while  $K_1$  will give the discrete  $k$  values in the direction of  $C_h$  due to the periodical boundary conditions. The relations can be expressed as followed:

$$C_h \cdot K_1 = 2\pi, \quad T \cdot K_1 = 0; \quad C_h \cdot K_2 = 0, \quad T \cdot K_2 = 2\pi. \quad (1.8)$$

$K_1$  and  $K_2$  can also be expressed in the following terms:

$$K_1 = (-t_2 b_1 + t_1 b_2)/N \quad K_2 = (m_2 b_1 - n b_2)/N, \quad (1.9)$$

This quantization can be seen in Figure 1.5 (Left), where the first Brillouin zone is visualized as a line of parallel segments with the length of  $|K_2|$  separated by the discrete values of  $|K_1|$ . Since  $NK_1 = (-t_2 b_1 + t_1 b_2)$  corresponds to a reciprocal lattice vector of 2D graphite, the two wave vectors which differ by  $NK_1$  are equivalent. Furthermore,  $t_1$  and  $t_2$  do not have a common divisor except for the unity and none of  $N-1$  vectors  $\mu K_1$  (where  $\mu = 1, \dots, N-1$ ) are reciprocal lattice vectors of the 2D graphite. Then the reciprocal vector can be expressed as

$$K = k \frac{K_2}{|K_2|} + \mu K_1, \quad \mu = 0, \dots, N-1 \quad \text{and} \quad -\pi/|T| < k < \pi/|T|. \quad (1.10)$$

As a consequence, each discrete value of the circumferential wave vectors gives rise to 1D electronic energy bands (one  $\pi$  and one  $\pi^*$  bands). In the following section, it will be discussed in-depth the electronic properties of SWCNTs on the basis of this structural considerations.

Considering the high-symmetry of the carbon nanotubes, their electronic structure can be calculated making use of a simple tight-binding approximation of the band structure of a graphene layer. This theoretical approach for the calculation of the electronic band structure uses an approximate set of wave functions based upon superposition of wave functions for isolated atoms located at each atomic site. In this model, the electrons should be tightly bound to the atom to which they belong and they should have limited interaction with states and potentials on surrounding atoms of the solid. As a consequence, the wave function of the electron will be rather similar to the atomic orbital of the free atom [22]. Three of the four C atoms form  $\sigma$  bonds with neighbouring atoms with a strong covalent interaction in

the particular case of SWCNTs. The remaining one forms the  $\pi$  band, which is the related to the electronic transport properties.

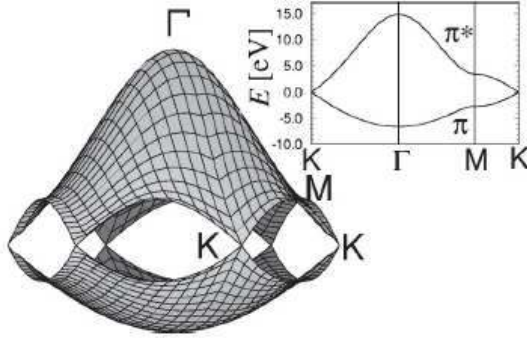
The dispersion relation of the  $\pi$  band of 2D graphite [1] is defined as follows:

$$E_{g2D}^{\pm}(k) = \frac{\epsilon_{2p} \pm \gamma_0 \omega(k)}{1 \mp s\omega(k)} \quad (1.11)$$

where  $\gamma_0$  is the hopping integral,  $\epsilon_{2p}$  is the site energy of the  $2p$  atomic orbital and  $s$  is the overlap integral between the nearest atoms. The  $\pm$  signs in the numerator and denominator account for the anti-bonding  $\pi^*$  energy band and the bonding  $\pi$  band, respectively. The function  $\omega(k)$  is given by:

$$\omega(k) = \left\{ 1 + 4 \cos\left(\frac{3k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right) \right\}^{1/2}. \quad (1.12)$$

The resulting energy dispersion relations of 2D graphite are plotted in Figure 1.6. Here, the Fermi surface is essentially reduced to the six distinct  $K$  points of the hexagonal Brillouin zone and the last valence and first conduction bands cross at the vertices of this zone.



**Figure 1.6.** Representation over the Brillouin zone of energy dispersion relation for the  $\pi$  and  $\pi^*$  bands in 2D graphene. The inset depicts the energy dispersion along the high-symmetry directions  $\Gamma MK$ . Exemplification of the three different types of carbon nanotubes [23].

In the inset of Figure 1.6, the energy dispersion relations is represented along the high-symmetry axis. Further details on the calculation of the band structure of 2D graphene monolayers can be widely found in the literature [24, 25].

From equation 1.10, and substituting into the expression of the graphite  $\pi$  band, one obtains

$$E_{1D}(K) = E_{g2D}\left(k \frac{K_2}{|K_2|} + \mu K_1\right), \quad (1.13)$$

with  $(-\pi/|T| < k < \pi/|T|)$  and  $(\mu = 0, \dots, N-1)$ .

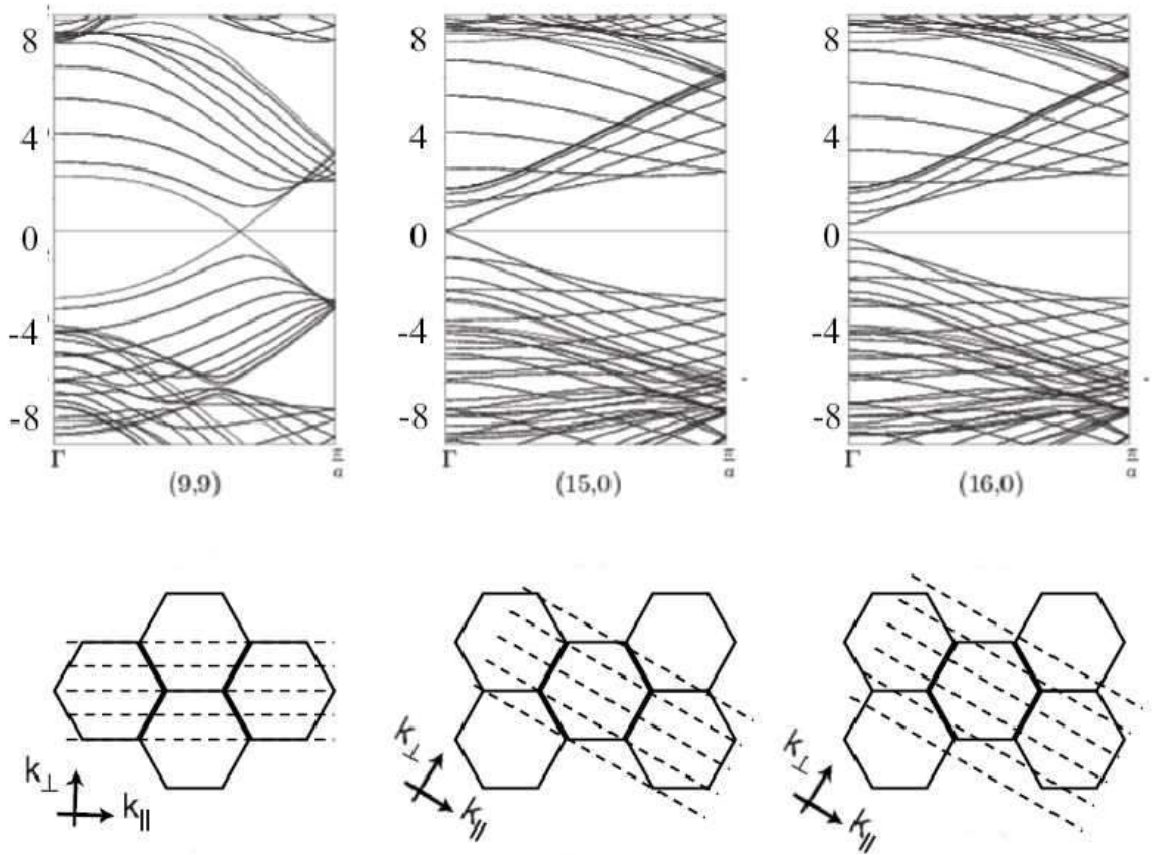
Combining the  $x$  and  $y$  components of  $K_1$  and  $K_2$ , the above equation can be rewritten as

$$E_{1D}(K) = \pm \gamma_0 \left\{ 1 + 4 \cos\left[\frac{3a_0}{2}\left(k \frac{K_{2x}}{|K_2|} + \mu K_{1x}\right)\right] \cos\left[\frac{a_0}{2}\left(k \frac{K_{2y}}{|K_2|} + \mu K_{1y}\right)\right] + 4 \cos^2\left[\frac{a_0}{2}\left(k \frac{K_{2y}}{|K_2|} + \mu K_{1y}\right)\right] \right\}^{1/2}. \quad (1.14)$$

Thus, considering the relation between the chirality  $(n, m)$  and the reciprocal vector  $K$ , the band structure of nanotubes (Figure 1.7) can be obtained from equation 1.14. Then the 1D density of states (DOS) in units of states/C-atom/eV can also be calculated by the following relation

$$D(E) = \frac{T}{2\pi N} \sum_{\pm} \sum_{v=1}^N \mathcal{R} \frac{1}{\left| \frac{dE_v^{\pm}(k)}{dk} \right|} \delta[E_v^{\pm}(k) - E] dE, \quad (1.15)$$

where the summation is taken for the  $N$  1D conduction (+) and valence (-) bands, respectively.



**Figure 1.7.** (From left to right) Band structure of a (9,9) armchair and (15,0) and (16,0) zigzag nanotubes. Under each graph, the quantization lines bands the reciprocal lattice of graphene. Depending on the point where they cut the hexagons, a metallic or a semiconducting tube can be determined.

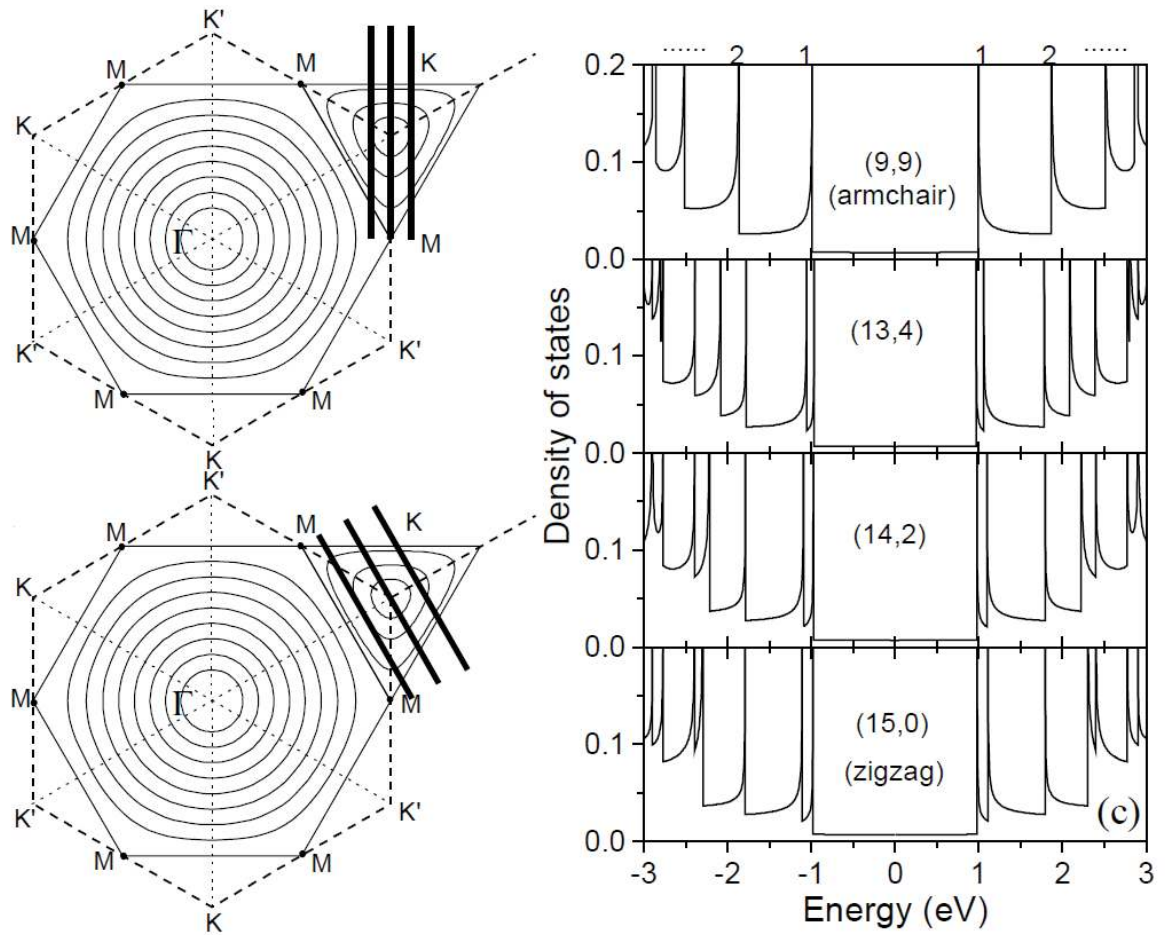
The  $k$ -vector projected onto the chiral vector  $k_{\parallel}$  (along the circumference) becomes quantized, while the  $k$ -vector ( $k_{\perp}$ ) along the tube axis is continuous for an infinite nanotube. Thus, the band structure will be defined by the energy bands related to this quantization (Figure 1.7). As a consequence, metal or semiconducting nanotubes can be defined depending on whether the cutting lines cross the  $K$ -point or not. The  $\pi$  and  $\pi^*$  energy bands of 2D graphite are degenerated. In Figure 1.7 (left), an example of an armchair

nanotube is plotted. Here, the center-line crosses two corners of the hexagon, suggesting that the armchair nanotubes should be always **metallic**. For  $(n, m)$  nanotubes, the theoretical analysis [1] has shown that, when  $(n - m)$  is not a multiple of three, the electronic states (cutting lines) miss the corner points (Figure 1.7 (right)) and the nanotubes are **semiconducting**. Consequently, for all other nanotubes certain electronic states land on the corner points of the first Brillouin zone (Figure 1.7 (middle)) yielding metallic character. However, due to a curvature induced orbital rehybridization effect [16], most of these types of tubes are driven into **small-gap semiconductors** with a band gap scaled by  $1/d^2$  [6] and of about 10 meV for nanotube with diameter around 1.4 nm.

The band structure (as shown in Figure 1.7) is also chirality dependent. Note here that the density of states of these 1D structures is not a continuous function of the energy, but it descends gradually and then increases in a discontinuous spike. These are the so-called **van Hove singularities**.

The energy separation between corresponding van Hove singularities is given by the relation of  $E_{11}^M = 6a_0\gamma_0/d$ . However, this is only correct within the linear  $k$  approximation for the energy dispersion relation of graphite. When the SWCNT has a smaller diameter  $d$ , the separation between two adjacent wave vectors,  $|K_1| = 2/d$ , becomes larger and the linear approximation is no longer correct. When the equi-energy lines near the  $K$  point are plotted, it is clearly shown that the circular contours only exist for smaller  $k$  values near the  $K$  points in the Brillouin zone. For larger  $k$  values, the equi-energy contour becomes a triangle which connects the three M points nearest to the  $K$  point, as shown in Figure 1.8 as the thin line curves. The distortion of the equi-energy lines away from the circular lines in the materials with a 3-fold symmetry axis is known as the trigonal warping effect [26]. In this case, the detailed form of the van Hove singularities in the 1D electronic DOS of metallic SWCNTs are chirality-dependent, as shown in Figure 1.8. The deviations for circular contours produce a splitting of the DOS singularities in metallic nanotubes. In armchair nanotubes (Figure 1.8 (top left)), the two wave vector lines near the  $K$  point are equivalent to each other and the DOS peak energies are equal, due to the symmetry of the energy contour in the  $KK'$  direction. While in metallic zigzag nanotubes (Figure 1.8 (bottom left)), the two lines are not equivalent in the reciprocal lattice space, which will give different energy separations relative to the  $K$  point. Thus the splitting of the DOS peak occurs, and the its value is a function of the chiral angle with a maximum for metallic zigzag nanotubes and zero splitting for armchair nanotubes [23, 26–28]. Figure 1.8 (right) shows an example of the calculated DOS in the metallic nanotubes from armchair (9, 9) to zigzag (15, 0) nanotubes with a diameter of about 1.22 nm.

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**Figure 1.8.** Schematic explanation of the splitting effect from armchair nanotube (above) to zigzag nanotube (below). The thin line curves are equi-energy contour. The three bold lines near the K point are possible reciprocal lattice vectors of the SWCNT. The minimum energy along the neighbouring two lines gives the energy positions of the van Hove singularities. On the right column, the calculated DOS for four selected metallic nanotubes with different chiral angle and a diameter of about 1.2 nm.

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## Controlled modification of the electronic properties of SWCNTs

The electronic properties of SWCNTs depend strongly on size and chirality. However, during the synthesis of SWCNTs, the just mentioned properties are not necessarily easily tailored. Shortly after the successful production of carbon nanotubes and the achievements in the characterization of their outstanding properties, several questions arouse regarding the possibilities to control their functionality to reach their full potential for applications. The outer wall of pristine carbon nanotubes has always been conceived as chemically inert and therefore not desirable for applications. This is what actually inspired the idea to functionalize SWCNTs making use of their extraordinary physical properties simultaneously. There are many possibilities to classify the types of functionalization but to facilitate the description and understanding of the experiments performed in this PhD thesis, this chapter will give a brief description about the possibilities to tune the electronic properties of SWCNTs via on-wall, endohedral and exohedral functionalization and their corresponding sub-classification. Undoubtedly, a number of successful achievements have been published using functionalized nanotubes, but several experimental limitations still remain unsolved.

### 2.1 Endohedral functionalization or filling

This classification involves the encapsulation of atoms, molecules or crystalline materials inside the nanotube hollow core [29, 30]. Filling can encompass a great number of application possibilities depending on the material, molecule or structure that gets encapsulated inside the SWCNT (See Figure 2.1). Although the filling of carbon nanotubes has been a very active field, in the latest years, these kind of filled SWCNTs have gained considerable attention, specially regarding synthesis routes [31–39]. The encapsulation of organic molecules inside SWNTs is tested intensively. Hybrid systems have been reported with modified electronic and optical properties, although there are still some difficulties preparing homogeneous samples.

## 2.2 Exohedral Functionalization

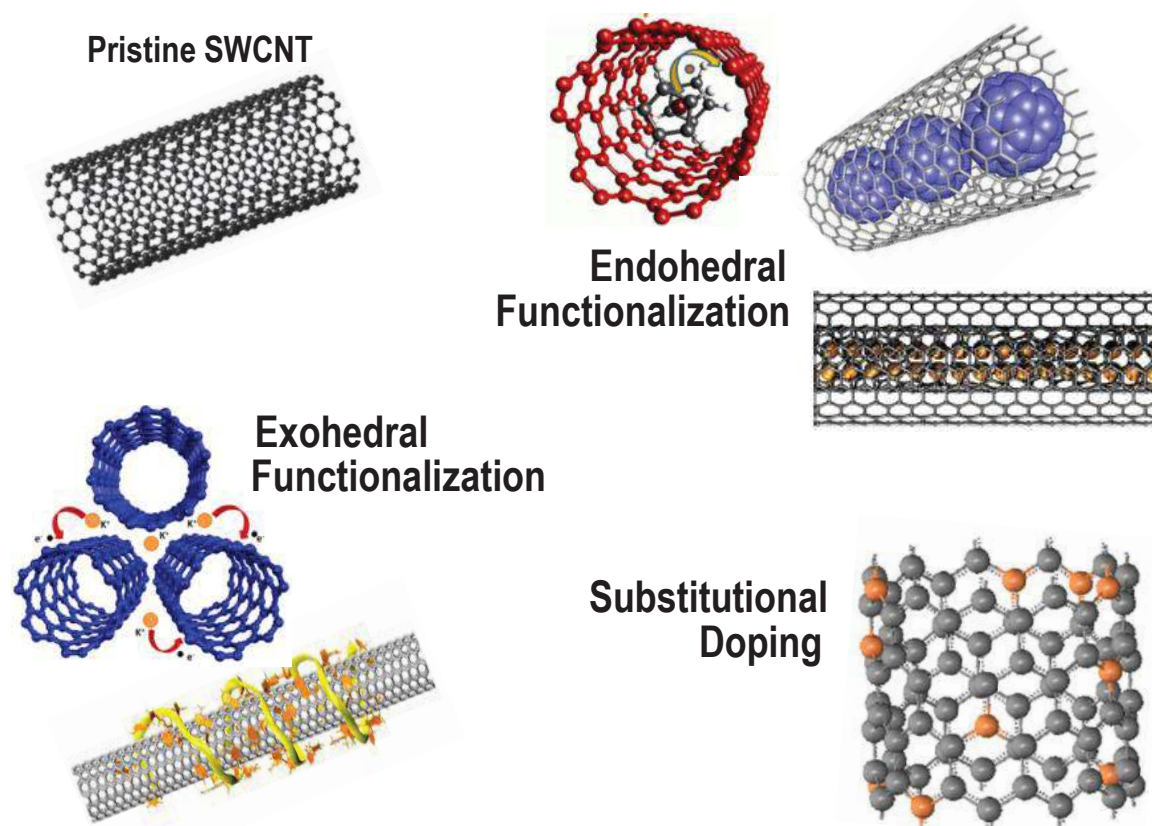
The use of the term 'exohedral' diverges within the literature but in this thesis, this type of classification will be explicitly considered for the cases in which the functionalizing agents remain outside the tube wall. The terms covalent and non-covalent functionalization are usually employed in chemical or biological studies with large molecules surrounding the nanotubes. Intercalation will be used when dealing with bundles of nanotubes and small molecules. Finally, a word on chemisorption vs. physisorption of molecules (regardless their size) will be given at the end of this section to understand the discussion of chapter six, which involves the use of SWCNTs as molecular sensors.

### 2.2.1 Covalent and non-covalent functionalization

The common approaches to understand this classification is associating chemical with covalent, and physical with non-covalent functionalization. Chemical functionalization is based on the covalent bond of functional groups onto carbon form of CNTs. It can be performed at the end caps of nanotubes or on their sidewalls which have many defects (this will be described also in the section related to on-wall doping). Direct covalent sidewall functionalization is associated with a change of hybridization from  $sp^2$  to  $sp^3$ . This process can be made by reaction with some molecules of a high chemical reactivity. Examples of this are fluorination, oxidative damage, acid treatment, among others [40–43]. The covalent method has a good advantage which that was soluble in various organic solvents because SWCNTs possess many functional groups such as polar or non-polar groups. However, these methods have two major drawbacks. First, during the functionalization reaction, especially during the ultrasonication process, where a large number of defects are inevitably created on the SWCNTs' sidewalls and, in some extreme cases, SWCNTs are fragmented into smaller pieces [44]. The damaging effects result in severe degradation of the mechanical properties of the tubes as well as a disruption of  $\pi$  electron system. This last is detrimental for transport properties, because defects sites scatter electrons and phonons that are responsible for the electrical and thermal conduction. Also, concentrated acids or strong oxidants are often used for this kind of functionalization, which are environmentally unfriendly [45].

The advantage of non-covalent functionalization is that it does not destroy the conjugated system of the SWCNTs' sidewalls, and therefore it does not affect the final structural properties of the material. Hence, it turns into an alternative method for tuning the interfacial properties of nanotubes. The CNTs can be functionalized in this way by aromatic compounds, surfactants and polymers, employing  $\pi$ - $\pi$  stacking or hydrophobic interactions for the most part. In these approaches, the non-covalent modifications of the tubes can do much to preserve their desired properties, while improving their solubilities quite remarkably [45].

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**Figure 2.1.** Representation of the possible functionalization paths for SWCNTs: intercalation, endohedral doping or filling and on-wall doping, respectively.

### 2.2.2 Intercalation

The term intercalation describes a bundle of SWCNTs, which allows the presence of atoms and small molecules within its interstitial channels. The bundle's properties are modified by the electron-donor or electron-acceptor character of the molecules. Taking advantage of this, the behavior of a collective of nanotubes as a whole can be changed. For instance, it has been observed that the Tomonaga-Luttinger liquid behavior proper of 1D systems can be changed to a common Fermi liquid by intercalation of potassium atoms[46–48].

### 2.2.3 Chemisorption vs. Physisorption

The large surface area to volume ratio of SWCNTs is particularly appealing for applications where the adsorption of other molecules plays an important role. Several studies are available, which use both MW and SWCNTs aiming at understanding the mechanisms that affect their electronic properties upon exposure to different molecular species and the natural question is to try understanding if the mechanisms involved are either chemisorption or physisorption.

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The behavior of MWCNTs can exhibit great differences from the same device employing SWCNTs and the performance is also different if the tubes are used in the form of films, as individual nano-components or as bulk product. Therefore, these questions that could seem fundamental and easy to answer, still need to be addressed.

## **2.3 Sidewall-functionalization**

Replacing the C atoms by impurity atoms in the walls is known as sidewall functionalization. The natural choices are N, B, P and Si although only the first two have been much more investigated. However, it is not always energetically favorable for most of the impurity atoms to reside in the hexagonal network of carbon network. In such case the presence of vacancies also needs to be considered. In other words, the presence of defects. The next subsections briefly describe how both sidewall-functionalization types are understood.

### **2.3.1 Defects**

Defects in SWCNTs are sites where the carbon atoms are removed from the hexagonal lattice or it has been rearranged in such manner that the formation of low-energy adsorption sites is promoted. This can also serve for the condensation of chemical species at high vapor concentrations.

### **2.3.2 Substitutional Doping**

This case specifically refers to the direct replacement of carbon atoms by heteroatoms. As the dopant is a heteroatom which takes the place of one of the C atoms in the lattice, the size of it is crucial. B and N are the nearest neighbors of the C in the periodic table. Both B and N have atomic radii similar to C. The replacement of carbon atoms by B or N eventually changes the local chemical reactivity and this chemical reactivity modifies the binding energy. B and N-doped CNTs can either be p-type or n-type CNTs, similar to the usual semi-conducting materials, resulting in several important applications in nanoelectronic devices. Note that B and N are not the only possible substitutional heteroatoms but the most extensively investigated. Si and P have already been shown as promising heteroatomic dopants.

A great part of this PhD thesis focused on the purification of B doped SWCNTs which were synthesized in our laboratory by high-vapor chemical deposition methods with only C/B feedstock. For the first time, a purification process was applied to this type of material and the electronic properties of a film of clean doped nanotubes were studied. This is the matter of discussion of chapter five.

## **2.4 Doping levels and bonding environments**

The literature regarding doped nanotubes, especially considering B and N as heteroatoms is really extensive. However, it has never been clearly stated what are the limits at which

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structures are still stable nanotubes with a defined percentage of doping atoms. In the same manner, it is still not understood what are the lowest amounts of heteroatoms that can be incorporated in the nanotube lattice so that the electronic properties of the tubes are profitable in the same fashion of Si based technology. Therefore, this section aims at giving a brief insight to the concepts behind low doping and formation of heteroatoms in order to understand the problems aimed to be solved within this thesis.

#### **2.4.1 Low doping**

For low doping levels of substitutional heteroatoms in CNTs, the rigid band model is most likely to be valid since these structures are similar to doped Si with only a small number of dopant related defect centers. any band structure modification can be considered negligible and the band structure of the doped system can be obtained by shifting the Fermi level in the band structure of the pristine system [49]. The applicability of a rigid band model has been proven for nanotubes by field-effect doping (p-n type) and intercalation with alkali metals even to very high doping levels (10%) n-type, and for p-type doping for Br<sub>2</sub>, I<sub>2</sub>, and FeCl<sub>3</sub> doping, among others [50–53].

#### **2.4.2 High doping and formation of heteronanotubes**

At this point it is worth recalling that a well-known procedure in the semiconducting technology to modify the solid state properties of materials is the addition of electron acceptor and donors [49]. To achieve it, heteroatoms are introduced to the CNTs system and depending on the position in relation to the tubes, there are different possibilities to affect their properties, i.e. some atoms or molecules can be encapsulated in the hollow core of the tubes or they can be trapped between the bundles (Figure 2.1). The different situation can be described as follows.

When the incorporation of heteroatom is higher, two situations are possible: high doping and formation of novel heteronanotubes. A heteronanotube of B, C and N is a 1D tubular structure with an essentially similar overall morphology compared to SWCNTs and the basic picture of a tubule with the honeycomb-like wall structure [54, 55]. However this wall structure is in principle a stable planar layer of C, B and N atoms arranged in hexagonal distribution with various stoichiometries. With the aid of an example, it will be easier to understand the concept of high doping and heteronanotubes.  $BC_3$ -SWCNT is not a highly B doped nanotube. In this case, due to the high doping, a  $BC_3$  planar graphite-like stable sheet is formed. Other examples of heteronanotubes theoretically predicted, are  $BC_2N$ ,  $C_3N_4$ , among others.



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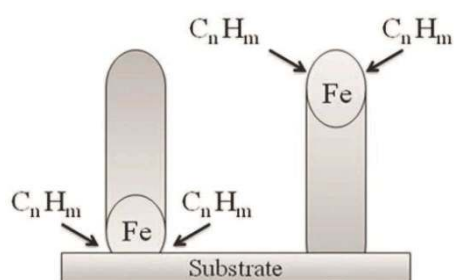
## Experimental Methods

After almost two and a half decades of research in carbon nanotubes, they have encountered several successful application possibilities in new emerging technologies. Several routes for SWCNTs growth in high yields were promptly discovered, but the controlled synthesis of tubes with specific chiralities or without impurities (e.g. amorphous carbon, metallic particles) caused trouble for a long time. The progress regarding methods to clean them and even separate them according to metallic character have been extremely useful. Trying to overcome this point, typical separation methods, inspired in the biochemistry field, have been adapted with a great success [56, 57].

The way in which nanotubes are formed is not exactly known and it seems to be related to the synthesis technique used. The growth mechanisms are intrinsically related to the type of catalytic mechanism (floating, supported or free catalyst synthesis). The literature regarding growth mechanisms is really abundant and it is out of the scope of this thesis, but to summarize this in a very simplistic manner, we can say that nanotubes can form either via the *base-growth* or the *tip-growth* models [58] (Figure 3.1). In the base-growth model, the nanotube lengthens with a close-end, while the catalyst particle remains on the supporting surface. The carbon feedstock is thus supplied from the "base" where the nanotube interfaces with the anchored metal catalyst [59]. In principle, base-growth operates when strong metal-support interactions exist so that the metal species remain pinned on the support surface. In contrast, in the tip-growth mechanism, the nanotube lengthening involves the catalyst particle lifted off from the support and carried along at the tube end. The carried-along particle is responsible for supplying carbon feedstock needed for the tube growth and this mode operates when the metal-support interaction is weak [59, 60]. As mentioned, this is not in the scope of this PhD research topic, but it is important to know that nanotubes with on-wall doping have not been as thoroughly studied in this respect as compared with their pristine counterparts. A more detailed information about all efforts done on the topic can be found in the vast literature available [61–71].

This chapter is devoted to giving an overall description of the most established routes

for the synthesis of pristine nanotubes. I have only used high vacuum chemical vapor deposition for the synthesis of doped SWCNTs during this PhD period, but other pristine nanotubes provided via collaborations have been synthesized mainly by high temperature methods and it is necessary to understand their properties, which are highly influenced by the used synthesis method. Additionally, it will be provided a general background related to the post-synthesis methods for cleaning and separation of SWCNTs.



**Figure 3.1.** Two general growth mode of nanotube in chemical vapor deposition. Left diagram: base-growth mode. Right diagram: tip-growth mode. Adapted from [72]

Both the production and all kind of post-manufacturing processes (i.e sorting tubes by length, diameter or chirality) enable the individualization of particular sort of nanotubes with very specific characteristics. For this reason, accessing these properties has required the use of more sensitive characterization techniques. This situation is reflected, for example, in the use of high energy spectroscopy techniques to identify different bonding environments due to doping, which turns to be crucial in determining extremely low doping levels. The end of this chapter will be dedicated to explain in detail the physical principles of the characterization methods as well as the theoretical approaches used throughout this work. Information about the specific equipment is also included.

### 3.1 Synthesis techniques

Since the discovery of carbon nanotubes, numerous ways of producing pristine material have been explored. The most widespread methods are electric arc-discharge, laser evaporation and chemical vapour deposition, but there have been developed several fashionable variations of them. The specific atomic geometrical arrangement determines the type of nanotubes and hence, the characteristics of the materials and its direct applications. Consequently, the growth technique and every single parameter involved in the process have a great influence in their properties. There are high and low temperature methods. Laser ablation and arc-discharge are part of the first group. Most of the low temperature methods are related to chemical vapour deposition technique.

#### Laser ablation

This is an efficient route for the synthesis of bundles of SWNTs with a narrow distribution. In this method, a piece of graphite target is vaporized by laser irradiation under high temperature in an inert atmosphere [73, 74]. The quality and yield of these products have been found to depend on the reaction temperature. In general, the yield of SWNTs strongly depends on the type of metal catalyst used and is seen to increase with furnace temperature,

among other factors. The laser technique is not economically advantageous because the process involves high-purity graphite rods and the laser powers required are high (in some cases two laser beams are necessary) [75].

### **Arc discharge**

CNTs are prepared by striking an arc between graphite electrodes in an inert atmosphere (argon or helium) [2, 76–78]. The carbon arc provides a convenient and traditional tool for generating the high temperatures needed to vaporize carbon atoms into a plasma ( $>3000^{\circ}\text{C}$ ). The yield of CNTs depends on the stability of the plasma formed between the electrodes, the current density, inert gas pressure and cooling of electrodes and chamber. Among the various inert gases, helium (He) gives the best results, probably due to its high ionization potential. The well-cooled electrodes and arc chamber help to maximize the nanotube yield in the arc growth process. The synthesis of doped nanotubes with this technique is usually achieved incorporating the dopant as part of the electrodes or as reaction atmosphere.

### **Chemical vapor deposition**

Chemical vapor deposition (CVD) has become the most important commercial approach for manufacturing carbon nanotubes. CVD is known as irreversible deposition of a solid from a gas/a mixture of gases through a heterogeneous chemical reaction. The process usually involves high temperature decomposition of hydrocarbons in presence of a catalyst. This reaction takes place at the interface of gas-solid substrate, and depending on the deposition conditions, the growth process can be controlled either by diffusion or by surface kinetics. CVD encompasses various techniques that are among the best suitable to produce SWCNTs at moderate temperatures. It offers better growth control because of the equilibrium nature of the chemical reactions involved. Common carbon precursor gases used in CVD of pristine SWCNTs are methane, ethylene, acetylene, benzene, carbon monoxide or ethanol [79]. Transition metals such as Fe, Co and Ni are frequently used as catalysts. In addition to these catalysts, other metals such as: Sc, Ti, V, Cr, Mn, Y, Zr, Nb, Mo, Hf, Ta, W or a combination of them, have also been reported [80, 81]. Frequently used substrates for bulk synthesis are ceramic particles such as magnesium oxide, aluminium oxide. Surface synthesis of SWCNTs is another possibility and it requires flat supporting substrates.

#### **3.1.1 Synthesis of doped SWCNTs**

Interestingly, the synthesis of SWCNTs with substitutional dopants is not as straight forward as the synthesis of pristine material. In the specific case of CVD, parameters such as the types of catalysts, the vapor pressure of the precursor used and the temperature have to be controlled in a different manner. The literature related to SWCNTs doped with different heteroatoms is really vast and I will therefore focus only on the B doped case, which is the only type of material that I report in this work. In this context, to achieve the milestones of

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this thesis, I have studied the possibility to particularly apply a high vacuum (HV) modified CVD method to grow B doped nanotubes in situ with very low amount of dopant.

Just as brief background, low amounts of substitutional doping and the formation of B/C heteronanotubes have been reported by using thermo-chemical treatments through substitutional reactions [82, 83], direct synthesis by arc discharge[84] and laser vaporization [85, 86]. Using high-vacuum chemical vapor deposition (HV-CVD), the first successful attempt to obtain high quality single-walled B-doped material was reported in Reference [87, 88]. This method presents interesting advantages such as the use of a high vacuum base atmosphere, and the possibility to control the decomposition of the catalysts in solid phase with continuous pumping, which avoids poisoning before the synthesis process starts. Additionally, we have used a pure liquid precursor that provides simultaneously a C and B[89].

### 3.2 Purification and Metallicity Sorting

Various methods have been developed in the last years towards the purification of nanotubes to get rid of the catalytic byproducts remaining after synthesis. Nowadays, purifying SWCNTs is almost a standard procedure and it can be achieved in different manners (e.g. electrophoresis, agarose gel, DNA assisted separation). From these, density gradient ultracentrifugation was the main technique used in this doctoral thesis. I have tried to investigate the possibility of finding methods to purify B-doped nanotubes, which in principle needs to be calibrated independently in comparison to samples made of only carbon nanotubes, where the catalytic remaining of the synthesis is essentially different. Once the purification step was overcome, additional experiments were performed to try to separate B-doped purified samples into metallic and semiconducting species.

Purification methods of SWCNTs can be basically classified into three categories, namely chemical, physical, and a combination of both.

In the **chemical method** it is necessary to first consider the amorphous carbon species, which are great part of the impurities existing in a pristine sample as-synthesized. Compared with SWCNTs, these impurities usually have higher oxidation activity, due to the presence of more dangling bonds and structural defects [90]. The chemical oxidation purification is based on the idea of selective oxidation etching, wherein carbonaceous impurities are oxidized at a faster rate than the nanotubes. In general, chemical oxidation includes *gas phase oxidation* (using air, O<sub>2</sub>, Cl<sub>2</sub>, H<sub>2</sub>O, etc.) [91], *liquid phase oxidation* (acid treatment and refluxing, etc.), and *electrochemical oxidation*. The disadvantages of this method are that it often opens the end of CNTs, cuts CNTs, damages surface structure and introduces oxygenated functional groups (OH, C=O, and COOH) on their walls. Interestingly, the SWCNTs purified with this method can serve as chemical reactors or a starting point for subsequent nanotube surface chemistry [92], unless the purification continues.

The **physical method** is ideal where non-oxidative treatments are highly desirable. The morphology and physical properties of carbon nanotubes are different from impurities and these differences enable the separation of CNTs from impurities by adopting some phys-

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ical techniques. Physical-based methods include *filtration* [93], *chromatography*, *centrifugation* [94–96], *electrophoresis*, and *high temperature annealing* (1400 to 2800 °C). The advantages of these treatments are their non-destructive and non-oxidizing response on the sample. Nevertheless, these purification processes are mostly performed in solution, which require the CNTs to be dispersed by using surfactants and/or sonication.



**Figure 3.2.** Density gradient ultracentrifugation (DGU) process. By using this method, it is possible to clean nanotubes as well as separate clean SWCNTs material according different characteristics. For example, by mixing the pristine SWNTs with surfactants, the metallic and semiconducting nanotubes can be separated from each other upon ultracentrifugation.

As mentioned, it is possible to combine physical and chemical methods. Indeed, a

multi-step purification method combines different purification techniques, leading to high yield and quality purified nanotube material. The part of this PhD thesis where purification was done, emphasizes on the feasibility of using a suitable modified density gradient ultracentrifugation method on in-situ B-doped material. It worth to remember that dopants on the nanotubes' lattice, as it is the case of substitutionally B-doped tubes, could represent sites with more reactivity upon interaction with chemical (e.g. surfactants).

*Density gradient ultracentrifugation* (DGU) works by exploiting subtle differences in buoyant density, as it is very well explained by Hersam et al. [97, 98]. The species of interest are loaded into an aqueous solution with a known density gradient. Under the centripetal force of an ultracentrifuge, the species sediment toward their respective isopycnic points (i.e. the position where their density matches that of the gradient). With suitable choice of the initial gradient, the species spatially separate by density at which point they can be removed by fractionation. For DGU to be successful, the buoyant density of a SWNT must be directly related to its physical and electronic structure. Since a SWNT is a hollow cylinder, all of its mass is located on its surface. The buoyant density (mass-to-volume ratio) of a SWNT will be proportional to the surface-to-volume ratio for a cylinder, which is inversely proportional to the diameter. If DGU occurred in vacuum, then the SWNT buoyant density would follow this simple inverse relationship with its diameter. However, since DGU occurs in aqueous solution and SWNTs are strongly hydrophobic, amphiphilic surfactants must be used to disperse the SWNTs. Consequently, the actual buoyant density of an SWNT in a DGU experiment will be a function both of the geometry of the SWNT and the thickness and hydration of the amphiphilic surfactant coating. When a surfactant is chosen that uniformly and identically encapsulates all of the SWNTs in solution, then the buoyant density is only a function of the SWNT diameter. Therefore, at low-speed centrifugation, amorphous carbon is removed and at high-speed centrifugation, metallic particles are separated from the nanotubes dispersion. The DGU technique was used for purification as well as separation of the B-doped nanotubes. The specific parameters used in the experiments will be summarized in the chapter corresponding to this topic.

### **3.3 Morphological characterization**

To make a morphological characterization and identification of the particular structures, several local probing methods are available. However, in this work, scanning electron microscopy (SEM) has been particularly used to have an overall overview of the morphology of the samples after synthesis, purification and other sample preparation methods, giving a first hint of the parameter needed to enhance the quality and the yield of the nanotubes. Scanning electron microscopy is a non-destructive method, which enables the visualization of the sample's surface (i.e. SWCNT network morphology) and also an elemental analysis of the sample. Here, an electron beam is produced by either field or thermionic emission, with primary electron energies of typically 1-10 keV. Thus, the beam is focused by an electromagnetic electron lens system into a spot of about 1-10 nm in diameter on a sample surface [99]. The focused beam is scanned in a raster across the surface by a deflection

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coil system in sync with an electron beam of a video tube, which is used as an optical display. Both beams are controlled by the same scan generator and the magnification given by the size ratio of the display and scanned area on sample. A two-dimensional map of the signal yields a SEM image. Usually systems have a separate detector-processing system, which is used for capturing images with a slower scan rate for better image quality.

For this PhD work, SEM images have been made in-house using a electron-microscope Zeiss Supra 55 VP, which belongs to the Faculty Centre for Nano Structure Research from the University of Vienna. It has four available detectors (three of which are sensitive to secondary electrons, and one is sensitive to backscattered electrons) and they can be used either under vacuum or in a low-pressure mode. The electron microscope is additionally equipped with two other detectors: EDX and WDX detectors, for a precise element analysis but they were not used in this PhD project.

To some extent, Raman spectroscopy also assisted identifying the morphology of our samples regarding diameters and diameter distribution. However, another subsection below will be devoted only to describe Raman spectroscopy and the gain from it specifically applied to nanotubes.

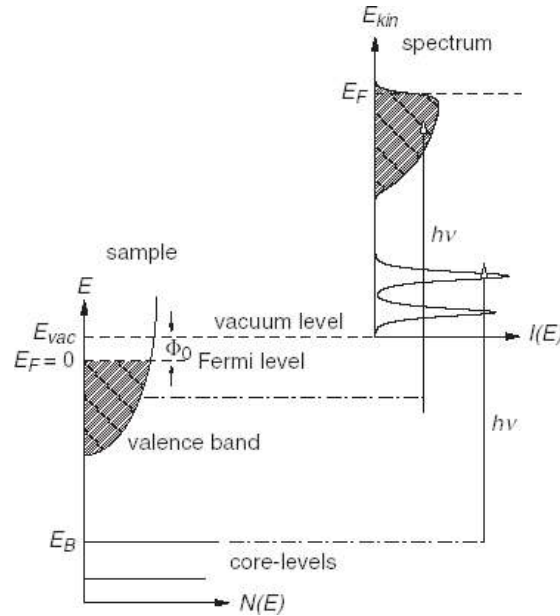
### 3.4 Photoemission spectroscopy

Photoemission Spectroscopy (PES) plays an essential role in the experimental characterization of the electronic structure of solids. It enables the study of low-dimensional systems, interfaces between different materials, chemisorption of gases, surface and interface chemical interactions and correlation effects.

This technique is based on the photoelectric effect proposed by A. Einstein. He assumed that the incoming radiation should be thought of as small packets (quanta) of energy  $2\pi\hbar\nu$ , where  $\nu$  and  $2\pi\hbar$  are the frequency and the Planck's constant, respectively. When light of high enough energy is shone onto a metal surface, this energy is transferred to the electrons and they are emitted from the surface. It takes certain energy to eject an electron from the surface, which is known as the work function ( $\phi$ ) and depends on the metal. Light below a certain threshold frequency, no matter how intense, will not cause any electrons to be emitted. Only light above this energy would cause electron to be emitted and by tuning the frequency of radiation, it would obtain a more energetic photoelectron. Under this consideration, PES happens when photons with a certain kinetic energy ( $2\pi\hbar\nu$ ) are directed on a sample expelling on electron form its orbit. To overcome the potential barrier determined by  $\phi$ , the ejected photoelectron is slowed down and leaves the solid with other kinetic energy ( $E_{kin}$ ), which is detected by an analyzer (Figure 3.3). This process can be completely described by the following formula:

$$E_{BE} = 2\pi\hbar\nu - E_{kin} - \phi \quad (3.1)$$

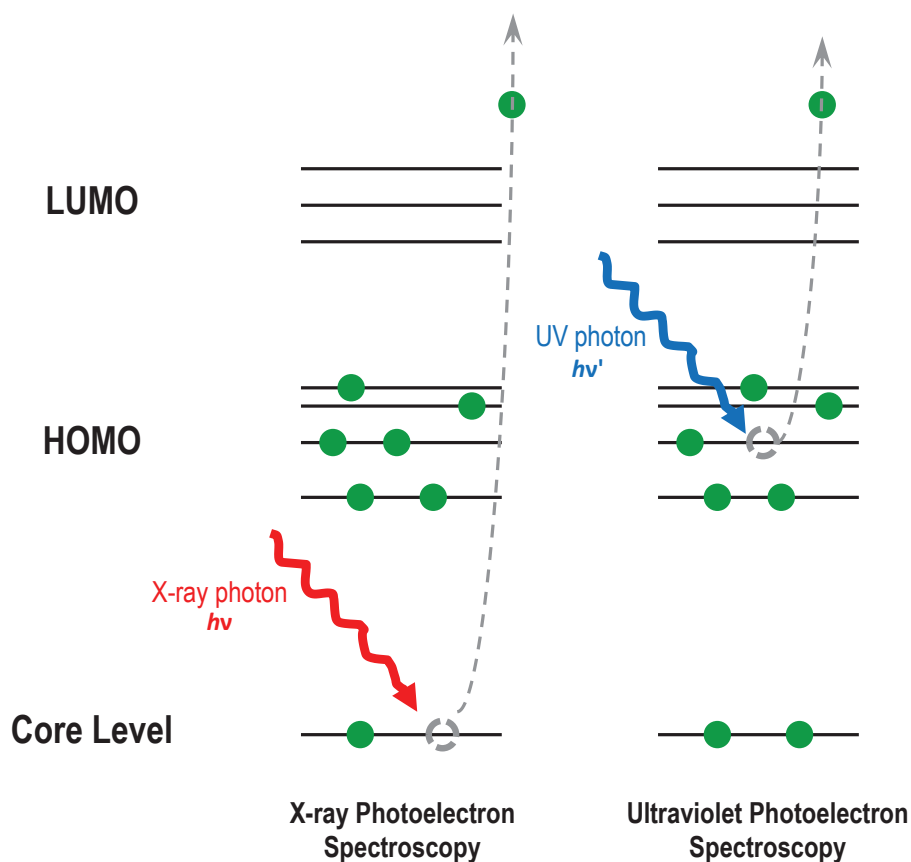
Despite its simple and qualitatively good form, the one-step model quantitatively fails. The three-steps model is a better model to interpret the experimental measurements and consists on three sequential steps:



**Figure 3.3.** Schematic view of the photoemission process in the single-particle picture. Electrons with binding energy  $E_B$  can be excited above the vacuum level  $E_{vac}$  by photons with energy  $2\pi\hbar\nu > E_B + \phi_0$ . The photoelectron distribution ( $E_{kin}$ ) can be measured by the analyzer and is -in first order- an image of the occupied density of electronic states  $N(E_B)$  in the sample [100].

- Optical excitation
- Electron transport through the solid, including inelastic scattering with the other electrons
- Electron escape from the surface, by travelling from the semi-infinite crystal to vacuum

The properties of the photoelectrons basically reflect the electronic eigenstates of the investigated system. Since the number of photoelectrons emitted at a particular energy is basically given by the density of states of the electron in a crystal, core-level photoemission and valence band photoemission give different types of spectra. For core level emission high energy X-rays are required and the spectra consist of sharp lines (Figure 3.4). This is known as **X-ray Photoelectron Spectroscopy** (XPS). In contrast, for the emission of valence electron only soft Xrays or hard UV radiation in an approximate energy range  $3 \text{ eV} \leq \hbar\omega \leq 100 \text{ eV}$  is required and the spectra are broad with characteristic structures. In this case, it is called **Ultraviolet Photoelectron Spectroscopy** (UPS). The basic property to be determined in the XPS and UPS experiments are the binding of the electron, which tabulated values for the core-level binding energies and photoemission cross-sections of most elements are very-well known for the free atoms [101, 102].

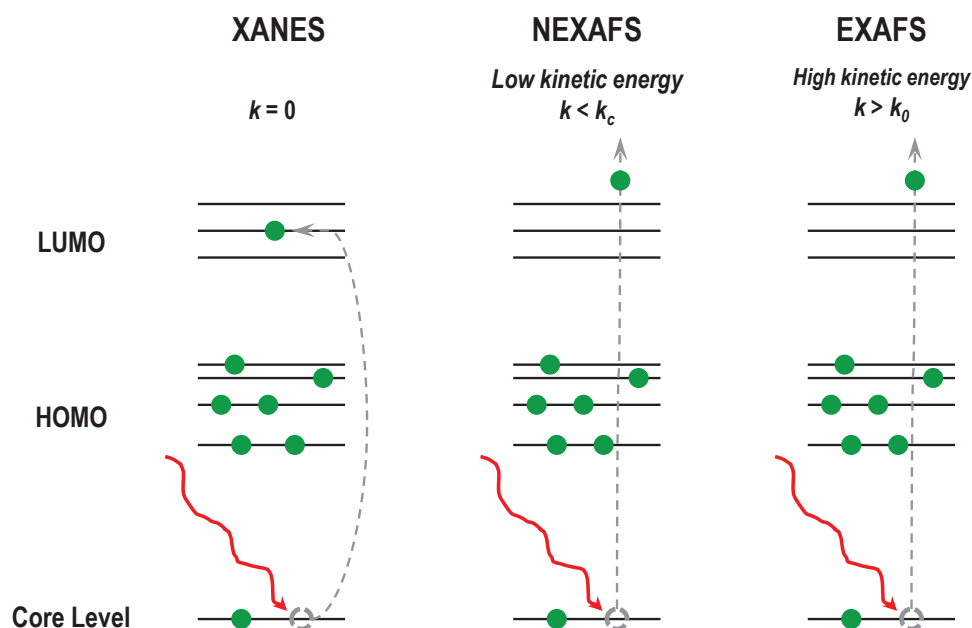


**Figure 3.4.** Schematic diagram of photoemission spectroscopy at the core level (X-ray Photoelectron Spectroscopy - green) and at the valence band (Ultraviolet photoemission spectroscopy - red).

### 3.5 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) has the advantage to probe disordered and amorphous materials and is capable of obtaining structural information in the immediate neighbourhood of the absorbing atom. XAS happens when a narrow parallel monochromatic X-ray beam of intensity  $I_0$  passing through a sample of thickness  $X$  will get a reduced intensity  $I$  according to the expression  $\ln(I_0/I) = \mu X$ , where  $\mu$  is the linear absorption coefficient, which depends on the types of atoms and the density  $\rho$  of the material.

At certain energies where the absorption increases drastically, and gives rise to an absorption edge. Such edge occurs when the energy of the incident photons is just sufficient to cause excitation of a core electron of the absorbing atom to a continuum state. These edges are at different energies due to the different nuclear charges of each element and different orbitals involved and the XAS spectrum can be approximately divided into regions, illustrated in Figure 3.5. They can be classified into the pre-edge range, X-ray absorption near edge structure (XANES), near edge X-ray absorption fine structure (NEXAFS) and extended x-ray absorption fine structure (EXAFS).

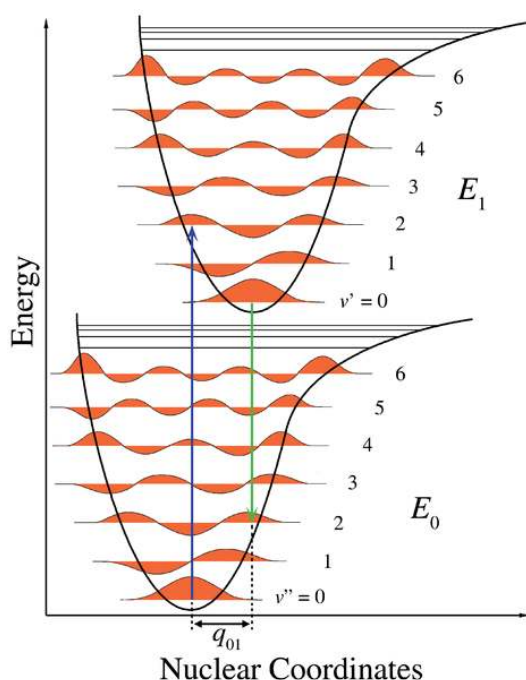


**Figure 3.5.** Energy level diagram showing excitation of core electrons observed at each of the possible transitions in XAS method. A neighbouring atom scatters the wave, resulting in interference at the origin. This can be constructive or destructive, depending on the interatomic distance and the photoelectron wavelength and originating a modulation of the likelihood of X-ray absorption at different energies.

Mostly NEXAFS has been used in this thesis and it refers to the fine structure of the X-ray absorption coefficient. The NEXAFS spectra provide information on the density of empty states in the conduction band of crystalline solids or states of antibonding molecular orbitals in the case of a molecule. It can also probe empty states due to defects. Furthermore, angular dependent NEXAFS measurements provide information on the symmetry of the material. Generally speaking, the NEXAFS spectrum is the fingerprint of the composition and symmetry of a compound.

#### **Franck-Condon Principle: fine structure**

It is necessary to introduce this principle to understand the interpretation of the results observed in the molecular adsorption of gases on SWCNTs described in this thesis. When a photon is absorbed, a molecule usually is not merely transferred into an excited electronic state, but also acquires some vibrational energy. According to the *Franck-Condon principle*, the absorption of a photon is a practically instantaneous process, since it involves only the rearrangement of practically inertia-free electrons. During light absorption, electrons can move but not the nuclei by the fact of being enormously heavy as compared to the electrons. Atomic nuclei have no time to readjust themselves during the absorption act, but have to do it after it is over, and this readjustment brings them into vibrations. The

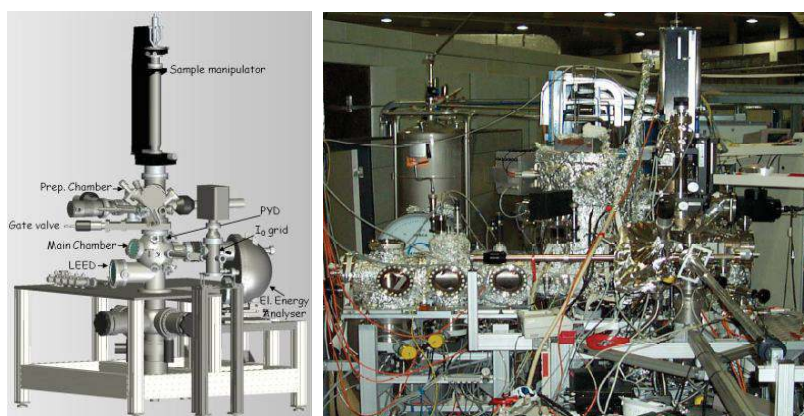


**Figure 3.6.** Potential energy curves for the ground state and an excited state of a diatomic molecule.

excitation occurs on a point slightly different to the non-vibrating state, which means that the molecule finds itself, after the absorption act, in a nonequilibrium state and begins to vibrate like a spring [103]. Since the usual lifetimes of excited electronic states are of the order of  $10^{-9}$  s, there is enough time during the excitation period for many thousands of vibrations. Fluorescence, when it comes, originates from near the bottom of the upper potential curve, and follows a vertical arrow down, until it strikes the lower potential curve. Again, it does not hit it in its deepest point, so that some excitation energy becomes converted into vibrational energy.

### 3.5.1 The Super ESCA beamline at ELETTRA

Photoemission and X-ray absorption (described in the next section) spectroscopy measurements were performed at the SuperESCA beamline from the ELETTRA synchrotron. One great advantage of using synchrotron radiation is the availability of the widest photon energy range with different excitation cross section using parallel modification of photon energy and electron kinetic energy analysis, depending upon the variety of methodologies of data collection. In principle, in these experiments the photon energy can be selected by use of a monochromator from a continuum spectra over a wide energy range. Also, high intensity and brightness are reachable and variable polarization can be used. The Super ESCA beamline has been nicely optimized for small photon spots and time-resolved measurements can be done on a very short time-scale, even below the nanosecond time-frame.



**Figure 3.7.** SuperESCA set-up used for X-ray photoemission and absorption spectroscopy measurements.

In particular, SuperESCA beamline has been designed for soft X-ray photoemission experiments on surfaces. To achieve high energy resolution keeping at the same time a high photon flux, the light produced by the insertion device is collected, monochromatized and brought to the experimental station following an special configuration (prefocusing-monochromator-refocusing scheme). The light source is a 2-section undulator, providing horizontally polarized photons. At 10 m from the source a pinhole selects the desired region of the undulator emission cone and a plane mirror is used to switch the light towards the beamline (Figure 3.7). The radiation is pre-focused into the monochromator entrance slit by a vertically oriented cylindrical mirror ( $2^\circ$  angle of incidence). The dispersed light coming out from the monochromator exit slit is finally re-focused by an ellipsoidal mirror on the sample in the experimental chamber. The energy resolution can be further improved by acting on the baffles placed along the optical path inside the monochromator in order to reduce stray light, where the monochromator resolving power ( $E/\Delta E$ ) is of the order of  $10^4$ .

The experimental station consists of two ultra-high vacuum chambers separated by a gate valve (Figure 3.7). The preparation chamber is the small-upper one and it has been designed for sample preparation. Therefore, it contains a sputter gun and a gas line, which is mainly used for standard cleaning procedures. The second chamber is the main one (bottom one) and is has been made of  $\mu$ -metal for optimum shielding, avoiding the influence of magnetic fields that could distort the experimental results. It is equipped with a 150 mm hemispherical electron energy analyzer with variable entrance slit, and a delay line detector. More technical specifications can be found in [www.elettra.trieste.it/elettra-beamlines/superesca](http://www.elettra.trieste.it/elettra-beamlines/superesca).

### 3.6 Optical spectroscopy techniques

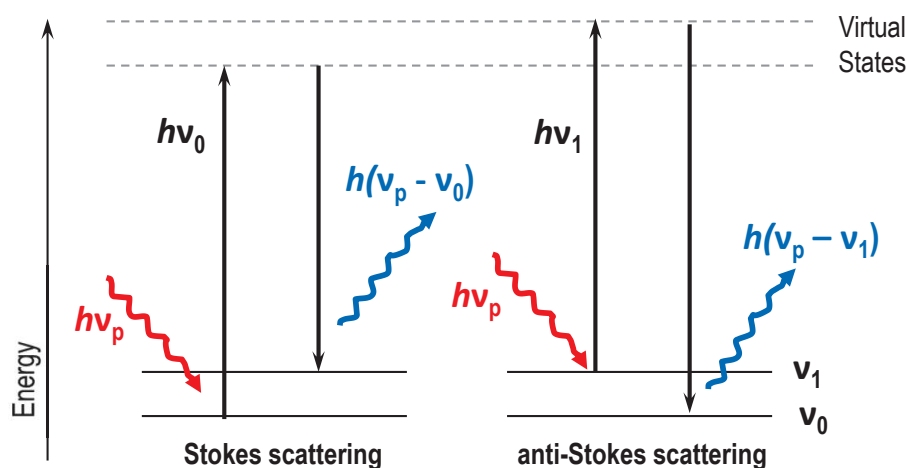
Optical spectroscopic techniques are widely used in the study of optical properties of nano-materials. They concentrate on measuring absorption, scattering or emission of light pro-

viding different information about the molecular properties of the materials. Commonly used techniques include a variety of processes, but in order to achieve the goals for this thesis, I have been used Raman scattering and optical absorption spectroscopy to access to the samples's properties.

In this section, several these spectroscopic techniques are reviewed with emphasis on their principle of operation as well as spectral interpretation. The main objective is to explain how one can get useful physical information about the nanomaterials under study from the optical spectrum measured experimentally.

### 3.6.1 Raman Spectroscopy

Raman spectroscopy is a non-destructive spectroscopic technique based on inelastic scattering of monochromatic light [104]. Photons of the laser light are absorbed by the sample and then re-emitted. The frequency of these photons is shifted up or down compared with original monochromatic frequency and this is the Raman effect. This shift provides information about vibrational, rotational and other low frequency transitions in molecules.



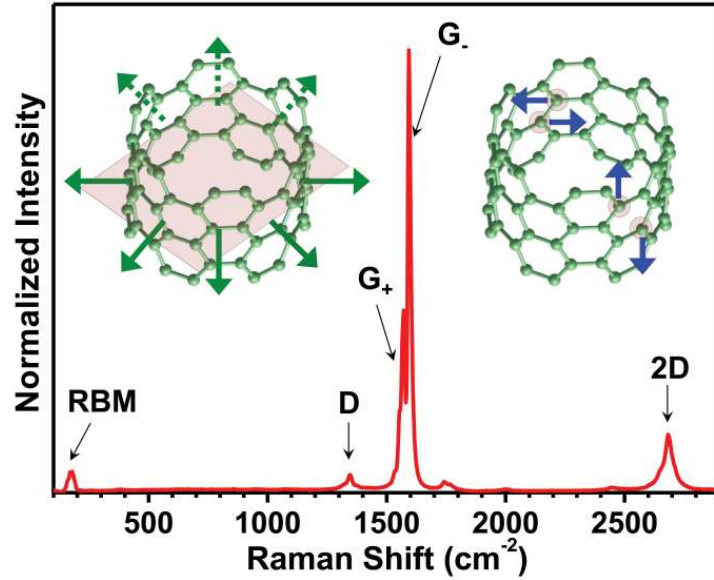
**Figure 3.8.** Diagrammatic representation of an energy transfer model of Stokes Raman and anti-Stokes Raman scattering [1].

Within the Raman effect, molecular deformations occur in the electric field  $\mathbf{E}$  determined by molecular polarizability  $\alpha$ . The laser beam can be considered as an oscillating electromagnetic wave with electrical vector  $\mathbf{E}$ . Upon interaction with the sample it induces electric dipole moment  $\mathbf{P} = \alpha\mathbf{E}$  which deforms molecules and, because of this periodical deformation, molecules start vibrating with characteristic frequency  $\nu$ . Taking this into account, it is possible to consider two different situations:

*Stokes scattering:* a photon with frequency  $\nu_p$  is absorbed by Raman-active molecule which at the time of interaction is in the basic vibrational state. Part of the photon's energy is transferred to the Raman-active mode with frequency  $\nu_0$  and the resulting frequency of scattered light is reduced to  $\nu_p - \nu_0$ .

*Anti-Stokes scattering:* a photon with frequency  $\nu_p$  is absorbed by a Raman-active molecule, which, at the time of interaction, is already in the excited vibrational state. Excessive energy of excited Raman active mode is released, molecule returns to the basic vibrational state and the resulting frequency of scattered light goes up to  $\nu_p + \nu_1$ .

Nanotubes, as molecular nanostructures have already been thoroughly investigated with this technique and the Raman scattering of light in presence of SWCNTs is fairly well understood. In this particular case, Raman spectroscopy is very useful for determining the diameter distribution, chirality, purity and morphology. Changing the laser excitation energies, it can be observed resonance-enhancement phenomena associated with the Raman intensity from which it can be assigned (n,m) values to individual SWNTs precisely [105]. Figure 3.9 shows an overview of the typical features appearing in a Raman spectrum of a



**Figure 3.9.** Raman spectrum from SWCNTs. Here are depicted the RBM, D, G and G' bands, which are the main observable features in this kind of response.

SWCNT[14]. The well-defined frequency features, can be identified as follows [106]:

**The radial breathing mode** These are the features appearing between 100-400  $\text{cm}^{-1}$ . The radial breathing mode (RBM) is associated with the vibrations of the carbon atoms, specifically to the coherent vibration of the C atoms in the radial direction, as if the tubes were breathing. The RBM has special importance because it is a footprint of nanotubes, which does not appear for other carbon systems and it is directly dependant on the SWCNT's diameter. There is an empirical equation that provides the proportionality relation between the frequencies and the nanotube diameter [107–109].

$$\omega_{RBM} = \frac{A}{d_t} + B \quad (3.2)$$

$A$  takes into account the force between C-C bonds. And  $B$  is an environmental factor, which is experimentally determined [110, 111]. It is then easily inferable why the RBM depen-

dence between the frequencies and the SWCNT diameter is specially used for the characterization of the diameter distribution in a nanotube sample [107]. The Raman spectra in the RBM region for a sample composed of an ensemble of different nanotubes chiralities is strongly dependent on  $E_L$  because for each value of  $E_L$ , the optical transition energies for different SWCNTs are in resonance with different excitation energies [112]. Therefore, the intensity of the RBM for these nanotubes is resonantly enhanced.

It is important to take into account that one-dimensional (1D) materials like SWCNTs excitonic effects need to be taken into account. Here, the exciton binding energy is much larger than the thermal energy at room temperature and thus exciton effects can be obtained even at room temperature. Because of the localized wavefunction of an exciton, the intensity of the optical process is enhanced significantly, and thus, Raman spectroscopy in SWNTs is dominated by excitons from photoexcited electron hole pairs.

**G Band** The intense peak between  $1500\text{--}1600\text{ cm}^{-1}$  is the so-called G-band, which is associated with the highest frequency optical phonon mode at the  $\Gamma$  point in the Brillouin zone [113, 114]. The G Band is composed by a set of modes called tangential modes (TM), which is identified with an in-plane tangential optical phonon involving the stretching of the bond between the two atoms in the graphene unit cell. In carbon nanotubes, it is composed of several peaks originating from the quantum confinement of the wave vector along the circumferential direction, and the zone folding of the graphite Brillouin zone into de SWCNTs Brillouin zone [115, 116]. These phonon modes have the symmetries  $A(A_{1g})$ ,  $E_1(E_{1g})$  and  $E_2(E_{2g})$  originate from the first-order Raman process. In the G band Raman spectrum, the  $G^-$  and  $G^+$  components can be observed. These two features are associated, respectively, with vibrations of the carbon atoms along the circumferential direction (TO phonon) and along the nanotube axis (LO phonon). The  $G^-$  feature is strongly sensitive to whether the nanotube is metallic or semiconducting. Due to the electron-phonon interaction, the phonon mode frequency at a certain wavevector is downshifted for one of the two G-modes. It is important to note that the assignment for the transversal optical (TO) and longitudinal optical (LO) phonon modes in metallic SWCNTs is opposite to the one in semiconducting tubes.

**D Band** The *disorder-induced* band appearing between  $1100\text{--}1300\text{ cm}^{-1}$ , is called the D-band. This is originated from a double resonance process, induced by the presence of amorphous carbon or by symmetry-breaking defects in the SWCNT structure [113]. The D band represents a defect induced mode from the zone boundary. It originates from phonons close to the K point of the graphite Brillouin zone and becomes active in NTs due to the presence of defects, such as impurities or missing atoms, among others. There is a strong dependence between  $E_L$  and the frequency, which is caused by a softening of the LO phonos near the K point due to the electron-phonon coupling. The dispersive behaviour of this band is explained by a double-resonance process involving a phonon and a defect. In this process, an electron-hole pair is created when the incident photon is absorbed. After that, the electron is scattered by a phonon (or a defect) with wavevector  $q$  and scattered back by a defect (or phonon) with wavevector  $-q$ , recombining with the hole and emitting a scattered photon.

**2D Band** Approximately at  $2600\text{ cm}^{-1}$  is located the 2D band, which is the overtone of the D-band. This feature is also observable in highly oriented graphite [117]. The 2D band

is the most intense feature in the second-order Raman spectrum of SWCNTs. This band originates from a double resonance process involving two phonons [113]. Basically, the 2D band is a single Lorentzian feature, where two features can also be observed in SWCNTs. The presence of these two peaks in this band indicates the resonance with two different van Hove singularities, one in resonance with incident photon and another in resonance with the scattered photon (anti-Stokes and Stokes process). For example, in the case of metallic NTs, the two peaks observed in the 2D band are caused by an anisotropy of the phonon dispersion around the K point, known as the phonon trigonal warping effect. In the case of doped SWCNTs, Maciel et al. [118] suggested that B doped SWCNTs exhibit a higher frequency 2D Raman peak, since one extra electron causes an electron and phonon renormalization near the defect site.

### **Spectrometers**

The Raman characterization of the samples used in this thesis, different Raman spectrometers were used. Basically, all systems consist in a microscope coupled to the laser source and a camera, where it is possible to capture the image of the analyzed region.

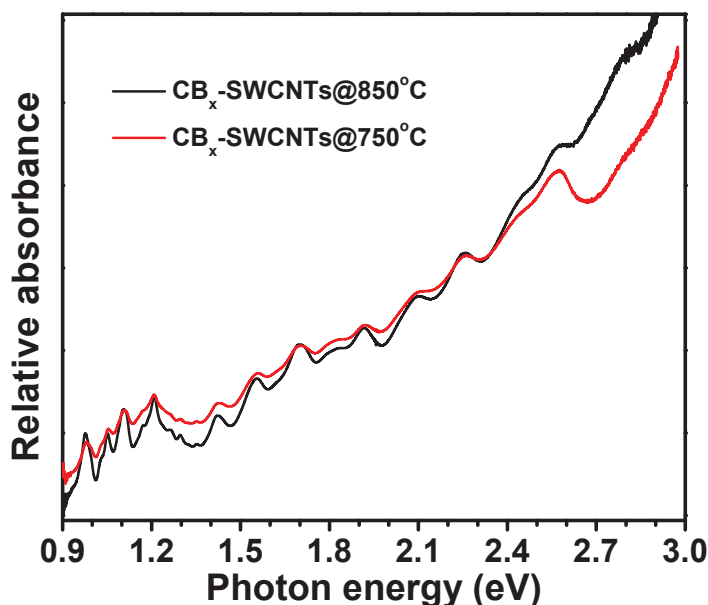
Mainly, a Horiba LabRam HR Raman micro-spectroscopy was used. It is equipped with a solid state 633 nm wavelength and coupled with a tunable Innova 70C spectrum laser (647 nm, 568 nm, 532 nm, 514 nm, 488 nm, and 452 nm laser lines). Particularly, this system provides ultra high spectroscopic and spatial resolution, from the order of 0.3  $\text{cm}^{-1}$  to 1  $\text{cm}^{-1}$ . Also, a FT-Raman spectrometer (IFS100 Bruker FT-Raman spectrometer) was used, which has a *Nd:YAG* laser with a wavelength of 1064 nm. It is equipped with a front measurement chamber and an attached Raman microscope. A resolution of 2  $\text{cm}^{-1}$  was usually used for the measurements with this spectrometer, taking into account the sought features. Finally, a Dilor xy triple monochromator spectrometer was utilized. The resolution depends on the wavelength of the laser and the chosen mode, but in the case of HR mode, a 0.5  $\text{cm}^{-1}$  of precision can be reached. The lasers used in the measurements were an *Ar+ / Kr+* ion laser (Spectra Physics, model Stabilite 2018) and a *He/Ne* laser (Spectra Physics, model 127). With both lasers, a range of discrete lines, between 488 and 632 nm excitation wavelengths can be used.

### **3.6.2 Optical Absorption Spectroscopy**

From the experimental and analytic points of view, optical absorption spectroscopy (OAS) is the simplest optical technique. OAS can be used easily to show the presence of SWNTs in the sample [119] from the observation of absorption peaks related to the first and second optical transition from semiconducting tubes, and the first optical level of metallic tubes (Figure 3.10). For higher optical levels, the optical absorption response gets blurred due to the absorption by s-bonded electrons.

In optical absorption spectroscopy, light will be absorbed when in resonance with  $E_{ii}$  values for the (n,m) nanotubes in the sample. The resonance width depends strongly on sample environment, and the broad peaks are actually related to groups of unresolved absorption profiles for different (n,m) SWNTs with similar  $E_{ii}$  values. The presence of groups

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**Figure 3.10.** Optical absorption spectra of B-doped SWCNTs synthesized at two different temperatures, where the optical transitions peaks reflect the broad diameter distribution of SWCNTs present in the sample.

absorbing at similar frequencies can be used, for example, to characterize the separation between metallic and semiconducting tubes.

The spectrometer used for the OAS measurements was a VERTEX 80v vacuum FT-IR spectrometer, which is based on the actively aligned interferometer, which provides PEAK spectral resolution. It is equipped with optical components to cover the spectral range from the far IR, or terahertz, through the mid and near IR and visible and up to the ultraviolet spectral range and its configuration provides apodized spectral resolution of better than  $0.2 \text{ cm}^{-1}$ .

More information can be found in [www.bruker.com/products/infrared-and-raman-spectroscopy/ft-ir-research-spectrometers/vertex-series/vertex-8080v/overview.htm](http://www.bruker.com/products/infrared-and-raman-spectroscopy/ft-ir-research-spectrometers/vertex-series/vertex-8080v/overview.htm)

### 3.7 Theoretical tools

A great part of the spectroscopy analysis described in Chapter 5 has been benefited by theoretical calculations done in collaboration with the Nano-Bio spectroscopy Group from San Sebastian-Spain. Core level estimations were obtained for adsorption experiments. The PWscf program of the Quantum Espresso suite [120] was used when it was necessary to consider various adsorbed species on SWCNTs in pristine and defected forms.

The electronic core levels of periodic SWCNTs and their adsorbates were computed

with the GPAW density functional theory code [121–123]. All calculations were performed with the LDA as exchange correlation functional [120]. It was ascertained that the predicted LDA core-level shifts are virtually the same as the ones obtained using the Perdew, Burke, and Ernzerhof (PBE) functional [124]. The optimized Quantum Espresso geometries were used without further modification as input for the GPAW code. All DFT calculations were spin-unpolarized.

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## Ultra pure B-doped SWCNTs

The synthesis of pure carbon SWCNTs has been enhanced along the years obtaining materials with very narrow diameter distribution, high yield and almost no presence of impurities. However, the production of SW doped material still faces several technical limitations. The most natural dopants are B and N because of the size and electronic configuration they have. However, other dopants like Si, P, and Ni have also been proposed. On-wall doping can be achieved by in-situ or post-synthesis processing of the carbon nanotubes with different kinds of heteroatoms, such as B, N or P, among others. [49, 87, 125].

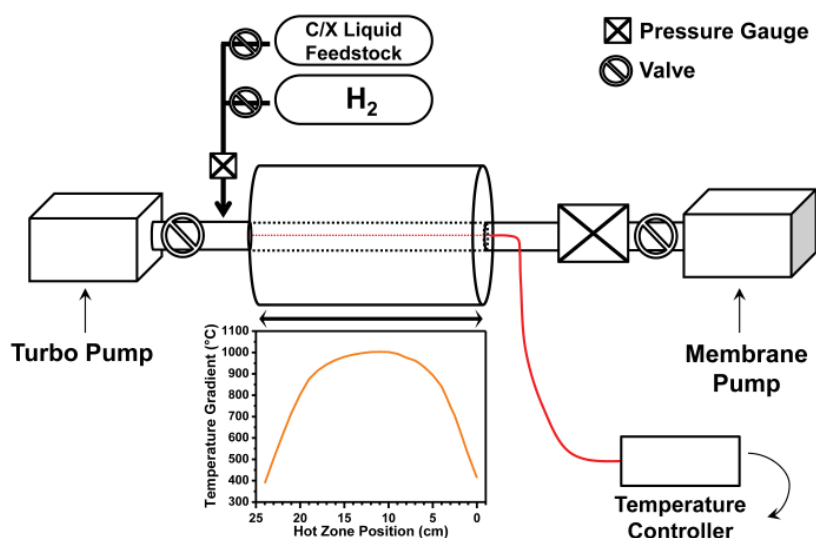
The possibility of accessing the intrinsic physical and electronic properties of SWCNTs can be strongly attributed to the difficulties in producing high purity material. As-synthesized material usually contains carbonaceous species, catalyst-supporting material or metallic impurities. Considerable progress in the purification of SWCNTs has been made and a number of methods including chemical oxidation, physical separation, and combinations of chemical and physical techniques have been developed. Since the purification methods for SWCNTs have been published and obtaining pure pristine samples turned into almost a standard procedure, several groups started the production of post-purification doping processes. Note that purified samples can undoubtedly allow studying the electronic properties of the samples in a much more realistic manner than any other study done so far. However, post-purification methods do not necessarily achieve substitutional doping and again, rests of the new chemical processes interfere in those kinds of studies.

In this chapter I describe my work related to the purification of B-doped nanotubes, which were produced in-situ by HV-CVD. It is important to remark that this was the first study to be published on the purification of doped SWCNTs.

### 4.1 Synthesis

The synthesis of B doped SWCNTS was performed in-house using a purpose built high-vacuum (HV)-CVD system (Figure 4.1)[87, 88]. The experimental system (Figure 4.1) con-

sists of an alumina tube located in the axis of a cylindrical furnace, which reaches an homogeneous temperature along approximately 20 cm of the tube. The temperature profile of the reactor can be seen in the "hot zone plot" in Figure 4.1. The vacuum system connected to the alumina tube has two rotary and one turbomolecular pumps, which allow working at a high vacuum ( $\sim 1 \times 10^{-9}$  mbar). The C/B feedstock, an air and hydrogen inlet are connected to one end of the alumina tube. Pressure gauges are used in the experimental system to control and avoid abrupt changes in the pressure of the synthesis chamber.



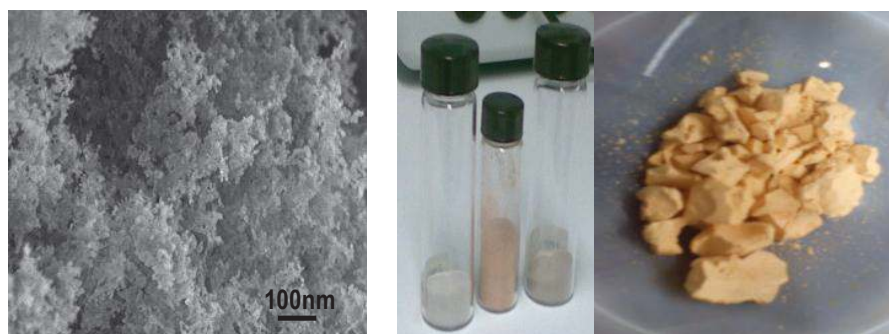
**Figure 4.1.** Schematic diagram of a chemical vapour deposition system adapted to work in high vacuum conditions [126, 127].

Dry metallic-based catalysts were employed, which were prepared with different compositions. Just to briefly comment about the catalysts, mainly, a mixture of iron nitrate ( $Fe(NO_3)_3$ ) and porous magnesium oxide nanopowders was used (Table 4.1). The compounds were sonicated in 2-propanol ( $C_3H_8O$ ) for about 2 hours. Then, they were dried removing the 2-propanol by evaporation and subsequently calcined. As final step, grinding was used to obtain a fine catalyst powder.

More specifically focusing on the synthesis, alumina crucibles with powder catalysts were placed inside the quartz tube. Then, the CVD reactor was evacuated with rotary and turbomolecular pumps until it reached a base pressure of  $10^{-8}$  mbar. The temperature was increased to attain the catalyst activation temperature. After the catalysts were placed in the reactors, the temperature increase was done carefully in the range from 90 to 200°C to avoid contamination of the synthesis chamber. Later, catalyst were reduced at 400°C for 5 hours under a flux of  $H_2$ . During this process, the pressure inside the quartz tube remained stable at 50 mbar and it was then again evacuated to the base pressure. This step in the synthesis process is done to remove any kind of oxygen containing functional groups, which are generated by the prolonged contact with air or the catalyst production itself. The SWCNTs synthesis was performed between 800°C and 900°C and Triisopropyl borate

**Table 4.1. Details on the catalyst preparation**

| height | MgO | Fe(NO <sub>3</sub> ) <sub>3</sub> | Evaporation Temperature [°C] |
|--------|-----|-----------------------------------|------------------------------|
| MF1    | 2   | 1                                 | 90                           |
| MF1-2  | 2   | 1                                 | 200                          |
| MF2    | 1   | 1                                 | 90                           |
| MF2-2  | 1   | 1                                 | 200                          |
| MF4    | 4   | 1                                 | 90                           |
| MF4-2  | 4   | 1                                 | 200                          |



**Figure 4.2.** (Left) SEM micrograph showing the overall characteristics of the catalyst (MF2) used in the synthesis of CB<sub>x</sub>-SWCNTs. (Right) After calcination, the powder is grinded obtaining the catalyst as it was employed in the experiments.

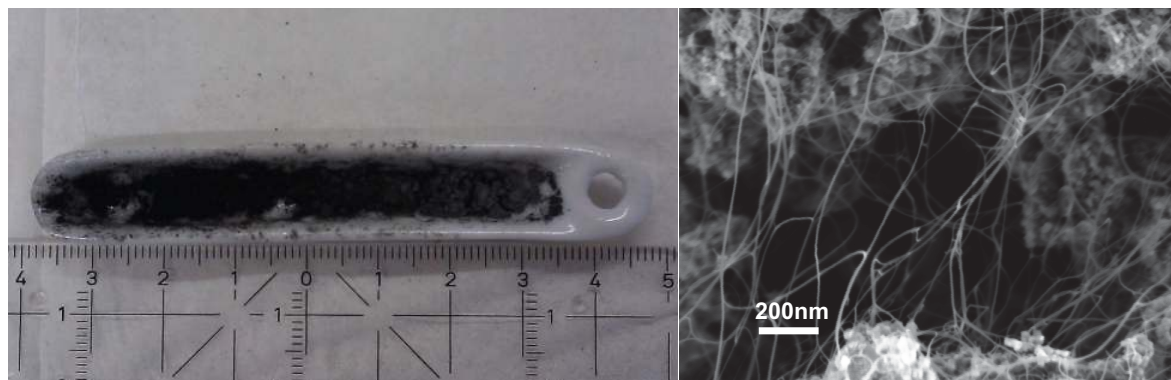
(C<sub>9</sub>BO<sub>21</sub>H<sub>3</sub>) and Triethyl borate (C<sub>6</sub>H<sub>15</sub>BO<sub>3</sub>) were used as C/B feedstocks. The catalysts were exposed to the C/B feedstock vapor (between 7-9 mbar). After different times up to 30 min of exposure to the feedstock flow, the system was cooled down in high vacuum to avoid contamination. Once the system cooled down, the chamber was vented and the samples were removed for further characterization. The inspection of B-doped SWCNTs fabricated by using Triethylborate (TEB) will be described here for illustrative reasons.

Part of these results have been published in the paper entitled *Spectroscopic study of the diameter distribution of B-doped single-walled carbon nanotubes* in Physica Status Solidi B [128] and other part of this study correspond to an ongoing study and a manuscript in preparation.

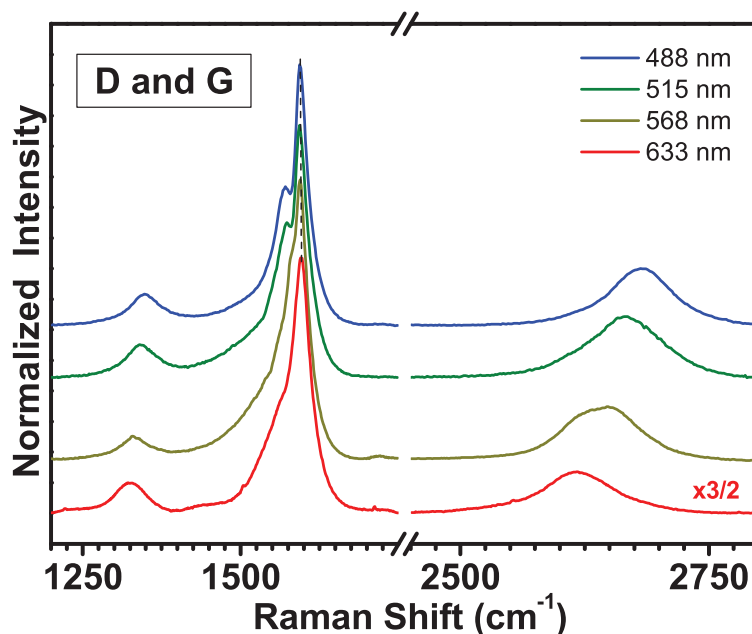
## 4.2 Overall Morphology of the samples

The as-grown material was a black powder consisting of B-doped nanotubes and by-products of the synthesis, which are composed mainly of magnesium oxide from the porous supporting material, metallic catalytic particles and, in a very low amount, amorphous car-

bon [87, 88]. A SEM micrograph of the typical overall morphology of such a sample is shown in Figure 4.3.



**Figure 4.3.** (Left) Powder catalyst is placed in alumina crucibles. In this case, the furnace has an inhomogeneous temperature profile, which allows to carry out experiments under the same conditions of pressure but with a temperature gradient. In the picture, it can be seen in the colour of the resulting nanotube-containing material. (Right) SEM micrograph of a typical  $CB_x$ -SWCNTs sample synthesized by HV-CVD from triethyl borate at 850 °C.



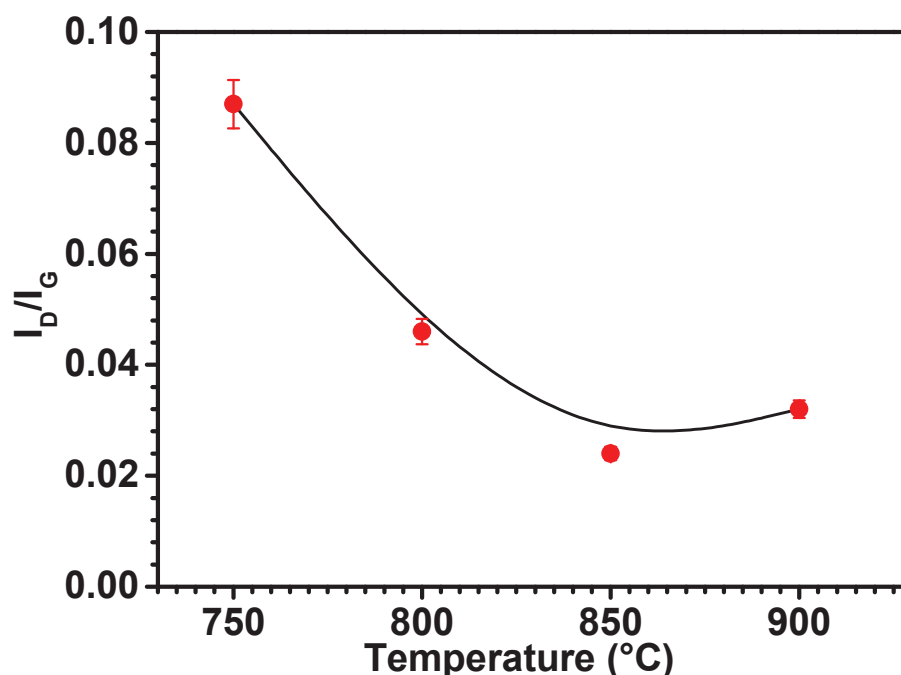
**Figure 4.4.** Resonance Raman spectra for the as-grown sample in the range of the tangential modes measured with the indicated laser lines.

Figure 4.4 shows the spectra recorded in the D, G and 2D regions with four laser lines on the sample. The tangential G mode exhibits a clear separation between the  $G^+$  and  $G^-$  [129], which gets more pronounced for higher laser energies. The  $G^+$  component is located at  $\sim 1569.4 \text{ cm}^{-1}$  for the measurement with 488 nm laser excitation. The response

corresponding to nanotubes with metallic character, measured for the 633 nm laser line, does not show a clear splitting of the G mode and the peak reveals a Fano behaviour, which is decreased in this case due to the p-type doping.

A similar observation has been previously reported for example in the intercalation of nanotubes with  $\text{FeCl}_3$  [130]. Further inspecting Figure 4.4, an upshift of the D line with the increasing laser energy was observed. If the Raman response for different samples recorded with one specific laser line is considered, it would in principle be possible to identify structural defects in the graphitic  $\text{sp}^2$  network and therefore, doping defects as it has been suggested in several papers. The overall D and 2D dispersion is about  $\sim 50 \text{ cm}^{-1}/\text{eV}$  and  $\sim 100 \text{ cm}^{-1}/\text{eV}$ ; respectively, which are in good agreement with previous results on pristine graphitic samples.

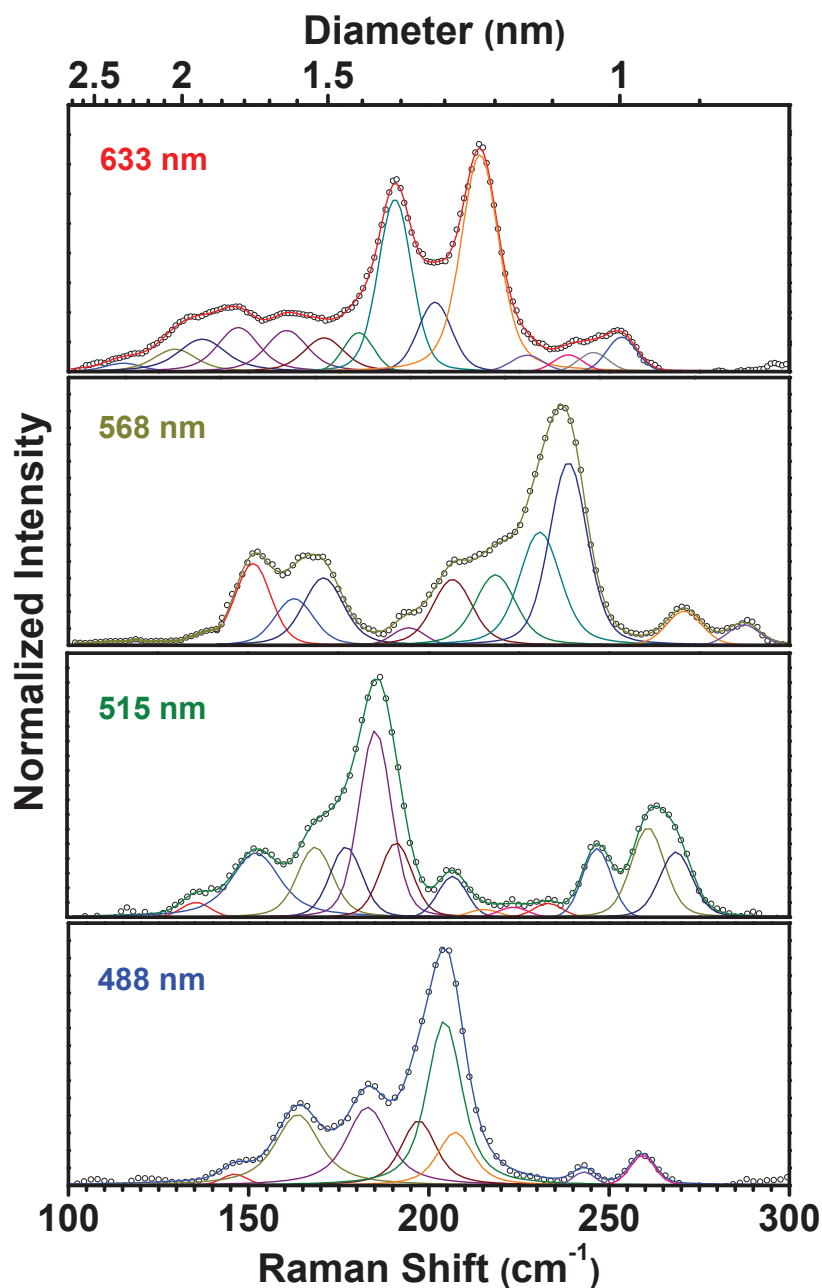
In addition, the relative defect content was analysed using the intensity ratio  $I_D/I_G$ . In Figure 4.5, this ratio is depicted for the different synthesis temperatures. Its values vary from  $\sim 0.09$  at  $750^\circ\text{C}$  to  $\sim 0.03$ , with a minimum value of 0.024 at the optimum synthesis conditions ( $850^\circ\text{C}$ ). Hence, the  $I_D/I_G$  ratio depends on the synthesis temperature. However, its values for higher temperatures than  $900^\circ\text{C}$  increase again, due to the formation of a major number of defects on the structure.



**Figure 4.5.**  $I_D/I_G$  in the Raman spectra recorded with a 633nm laser line for samples synthesized at different temperatures.

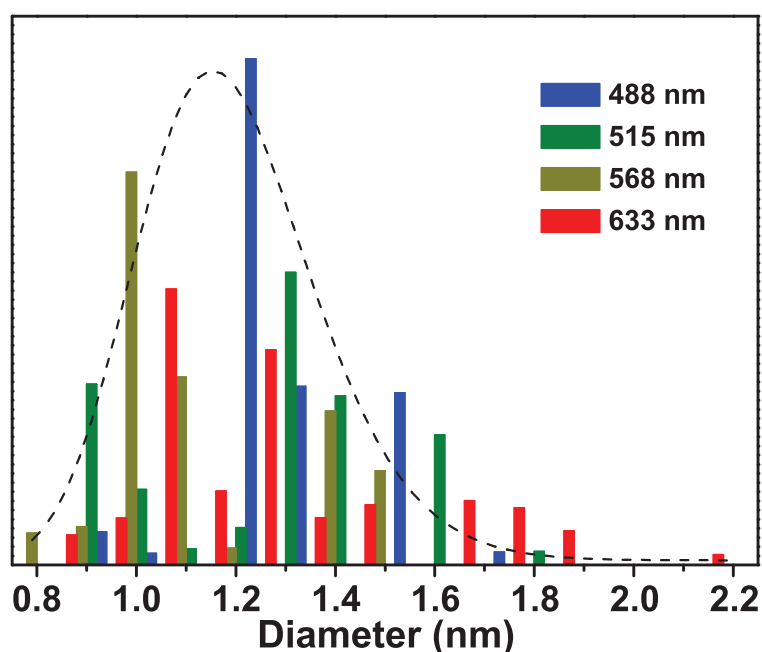
### Diameter distribution

In order to study the diameter distribution of the sample, the RBM region has been inspected with multi-frequency Raman spectroscopy. It is well-known that different laser excitation wavelengths are necessary to obtain a reasonable estimation of the tube-diameters and the diameter distribution.



**Figure 4.6.** Multi-frequency Raman response in the radial breathing mode (RBM) region with different laser excitation-energies of a sample synthesized at 850°C and its corresponding fitting. The diameter range is broad, although it is narrower than what was reported for B-doped SWCNTs synthesized by HV-CVD with triisopropyl borate as precursor [87, 131].

Figure 4.6 shows the spectra scanned with the 633 nm, 568 nm, 515 nm and 488 nm wavelengths for the samples synthesized at optimal conditions. Taking into account the resolution employed in the measurements, the RBM spectra were fitted using Voigtian functions. The deconvolution of these spectra is included in Figure 4.6. The upper scale bar gives us an estimation of the diameters of the tubes taking into account the simple lineal relation of the  $\omega_{RBM}$  and the diameter of the tubes ( $d_t$ ) [132]. Under these considerations, it was found that the  $d_t$  varies mainly from  $\sim 1$  to  $\sim 2.1$  nm. Although a full analysis of population of diameters in the sample would require optical absorption studies, this would imply an additional treatment of the samples [131]. Therefore non-invasive multi-frequency Raman spectroscopy on raw samples was employed. Note that there are complicated models that even allow the direct and complete study of the tube diameters using only one laser line [133]. These measurements provide a reasonably good estimate of the full sample characteristics. This can also be associated with the yield of nanotubes in both types of samples. As mentioned above the TEB samples produce larger amount of raw material. From the multi-frequency Raman measurements, a normalization to the laser intensity was



**Figure 4.7.** Overview of the diameter distribution obtained from the different laser excitations for B-doped SWCNTs from HV-CVD of triethyl borate.

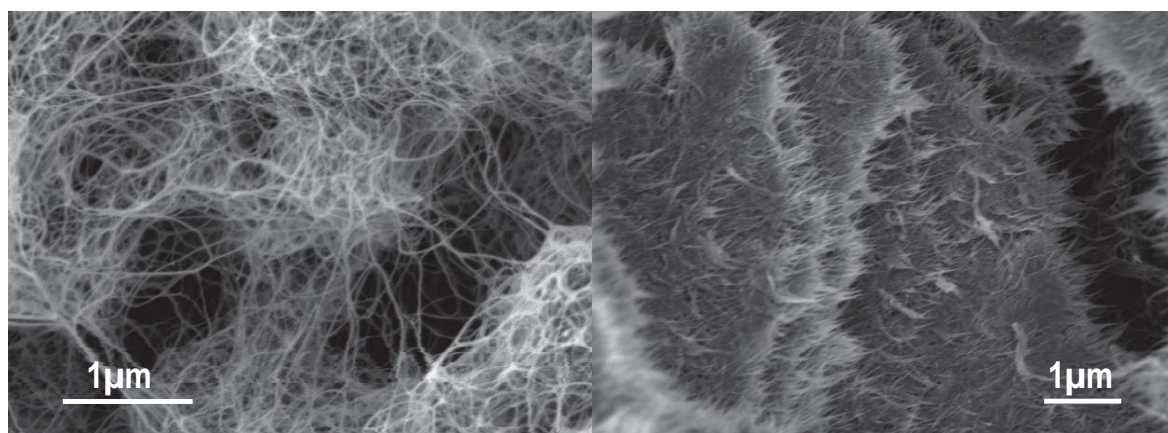
done and the area under the curve for each peak was used in order to plot Figure 4.7. This image summarizes the diameter populations obtained for the different laser lines. As a guide for the eye, a Poisson distribution of the catalytic particles with a mean value at  $\sim 1.15$  nm was shown. B-doped nanotubes synthesized from TEB exhibit a large diameter distribution compared to other B-doped samples produced by CVD [87, 134] with other C/B

source but they are small compared to pristine nanotubes made with a similar process.

### 4.3 Non-destructive cleaning of doped SWCNTs surface

The possible application of doped material in nanostructured devices requires an strict control of the dopant concentration and the bonding environments, becoming of crucial importance the optimization of existing methods to purify doped nanotubes. Therefore, modification on a standard purification method was done and subsequently applied on  $\text{CB}_x$ -SWNTs synthesized with Triisopropylborate.

Results described here were published in the paper entitled *On the purification of CVD grown boron doped single-walled carbon nanotubes* in Physica Status Solidi B [131]. As commented before, the aspect of the samples synthesized with carbon source remains similar to what has been thoroughly studied by Ayala et al. [87, 88]. However, a deep inspection is required to analyze possible changes upon the chemical process during purification. To have a first hint of these effects in the physical properties of these tubes, SEM imaging was performed and later, a comparison with the non-purified material. For practical purposes, the as-grown  $\text{CB}_x$ -SWNTs will be called 'pristine' throughout the following paragraphs.

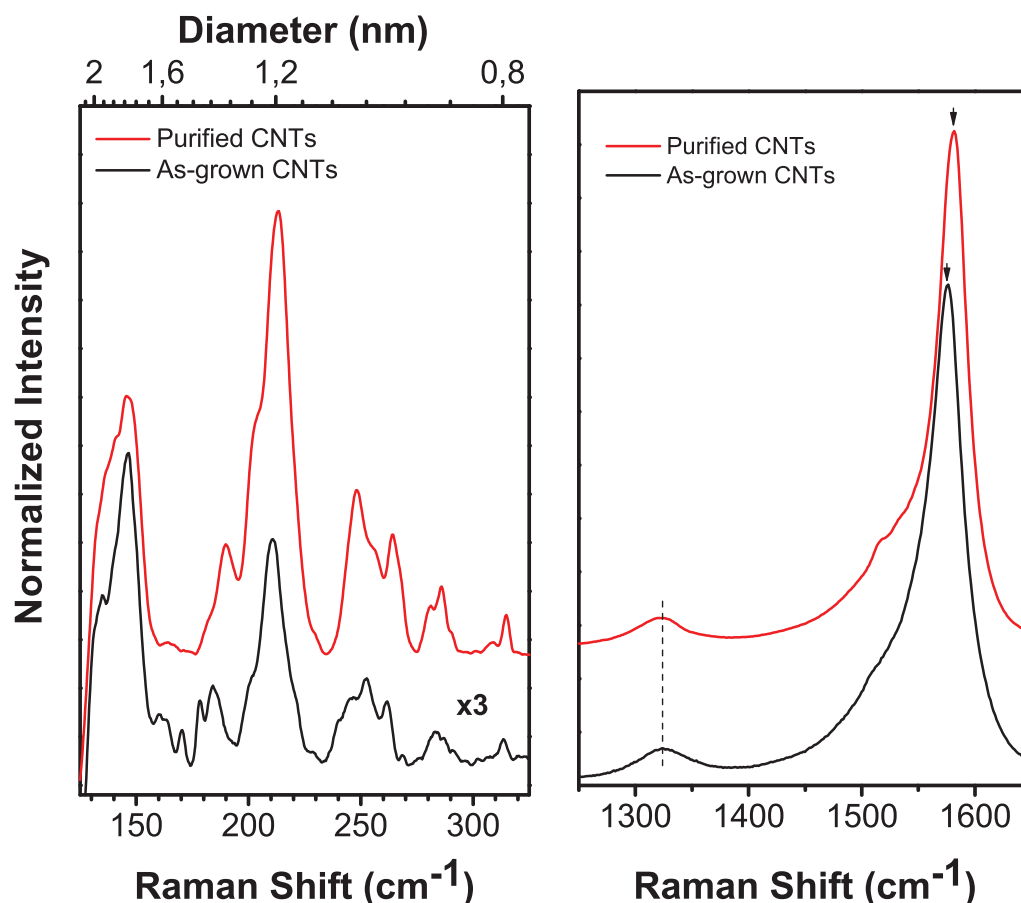


**Figure 4.8.** SEM imaging of the  $\text{CB}_x$ -SWNTs material, which has been grown via HV-CVD, before purification (left) and after purification (right).

In the left side image in Figure 4.8, the low magnification image shows the mixture of nanotubes and the catalytic remaining, where no formation of a appreciable amount of amorphous [134] carbon and MWCNTs. In the right image in Figure 4.8, the purified material was evaluated showing the morphology of a buckypaper. Clearly, all contaminants disappear and a compact layer of nanotubes is formed. It is a first clear proof of the efficiency of this method to purify doped nanotube material.

In general, when evaluating the quality of pristine SWCNTs, two independent parameters are crucial: purity and defect density. The purity is basically related to the content ratio

of SWCNTs to impurities. On the other hand, the defect density is related to the abundance of structural defects on the nanotube walls. However, in this case, the substitutional dopants can also be considered as relative wall defects. For this reason it is important to carefully consider the variations observable with standard nanotube characterization techniques.

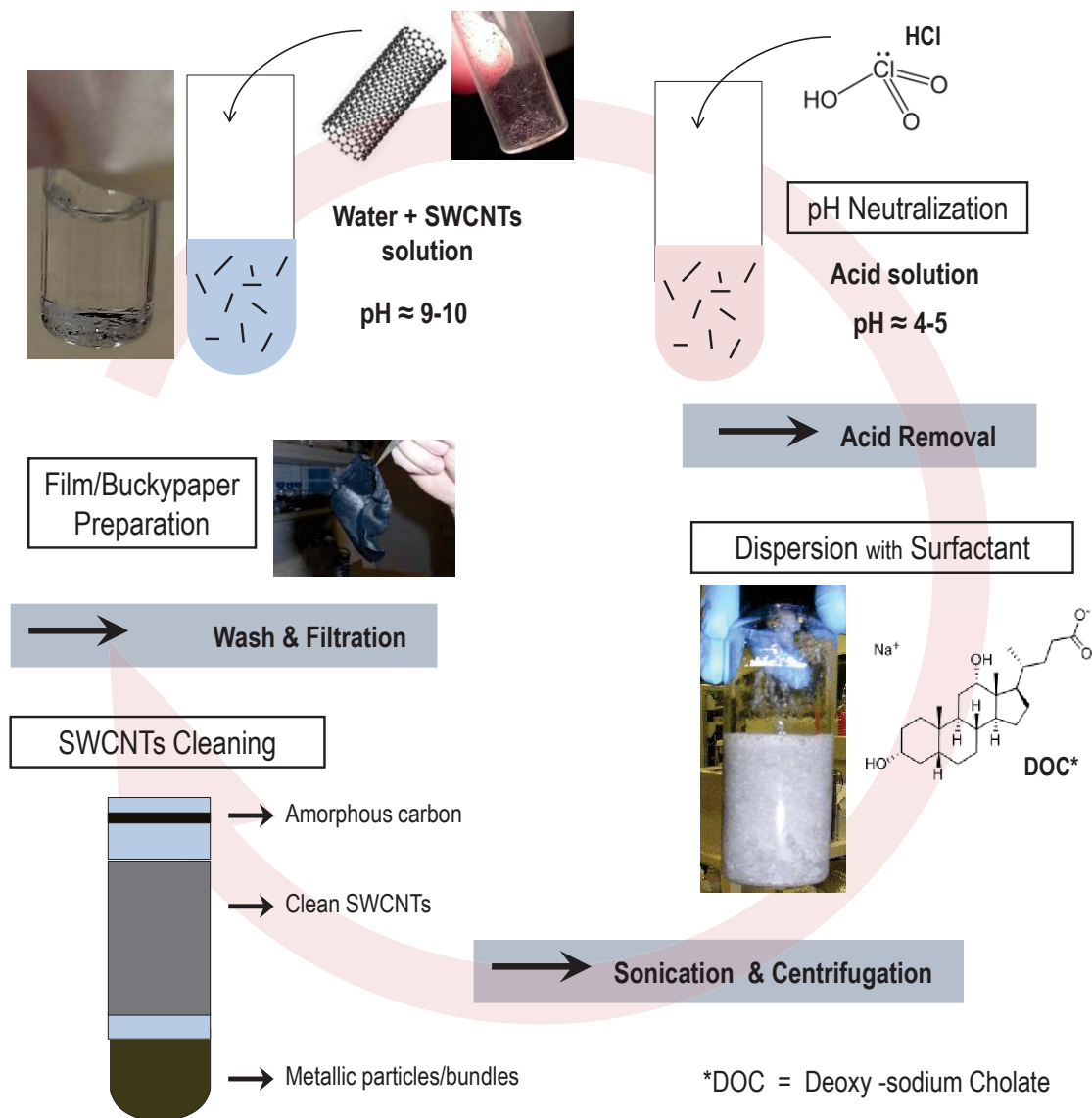


**Figure 4.9.** Resonance Raman spectra measured with the laser excitation of  $568\text{ cm}^{-1}$  for the as-grown and purified samples. Spectra are shown in the range of the radial breathing modes (left) and the tangential modes (right). A splitting in the G-band (arrows) is observed. The D-band remains in the same position (dashed-line).

### Purification process

In Figure 4.10, the modified DGU process used for the purification of  $\text{CB}_x\text{-SWNTS}$  is represented. SWNTs were suspended in deionized water ( $\text{pH}=10$ ) and the pH of the suspension was neutralized using a mild acid solution (30 wt.% HCl solution). The nanotubes were then dispersed in a 1% Deoxy Cholate Sodium Salt (DOC) aqueous solution by sonication for 4 h. The dispersions were then ultracentrifuged for 30 min at  $151000\text{ xg}$  and the upper 80% supernatant was collected. In this process, the condensed fraction at the bottom of the centrifuge tubes was removed as it mainly contained amorphous carbon,

similarly to the material obtained in other nanotube purification procedures [135, 136]. The samples obtained were filtrated through PTFE membrane filters (Milipore, pore size 0,2nm) and rinsed thoroughly with methanol water and toluene.



**Figure 4.10.** Representation of the modified DGU process used for the purification of CB<sub>x</sub>-SWNTs. Considering the specific composition of the byproducts in my experiments, a mild acid solution is used to remove the supporting material. Lately, metallic particles and the small amount of amorphous carbon are removed by fase-separation with optimal conditions during the centrifugation.

All parameters used in the process are listed in Table 4.3

**Table 4.2. Experimental parameters used Density Gradient Ultracentrifugation**

| <b>Purification</b>    |                                 |
|------------------------|---------------------------------|
| pH Adjustment          | 30% vol. HCl                    |
| Surfactant             | 1% DOC                          |
| Homogeneization        | 30 min, 25°C                    |
| Sonication             | 20W/cm <sup>2</sup> , 4h        |
| Centrifugation         | 40000RPM, 30min                 |
| Supernatant extraction |                                 |
| Wash & filtration      | Warm water, PTFE membrane 0.2μm |
| <b>Separation</b>      |                                 |
| Surfactant             | 2% DOC                          |
| Sonication             | 20W/cm <sup>2</sup> , 8h        |
| Centrifugation         | 4000RPM, 30min                  |
| Impurities extraction  |                                 |
| Centrifugation         | 50000RPM, 9-22h                 |
| Fraction extraction    |                                 |

#### 4.4 Optical characterization of the purified material

First, the intensity ratio of the tangential mode of these SWCNTs (G-band to the D-band) was used to estimate the nanotube yield. In the right panel of Figure 4.9, the D and G bands of the Raman spectra are depicted for the raw (black line) and the purified material (red line). Considering first the D peak, there is no noticeable modification of its position, shape or intensity, which suggests that there is no formation of additional defects during purification. This is a crucial matter when to keep the original morphology of the SWCNTs is desirable. Purification requires the dispersion, sonication and centrifugation of the material, commonly originating defects or molecules depositions from the surfactant solutions. For this reason, a post purification is performed before preparing the final buckypaper. However, this post purification treatment before the buckypaper preparation does not induce additional changes in the D band.

Regarding the G band of the raw material, a narrowing and upshift of about ~5 wavelengths after purification are observed, which in turn suggests that the purification process contributes to get rid off common impurities, such as big catalyst particles. Surprisingly, the  $I_D/I_G$  ratio increases only from 0.07 to 0.08 with use of DOC during purification. In investigations related to doped nanotubes, Blackburn et al. [86] suggested that depending on the dopant concentration, a delocalized positive charge is generated over the tube. This should be particularly observable in the G band and its components. However in this case, this observation can be disregarded because I am dealing with low dopant concentrations, which do not seem to have a big effect in the bulk samples.

### Annihilation of small-diameter tubes

One important characteristic of the HV-CVD material is that it is grown with very small diameters, which is unusual for pure carbon CVD tubes. These small-diameter B-doped tubes have a diameter of about 0.5-0.7 nm and a length of about 5  $\mu\text{m}$  in great abundance. These characteristics turn them into very reactive structures due to their higher curvature and also excellent candidates for field-emission transistors components or gas sensors devices fabrication. In particular, the high sensitivity of these tubes to the interaction with chemical species is a key point of these study, aiming at finding the right parameters to stabilize and keep them in the sample after purification.

The RBM region has been inspected with a multifrequency Raman spectroscopy analysis on the raw and purified samples and depicted in Figure 4.11, where the best-fit curves are Voigtian functions. Tubes with diameters between  $\sim 0.5$  to  $\sim 1.7$  nm were found with the three laser inspection (633 nm, 568 nm and 488 nm wavelengths) shown in Figure 4.11, taking into account the dependence relation of the RBM and the diameter of the tubes using an environmental factor of a  $0.05786 \text{ nm}^{-2}$  as estimated in reference [132].

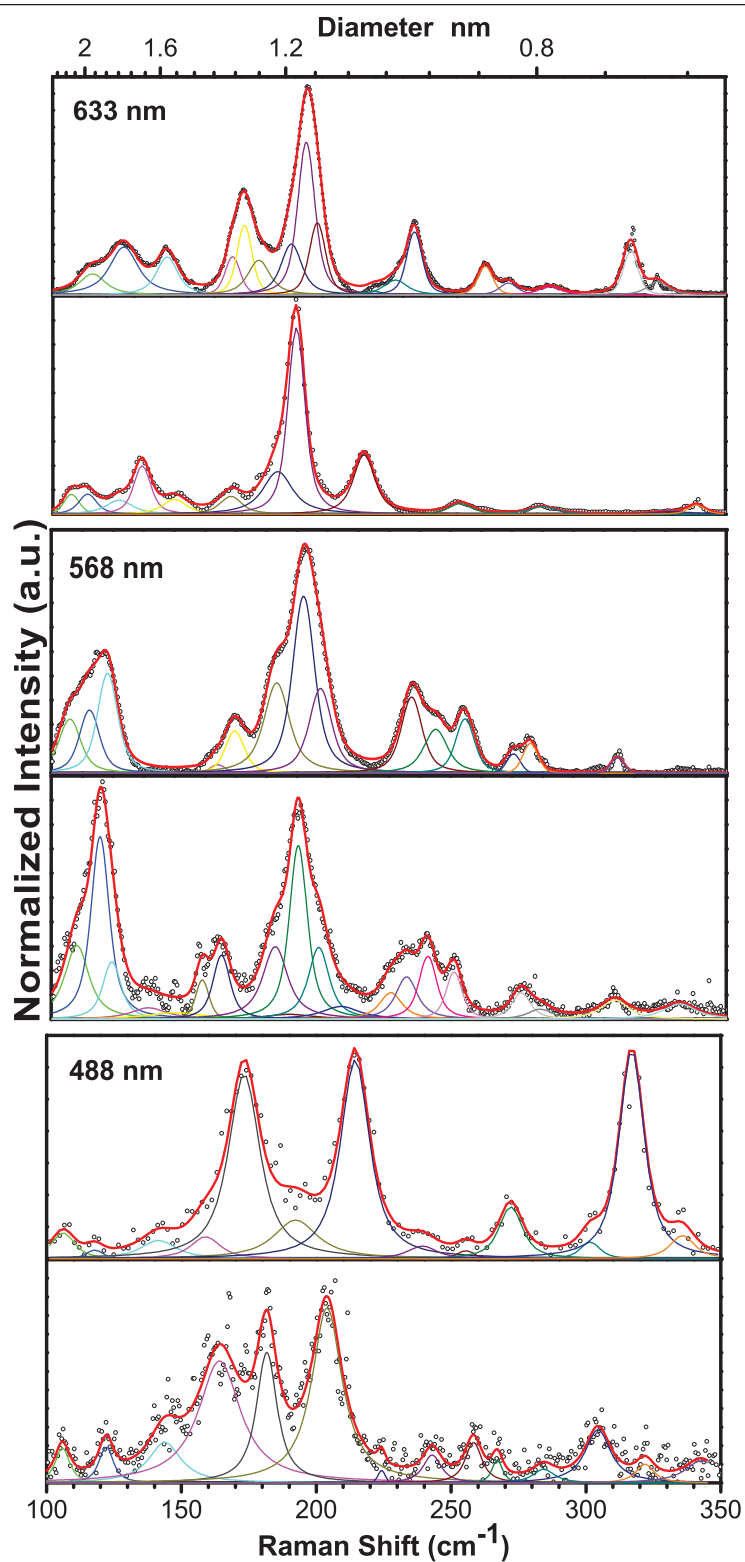
Comparing the raw material spectra with the purified ones, a clear modification in the diameter range is observed. The RBM corresponding to the smaller diameter tubes are noticeably reduced in intensity after purification for all laser lines. The intense lines shown in all upper spectra corresponding to the raw material are significantly lowered after purification. This result suggests that the purification method can be successfully applied to get rid off the common by-products present in these kind of samples, but unfortunately the smaller diameter tubes tend not to survive. Even though this statement has been generalized for all kinds of nanotubes, it can be safely state that there is a crucial difference with this material. The presence of B in the nanotube lattice induces the formation of a higher amount of zigzag nanotubes, which in principle should favor the stability of even smaller diameter tubes [137]. This can be then associated to the fact that nanotubes with diameters ranging from  $\sim 0.8$  to  $\sim 1.0$  nm are still present in the sample with a low detrimental ratio.

## 4.5 Doping level in purified samples

Concerning the B substitutional content, our starting material was measured by XPS. In reference [87], it was reported that the B atomic concentration in was around 1%at. However, this percentage estimated the total amount of boron atoms compared to the carbon ones, disregarding the different bonding environments. Given that B seems to form terraces on top of the Fe catalytic remaining, as reported in the same reference, it is expected that only around 0.1 %at (or even much less) is present in the purified samples. There are very limited reports on SWCNTs which have been able to detect these low amounts with a proper identification of bonding environments and based on the fact that I purified the material, several types of tubes unfortunately do not survive the process and also lower the concentration of boron. I expect that the boron incorporation happens with a preferential manner in the thinner diameter tubes, which again means that the content turns even lower. Implicitly the methods for detection start facing sensitivity limitations.

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As ongoing work related to this topic, I have started to study the dopant concentration of B atoms in films and buckypapers of purified material using XAS, which has already provided a proof of less than parts per mil. This is already in a range of ultra-low dopant concentration for nanotubes. Valence band photoemission measurements in these kinds of films have allowed us to identify a rigid band shift, which is highly desirable for future applications in the semiconductor technology.



**Figure 4.11.** Multi-frequency Raman response in the RBM region with different laser excitation energies of the raw and purified material and its corresponding fitting. The diameter range is broad and remain constant after purification. However, small diameter nanotubes signal was significantly reduced in intensity due to the purification process in all energies excitations.

## NO<sub>x</sub> absorption on single-walled carbon nanotubes

Every single factor implicated on the production and processing chain of SWCNTs as well as their intrinsic structural characteristics (e.g. defects and metallicity) can influence on their behaviour against other agents, specially if they are conceived as chemical sensors. These limitations were gradually avoided by making use of the great advances on the purification and separation methods and ultra-pure semiconducting and metallic SWCNT samples were rapidly obtained. Combining this kind of material with the use of high-sensitivity spectroscopy techniques, the specific role of the interaction of the tube wall and the adsorption process during gas phase reactions was studied.

In this chapter, I aim to demonstrate that the electronic response of pure metallicity separated SWCNTs upon the exposure of toxic gases (particularly, NO<sub>2</sub>) is completely different from what it was observed on mixed samples. This work allows to comprehend the basis for our proposed chemical pathway, which undoubtedly represents a big step towards the development of more sensitive and selective sensing devices. Part of these results are described in the manuscript entitled *Revealing the adsorption mechanisms of nitroxides on ultra-pure, metallicity-sorted carbon nanotubes*, which has been submitted to ACS Nano.

### 5.1 Metallicity sorted material

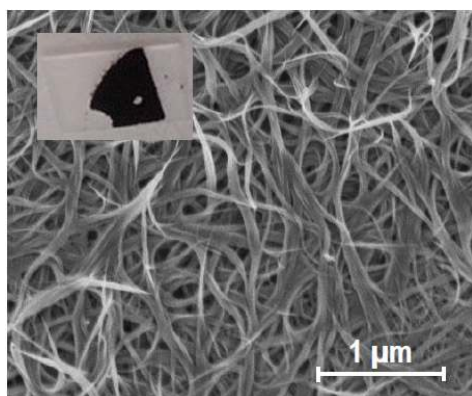
As starting point of this study, a complete characterization of the samples was done, mainly comprising a morphological description as well as the determination of the cleanliness of the sample. This last point is a crucial aspect in the disentanglement of the inherent nanotubes capability to interact with potential chemical absorbants and, therefore, much attention has been paid to this issue.

The material used for this set of experiments was synthesized by arc-discharge and, subsequently, purified and separated by using a variation of the DGU method (as proposed by Yanagi et al. [96]), obtaining metallic and semiconducting SWCNTs with high-purity of about 95 % and 99 % compared to the pristine sample, correspondingly. Samples were

deposited as thin films, with a thickness of  $\approx 1 \mu\text{m}$ , on sapphire substrates [96, 138] (Inset Figure 5.1).

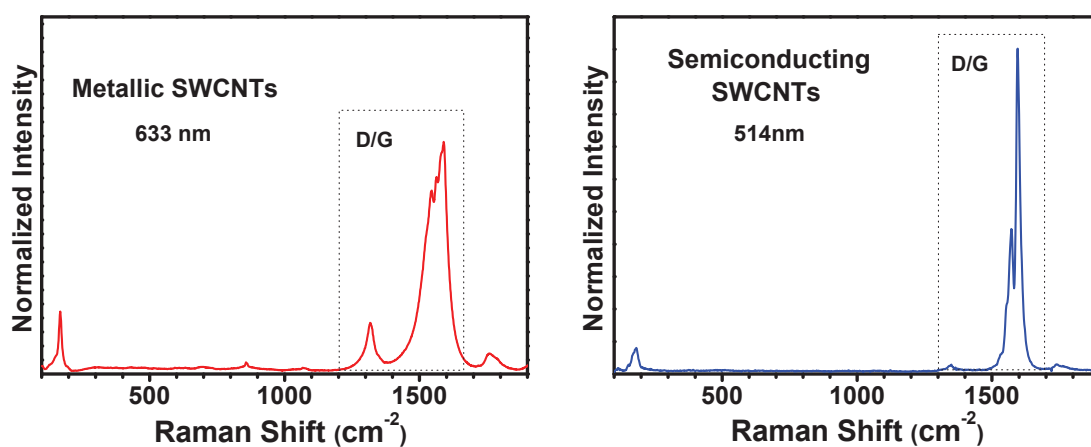
### 5.1.1 Morphological details

Metallic and semiconducting SWCNTs films presents the typical reddish and greenish coloration expected for metallicity sorted materials, correspondingly. The overall morphology of this thin films was firstly observed by using SEM, as it is shown in Figure 5.1. This micrograph evidences the formation of a high-purity network [98] of semiconducting tubes and no presence of any kind of impurities. Notice that no image from the metallic tubes was included since no observable difference between both types of films was perceived with this imaging technique.



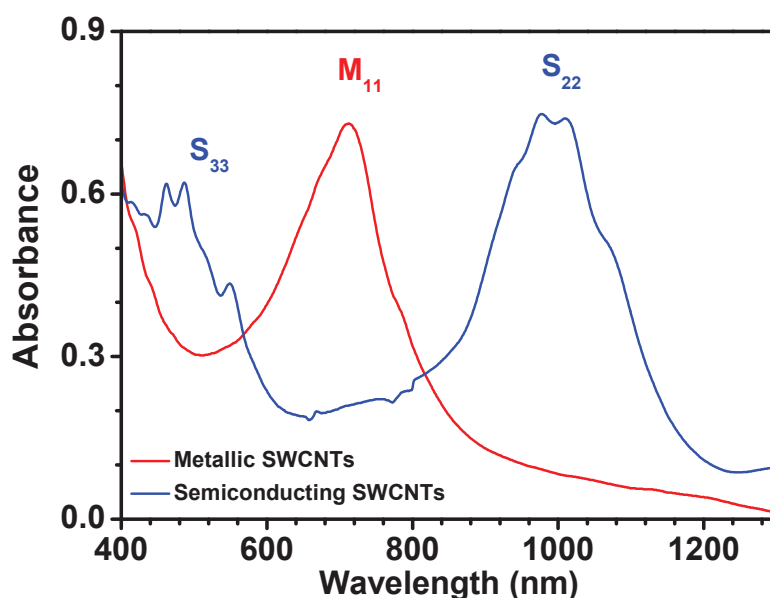
**Figure 5.1.** SEM micrograph at intermediate magnification showing the overall morphology of the nanotube films used in the experiments. In the inset, a film' snapshot is depicted.

Complementary to SEM, Raman resonance spectroscopy and optical absorption measurements were performed to rule out other characteristics of the samples and to settle the purity of the material, as it is explained in the subsequence section.



**Figure 5.2.** Room temperature Raman response for a) metallic and b) semiconducting tubes conducted at 633 nm and 514 nm laser excitation in the range between 100 and  $1900 \text{ cm}^{-1}$ , respectively.

The Raman response of metallic and semiconducting SWCNTs measured at 514 nm and 633 nm, correspondingly, is shown in Figure 5.2. For both cases, the D/G ratio was evaluated in the range of 1200-1800 cm<sup>-1</sup>, where a very little defect line is detected with a D/G ratio better than 3-5 %, as previously determined for similar tubes. Additionally, the radial breathing mode region was inspected and SWCNTs with a mean diameter of 1.4 nm was found.



**Figure 5.3.** OAS spectra of high purity SWCNTs: metallic (red) and semiconducting (blue) nanotubes.

As explained in the previous chapters, DGU method is a separation method in which the difference of mass enable the molecules/particles to be distributed by several ultra fast centrifugation cycles. Consequently, this process is used to separate impurities from the nanotube-material as well as to subsequently separate the clean tubes by either metallicity, length or diameter (chirality). A direct way to evidence the successful application of the method is optical absorption spectroscopy. In Figure 5.3, OAS spectra from both samples are shown. The high purity is attested anew by the absence of a broadening in the range of 1100-1300 nm, where amorphous carbon is recognized and estimated by the statistical averaging of the area under the each curve. Furthermore, the intrinsic  $S_{11}$  and  $S_{22}$  adsorption bands of semiconducting tubes and the  $M_{11}$  from the metallic ones can be clearly identified with no bands associated with the other conduction type in either spectra. The good dispersion evinced in the intense OAS response leads to an homogeneous deposition of the tubes while preparing the thin films (seen in the SEM image from Figure 5.1).

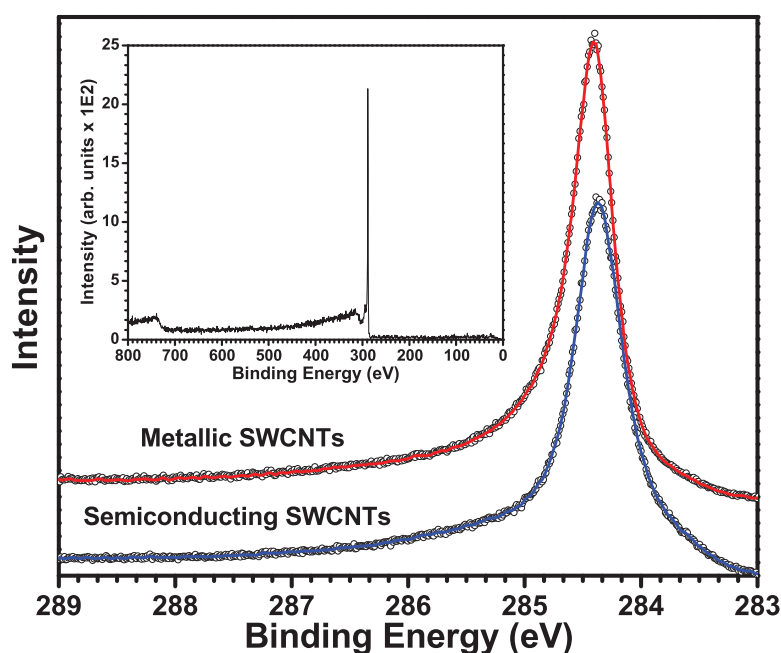
PES was also used to characterize the pristine material. Here, it has been shown that the SWCNTs in a buckypaper form have less than 1 % wt. of processing residuals, with negligible residual magnetic metal impurity content. Typically, in these samples the remaining amount of surfactants, such as deoxycholate sodium salt, is below the the detection

limit of XPS and FTIR spectroscopy. Thus, the use of this standard method allows to suggest that the starting sorted samples are highly purified and successfully separated into metallicities.

### 5.1.2 Cleanliness of the samples

The ultimate goal of this sample preparation process is to expose this kind of carbon nanotubes to different gases and measure their photoemission response, where any post-production contamination can dramatically affect the sensing performance.

Certainly, sorted samples were deposited on substrates and manipulated, being exposed to surfactants, filter membranes and the atmosphere (molecular oxygen). Hence, before starting with the experiments, samples were located on a vertical Ta holder, which was attached on the backside to a resistive heating system and placed facing an e-beam heating system.

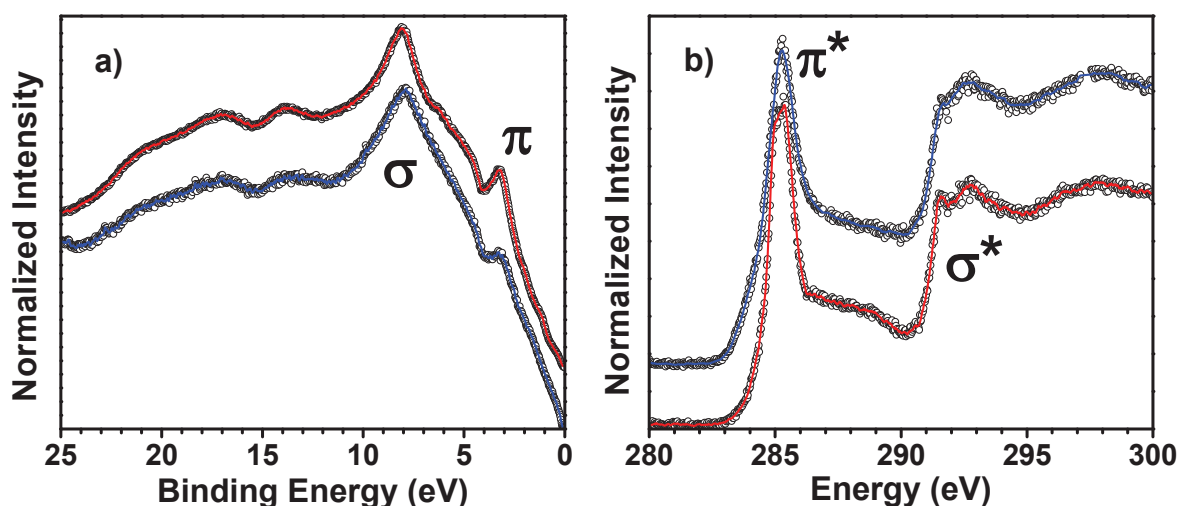


**Figure 5.4.** XPS spectrum measured at 400eV photon energy and at 101K and 105K for metallic (red line) and semiconducting (blue line) SWCNTs, respectively. The inset spectrum depicts a typical survey scan for metallic tubes after finishing the annealing cycles. It has been taken to evaluate residual contamination.

With a base pressure of  $2.5 \times 10^{-10}$  mbar, resistive and e-beam annealing cycles were carried out up to 900K for several hours and a photoemission survey scan was measured (inset Figure 5.4). This overall inspection shows only the presence of C atoms and no other chemical species. Additionally, C 1s high resolution XPS response was inspected (Figure 5.4). The C 1s response for the metallic and semiconducting ultra-clean samples

reveal an overall Doniac-Sunjic line shape of the metallic tubes and the symmetric line of the semiconducting nanotubes. A line shape analysis reveals respective peak positions, located at about  $\sim 284.43$  eV and  $\sim 284.41$  eV binding energy, and corresponding linewidths of 0.31 eV and 0.33 eV, for semiconducting and metallic samples, respectively. This is in good agreement with previous results on pure metallicity sorted reference material [48].

In addition, the clear fingerprint of the SWCNTs van Hove singularities (vHs) in the occupied and matrix element weighted unoccupied density of states is revealed using valence band photoemission and C 1s absorption, depicted in Figure 5.5. The line shape analysis evidences that the positions of the vHs are in good agreement with previous results [48], which proves the very high quality of our samples. It worth to notice that the slight linewidth broadening in the XAS response is due to the experimental resolution of the the different beam lines in the ELETTRA synchrotron.



**Figure 5.5.** a) Valence band photoemission conducted at 100 eV photon energy on metallic (red curve) and semiconducting (blue curve) SWCNTs, measured at 101K and 105K respectively. b) Complementary C 1s XAS studies in the range of the  $\pi^*$  response reveal a corresponding fine structure in the unoccupied DOS.

Considering the very small D/G ratio seen before by Raman spectroscopy of about 3%-5%, a low-defect content was assigned (See Figure 5.2). After the high-temperature annealing, a thermal healing of the nanotube' lattice takes place, as it was demonstrated in the literature [139]. Consequently, the defect content is highly reduced which is of crucial importance while settling the rules that governs the absorption mechanism for sorted nanotubes.

## 5.2 Testing the SWCNT' sensing performance

Once metallic and semiconducting SWCNTs were out-gassed and a factual evidence of their ultra-cleanness was given, sensing experiments were carried out in ultra-high vacuum

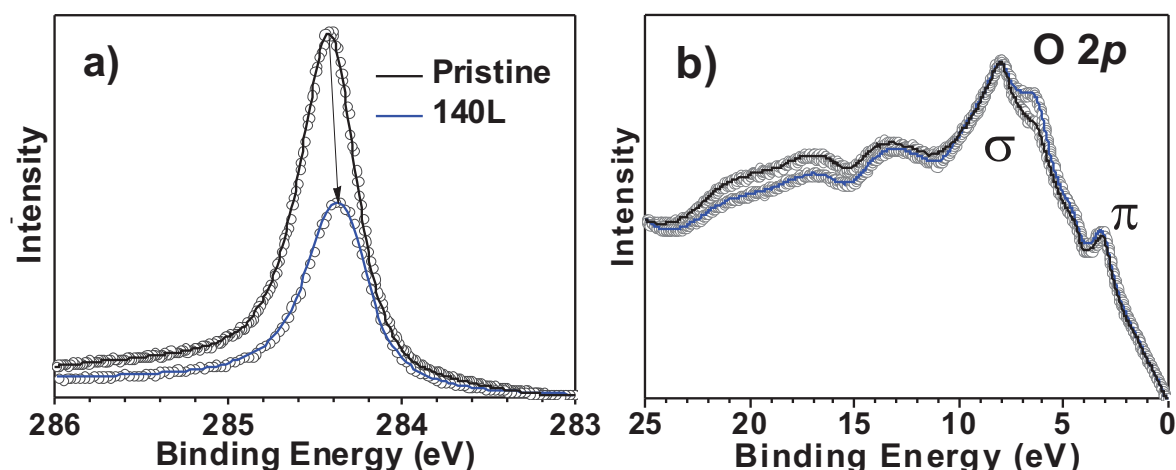
at a temperature of 100K. Samples were exposed to pure O<sub>2</sub>, NO and NO<sub>2</sub> gases, which were inserted by a needle valve allowing to control the dosis of the uptake. Note that all dosis will be expressed in Langmuir (L), which is defined as  $1\text{ L} \approx 1.33 \times 10^{-6} \text{ mbar} \cdot \text{s}$ . By using the facilities of the SuperESCA beamline at the Elettra Synchrotron [140], core level spectra were recorded for the C 1s, N 1s and O 1s signals using photon energies of 400, 525, and 650 eV, with corresponding overall energy resolution of 100, 150, and 200 meV, respectively. Moreover, X-ray absorption spectroscopy was measured using the Auger yield of the respective core levels. For calibration purposes, the tantalium (Ta) from the sample holder was measured as the reference.

Results on the absorption of each chemical species certainly suggest a distinct behaviour. They will be presented separately to highlight their particular mechanism as a function of the metallicity of the samples.

### 5.2.1 Oxygenation of the tubes

The interaction of oxygen with carbon nanotubes has always been an important subject when underlying the physical mechanism of any gas adsorption. The incorporation of oxygen is unavoidable in the processes of production, purification and separation of carbon nanotubes and can greatly alter their electronic structures, making it sometimes difficult to discern the intrinsic properties of SWCNTs.

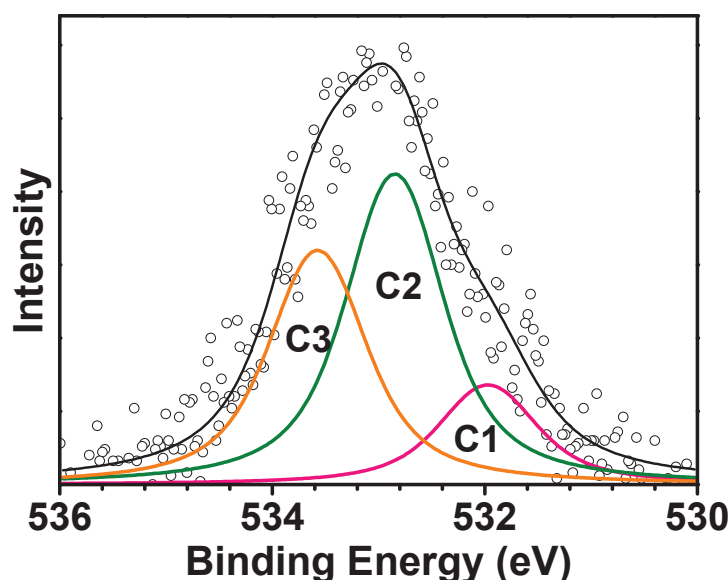
Metallicity sorted samples were exposed to 140L dose. However, results will be presented for semiconducting tubes considering that the effects are representative for both metallicities.



**Figure 5.6.** a) C 1s XPS spectra of the clean s-SWCNTs and after exposure to 140L molecular oxygen measured at 400 eV. Here, a small shift of  $\sim 0.6$  eV and a small intensity attenuation are found. b) VB XPS measurement conducted at 100 eV upon exposure of 140L of O<sub>2</sub>, where a small O 2p peak is observed.

In Figure 5.6 a), a  $\sim 0.6$  eV shift of the C 1s response towards lower binding energy without additional broadening is observed. The unaffected C-C peak signal suggests that

there is no significant charge transfer from the molecular oxygen to the C atoms. Furthermore, the C 1s emission do not show any extra contribution related to a C-O bond, which is located at the energy range 286-289 eV [141]. However, the small shift observed in the C-C peak can be assigned to a weak hybridization.



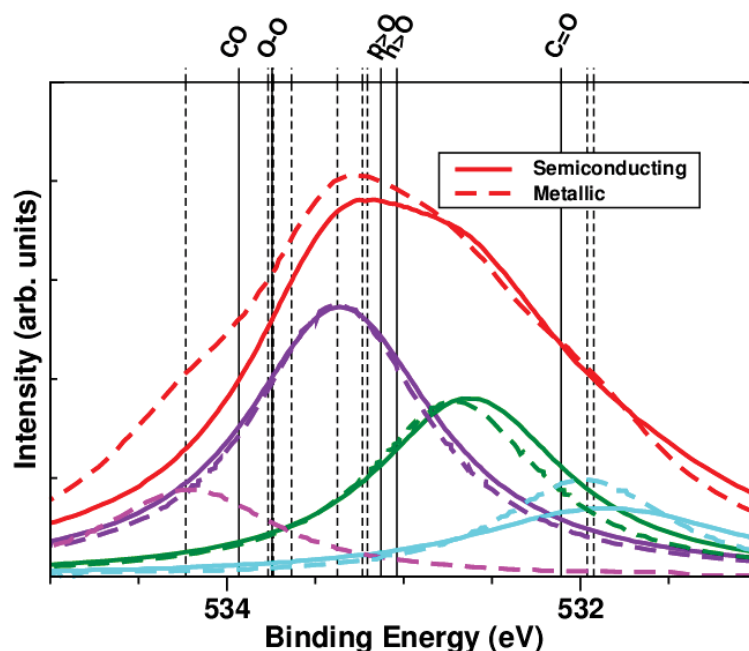
**Figure 5.7.** An insight into the chemical reaction of O<sub>2</sub> on SWCNTs was studied by measuring the O 1s XPS. The deconvolution of the O 1s reveals the rich bonding environment resulting from the oxidation of the tubes.

To follow the chemical reaction, the corresponding O 1s signal was recorded, allowing a cyclic probing of the oxygen uptake. A negligible time-dependant deviation of the line shape was observed, indicating that an oxidative limit was reached within 2 min of exposure. This response was deconvoluted using Voigt function and the best-fit curves are displayed in Figure 5.7, where components were found at binding energies of 531.9 eV (C1), 532.8 eV (C2) and 533.6 eV (C3). Differently from the case of the C 1s core level, where only a very small O contribution was detected, the case of the O 1s spectra allows to study the nature and complexity of the adsorption mechanism in our system. Taking into account the possible radical formation and their most stable configurations[142–144], it is reasonable to assign the C1 components to a C=O carbonyl group, while C2 indicates the presence of a C-O-C epoxy structures and the C3 should be attributed to a carboxylate group O-C=O. The mechanism is undoubtedly dominated by van der Waals interaction but the process in which the O<sub>2</sub> dissociates is still not completely understood. The breaking of the O-O bond of a physisorbed O<sub>2</sub> molecule is unlikely owing to the weak interaction with the SWCNT. However, it was shown that near the defect sites of the graphite surface O<sub>2</sub> molecule can dissociate [145]. A carbon nanotube is normally more reactive than the surface of graphite. As a result, O<sub>2</sub> physisorbed near the defect sites of a SWCNT can be the origin of the dissociation into atomic oxygen[146]. This will be studied in more detail in the theoretical modelling bellow.

The valence band spectra measured on the clean sample and at 140L dosis are shown in Figure 5.6 b). In both spectra, peaks at 3.1 eV and 8.1 eV correspond to valence band electrons originating from the  $p$ - $\pi$  and  $p$ - $\sigma$  bands. Exposure to  $O_2$  induces the growth of another feature at  $\sim 6.3$  eV, which is interpreted as the O  $2p$ . Less than 5% of variation of the intensity O  $2p$  line is detected. The same holds for the unoccupied DOS vHs revealed in the C  $1s$  XAS signal, which stays unaltered after oxygen exposure. These observations attest that pure SWCNTs are sensitive to  $O_2$  and gas adsorption most probable only happens on the few remaining defective sites on the SWCNTs' walls. These zones act like 'reaction catalyst places', generating a very rich and fast dissociation of the O molecules. Interestingly, oxygen and their derivatives forms only physisorbs on the tubes saturating in a very low dosis.

### Modelling the $O_2$ bonding environment

To have a complete picture, theoretical calculations were done exploring all possible forms of absorbed oxygen on (6,6) and (10,0) SWCNT. Notice that all simulations were performed using these chiralities since they are representative for the samples employed along the gas sensing experiments. Previously, in Figure 5.8, an abundant bonding environment is revealed and the following simulations try to address on the mechanism of  $O_2$ -CNT interaction obtained by a core-level study.



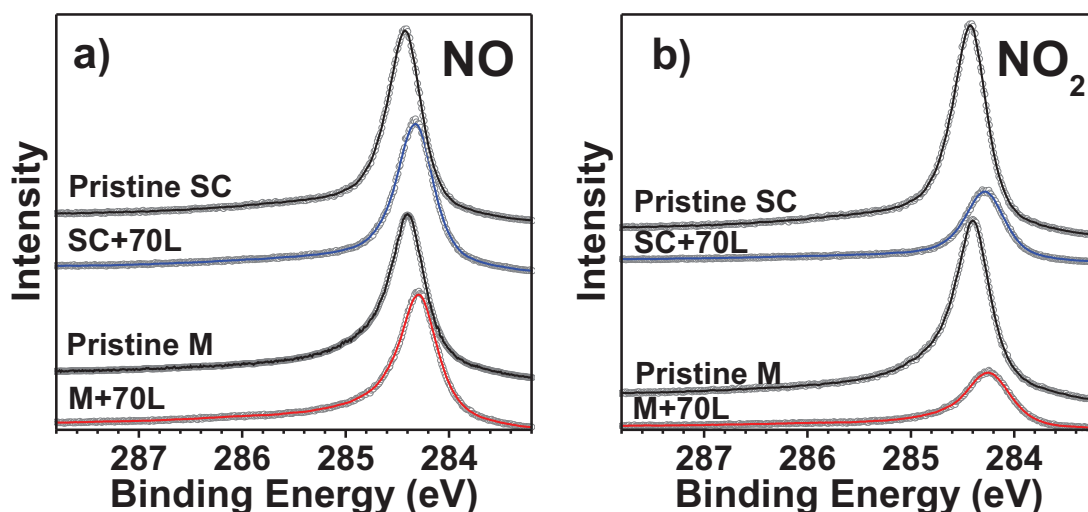
**Figure 5.8.** Making use of theoretical tools, a simulation of the bonding environments for  $O_2$  adsorption was done. The identification of the compounds and functional groups involved in this process gives a hint of dynamics of the adsorption mechanism.

The O<sub>2</sub> molecule first spontaneously dissociates on the monovacancy, leading to an epoxide group on a pentagon (p>O) and a carbonyl group (C=O). Then, p>O can migrate away from the monovacancy and deposit on a hexagon (h>O). Results suggests that the main peak is due to this atomic oxygen on the pristine SWCNT (epoxide group on a hexagon, h>O). Finally, a fraction of the atomic oxygen on the pristine CNT (h>O) rip a C atom out of the tube, forming another monovacancy with CO adsorbed (C-CO). In contrast, for the (10,0) SWCNT, the calculated C-CO peak is significantly shifted (by 0.3 eV) to the right, while the other peaks (C=O, h>O, p>O, O-O) are nearly unchanged. This fact explains why the left shoulder was only evident on the metallic CNTs. Also, no chemisorbed O<sub>2</sub> (O-O) was found to bond on the sidewalls of the tubes, neither on the defective sites nor the crystalline zones.

As mentioned before, this specific reaction between oxygen and CNTs is very controversial and there is plenty of publication in favor or against the potential reactivity of oxygen, depending on the morphological characteristics of the tubes. However, in this work, it can be ensured that the purity, metallicity and the defect content are interconnected factors that plays an important role in determining the reactivity of SWCNTs to the presence of oxygen.

### 5.2.2 NO vs. NO<sub>2</sub>

Then, the sensitivity of these samples was studied under the exposure to N-containing compounds, particularly NO and NO<sub>2</sub>. Changes observed for both situations indicates that NO is less reactive. Hence, the modification in the response are less evident than the other case. Consequently, a preliminar appraisal was done considering both circumstances at a 70L dose to better illustrate the results.



**Figure 5.9.** C 1s photoemission spectra recorded on the semiconducting (top) and metallic (bottom) SWCNT-samples after exposure to 70 L of (a) NO and (b) NO<sub>2</sub>, compared to their pristine material.

Figure 5.9 show the changes in the C 1s line recorded in XPS. Here, the exposure

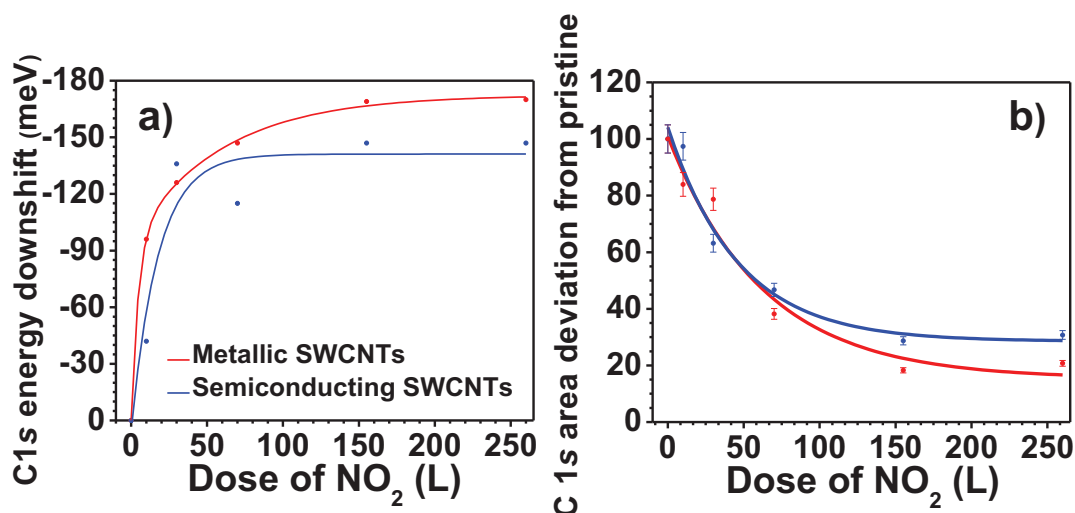
to NO produces an intensity attenuation of 12 % and an increase of the full width at half maximum (FWHM) to 0.41 eV in the C 1s of pristine semiconducting samples. In the case of metallic tubes exposed to NO, the intensity is reduced by 17 % and the line exhibits an even larger broadening to 0.64 eV. The exposure to a comparable dosage of NO<sub>2</sub> not only induces a larger shift ( $\sim 150$  meV) but also a larger broadening. The shift of the C 1s line to lower binding energies in comparison to pristine samples for the metallic (from 284.48 to 284.37 eV) and semiconducting tubes (from 284.43 to 284.34 eV) [48] is the first evidence of a different core-level shift from what has been previously reported for unsorted material [147, 148]. Additionally, the intensity attenuation is around 25 % and 70 % for the semiconducting and metallic samples respectively. This is another remarkably different result from previous studies on unsorted SWCNT-material, where the C 1s response of sorted SWCNTs upon exposure to NO<sub>2</sub> was conversely four times more intense than for NO.

### 5.3 NO<sub>2</sub> adsorption

Keeping in mind that NO<sub>2</sub> is a very reactive molecule with a rich chemistry and that nanotube-material presents a high sensitivity to this compounds, the following section will be centred on inquiring the chemical pathway when working with ultra-pure sorted samples.

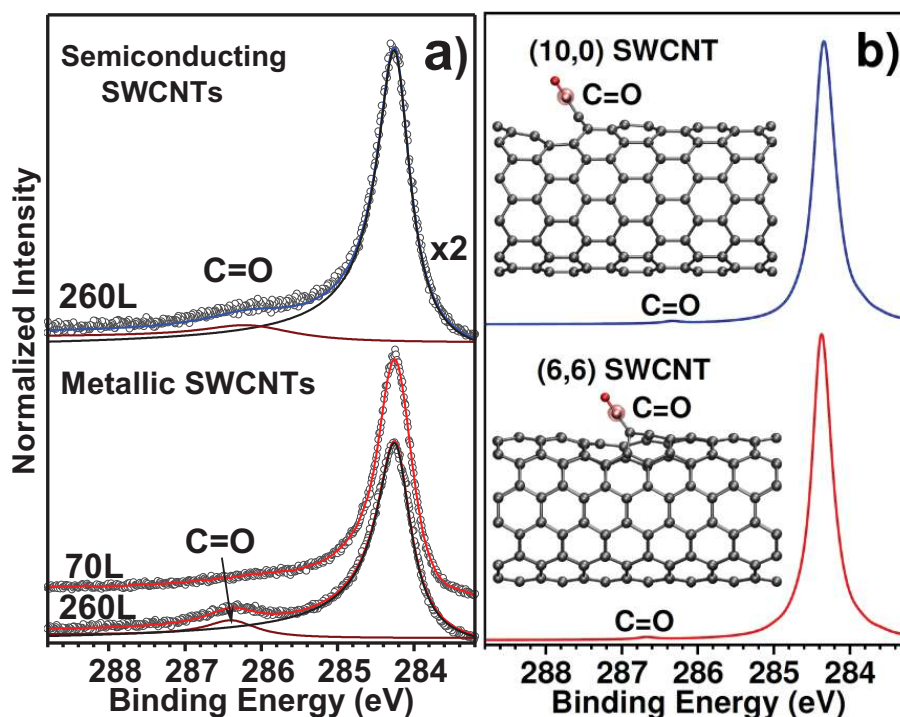
#### 5.3.1 C 1s core level analysis

Semiconducting and metallic SWCNTs were dosed at 10 L, 30 L, 70 L, 155 L and 260 L to observe the spectral evolution of the C 1s line.



**Figure 5.10.** (a) Overall area and (b) binding energy shift of the C 1s line as a function of increasing NO<sub>2</sub> dosage observed for semiconducting and metallic samples.

The C 1s shift from the main peak position is shown in Figure 5.10 a), whereas Figure 5.10 b) depicts the change of the area under the curve relative to the pristine material. This exponential dependence with increasing dosage in both the C 1s relative area and the peak downshift can have different explanations. These include the oxidation of the tubes by the NO<sub>2</sub> molecules, the chemisorption of molecular species as products of a reaction or simply the presence of reactive defects. Whatever the case may be, these new observations strongly suggest that the reaction pathways of the NO<sub>x</sub> molecules are very different to what has been reported so far. Previous studies suggested that metal impurities were responsible for the tremendous increased sensitivity to NO<sub>2</sub> absorption [149]. However, changes in the C 1s and N 1s in photoemission strongly hint that working with purified and sorted samples provides additional information. This requires rethinking of the adsorption processes that have been proposed so far in similar studies with unpurified SWCNTs.



**Figure 5.11.** (a) C 1s XPS spectra recorded on the metallic (bottom) and semiconducting (top) SWCNT-samples after exposure to the 260 L saturation limit of NO<sub>2</sub>. An additional spectrum at 70 L for the metallic sample is depicted for comparison purposes (see text). (b) C 1s simulated spectra for defective semiconducting (10,0) (top) and metallic (6,6) (bottom) SWCNTs with adsorbed atomic oxygen extracting a carbon atom to form a ketene group at the monovacancy. The maximum of the simulated C 1s and the corresponding experimental spectrum were aligned. The inset shows a ball-and-stick model with carbon and oxygen atoms as grey and red spheres, respectively. An isosurface representation ( $0.11 \text{ e}/\text{\AA}^{3/2}$ ) of the ketene C=O C 1s orbital is also shown.

The investigation of the adsorption process was considered at the highest possible coverage, which corresponds to 260 L NO<sub>2</sub> close to the saturation dosage. Figure 5.11 a)

provides insight in the vicinity of the main peak of the C 1s in XPS, which is proportionally downshifted about 180 meV for both types of samples at this dosage. Additionally, upon exposure to NO<sub>2</sub>, a component independent from the  $\pi$  plasmon satellite and the shake-up features related to low energy  $\pi - \pi^*$  interband transitions [150] is observed. This feature is located at 286.4 and 286.2 eV for the metallic and the semiconducting samples, respectively. Its intensity appears to be directly related to the hybridization of the system and clearly depends on the metallicity of the samples, as it is about five times higher for metallic tubes.

### Simulated C 1s spectra

In order to understand the nature of this feature, DFT calculations on semiconducting (10,0) and metallic (6,6) SWCNTs were performed. Various adsorbed molecules were evaluated (Table 5.1) and then, a monovacancy defect were introduced on the SWCNTs with various C–N and C–O adsorbed configurations to understand the origin of this signal. To this end, it has been employed more than 6 Å of vacuum and non-periodic boundary conditions in all directions. In this way, a common vacuum-level reference between the all-electron C 1s eigenenergies was ensured. The C 1s spectra was then simulated by employing a Lorentzian broadening with an inverse lifetime of 0.27 eV, and aligning the calculated and experimental C 1s levels of the C–C species in acetone [151].

**Table 5.1. Carbon Species, Isolated Gas Phase Molecules, and Functional Groups Studied.**

| C Species | Molecule         | Formula                                       | Group               |
|-----------|------------------|-----------------------------------------------|---------------------|
| O=C=O     | carbon dioxide   | CO <sub>2</sub>                               |                     |
| C≡O       | carbon monoxide  | CO                                            |                     |
| C=O       | ethenone         | CH <sub>2</sub> CO                            | ketene              |
|           | formaldehyde     | CH <sub>2</sub> O                             | aldehyde / carbonyl |
|           | acetyl radical   | CH <sub>3</sub> CO                            | acetyl              |
|           | acetone          | (CH <sub>3</sub> ) <sub>2</sub> CO            | ketone / carbonyl   |
| C–O       | phenol           | C <sub>6</sub> H <sub>5</sub> OH              | hydroxyl            |
|           | ethylene oxide   | C <sub>2</sub> H <sub>4</sub> O               | epoxide             |
| C–N       | nitrobenzene     | C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> | nitro               |
|           | pyridine-N-oxide | C <sub>5</sub> H <sub>5</sub> NO              | amine oxide         |
|           | pyridine         | C <sub>5</sub> H <sub>5</sub> N               | pyridyl height      |

The first approach using nitrogen-containing molecules was not able to reproduce the feature at the binding energies observed experimentally. The calculated separation between the C 1s main peak and this feature was never more than 1.1 eV to higher binding energies, with a charge transfer of 0.33 and 0.38 electrons from the (10,0) and (6,6) SWCNTs to NO<sub>2</sub>, respectively. Also, only a slight chemisorption of NO<sub>2</sub> at high coverages was found but in general it was physisorbed. Consequently, the focus centred to the possible adsorption of oxygen.

Considering a pristine nanotube, the adsorption of molecular oxygen is weak, with a small charge transfer, and in this case no significant shift of the C 1s was observed [120, 152–155]. Therefore, a monovacancy was introduced to the lattice a monovacancy and the adsorption of atomic oxygen was inspected. The monovacancy resembles a bicyclo[7.3.0]dodecane, which consists of a nine-membered ring and a five-membered ring. In this defective site, there is one unsaturated hexagon carbon with divalent carbene character that sticks out of the SWCNT, as shown in Figure 5.11 b). To this electrophile site, a CO molecule leading to the formation of a ketene group was attached. This describes the likely scenario of an atomic oxygen extracting a carbon atom and creating a defect in the lattice [156–158]. For both SWCNTs, the calculated C=C bond length is 1.31 Å and the C=O bond length is 1.17 Å, as is the case for the ethenone molecule. The calculated C 1s core-levels for the C=O species of the ketene group are 286.67 and 286.33 eV for the (6,6) and (10,0) SWCNTs, respectively, as shown in Figure 5.11 b). This is in semi-quantitative agreement with the experimentally observed features in the C 1s spectra at 286.4 and 286.2 eV for the metallic and semiconducting samples, respectively. The differences in the core-level shifts between the metallic and semiconducting samples is also reproduced, and may be related to the different charges of 0.64 and 0.62 *e* calculated for the C=O species in the (6,6) and (10,0) SWCNTs, respectively. For all other oxygen containing groups considered, such as carbonyls and epoxides, the C 1s core levels are at most 1.6 eV. These clearly demonstrates that the experimentally observed features are caused by the presence of the C=O species of ketene groups formed as reaction by-products.

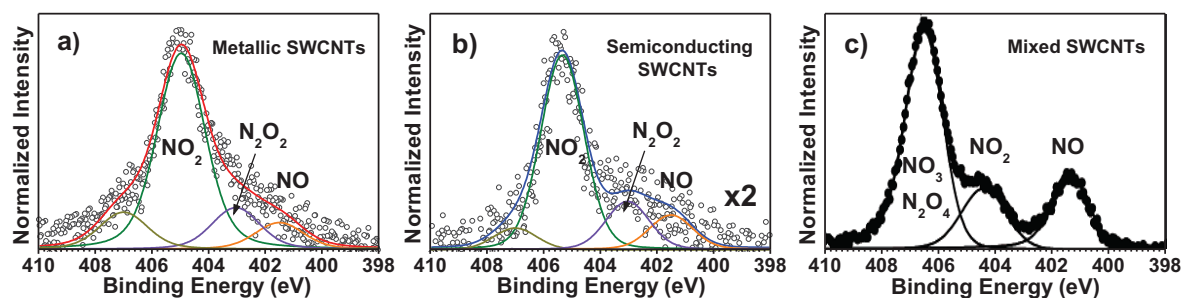
With the aim of further confirming that the features observed at high binding energy in the C 1s photoemission signal are due to a C=O species in a ketene group, a separate calculations for isolated molecules (Table 5.1) containing a variety of C–N and C–O chemical environments was performed. Results clearly showed that the experimentally observed feature can only be attributed to a C=O species within a ketene group. For both types of SWCNT, it has been found that the C=O species of a carbonyl group and C–O species are at too weak binding energy to give rise to the experimentally observed feature. However, it should be noted that the presence of carboxyl and epoxide groups in the experimental spectra cannot be ruled out as their signals may appear in the region between the main and ketene peaks. As described below in more detail, the atomic oxygen is available via a new reaction pathway which is generated by the photoinduced interaction with synchrotron radiation. This observation contrasts with previous studies on less purified metallicity mixed samples [147–149].

### 5.3.2 N 1s core level analysis

An important part in interpretation of the absorption process is the analysis of the chemical bonding environment obtained, in this case, by the study of the N 1s response. In Figure 5.12, the N 1s spectra recorded for metallic (a) and semiconducting (b) samples are shown as compared to the previously reported N 1s signal from mixed SWCNTs [149] exposed to a comparable dose of NO<sub>2</sub> (c). Here, a spectral deconvolution has been done with Voigtian functions, taking into account the experimental resolution. At the 260 L satu-

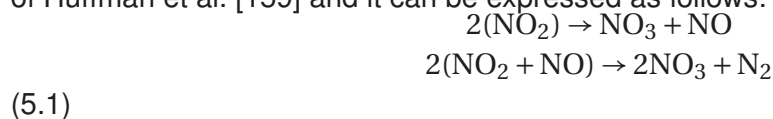
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ration dosage the N/C ratios are  $\sim 15\%$  and  $\sim 8\%$  for the metallic and the semiconducting tubes, respectively. It means that the metallic tubes are twice as prone to adsorb  $\text{NO}_2$  (and products of its reaction) than their semiconducting counterparts. The strongest component identified at 405.5 eV in Figures 5.12 a) and 5.12 b) corresponds to  $\text{NO}_2$ , which is remarkably different from the case observed in the mixed samples. This suggests that the reaction pathway is different when only ultra-clean nanotubes are used. The chemical reactions are different and take place at a different speed from what has been reported for unsorted material.  $\text{NO}_2$  is weakly hybridized with the SWCNTs and the relative intensities of the reaction products as compared to the main  $\text{NO}_2$  contribution are much smaller than previously reported. The other components that can be identified are:  $\text{NO}$  ( $\sim 401.2$  eV),  $\text{N}_2\text{O}_2$  ( $\sim 403$  eV),  $\text{N}_2\text{O}_4$  and  $\text{NO}_3$  ( $\sim 407.1$  eV). Bearing this in mind, the type of reaction that occurs once the  $\text{NO}_2$  molecules approach the nanotube's surface can now be analysed [159].



**Figure 5.12.** N 1s core level photoemission spectra recorded at 100 K of metallic (left) and semiconducting (middle) SWCNTs after exposure to  $\text{NO}_2$  at the saturation limit of 260 L, compared to the N 1s spectrum reported in Reference [149] (right). Note that the intensity of the response for the metallic sample is twice as high as that corresponding to the semiconducting one.

Previous studies on unsorted SWCNT-material [147, 148] proposed  $\text{NO}$  and  $\text{NO}_3$  (or  $\text{N}_2\text{O}_4$ ) as major products of the chemical reaction as can be clearly observed in Figure 5.12 c). However, these are hardly observed in spectra in Figures 5.12 a) and 5.12 b). In principal, it can be attributed to a preferential physisorption of  $\text{NO}_2$  on the metallicity sorted SWCNTs and its inability to dissociate rapidly due to the much smaller number of defects and almost nonexistent metallic impurities in these samples. From the weaker N 1s signal strength it can be inferred that semiconducting SWCNTs induce more dissociation of  $\text{NO}_2$  than the metallic ones. It is then clear that physisorption is the predominant adsorption mechanism so far but it cannot be ruled out that a weak chemisorption can take place. The reported chemical reaction for the case of mixed material was proposed based on the work of Huffman et al. [159] and it can be expressed as follows:

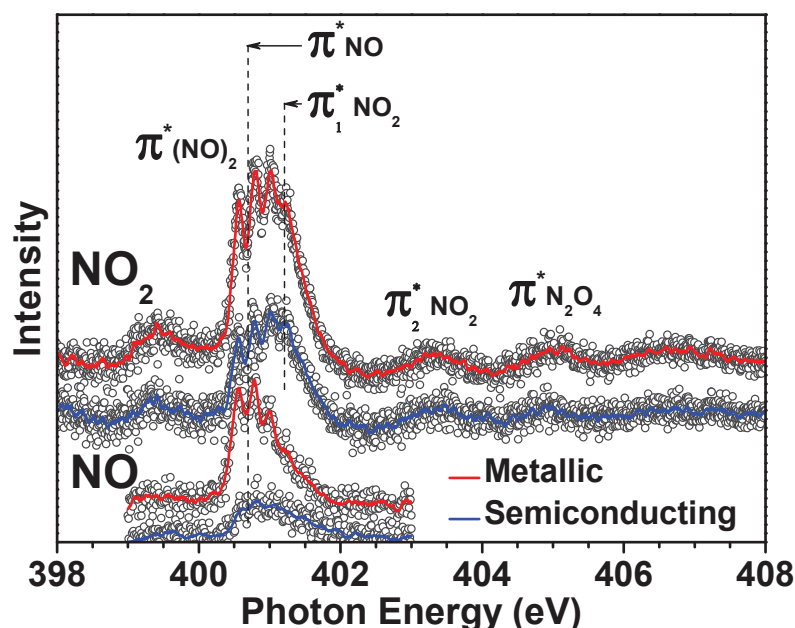


This expression cannot describe the scenario in which the absorption on ultra-clean sorted nanotubes takes place. Fundamentally,  $\text{NO}_2$  is by far the strongest component after

it interacts with the nanotubes and this is not provided by Equation 5.1. A proposed explanation for this difference is the low NO<sub>2</sub> decomposition rate in comparison to the gas injection rate. The divergence between the reaction of ultra-clean metallicity-sorted SWCNTs and the one from unpurified material are compelling evidence that the effect of impurities is still not understood and may not be neglected.

### 5.3.3 Vibrational fine structure

Thus far, N 1s provided details about the chemical species involved in the reaction as well as the speed of the dissociation. Also, the presence of the dimers from N<sub>2</sub>O<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> was detected, which stoichiometric equilibrium with their monomers at low temperature has been very-well established in Reference [159]. Therefore, X-ray absorption spectroscopy was performed considering that this is a more sensitive technique and allows the analysis of samples with an ultra-low amount of dopants/adsorbates [49].



**Figure 5.13.** N 1s XAS spectra of sorted SWCNTs upon the exposure of a comparable dose of NO and NO<sub>2</sub>.

Comparing NO and NO<sub>2</sub> adsorption, Figure 5.13 shows the overall XAS response in the N 1s recorded for the metallic and semiconducting samples exposed to a dose of 70 L of NO (bottom) and NO<sub>2</sub> (top). The response for NO onto metallic tubes is five times more intense than that for the semiconducting ones. In the case of exposure to NO<sub>2</sub>, it is about twice as intense. The clearly discernible features in all spectra correspond to the different

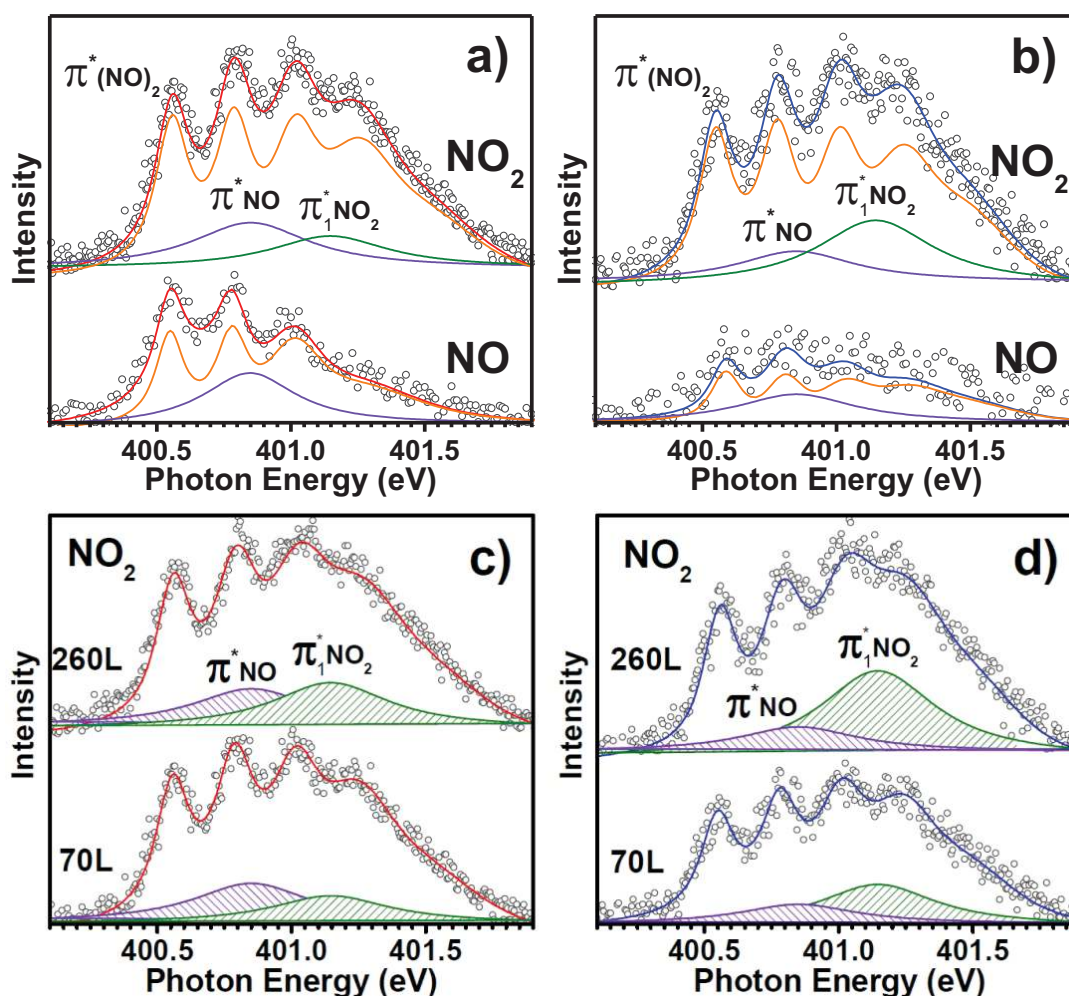
$\pi^*$  resonances related to the N-containing species. However, the spectra corresponding to  $\text{NO}_2$  exposure are much richer in nature and clearly exhibit additional signals above 402 eV.

In studies of adsorption of  $\text{NO}_2$  on the Ni(100), the features between 400 and 402 eV have previously been assigned to transitions into unoccupied  $\pi^*$  orbitals of NO and NO dimers [160]. The additional intensity at around 401.3 eV in the two top spectra of Figure 5.13 can be assigned to the lowest unoccupied  $\pi$  orbital of  $\text{NO}_2$  as reported in Reference [160–162]. The component at 403.3 eV is also associated to the  $\pi^*$  of  $\text{NO}_2$ , whereas the one at 405.1 eV corresponds to  $\text{N}_2\text{O}_4$  [161, 163, 164]. This confirms that the small component at high binding energies in the spectra in Figures 5.12 a) and 5.12 b) can be related to  $\text{N}_2\text{O}_4$ , and it is minimal. Therefore, it can be related to direct physisorption of a small amount of  $\text{NO}_2$  dimers.

Now the focus will be centred on the N 1s close-up into the region between 400 and 402 eV. To the best of my knowledge, the nicely revealed fine structure in the N 1s edge has not been investigated in studies with carbon nanotubes. In molecular systems, this fine structure is assigned to vibrational shake ups, the so-called Franck-Condon satellites (FCS). Studies identifying FCS by XAS and electron energy loss spectroscopy (EELS) in gas phase experiments have been widely reported, mostly dealing with CO and  $\text{N}_2$  [165, 166]. Also in the gas phase, studies on NO and its dimers have found a separation of the FCS of 235 meV [160, 167]. Much less is reported on the observation of FCS of gases adsorbed on substrates. Among these, investigations of CO adsorption on different metals (e.g. Ni, Rh or Cu) have shown that the line profile is dominated by the excitation of the stretch vibrations of the adsorbed molecules [168–170]. In general, the shake-up intensity decreases with increasing chemisorption strength, which is related to the electronic relaxation of the adsorbate. Hence, in physisorbed and weakly chemisorbed systems, the adsorbate retains its molecular character with the molecular orbital closely resembling the free molecule. In strongly chemisorbed molecules, adsorbate-substrate hybrid orbitals are formed. Their influence on observations for gas absorption on different substrates is well understood [171]. Additionally, it has been observed that the absorption on SWCNTs leads to an upshift of the energy for NO and to a downshift for  $\text{NO}_2$ .

Turning to a quantitative analysis of the N 1s XAS  $\pi^*$  response, the first FCS at around 400.8 eV varies slightly in position when adsorption occurs onto metallic or semiconducting samples. This suggests that the strongest interaction is the one between the NO dimer and the nanotubes independently from the metallicity of the sample, for both NO and  $\text{NO}_2$  adsorption. Therefore, the  $\pi^*$  response of the FCS is assigned to the NO dimers. The relative percentage area of the  $\pi^*$  response corresponding to NO and the  $(\text{NO})_2$  FCS compared to the  $\pi_{\text{NO}_2}^*$  is summarized in Table 5.2.

The region between 400 and 402 eV in the N 1s XAS can be analysed regarding the first  $\pi_1^*$  resonances of  $\text{NO}_2$  and NO, and a set of correlated Voigtians revealing the FCS, which are separated by the phonon frequency and broadened by the lifetime. The top panels in Figure 5.14 show the corresponding line shape analysis of spectra recorded on the metallic (Figure 5.14 a) and semiconducting (Figure 5.14 b) samples after an exposure to 70 L of both  $\text{NO}_2$  and NO. The  $\pi_{\text{NO}}^*$  resonance at ca. 400.8 eV represents the first unoccupied  $\pi$  orbital, which can either be related to adsorbed NO or to its dimers. The intensity variation



**Figure 5.14.** Close-up into Franck-Condon satellites region of the main peak of N 1s XAS response for (a) metallic and (b) semiconducting SWCNTs. These spectra were recorded upon the exposure to 70 L of NO and NO<sub>2</sub>. The bottom spectra show a comparison of the response obtained upon exposure to 70 L and 260 L of NO<sub>2</sub> in both, the metallic (c) and semiconducting (d) samples. The shaded areas represent only the components corresponding to molecular NO product of the NO<sub>2</sub> decomposition.

of this component explains why the NO molecules are co-adsorbed on the surface of the nanotubes at different rates depending on the nanotube's metallicity. When the samples were exposed to NO<sub>2</sub>, the spectral response is surprisingly similar. Only an additional peak at 401.1 eV corresponding to the  $\pi^*$  was observed, which is the transition into the lowest unoccupied  $\pi_{\text{NO}_2}^*$  orbital of NO<sub>2</sub> [162]. This is a further indication that many of the adsorbed NO<sub>2</sub> molecules undergo a chemical reaction with the SWCNT forming NO and NO dimers. A quantitative analysis of the vibrational frequencies and the relative strength of the FCS as compared to the  $\pi^*$  signal of NO and NO<sub>2</sub> provides information related to the relative hybridization strength of the adsorbed species and their nature. In the case of NO, the

**Table 5.2. Relative percentage area of the  $\pi^*$  response corresponding to NO and the  $\text{N}_2\text{O}_2$  FCS compared to the  $\pi_{\text{NO}_2}^*$**

| Dose (L)               | $\pi^* (\text{NO})_2$ | $\pi^* \text{NO}$ | $\pi_1^* \text{NO}_2$ |
|------------------------|-----------------------|-------------------|-----------------------|
| Semiconducting SWCNTs: |                       |                   |                       |
| 30 L                   | 74.68                 | 6.13              | 19.18                 |
| 70 L                   | 71.63                 | 9.03              | 19.33                 |
| 260 L                  | 60.06                 | 8.78              | 31.15                 |
| Metallic SWCNTs:       |                       |                   |                       |
| 30 L                   | 55.58                 | 15.86             | 8.56                  |
| 70 L                   | 71.26                 | 16.89             | 11.84                 |
| 260 L                  | 67.41                 | 14.57             | 18.02 height          |

stretching frequency ( $\nu$ ) is around 236 meV, which corresponds to the  $\text{C}_{2v}$  asymmetric N-O stretching mode of the dimer ( $\text{N}_2\text{O}_2$ ) which is close to NO. To gain further information, the changes in the XAS response were also studied as a function of  $\text{NO}_2$  dosage. These are depicted in Figures 5.14 c) and 5.14 d), comparing the metallic and semiconducting samples after exposure to 70 L and 260 L of  $\text{NO}_2$ . The vibrational frequencies of the FCS become slightly harder for higher doses and for metallic samples.

**Table 5.3. Frequencies of the FCSs in Figures 5.14c and 5.14d**

|       | Semiconducting SWCNTs | Metallic SWCNTs |
|-------|-----------------------|-----------------|
| 70 L  | 232 meV               | 229 meV         |
| 260 L | 235 meV               | 233 meV height  |

Table 5.3 summarizes the values of the FCS frequencies at 70 L exposure and at the saturation dosage of 260 L to  $\text{NO}_2$ . The frequency hardening with dosage and metallicity can be explained by an increased hybridization with the SWCNT. This is consistent with previous experiments of FCS on metallic substrates [168–170]. Concomitantly, the increased hybridization also reveals a change in the relative intensity of the  $\pi^*$  response of  $\text{NO}_2$  as compared to NO and the NO dimer FCS. These results are shown in Table 5.2. The relative  $\text{NO}_2$  intensity increases with increasing  $\text{NO}_2$  dosage and it is about three times stronger for the semiconducting nanotubes. This further confirms that part of the  $\text{NO}_2$  is transformed into NO dimers following the endothermic chemical reaction of  $2\text{NO}_2 \rightarrow 2\text{NO} + 2\text{O}$  proposed in Reference [159]. The oxygen from the chemical reaction with the SWCNTs may be physisorbed as  $\text{O}_2$  or chemisorbed on pristine SWCNTs forming epoxide groups or at defects as carbonyl or ketene groups. However, it is the C=O species of ketene groups that gives rise to the extra peak in the C 1s XPS response, as explained above. The higher  $\text{NO}_2$  response at the saturation dosage is related to the higher coverage, which lowers the

molecular interaction with the SWCNTs. The apparent sensitivity of the NO dimer to the electronic nature of the surfaces upon adsorption represents an ideal situation to understand the differences found between semiconducting and metallic SWCNTs while exposed to different gases.

### **Limit for the desorption energy of NO<sub>2</sub> on sorted SWCNT**

The last part of our experiments involved heating up the SWCNTs covered with NO<sub>2</sub> in order to estimate a lower bound for the desorption energy in metallicity-sorted material. After the saturation dose was reached, and properly measured at low temperatures, thermal desorption was studied by resistive heating. Due to fast thermal desorption the whole desorption cycle could not be followed by in-situ measurements as in previous studies on the adsorption and desorption of different gases and solvents on surfaces of mixed nanotubes [161, 172]. However, using the partial pressure of the analysis chamber and the heating time allowed us to estimate a lower bound for the desorption energy. For both metallicities desorption started after 2 min at 140 K, and it finished shortly after recovering the base pressure of the chamber. Here, a complete recovery of the C 1s line of the pristine SWCNTs and vanishing of the N 1s and O 1s responses was observed. It is estimated a lower bound of the activation energy for desorption ( $E_a$ ) of about 20 kJ/mol for the semiconducting tubes and 37 kJ/mol for the metallic ones. Previous results on HOPG [172] reported an  $E_a$  of 37 kJ/mol comparable to our estimation for metallic tubes. However, the purely semiconducting tubes interestingly show a much lower estimated value. In any case, both types of metallicity sorted nanotubes exhibit much lower values than the calculated  $E_a$  of 114 kJ/mol reported for unsorted nanotubes [161]. The lower desorption/adsorption energy for the semiconducting sample is also consistent with a weaker hybridization of the adsorbed nitric oxides due to the absence of conduction electrons. Concomitant with the strong interaction of nitroxides with different metallic systems, this study paves the way to tailor the interaction with SWCNTs by advanced filling reactions with metals and metal compounds.





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## Conclusion and further perspective

The main goal of this PhD thesis project has been the execution of an exhaustive spectroscopic study of the changes in the electronic properties of SWCNTs caused by surface functionalization.

Within the first approach, the potential of synthesizing B doped SWCNTs with a very low content of dopants using different C/B feedstocks has been investigated. By combining Raman spectroscopy and imaging techniques, the characteristics of the as-grown materials were perfectly determined and all parameters like temperature and carbon source exposure of the catalyst have been completely identified for the case of the optimized material. The most intriguing fact has been discovered while performing purification on these samples with density gradient ultracentrifugation. In the case of pristine nanotubes, this process has shown to be non-destructive and the etching effect of surfactant, acid solution, sonication or/and centrifugation has been extensively studied and completely controlled. Nevertheless, in doped material, dopants generates very reactive sites where chemical reactions tend to be highly intensified and accelerated. The characterization of my samples has shown that the catalytic compounds as well as the metallic particles were removed, keeping the factual doping level reached in the synthesis. Multifrequency Raman response has revealed that the diameter distribution remains almost the same as in the as-grown material, only very small diameter (in the range of 0.5-0.8 nm) tubes has been annihilated in the process. Due to curvature effects, these tubes tend to be chemically unstable and clearly this modified process cannot ensure the survival of this type of tubes. In this part of the thesis, it has been fully demonstrated that small modifications in standardized techniques leads to practical advances in the cleaning of doped material. This point must be considered of great interest in the design of new technologies. It worth to remember that one key aspect in e.g. electronic devices fabrication is the feasibility of use material without by-products, which could cause interferences or changes in the intrinsic characteristics of the material. But if, in addition to cleanliness, well-controlled in-situ SWCNTs can be obtained, the outcome will be a entirely new range of application and an enhancement of the

state-of-the-art high-tech products.

The second part of this thesis has been advocated to the study of the  $\text{NO}_x$  adsorption on ultra-pure metallic and semiconducting SWCNTs. Using this kind of nanotubes have allowed to identify that the chemical reactions are different and take place at a different speed from what has been reported for unsorted material. The adsorption reaction directly depends on the metallic character of the samples, and it is twice as high for the metallic tubes as for the semiconducting ones. Franck Condon satellites were resolved in the N 1s on this gas-nanotube system, revealing a weak chemisorption, which is related to NO dimer molecules. Complementary experiments on the desorption of the system show a very fast recovery and hence, give an evidence of the reversibility of the process. This study settles the limit for the strength of the interaction of SWCNT with nitroxides and paves the way to tailor the interaction with SWCNT by for instance advanced filling reactions with metals and metal compounds. This will allow to control the selectivity of the interaction with different nitroxides towards utmost sensitivity and selectivity of nanotube sensors at room temperature.

Combining all results discussed in this thesis, the new step in my research is the use of B-doped SWCNTs to study their gas sensing behaviour. This very promising analysis will lead to the production of other kind of purified doped material as well as a real determination of the effect of different doping levels in the complexity of the adsorption mechanism.

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## Curriculum Vitae

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### Education

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Thesis: *Influence of purity and metallicity on gas sensing applications of single walled carbon nanotubes and their heteroatomic doping at low doping levels*

2. Faculty of Physics, University of Vienna. Vienna, Austria

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## Publications

### Published, accepted or submitted for publication

1. M. Sauer, H. Shiozawa, P. Ayala, G. Ruiz-Soria, X. Liu, K. Yanagi, H. Kataura, S. Krause, T. Pichler  
*Environmental stability of ferrocene filled in purely metallic single-walled carbon nanotubes*

**Accepted for publication in Physica Status Solidi B**

2. G. Ruiz-Soria, A. Perez, M. Sauer, D.J. Mowbray, P. Lacovig, M. Dalmiglio, S. Lizzit, K. Yanagi, A. Rubio, A. Goldoni, P. Ayala, T. Pichler  
*Revealing the adsorption mechanisms of nitroxides on ultra-pure, metallicity-sorted carbon nanotubes*

**Submitted to ACS Nano**

3. M. Sauer, H. Shiozawa, P. Ayala, G. Ruiz-Soria, X. Liu, A. Chernov, S. Krause, K. Yanagi, H. Kataura, T. Pichler  
*Internal charge transfer in metallicity sorted ferrocene filled carbon nanotubes hybrids*  
**Carbon** 59 (2013) 237

4. G. Dabera, I. Jayawardena, M.R.R. Prabhath, I. Yahya, Y.Y. Tan, N.A. Nismy, H. Shiozawa, M. Sauer, G. Ruiz-Soria, P. Ayala, V. Stolojan, A.A.D.T. Adikaari, P.D. Jarowski, T. Pichler, S.R.P. Silva  
*Hybrid carbon nanotubes networks as efficient hole extraction layers for organic photovoltaics*

**ACS Nano** 7 (2013) 1

5. M. Sauer, H. Shiozawa, P. Ayala, G. Ruiz-Soria, H. Kataura, K. Yanagi, S. Krause, T. Pichler  
*In situ filling of metallic single-walled carbon nanotubes with ferrocene molecules*  
**Physica Status Solidi B** 249 (2012) 2408

6. G. Ruiz-Soria, S. Daothong, T. Pichler, P. Ayala  
*Spectroscopic study of the diameter distribution of B-doped single-walled carbon nanotubes*

**Physica Status Solidi B** 249 (2012) 2469

7. G. Ruiz-Soria, P. Ayala, S. Puchegger, H. Kataura, K. Yanagi, T. Pichler  
*On the purification of CVD grown boron doped single-walled carbon nanotubes*  
**Physica Status Solidi B** 248 (2011) 2504

8. T. Susi, Z. Zhu, G. Ruiz-Soria, R. Arenal, P. Ayala, A.G. Nasibulin, H. Lin, H. Jiang, O. Stephan, T. Pichler, A. Loiseau, E.I. Kauppinen  
*Nitrogen-doped SWCNT synthesis using ammonia and carbon monoxide*  
**Physica Status Solidi B** 247 (2010) 2726
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