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Abstract

Semiconductor technology is one of the fields where the research using carbon nanostructured materials has a very promising scope of applications. However, to make their use possible in nanoelectronics it is necessary to have an accurate control of their structural properties. There are many ways of doing this. This PhD thesis focuses on the synthesis of one-dimensional carbon nanostructures, namely single-walled carbon nanotubes and carbyne, inside a protective nanoreactor, which is the hollow core of an outer single-walled carbon nanotube. To date, structures like these can be made with methods like chemical vapor deposition and other chemical methods. This PhD work focuses strongly on realizing an experimental technique to make this synthesis feasible on a localized spot combining the principles of CVD and focused laser annealing. The same laser is also used for in situ Raman spectroscopy. I implemented a vacuum system where the single-walled carbon nanotubes could be placed on top of a suitable substrate and then heated and used as chemical reactors while they were exposed to a hydrocarbon source to grow a new structure inside the hollow core. Coupling this setup to the Raman spectrometer was a key feature that allowed combining synthesis and spectroscopy for in situ studies of growth kinetics.

In this manner, it is possible to promote the synthesis and viabilize Raman measurements *in-situ* as a very promising solution for applications. Localized synthesis has been tried in other labs indeed. However, the advantage of this work relies on the starting material, which are nanotubes with a controlled diameter distribution and a known chirality. This provides an advantage to understand the material that grows inside and allows us going one step forward in the understanding of the properties of the inner tubes and linear carbon chains. This is a novel approach to make the chains and the work presented here paves the way for promising future work. The first chapter is devoted to provide a thorough introduction to the field of carbon nanomaterials and the second chapter gives a background on their electronic and optical properties. The description of graphene has been taken into account in several sections for practical purposes. The third chapter provides in the first part an overview of the common synthesis methods.

Abstract

The second part focuses on the theoretical background of Raman Spectroscopy applied to carbon materials. Subsequently a description of *in-situ* methods is provided. The fourth, fifth and sixth chapters contain the results of the experiments with a thorough discussion. This also includes considerations regarding metallicity of the tubes, length of the chains and other aspects that are related to the state-of-the-art in the field. Finally, I have included a chapter providing brief conclusions and a perspective of where to go with these results and how to inspire new experiments.

Kurzfassung

Die Halbleitertechnologie ist eines der Gebiete, in denen die Forschung mit nanostrukturierten Kohlenstoffmaterialien einen vielversprechenden Anwendungsbereich hat. Um ihre Verwendung in der Nanoelektronik zu ermöglichen, ist jedoch eine genaue Kontrolle ihrer strukturellen Eigenschaften erforderlich. Es gibt viele Möglichkeiten, dies zu tun. Diese Doktorarbeit konzentriert sich auf die Synthese eindimensionaler Kohlenstoffnanostrukturen, nämlich einwandiger Kohlenstoffnanoröhren und Carbone, in einem schützenden Nanoreaktor, der selbst wieder der Hohlraum in einer äußeren einwandigen Kohlenstoffnanoröhre ist. Bisher können solche Strukturen mit Methoden wie der chemischen Gasphasenabscheidung und anderen chemischen Methoden hergestellt werden. Diese Doktorarbeit konzentriert sich jedoch stark auf die experimentelle Realisierung der Synthese an nur einem lokalisierten Punkt. Der Punkt wird lokal durch einen fokussierten Laserstrahl geheizt und befindet sich in einer für Gasphasenabscheidung geeigneten chemischen Umgebung. Der Laser kann nicht nur zum lokalen Heizen sondern auch mithilfe eines Raman-Spektrometers zur spektroskopischen Untersuchung der lokalen Syntheseprodukte verwendet werden. Wir haben ein Vakuumsystem implementiert, bei dem die einwandigen Kohlenstoffnanoröhren auf ein geeignetes Substrat gelegt und dann erhitzt und als chemische Reaktoren verwendet werden können, während sie einer Kohlenwasserstoffquelle ausgesetzt werden, um neue Strukturen im inneren Hohlraum zu bilden. Die Kopplung dieses Aufbaus an das Raman-Spektrometer ist entscheidend, damit Syntheseprozesse und spektroskopische Untersuchungen unmittelbar verknüpft werden können. Die lokalisierte Synthese wurde in der Tat schon in anderen Labors versucht. Der Vorteil dieser Arbeit beruht jedoch auf dem Ausgangsmaterial, bei dem es sich um Nanoröhren mit einer kontrollierten Durchmesser- und einer bekannten Chiralität handelt. Dies bietet den Vorteil, das Material, das im Inneren wächst, sehr genau zu kennen, und ermöglicht es uns, die Eigenschaften der Innenröhre und linearer Kohlenstoffketten besser zu verstehen. Dies ist ein neuartiger Ansatz, um Kohlenstoffketten herzustellen, und die hier vorgestellte wissenschaftliche Arbeit ebnet den Weg für weiterführende zukünftige Arbeiten.

Das erste Kapitel bietet eine gründliche Einführung in das Gebiet der Kohlenstoffnanomaterialien und das zweite einen Hintergrund zu deren elektronischen und optischen Eigenschaften. Die Beschreibung von Graphen wurde aus praktischen Gründen in mehreren Abschnitten berücksichtigt. Im dritten Kapitel gibt es zunächst einen Überblick über die gängigen Synthesemethoden und dann den theoretischen Hintergrund der Raman-Spektroskopie auf Kohlenstoffmaterialien. Anschließend wird eine Beschreibung der *in-situ* Methoden bereitgestellt. Das vierte, fünfte und sechste Kapitel enthalten die Ergebnisse der Experimente mit einer gründlichen Diskussion. Hier wird insbesondere auf Überlegungen bezüglich der Metallizität der Nanoröhren, der Länge der Ketten und anderer Aspekte, die mit dem Stand der Technik auf dem Gebiet zusammenhängen eingegangen. Schließlich habe ich ein Kapitel beigefügt, das kurze Schlussfolgerungen und eine Perspektive darüber enthält, wohin diese Ergebnisse führen und wie neue Experimente inspiriert werden können.

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1 Introduction

The research related to carbon materials has been extremely active during the last century. A variety of applications have been accomplished particularly with bulk carbon materials like diamond-like amorphous carbon, carbon fibers, tetrahedral amorphous, among others. Most of the bulk carbon materials have been used for over a century. The use of carbon fibers provided several technological breakthroughs in the second half of the last century. However, the carbon nanotechnology era was only born with the discovery of fullerenes. These are point molecular structures consisting of different specific numbers of carbon atoms. The C_{60} Buckminsterfullerene was discovered experimentally in the arc-discharge experiments performed in the Krätschmer-Huffman system [1], which were inspired in the research by Sir Harry Kroto (in Sussex), Richard Smalley and Robert Curl (at Rice University), who were trying to understand the mechanism by which long-chain carbon molecules are formed in interstellar space and circumstellar shells [2]. The C_{60} molecule was named after the architectural shapes designed by Buckminster Fuller. The geodesic domes designed in the 1960s resemble the geometric structure of the nanostructures described. The discovery of fullerenes accounted for the Chemistry Nobel Prize to Curl, Kroto and Smalley in 1996. However, the last two decades of the past century witnessed important breakthroughs in nanotechnology, and part of this was the discovery of the carbon allotropes with great significance for a new era revolutionized by novel materials. Besides Fullerenes, in 1991, Sumio Iijima reported experimentally the observation of elongated coaxial structures, namely carbon nanotubes (CNTs). The discovery of carbon nanotubes has been under constant debate inside the carbon community. Nevertheless, the report in 1991 by Sumio Iijima brought for the first time tremendous attention to this quasi-1 dimensional material with over 50000 citations [3]. They can exist in two forms according to their number of concentric walls: as single-walled nanotubes (SWCNTs) or in concentric arrangement of tubes with random crystal orientation, namely multi-walled carbon nanotubes (MWCNTs). The possibility to have a variety of structures made exclusively from carbon atoms is actually given by the unique electronic structure of this element. Carbon is an atom

that appears in several types of structures and molecules. A lot of them are organic compounds and hydrocarbons.

1.1 Atomic structure of the carbon atom

Describing them all is out of the scope of this work. However, it will be worthwhile to know the properties of nanostructures made out of carbon to understand the driving force to perform the experimental work here reported. Carbon is an atom with a peculiar electronic configuration. It has 6 electrons, two of which are in the core level $1s^2$. The 4 remaining valance electrons are responsible for the atomic interaction with neighboring atoms. Due to the core screening, the valence electronic orbitals can hybridize in a versatile manner, making different combinations of hybrid orbitals as seen in Figure 1.1.

The crystalline structure of diamond is made of C atoms covalently bonded from

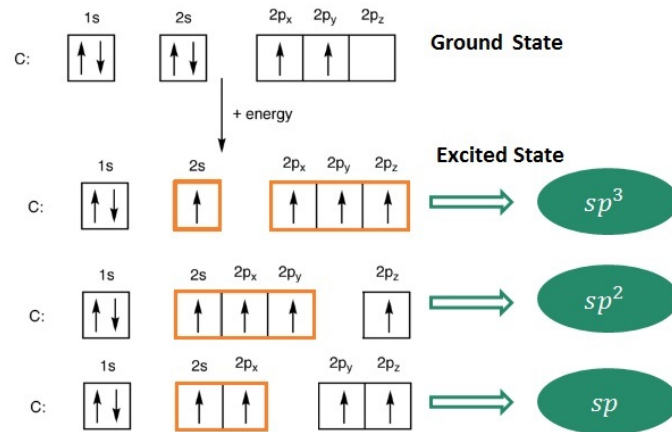


Figure 1.1: Hybridization of Carbon (adapted from © 2020, BYJU'S).

electrons purely in sp^3 orbitals. On the other hand, fullerenes, graphene and carbon nanotubes are all sp^2 -type of allotropes. All these materials have been extensively studied over the past decades from nanotechnology point of view. However, recently the true one dimensional carbon allotrope, namely carbyne, was materialized. This a structure rich in sp^1 -type of configuration. Last but not least, graphene, a one-layered two-dimensional sheet made exclusively of sp^2 hybridized carbon was achieved from the experimental point of view through the micromechanical cleavage (often called the Scotch tape method). This brought the second nobel prize to the carbon nanoscience field, awarded to Andre Geim and Konstantin Novoselov in 2010 [4]. This provides us an idea of how active the research field is and how important the related materials

are. The next sections are focused on the structural properties and the derived physical properties of the nanostructured carbon materials.

1.2 Carbon allotropes: structure

As mentioned above, the availability of different hybridization types of the electronic orbitals in the carbon atom, a range of structures can be formed. In this section, we will focus on a very brief overview of the allotropes that are of particular interest in nanotechnology research. Furthermore, we will pay special attention to carbon nanotubes and, implicitly graphene, as parent material given the relationship of their physical properties. Additionally, an insight to carbyne through the description of linear carbon chains will be provided.

1.2.1 Fullerenes

The fullerenes are clusters of C atoms. Their structure can be described from a geometrical point of view like a Soccer ball, a truncated icosahedron formed by 12 pentagonal faces, and 20 hexagonal faces [5], as shown in Figure 1.2. This kind of three-

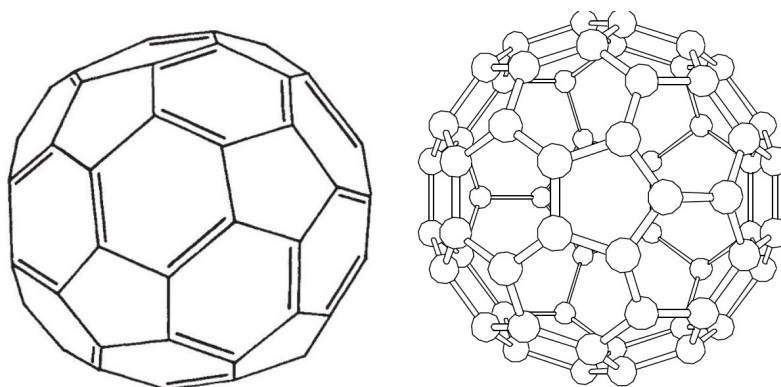


Figure 1.2: C_{60} fullerene. The left side represents a bar molecular model showing the double bonds present only in the hexagons [6]. The right side is a ball-stick model to better visualize the structure (from [1]).

dimensional figure called a closed polyhedron fulfills the Euler rule $\chi = V + E - F = 2$, where V , E , and F are the number of vertices, edges and faces respectively. In 1987 Kroto proposed that the most stable fullerenes are those in which no two pentagons share an edge, which means that each pentagon is surrounded by hexagons. This isolated-pentagon rule minimizes the steric strain that results from the misalignment of the p-orbitals on the fullerene surface [6, 7, 8]. The most common of fullerenes are

C_{60} and C_{70} . However, it has been seen experimentally that Fullerenes from C_{40} to up C_{400} can exist. Specifically, molecules with the composition C_{20+2m} can be stable hollow nets composed of 12 pentagons and m hexagons [9, 10]. Fullerenes with more than 70 C atoms are called higher fullerenes [11]. The most effective technique to separate fullerenes is high-performance liquid chromatography (HPLC), where a pressurized mixture of fullerenes and solvents passes through a column filled with a solid adsorbent material. The change in the velocity of the flow for the different components produces the separation of the components as they flow out of the column [12].

1.2.2 Graphene and Graphite

Graphene is a single layer of C atoms with sp^2 hybridization, each C atom has 3 covalent bonds in-plane and one electron in a π orbital. Its structure reminds of a honeycomb [13]. In the real space, the rhombic unit cell contains two atoms A y B separated by a distance $a_{C-C} = 1.42$. Their carbon atoms are located at the vertices of the hexagons, as is shown in Figure 1.3a, where $\vec{a}_1$ and $\vec{a}_2$ are the unit vectors in the real space, and defined by

$$\begin{aligned}\vec{a}_1 &= \left(\frac{\sqrt{3}}{2}a, \frac{a}{2}\right) \\ \vec{a}_2 &= \left(\frac{\sqrt{3}}{2}a, -\frac{a}{2}\right)\end{aligned}\tag{1.1}$$

Here a is the lattice constant of monolayer graphene which is defined by $a = |a_1| = |a_2| = a_{C-C}\sqrt{3} = 1.42\sqrt{3} = 2.46$, that is also the module of the unit vectors $\vec{a}_1$ and $\vec{a}_2$. The reciprocal space as shown in Figure 1.3b, is also a honeycomb, where $\vec{b}_1$ and $\vec{b}_2$ are the unit vectors in the reciprocal space and they are 30° rotated from the $\vec{a}_1$ and $\vec{a}_2$ real unit vectors. The reciprocal unit vectors are given by

$$\begin{aligned}\vec{b}_1 &= \left(\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{2a}\right) \\ \vec{b}_2 &= \left(\frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{2a}\right)\end{aligned}\tag{1.2}$$

1.2.3 Carbon nanotubes

Carbon nanotubes are cylindrical molecules that consist of rolled-up sheets of single-layer carbon atoms (graphene). They can be single-walled with a diameter between 1 to 2 nm or multi-walled, consisting of several concentrically arranged nanotubes, with

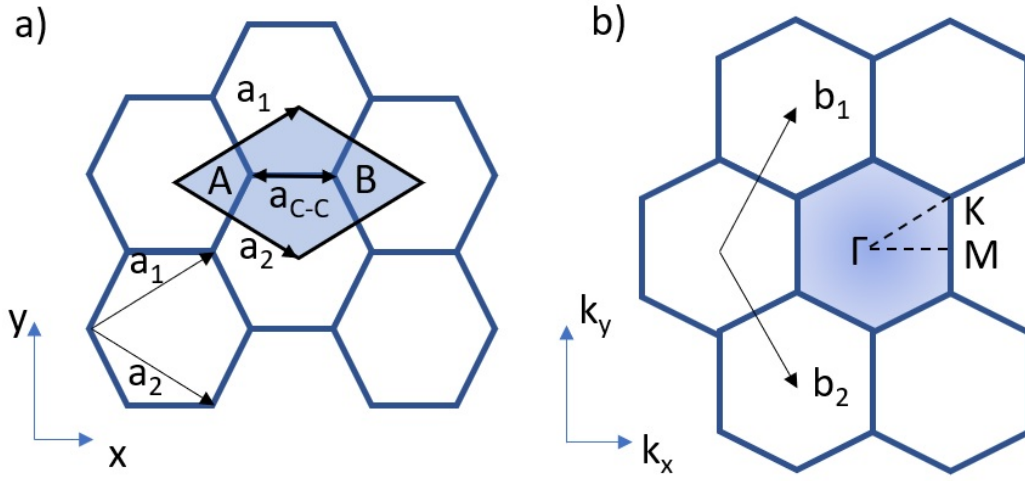


Figure 1.3: a) Representation of the lattice vectors in the honeycomb-like lattice of graphene. b) The reciprocal space is pictured with the unit vectors and the high symmetry points.

diameters usually up to more than 100 nm. Their length can reach several micrometers or even millimeters. Since their discovery in 1991, CNTs have been the subject of intensive research and attracted great attention for fundamental research and industrial applications. CNTs are composed of sp^2 -bonded C atoms assembled. This unique molecular structure gives stability, as well as, excellent qualities in mechanical strength, electrical and thermal conductivity. CNTs can be classified into single-walled CNTs (SWCNTs), double-walled CNTs (DWCNTs), and multiwalled CNTs (MWCNTs) based on the number of graphitic layers. Classified by their electronic properties, SWCNTs can be either semiconducting or metallic depending on their chirality and diameter. This structure dependence on electronics, as well as, optic properties brings them great potential in applications for electronics and optoelectronics [14].

Single wall carbon nanotubes have properties that MWCNTs do not have, as they are at least masked by multiple tube interactions. In 1993, two different groups successfully worked on synthesized of SWCNTs: one Bethune and coworkers and on the other S. Iijima and T. Ichihashi [15, 16, 17]. SWCNTs do not naturally exist as individual tubes; van der Waals forces between the molecules cause them to aggregate into microscopic bundles or ropes, which in turn agglomerate loosely into small clumps [18]. SWCNTs possess remarkable properties such as an excellent mechanical performance due to their Young's modulus in the range of $0.3 - 1 TPa$ [19], high conductivity up to $4 \times 10^5 S/cm$ [14], excellent current-carrying capacity exceeding $10^9 A/cm^2$ [20], excellent charge-carrier

mobility $> 10^5 \text{ cm}^2/\text{Vs}$ at 50K [21] and excellent thermal conductivity $\sim 3500 \text{ W/mK}$ at room temperature [22].

As mentioned, an SWCNT is a nanosize tube formed by bonded carbon atoms arranged in a hexagonal pattern, which can be pictured like a roll-up graphene sheet, as shown in Figure 1.4. The unit vectors in real space for graphene were briefly mentioned in the previous section. Based on then, other vectors and quantities can be defined. For instance, the SWCNT is characterized by the chiral vector ($\vec{C}_h$) which is the vector that extends around the circumference of the cylinder that is formed by rolling the graphene sheet, that means that $|\vec{C}_h| = \pi d_t$, where d_t is the diameter of the SWCNT. where the circumference of the cylinder turns into the chiral vector $\vec{C}_h$. The translation vector $\vec{T}$ is aligned along the cylinder axis, $\vec{R}$ is the symmetry vector and θ is the chiral angle. The chiral vector can be expressed as $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$, where (n, m) are integer and

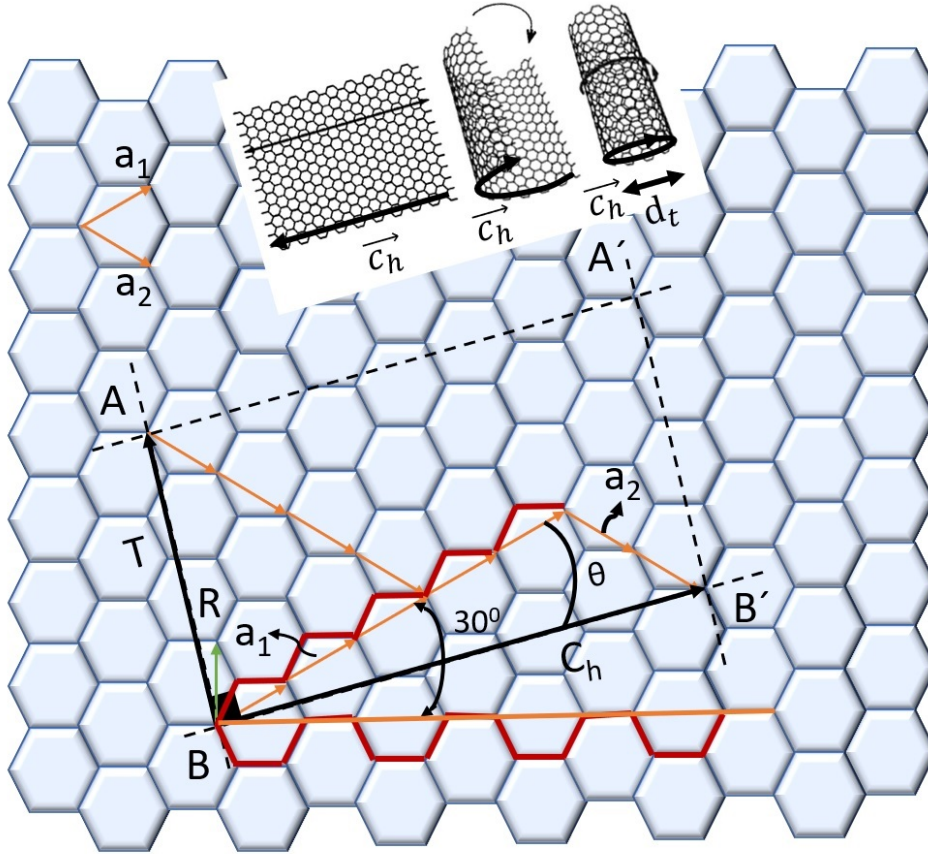


Figure 1.4: The unrolled nanotube projected on honeycomb lattice of the graphene layer, where the circumference of the cylinder turns into the chiral vector $\vec{C}_h$, the translation vector $\vec{T}$ is aligned along the cylinder axis, $\vec{R}$ is the symmetry vector and θ is the chiral angle (adapted from [23]).

$(\vec{a}_1, \vec{a}_2)$ are the lattice unit vectors. The chiral angle is measured in reference to zig-zag

direction (see Figure 1.4). From θ , it is possible to classify the nanotubes according to their morphology as follows:

$\theta = 0^\circ$ zig-zag nanotube

$\theta = 30^\circ$ armchair nanotube

$0^\circ < \theta < 30^\circ$ chiral nanotube

These can be observed in the Figure 1.5. Furthermore, the d_t and θ are obtained as

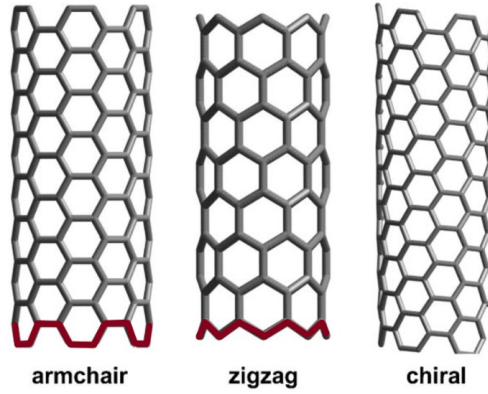


Figure 1.5: Classification of carbon nanotubes by their morphology according to the enrollment direction of the graphene parent sheet: armchair, zigzag and chiral (adapted from [24]).

function of (n, m) respectively as follows,

$$\begin{aligned} d_t &= a \frac{\sqrt{n^2 + mn + m^2}}{\pi} \\ \theta &= \arctan \frac{\sqrt{3}m}{m + 2n} \end{aligned} \quad (1.3)$$

The unit cell of a SWCNT is the rectangle formed by $\vec{C}_h$ and the translational vector ($\vec{T}$). The $\vec{T}$ vector is perpendicular to the $\vec{C}_h$ vector and goes from the point of origin to the first similar point in the network. The $\vec{T}$ is defined by $\vec{T} = t_1 \vec{a}_1 + t_2 \vec{a}_2 = (t_1, t_2)$ where

$$\begin{aligned} t_1 &= \frac{n + 2m}{d_r} \\ t_2 &= \frac{2n + m}{d_r} \\ d_r &= \gcd(2n + m, 2m + n) \end{aligned} \quad (1.4)$$

gcd : the greatest common divisor

1 Introduction

The number of hexagons (N) in the unit cell of a SWCNT can be obtained by dividing the area of the rectangle $|\vec{C}_h \times \vec{T}| = \sqrt{3}a^2(n^2 + nm + m^2/dr)$ by the area of the unit cell of the graphene $|\vec{a}_1 \times \vec{a}_2| = \sqrt{3}a^2/2$, then

$$N = 2(n^2 + nm + m^2/dr). \quad (1.5)$$

The vector in the reciprocal space of SWCNT related with the circumferential direction vector $\vec{C}_h$ is $\vec{K}_1$, and the vector in the reciprocal space of SWCNT related with the axis direction vector $\vec{T}$ of the tube is $\vec{K}_2$, so $\vec{K}_1$ and $\vec{K}_2$ vectors are perpendicular. Since an SWCNT is a cylinder, it can be seen as a 2π periodic infinite graphene sheet in circumferential direction, that makes the $\vec{K}_1$ is discrete and $\vec{K}_2$ is continue in axial direction. With these conditions $\vec{C}_h \cdot \vec{K}_1 = 2\pi$, $\vec{C}_h \cdot \vec{K}_2 = 0$, $\vec{T} \cdot \vec{K}_1 = 0$, $\vec{T} \cdot \vec{K}_2 = 2\pi$. The vectors $\vec{K}_1$ and $\vec{K}_2$ are given by the following equations:

$$\begin{aligned} \vec{K}_1 &= \frac{1}{N}(-t_2\vec{b}_1 + t_1\vec{b}_2) \\ \vec{K}_2 &= \frac{1}{N}(m\vec{b}_1 - n\vec{b}_2) \end{aligned} \quad (1.6)$$

To better visualize this, Figure 1.6 shows the graphene reciprocal space where the reciprocal lattice unit vectors $\vec{K}_1$ and $\vec{K}_2$ of a nanotube are represented. The example here corresponds to a nanotube with the (4, 2) chirality. Using $(\vec{K}_1, \vec{K}_2)$, the cutting lines for the nanotubes are constructed. These cutting lines are defined as zone-folded one-dimensional (1D) Brillouin zone (BZ) line segments, expressed in relation to their two-dimensional (2D) BZ counterparts. The cutting lines serve to correlate the physical properties of the CNTs with the corresponding properties of graphene by a zone folding scheme. To construct the cutting lines, it is necessary to consider that the vectors $(\vec{K}_1, \vec{K}_2)$ are orthogonal and $\vec{K}_2$ is directed along the nanotube axis. Then, the cutting lines are aligned along the tube axis given by the wave vector $\vec{K}_2$, and the separation between two adjacent cutting lines is given by the wave vector $\vec{K}_1$ [25].

From equations 1.6, $N\vec{K}_1 = -t_1\vec{b}_1 + t_2\vec{b}_2$ corresponds to a translational reciprocal lattice vector of graphene. Two wave vectors which differ by $N\vec{K}_1$ are equivalent [26]. The N wave vectors $\mu\vec{K}_1$ form the N quantized states in the direction $\vec{K}_1$ of the unrolled reciprocal space of the nanotube, where μ is an integer number varying from $(1 - N/2)$ to $N/2$, and N is always even. Each of these N quantized states gives rise to a line segment of length $|\vec{K}_2|$ along the direction $\vec{K}_2$ in the unrolled reciprocal space of the nanotube. For the (4, 2) nanotube shown in Figure 1.6, μ varies from $(1 - N/2 = -13)$ to $N/2 = 14$ (because $N = 28$). Here the middle cutting line $\mu = 0$ passes the Γ point,

the center of the first Brillouin zone of the graphene [27].

Double wall carbon nanotubes are a very interesting case of analysis. Many poten-

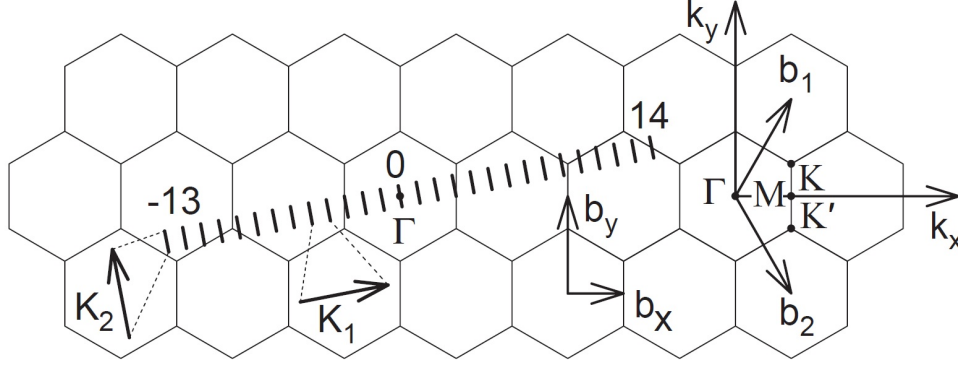


Figure 1.6: Reciprocal space of the graphene layer and the cutting lines for the (4, 2) nanotube, where $(\vec{b}_1, \vec{b}_2)$ are graphene reciprocal lattice unit vectors and $(\vec{K}_1, \vec{K}_2)$ are the reciprocal lattice unit vectors of the tube (from [27]).

tial applications in nanomechanics, energy production, optoelectronics, and lithography make DWCNTs an interesting material for researchers [28, 29, 30, 31, 32, 33, 34]. They are the most simple of multiwall carbon nanotubes. They are two concentric SWCNTs separated by a inter wall distance $d_{g-g} = 0.34nm$ that is the distance between graphene layers in graphite. The inner and the outer tube interact with each other through interlayer interactions, which are mediated by weak van der Waals forces [35]. DWCNTs can appear in four different flavors as (inner tube@outer tube), as shown in Figure 1.7.

In the development of this thesis two advantages of DWCNTs, compared to SWCNTs,

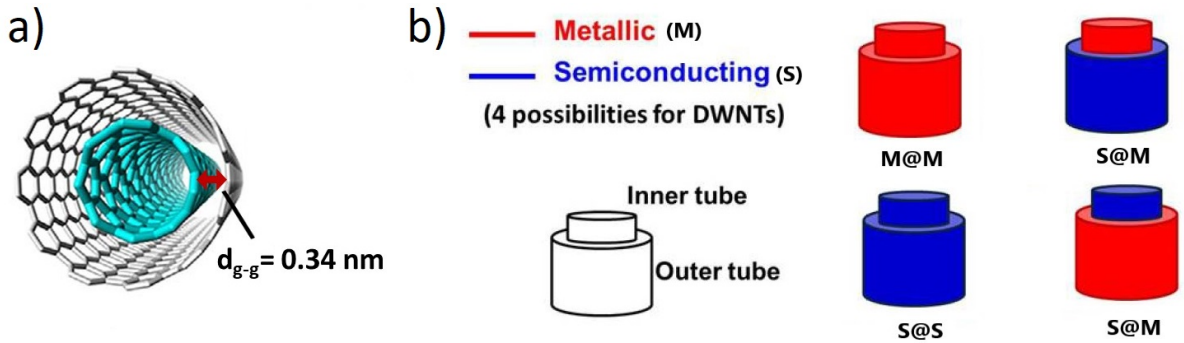


Figure 1.7: a) Double wall carbon nanotubes, where $d_{g-g} = 0.34nm$ is the distance between walls of inner and outer tube (from [36]). b) Different possibilities of DWCNTs according to which the tubes that form they are metallic or semiconductors (from [35]).

were especially used, the first was that the inner tube is well protected by the outer wall,

hence even with high functionalization, the optical and electronic properties of inner tubes are still preserved [37, 38, 39, 40]. Second, the small diameter of the inner tube could be used like nanoreactor to synthesize linear carbon chains, which are in the scope of the experiments performed in this thesis.

Different methods have been developed to synthesize DWCNTs [41]. All of them exhibit advantages and disadvantages. The arc discharge method normally produces a high quality DWCNTs [42]. However, a lot of carbon impurities like graphitic onions are formed at the same time, which are usually very difficult to remove [43]. Chemical vapor deposition (CVD), as an alternative, is the most frequently used method [44]. It can produce a high yield of DWCNTs by controlling the precursors, catalysts, and synthesis temperature [28]. However, the diameter distribution of the tubes synthesized by CVD is usually very broad, and the quality of the DWCNTs is lower than the arc-discharge ones [35]. In addition, DWCNTs can be obtained by the annealing of SWCNTs encapsulated with nano compounds, e.g. C_{60} , ferrocene, nanoribbons, or some organic solvents [45, 46, 47, 48, 49]. Kramberger and co-workers proposed an *in-situ* laser annealing experiment to transform C_{60} peapods into DWCNTs [50, 51]. The method was very effective but very high laser power was used, which is not necessarily optimal. Although, all these methods have proposed creative and effective solutions to produce DWCNTs, such as the latest work employing twisted graphene nanoribbons [36], having a method where the chirality of the inner tubes can be controlled is still challenging and elusive. This will be discussed in further detail in the next chapters.

Finally, **multi wall carbon nanotubes** are also worth describing although they are not in the scope of this thesis. The first carbon nanotubes observed were MCWNTs (Iijima 1991 [3]). MWCNTs are carbon nanotubes formed of concentrically nested multiple graphene sheets with interlayer distance of 0.34 nm [17]. Examples are shown in Figure 1.8. This kind of carbon nanotube can occur as a byproduct of natural and industrial processes. They have ever been found from forest fires and household cooking with propane and natural gas stoves [52, 53]. At the end of the first decade of the 21st century, the bulk volumes of manufactured MWCNTs reach a few hundred tons, unlike SWCNTs that were produced much less [54, 52]. However, the difficulty of obtaining reproducible and statistically valid samples in the most favorable laboratory conditions, made the SWCNTs be the most studied instead [52, 55]. The advantages that MWCNTs show due to the Russian-doll structure are better mechanical stability and higher rigidity, properties that are for instance needed for scanning probe tip applications. In the

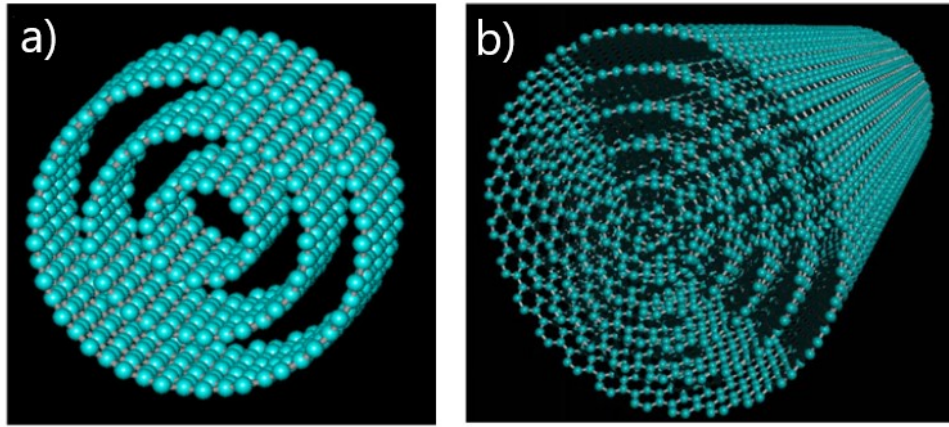


Figure 1.8: a) Triple wall carbon nanotube, multi wall carbon nanotube formed by three concentric single wall carbon nanotubes. b) Multi wall carbon nanotube formed by more than three concentric single wall carbon nanotubes (from [52]).

fabrication of nanotube composites, the MWCNTs configuration is more advantageous. Since the first step is the chemical functionalization of the tube walls, the load transfer can be achieved without damaging the stiffness of the internal tubes. It is important to mention too that MWCNTs can be grown without magnetic catalytic particles [55], which is interesting for some applications.

1.2.4 Long linear carbon chains and carbyne

A Linear carbon chain (LCC) is a one-dimensional monoatomic chain consisting of sp -hybridized carbon atoms. Theoretical studies on LCC have proposed stronger mechanical strength than diamond and higher electron mobility than graphene and carbon nanotubes. LCC are expected to have two different configurations of carbon atoms: one is an alternating triple and single bonds called polyyne and the other is sequential double bonds called cumulene (this is shown in Figure 1.9 a, b respectively). Classifying LCC by their length, when it is formed from 10 to hundred atoms it is simply called LCC, but when it is formed by thousands of atoms it is usually named long LCC (LLCC). Finally, carbyne is formed by an infinite number of C atoms.

The promise of this allotrope is to allow control of the bandgap (which can also show superconductive behavior), as well as the control of the electronic and optical properties. They can be modified by altering the number of carbon atoms and the terminal groups. This will allow in the future to use of LCC in the next generation electronic devices, such as molecular wires, and optical an energy storage devices [57]. On the other hand, its

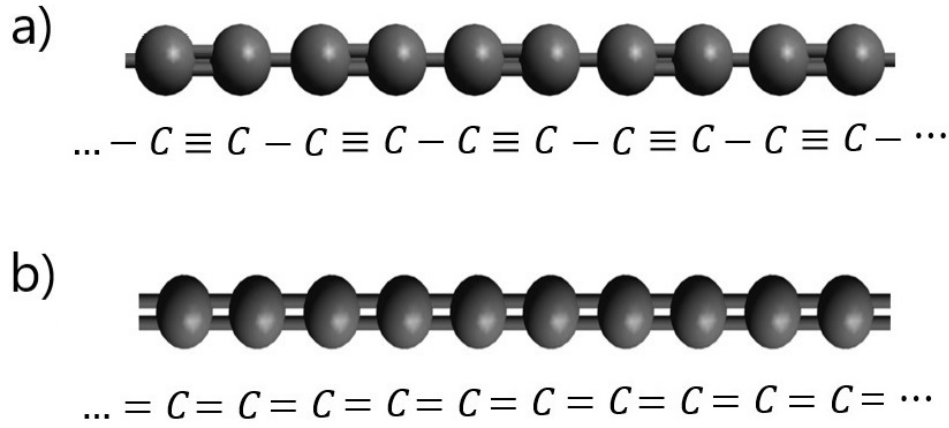


Figure 1.9: Linear carbon chain: a) α - *carbyne* or polyynes; b) β - *carbyne* or cumulene (adapted from [56]).

high thermal conductivities on the order of 6000 W/wK are useful for heat dissipation in nanodevices [58].

The Synthesis of pure carbyne crystal or long isolated carbon chains represents a big technologic challenge, due to the extreme instability and chemical reactivity of sp^1 carbon [59]. At the moment, there are two efficient methods to synthesize chain. The first requires stabilization attained either by attaching bulky groups on the edges, in which the longest synthesized chain so far is formed by around 50 atoms [60], and the second is by encapsulation into nanotubes in which is possible to obtain sequence of more than 6000 atoms [61]. The later method has been used in this thesis assisted by the stability and protection that grant to LCC the nanotubes.

2 Electronic and Optical Properties of the materials

The physical properties of SWCNTs and DWCNTs are based on those of the parent material graphene, which can be pictured as a flat structure that is rolled into a tubular one. This is why CNTs offer a range of interesting properties which are strongly related with the description of graphene. Great part of this thesis encompasses the analysis of the Raman spectra measured during the growth of SWCNTs and LLCs inside the hollow core of a nanotube. To understand this optical response we need to understand in detail their electronic and optical properties. This chapter focuses on these aspects.

2.1 Electronic and Optical properties of graphene

2.1.1 Electronic band structure of graphene

The carbons atoms in graphene mix their sp^2 orbitals in the $xy - plane$ with three neighbors to form $\sigma - bonds$, and the remaining electron in $z - direction$ forms the $\pi - bond$. These delocalized $\pi - electrons$ give origin to the electronic bands of graphene and determine its electronic properties. When the carbon atoms are in the hexagonal lattice, the electronic wavefunctions overlap, however, by symmetry the overlap between $\pi - orbitals$ and the orbitals in the $xy - plane$ are zero. In this way, the $\pi - electrons$ can be treated independently from the other valence electrons [54]. From the tight-binding model, the eigenvalues of the energy dispersion in function of the set of available electronic momenta, that are the vectors of the first hexagonal Brillouin zone (BZ) $E(k_x, k_y)$ [54], is given by

$$E(k_x, k_y) = \frac{\varepsilon_p \pm tw(k_x, k_y)}{1 \pm sw(k_x, k_y)} \quad (2.1)$$

where ε_p is the atomic level energy of an isolated carbon atom, s the graphene overlap integral, while $w(k_x, k_y)$ is

$$w(k_x, k_y) = \sqrt{1 + 4 \cos \frac{\sqrt{3}k_x}{2} \cos \frac{k_y}{2} + 4 \cos^2 \frac{k_y}{2}} \quad (2.2)$$

The + signs gives the bonding π energy band and $-$ the antibonding π energy band. Since there are two π electrons per unit cell, these two π electrons fully occupy the lower π -band. Then, the π -band is filled by spin up and spin down electrons, while the π^* -band is empty. When the graphene overlap integral s becomes zero, the π and π^* band become symmetrical around $E = \varepsilon_p$ and this is defined by the equation

$$E(k_x, k_y) = \pm\gamma_0 \left\{ 1 + 4 \cos\left(\frac{\sqrt{3}k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right) \right\} \quad (2.3)$$

where γ_0 is the transfer integral between first-neighboring π – *orbitals* that give a direct measure of the width in energy of a band. The typical values are 2.9 – 3.1 eV (hopping energy), with one π – *atom* per atom. The positive branch (conductive band) is empty while the negative band (valance band) is fully occupied. It can be seen in Figure 2.1 that the valence and conduction bands touch at the Fermi level in only four K – *points*, called also Dirac points.

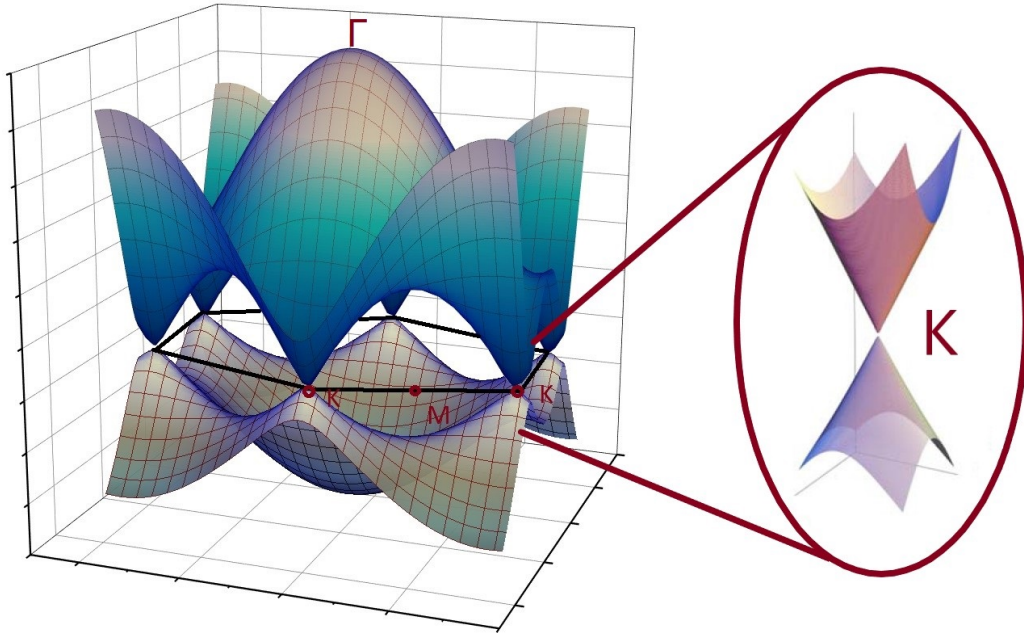


Figure 2.1: The energy dispersion ratios for graphene shown in the Brillouin zone region. The valence and conduction bands of graphene touch at the points K and K' (from [62]).

2.1.2 Density of states

From the tight-binding Hamiltonian for electrons in graphene it is possible obtain the density of states per unit cell (DOS) [63]. The DOS shows Van Hove singularities as

shown in Figure 2.2 [64, 65, 66]. The band structure of massless Dirac fermions has a unique character, since they have linear energy dispersion in the vicinity of the two nonequivalent symmetric points, K and K' points, in the Brillouin zone, where the conduction and valence bands conically touch. As mentioned above, this structure is called Dirac cone and the K points Dirac points. The DOS is 0 at the K points, and the dispersion is linear close to them. Therefore, close to K points, the electrons in graphene have similar behavior to massless Dirac electrons, that means that energy electrons fulfill

$$E_{\pm}(k) = \pm \hbar v_F |k|$$

$$v_F = \frac{\sqrt{3}\gamma_0 a}{2\hbar} \quad (2.4)$$

where v_F is the Fermi velocity of π electrons ($\sim 10^6$ Km/h), γ_0 is the transfer integral between first nearest neighbor orbitals (hopping energy), $a = \sqrt{3}a_{C-C}$ and $a_{C-C} = 1.42$ with this, it is possible observe intriguing physical properties such as barrierless tunnelling, as discovered by Oskar Klein in 1928, which is scaled Klein paradox [67] or half-integer quantum Hall effect [68]. However, graphene has one very severe limitation from the point of view of electronic applications: it has no bandgap and a vanishingly small density of states at the Fermi level, making it a zero band gap semiconductor [69].

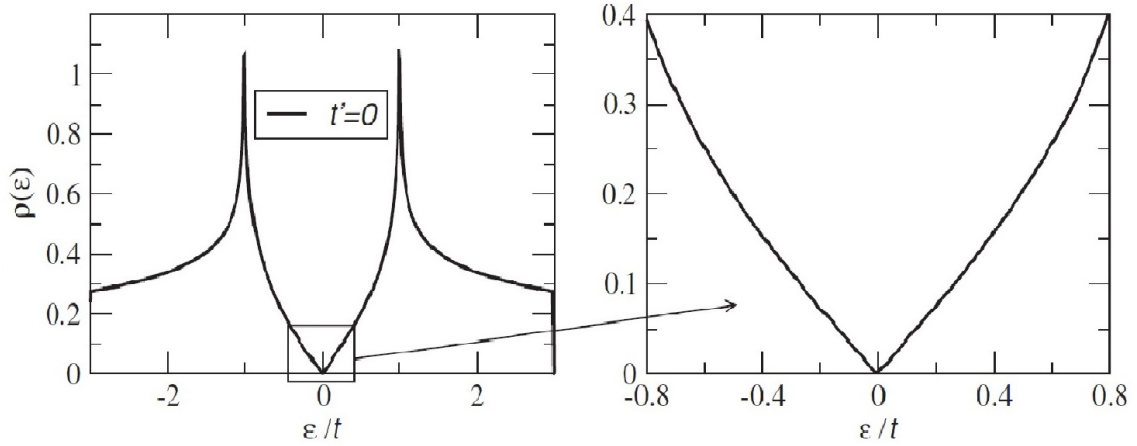


Figure 2.2: DOS of Graphene: a) Density of states per unit cell as a function of energy, in units of t , computed from the energy dispersion $t' = 0$, where t is the nearest-neighbor hopping energy (hopping between different sublattices) and t' is the next nearest-neighbor (hopping in the same sublattice) (from [63]).

2.1.3 Zone folding

When we move from bulk material to low-dimension material, electronic states are limited in the nanoscale direction due to quantum effects. The components of the wave vector in the nanoscale directions can only take discrete values to maintain an integral number of wave function nodes, that is, these components of the wave vector are quantized. The number of quantized states equals the number of unit cells of the main bulk material in the nanoscale directions of the low-dimensional structure [70]. The Brillouin zones have an important property due to the reciprocal lattice is periodic. This is that for any point outside the first Brillouin zone exists a unique reciprocal lattice vector that will translate that point back inside the first zone. So, each point is unique, and each zone contains every single physically distinguishable point. These made that all zones have the same area or volume. So, in a superlattice, that consists of lattice constants a and b and has a period $a + b$. The first Brillouin zone edge is given by $2\pi/(a + b)$, indicating that a larger unit cell results in a smaller Brillouin zone. In other words, Brillouin zones of bulk materials $2\pi/a$ and $2\pi/b$, are folded into a smaller zone with $2\pi/(a + b)$ in the superlattice. Therefore, many mini bands are formed in a superlattice. This typical feature for superlattice and is called zone folding effect [71]. For instance, if we intercalate the graphite layer (graphene) with other layers to form a periodic structure, new planes of energy discontinuity in momentum space appear parallel to k_z axis. If the structure in the intercalate layer is proportional to that of the graphite layer, these new planes of energy discontinuity cut the initial graphite Brillouin zone into smaller but equal parts. That can be seen in Figure 2.3 for graphite-alkali metal. The outer hexagon represents the Brillouin zone for the graphite layer while the inner hexagon represents the Brillouin zone for the intercalate layer [72]. The method is also used to construct 1D electronic energy sub bands by cutting 2D electron scatter ratios when the 1D nanotube is wound from 2D graphene sheets, it is known as the zone folding scheme and will be discussed in more detail for SWCNTs.

2.1.4 Optical properties

The optical properties of graphene depend of the linear band structure, zero band-gap and strong interaction of Dirac electrons with the electromagnetic radiation. The energy dispersion near the Dirac point is linear, such that the electrons and holes in the background of a honeycomb lattice mimic relativistic particles that are described by

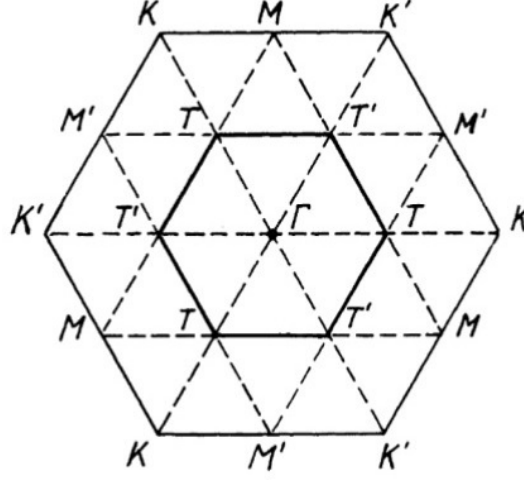


Figure 2.3: Brillouin zone for graphite layer (outer hexagon) and the projection of Brillouin zone for graphite-alkali metal (C_8) on the plane perpendicular to the k_z axis (from [72]).

the Dirac relativistic equation. For pristine graphene at zero temperature, the optical conductivity in the linear dispersion regime of graphene is found to be independent of the frequency. The corresponding optical conductance of graphene is determined solely by fundamental constants and assumes the value of

$$\sigma(\omega) = \frac{\pi e^2}{2h} \quad (2.5)$$

where ω is the frequency e is electron charge and h is Planck's constant, so the optical absorbance is

$$A(\omega) = \frac{4\pi}{c} \sigma(\omega) = \pi\alpha \approx 2.29\% \quad (2.6)$$

Thus, the absorption of graphene from visible to near infrared region is modeled by interband transitions and it is frequency independent, described by the fine structure constant α [73, 74]. In this way, its absorbance is not only independent of the frequency of the electromagnetic radiation, but it is also independent of any material properties of the absorber.

2.2 Electronic and optical properties of carbon nanotubes

2.2.1 Electronic band structure

The electronic structure of SWCNT can be obtained from the electronic structure of graphene, using the concept of cutting lines, that was defined in the subsection 1.2.3 of the chapter 1. For these purposes is necessary to take into account the quantum 1D confinement of electronic states. That means, to take into account the periodic boundary conditions in the circumferential direction of $\vec{C}_h$ and the continuous periodicity of $\vec{T}$. With these considerations, the reciprocal lattice vectors $\vec{K}_1$ and $\vec{K}_2$ are related with the circumferential direction and the nanotube axis respectively. The first Brillouin zone of nanotube is given by a line of length $|\vec{K}_2|$, which is a line because nanotube is a 1D object. However, the first Brillouin zone of nanotube can be expanded into the 2D reciprocal space of graphene in the form of the cutting lines, in the same form as the 1D nanotube can be un rolled and placed on a 2D graphene layer, this procedure is known as zone-unfolding and is opposite to the zone folding scheme [25].

The area of the bordering rectangle formed by the set of cutting lines is formed for $N\vec{K}_1$

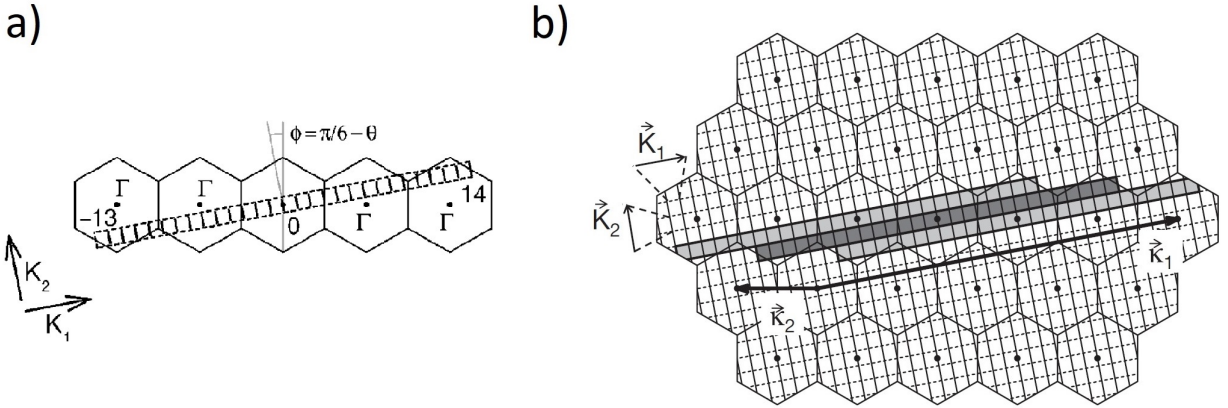


Figure 2.4: Reciprocal space of the graphene layer: a) The fully K_1 -extended representation of the cutting lines for the (4, 2) nanotube. The two arrows indicate the zoomed $\vec{K}_1$ and $\vec{K}_2$ of the nanotube [25]. b) The $\vec{K}_1$ and $\vec{K}_2$ reciprocal lattice vectors. Parallel equidistant lines represent the cutting lines for the (4, 2) nanotube (from [27]).

and $\vec{K}_2$ and has an inclination angle $\phi = \pi/6 - \theta$, where θ is the nanotube chiral angle. This area can be calculated from $N|\vec{K}_1 \times \vec{K}_2|$. Using the equations 1.6 the area of the bordering rectangle is obtained as $(t_1m - t_2n)|\vec{b}_1 \times \vec{b}_2|/N$. For the relation between t_1 , t_2 and N from equations 1.4 and 1.5, it can be found that $N = t_1m - t_2n$, then the area

of the bordering rectangle is equal to $|\vec{K}_1 \times \vec{K}_2|$. That is the area of the first Brillouin zone of graphene $8\pi^2/\sqrt{3}a^2$ [25]. In Figure 2.4 b), the first Brillouin zone of a SWCNT, is seen in dark gray and it can be compared with the first Brillouin zone of graphene.

The electronic structure of SWCNT can be obtained superimposing the 1D cutting

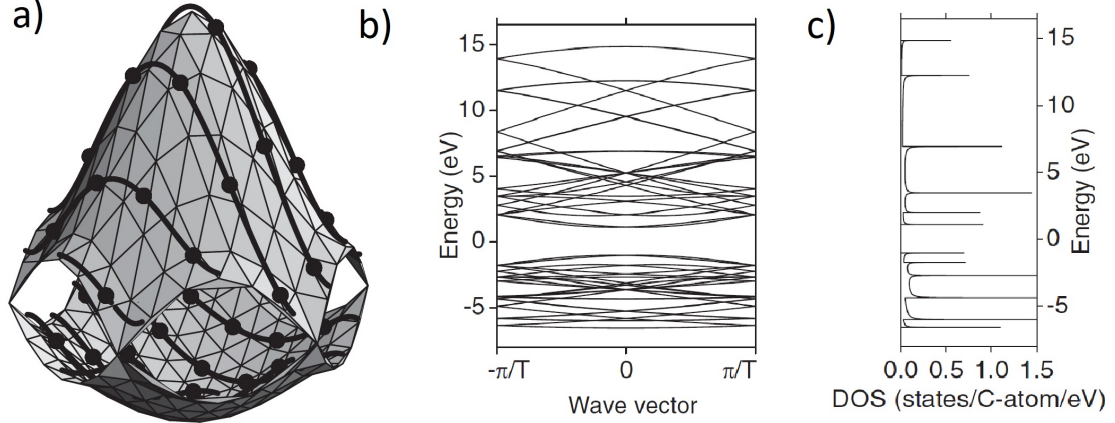


Figure 2.5: a) Reciprocal space of the graphene layer, the conduction and valance band structure of graphene superimposed the cutting line for (4,2) [75]. b) Electronic energy band diagram for the (4, 2) nanotube obtained by zone-folding [75]. c) Density of electronic states for the energy band diagram (from [75]).

lines on the conduction and valance band structure of graphene. The total number of electronic subbands is equal too the number of hexagons in the nanotube unit cell N , therefore there are $2N$ electronic energy subbands in the 1D reciprocal space of the nanotube by superposing the cutting lines in conduction and valance bands. As there are two carbon atoms A and B, per unit cell of the graphene and they have one free electron each, the total number of electronic energy subbands in the 1D reciprocal space of the nanotube is equal to the total number of atoms in the nanotube unit cell. However, the total number of distinct electronic energy subbands is less than $2N$, since most of them are doubly degenerate. That is, the $2(N/2 - 1)$ pairs of the subbands arising from the cutting lines of the indices μ and $-\mu$, where $\mu = 1, \dots, (N/2 - 1)$ belong to the E irreducible representations and are doubly degenerate, whereas the 4 subbands arising from the cutting lines of the indices $\mu = 0$ $\mu = N/2$ belong to the E irreducible representation a and are non-degenerate, so that the total number of the distinct electronic energy subbands is $(N+2)$ [25].

In Figure 2.5 a), the energy-momentum contours indicate the cutting lines for a (4, 2) nanotube, and the solid dots stand for the ends of the cutting lines in the K1-extended

representation [25]. The electronic band structure of the nanotube, shown in Figure 2.5 b) for (4, 2) nanotube, is the set of N pairs of 1D energy dispersion relations $E_\mu(k)$. The set is obtained, when the energy dispersion relations of graphene are folded. These 1D energy dispersion relations are given by

$$E_\mu(K_1, K_2) = E_{g2D} \left(k \frac{K_2}{|K_2| + \mu K_1} \right), \quad \mu = 0, \dots, N-1 \quad \text{and} \quad \frac{-\pi}{T} < k < \frac{\pi}{T} \quad (2.7)$$

which correspond to the energy dispersion relations of a SWCNT, where E_{g2D} comes from equation 2.2. The N pairs of energy dispersion curves given by equation 2.8 correspond to the cross-section of the two dimensional energy dispersion surface shown in Figure 2.5 a), where the cuts are made on the lines of $K_2/|K_2| + \mu K_1$ for a (4,2) nanotube [54]. The electronic properties of CNTs depend of their morphology because the distance of

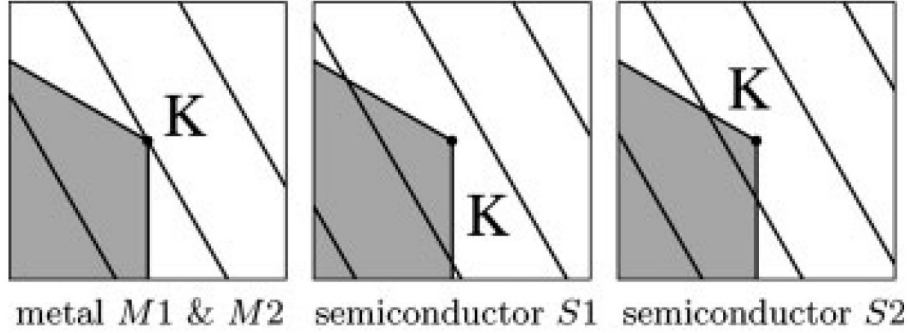


Figure 2.6: The cutting lines the cutting lines in the vicinity of the K – point, $n - m$ multiple of 3 to metallic tubes, $n - m$ different multiple of 3 to semiconducting tubes (from [27]).

cutting lines is dependent of the diameter, therefore of chirality. When the cutting line goes through the K – points in a SWCNT (n, m) the energy gap between conductive and valance band is zero, then the SWCNT is metallic. However, if the cutting line pass near of the K – point, the SWCNT has a semiconducting behavior. From there the condition $(n - m)$ or $2n + m$ multiple of 3 to metallic tubes otherwise semiconducting. This can be see in Figure 2.6. For instance, the zig-zag $(n, 0)$ are metallic when n is a multiple of 3. Furthermore, It is important to mention that the armchair (n, n) SWCNTs that is $(m = n)$ are truly metallic. However for other cases where the SWCNT satisfy the condition with $(m \neq n)$ a small energy band gap at lower temperature can appear, which means that they have a quasi-metallic behavior. This effect is due to curvature, therefore it is more evident in small diameter SWCNTs.

2.2.2 Density of the states

The concept of the DOS for a CNT is very important to understand the allowed states at specific energy levels. The DOS are strongly related to the dimensionality of the materials as shown in the Figure 2.7 a). For SWCNT, the DOS emerge of the cutting lines of the reciprocal space of the rolled up graphene sheet. In Figure 2.5 c) the corresponding DOS for the band structure of (4, 2) nanotube is shown.

In the Figure 2.7 a), we can see the relation between the SWCNT electronic bands and the DOS. Each cutting line except for the one that crosses the K – point produces a local maximum in the DOS, which is called van Hove singularity (vHs). Each vHs arises from a different cutting line, and they appear at those points where the cutting lines are tangential to the electronic equienergy contours of the graphene layer in the 2D reciprocal space. The presence of vHs in the DOS of carbon nanotubes has a great impact on their physical properties, such as transport processes, optical absorption, electron-phonon interaction [25]. For all metallic nanotubes, independent of their diameter and chirality

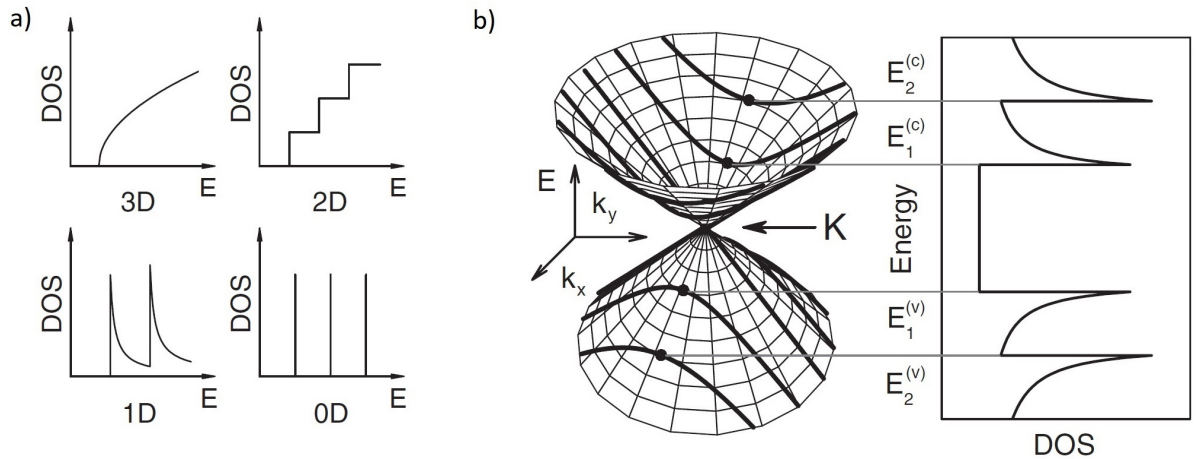


Figure 2.7: a) The electronic density of states for 1D, 2D, 3D systems [27]. b) The valence and conduction bands for graphene near of the point K where the two bands touch. The cutting lines of these contours denote the dispersion relations for the 1D system derived from the 2D system. The energy extremum E_i for each cutting line at the wave vector k_i is known as the van Hove singularity (from [27]).

a cutting line crosses the Fermi level E_F at the K point, then the density of states per unit length along the nanotube axis is a constant and it is given by

$$N(E_F) = \frac{8}{\sqrt{3}\pi a|t|} \quad (2.8)$$

where a is the lattice constant of the graphene layer and $|t|$ is the nearest neighbor $C - C$ tight-binding overlap energy usually denoted by γ_0 in the graphite literature [54]. For semiconducting nanotubes the DOS is zero up to the first van Hove singularities, and their energy gap depends upon the reciprocal nanotube diameter $1/d_t$

$$E_g = \frac{|t|a_{c-c}}{d_t} \quad (2.9)$$

Where where a_{c-c} is the nearest neighbor C–C distance on a graphene sheet. The DOS is Zero for semiconducting nanotubes and small for metallic nanotubes, which is shown in Figure 2.8 for metallic (9,0) and semiconducting (10,0) zigzag nanotubes and compared with the DOS for graphene.

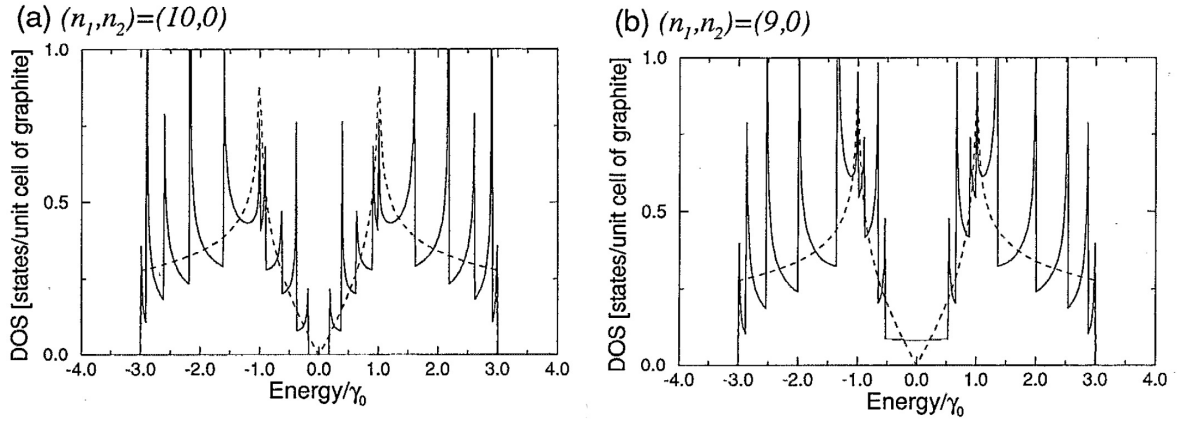


Figure 2.8: a) DOS of Semiconducting SWCNT (10,0) b) DOS of Semiconducting SWCNT (9,0). The cutting line shown the DOS for Graphene [26].

2.2.3 Optical Properties of SWCNT

In SWCNTs, the optical absorption and emission are related to its density of the states. The energy for a photon in the optical range is between 1.8 – 3.1 eV. It is necessary to take into account the energy dispersion relations for graphene. The optical process for both graphene and SWCNT will be near to the $K - point$ in Dirac cone as shown in Figure 2.9. In the case of SWCNTs the optical transition will be take account the vHss.

In Figure 2.6, the distance of $K - point$ to the cutting lines related with de diameter of de SWCNT is given by $K = 2/d$. With this we can clearly observe that the distances between the vHs is inversely proportional to the diameter $1/d$. Additionally, the direction of the cutting lines depends of the chiral angle, so the energy where the vHs occur is dependent of the chirality. In this way each (n,m) SWCNT has a different set of

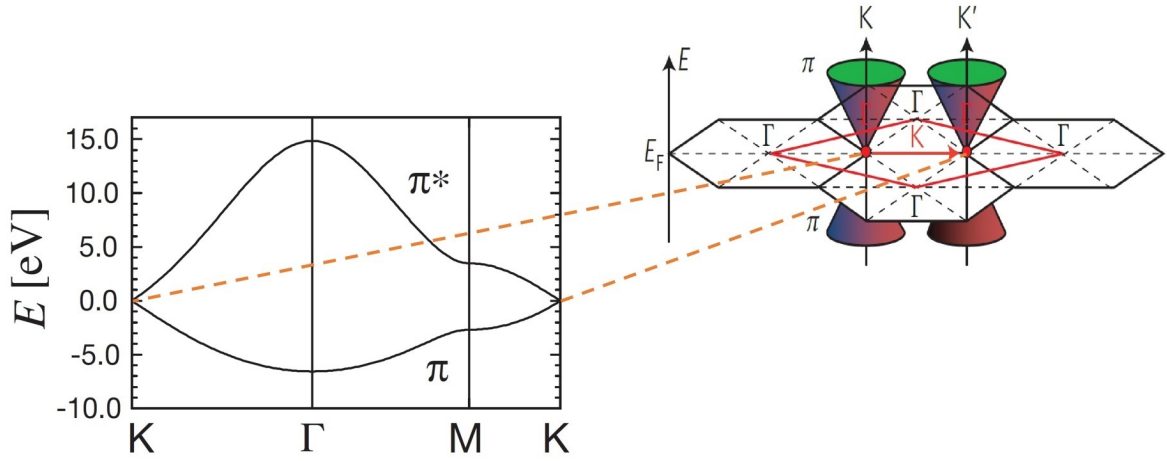


Figure 2.9: The energy dispersion $E(k)$ along the high symmetry Γ M K and related with the Dirac cone (adapted from [76, 77]).

vHs in its valance and conduction bands and therefore a different set of electronic transition energies for optical transition between its valance and conduction bands vHss. Visualizing where the optical transitions for all nanotubes are can be very useful therefore a plot of the electronic transition energies between the electronic valence and conduction bands with the same symmetry (E_{ii}) vs the diameter of the SWCNT was developed (see Figure 2.10). This is know as a Kataura Plot. Each point in the plot represents one optically allowed E_{ii} from a given (n,m) SWNT.

2.2.4 Joint density of states

For the optical process, it is necessary introduce the concept of the joint density of the states (JDOS), that is the density of electronic states that can absorb or emit photons as a function of photon energy. This is different from the DOS, which is the density of electronic states vs. the energy above and below the Fermi level. Therefore, the JDOS starts from zero energy, and exhibits vHss at energies equivalent to the energy difference between vHss in the DOS, subject to optical selection rules [75]. The electronic states that are preferably excited by a photon of determined energy are those that have transition energy between the valence and conduction bands like the energy of the photon. The electronic states that fulfill this condition are those found along the contours of energy, which form distorted circles exhibiting threefold symmetry around the K and K' points in the Brillouin zone of the graphene layer [25], as is shown in the Figure 2.11 a).

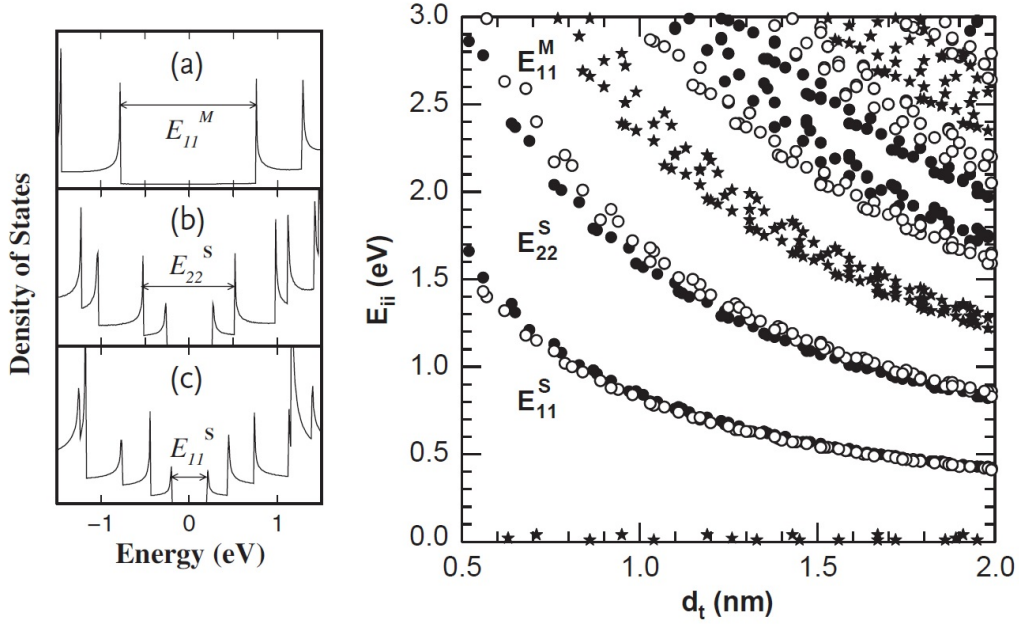


Figure 2.10: Density of electronic states for a) armchair (10, 10) SWNT, b) chiral (11, 9) SWNT, and c) a zigzag (22, 0) SWNT obtained with the tight-binding model. d) Kataura Plot, where shown the electronic transition energies E_{ii} for all the (n, m) SWNTs with diameters from 0.4 nm to 3.0 nm using a simple first-neighbor tight binding model (from [27]).

The allowed electronic states of the found at the intersections of the equienergy contour and cut lines strongly participate in optical absorption. So, the resonance case takes place when the energy of the photon coincides with the energy of transition E_{ii} between the two vHs in the valance and conduction bands (E_{vi} , E_{ci}), that means the equi-energy contour corresponding to the energy of the photon touches one of the cutting lines tangentially as shown in the Figure 2.11 b). In practice, the resonance case is rarely satisfied, since it has a preresonance condition, where the equi-energy contour is slightly shifted in either direction from the point where it would have been tangential to the cutting line at the cross point of the contour and the line. In this way, there are had two cases, when the photon energy decreases below the vHs and the photon energy increases above the vHs, as shown in Figure 2.11 c) and d) respectively. In the first case (preresonance), where there are no resonant states present, and the second case when the photon energy lies above the vHs, where there are both types of electronic wave vectors, preresonant and softresonant (bold gray and black bold respectively), as shown in the Figure 2.11 d). The photon energy increases the number of resonant states shown by the bold black lines and decreases gradually bold black lines. Figure 2.11 e) shows a

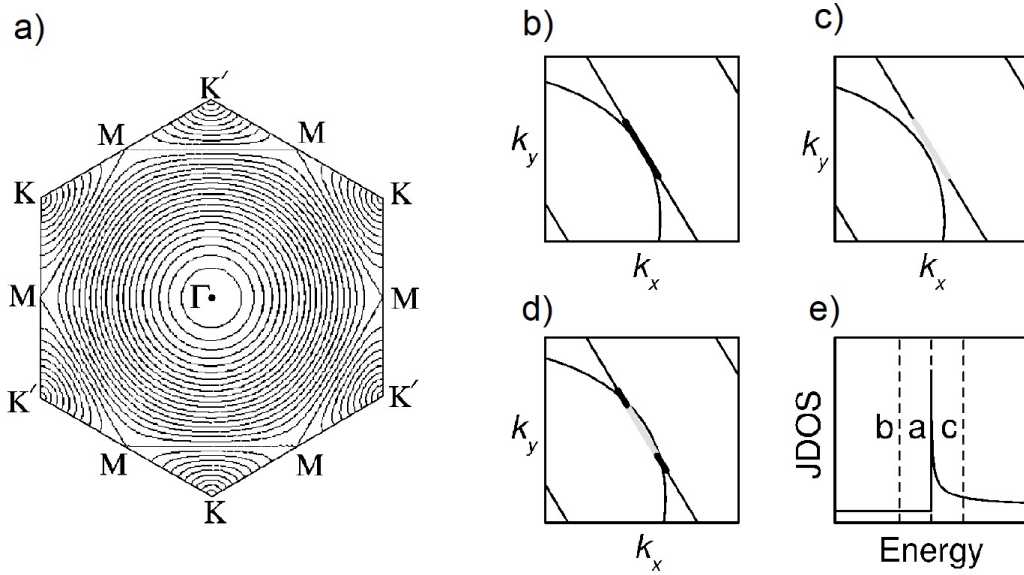


Figure 2.11: a) The contour plot of 2D energy of graphite. The equi-energy lines are circles near the K point and near the center of the hexagonal Brillouin zone, however are straight lines which connect nearest M points [76]. b) The resonance condition $E_{\text{photon}} = E_{ii}$ c) d) Kataura Plot, where shown the electronic transition energies E_{ii} for all the (n, m) SWNTs with diameters from 0.4 nm to 3.0 nm using a simple first-neighbor tight binding model (from [25]).

JDOS profile in the vicinity of the VHS generated by the cutting lines from Figure 2.11 b) to d).

2.2.5 Excitons in carbon nanotubes

The exciton is a bounded electron-hole pair. An exciton in a semiconducting material consists of a photoexcited electron and a hole bound to each other by an attractive Coulomb interaction[78]. In an optical transition in a crystal, we expect a vertical transition $k_c = k_v$, where k_c is the wave vector of the electron and k_v of the hole, as shown in Figure 2.12 a . The exciton wave vector of the center of mass is defined by $K = k_c - k_v/2$, here the hole, created by exciting an electron, has the opposite sign for its wave vector and effective mass to the electron excited. The translational motion of an exciton is represented by its energy dispersion in function of K. So, an exciton can recombine by emitting a photon when $K = 0$ and can not recombine directly to emit a photon if $K \neq 0$. This last one is a dark exciton. For $K \neq 0$ the recombination emission is possible by a phonon-assisted process involving an indirect optical transition.

Another possibility is when an electron with spin up absorbs a photon, and it is excited

to an excited state, leaving a hole at energy level at which the electron was. This hole has a wave vector of $-k$ and an effective mass of $-m^*$ and also a spin-down hole state, opposite to the electron excited, as shown in Figure 2.12 b. This kind of exciton is called spin singlet, with $S = 0$ and it does not represent an eigenstate. An eigenstate of this exciton will be the antisymmetric combination of its state. On the other hand, a triplet exciton $S = 1$ two electrons, one in the ground state and other in an excited state give a total spin of $S = 1$ as shown in Figure 2.12 c. The triplet exciton cannot recombine by emitting a photon due to Pauli's principle, so it is a dark exciton. The exciton effect is common in 3D semiconductors with a binding energy on the order of 10meV , for this reason the optical absorption is usually observed at low temperature. However, in a SWCNT the binding energy of exciton is around 1eV . Since it is two orders, the excitonic effect can be observed at room temperature.

In the electronic structure of SWCNT and graphite, there are well defined region

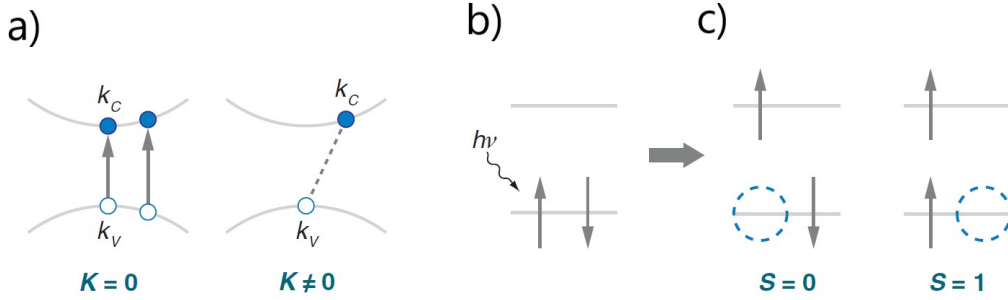


Figure 2.12: a) singlet exciton formed at $K = 0$ in a crystal, where $k_c = k_v$ and dark exciton, giving rise to a dark exciton b) Photon absorbed by an electron with spin and it gets a singlet exciton $S = 0$. If the spin of the electron is, we here define the spin of the hole left behind as. c) A triplet exciton ($S = 1$) that is a dark exciton (from [79]).

around the K – points called valleys. When, an optical transition occurs vertically in k space the hole and the electron produced can be considered a pair electron-hole. They can recombine radiatively (bright exciton). Also, it is possible that the electron is in one valley and the hole in other, in this case the radiative recombination is not possible because they do not have the same k value. This is an E-symmetry exciton: a type of dark exciton. This coexistence of different types of excitons is important to understand the optical properties of SWCNTs.

For a single SWCNT it is possible to observe resonance Raman spectra, photoluminescence or resonance Rayleigh scattering. This strong enhancement of the optical intensities can be understood from a point of view of an optical process like a connection

of the valance and conduction bands by the 1D vHss in the JDOS. On the other hand, an exciton has an energy dispersion as a function of the wave vector of the center of mass vHs in the excitonic density of states from the ground states are expected to be observed, where optical absorption becomes strong. This occurs when the wave vector of the center of mass vanishes [78]. In a thin film of SWCNTs, the exciton effect was proven experimentally by absorption spectra, in which the excitons existence was deduced from the difference between the observed absorption peaks and the energies calculated in a simple tight-binding model [80, 81]. Other evidence of the effect of excitons in optical spectra is the ratio problem of E_{22}^s/E_{22}^s that is 2 in the large-diameter limit within the tight-binding model, where E_{nn}^s denotes the excitation energy from the $n - th$ highest valence to the $n - th$ lowest conduction bands of a semiconducting SWCNTs. From extrapolation the photoluminescence (PL) mapping data, the ratio approaches 1.7, this problem was resolved considering the exciton effect [82].

The exciton evience has been demonstrated by two-photon PL. The typical absorbtion and PL spectra are observed as a one-photon process. However at high excitation power densities, two-photon absorption occurs. The selection rules for two-photon absorption differ from those of one-photon absorption; thus complementary information of excitons is obtained from the two-photon absorption [83].

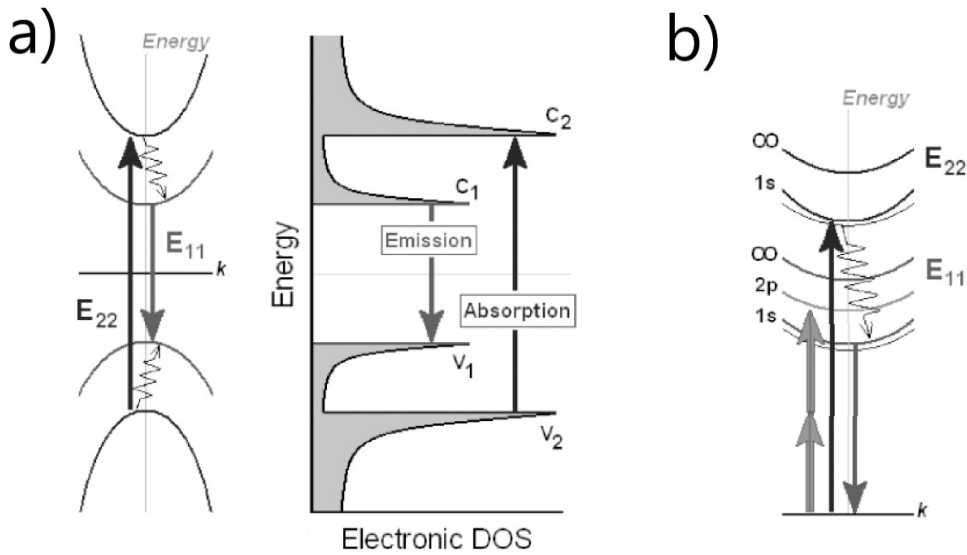


Figure 2.13: a) The band structure and optical transitions of a one-photon process, b) A simplified picture of the exciton band structure and optical transition. One-photon processes are shown as in (a) and a two-photon process (from [54]).

2.3 Physical properties of linear carbon chains and carbyne

The Linear Carbon Chain (LCC) is a promising material with several interesting properties. One of the core chapters of this thesis focuses on the *in-situ* synthesis via laser annealing and Raman spectroscopy of LCC inside CNT. Theoretical studies predict that the LCC can have superconductivity and ferromagnetism. There is a possibility the control of electronic properties changing the length of the LCC, and its reasonably chemical stability, when it is encapsulate in SWCNT (LCC@SWCNT).

The possibility of superconductivity and ferromagnetism for this combined system LCC encapsulated in SWCNT semiconducting was studied by Chen et al [84], using tight-binding calculations. In this study was predicted that the C atoms of the chain have a low and weak coupling with the atoms of the tube, producing a flat bands near the Fermi level. This can increase the possibility of superconductivity and ferromagnetism for this combined system. Also using tight-binding calculations Wang et al. studied the LCC in zigzag SWCNT [85] and showed the metallic behavior with zero band gap for all LCC of two and one C atoms in zigzag SWCNT ($C_2@(n, 0)$, $C@(n, 0)$ respectively). The properties of LCC@SWCNT can be controlled by changing the filling density of LCC atoms. Other studies with density-functional theory and periodic boundary conditions of LCC encapsulated in SWCNTs ((7,1), (5,5), (6,4) and (9,0)) developed by Rusznyák et al., suggested the suppression of the Peierls dimerization due to a combined effect of hybridization and charge transfer [86]. Xu et al using first-principles calculations based on spin density functional theory observed that dimerization for LCC@SWCNT is produced when the chain is formed by an even number of C atoms, but it is not when the chain has an odd number of atoms [87]. Theory studies developed by Bonabi et al [88], about the excitonic optical response of the combined system of LCC@SWCNT show that the interaction between the CNT and chain results in new bright excitons as well as charge transfer excitons, where electrons are localized on the CNT and holes on the chain, yielding new dark excitons in the combined system.

For a quasi-1-D conjugated chain system, the band gap is strongly dependent on the bond length alternation, which is the bond length difference between the single and triple bonds of polyynes (short carbon chain), in this way the bond length alternation decreases along with the increasing length of the LCC, which changes the electronic structure and results in a smaller band gap [89]. Experimentally, for polyynes of 44

carbons atoms, spectroscopic analyses show a band gap about of 2.56 eV [60]. Shi et al, determined experimentally the band gaps of long LCC@DWCNT (about 6000 C atoms encapsulated in DWCNTs) with a range from 2.253 to 1.848 eV [90]. Which represent a downshift of the band gap, due to the interaction between the carbon chain and the host tube, compared to measurements in gas suspension or in solution. This also modifies the chain's bond length alternation. LLCCs@DWCNTs have also served to determine the vibronic and electronic properties of the encapsulated LLCC. So, It is possible the control of the fundamental Raman mode of the chain by 95 cm^{-1} and its band gap by 0.6 eV, which suggest that this 1D hybrid system to be a promising block for nanoscale optoelectronics [91, 92].

3 Methods

This PhD thesis has its main focus on the development of a method to grow structures inside the hollow core of SWCNTs using the laser beam of the Raman spectrometer while performing measurements *in-situ*. The development of our system has brought some technical challenges that have been somewhat guided by previous trial and error attempts in previously reported experiments. The present chapter has two main parts. The first is related to the synthesis methods commonly used for the synthesis of carbon nanostructures and the second is focused on a thorough description of Raman spectroscopy. This chapter has the purpose to provide an insight to both topics without going into great detail about the specific experiments done in the PhD work. It is primarily a background description.

3.1 Production of graphene, carbon nanotubes and carbyne

3.1.1 Synthesis of graphene

In 1975, graphene (mono and multilayered graphite) was already synthesized by the thermal decomposition of carbon on a single crystal of Platinum substrates by Lang et al [93]. However, due to lack consistency of properties and beneficial applications, it was not extensively studied at that time. Likewise, other efforts made in the late 70's [94, 95] and 90's [96, 97], where their electronic properties were not investigated because of the difficulty in isolating and transferring them onto insulating substrates. In 2004 and 2005, the experimental evidence of 2D crystals came with Novoselov et al. [98, 4] when thin flakes of graphene and other materials were exfoliated from their bulk material. At the moment, there are various techniques have been established for the graphene synthesis, however the most commonly are mechanical cleaving, chemical exfoliation and thermal chemical vapor deposition [99].

Micromechanical cleavage is the first recognized method of graphene synthesis, an schematic is shown in Figure 3.1. This is a top-down technique (decomposition

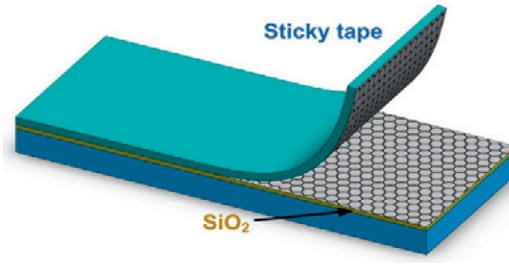


Figure 3.1: Schematic illustration of the graphene production techniques Micromechanical Clavage (from [100]).

technique) in nanotechnology, by which longitudinal or transverse stress is created on the surface of the layered structure materials. Graphite is formed by mono-atomic graphene layers, separated by a distance of 0.34 nm and on interlayer bond energy of $2eV/nm^2$. The layers are stacked together by weak van der Waals forces. Thus, it is possible to produce graphene from a high purity graphite sheet, if these bonds can be broken. In the cleavage method, the mechanical energy is used to break these weak bonds and separate out individual graphene sheets, where an external force of $\sim 300nN/\mu m^2$ is required to separate one mono-atomic layer from graphite.

Next, **the chemical exfoliation** method is considered to be the most effective and

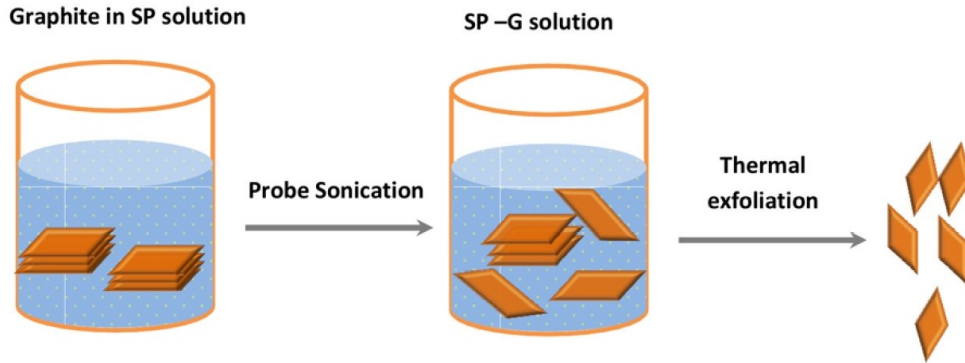


Figure 3.2: Schematic illustration of the graphene production techniques Chemical exfoliation, SP-solution (soap-polyvinylpyrrolidone solution) is a solution use for stabilizing the dispersion of graphene (from [101]).

economical way to prepare graphene sheets in large quantity from bulk graphite [102]. In this method a colloidal suspension is used which modify graphene from graphite and graphite intercalation compound, as shown in Figure 3.2. The production of graphene, with the chemical method is commonly used applications in polymer composites, energy storage materials and transparent conductive electrodes [99]. There are two-steps in

chemical exfoliation. In the first step, the interlayer van der Waals forces are reduced to increase the interlayer spacing to form graphene intercalated compounds (GICs). In the second step, graphene is exfoliate from with single to few layers by rapid heating or sonication. Alternatively, the graphite can be oxidized to obtain completely to obtain graphite oxide. Then, by sonication graphene oxide can be obtained and finally a thermal or electrochemical reduction process is used to convert in to graphene sheets [103].

Finally, **chemical vapor deposition (CVD)**, a large scale oriented method where

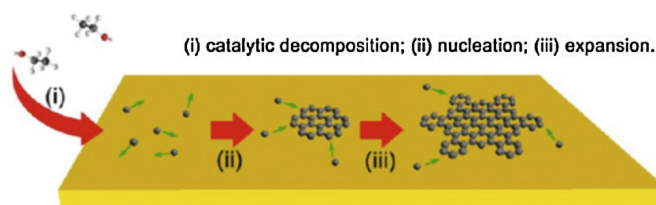


Figure 3.3: Schematic illustration of the graphene production techniques chemical vapor deposition. (i) At a high temperature ethanol decomposes into different products as carbon suppliers. (ii) The diffused carbon atoms on the copper surface are captured by the edge of the nuclei and form a circular shape. (iii) The expansion of graphene domains (from [104]).

vapors of hydrocarbons are used as C source to condense as a 3D graphene. There are many variation of this technique, which focus on different aspect like the carbon source, and the catalytical surface. For instance, the first report on the CVD synthesis of few-layer graphene was published in 2006 [105], it has afterwards evolved as an important method for preparation and production of graphene. The deposition process can involve two; homogeneous gas-phase reactions, which occur in the gas phase, and heterogeneous chemical reactions which occur on/near a heated surface leading, in each case, to the formation of powders or films [106, 107]. Amplified sketch can be seen in Figure 3.3.

3.1.2 Synthesis of CNTs

Nano-materials have an important economic potential and developing efficient procedures for synthesis is essential. Among the most popular nano-material to date are carbon nanotubes, with remarkable mechanical, electrical, chemical and thermal properties, that make them useful in various applications [108]. CNTs have stimulated extensive research since the report by Sumio Iijima in the early 90s [3, 109]. A controllable synthesis continues to be a challenge. However, it is important to remark that the last

three decades have witnessed the development of a great number of creative solutions in this respect. This section is only brief of the most popular and widely used nanotube synthesis techniques, namely: Arc Discharge, Chemical Vapor Deposition and Laser Ablation.

Arc discharge is the oldest technique to produce carbon nanotubes, it was used by

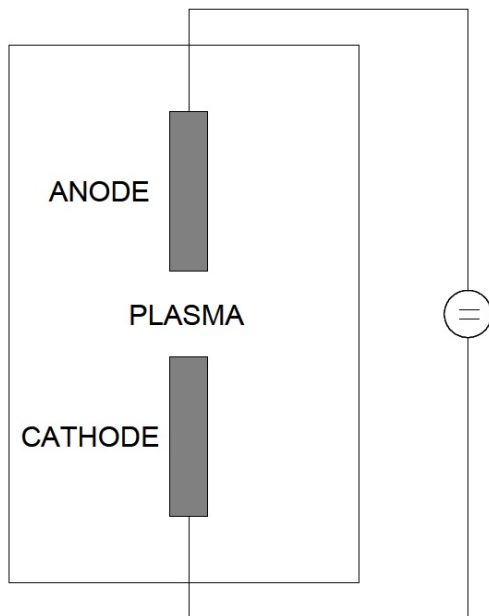


Figure 3.4: Schematic of an arc discharge setup (from [110]).

Iijima in 1991 to produce for first reported CNTs [3]. In Figure 3.4 a schematic of an arc discharge chamber is shown. It consists of two electrodes. The anode is filled with powder carbon precursor mixed with the catalyst and the cathode is usually a pure graphite rod. The environment could be filled with a gas or a liquid. The electrodes touch to produce an arc, that produce a plasma that is at 4000-9000 K of temperature. The precursor of the anode aggregates deposits near the cathode [111].

Another common high temperature method is **laser ablation** that use a carbon rich target, which is evaporated with a laser in presence of catalyst and the carbon nanotubes are then condensed with a cooling mechanism like a cold finger. It is used for the production of SWCNTs and the material has a very narrow diameter distribution [112, 113, 114]. This is a characteristic of high temperature methods. Figure 3.5 is shows a schematic diagram of f laser ablation setup.

The last, but certainly the most commonly used method for the synthesis of CNTs is **chemical vapor deposition** in a wide range of variations [109]. To synthesize CNTs

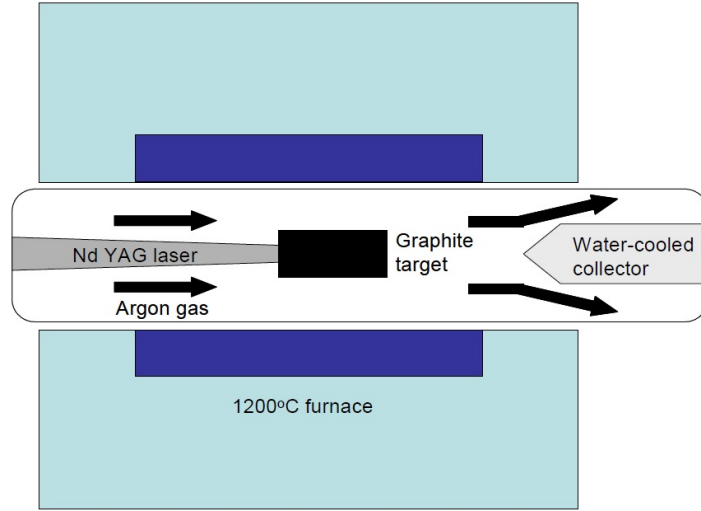


Figure 3.5: Schematic diagram of laser ablation setup (from [108]).

by CVD, a catalyst is required, which is nucleated via thermal annealing or chemical etching. The reaction temperature are usually between $600 - 2000^{\circ}$ depending on decomposition temperature of the source that can be a hydrocarbons such as: Methane, Ethylene, Acetylene, Benzene, Toluene, etc. This hydrocarbon gas in some cases is mixed with a carries gas that is usually nitrogen, hydrogen or argon. This mixture with pure gas is made to react in a reaction chamber over the surface of metal catalyst for a given time period and when the decomposition of the carbon precursor takes place CNTs grow assisted by the catalyst particle in the reactor. To increase the efficiency it is necessary to have a good control of the preassure, temperature, vapor or rate of the carbon source and catalyst support [115, 116]. Figure 3.6 is shows a schematic diagram of a CVD setup for CNTs.

One of the variations of CVD was used for the synthesis of SWCNTs used in this work. This is **enhanced-direct-injection-pyrolytic-synthesis (eDIPS)**, this is an approach for selective control of SWCNT in the gas-phase growth using two kinds of carbon sources with different decomposition properties. The 1st source, toluene solution of catalyst or their precursors are directly injected into vertical reactor through a spray nozzle, where the gradual and selective control of the tube diameter distribution is achieved by tuning of the flow rate of the 2nd carbon source could be ethylene. The increasing the flow rate of 2nd carbon source tends to decrease the tube diameter [118]. An schematic diagram of eDIPS setup is shown in Figure 3.7.

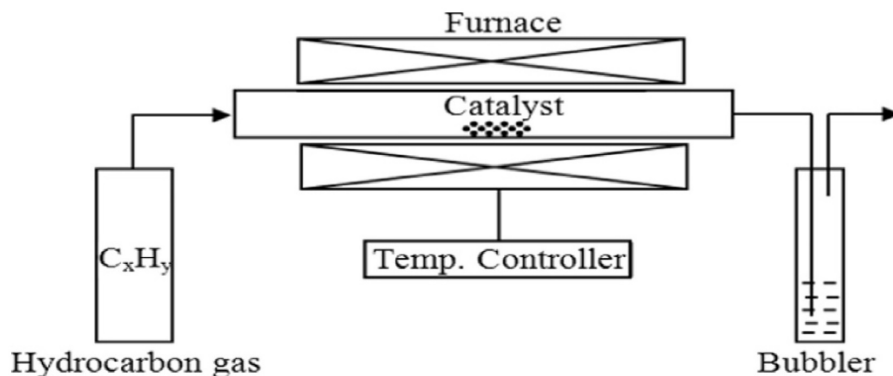


Figure 3.6: Schematic diagram of a CVD setup CNTs (from [117]).

3.1.3 Synthesis of carbyne

The first attempt to fabricate a one-dimensional polymer of C was done by Baeyer in 1885 describing it as a “explosive diamond” [119]. Between 1959 and 1960, A.N. Nesmeyanov reported the synthesis of diacetylene (C_4H_2) but without terminal hydrogen atoms [120, 121].

There are several theoretical works focused on understanding the morphology and physical properties of carbyne. However, making a linear chain with infinite length has not been possible so far. Carbyne was predicted by the beginning of the past century but its experimental production recently. In 1984 a group of researchers working at Exxon reported clusters between 30 and 180 atoms that could count as the first experimental identification of carbyne but it is disputed, that they were dealing with fullerenes instead of carbyne. Several chemical methods to create carbon chains have been developed. However the chains are hardly stable. The efforts for increasing the large and stable chain of carbons start with a method to produce the End-Cap Stabilized Oligynes (polyyynes of 20 atoms) [122], MWNTs with a linear carbon chain (C chain) inserted in its innermost tube have been made via chemical methods too.

3.2 Raman Spectroscopy

This spectroscopy method is the most widely used for the characterization of CNTs and other carbon nanostructures given its strong spectral features. This section provides the theoretical background of Raman spectroscopy focused on its response to the materials that are the core of this PhD thesis, to then follow with the specific experimental work in chapter number 4.

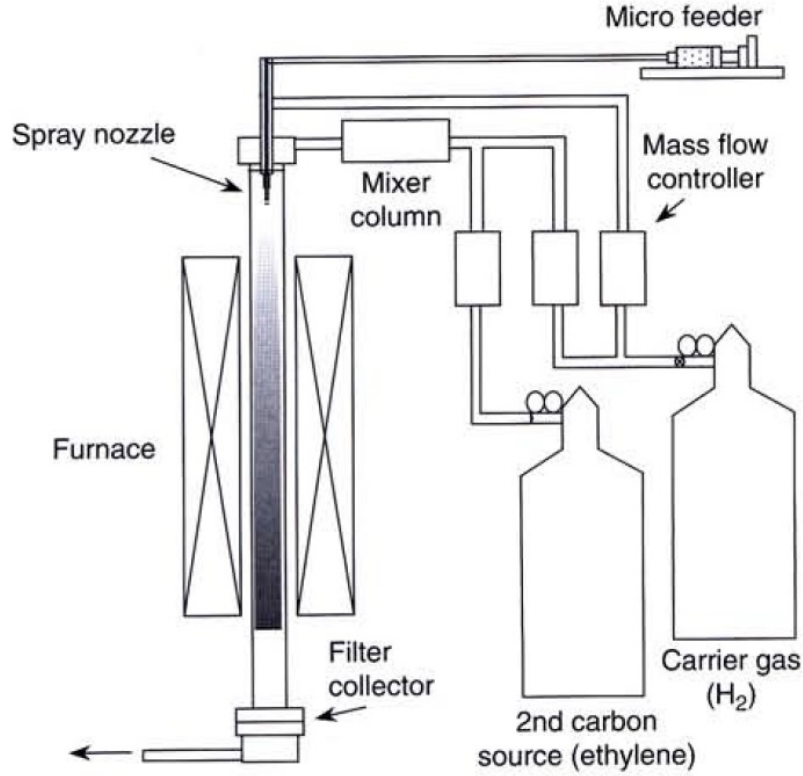


Figure 3.7: Schematic diagram of enhanced-direct-injection-pyrolytic-synthesis setup (from [118]).

3.2.1 Phonons

Raman spectroscopy is defined as the inelastic interaction of light with matter. While studying the effects of how this interaction takes place, it is important first to take into account how a solid is structured and based on this, how the interactions with light can be measured. In a solid, the atoms can be considered to be in an equilibrium position. When they move from these equilibrium positions, they experience restoring forces and vibrate at characteristic frequencies. From the classical formalism, the vibratory frequencies are described with an orthogonal set of harmonic oscillators representing normal modes of vibration. Taking into account the quantum nature of the atoms in this scenario it is necessary to consider the time-dependent Schrödinger equation for the quantum harmonic oscillator

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} K x^2 \right] \psi_n = E_n \psi_n, \quad n = 1, 2, 3, \dots \quad (3.1)$$

in which m is the mass, K is the force constant for the harmonic oscillator, ψ_n is a wave function of the harmonic oscillator and n labels the quantum state of the harmonic oscillator. The vibrational amplitude for ψ_n , which is proportional to n , is quantized and

3 Methods

the different vibrational levels are described by the number of vibrational quanta, which in this case are the phonons, described by the quantum number n . The annihilation a and the creation $a^\dagger$ operators are defined by

$$a = \frac{p - i\omega m x}{\sqrt{2\hbar\omega m}} \quad \text{and} \quad a^\dagger = \frac{p + i\omega m x}{\sqrt{2\hbar\omega m}} \quad (3.2)$$

so that the Hamiltonian for the harmonic oscillator is

$$\begin{aligned} H &= \frac{1}{2m} [(p + i\omega m x)(p - i\omega m x) + m\hbar\omega] \\ &= \hbar\omega [aa^\dagger + 1/2] \end{aligned} \quad (3.3)$$

Taking into consideration the number operator $N = a^\dagger a$, the Hamiltonian can be written as

$$Hn = \hbar\omega [N + 1/2] n = \hbar\omega(n + 1/2)n \quad (3.4)$$

So, the eigenvalues for the harmonic oscillator are written as

$$E = \hbar\omega(n + 1/2), \quad n = 1, 2, 3, .. \quad (3.5)$$

Here n corresponds to the number of phonons with frequency ω . For the vibration in a molecule with N atoms, there are $3N - 6$ degrees of freedom. The subtraction of 6 degrees of freedom correspond to the zero frequency for translations and very small frequencies due to the rotation of the center of mass. Therefore, the atomic motion of the molecule can be represented by a linear combination of the $3N - 6$ independent orthogonal vibration modes. The vibrational structure of crystalline solids can be described using the same concepts to describe the behavior of electrons in a crystalline solid such as the real unit cell, reciprocal unit cell, the Brillouin zone, etc. However instead of bands the term branches is used instead of bands to designate the phonon dispersion relations. Considering N as the number of atoms in the unit cell and the number of unit cells in a mol of crystal as $N_\Omega \sim 10^{23}$ per mole. Then, the vibrational modes are $3 \times N_\Omega \times N$, where the quasi-infinite number of vibrational modes are grouped into the various phonon branches. In the case of electronic bands, their number is defined by the number of electrons in the unit cell, while for the phonon branches, their number is defined by the number of atoms in the unit cell. The difference between one phonon to another within the branch is given by the change in the phase of the vibration from one-unit cell to the next, different for the electrons that is given by the atomic motion. This difference among phonons within the unit cell is described by phonon

wave vectors $\vec{q}$, where $\vec{k}$ is used for the electron wave vector and their energies are given by $E_q = \hbar\omega_q$.

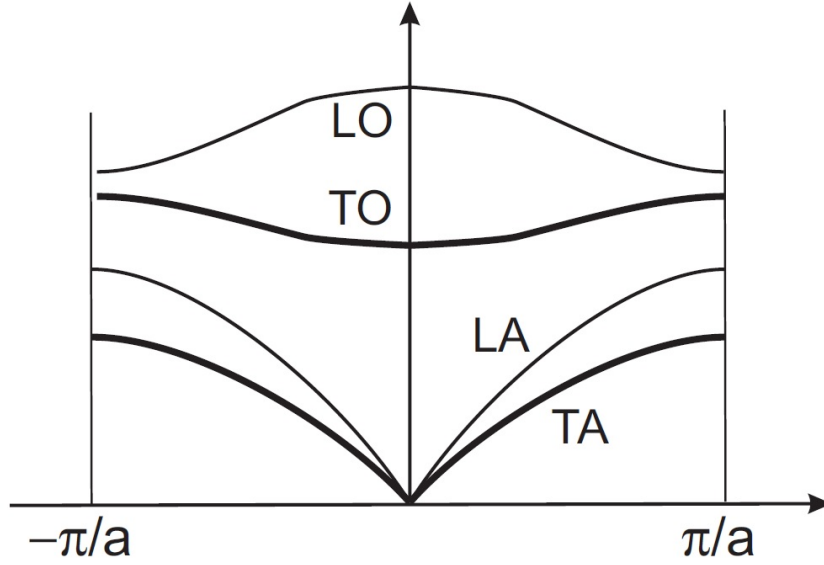


Figure 3.8: Schematic phonon dispersion relations for a 1D crystal made by the repetition of two different atoms (from [27]).

In high symmetry crystals such as graphene and graphite, the wave propagation direction is defined by the wave vector $\vec{q}$, and for a given $\vec{q}$ it can be defined one longitudinal acoustic (LA) branch, where the vibrational amplitude is parallel to the wave propagation direction $\vec{q}$, and two transverse acoustic (TA) branches, whose amplitudes are perpendicular to $\vec{q}$. Figure 3.8 shows the phonon dispersion relation for a theoretical 1D crystal formed with two different alternating atoms. The two lower energy branches are for the acoustic phonons and two higher energy branches are for the optical phonons, in the case of the 1D crystal, two acoustic and two optical modes are degenerate since atomic vibrations along x or y will have the same energies. In the case of graphite, up to six branches are present (3 acoustic and 3 optical), since it has two atoms in the unit cell.

When the light interacts with the matter part of the energy pass across of sample, that means the energy is transmitted. In the meantime, the remain interacts with the material through light absorption, reflection photoluminescence or light scattering. All these transmitted and light-matter interactions will depend on the electronic and vibrational properties of the material, and different phenomena related to different

optical transitions occur when photons with different energy interact with the matter, as shown in Figure 3.9. An example is heat, which is produced when the photon energy

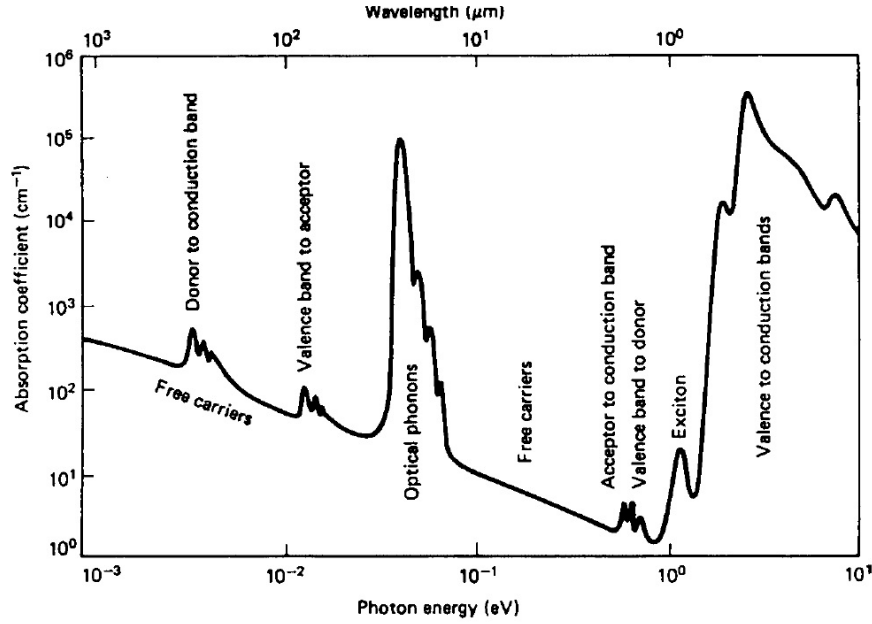


Figure 3.9: Schematic optical absorption curve for a semiconducting material where is shown the photophysical mechanisms operative for various regions of the electromagnetic spectrum (from [27]).

is absorbed and transformed in to atomic vibration. If the energy match allows phonon transitions, it can create acoustic or optical phonons, which corresponds to infrared (IR) absorption because phonon energies are at IR frequencies. Regardless of the energy of the photons, if they do not match the energy of optical phonons, the energy can still be transferred to the electrons. When the electrons are shaken by the photons, an oscillating electric field is formed and a virtual absorption is produced, following that energy scatters back to another photon with the same energy (elastic process). This elastic scattering process is called Rayleigh. When the Photons shake the electrons, with no real absorption, causing vibrations of the atoms at their natural vibrational frequencies, then phonons are generated. The electrons scatter the energy back into another photon with more or less energy than the original photon. This inelastic scattering process that creates or absorbs a phonon it is called Raman scattering. When the photon loses energy by creating a phonon, it is a Stokes process, and when the photon gains energy by absorbing a phonon is an anti-Stokes process. When both the Raman process occur, but incident light is at an energy near an electronic transition, this provides enough energy to excite the electrons to a higher electronic state. In this

case, we deal with a resonant process.

Light scattering techniques provide a very good tool to study solids and molecules.

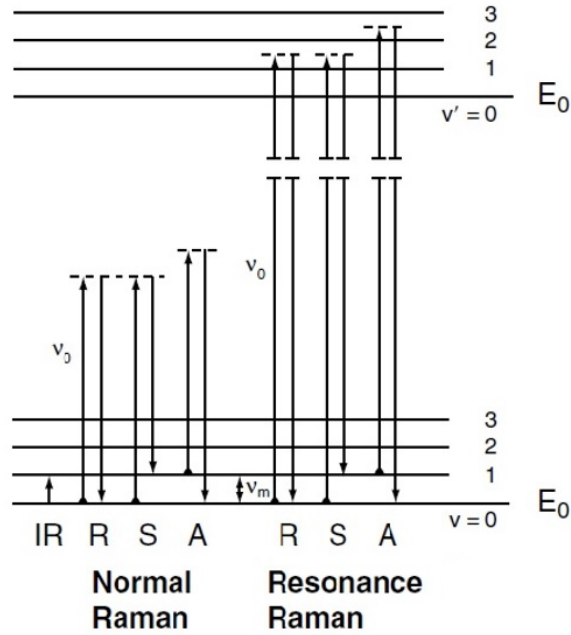


Figure 3.10: Infrared absorption(IR), Rayleigh scattering (R), Stokes (S) and anti-Stokes (A) Raman scattering (from [123]).

Since the incident and scattered light can be studied together with the properties of the material. The ability of the photon to shake the electrons is measured by the polarizability. Normal modes are related to the chemical and structural properties of the material, so each material has a unique set of normal modes and thus also a unique Raman spectrum.

3.2.2 Resonant Raman scattering process

For nano-scale structures, the resonant Raman effect is very important. In normal Raman effect, the photon energy is not enough for electrons to realize a real electronic transition, so the electron that absorbs the incident photon energy is excited a "virtual state" from where it couples to the lattice, generating the Raman scattering process. Nevertheless, when the energy of the incident photon, that is generally originated by a laser (laser energy E_{laser}), matches the energy gap (E_{ii}) between an occupied initial state and an unoccupied final state, that means between the valance and conduction band. In a semiconducting medium, the probability for a scattering event increases in

10^3 . Therefore, the large resonance enhancement permits the observation of Raman signals from nanostructures. The intensity of the Raman scattering can be expressed as

$$I(E_{laser}) \propto \left\{ \frac{A}{(E_{laser} - E_{ii} - i\gamma_r)(E_{laser} - (E_{ii} \pm E_{ph}) - i\gamma_r)} \right\}^2 \quad (3.6)$$

Where E_{laser} is the laser energy, E_{ii} is the electronic transition energy, E_{ph} is the phonon energy, γ_r is the resonance window width. It is easy to see from this that the intensity of Raman scattering increases when E_{laser} is near E_{ii} . Regarding the energy units, let us consider the emission and absorption of a photon. Here the following relations are valid:

$$\Delta E = E_2 - E_1 = h\nu = h \frac{hc}{\lambda} = hc\tilde{\nu} \quad (3.7)$$

where h is the Planck constant, c is velocity of the light, ν is frequency and $\tilde{\nu}$ is the wavenumber defined by $\tilde{\nu} = \nu/c$, $\tilde{\nu}$ is directly proportional to the energy of the transition with units $(\text{longitudinal})^{-1}$. Henceforth, 1 cm^{-1} is the energy of a photon whose wavelength is $2\pi \text{ cm}$, and the energy conversion factors are $1\text{eV} = 8065.5 \text{ cm}^{-1} = 2.418 \times 10^{14} \text{ Hz}$.

3.2.3 Raman Spectrum of Graphene

The main contribution to the Raman spectra are the phonons. The unit cell of graphene has two C atoms then we have six degrees of freedom, where three of them are translational and three vibrational. In such case we deal with six phonon branches, as shown in Figure 3.12, in which three are acoustic branches (A) and the other three are optic (O). Two are perpendicular to the graphene plane one acoustic and one optic, which correspond to the out-of-the plane (o) phonon modes. The other four two acoustic and two optic phonon branches correspond to vibrations in-plane (i). The reference vibration is considered the direction of the nearest $C - C$ atoms, then the phonons are classified as longitudinal (L) when parallel to the nearest $C - C$ atoms or transverse (T) if is perpendicular. Then, the six branches are assigned to LO, iTO, oTO, LA, iTA, and oTA phonon modes along of the high symmetry directions ΓM and ΓK . Graphene is the simplest of the sp^2 nanostructured carbon materials and its study is the prototype for studying more complicated carbon nanostructures. The Raman spectrum of graphene is simple as is it shown in Figure 3.12. However, it gives a lot of information. The most dominant peaks are the G and G' bands. These bands appear at 1580 cm^{-1} and 2700 cm^{-1} respectively using a laser excitation of 515 nm (2.41eV). The G band is characteristic in Raman spectra of all sp^2 nanostructured carbon systems, it is associated

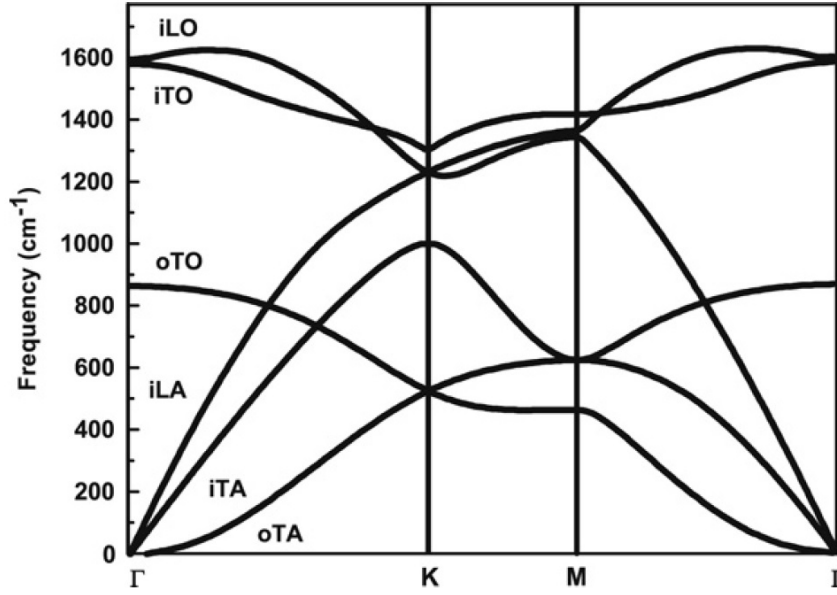


Figure 3.11: Calculated phonon dispersion relation of graphene showing the iLO, iTO, oTO, iLA, iTA and oTA phonon branches, where (i) in-plane, (o) out-of-the plane, (A) acoustic, (L) Longitudinal and (T) Transversal (from [124]).

with the doubly degenerate iTO and LO phonon mode at the Brillouin zone and is the only band coming from a normal first-order Raman scattering process, because of the strong $C - C$ bonding and small mass of the C atoms the G band has a relatively high Raman frequency in comparison to other materials. The G' , called also 2D band, originates from a second-order process, involving iTO phonons near the K point. The D-band around 1350 cm^{-1} (with laser 515 nm) originates from a second-order process and one defect. The D' - band is another weak disorder-induced feature at 1620 cm^{-1} related to the edges in graphene.

3.2.4 Raman Spectrum of SWCNT

SWCNTs can be considered as a rolled up graphene sheets obtain the electronic structure, as explained to some extent in the chapter 2.2 of the thesis. In the same way, this approximations is used to obtain the phonon structure. In the unit cell of graphene, the two atoms A and B give rise to six phonon modes, because there are three degrees of freedom per atom. Superimposing the N cutting lines in the K_1 -extended representation on the six phonon frequency surfaces in the reciprocal space of the graphene layer, according to the zone-folding scheme as described in section 2.2.1, produce $6N$ phonon modes for each CNTs. The $6(N/2 - 1)$ pairs of the phonon modes arising from the

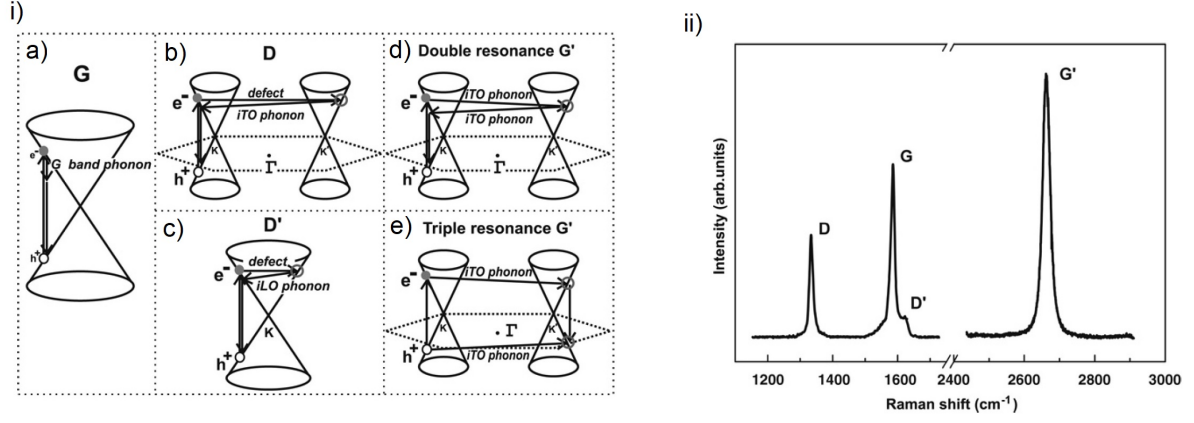


Figure 3.12: i) Raman scattering process: a) First-order G-band process, b) and c) one-phonon second-order double resonant process for the D-band and D'-band respectively intravalley process, and d) for the triple resonance G' band process for graphene. ii) Raman spectrum of graphene (from [124]).

cutting lines of the indices μ and $-\mu$, where $\mu = 1, \dots, (N/2 - 1)$, are expected to be doubly degenerate, similar to the case of the electronic subbands in section 2.2.1, whereas the 12 phonon modes arising from the cutting lines of the indices $\mu = 0$ and $\mu = N/2$ are nondegenerate, so that the total number of distinct phonon branches is $3(N + 2)$. For instance in the (4,2) nanotube, there are 90 distinct phonon branches [25]. The 1D nature of SWCNTs emerges from the quantum confinement of the phonon states into vHs. An example is the phonon dispersion of a (10,10) SWCNT, which is shown in Figure 3.13, with DOS in which it is possible to see many phonon branches. Their amount can be obtained by $3(N + 2)$. In the case of (10,10) SWCNT there are 66.

These many vibrational degrees of freedom are originated by a large number of atoms in its unit cell. A SWCNT of $\sim 1\text{nm}$ of diameter could have between 100 – 150 phonon branches for achiral tubes, which can duplicate or triplicate for chiral tubes. Only a small fraction of them are Raman active. The Raman-active modes have a low-energy when the radial vibration is observed, high-energy range with inplane $C - C$ vibrations and an intermediate-frequency range. The low and high energy phonons are the most studied; their strong Raman signal gives information about the morphology, electronic and optical properties. Something important to mention about the higher Raman signal intensity is that has the contribution of the resonant enhancement and the vHs energy in the JDOS. It is therefore possible to measure a single isolated SWCNT.

In the Raman typical spectrum of SWNTs like the one shown in Figure 3.18, the strong spectral features are the G band around 1580 cm^{-1} similar to that in graphene. However,

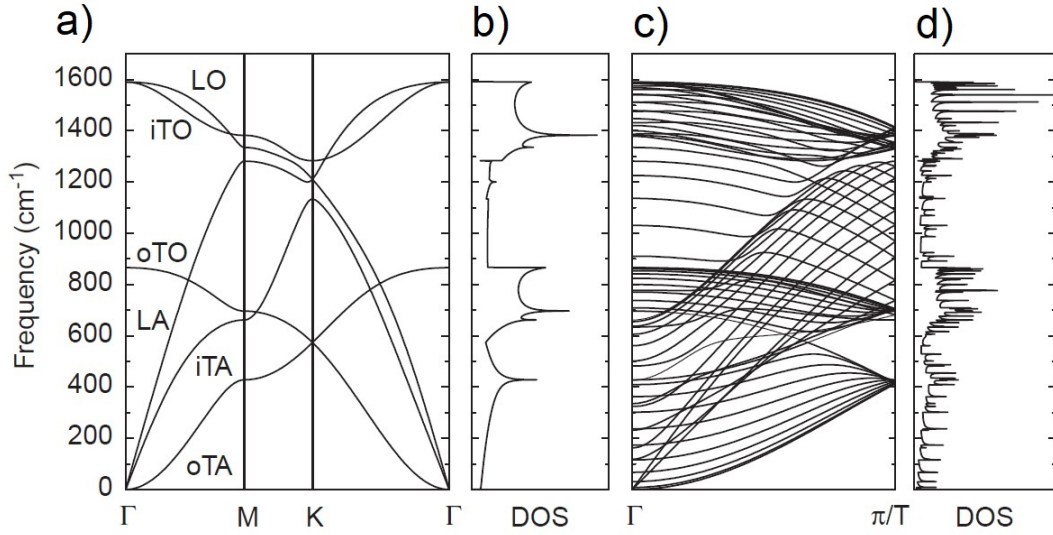


Figure 3.13: a) Phonon dispersion of Graphene. b) The phonon density of states for graphene. c) The phonon dispersion relations of an armchair carbon nanotube with (10,10), for which there are 120 degrees of freedom and 66 distinct phonon branches. d) The phonon density of states for a (10,10) nanotube(from [75]).

for SWCNT it splits in two G^+ and G^- . The lower frequency band called radial breathing mode 0RBM can also be observed. Both are first-order Raman modes. Additionally, it is possible to see the defect-induced band denoted like D-band at 1350 cm^{-1} and its overtone 2D-band called too G' at around 2700 cm^{-1} when measuring with a 515 nm ($2,41 \text{ eV}$) laser; both originate from double-resonance process.

The new feature in a SWCNT spectrum is **the Radial breathing mode** band (RBM), which is unique to these structures. RBM feature is originated by the coherent vibration of the C atoms in the radial direction as if the tube were breathing (see SWCNT in Figure 3.15a)). The RBM appears only in CNTs and its presence in the Raman spectrum proves that a sample contains SWCNTs. In the roll-up graphene vision shown in Figure 3.15a), the out of plane tangential acoustic modes give rise to RBM in the SWCNT. These features are an important mode for the characterization and identification of specific SWCNTs. The RBMs occur with frequencies between 100 and 350 cm^{-1} for diameters in the range of 2.6 and 0.7 nm . The RBM frequency (ω_{RBM}) is inversely proportional to the nanotube diameter d_t , this dependence comes from the fact that the mass of all the C atoms along the circumferential direction is proportional to the diameter, and it follows the equation

$$\omega_{RBM} = \frac{A}{d_t} + B \quad (3.8)$$

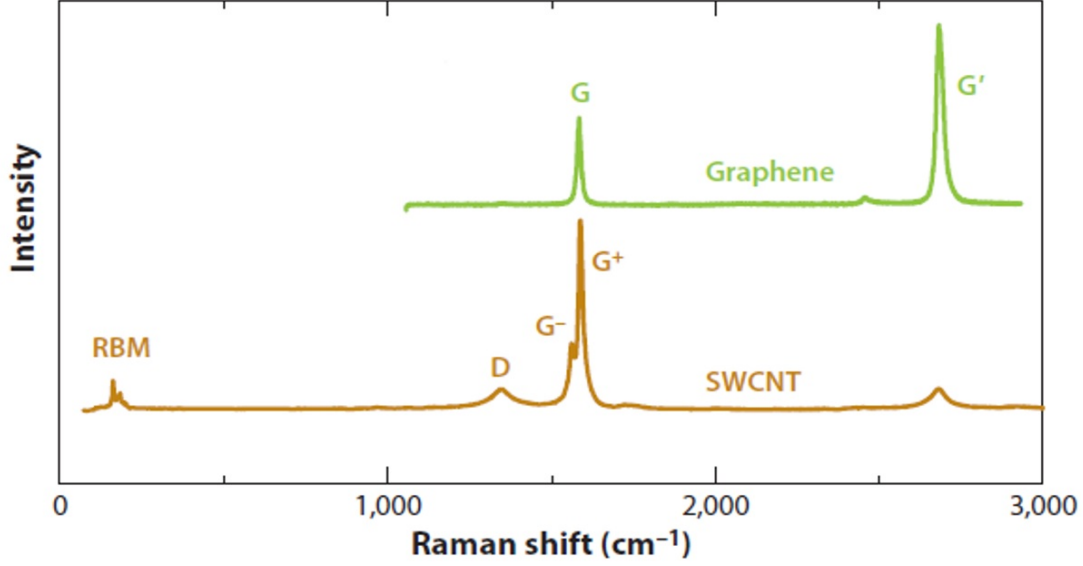


Figure 3.14: SWCNT Raman spectrum compared to the graphene Raman spectrum (from [125]).

where $B = 10 \text{ cm}^{-1}$ is the environment coefficient (for instance an upshift is assigned to tube-tube interaction) and A is a constant value typically around 234 cm^{-1} , for SWCNT bundles. The Raman intensity for the RBM is strongly enhanced when the incident or scattered light is in resonance with an excitonic transition that is when an energy separation E_{ii} between van Hove singularities (vHs) is close to the laser excitation energy.

The next stronger features in the Raman Spectrum is the **G-band**. It is identified with an in-plane tangential optical phonon involving the stretching of the bond between the two atoms in the graphene unit cell. Unlike the G-band in graphene that exhibits a single Lorentzian around 1580 cm^{-1} , for SWCNT it is the result of various components originated from the quantum confinement of the wavevector along the SWNT circumferential direction, and the folding of the graphene Brillouin zone into the SWCNT Brillouin zone. The main features are two G^+ 1590 cm^{-1} and G^- 1570 cm^{-1} . G^+ is associated with the vibration along the SWCNT axis (LO phonon), and the G^+ feature is independent of the diameter and chiral-angle. However, the G^+ is sensitive to charge transfer from and to dopant (upshift for acceptors and downshift for donors). For the case of G^- , it is dependant on the diameter, because of the vibration of C atoms along the circumferential direction (TO phonon). Furthermore, the lineshape of the G bands changes for metallic and semiconducting SWCNT with a Breit-Wigner-Fano or Lorent-

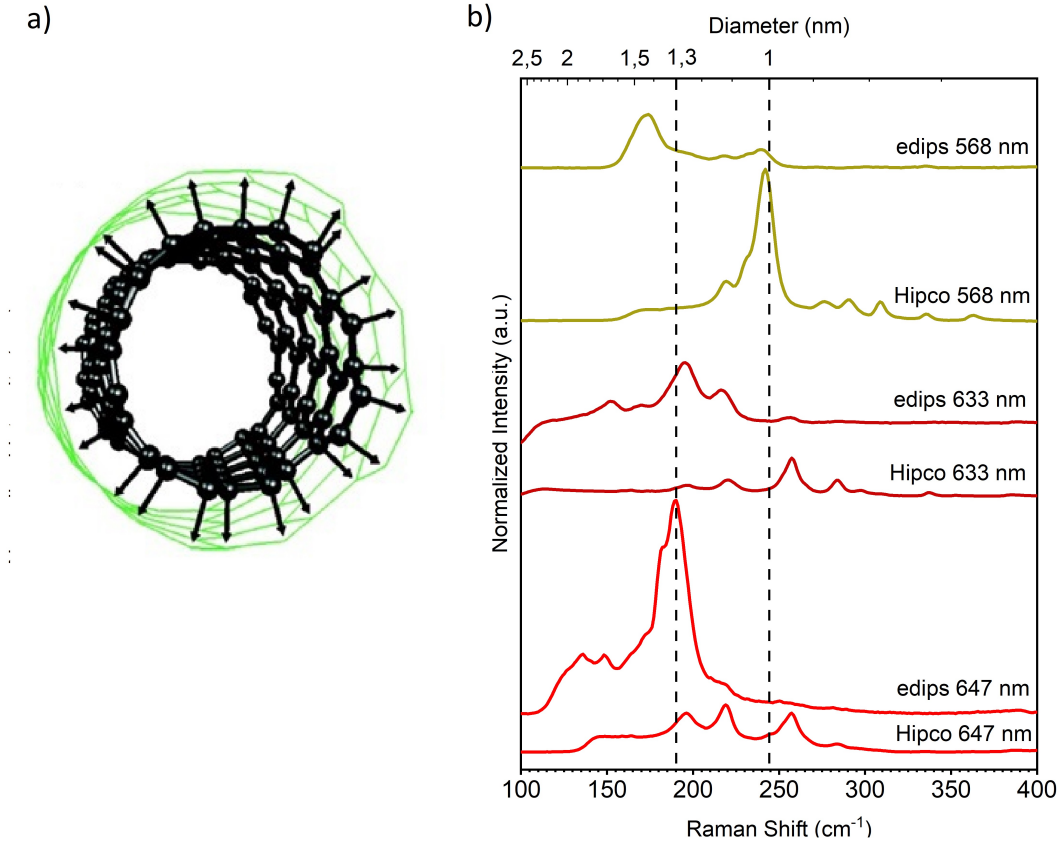


Figure 3.15: a) Schematics of the Radial Breathing Mode (from [126]). b) Raman response in the RBM region of edips and Hipco SWCNT of laser 647 nm, 633 nm and 568 nm.

zian lineshape. The next observable spectral line is disorder induced **D-band**, which is a weak feature in the second-order Raman spectrum of SWCNT and it is observed between 1250 and 1450 cm^{-1} . For Graphene and SWCNT, it originates when there is symmetry breaking on the hexagonal sp^2 – *bonding* lattice. Its major contribution comes from the iTO phono branch near the K point in the Brillouin zone. In SWCNT, the D-band is sensitive to the diameter and chirality. It becomes active in SWCNT due to the presence of defects, impurities, missing atoms, finite-size effects and molecules linked to the sidewalls. It is dependent on the excitation laser energy, caused by a softening of the LO phonons near the K(K') point due to the electron–phonon coupling. The ratio I_D/I_G is used usually as a metric: the more defective sample will have larger and broader D band so larger I_D/I_G .

The last is the **2D band** also called G' and it is the most intense feature in the second-order Raman spectra. It is the overtone of the D-band, its frequency dispersion is twice as that of the the D-band. The 2D-band arises from a double resonance process,

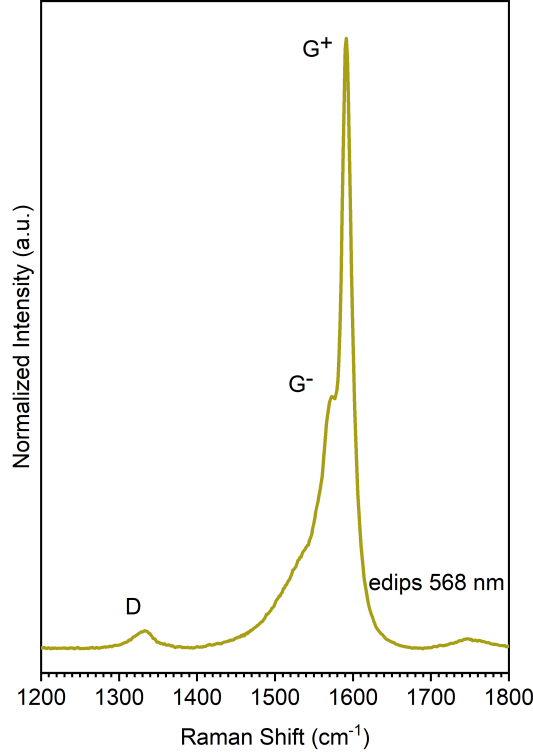


Figure 3.16: Example of Raman spectrum recorded on aSWCNT sample with a laser wavelength of 568nm. The characterizing features observed with this technique are labeled in the graph namely D, G-, G+ and D modes.

unlike of the D-band where a phonon and a defect are involved. For the 2D-band another phonon originates the momentum conservation in the double-resonance process. When a photon of the incident light excites an electron from valance to the conduction band, the electron can be resonantly scattered by a phonon with the correct wave vector (q) and phonon energy E_q to satisfy the double resonance conditions. That means, if the energy of the incident photon changes (E_{laser}), the wave vector and the phonon energy to fulfill the resonance condition change too as shows in Figure 3.17, this explains the dispersive nature of the 2D-band. This dispersive effect is used to characterize graphene layers and distinguish different kinds of graphene according to the numbers of layers of the stacking of these layers. At the individual nanotubes level, sometimes, the 2D-band appear like two peaks for semiconducting and metallic SWCNTs. In semiconducting SWCNTs the presence of two peaks indicates resonance with two different vHss of the same nanotube, independently one with the incident and another with the scattered energy of the photons, when the vHSS are sufficiently separated in energy. Thus, the two different features observed in the 2D-band are related to phonons with different

wavevectors in the phonon dispersion around the K point. In metallic SWCNTs, the electron wavevector, and also the phonon wavevectors for the two resonance states, show almost similar magnitude but opposite signs in the wavevector relative to the K point. Therefore the two peaks in the 2D-band arise from the anisotropy of the phonon dispersion E_q around the K point, known as the phonon trigonal warping effect.

Less commonly studied, the **M** and **iTOLA** modes are also part of SWCNT spectra.

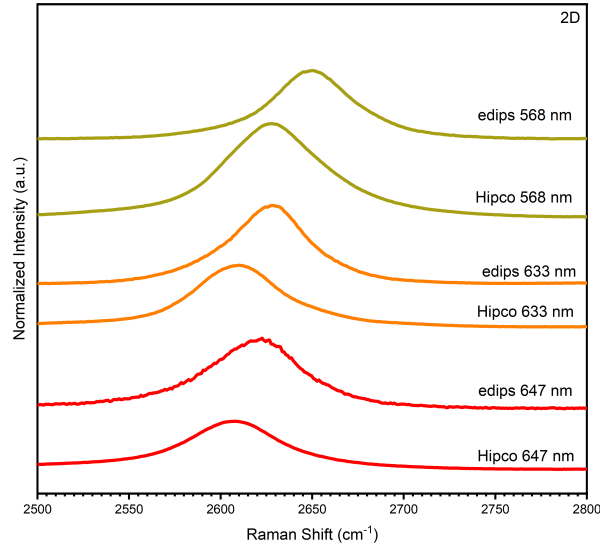


Figure 3.17: 2D Raman spectra of edips and Hipco SWCNT with excited laser 647 nm, 633 nm and 568 nm.

The M feature is observed around 1750 cm^{-1} . It can be studied like a two component-line M^- and M^+ . The lower frequency mode M^- shows a weakly dispersive behavior with the energy of the incident photon, unlike M^+ that is basically independent. Both features are attributed to overtones of the "out of the plane" (oTO) infrared-active mode at 867 cm^{-1} . It is not Raman-active in the first-order spectrum of graphene, but, it can be observed in the second-order spectrum of graphene through the double resonance process. In general, the overtones produce too weak features by the dispersion effects. However, in SWCNTs they are enhanced due to the vHss effects and the effects associated with SWCNT curvature that break the symmetry. The iTOLA feature is highly dispersive and upshifts from 1864 cm^{-1} to 2000 cm^{-1} depending on the photon incident energy. It is attributed to a combination of two intravalley phonons, one from the in-plane transverse optical branch (iTOLA) and the second phonon from the longitudinal acoustic (LA) branch, (iTOLA+LA), these combination modes are not seen in graphene.

However, it is enhanced by the double resonance process. The responsible for the dispersion is the acoustic LA phonon.

3.2.5 Raman spectrum of a linear carbon chain

As mentioned in the previous chapter, the linear carbon chain has been studied for its interesting properties such as higher thermal conductivity than graphene, electronic and optical properties that depend on the length of the chain, as well as the sequence of double bonds (cumulenes), that result into a 1D metal or an alternating sequence of single-triple bonds (polyyne), which are expected to show semiconductor properties, etc. [127, 128, 129]. Raman is also a powerful tool for characterizing linear carbon materials is Raman spectroscopy [130].

Wakabayashi et al, with resonance Raman and laser excitation of 515 nm obtained

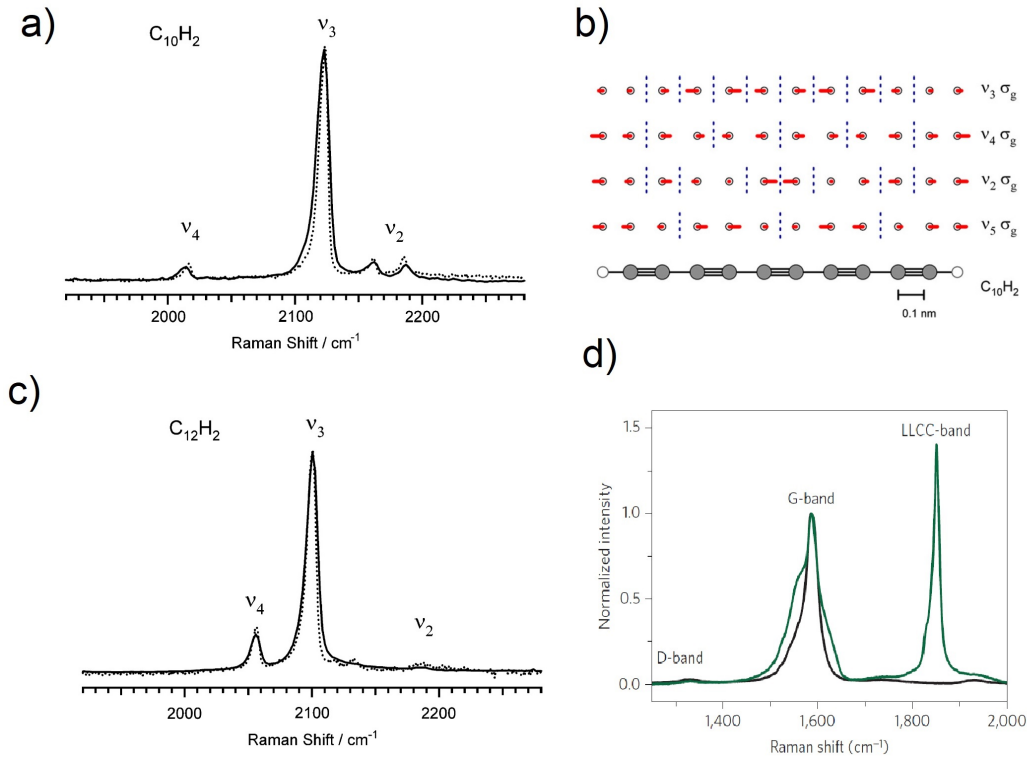


Figure 3.18: Resonance Raman spectra of (a) $C_{10}H_2$ and (b) $C_{12}H_2$ in n-hexane, with laser excitation wavelength of 262 nm and 270 nm respectively and the dotted line shows for 514.5 nm. (c) Vibrational modes of $C_{10}H_2$ in its ground state. The displacements of the atoms are represented by horizontal red bars and the vertical dotted line indicate the positions of nodes. (d) D-band, G-band and LLCC-band (green line) of a sample compared to pristine DWCNTs (black line) with laser excitation wavelength of 568 nm (from [131, 61]).

the spectra of polyynes $C_{10}H_2$ with peaks at 2123 cm^{-1} and 2017 cm^{-1} and $C_{12}H_2$ with peaks in 2097 cm^{-1} , 2097 and 2053 cm^{-1} in n-hexane [131]. On the other hand Nishide et al obtained the Raman spectra of the $C_{10}H_2$ polyyne molecules in SWCNT ($C_{10}H_2@SWCNT$) excited with laser of 532 nm with a peak at 2066 cm^{-1} [132] and in general identify the Raman band for polyyne molecules ($C_{2n}H_2$, $n = 4 - 6$ in the region of $2000\text{--}2200\text{ cm}^{-1}$ [133]. In a study developed by Fatinni et al, resonance Raman with DWCNT with and without B doping the Raman peak observed at 1850 cm^{-1} was concluded to be coalescence-inducing mode CIM produced when the DWCNT were treated with high temperature between 1300 and 1500 C [134]. Malard et al observed that a strong enhancement of the polyyne Raman features around 590 nm (2.1 eV) of excited laser, different to the polyynes that is 4.9 and 4.5 eV for $C_{10}H_2$ and $C_{12}H_2$ respectively [135]. Conversely, for cumulenic Raman intensities computed for chains of different lengths, Innocenti et al [136] concluded that cumulenic molecules could be detected by Raman spectroscopy. However, the intensity of the signal is lower than the polyynes. Agarwal et al studied and characterized long polyynes in the range of $2300\text{--}1900\text{ cm}^{-1}$ for polyynes in the range of $4 - 20$ triple bonds by Raman spectroscopy exciting with an infrared laser [137]. For LCC in MWCNT and DWCNTs the strong Raman peak was characterized around 1850 cm^{-1} [138, 61]. Other studies developed with LLCCs@DWCNTs reveal that the nanotube host, characterized by its chirality, determines the vibronic and electronic properties of the encapsulated LLCC. The fundamental Raman mode of the chain lies around 95 cm^{-1} and its band gap around 0.6 eV , with promising perspectives for optoelectronics [91, 92]. In summary, from the various papers published in the last decades related to the 1-D carbon chains it has been very difficult to make generalizations because different suspension media used for stabilization have always had an influence. Nevertheless, one solid conclusion is the fact there is a linear carbon chain band (LCC band), which shifts according to the nanotube length [61].

4 Experimental design and initial considerations

In the previous chapters an overview was presented on how synthesis methods for 1D carbon nanostructures work from a broad perspective. In this chapter I summarize a great part of the experiments that I performed during my studies taking into account the development of the appropriate setup. This was a high vacuum chamber coupled to a multi frequency Raman spectrometer where different solvents could be injected. The synthesis took place *in-situ*. Therefore, optimizing the optics for efficient use of the power laser was taken into account. The methods for *in-situ* synthesis and analysis can provide dynamic information in real time [139]. For instance in the study by Dittmer et al [140], one of the first reports of CVD and *in-situ* Raman spectroscopy, reported the successful growth of SWCNTs by local catalyst heating. An *in-situ* method for preparing aligned MWCNTs on electrically insulating substrates, based on the catalytic decomposition of ferrocene-xylene mixture [141] has also been reported. From the sections before we already understand that Raman spectroscopy is a very useful technique to characterize carbon nanomaterials but beyond that, it is especially practical because it can be used at very high temperatures and imposes no restriction on the gas pressure so synthesis while measuring is fully viable. It is therefore possible to obtain both qualitative and quantitative information on the growth kinetics of SWCNTs as a function of the growth conditions [142]. In our experiments, we can use a small quantity of material for our probes, due to use of microscopy used for Raman spectroscopy and laser annealing treatment. For our experiments we placed the SWCNTs on a grid and the laser beam could be focused on the sample adjusted with the maximum intensity of the received Raman signal. In this manner, efficient laser annealing treatment could be achieved at a specific location.

4.1 On the development of the experimental setup

Ideally, we would like to detect individual nanotubes and assemblies of them, as they grow and at the same time measure their physical properties while imposing minimal restrictions on the synthesis method [143]. This is the reason why the first goal of the PhD project was to focus on the experimental setup. We implemented a vacuum chamber coupled to a multi-frequency Raman spectrometer (Horiba Jobin Yvon LabRAM). The first task was to place the samples on the laser path with enough signal and to perform the Raman measurements and to promote the synthesis via laser annealing. A diagram of the experimental setup is shown in Fig. 4.1. No changes were made to the spectrometer but the challenge was associated to focusing the beam on the sample which was coupled to a vacuum system. Therefore, two important considerations had to be taken into account: to have a focused laser spot and to minimize mechanical vibrations in the purpose-built cubic synthesis chamber with a quartz window. Behind the quartz window, a plate with nine supports for the sample was placed. The quartz window was located below an objective (Olympus LMPLFLN $50\times/0.5/\infty/0/\text{FN26.5}$) and it was pumped to 3.0×10^{-5} mbar for all the *in-situ* laser annealing process.

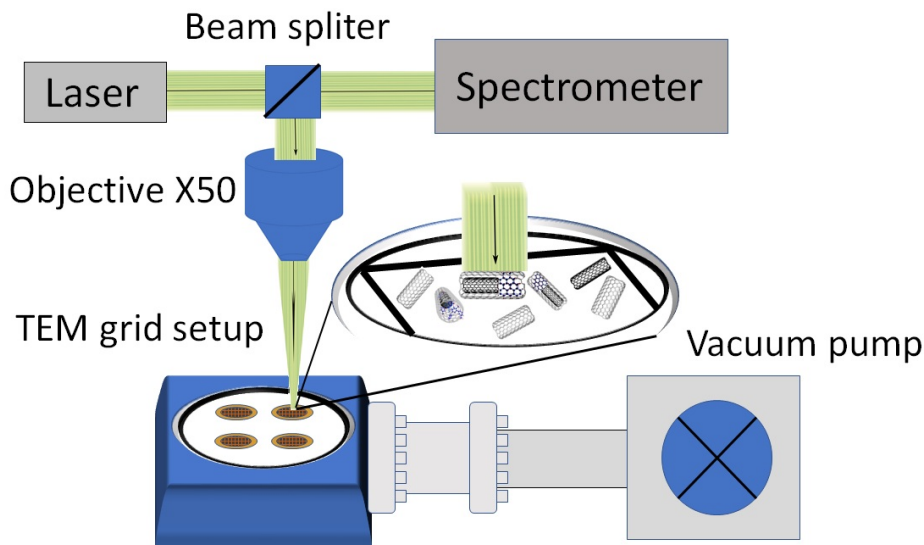


Figure 4.1: Experimental setup: a high vacuum chamber with a feedstock inlet was placed under the focused laser beam of a Raman Spectrometer. The laser was used for both: inducing the formation of structures inside the SWCNT nanoreactors and recording Raman spectra.

The Raman spectrometer used in these experiments was a multi-frequency Horiba Jobin Yvon LabRAM a system. The spectra are recorded by a liquid N_2 cooled CCD

detector. The resolution is laser-dependent, but it is in general between 1 and 2 cm^{-1} . The following sources are coupled to the system: an Ar^+/Kr^+ laser (458, 488, 515, 531, 568, 647 nm) and a He-Ne laser (633 nm). The laser power depends on the optical arrangement and also depends on the type of laser used. For instance, it can be controlled up to a maximum of 50mW with the 647nm and 488nm wavelength at the microscope output. Note that using a 50x objective allows a laser spot of $2\mu\text{m}$ to be used. The system, as described, was used for all the experiments in the following sections explaining how inner tubes and linear carbon chains were grown via laser annealing using SWCNTs as nanoreactors.

4.2 The starting material: SWCNTs

The experiments in this work rely on the quality and characteristics of the nanotube material used for the subsequent laser annealing treatments where additional inner structures are to be grown. Recalling that SWCNTs can be either metallic and semiconducting, that they can have different chiralities and that their diameters can vary, we can understand that we are dealing with experiments with several variable parameters. Therefore, having previous knowledge of the nanotube-material to be used as nanoreactors is crucial. The SWCNTs used as starting material in the experiments were produced with the eDIPS (enhanced direct injection pyrolysis) method described in chapter 3 [118]. The advantage of this technique is mainly that while being a CVD technique, it is able to produce large amounts of material, but the nanotubes have a relatively small diameter distribution. This is not the case of standard supported CVD. The nanotubes used in the work to be described ahead are purified eDIPS material that had an average diameter between 1.3 and 1.7 nm. They were obtained from a collaboration with Prof. Takeshi Saito at AIST in Japan. After confirming the purity and crystallinity, the pristine SWCNTs were used in our study without further purification.

To gain proper understanding on the efficiency of the method, our goal was far from working with bulk quantities. Therefore, we decided to use plain metal transmission electron microscopy grids (TEM grids). More explicitly, Cu grids. This gave the advantage to use small amounts of SWCNTs but here again, the challenges like making the nine pin holder for the grid mentioned above and handling the vacuum were not trivial. The SWCNTs were dispersed in toluene (Sigma-Aldrich, 99.5% purity) by bath-ultrasonication (Elmasonic S30H, 37 kHz) for four hours. Then, $5\mu\text{l}$ of this well-dispersed

4 Results 1: Experimental Design

SWCNT solution was drop-casted on a TEM grid and dried in a furnace at 80°C for 5 min. Finally, the grid was placed inside the purpose built cell for *in-situ* synthesis and Raman spectroscopy.

5 Double Walled carbon nanotubes by *in-situ* annealing and Raman Spectroscopy

When we completed the system to operate *in-situ* the first natural test was to induce the formation of thinner nanotubes inside the SWCNT templates. This is of important technological interest because double-walled carbon nanotubes (DWCNTs) have many advantages over their singled-walled counterparts such as higher mechanical strength and thermal stability. They can be synthesized by well-established methods like arc-discharge, chemical vapor deposition and the annealing of molecules and nano compounds encapsulated in SWCNTs. However, the material grown with these methods does not necessarily have a homogeneous morphology across an entire sample. As starting point we had a big advantage compared to studies reported before, which was having a known diameter of the starting material. Our goal was to obtain DWCNTs inspired on the proven feasible synthesis of other nanostructures inside nanotubes [50, 144, 145, 146]. We investigated the decomposition and changes of solvents and explored the possibility to grow inner tubes with specific chiralities. In this context, we have also observed that monitoring the laser wavelength, power and choosing the host's diameter, the chirality of the inner tubes can be tailored in a controlled manner. Specifically related to the DWCNTs, we noticed it is possible to promote the process towards the growth of both metallic and semiconducting inner tubes, and even more, a selective inner tube growth with chirality enrichment. Note that the results in this section were published in Ref. [147], therefore, most of the description in the paper has been used here. At the time the publication was submitted, we were running the first experiments towards the synthesis of LCCs. Those were only pilot experiments from which only one conclusion could be drawn and that was that the dynamic of the chains annealed at higher power indicated the decomposition of the long into shorter ones. This is also briefly mentioned at the end of this chapter.

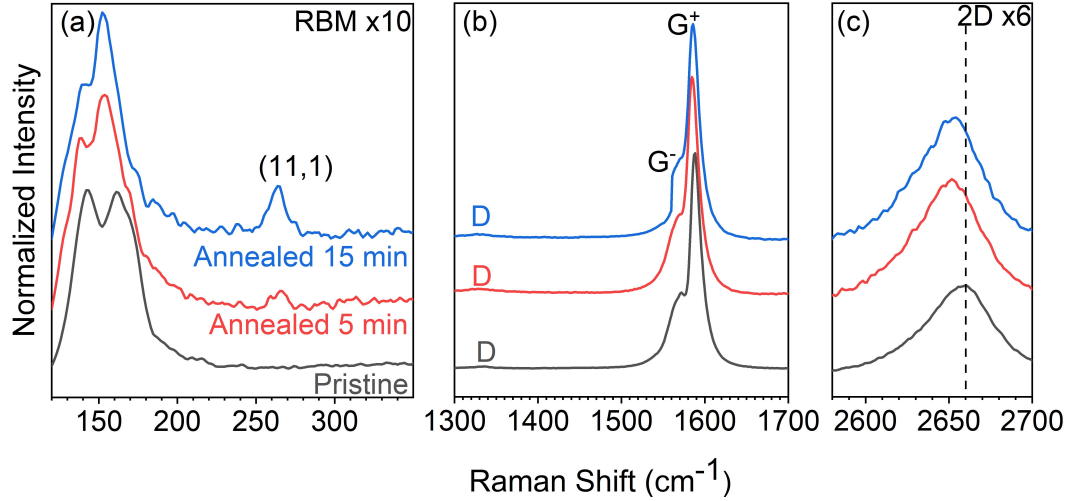


Figure 5.1: Raman spectra excited by a 568nm laser of eDIPS SWCNTs with an average diameter of 1.7nm before and after in situ laser annealing at a power of 6 mW for 5 and 15min: (a) RBM, (b) D and G bands, and (c) 2D-band. A dashed line in (c) is used to guide the eye.

5.1 Possibility to create inner tubes

While using Raman spectroscopy in our experiments, *in-situ* laser annealing allowed us to create the inner tubes in a short time under a micrometer sized spot, resulting in real-time monitoring and chirality control by selecting defined diameter SWCNTs as the starting material. This represents a different approach toward the use of laser annealing on SWCNTs. Note that this is a technique, which had previously been used to increase the tubes crystallinity through the reduction of defects.

Identifying DWCNTs is straightforward using Raman spectroscopy. The wall separation between an inner and an outer tube should be comparable to the interplanar distance in graphite, which is around 0.33 to 0.41 nm considering van der Waals forces. Given that the Raman shift in the RBM region in the Raman spectrum can be inversely associated with the diameter, both, inner and outer tubes can be identified under this principle. For instance, let us first, analyze a sample rich in nanotubes with 1.7 nm in average diameter with a constant power density of 6 mW for different times. Fig. 5.1a shows the radial breathing mode (RBM) region, where after 5 min of laser annealing a new peak raises at 264 cm^{-1} , and its intensity increases with the time as observed in the spectrum recorded after 15 min. This increment suggests the formation of more

and longer tubes through the annealing process. The newly formed nanotubes are very thin with a diameter of about 0.92 nm calculated by $\nu_{RBM} = 234/d + 10$, where d is the diameter of the tubes and ν_{RBM} the frequency of the RBM [148, 149]. Assisted by a Kataura plot [150], this peak can be assigned to an (11,1) tube. The lower frequency peak that appears at 159 cm^{-1} corresponds to 1.57 nm tubes, which compared to the diameter of the newly formed tubes is about $\sim 0.65 \text{ nm}$, which is around two times the van der Waals distance between planes in graphite [151], suggesting that DWCNTs have been created by a simple laser annealing process. This is a very illustrative case because both the inner and outer tubes are in resonance with the same laser. This is in good agreement with the study of Levshov et al [152], that attributes this to an inter-layer distance less than the nominal van der Waals 0.34 nm. Looking at Fig. 5.1b

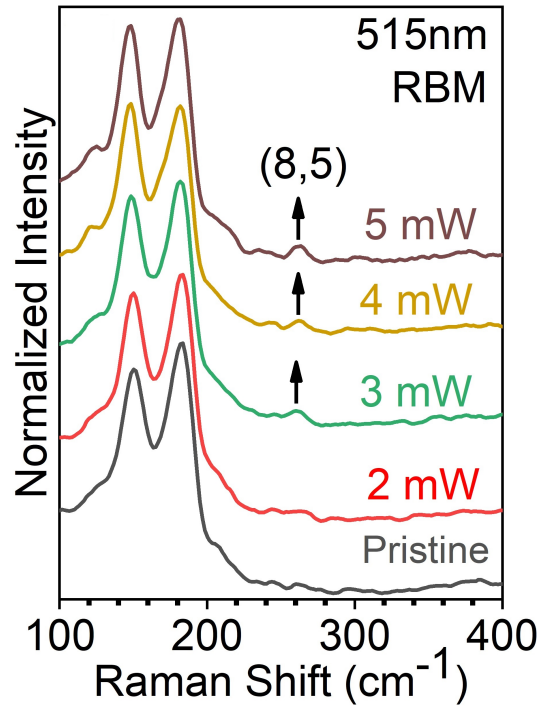


Figure 5.2: Study of an eDIPS SWCNT 1.43 nm diameter sample annealed *in-situ* by a 515 nm laser. Raman spectra recorded during laser annealing in high vacuum by a step of 1 mW.

one can observe that for the D-band almost no change can be found before and after laser annealing, which shows us that the used laser power does not dramatically damage the nanotubes by creating defects. Huang *et al.* [153] reported that when the SWCNTs are not heavily bundled and under vacuum, the temperature induced by laser annealing can even slightly reduce the defects of the SWCNTs. As shown in Fig. 5.1c, the 2D-band

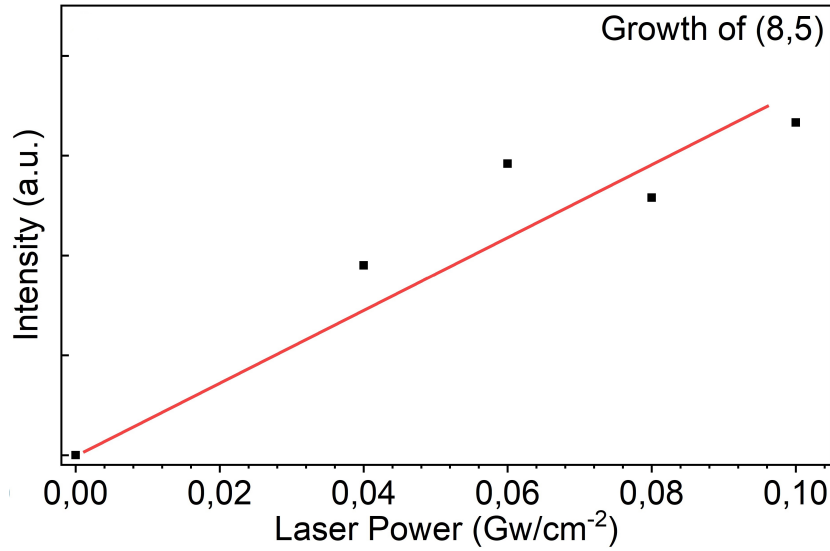


Figure 5.3: Study of an eDIPS SWCNT 1.43 nm diameter sample annealed *in-situ* by a 515 nm laser. Intensity of newly-formed inner tubes as a function of laser power for annealing.

shifts to lower frequency appear after laser annealing, confirming the formation of the small nanotubes as well. This feature is used for differentiating between single and double layer graphene [75, 154], so in the same way this change in the 2D-band can be attributed to the formation of the new inner wall that changes the π electronic structure when a second wall is formed.

5.2 Understanding the origin of the C atoms that generate the inner SWCNT and finding the growth onset

So far we have seen that effectively it is possible to induce the formation of inner tubes. The following question to be addressed is what the inner tube carbon source is. Previous laser annealing studies on buckypapers of peapods (C60@SWCNTs) have shown that very high laser power (about 300 mW) opens the possibility to use buckyballs to generate the inner tubes. [50, 51]. In our study, samples are just tens of nanotubes in small bundles, therefore a few mW of power was enough to create inner nanotubes. A first possible source could be the carbonaceous impurities that always exist in SWCNTs [155], which can be reconstructed during the laser annealing. A second source could be incorporated during the sonication process used for dispersion, when the toluene molecules can go into the nanotubes and stay inside [49, 156]. Assuming the presence of both when the laser

shines on the nanotubes, the formation mechanism can be triggered when the toluene molecules decompose into small species and the power is high enough to activate the nano-chemical reaction using SWCNT templates, so that the inner tubes start forming.

To better illustrate and understand the onset of the formation the inner tubes let us now focus on the laser power required for these purposes taking as example pristine eDIPS nanotubes with an average diameter of 1.43 nm. We carried out experiments increasing gradually the power in steps of 1 mW starting from 2 mW. As shown in Fig. 5.2, the pristine starting material shows strong Raman signals below 200 wave numbers and it remains almost unaltered during the first annealing step. It is only from 0.06 GW/cm^2 that a peak in the RBM region at $\sim 262 \text{ cm}^{-1}$ appears and it's intensity gradually increases with the laser power following a linear trend as plotted in Fig. 5.3. In this case, the inner tube was assigned as a metallic tube (8,5). Therefore, the laser annealing method enables to synthesize both metallic and semiconducting tubes, as well as identifying when the growth occurs.

5.3 Possibility to control the chirality of the inner tubes in the DWCNTs

Once the growth upon laser intensity and time of exposure were determined for various types of samples, a more exhaustive multi-frequency exploration with further laser lines was carried out. In different resonance conditions, a few more inner tubes were observed and assigned, as shown in Fig. 5.4 and table 5.1. Interestingly in addition to

Table 5.1: Summary of types of the SWCNTs used, experimental parameters, and the main results. $D_{average}$, λ_{LA} , λ_{RS} , RBM, D_{inner} , and Ch represent the average diameter of SWCNTs, laser wavelength for the laser annealing, laser wavelength for the Raman spectral measurements, RBM of the inner tube, diameter of the inner tube, and the chirality assignment for the inner tube, respectively.

$D_{average}$ (nm)	λ_{LA} (nm)	λ_{RS} (nm)	RBM (cm^{-1})	D_{inner} (nm)	Ch (n,m)
1.70	568	568	264	0.92	(11,1)
1.70	568	515	289	0.84	(10,1)
1.70	568	488	379	0.63	(5,4)
1.43	515	531	263	0.93	(8,5)
1.43	515	515	283	0.85	(10,1)
1.30	568	568	271	0.90	(11,1)

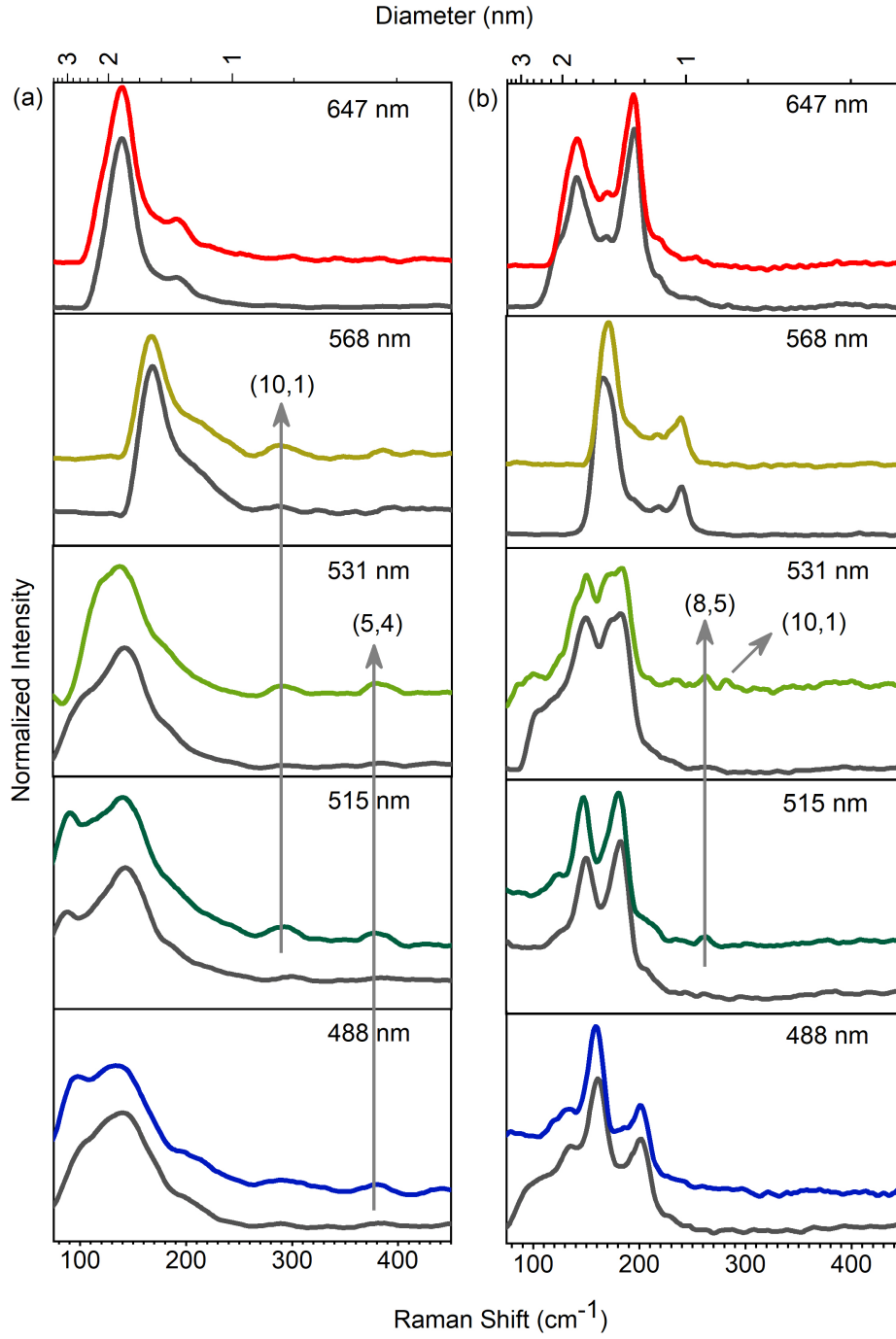


Figure 5.4: Raman spectra of eDIPS SWCNTs with average diameter of (a) 1.7 nm, (b) 1.43 nm before and after laser annealing excited by multi-frequency lasers.

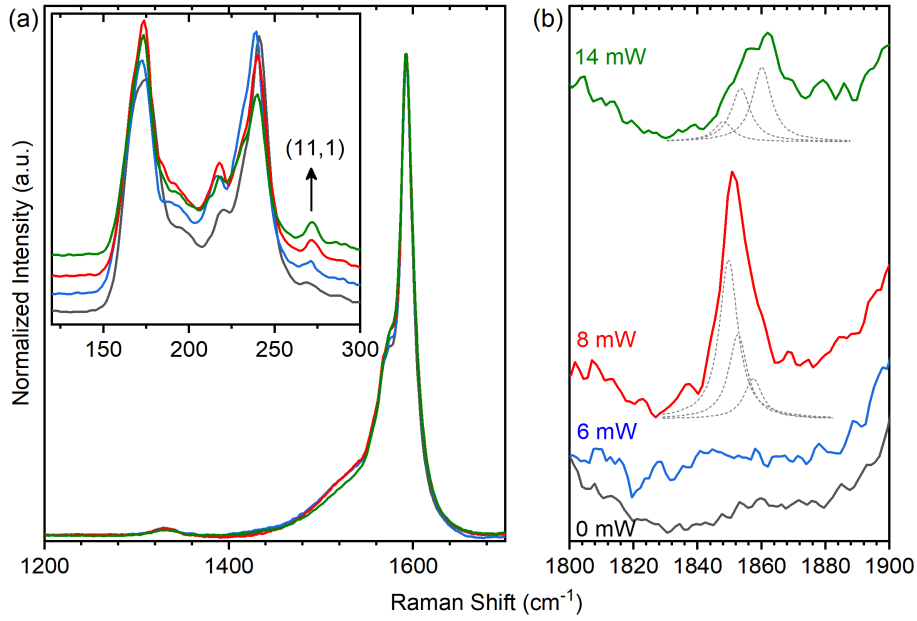


Figure 5.5: Raman spectra of eDIPS SWCNTs with average diameter of 1.30 nm before and after laser annealing excited by a 568 nm laser. Raman signals from both of the inner tubes and the linear carbon chains were observed.

the growth of inner tubes with different chirality depending on the host diameter, laser wavelength and annealing power, both (11,1) and (10,1) were frequently identified in nearly all samples. This suggests that this laser annealing method allows us to control the synthesized nanotube chirality and, in addition, yields the preferred enhanced growth of some selected chiralities. Usually the synthesis of thin inner tubes, *e.g.* (6,5) and (6,4), is more favorable. Here a few other thin nanotubes, which were not frequently seen in the traditional methods, were introduced by the laser annealing. The growth mechanism of these "laser-introduced" inner tubes differs from that of those made by traditional methods, as cited before [28, 41, 42, 43, 44, 35, 45, 46, 47, 48, 49, 50, 51]. This is the matter of an unexplored playground worth investing experimental and theoretical investigations.

5.4 Possibility to grow LCCs inside the DWCNTs

Further analyzing the spectra, the RBM frequencies of (11,1) and (10,1) nanotubes are located at positions with a few wavenumbers difference when synthesized inside different SWCNTs. This interesting finding could be explained by the van der Waals interaction between the inner and outer tubes[157].

In several experiments, peaks located at around 1850 cm^{-1} appear together with

those corresponding to the inner tubes during the laser annealing process, as shown in Fig. 5.5. In particular, measurements with a 568 nm laser while annealing with fine-controlled power reveal a particularly strong intensity of this new mode, where a few sub-components could also be identified. This mode has been reported as fingerprint of LCCs [61, 158] and the chain length has been associated to the frequency of the mode [159, 91]. The deconvolution in grey dashed lines corresponds to the three main peaks that were extracted from the linear carbon chain mode (LCC-band). These correspond to the carbon chains consisting of tens of carbon atoms. Since those LCCs were in resonance with the 568 nm laser, a higher intensity was detected [160]. We have found that the LCCs are very sensitive to the laser power. They can be damaged completely if the power is too high. As intermediate states, the LCCs can be decomposed into shorter fragments, as indicated by the peak shifts to a higher frequency as shown in Fig. 5.5b. In contrast, the inner tubes remain well preserved under the same laser power suggesting that the LCCs, are much less stable than the thin inner tubes. Furthermore, we evidenced that the LCCs always start to appear subsequent to the formation of the inner tubes. This is consistent with the role of the inner tubes as templates for the LCC growth and later on stabilizing the LCCs as hosts. We believe that laser annealing would be an effective method to tailor the length of synthesized LCCs in the future.

Although in this chapter we focused on samples produced using toluene as feedstock, other solvents were tested as well but with less pronounced spectra. However, looking into the formation of linear carbon chains brings different mechanistic perspectives and their capability to grow also had to be tested. The next chapter summarizes the experiments performed with different types of organic solvents pursuing mainly the growth of linear carbon chains protected by the DWNTs.

6 Growth of encapsulated linear carbon chains

Once we successfully synthesized DWCNTs with the laser annealing *in-situ*, and after we noticed the formation of LCCs inside the DWCNTs grown in the presence of the toluene feedstock, we decided to orient our experiments to the growth of LCCs. To have some background on how such materials have been synthesized so far we can recall first the studies from Thomas Gibtner et al., who developed a method to produce the end-cap stabilized oligynes, which are polyynes of 20 atoms [122]. One year later in 2003, Xinluo Zhao et al. proposed a new type of one-dimensional carbon structure [122], consisting of a MWCNT with a LCC inserted into its innermost tube of 0.7 nm in diameter. In the same year Yi Liu and R. O. Jones calculated that carbon chains can be inserted coaxially into 0.7 nm -1.0 nm diameter tubes [161]. In the same line in 2006, Daisuke Nishide et al. encapsulated Polyynes $C_{10}H_2$ in Carbon nanotubes exhibiting a Raman peak at 2066 cm^{-1} [132], and E. Cazzanelli et al. studied MWCNTs deposited on graphite cathodes by the arc discharge technique in a He atmosphere, and found by micro-Raman mapping that in some regions of the sample, strong bands in the $1780\text{-}1860\text{ cm}^{-1}$ range corresponding to linear carbon chains inside the nanotubes [162]. In 2010, Wesley A. et al described the synthesis of a series of conjugated polyynes, which the longest was of 44 C [60]. Encapsulated polyyne $C_{10}H_2$ molecules in DWCNT and annealing the sample to high temperature and vacuum C. Zhao growth a linear carbon chain of more of 50 C atoms in 2011, the Raman peak appear around 1800 and 1850 cm^{-1} [163]. It was only in 2016 that Shi et al [61] proposed the use of DWCNTs to template the growth of long LCC inside carbon nanotubes and successfully grew the longest chains ever observed, reaching around 6000 atoms.

Inspired on the availability of thin nanotubes and taking as starting point the example from the previous chapter, our next goal was to encapsulate linear carbon chains inside the SWCNTs by exposure to different organic solvents while exploring the best synthesis parameters under the laser beam. In this chapter, the study the results presented by the

end of the previous chapter are complemented with further observations. Additionally, three new solvents came in question namely: isopropanol, methanol and ethanol.

6.1 Study using different solvents

As stated previously, we believe that great part of the carbon atoms present in the solvents used for sonication of our starting nanotube material have significant influence on the possibility to further grow something inside them. This brought us to further investigate this possibility using three additional hydrocarbons besides toluene; namely methanol, ethanol, and isopropanol. Let us recall their structure in the molecular diagrams in Fig. 6.1.

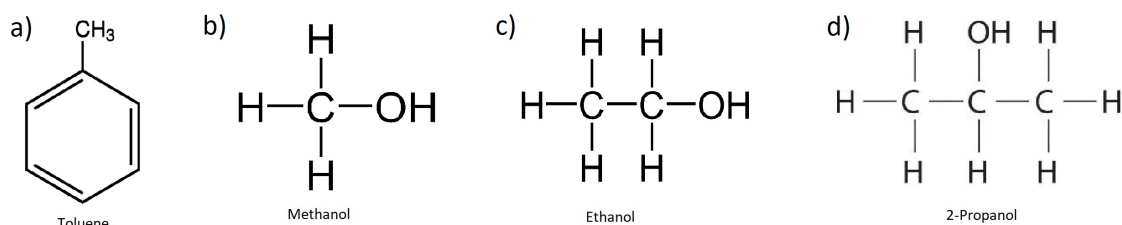


Figure 6.1: Molecular structure of: (a) toluene, (b) methanol, (c) ethanol, (d) isopropanol (adapted from Wikipedia).

They were chosen to perform the pilot experiments because they have been successfully used in the synthesis of SWCNTs, and also because, apart from toluene and methanol, the following two have double and triple C atoms bonded in their stable form. This could be one of the factors facilitating the formation of chains inside the SWCNTs.

The experimental considerations aiming at synthesizing the linear carbon chains are very similar to those described in chapter 4. However, the starting material was limited to the SWCNT-samples rich in 1.3 nm diameter nanotubes. This was first inspected with toluene, as already explained in chapter 5. Then, eDIPS SWCNTs (1.3 nm average diameter) were sonicated following also the procedure mentioned before, which combines a preliminary bath sonication and then tip sonication for 2 hours. The SWCNTs were drop casted onto the TEM grid as also described previously. The samples were treated first with at least two wavelengths. Additionally, different wavelengths were used to perform Raman measurements.

Table 6.1: Summary of the experimental parameters used for the samples sonicated with isopropanol, and main results. λ_{LA} , λ_{RS} , RBM, D_{inner} , Ch and LCC represent the laser wavelength for the laser annealing, laser wavelength for the Raman spectral measurements, RBM of the inner tube, diameter of the inner tube, the chirality assignment for the inner tube and LCC Raman peak, respectively.

Solvent	λ_{LA} (nm)	λ_{RS} (nm)	RBM (cm^{-1})	D_{inner} (nm)	Ch (n,m)	LCC (cm^{-1})
2-Propanol	568	647	-	-	-	$\sim 2006, \sim 2045$
2-Propanol	568	568	271	0.90	(11,1)	~ 1855
2-Propanol	568	531	355	0.68	(6,4)	-
2-Propanol	568	531	381	0.63	(7,2)	-
2-Propanol	568	515	355	0.68	(6,4)	-
2-Propanol	647	647	-	-	-	$\sim 2006, \sim 2045$
2-Propanol	647	568	-	-	-	~ 1855
2-Propanol	647	568	272	0.89	(11,1)	~ 1855
2-Propanol	647	531	355	0.68	(6,4)	~ 1855
2-Propanol	647	531	224	1.09	(12,3)	~ 1855
2-Propanol	647	515	-	-	-	~ 1855
2-Propanol	647	488	-	-	-	~ 1855

6.1.1 LCC@SWCNT from isopropanol

We start by this solvent because we have obtained the best results from using it. Since the experiments were all done in situ, we had to look for resonant features with the different lines. In the case of isopropanol, the laser annealing treatment was carried out using two frequencies, whereas the inspection of the RBMs and LCC-band was done using four different wavelengths: 647 nm (1.92 eV), 568 nm (2.18 eV), 515 nm (2.41 eV) and 488 nm (2.58 eV). This is summarized in table 6.1. Note that these steps were required for optimization. Additionally, analyzing the irradiation time and the laser power during the laser annealing were crucial parameters. This had to be done gradually because in this particular case the power of the laser can rapidly induce the growth but it can also destroy the LCCs. To better understand how the laser power affects the formation of the LCCs, spectra recorded with a 647 nm (1.2 eV) laser are shown in figure 6.4. We increased the power of the laser step by step until we reached 50 mW, as shown in Fig. 6.2. After 100 minutes of annealing and 20 mW two peaks at ~ 2007 and $\sim 2047 \text{ cm}^{-1}$ could be observed within the LCC-band range. We continued the

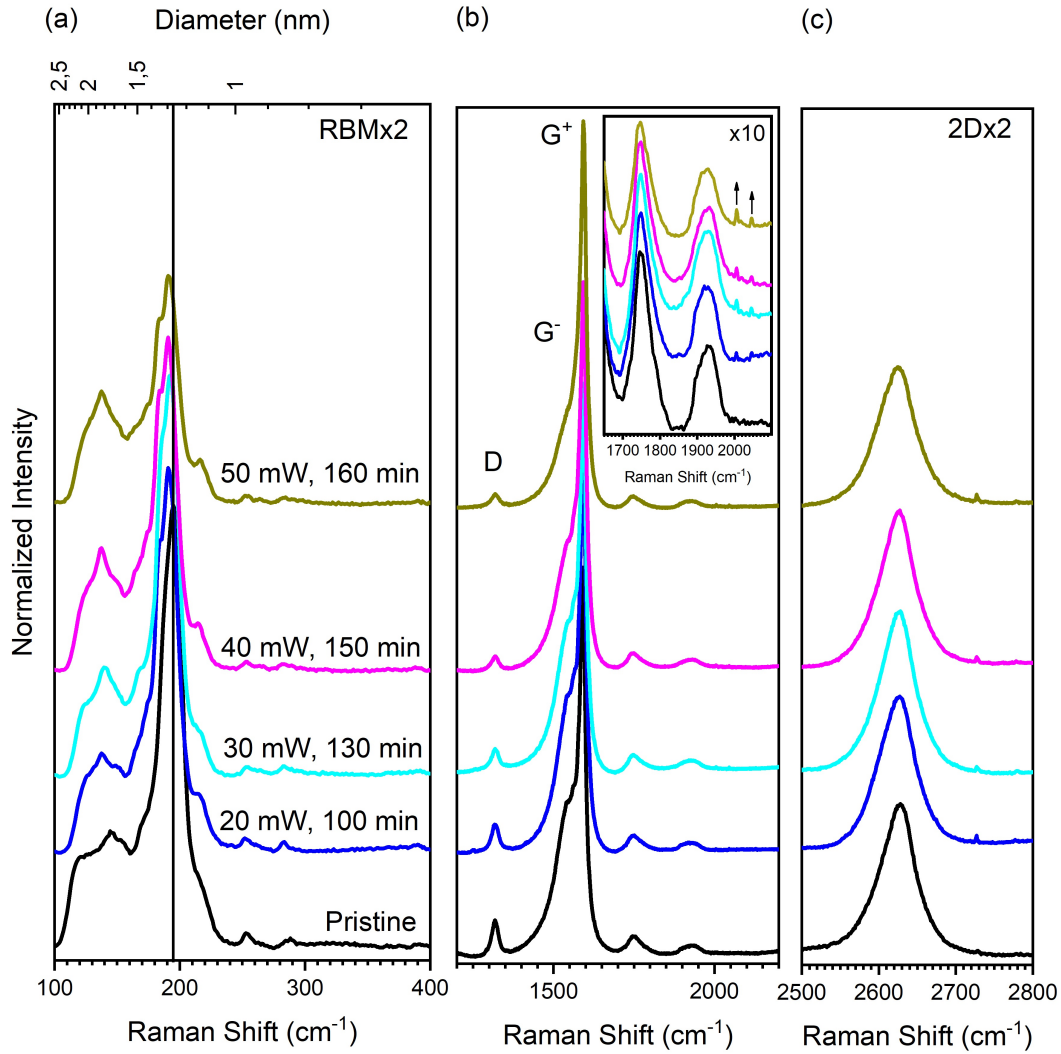


Figure 6.2: LCC@SWCNT in presence of isopropanol. Raman spectra recorded with the 647 nm excitation wavelength. SWCNTs with average diameter of 1.3 nm. The laser annealing was done for 160 minutes increasing the laser intensity up to 50mW. (a) RBM, (b) D and G bands, (c) 2D-band.

irradiation for 60 more minutes until the laser power reached 50 mW. Intuitively we can draw the conclusion that the higher laser power had a stronger influence over the time of exposure during the LCC growth. Now, if we look at the D band we notice that it interestingly decreases. The D band is related to the defects. Therefore, it cannot be discarded that the laser heating in presence of additional C atoms at this power can also have an effect on healing. Now focusing on the changes of the RBM on the left side spectra of Fig. 6.2, we can see that increasing the laser power and finding the onset for the growth of the LCC can also be related with a shift related to a charge transfer while the LCC grow inside the tubes, as already mentioned. We observed a gentle shift of the

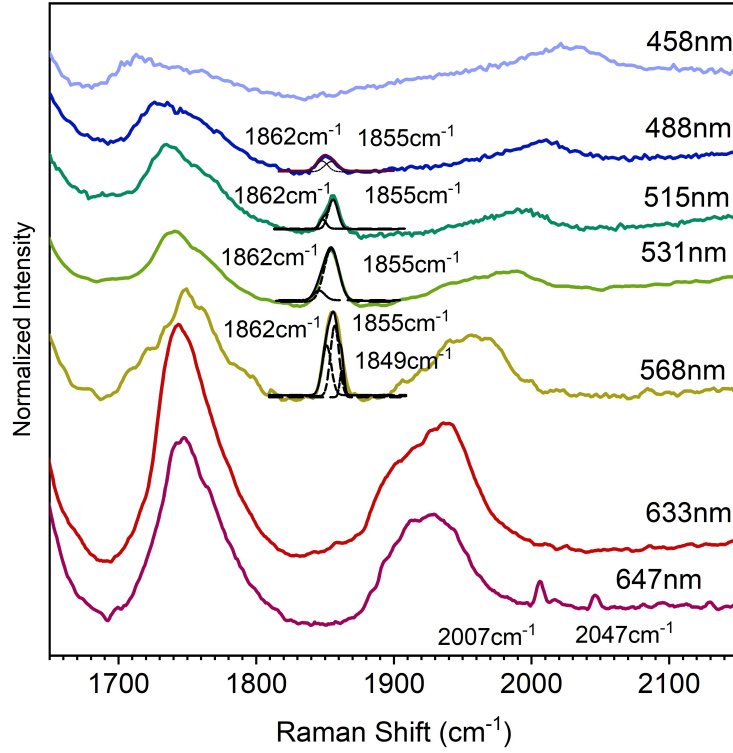


Figure 6.3: LCC@SWCNT in presence of isopropanol. Multifrequency Raman on the LCC- band region. The LCC-band has been fitted with different components represented by the dashed lines.

peak from 194 cm^{-1} to 191 cm^{-1} . In fact, this could mean that the diameter of the SWCNTs expands from ~ 1.27 to $\sim 1.3 \text{ nm}$ due to the presence of the LCC.

The samples were further inspected with multi-frequency Raman and the spectra are shown in Fig. 6.3. We have paid special attention on the LCC band, which was seen around 1855 cm^{-1} with the 531 nm excitation. The intensity of the LCC-band is different when recorded with different excitations. Note that the spectra were normalized to the laser power. For the spectra recorded with 568 , 531 , 515 , and 488 nm excitation wavelength, three components could be identified in $\sim 1862 \text{ cm}^{-1}$, $\sim 1855 \text{ cm}^{-1}$, and $\sim 1849 \text{ cm}^{-1}$. The center of the component corresponds to chains that differ in length and their intensity is dictated by their population. Note also that using 647 nm we could identify two peaks at 2007 and 2048 cm^{-1} , whereas no chain was in resonance with the 458 nm , including the Raman feature around $\sim 1855 \text{ cm}^{-1}$ became zero.

Let us analyze this in further detail. In Fig. 6.3 we could see that the LCC is formed by two well defined components at $\sim 1862 \text{ cm}^{-1}$, and $\sim 1855 \text{ cm}^{-1}$. Now, in Fig. 6.4 spectra of a sample annealed for 160 minutes with 647 nm laser wavelength but recorded

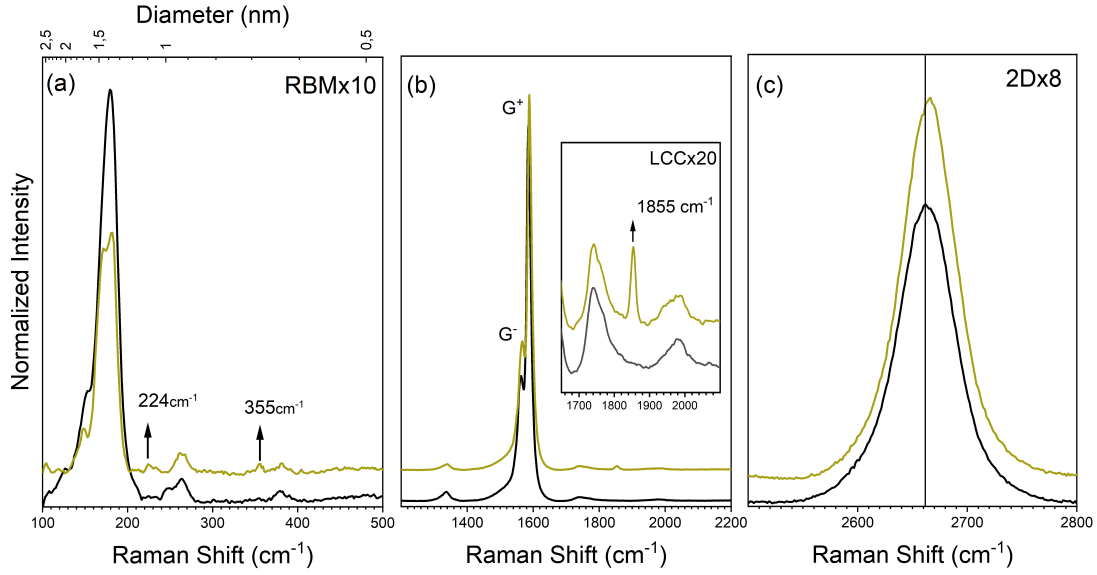


Figure 6.4: LCC@SWCNT in presence of isopropanol: Raman spectra before and after laser annealing with a 647 nm laser recorded with 531 nm wavelength. The signals from both, inner tubes and the LCCs can be observed. The line in (a) and (c) is a guide to the eye.

with the one of 531nm (2.33 eV) laser excitation are shown. In the the RBM region we can clearly observe the formation of two new peaks at 224 and 355 cm^{-1} comparing spectra pre and post annealing treatment. These correspond to the formation of new inner tubes of 1.09 and 0.68 nm diameter respectively. Assisted by the Kataura plot, the multifrequency Raman study allows assigning this signals to the (12,3) and (6,4) chiralities which are a metallic and a semiconducting nanotube respectively. The D band decreases after the treatment, which hints for a healing of defects in this case as well. Regarding the LCC-band, note that around the $\sim 1850 \text{ cm}^{-1}$ the lenght of the LCC is around of ~ 10 C atoms. For the 2D band, we can see a slight shift, which can be attributed to the formation of the new components inside of the SWCNT that alter the π electronic structure.

To better visualize the population of the chains with different lengths, the intensity of the different components of the LLC-band taking into account a normalization with the laser power has been plotted versus the energy of the laser excitation. Fig. 6.5 allows us visualizing that a maximum can be identified always around 2.18 eV, which is the resonance energy. The population of chains in specific lengths is consistent independently from the excitation wavelength used to measure them.

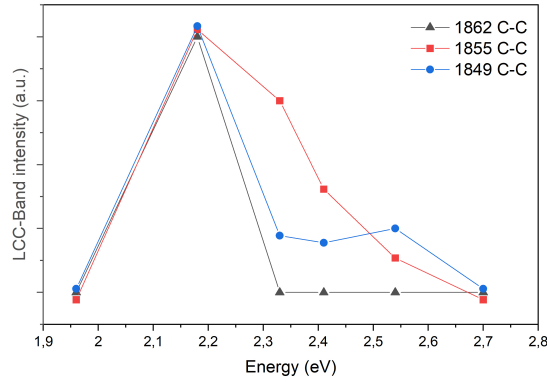


Figure 6.5: The intensity of the LCC subcomponents (1862, 1855, 1849 cm^{-1}) obtained by laser annealing with SWCNT dispersed in isopropanol as a function of the laser energy used for the annealing.

6.1.2 LCC@SWCNT from methanol

The next solvent we used was methanol. As well as in the previous cases presented, we used samples synthesized by eDIPS with a narrow diameter distribution centered on 1.3 nm and subsequently dispersed the SWCNT in methanol following the same procedures of sonication using bath and tip sonication.

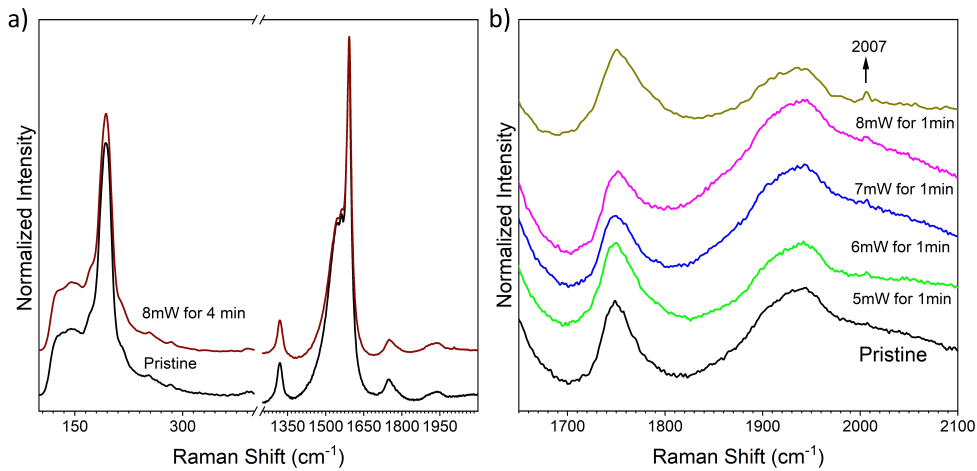


Figure 6.6: LCC@SWCNT in presence of methanol recorded with a 647nm laser excitation wavelength: a) Raman spectra before and after laser annealing of SWCNTs dispersed in methanol . b) Progressive increase of intensity of a peak located at 2007 cm^{-1} .

The full Raman spectrum is shown in Fig. 6.6 where the very pronounced RBM corresponding to the initial tubes and the other features corresponding to the SWCNTs were not altered in any manner after the annealing treatment with 8 mW for 4 minutes.

Somewhat, changes in intensity could be registered but neither additional peaks nor alteration of the spectral features were seen. We also performed multi-frequency Raman but no internal tube formation could be identified with the different available lasers. However, while using the 647nm wavelength laser as shown in the right panel of Fig. 6.6, the formation of a new peak at $\sim 2007 \text{ cm}^{-1}$ in the LCC-band could be identified. Interestingly, the formation of a LCC left some evidence but we saw no formation of an inner SWCNT.

Table 6.2: Summary of the experimental parameters used for the samples sonicated with ethanol, and main results. λ_{LA} , λ_{RS} , RBM, D_{inner} , Ch and LCC represent the laser wavelength for the laser annealing, laser wavelength for the Raman spectral measurements, RBM of the inner tube, diameter of the inner tube, the chirality assignment for the inner tube and LCC Raman peak, respectively.

Solvent	λ_{LA} (nm)	λ_{RS} (nm)	RBM (cm^{-1})	D_{inner} (nm)	Ch (n,m)	LCC (cm^{-1})
Ethanol	647	647	-	-	-	~ 2006
Ethanol	647	568	314	0.77	(10,0)	~ 1855
Ethanol	647	647	-	-	-	~ 1855

6.1.3 LCC@SWCNT from ethanol

Next, ethanol was used attempting to grow LLCs also using the 1.3 nm diameter eDIPS SWCNTs. Since the 647nm excitation wavelength had given so far the best results during the annealing process, we did these experiments using that specific laser. Note that the same wavelength has allowed us to better identify the LCCs in previous experiments. As shown in the left panel of Fig.6.7 the intensity of the RBMs after exposure to the beam decreased significantly. Furthermore, although there is no significant formation of chains, we still were able to identify a signal at 2007 cm^{-1} as shown in the middle panel of Fig. 6.7. These measurements were made with 647 nm and the annealing to promote the growth was followed with 568 nm excitation wavelength. Surprisingly, in the right side panel of Fig. 6.7 an LCC band around 1855 cm^{-1} could be identified and its intensity increased according to the laser power. At this point it is important to remark that ethanol was the feedstock used in Ref. [61]. In that report, the material grown in high vacuum systems with up to 6000 atoms in length could be demonstrated. Surprisingly, working at very small volumes has not resulted into the efficient production of LCCs that is observed at larger volumes.

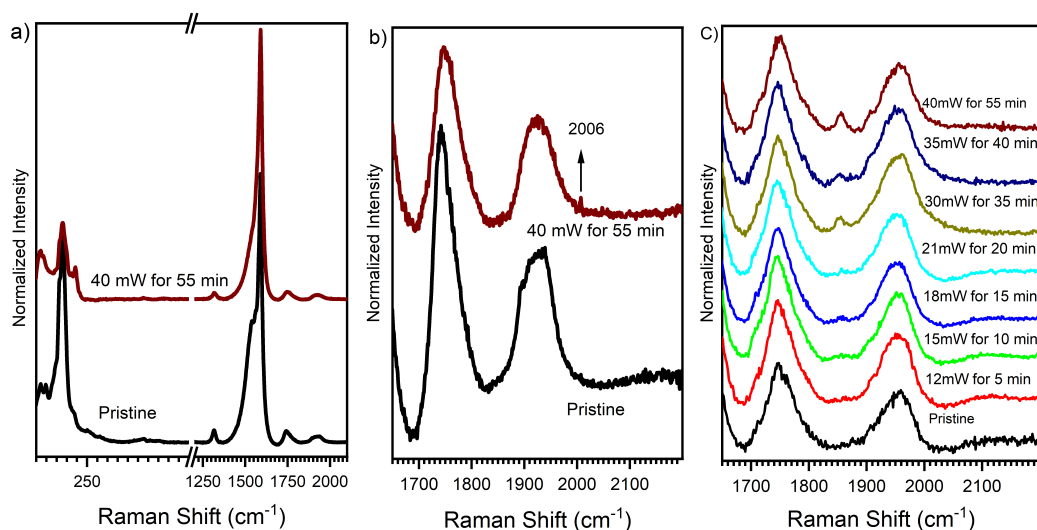


Figure 6.7: LCC@SWCNT in presence of ethanol: Raman study. a) Full Raman spectra recorded with a 647nm wavelength b) LCC band showing the formation a small peak in 2007 cm^{-1} . In RBM the inner tube is not observed. c) The same sample was follow with RAMAN spectroscopy 568 cm^{-1} laser excitation, it is observed the formation of peak in 1855 cm^{-1} LCC band.

6.1.4 LCC@SWCNT from toluene

The last solvent was toluene. It had actually been the first one to be tested, as reported in the previous chapter. We had only observed that the possibility to grow chains existed and the growth was observed to occur when lasers with wavelengths of 647 nm (1.92 eV) and 568 nm (2.18 eV) were used for the laser annealing. It is important to remark that toluene made possible the growth of a large amount of inner tubes. Compared to the other three solvents, the structure of toluene has a benzene ring, which can be responsible for the preferential formation of tubes and not of LCCs.

When laser annealing is applied to toluene dispersed SWCNT, the formation of chains cannot be systematically identified. However, in the Raman spectra, peaks located around 1850 cm^{-1} occasionally appear along with the inner tubes when measuring with the 568 nm laser wavelength. The signal is high and has more than one component but it is not consistently observed in a systematic study. Also as expected, we found that the LCCs were very sensitive to the laser power. As intermediate states, the LCCs can be decomposed into shorter fragments whereas the inner tubes are still well protected and stable under the same laser power. Furthermore, we noticed that the LCC band always starts to appear after the formation of the inner tubes. This confirms that the inner tube plays a role as template for the LCC growth.

Table 6.3: Summary of the experimental parameters used for the samples sonicated with toluene, and main results. λ_{LA} , λ_{RS} , RBM, D_{inner} , Ch and LCC represent the laser wavelength for the laser annealing, laser wavelength for the Raman spectral measurements, RBM of the inner tube, diameter of the inner tube, the chirality assignment for the inner tube and LCC Raman peak, respectively.

Solvent	λ_{LA} (nm)	λ_{RS} (nm)	RBM (cm^{-1})	D_{inner} (nm)	Ch (n,m)	LCC (cm^{-1})
Toluene	568	647	-	-	-	~ 2005
Toluene	568	568	271	0.90	(11,1)	~ 1855
Toluene	568	568	377	0.64	(7,2)	-
Toluene	568	568	336	0.72	(6,5)	-
Toluene	568	568	308	0.79	(10,0)	-
Toluene	568	515	409	0.59	(5,4)	~ 1855
Toluene	568	515	378	0.64	(7,2)	-

6.1.5 Growth of linear carbon chains inside B-doped SWCNTs

In the spirit of finding a broader applicability of the method, additional experiments were done using as templates boron doped SWCNTs (CB_xSWNT) produced in our lab. The peculiarity on this starting material is the fact that nanotubes grown by HV-CVD from triisopropyl borate have a very narrow diameter distribution and their diameters are significantly smaller compared with pristine tubes grown with other carbon feedstocks used in standard CVD. These nanotubes are produced in our laboratory and they have carefully been optimized. They have also been purified in collaboration with the group of professor Hiromichi Kataura at AIST in Japan. In summary, the CB_xSWNT starting material are tubes with diameters in the range from 0.9 to 1.3 nm primarily. This diameter distribution is not shown in this PhD thesis, as it has been previously been reported in our groups publications. For the purpose of growing linear carbon chains, only pilot experiments were performed using toluene as solvent. The 568 nm excitation wavelength was used for measuring and annealing the samples. It is important to remark that theoretical work reported by Kang et al. [57] has suggested that the use of CB_xSWNT may increase the possibility to encapsulate LCCs. Since CB_xSWNT are expected to be p-type doped, having a system of a SWCNT with an encapsulated chain is particularly attractive from the point of view, that it provides an extra tool to control the electronic properties of the hybrid system. In order to asses the degree of control, we would need a reference undoped sample but this was still not available. More related

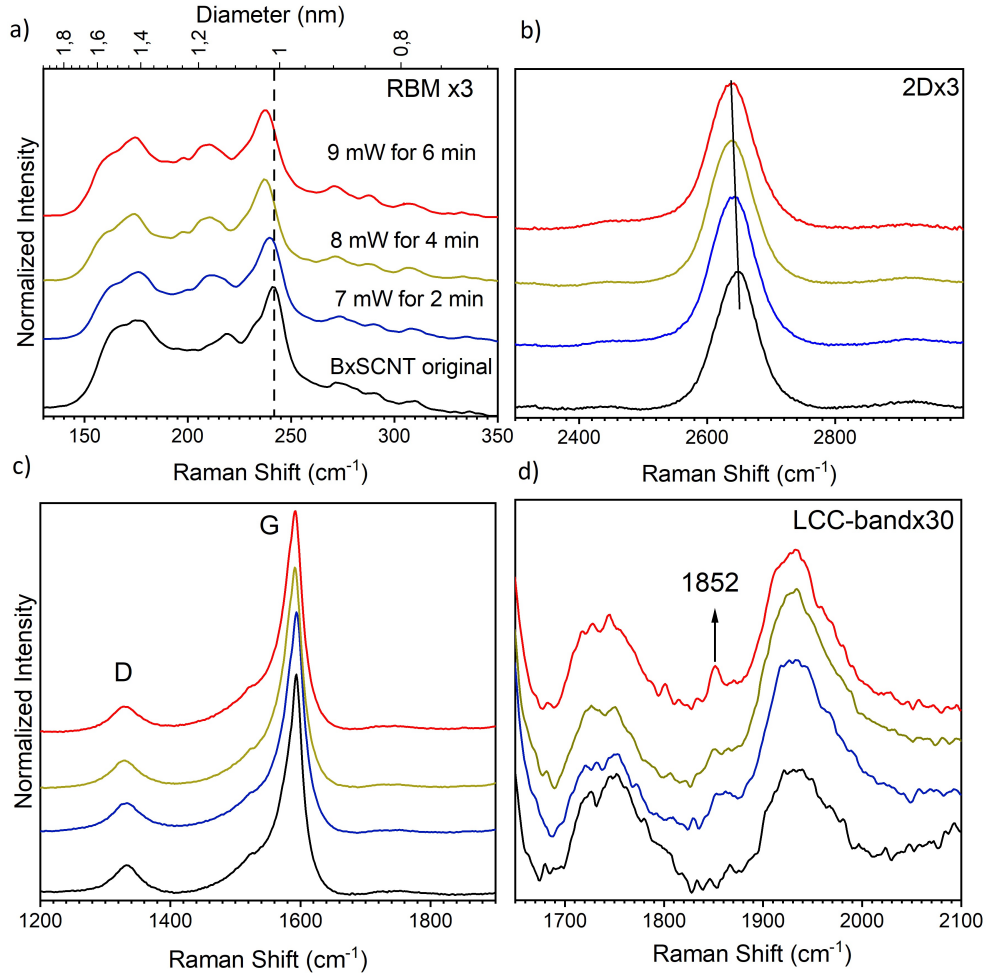


Figure 6.8: LCCs@CB_xSWNTs: Raman spectra excited by a 568 nm laser. Spectral evolution during the formation of LCC within a time interval of 9 minutes increasing the intensity of the laser up to 9 mW (the spectra show the initial stage in the bottom and the three last recordings at 7, 8 and 9 mW respectively: (a) RBM , (b) 2D-band , (c) D and G bands (d) LCC-band.

to the specific experiments, the samples were inspected by Raman Spectroscopy at the beginning with the 568 nm excitation wavelength. In the RBM region, a shift from 242 to 236 cm^{-1} can be observed, which corresponds to 1.01 to 1.04 nm respectively. This is the first indicator that a charge transfer is taking place and it can at least partially be attributed to the growth of inner material. Also the shift in the 2D band shown top right panel of Fig. 6.8 from ~ 2649 to ~ 2639 cm^{-1} can be related to this exchange. On the other hand, looking at the bottom left figure, we have observed that the D band is not altered, suggesting a minimal creation of defects (if at all) during the laser annealing process. Finally the bottom right spectrum provides the confirmation of the chain growth where the LCC band can be seen around ~ 1850 cm^{-1} .

7 Conclusions and future perspectives

The primary goal of this work was inspired on applications where placing carbon nanotubes with known electronic properties on a specific spot is necessary. With this challenge in mind, a setup to perform *in-situ* annealing while measuring Raman spectroscopy on carbon nanotubes was designed. The system developed during this PhD work is a vacuum chamber with a quartz window under which, a sample can be placed and irradiated with the laser beam of a Raman spectrometer. Although there were some technical challenges, the system could run without any problem and the planned experiments were performed. These experiments and the relevant results have been thoroughly described in chapters 4 to 6. One of the key aspects for the successful experiments shown here was the availability of the eDIPS samples. We had samples with different diameters (on average between 1.3 and 1.7 nm). Although the growth mechanism could not be determined, the availability of small diameters was crucial to make the synthesis feasible. Larger nanotubes are more prone to radiation damage with the focused beam power we used and for these optimization phase the very stable samples were extremely important. We have achieved the growth of tubes inside the hollow core of SWCNTs. This resulted into DWCNTs where the chirality and metallicity control were hinted. This is a key result for applications since the overall properties of DWNTs depend on both, the inner and the outer tube. Furthermore, a question we consider important to solve is the source for the carbon atoms that take part on the growth of the tubes. Since we used different solvents for all tests, the bath sonication seems to have a very particular role. We believe the main C source is the solvent where the tubes were dispersed and in second place the carbonaceous impurities that might exist inside the tube. Therefore, the duration of sonication is an important step to form the inner tube. It is also important that the molecules reach the hollow core of the tubes and therefore the sonication times are crucial. Ideally, a future study should focus on a more mechanistic approach to the growth but adding an imaging

study with enough space resolution. Damaging the tubes with the sonication process is unavoidable. To optimize this without compromising the onset for the growth of inner material, different time intervals were tested, and we concluded the best recipe was a combination ultrasonic bath and subsequently the tip sonicator. The next variable we had to consider was the laser wavelength and power to be used. We tested the following lines for annealing: 647 nm (1.92 eV), 568 nm (2.18 eV), 515 nm (2.4 eV), and 488 nm (2.54 eV) and set a maximum at 50mW for our trials at the beginning. However, we noticed it was extremely important to use lower power. Previous experiments on DWCNTs from the decomposition of C60 peapods using a high laser power (300mW) were our first guide but we noticed a few milliwatts of power were enough to create inner nanotubes. This was suspected but it can only be concluded because we placed very small amounts of materials on TEM grids. This meant that we were dealing with tens of nanotubes in small bundles. From the gradual increase of the RBM we could conclude that the laser power is linearly related to the formation of the inner tube. Now, regarding the use of multi-frequency Raman it is important to recall that it was our main guide to the feasibility to grow as well as to the quality of the result. Since we realized the laser characteristics can influence the type of nanotubes that can grow inside, controlling the chirality and metalicity by these means is the ultimate goal. Since this requires considerable time for optimization, it was not possible during my PhD time but such promising experiments should be considered for future studies. Now turning to the growth of LCCs inside the tubes, our success limit were LCCs with a length of ~ 20 atoms in eDIPS SWCNTs of 1.3 nm of diameter in average. However, this is a very solid standpoint since this could be confirmed with Raman spectroscopy, which revealed a LCC band where DWCNTs were not necessarily identified. The growth of LCC was mostly successful with the 647nm and 568nm lasers for the four solvents (methanol, ethanol, iso-propanol, and toluene). This outcome might be related to the fact that the dissociation of the feedstock is not produced drastically when the energy of the photon is not high and potentially only increases the probability of carbon atoms to bond. Toluene is the solvent, with which the largest number of inner tubes with different chiralities were formed. We believe that the benzene ring in toluene helps in the formation of the inner tubes. With Methanol, which has one C atom in its chemical structure, the formation of inner tubes was not observed, however, a peak grew around 2007 cm^{-1} , which is assigned to the LCC a few atoms could be seen and it might be a proof of possibility to grow a chain without an inner tube. In the case of

ethanol, that has 2 carbon atoms in its chemical structure, the formation of a single 0.77 nm (10,0) inner tubes was observed, in addition to the formation of LCC with a dozen atoms assigned from a Raman response about 1855 cm^{-1} . The best LCC growth was obtained with isopropanol. Note that we performed TEM studies but I did not include them in this PhD thesis because they were not conclusive. Furthermore, we found that LCCs are very sensitive to the power of 568 nm laser wavelength. The power in this case is crucial, since there is a threshold at which the LCCs get completely destroyed. As intermediate states, the LCCs can be decomposed into shorter fragments. Finally looking into different materials with interesting physical properties, the laser annealing treatment was applied to BC_xSWNTs dispersed in toluene where we could successfully prove the feasibility to grow LCC.

This PhD work has been extensively devoted to optimization rather than the exploration of the physical phenomena or applicability of the new structures. However, it has provided some key insight into the real feasibility to make DWCNTs and LCCs on specific spots. Therefore, there is still a very rich playground in which I would like to devote some of my future research time.

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