Chapter 1: Literature Review on Carbon Nanotubes

1.1. Introduction

Carbon Nanotubes (CNTs) are believed to be the ultimate nanomaterial, due to their exceptional thermal conductivity, electronic properties, and mechanical strength. Discovered by Iijima Sukumo\(^1\), an electron microscopist from the NEC laboratory in Japan in 1991, they have been capturing the imagination of physicists as well as chemists for the last thirteen years. They are the fifth existing form of solid-state carbon; the four other forms have been: diamond, graphite, non-crystalline structures like charcoal, and fullerene.

The discovery of CNTs is a direct consequence of the discovery of cage-like molecules named fullerenes (C\(_{60}\)) that are solely composed of sixty carbon atoms arranged in pentagonal and hexagonal rings. Fullerenes were discovered in 1985 by Kroto et al.\(^2\) who synthesized very small amounts of C\(_{60}\) by laser vaporization of graphite in a helium atmosphere. Their discovery was closely followed by the work of Krätschmer et al.\(^3\) who synthesized larger amounts of C\(_{60}\) by carbon arc-discharge. Iijima\(^1\) subsequently discovered CNTs by studying with High-Resolution Transmission Electron Microscopy (HRTEM) the cylindrical deposit that was formed on the graphite cathode after arc-evaporation.

CNTs can be viewed as wrapped sheets of graphene, closed at each end with half fullerene caps. They are a few nanometers wide, several micrometers long, and one atom in wall thickness. The CNTs’ formation comes from the energy lowering of the graphene sheets’ dangling bonds, leading to the rolling-up of the sheets. The bonding of carbon atoms in a CNT and a graphene sheet are very similar, and the sp\(^2\) hybridization structure of graphene is the major constituent of CNTs.

Two types of CNTs possess a high structural perfection. Single-Walled CNTs (SWNTs) consist of a single graphene sheet wrapped in a cylindrical fashion (Figure 1.1). Multi-Walled CNTs (MWNTs) are composed of multiple graphene sheets concentrically rolled-up. SWNTs present loops and curves while MWNTs are most of the time straight. MWNTs were the first type of CNTs that were discovered in 1991. Less than two years
later, Iijima et al.\textsuperscript{4} in Japan and Bethune et al.\textsuperscript{5} in the United States simultaneously discovered SWNTs.

![Wrapped sheet of graphene](image)

**Figure 1.1.** Wrapped sheet of graphene\textsuperscript{6}.

CNTs can be synthesized by carbon arc-discharge, laser ablation, and chemical vaporization. In the arc-discharge method, carbon atoms are evaporated by plasma of helium gas ignited by high currents passed through opposing graphite anode and cathode, and condensed on the surface of the graphite cathode. The laser ablation method involves the ablation of a carbon target containing a small percentage of catalyst materials like nickel and cobalt with intense laser pulses. During the experiment, a flow of inert gas is passed through the growth chamber to collect the grown CNTs. In the chemical vapor deposition technique a catalyst is heated to high temperature in a tube furnace while a hydrocarbon gas is flowed through the tube at the same time. Cooling the system at room temperature enables collection of the produced CNTs.

CNTs behave conceptually as a prototype one-dimensional quantum wire, and are therefore of great interest in the fabrication of electronic devices. Small-angle scattering of electrons or holes by defects or phonons that usually occurs in a three-dimensional system do not occur because carriers inside the CNT can only move forward or backward. This ballistic behavior is responsible for the large amount of current that can flow through the system.

In the following sections, theoretical aspects relevant to the structure and properties of CNTs are provided. Methods of purifying and solubilizing CNTs in aqueous and organic solvents are also covered. A section dedicated to selected applications of CNTs follows.
1.2 Literature review

1.2.1 Structure and Properties of Carbon Nanotubes

The structure and properties of CNTs are closely interrelated. The various properties of CNTs will depend on the different geometries that can be created on the surface of the cylindrical graphene sheet composing them. The following paragraphs present the different geometrical characteristics of CNTs and the different electronic properties arising from these features7-18.

1.2.1.1 Geometrical Structure of Carbon Nanotubes

The structure of a CNT is defined by the tube diameter $d_t$, the chiral angle $\theta$, and the chiral vector $C_h$, which connects two crystallographically equivalent sites on a graphene sheet. $C_h$ is expressed as:

$$C_h = n\mathbf{a}_1 + m\mathbf{a}_2 = (n,m)$$

(1.1)

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the basis vectors of the graphene lattice, and $n$ and $m$ are integers defining $d_t$ and $\theta$. Figure 1.2 shows a schematic of a graphene sheet displaying the lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, the chiral vector $C_h$, and the limiting zigzag $(n,0)$ and armchair $(n,n)$ cases. The graphene layer can be rolled up along $C_h$ to join the vectors OB and AB’, and form a CNT. The length, a, of $\mathbf{a}_1$ and $\mathbf{a}_2$ is directly deduced from the distance $a_{C-C}$ between two carbon atoms:

$$a = \sqrt{3} a_{C-C}$$

(1.2)

Therefore:

$$\mathbf{a}_1 = \left(\frac{\sqrt{3}a}{2}, \frac{a}{2}\right) \quad \text{and} \quad \mathbf{a}_2 = \left(\frac{\sqrt{3}a}{2}, -\frac{a}{2}\right)$$

(1.3)

The circumference of the CNT is expressed as:

$$L = |C_h| = a\sqrt{n^2 + m^2 + mn} \quad 0 \leq |m| \leq n$$

(1.4)

The diameter of the nanotube can be directly deduced from equation (1.4):
The chiral angle $\theta$ is defined as the angle between the zigzag axis and $C_h$, and is given as a function of $n$ and $m$:

\[
\sin \theta = \frac{\sqrt{3m}}{2\sqrt{n^2 + m^2 + nm}} \quad 0 \leq |\theta| \leq 30^\circ
\]  

(1.6)

\[
\cos \theta = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}
\]  

(1.7)

\[
\tan \theta = \frac{\sqrt{3m}}{2n + m}
\]  

(1.8)

**Figure 1.2.** Schematic of a 2D graphene sheet illustrating the lattice vectors $a_1$ and $a_2$, and the roll-up vector $C_h$.  

The vector $T$ perpendicular to $C_h$ is the translation vector of the nanotube, and defines its 1D unit cell. $T$ is given by:

\[
T = t_1a_1 + t_2a_2 \equiv (t_1, t_2)
\]  

(1.9)

with

\[
t_1 = \frac{2m + n}{R_d} \quad \text{and} \quad t_2 = -\frac{2n + m}{R_d}
\]  

(1.10)

where $d_R$=d, the highest common divisor of (n,m), if n-m$\neq$3dr, and $d_R=3d$ if n-m=3dr, $r$ been an integer.
The length of $T$ is given by:

$$T = \frac{\sqrt{3}L}{d_R}$$  \hspace{1cm} (1.11)

The number of hexagons $N$ per unit cell of an achiral CNT is governed by:

$$N = \frac{2(m^2 + n^2 + nm)}{d_R}$$  \hspace{1cm} (1.12)

CNTs can be either zigzag $(n,0)$, armchair $(n,n)$ or chiral $(n,m)$. Figure 1.3 shows the structures of these three different types of CNTs.

![Figure 1.3. Examples of armchair, zigzag and chiral nanotubes](image13.png)

The different names stand for the way the carbon atoms align in a CNT. For the armchair nanotube, $\theta=30^\circ$, and for the zigzag nanotube, $\theta=0^\circ$. Armchair and zigzag nanotubes have a mirror plane and are thus achiral. All the other nanotubes possess chiral angles between these two values and are termed chiral.

### 1.2.1.2 Electronic Properties of Carbon Nanotubes

Metallic CNTs can carry current densities two to three orders of magnitude higher than metals such as copper or aluminum. Field-Effect Transistors based on semiconducting CNTs (FET-CNTs) can exhibit electron mobility as high as $9000 \, \text{cm}^2/\text{Vs}$. 

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which is twenty times higher than common semiconductors like silicon. These exceptional electronic properties of CNTs are directly related to their geometrical and electronic structure. In this section, the electronic properties of Single-Walled Carbon Nanotubes (SWNTs) will be emphasized. Multi-Walled Carbon Nanotubes being built from concentrically nested SWNTs, their overall electronic properties can be derived from those of SWNTs and will be determined by the external shell of the MWNT.

The electronic band structure theory of graphite, coupled with boundary conditions imposed by the rolling-up of the graphene sheet forming a CNT enables to determine the band structure of a CNT. Once the band structure of a CNT is known, it is possible to determine its metallic or semi-conducting nature.

A graphene sheet is composed of a hexagonal lattice of carbon atoms (Figure 1.2). Among the four valence electrons of the carbon atoms, only one of them, in the $\pi$($2p_z$) state, participates in the conductivity of graphite. The three other electrons are tightly bound to their neighbors, and do influence the conductivity. The electronic band structure theory of graphite is based on the energy of dispersion of graphite for the $\pi$ ($2p_z$) electrons (equation (2.13)) developed using the “tight binding approximation”.

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

where $\gamma_0$ is the energy overlap integral between nearest neighbors, $a=1.42 \times \sqrt{3}$ Å is the lattice constant, and $k_x, k_y$ are the component of the electron wave vector $k$.

The 3-dimensional plot of the energy of dispersion displays the conduction and valence bands of graphite. The points $\mathbf{K}$ where these two bands touch and are degenerate define the Brillouin zone (Figure 1.4). The Brillouin zone is a geometrical shape that contains the valence electrons of the graphite crystal. Its planes define in momentum space ($k$-space) the location of the band gap. Electron wave vectors lying within the Brillouin zone are in the same energy band. The Brillouin zone geometrically corresponds to the reciprocal lattice of the graphene sheet hexagonal lattice (Figure 1.5). Folding the Brillouin zone enables definition of the allowed electronic states (band structure of CNTs) resulting from the quantization of the wave vector in the direction perpendicular to the fiber axis.
Figure 1.4. Band structure of the 2D graphene sheet. The valence and conduction band meet at 6 points defining the Brillouin zone$^6$.

This quantization results in periodic boundary conditions along the circumferential direction defined by:

$$C_h \cdot k = 2\pi q$$  \hspace{1cm} (1.14)

where q is an integer and the chiral vector $C_h$ is determined by the indices n and m.

Only a certain set of “$k$” states of the graphene sheet is allowed. These allowed electronic states (subbands) lie along parallel lines separated by a spacing of $\frac{2\pi}{|C_h|}$ in the Brillouin zone. Figure 1.6 shows examples of the allowed states for a metallic tube (Figure 1.6b) and a semiconducting tube (Figure 1.6c). The nanotubes are metallic if one of the subbands passes through a $K$ point, and semiconducting otherwise.
Figure 1.5. Unit cell of the hexagonal lattice of a sheet of graphene and the corresponding Brillouin zone. $a_1$ and $a_2$ are the basis vectors and $b_1$ and $b_2$ the reciprocal lattice vectors.$^6$

Figure 1.6. (b) Example of the allowed 1D subbands for a metallic tube. (c) Example of the quantized 1D subbands for a semiconducting nanotube.$^6$

The periodic boundary conditions associated with the two limiting cases armchair and zigzag nanotubes can be deduced from equation (1.14):

$$k_{x(armchair)} = \frac{q}{n_x} \frac{2\pi}{\sqrt{3}a} \quad \text{with} \quad q = 1, \ldots, n_x \quad (1.15)$$

$$k_{y(zigzag)} = \frac{q}{n_y} \frac{2\pi}{a} \quad \text{with} \quad q = 1, \ldots, n_y \quad (1.16)$$

The 1-D energies of dispersion associated with these conditions are obtained by inserting equations (1.15) and (1.16) in equation (1.13):

$$E_{q(armchair)}(k) = \pm \gamma_0 \left\{ 1 \pm 4 \cos \left( \frac{q\pi}{n} \right) \cos \left( \frac{ka}{2} \right) + 4 \cos^2 \left( \frac{ka}{2} \right) \right\}^{\frac{1}{2}} \quad (1.17)$$
with $-\pi < ka < \pi$ and $q = 1, \ldots, n_x$

$$E_{q(zigzag)}(k) = \pm \gamma_0 \left[ 1 \pm 4 \cos \left( \frac{\sqrt{3}ka}{2} \right) \cos \left( \frac{q\pi}{n} \right) + 4 \cos^2 \left( \frac{q\pi}{n} \right) \right]^{1/2} \quad (1.18)$$

with $-\frac{\pi}{\sqrt{3}} < ka < \frac{\pi}{\sqrt{3}}$ and $q = 1, \ldots, n_y$

The periodic boundary condition associated with chiral CNTs is given by:

$$\sqrt{3}n_x k_x + n_y k_y a = 2\pi q \quad (1.19)$$

Inserting equation (1.19) in equation (1.13), and eliminating $k_x$ enables the determination of the 1-D energy of dispersion associated with chiral nanotubes:

$$E_{q(chiral)}(k) = \pm \gamma_0 \left[ 1 \pm 4 \cos \left( \frac{q\pi}{n_x} - \frac{n_x ka}{n_y} \right) \cos \left( \frac{ka}{2} \right) + 4 \cos^2 \left( \frac{ka}{2} \right) \right]^{1/2} \quad (1.20)$$

with $(-\pi < ka < \pi)$ and $(q = 1, \ldots, n_x)$

The electronic density of states (DOS) can be determined by summing the number of states at each dispersion energy level$^6$. In Figure 1.7, the density of states for two CNTs is plotted. When the density of states at the Fermi level ($E=0$) is finite, the CNT is metallic and when there is an energy gap at $E=0$, the CNT is semi-conducting. Armchair CNTs are metallic, while zigzag or chiral CNTs are metallic when $\frac{|n-m|}{3}$ is an integer, and otherwise semiconducting$^{11}$.

![Figure 1.7. Electronic density of states of CNTs](image-url)
1.2.2 Purification of Carbon Nanotubes

All currently used CNTs synthesis techniques produce not only CNTs, but also byproducts like amorphous carbon, incomplete fullerenes, metal catalyst, and carbon shells enclosing the metallic particles. The presence of these impurities hinders the CNTs properties, and therefore affects their applicability. Several research groups performed extensive work in order to obtain highly purified CNTs. Nitric acid treatment, sulfuric acid/nitric acid treatment, isothermal treatment and alternative treatments are discussed in the next sections.

1.2.2.1 Strong acids purification

Nitric acid treatment is the most commonly used approach to purify and functionalize CNTs with carboxylic groups that enable the solubilization of CNTs. It removes the metal catalyst particles from the CNTs soot, but also consumes the CNTs by attacking their sidewalls and produces carbonaceous impurities, which need to be further removed by centrifugation and washing with slightly basic water. It was first introduced by Liu et al.21. A method was developed that consisted of refluxing 8.5 g of laser-oven produced CNTs in 1.2 liters of 2.6M nitric acid for 45 hours. The resulting solution was centrifuged for two hours at 2400 rpm, and the supernatant decanted off. The sediment was then suspended in de-ionized water, and the solution centrifuged a second time. The final solids were then re-suspended in 1.8 liters of water and filtered through a poly(tetrafluoroethylene) (PTFE) filter membrane. Figure 1.8 shows pictures of raw CNTs and CNTs purified with nitric acid.
This research group extended this process to larger quantities of CNTs\textsuperscript{22}. They typically used one liter of 2-3 M, nitric acid for 10g of raw CNTs, 45 hours refluxing time, one centrifugation step and 3-4 washing steps after the acid treatment. The washing steps consisted of re-suspending in de-ionized water the sediment obtained after the first centrifugation, centrifuging the solution and decanting-off the resulting supernatant. The filtration method was also adapted to larger quantities of CNTs. A cross-flow filtration set-up was utilized in order to avoid the blocking of the filter membrane by the thickening of the CNTs filter cake. The yield obtained ranged from 10 to 20\%, depending on the quality of the starting material. Several research groups further studied and adapted this treatment. Dillon et al.\textsuperscript{23} refluxed 80 mg of CNTs produced by laser vaporization in 60 ml of a 3M solution of nitric acid for 16h at 120\degree C. The authors filtered the solution and obtained an 82 wt.-\% yield. The resulting CNTs were further oxidized in air at 550\degree C during 30 minutes, in order to remove the thick carbonaceous matrix encasing them after the acid treatment. The final yield was 20 wt.-\%. Figure 1.9 displays TEM pictures of the raw and purified CNTs.
Valentini et al.\textsuperscript{24} ultrasonicated 0.05g of CNTs in 60 ml of a 2.2M solution of nitric acid for 30 minutes at room temperature, and let it seat for 20 hours. Hu et al.\textsuperscript{25} studied different nitric acid treatment conditions to remove metal catalyst particles from electric arc-produced CNTs. They used 150 ml of nitric acid for 1g of CNTs. The raw CNTs were refluxed in a 3M solution of nitric acid for 12, 24, and 48h, in a 7M solution of nitric acid for 6 and 12h, and in 16M solution of nitric acid for 6 and 12h. Both the concentration and the refluxing time played a role in the yield and quality of the purified CNTs. Refluxing CNTs in a 3M solution of nitric acid for 12h resulted in a yield of 69\% of the starting material, while refluxing them in the same concentration of nitric acid for 24h resulted in a yield of 63\% of the starting material. These results confirmed that CNTs were not only purified but consumed by the nitric acid, which resulted in the apparition of additional carbonaceous impurities. Refluxing CNTs in higher concentrations of nitric acid (7 or 16M) for 6h resulted in lower yields, which was expected due to the increased acidic conditions. Refluxing CNTs in a 16M nitric acid solution for 6h resulted in a 28\% yield of the starting material, while refluxing them in a 16M nitric acid solution for 12h resulted in an almost complete destruction of the CNTs. The authors concluded that the 3 M/12h and the 7M/6h nitric conditions were the most efficient at removing metal catalyst particles from the CNTs, but also that a post
treatment was necessary in order to remove the carbonaceous impurities produced during the treatment.

A variation of the nitric acid treatment consists of using a combination of sulfuric acid and nitric acid to functionalize and exfoliate CNTs. Liu et al.\textsuperscript{21} sonicated CNTs in a (3:1) mixture of sulfuric acid and nitric acid for 24 hours at 40°C, in order to cut the nanotubes into smaller pieces. The tubes’ size decreased at a rate of 130 nm per hour. The authors explained the cutting of the nanotubes by the apparition of high temperature microscopic domains due to the sonication of the solution. Ando et al.\textsuperscript{26} first refluxed CNTs for 45h in hydrogen peroxide and then for 24 hours in a (3:1) sulfuric acid/nitric acid solution.

Zhang et al.\textsuperscript{27} compared the effect of the nitric acid treatment and the sulfuric acid/nitric acid treatment on the structure of CNTs. The as-produced CNTs were first purified with a 37% hydrochloric acid solution, in order to remove the catalyst particles utilized during the synthesis of the CNTs. The authors used a nitric acid treatment that consisted of refluxing 80 mg of purified CNTs in 50 ml of a 2.6M nitric acid solution for 48h. The sulfuric acid/nitric acid treatment consisted of sonicating 60mg of purified CNTs in 50 ml of a 3:1 mixture of sulfuric acid/nitric acid, for 24h. The comparison that the authors made was based on the FTIR (Fourier Transform Infrared) spectra of the resulting CNTs. For the CNTs treated with the mixture of acids, the peak assigned to the C=O vibration in the COOH (carboxylic) group shifted from 1737 cm\(^{-1}\) to 1720 cm\(^{-1}\), as the time of the treatment increased, while for the CNTs treated with nitric acid only, the peak assigned to the C=O vibration at 1740 cm\(^{-1}\) did not shift. These results indicated that for the mixture of acid, the number of carboxylic groups along the nanotube sidewalls increased with treatment time, while for the nitric acid, the amount of carboxylic groups stayed constant. This difference was attributed to the capacity of the mixture of acids to etch into the aromatic rings of the nanotubes, which led to the creation of more COOH groups.
1.2.2.2. Isothermal treatment

The isothermal treatment is an alternative oxidative treatment widely used to purify CNTs. Although it also purifies the CNTs, it does not cut them, and the damage usually occasioned to their electronic structure by strong acids purification treatments are strongly reduced. Chiang et al. developed the oxidative treatment first experimented by Dillon et al. CNTs initially cleaned with nitric acid were heated under a 5% O$_2$/Ar atmosphere, in a tube furnace at increasing temperatures and sonicated in hydrochloric acid during 10 minutes after each one hour heating step. The temperatures used were: 300, 400, 450 and 500°C. Table 1.1 displays the metal atomic percentage as well as the weight loss obtained after each heating step. The authors further refined this method by using only two temperatures 300 and 500°C, in order to maximize the removal of metal catalysts particles while minimizing the weight loss. These two temperatures were chosen based on the rate of oxidation of the different CNTs samples held at 425°C in air for 6h. Figure 1.10 gives the TGA (Thermal Gravimetric Analysis) curves for the four different oxidative temperatures. It shows that the largest changes in the oxidation rate occurred for samples, which were oxidized at 300 and 500°C. From Table 1.1, the authors deduced that the largest loss in metal catalyst particles also occurred after the oxidation steps at 300 and 500°C. Figure 1.11 shows TEM pictures of CNTs before and after treatment. It can be noticed that the black points corresponding to the metallic particles have almost completely disappeared for the purified sample.

Table 1.1. Metal atomic percentage and weight loss after each heating step$^{28}$.

<table>
<thead>
<tr>
<th>Step</th>
<th>metal atomic %$^a$</th>
<th>weight loss$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) as-purified Tubes@Rice SWNTs</td>
<td>1.71</td>
<td></td>
</tr>
<tr>
<td>(b) after water reflux</td>
<td>1.56</td>
<td>9.2</td>
</tr>
<tr>
<td>(c) heated in 300 °C, 5% O$_2$/Ar</td>
<td>1.44</td>
<td>8.7</td>
</tr>
<tr>
<td>(d) heated in 400 °C, 5% O$_2$/Ar</td>
<td>1.41</td>
<td>8.8</td>
</tr>
<tr>
<td>(e) heated in 450 °C, 5% O$_2$/Ar</td>
<td>1.43</td>
<td>12.2</td>
</tr>
<tr>
<td>(f) heated in 500 °C, 5% O$_2$/Ar</td>
<td>0.17</td>
<td>18.9</td>
</tr>
</tbody>
</table>

$^a$ $M_X/M_C \times 100$, where $M$ = atomic %, $X$ = Co + Ni, C = carbon.

$^b$ Total weight loss from the process is 57.8%.
Chiang et al.\textsuperscript{29} further modified this treatment, in order to improve the yield without altering the efficiency of the purification. A three-stage method was used with three oxidative temperatures: 225, 325, and 425°C. After each heating step, the CNTs were sonicated during 15 minutes in hydrochloric acid. The CNTs were then rinsed several times with water until the pH of the filtrate became neutral. An additional annealing stage was sometimes added, in order to further remove the residual acid possibly remaining in the CNTs after the treatment. Table 1.2 displays the metal catalyst particles’ atomic percentage as well as the weight loss after each treatment step.
The total weight loss was 69.1%, and the final metal particle atomic percentage was 0.03%. Figure 1.12 shows TEM pictures of CNTs before and after treatment. It can be noticed that the black points corresponding to the metallic particles have totally disappeared.

Other authors used modified versions of the method implemented by Chiang et al. Gajewski et al.\textsuperscript{30} heated CNTs in a tube furnace in an O\textsubscript{2}/Ar atmosphere, at 355°C, for 3 hours and 20 minutes, and subsequently washed them with hydrochloric acid. Valentini et al.\textsuperscript{24} oxidized CNTs at 400°C, for 1 hour, in air, and sonicated the resulting CNTs in 60 ml of hydrochloric acid for 4 hours. Moon et al.\textsuperscript{31} heated the CNTs in air, for 50 minutes at 470°C. The oxidized CNTs were immersed in hydrochloric acid and filtered several
times, until the color of the acid remained unchanged. The total yield that was obtained ranged from 25 to 30%, with less than 1% of the metal catalyst particles remaining. Strong et al.\textsuperscript{32} oxidized CNTs at 250°C for 12 hours in air, and extracted them in a Soxhlet extractor for 68-72 h with 600ml of hydrochloric acid diluted to 1 liter with de-ionized water. The resulting percentage of metal catalyst left was 0.2%. For each treatment presented, the purified CNTs were rinsed several times with water, in order to remove the residual hydrochloric acid trapped inside the CNTs.

### 1.2.2.3 Alternative treatments

Studies can be found in the literature that present purification treatments that differ from the strong acids treatment or isothermal treatments. Zhang et al.\textsuperscript{27} refluxed 50mg of CNTs in 30 ml of a solution of 0.2 M potassium permanganate and 0.2 M sodium hydroxide for 40 minutes, and subsequently added up 1.5g of sodium sulfate and 15 ml of sulfuric acid. The solution was then filtered and rinsed with slightly basic de-ionized water. Harutyunyan et al.\textsuperscript{33} heated 100mg of CNTs produced by the arc-discharge method in a microwave system (1.5kW, 2.45GHz) under a flow of dry air, for 30 minutes, at 405°C. The resulting CNTs were refluxed in a 4M solution of hydrochloric acid for 6 hours, rinsed and filtered with water. The authors obtained an approximate yield of 35%, and a residual metal content of less than 0.2 wt. %.

Georgakilas et al.\textsuperscript{34} proposed a purification method aimed at reducing the structural defects usually produced by classical oxidative treatments. It consisted of first functionalizing the CNTs, then purifying them, and finally removing the functional groups by heating the CNTs at 350°C, and annealing them at 900°C. The CNTs functionalization was based on the condensation of an aldehyde and a α-amino acid (glycine). The purification step consisted of slowly adding diethyl ether to a chloroform solution of the functionalized CNTs, which led to the precipitation of the carbonaceous particles. The metallic content was reduced to 0.4%.

Dalton et al.\textsuperscript{35-37} purified CNTs produced by the arc-discharge method by solubilizing them with a conjugated polymer (poly(p-phenylenevinylene-co-2,5-dioctyloxy-m-phenylenevinylene)), that adsorbed on the surface of the CNTs due to van
der Waals interactions between the phenyl rings of the polymer and the hexagonal lattice of the CNTs. The CNTs were effectively suspended in solution, while the carbonaceous particles precipitated at the bottom of the solution. Figure 1.13 (a) and 1.13 (b) display respectively the Raman spectra of a powder of raw CNTs and of the PmPV-CNTs composite material. The peak at 1350 cm$^{-1}$ is assigned to graphitic impurities and defects. The peak at 1581 cm$^{-1}$ is assigned to pure CNTs. The ratio of the intensities of the 1581 cm$^{-1}$ peak relative to the 1350 cm$^{-1}$ peak gives an indication of the ratio of impurities to pure material present in the system. The comparison of Figure 1.13 (a) and 1.13 (b) enabled the authors to conclude that the quantity of pure CNTs was higher for the composite material.

![Figure 1.13.](image)

**Figure 1.13.** (a) Raman spectrum of raw CNTS. (b) raman spectrum of the composite material$^{37}$. 

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1.2.3 Solubilization of Carbon Nanotubes

Carbon nanotubes form naturally packed and entangled crystalline ropes due to strong van der Waals attractions. This aggregation phenomenon hinders their applicability and diminishes the specific mechanical and electronic properties of each nanotube. In order to insert them into composites, or use them as components of electronic devices, it is essential to be able to obtain well-separated CNTs. Substantial efforts have been dedicated to the solubilization and dispersion of CNTs. The different strong acid treatments presented in section 1.2.2.2 are not only used to purify CNTs, but also to functionalize them with carboxylic groups in order to render the CNTs soluble in water. Due to their shortening effect on the size of the CNTs, it appeared necessary to developed alternative treatments. The existing alternative techniques used to solubilize CNTs can be separated into two different approaches: covalent and non-covalent functionalization. These two approaches are described in the following paragraphs.

1.2.3.1 Covalent Functionalization of Carbon Nanotubes

Boul et al. rendered CNTs soluble in different types of solvents like chloroform, methylene chloride and tetrahydrofuran by covalently attaching alkanes to their sidewalls. The CNTs were fluorinated by passing fluorine diluted with helium through a Monel flow reactor containing a sample of CNTs. The F₂ and He flow rates were 2 and 20 sccm respectively, and the reaction time 5 hours. The CNTs could survive the fluorination process for temperatures as high as 325°C. Two approaches were used to attach the alkanes on the surface of the fluorinated CNTs. The first approach consisted of reacting the fluorinated CNTs with an excess of alkyl-lithium species. The second approach consisted of using a Grignard synthesis with alkyl magnesium bromides in tetrahydrofuran as the alkyl precursor.

Bahr et al. electrochemically reduced aryl diazonium salts in the presence of CNTs. The reduction gave an aryl radical that covalently attached to the carbon surface (Figure 1.14). The authors used different types of aryl diazonium salts, among them 4-
tert-butylbenzene moiety, which was found to significantly enhance the solubility of CNTs in organic solvents.

![Figure 1.14. Reduction of aryl diazonium salts in the presence of CNTs.](image)

Chen et al. covalently modified the open ends of acid purified CNTs by first reacting them with dichlorocarbene at 70°C for 24 hours. The functionalized CNTs were then reacted with octadodecylamine at 90-100°C for 96 hours (Figure 1.15). The final product was washed with ethanol, dissolved in dichloromethane, filtered and dried under vacuum. The resulting CNTs were soluble in chloroform, dichloromethane, aromatic solvents (benzene, toluene, chlorobenzene, 1,2-dichlorobenzene) and CS₂.

![Figure 1.15. Functionalization of CNTs with octadodecylamine.](image)

Chen et al. solubilized CNTs in organic solvents by functionalizing nitric acid purified CNTs with octadodecylamine (ODA). They formed an ODA/CNT-carboxylate zwitterion by an acid-base reaction with the ends of the nanotubes (Figure 1.16). A purified CNTs sample was heated in ODA at 120-130°C for 4-8 days. The resulting mixture was then sonicated in 800 ml of ethanol for 30 minutes, filtered and dried at room temperature. The CNTs obtained were soluble in tetrahydrofuran, 1,2-dichlorobenzene, and partially soluble in dichloromethane.
Chattopadhyay et al.\textsuperscript{43} also utilized ODA to functionalize the CNTs. They demonstrated that ODA was not only attached to the CNTs by forming a zwitterion, but also because of the adsorption of the ODA amino groups along the sidewalls of the CNTs.

Qin et al.\textsuperscript{44} grafted poly(sodium 4-stryrenesulfonate) on CNTs by polymerizing sodium 4-stryrenesulfonate in the presence of CNTs, in order to disperse the CNTs in water. This treatment did not require high shear mixing or sonication to disperse the CNTs. The in situ radical polymerization was achieved by stirring at 65°C for 48h, a mixture of 40mg of pristine CNTs, 4 g of sodium 4-styrene sulfonate and 40 mg of potassium persulfate as the free radical initiator. AFM pictures showed that the dispersed CNTs presented lengths comprised between several hundred nanometers and several micrometers and an average diameter of 1.2 nm.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure16.png}
\caption{Figure 1.16. ODA/CNT-carboxylate zwitterions formation\textsuperscript{42}.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure17.png}
\caption{Figure 1.17. Adsorption of ODA groups on the surface of a CNT\textsuperscript{43}.}
\end{figure}
1.2.3.2 Noncovalent functionalization of Carbon Nanotubes

Aside from the work performed by Quin et al., the different functionalization techniques presented so far enabled one to dissolve or disperse CNTs in organic solvents. Lots of applications, especially biomedical and biophysical require CNTs to be soluble in aqueous media. Surfactants and polymers have been used to dissolve CNTs in water, as well as in organic solvents. The use of surfactants or polymers involves the physical adsorption of molecules along the sidewalls of the CNTs. While providing new functionalities on the surface of the CNTs and tailoring their properties, these non-covalent modifications do not destroy the surface of the nanotubes and do not alter their intrinsic electronic nature.

Islam et al. compared the dispersing capacity of different types of surfactants: sodium dodecylbenzene sulfonate (NaDDBS), sodium octylbenzene sulfonate (NaOBS), sodium butylbenzene sulfonate (NaBBS), sodium benzoate (C₆H₅CO₂Na), sodium dodecyl sulfate (SDS), Triton-X 100 (TX100), dodecyltrimethylammonium bromide (DTAB), dextrin and poly(styrene)-poly(ethylene oxide) diblock copolymer. Figure 1.18 depicts examples of how surfactant molecules could adsorb on a CNT surface. The CNTs were typically mixed with the surfactant and the resulting solution sonicated for 16 to 24 hours. The optimum surfactant/CNTs ratio varied from 1:5 to 1:10 depending on the surfactant used. Sodium dodecylbenzene sulfonate (NaDDBS) enabled to obtain a fraction of single tubes in solution greater than 63%. Stable suspensions could not be obtained with the other surfactants for CNTs concentration greater than 0.5mg/ml. The differences in dispersion were attributed to the differences existing in the surfactant structures. It was found that the presence of benzene moieties, small and charged headgroups, and long alkyl chains increased the dispersion capacity of a surfactant.
Moore et al.\textsuperscript{46} compared the dispersion capacity as well as the quality of the absorbance and fluorescence spectra of different surfactants and polymers (Table 1.3). It was concluded that NaDDBS was the most efficient ionic surfactant for dispersing high quantities of CNTs and, that solutions of CNTs dispersed with NaDDBS presented the most well defined absorbance and fluorescence spectra. In the case of ionic surfactants, charge repulsion was the main parameter impeding the aggregation of the CNTs. For nonionic surfactants and polymers, a higher molecular weight increased the dispersion of CNTs. This was explained by the steric stabilization induced by the longer chains of the species adsorbed on the CNTs.

Paredes et al.\textsuperscript{47} developed a method based on sequential ultrasonication steps to exfoliate and disperse CNTs in sodium dodecylbenzene sulfonate and at the same time optimize the CNTs length, and preserve their electronic structure. A combination of tip and bath ultrasonication was used. The solution was tip sonicated with a small number of pulses with 0.5-s-on/0.5-s-off pulse cycles at 40 W/cm\textsuperscript{2}. The resulting dispersion was centrifuged and further sonicated in a bath sonicator for different times ranging from a few minutes to several hours. Sonication times inferior to 30 minutes led to long dispersed tubes. Figure 1.19 displays the length distribution histogram of dispersed CNTs prepared by a five pulses tip sonication, 30 minutes centrifugation and 30 minutes bath sonication procedure.
Table 1.3. Dispersion capacity of different surfactants

<table>
<thead>
<tr>
<th>surfactant/polymer&lt;sup&gt;a&lt;/sup&gt;</th>
<th>molecular weight</th>
<th>mass percent conversion</th>
<th>68.30 fluoro. C peak</th>
<th>68.30 fluoro. pos. relative to SDS (cm&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</th>
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</thead>
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<tr>
<td>antionic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SDS</td>
<td>288.4</td>
<td>3.3 ± 0.5</td>
<td>3.6 ± 0.5</td>
<td>0 ± 10</td>
</tr>
<tr>
<td>SDS-BS</td>
<td>348.5</td>
<td>3.9</td>
<td>4.6</td>
<td>2</td>
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<tr>
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<td>4.5</td>
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<td>Sorbsol</td>
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<tr>
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<td>CTAB</td>
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<td>2.3</td>
<td>−124</td>
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<tr>
<td>nonionic</td>
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<td>Tween 85&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>Triton X-405&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>3.6</td>
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<td>Pluronic F 103&lt;sup&gt;f&lt;/sup&gt;</td>
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<tr>
<td>Pluronic F 85&lt;sup&gt;f&lt;/sup&gt;</td>
<td>4,620 (2.310)&lt;sup&gt;d&lt;/sup&gt;</td>
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<td></td>
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</tbody>
</table>

<sup>a</sup> Sodium dodecyl sulfate (SDS - Aldrich); sodium dodecylbenzenesulfonate (SDBS - Aldrich); sodium dodecylsulfate (SDS - Aldrich); sodium n-lauroyl sarcosinate (Sorbsol - Aldrich); sodium alkyl allyl sulfosuccinate (TREM - Cognis Corporation); poly(vinyl sulfonate) (PSS - Aldrich); dodecyltrimethylammonium bromide (DTAB - Aldrich); cetyltrimethylammonium bromide (CTAB - Aldrich); Brij (Aldrich); Tween (Aldrich); Triton X-100 (Aldrich); poly(vinylpyridine) (PVP - Aldrich); PEG-PPO-PPO-PEG triblock polymer (EIE - DoW); PEG-PPO-PPO triblock polymer (Pluronic - BASF). See Supporting Information for structures.  
<sup>b</sup> Position of the (8,3) fluorescence feature in SPS suspended nanotubes is at 10.565 cm<sup>−1</sup> or 952 nm.  
<sup>c</sup> Lower molecular weight Tween and Triton X surfactants and PVP and Pluronic polymers were tried, but none yielded nanotubes in the decim.  
<sup>d</sup> Number in parentheses is PEG molecular weight.

Figure 1.19. Length distribution of dispersed CNTs<sup>47</sup>.
Polymers not only adsorb on the surface of CNTs, like surfactants, but also wrap themselves around the nanotubes and can provide functionalities on their sidewalls and ends for further manipulation. The wrapping is primarily due to the disruption of the thermodynamically unfavorable hydrophobic interface between the CNTs and the water. Depending on the affinity of the polymer for the nanotubes, the polymer will wrap around bundles of CNTs or ideally exfoliate the bundles by an intercalation process and wrap around single CNTs (Figure 1.20).

![Figure 1.20. Exfoliation of bundles of CNTs induced by polymer chains](image)

O’Connell et al.\(^{48}\) utilized polyvinyl pyrrolidone (PVP) and polystyrene sulfonate (PSS) to solubilize CNTs in water. The CNTs were first dispersed in water with 1\%w sodium dodecyl sulfate (SDS) at a concentration of 50 mg/l. A 1\%w PVP or PSS was added to the solution, which was subsequently incubated at 50°C for 12h. The resulting mixture was centrifuged to remove the residual polymer and surfactant, giving polymer-wrapped CNTs that could be dispersed in water at a concentration as high as 1.4g/l. Figure 1.21 shows AFM pictures of these polymer wrapped CNTs adsorbed on amine functionalized substrates.

![Figure 1.21. Tapping–mode AFM images of PVP-CNTs on an amine-functionalized substrate. 1µm height images (left) and phase image (right)](image)
Wang et al.\textsuperscript{49} were able to suspend CNTs in a solution of Nafion, a perfluorosulfonated polymer, in phosphate buffer or alcohol. The solubility of the CNTs in the Nafion solution was enhanced when the polymer content was increased from 0.1\% to 5\%. Figure 1.22 shows the influence of the Nafion percentage in solution on the solubility of CNTs.

**Figure 1.22.** Influence of Nafion percentage on the solubility of CNTs: (a) phosphate buffer (b) 98\% ethanol. (c) 10\% ethanol in phosphate buffer. (d) 0.1\% Nafion in phosphate buffer (e) 0.5\% Nafion in phosphate buffer (f) 5\% Nafion in ethanol\textsuperscript{49}.

The need for biocompatibility of CNTs has led several research groups to study the dispersion of CNTs with the help of natural compounds and natural polymers. Bandyopadhyaya et al.\textsuperscript{50} dispersed raw CNTs in aqueous solutions of Gum Arabic (GA), a polysaccharide soluble in water. Concentrations of 0.05wt \% of CNTs were dispersed in solutions of 0.5 wt\% to 15wt\% of GA. The authors carried out WAXS (Wide-Angle X-ray Scattering) measurements of raw CNTs and of a dried powder of CNTs dispersed in GA. The peak representing the intertube interactions disappeared for the CNTs dispersed with GA, indicating that a significant amount of individual CNTs were present in the solution. The dispersing efficiency of GA and other dispersing agents were visually compared. As can be seen in Figure 1.23, the solution of CNTs dispersed with GA stayed homogeneous over a long period of time (3 months), while a significant amount of CNTs dispersed with surfactants like sodium dodecyl sulfate or cetyltrimethylammoniumchloride precipitated at the bottom of the solution.
Zheng et al.\textsuperscript{51} explored the potential of single-stranded DNA as CNTs dispersing agent, in order to expand the use of CNTs in biotechnology. Single–stranded DNA molecules (ssDNA) could readily wrap around CNTs with mild-sonication in the presence of a denaturant that suppressed the G(guanine):C(cytosine) and A(adenine):T(thymine) base pairings. More intense sonication was required in order to disperse CNTs in short double stranded DNA molecules. The solutions obtained were stable for months at room temperature. AFM measurements (Figure 1.24) showed that the length of the CNTs ranged from 50 to 1000 nm, and their diameter varied from 1 to 2 nm.

\textbf{Figure 1.23:} Vials containing aqueous dispersions of CNTs (0.05\%w) after 3 months of incubation at room temperature: (A) 2\%w GA; (B) 5\%w GA; (C) 5\%w SDS; (D) 15\%w SDS; (E) 5\%w CTAC; (F) 15\%w CTAC\textsuperscript{50}.

\textbf{Figure 1.24.} CNTs dispersed with DNA\textsuperscript{51}. 

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A simulation of the wrapping of ssDNA around CNTs was performed and showed that the DNA molecules could adsorb on the CNTs’ surface via helical wrapping or surface binding. The simulation of the helical wrapping ssDNA around a (10,0) CNT is displayed in Figure 1.25. The bases (G, C, A, T) adsorbed on the surface, while the sugar-phosphate backbone remained exposed and soluble in water.

![Simulation of the wrapping of ssDNA around a CNT](image)

**Figure 1.25.** Simulation of the wrapping of ssDNA around a CNT$^{51}$.  

Dieckmann et al.$^{52}$ synthesized specific peptides, wrapped them around CNTs and formed macromolecular structures via interaction between the peptides assembled on the nanotubes. They demonstrated that the peptides formed an amphiphilic α-helix that could adsorb on the surface of the CNTs thereby providing their solubilization (Figure 1.26).

![Adsorption of an amphiphilic α-helix around a CNT](image)

**Figure 1.26.** Adsorption of an amphiphilic α-helix around a CNT$^{52}$.  

The authors designed their peptides in order to have a helix presenting a hydrophobic face (apolar residues) that could interact with the side of the CNTs, as well
as a hydrophilic face (polar residues) that could provide the solubility of the CNTs-peptide complex. The peptide took a helical configuration depending on the concentration of the solution and also on the presence of CNTs in the solution. For a sufficiently high concentration (200μM), it presented a helical configuration without added CNTs. For a 100μM solution, it only folded in a helical configuration in the presence of CNTs through hydrophobic interactions with the nanotubes. The CNTs solubility in a 100μM solution was 0.7mg.mL⁻¹. Diluting this solution 10 times led to the self-assembly of the CNTs/peptide complex into microscopic fibrillar structures (Figure 1.27).

![Image](image1)

**Figure 1.27.** Optical micrograph of the fibers and microfibers that form within 36 h from the peptide/CNTs solution after 10 fold dilution with water⁵².

Zorbas et al.⁵³ further demonstrated the ability of the peptide/CNTs complex to self-assemble into Y-, X-, and intraloop junctions (Figure 1.28).

![Image](image2)

**Figure 1.28.** AFM image of nano-1/SWNT sample exhibiting a Y-junction and a X-junction⁵³.
Star et al.\textsuperscript{54} used a starch-iodine complex to suspend CNTs. Amylose, the linear component of starch adopts a helical conformation in an aqueous solution by wrapping itself around guest molecules like iodine. Once sonicated with CNTs, the iodine small molecules were replaced by CNTs via a “pea-shooting” mechanism (Figure 1.29). A 5:1 mixture of starch and CNTs could be obtained by dispersing 10mg of CNTs in a 10.L\textsuperscript{−1} starch/iodine complex solution. The solution was sonicated and centrifuged and the sediment was dispersed in water. The resulting aqueous solution was then brought to a boil in order to precipitate the starch/CNTs complexes out of solution.

![Figure 1.29](image.png)

\textbf{Figure 1.29.} Schematic representation of the “pea-shooting” type of mechanism whereby carbon nanotubes displace iodine molecules from the amylose helix\textsuperscript{54}.

Two different research groups studied poly(p-phenylenevinylene-co-2,5-dioctyloxy-m-phenylenevinylene) or its derivatives, in order to solubilize CNTs. This family of copolymers possesses not only side chains enabling the wrapping of the copolymer around the CNTs, but also phenyl rings capable of interacting with the hexagonal lattice of the CNTs via \(\pi-\pi\) interactions,
Dalton et al.\textsuperscript{36,55-57} synthesized poly(p-phenylenevinylene-co-2,5-dioctyloxy-m-phenylenevinylene) (PmPV-co-DOctOPV). PmPV-co-DOctOPV enabled this research group to solubilize CNTs and also to purify them as mentioned in section 1.2.2.4. Figure 1.30 shows the structure of this copolymer. The authors solubilized different mass fractions of CNTs in $10^{-5}$ M solutions of copolymer in toluene. The resulting suspensions were sonicated for several hours at low power and left to decant for several days. Transmission Electron Microscopy (TEM) pictures showed the presence of a certain amount of individual CNTs covered by the copolymer (Figure 1.31). No traces of graphitic particles were found, which indicated that the impurities present in the initial soot of CNTs had precipitated at the bottom of the solution. The decanted solutions were stable over a period of several months. Scanning Tunneling Microscopy (STM) pictures showed that the copolymer was effectively wrapped around the CNTs (Figure 1.32). While most of the time the wrapping along the CNTs was disordered, in some cases some order could be found\textsuperscript{56}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig130.png}
\caption{PmPV structure\textsuperscript{36}.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig131.png}
\caption{TEM picture of CNTs protruding from the edge of a PmPV-CNTs film\textsuperscript{55}.}
\end{figure}
Figure 1.32. (a) STM image of two polymer wrapped CNTs lying on HOPG. STM parameters were an applied voltage of 200 meV, and a tunneling current of 10s of pA. The line A denotes the position at which the cross-section in (b) is taken. The approximate height of the tube on the left is 15Å. The approximate height of the tube on the right is 20 Å.

Star et al. similarly investigated the solubility of CNTs in a solution of PmPV in chloroform (CHCl₃). AFM was used to demonstrate the dispersion of the nanotube bundles into smaller diameter ropes when PmPV was used as dispersing agent. The size of the ropes was significantly smaller than for CNTs dispersed in dimethylformamide (DMF) (Figure 1.33).

Figure 1.33. (a) SWNTs prepared from 0.32mg of SWNTs in 5 mL of DMF; (b) solution containing 0.32mg of SWNTs with 0.2 mg of PmPV in 5 mL of CHCl₃; (c) solution containing 0.24mg of SWNTs with 1mg of PmPV in 5 mL of CHCl₃.
The same research group\textsuperscript{59} studied the solubilization in CHCl$_3$ of CNTs with one of the derivatives of PmPV, PPyPV (poly\{(2,6-pyridinylenevinylene)-co-[(2,5-dioctyloxy-p-phenylene)vinylene]\})(Figure 1.34).

![PPyPV structure](image)

**Figure 1.34.** PPyPV structure\textsuperscript{59}.

The authors reported that an excess of polymer was required to disperse the CNTs, and that the length and diameter of the resulting nanotubes depended on the ratio of polymer to CNTs present in solution. Compared to PmPV, PPyPV could be protonated by adding hydrochloric acid to the polymer-CHCl$_3$ solution (Figure 2.34).

![Protonation of PPyPV](image)

**Figure 1.35.** Protonation of PPyPV\textsuperscript{59}.

While PmPV interacted with CNTs in its neutral form, PPyPV and CNTs interacted predominantly via the protonated form of PPyPV. As shown in Figure 1.36, when the quantity of CNTs present in solution was increased, the amount of protonated PPyPV also increased. This phenomenon was attributed to the decrease of the pK$_a$ of the polymer due to charge stabilization induced by the interaction between the polymer and the CNTs.
Figure 1.36. The y-axis is the ratio of the red (protonated) to the blue (charge neutral) absorption features in the absorption spectrum of PPyPV$^{59}$.

A hyperbranched polymer derived from PmPV was synthesized$^{60}$, in an attempt to selectively separate the CNTs based on their diameter. Figure 1.37 shows a schematic representation of this polymer.

![Hyperbranched Polymer Schematic](image)

Figure 1.37. Schematic representation of a hyperbranched polymer derived from PmPV$^{60}$.

A generation 3 hyperbranched PmPV derivative possessed pockets of definite size (2 nm) that could clip or slide around the CNTs, as well as a planar configuration that made the pockets accessible for the CNTs (Figure 1.37). The CNTs could be suspended in a solution of the hyperbranched polymer in CHCl$_3$ at a 5:1 ratio, by sonicating for one hour.

Chen et al.$^{61}$ synthesized different types of conjugated poly(aryleneethynylene)s (PPEs) (Figure 1.38) which possessed rigid backbones that could not wrap around the CNTs, but interacted with them via $\pi$-stacking (Figure 1.39). A solubility of 2.2mg/mL
in CHCl₃ was obtained with the (1a) polymer, which represented a 20-fold enhancement in CNTs solubility compared to other solubilization techniques.

The authors tested the impact of PPEs’ rigidity on the solubility by varying the length of the different types of PPEs. PPEs with backbone lengths shorter than 15 nm triggered the highest CNTs solubility.

The different techniques presented in this section for obtaining the solubilization of CNTs in aqueous solutions or organic solvents are essential for the processing of CNTs into different types of applications. The number of applications incorporating CNTs is proportional to the tremendous interest that CNTs have been engendering for the last ten years. The interest of the author is mainly directed toward electronic devices, mostly Field-Effect Transistors based on CNTs, CNTs based hybrid nanostructures, and

\[ \text{Figure 1.38. PPE structure}^{61}. \]

\[ \text{Figure 1.39. Interaction of PPE with a CNT}^{61}. \]
CNTs multilayers. These three types of applications are discussed in the following section.

1.2.4 Selected Applications

1.2.4.1 Carbon Nanotubes Field-Effect Transistors

Over the past several decades, tremendous advances have been made in silicon based electronic devices leading to smaller and smaller devices with higher speed, and higher density. However, it is now widely accepted that the scaling limits of silicon devices will be reached in a few years from now. Researchers have started to explore new directions for the fabrication of reduced size devices. One of the most promising paths is the use of one or a few molecules as the active part of the device. Carbon Nanotubes (CNTs) are among the most promising building blocks for these molecular nanoscale electronics due to their unique structural, mechanical, and electrical properties. Recently, several Field-Effect Transistors (FETs) based on CNTs have been fabricated and characterized. FETs are usually used for weak signal amplification and to implement electronic switches and memory devices. In a FET, current flows along a semiconductor path called the channel. The channel is enclosed between a source and a drain electrode. The physical diameter of the channel is fixed, but its effective electrical diameter can be varied by the application of a voltage to a control electrode called the gate. The conductivity of the FET depends, at any given instant in time, on the electrical diameter of the channel. A small change in gate voltage can cause a large variation in the current from the source to the drain. The highest the field-effect mobility of the semi-conductor channel is, the better the characteristic of the transistor will be. Most of the FETs fabricated are based on individual Single-Walled Carbon Nanotubes (SWNTs) and require high-cost fabrication techniques. However, for many applications individual SWNTs can be replaced by interconnected arrays of SWNTs. FETs based on individual CNTs are briefly presented in the following paragraph. A discussion on FETs based on random networks of CNTs follows.
1.2.4.1.1 Field-Effect Transistors (FETs) based on individual carbon nanotubes

Individual CNT-FETs are usually based on one SWNT that is either directly grown on a silicon substrate between two electrodes via chemical vapor deposition or deposited on two electrodes by spin coating of a SWNT solution. The SWNT represent in this case the semi-conducting channel of the FET. FETs based on semi-conducting SWNTs can usually exhibit electron mobility as high as 9000 cm$^2$/Vs$^{19}$, which is twenty times higher than common semiconductors like silicon, and 90 000 times higher than FETs based on organic molecules like pentacene. A field-effect mobility of 79 000 cm$^2$/Vs has also been reported for a FET based on an ultralong SWNT of 300 μm$^62$.

Several research groups studied the characteristics of individual SWNT based transistors$^{63-71}$. The pioneering work was performed by Tans et al.$^{71}$ who were the first to experimentally confirm the theoretical prediction that stated that SWNTs acted like quantum wires and may be utilized in electronic devices. Figure 1.40 shows an AFM picture of a SWNT that was deposited by spin coating of a SWNT solution. It had a diameter of 1 nm and a length of 3 μm.

![AFM tapping-mode image of a SWNT on top of a Si/SiO2 substrate with two 15 nm-thick Pt electrodes](image)

**Figure 1.40.** AFM tapping-mode image of a SWNT on top of a Si/SiO2 substrate with two 15 nm-thick Pt electrodes$^{71}$.

The contact resistance of the individual SWNT was 300 kΩ at room temperature and 1MΩ at 4K. The current-voltage characteristics at different gate voltages were
determined and are displayed in Figure 1.41. The measurements were performed in a dilution refrigerator at 5mK. The current increased by steps and showed a gap around zero bias voltage. This behavior was attributed to Coulomb charging of the nanotubes.

![Current–voltage curves of the nanotube at a gate voltage of 88.2mV (trace A), 104.1mV (trace B) and 120 mV (trace C).](image)

**Figure 1.41.** Current–voltage curves of the nanotube at a gate voltage of 88.2mV (trace A), 104.1mV (trace B) and 120 mV (trace C).

The authors used the same device configuration to refine their study. A semiconducting SWNT replaced the metallic SWNT, and the measurements were performed at room temperature. As shown in Figure 1.42, well-defined p-type FET characteristics were obtained. A p-type FET is defined by a decrease in the amount of current that flows in the channel when the gate voltage is increased.

![Two probe I-V bias curves for various values of the gate voltage (V_gate).](image)

**Figure 1.42.** Two probe I-V bias curves for various values of the gate voltage ($V_{\text{gate}}$).
1.2.4.1.2 Field-Effect Transistors Based on Networks of Carbon Nanotubes

Due to the difficulty and the cost involved in reproducing individual SWNT-FET possessing high field-effect mobilities, as well as the necessity to have multiple SWNTs side by side to surpass the current drive of silicon based devices, one research group started to focus its attention on building FETs based on random networks of SWNTs. Two different approaches were used to obtain SWNTs networks: direct growth on a catalyzed substrate (for example by Chemical Vapor Deposition) or solution based deposition.

Snow et al. fabricated different FETs based on networks of SWNTs (Figure 1.43) that exhibited field-effect mobilities up to 270 cm²/Vs. The channel length (L) was varied from 1 to 25 μm, and the channel width (W) from 35 to 100μm. Networks with a low density of SWNTs presented field-effect mobilities around 10 cm²/Vs. Networks with a high density of SWNTs presented field-effect mobilities around 100 cm²/Vs, but a high off-state current. The SWNT networks exhibited a sheet resistance of 108 kΩ/square.

![Figure 1.43](image)

**Figure 1.43.** Schematic of the network based FET.

Figure 1.44 displays the variation of the current that flowed through the transistor as a function of the applied gate voltage for a bias voltage of 0.1V, and four different network
growths. The channel width used in this case was 35 μm, and the channel length 10μm. The curves were indicative of a p-type behavior. The intrinsic high mobility of individual SWNTs, and the low resistance of the contacts between the interconnected SWNTs were responsible for the high field effect mobility of the fabricated transistors.

![Figure 1.44. Current versus gate voltage at V_{bias}=0.1V^{73}.](image)

The percolation threshold that corresponded to the minimum density of SWNTs that was necessary to obtain electrical connection was defined as the density at which the average distance between the SWNTs equaled the average length of the SWNTs:

\[ \rho_{th} \approx \frac{1}{\langle L \rangle^2} \quad (1.21) \]

For growth conditions that provided SWNTs lengths between 1 and 3 μm, the threshold density was equal to 0.3 μm².

The same authors further developed a simple technique to fabricate FETs based on solution deposited aligned SWNTs^{74,75}. Solutions of varying concentrations of SWNTs were dispersed in a 1% w sodium dodecyl sulfate (SDS) solution. The resulting mixtures were sonicated and centrifuged to remove non-dispersed SWNTs. Amino functionalized silicon substrates (Si/SiO₂) were grazed on the SWNTs solution, and subsequently blown dry with a stream of nitrogen to align the SWNTs in the direction of the nitrogen flux. The chip was then rinsed to remove the SDS and dried again. This
step was repeated until a suitable resistance was obtained. Figure 1.45 shows an AFM picture of an aligned network of SWNTs fabricated by this method. The authors reported that 90% of the SWNTs presented a 95% alignment.

**Figure 1.45.** AFM image of SWNTs aligned on a surface using a directional solution drying procedure.74

FETs were fabricated based on aligned SWNTs parallel or perpendicular to the current flow. Figure 1.46 shows that the FETs current-gate voltage characteristics strongly depended on the alignment of the SWNTs. The on/off ratio was higher for the perpendicular device ($10^4$) than for the parallel one ($10^2$).

**Figure 1.46.** Log plot of the source-drain current (ISD) as a function of gate voltage (VG) as the source-drain voltage (VSD) is held constant at 0.100V for a p-channel SWNT transistor with gate length of 7$\mu$m.74
1.2.4.2 Self-Assembly of Carbon Nanotubes Multilayers

As described in section 1.2.2 and 1.2.3, CNTs could be oxidized with strong acids like sulfuric acid and nitric acid in order to generate carboxylic groups on their surface. These carboxylic groups enabled the self-assembly of positively charged species on the CNTs via electrostatic interactions. This process was extended to the self-assembly of functionalized CNTs on oppositely charged surfaces, which could further lead to the formation of CNTs multilayers. CNTs multilayers have numerous applications. They can serve for example, after further chemical processing, as strong CNTs/polymer composites with improved mechanical properties\textsuperscript{76} or as scaffolds for the fabrication of novel hybrid nanostructures\textsuperscript{77}.

Rouse et al.\textsuperscript{78} self-assembled multilayers of CNTs with poly(diallyldimethylammonium chloride) (PDDA) as the polyelectrolyte interlayer. A negatively charged silicon wafer was dipped in a 1%w aqueous solution of PDDA containing 1.0 M NaCl for 10 min, subsequently rinsed and dried under a flux of nitrogen. The PDDA functionalized wafer was then dipped into a dispersion of acid treated CNTs dispersed in dimethylformamide (DMF) (0.005mg CNTs/1ml DMF) for 100 min, rinsed and dried. The resulting wafer was dipped again in a solution of PDDA for 10 min. These three steps were repeated until the desired numbers of multilayers were formed. Figure 1.47 displays AFM pictures of one, three, six and nine PDDA/CNTs bilayers. The networks obtained were composed of bundles of CNTs possessing lengths ranging from 1 to 3 μm, and diameters ranging from 5 to 10 nm. Globular domains of PDDA could be noticed on the surface of the CNTs, that enabled the self-assembly of CNTs on the PDDA treated CNTs bundles. A UV-Vis-NIR study of the different films fabricated confirmed the increase in thickness of the films, after each treatment cycle.
Figure 1.47. Tapping mode AFM images of a PDDA/SWNT multilayer film prepared on a silicon wafer after various numbers of adsorption treatments: (a) PDDA/SWNT, (b) (PDDA/SWNT)$_3$, (c) (PDDA/SWNT)$_6$, (d) (PDDA/SWNT)$_9$. The scale bar is 1.25 micron and the z-scale in all images is 50 nm.$^{78}$

In another study, Rouse et al.$^{77}$ built multilayer of CNTs in order to utilize them as scaffolds for silica deposition. Poly(ethyleneimine) (PEI), poly(allylamine) (PA), and poly(4-vinylpyridine) (P4VP) were used as the interlayer species. CNTs multilayers could be fabricated by using the amino group affinity for the sidewalls of non-oxidized CNTs for CNTs/PEI or CNTs/PA multilayers and the affinity of the basic nitrogen of the pyridine ring for the CNTs sidewalls for CNTs/P4VP multilayers. Alternate dipping of a Pirahna (2:1 v/v% concentrated H$_2$SO$_4$ and 30%H$_2$O$_2$ for 1h) and APTES (0.05 M 3-aminopropyltriethoxysilane solution in toluene for 4-6h) pre-treated glass substrate in a pristine CNTs solution and a polyelectrolyte solution (PEI, PAH or P4VP) led to the build up of the desired multilayered structures. Figure 1.48 shows AFM pictures of PEI/CNTs multilayers. The same type of film morphology was obtained for P4VP/CNTs and PAH/CNTs multilayers. Due to the possibility of catalyzing the hydrolysis and
condensation of tetraethyl orthosilicate (TEOS) with P4VP, the authors were capable of using the P4VP/CNTs multilayers as scaffolds for the formation of silica.

Figure 1.48. Tapping mode AFM images of a (PEI/CNTs) film prepared on a silicon wafer after each adsorption cycle.

Zhang et al.79 self-assembled multilayers of MWNTs on glassy carbon electrodes. The electrochemical properties and electrocatalytic activity toward O₂ reduction of the resulting films were studied, in order to evaluate the use of MWNTs multilayers for the fabrication of efficient alkaline air electrodes. The polyelectrolyte interlayer was PDDA. The multilayers were fabricated by alternately dipping the carbon electrodes in a 1%w PDDA solution containing 0.5MNaCl, and a 1mg/mL MWNT dispersion each for 30 min. SEM showed that the coverage of the glassy carbon substrate increased with the number of MWNTs layers deposited (Figure 1.49). The films obtained exhibited excellent electrochemical activity and electrocatalytic activity toward O₂ reduction.
The exceptional mechanical properties of CNTs (strength, stiffness) coupled with their low mass density and exceptional electrical and thermal properties make them ideal candidates as fibrous reinforcements in polymer composite materials. One of the problems encountered in the fabrication of CNTs reinforced polymers though, is the lack of compatibility of the CNTs with the polymeric matrix. This lack of compatibility often leads to the mechanical failure of the composite. Several paths involving mixing and functionalization of the CNTs have been explored in order to improve CNTs reinforced composite performances. One of the most efficient and recent solutions proposed consisted of utilizing self-assembled CNTs multilayers with polyelectrolytes interlayer and chemically cross-linking the resulting structure in order to build homogeneous and mechanically reliable composites. A few pioneering works have been performed in order to build cross-linkable CNTs/polyelectrolytes multilayers.

Mamedov et al. built multilayers of SWNTs with PEI as the polyelectrolyte interlayer by alternately dipping a negatively charged glass substrate in a positively charged 1%w PEI solution at pH=8.5 for 10 min and a negatively charged SWNTs solution at pH=6.8 for 30 min. Due to the small amount of negative charges present on the surface of the nanotubes, after every fifth deposition cycle, the SWNTs layer was replaced by a layer of poly(acrylic acid) (PAA) in order to improve the quality of the resulting structure. Optimized assembly parameters enabled to obtain films composed of 30 and 40 PEI/CNTs bilayers. PEI amino groups could subsequently be cross-linked, either with themselves or with the carboxylic groups of PAA or SWNTs via chemical
treatment. The cross-linking of the multilayers was obtained by heating the films at 120°C after every fifth deposition cycle, and by dipping the final film in a 0.5% glutaraldehyde solution in phosphonate buffer for 1h at room temperature. After rinsing with water, the resulting film could be delaminated from the surface with hydrofluoric acid and its mechanical properties determined. The SWNTs loading inside the composites could be as high as 50%, compared to 1-15% for classical polymer/SWNTs composites made by mixing, solution casting or in-situ polymerization, and no phase segregation was reported. Tensile strengths approaching those of hard ceramics were obtained due to the high connectivity between the components of the composite, which dramatically increased the load transfer.

Olek et al. applied this technique to the fabrication of MWNTs (Multi-Walled CNTS)/polymer composites. The MWNTs used in this case were “hollow” and “bamboo” types MWNTs (Figure 1.50), reputed to be less expensive than SWNTs. PEI and PAA were used as the polyelectrolyte interlayer, and an experimental protocol similar to Mamedov et al. was employed to build and crosslink the multilayers. Films possessing up to 100 PEI/MWNTs bilayers could be built, cross-linked and delaminated in order to obtain homogeneous free-standing composite films (Figure 1.51). Due to the “knots” present on the surface of the “bamboo” type MWNTs, a better connectivity could be obtained between the MWNTs and the matrix, giving rise to better composite mechanical properties than for “hollow” type MWNTs. The Young’s modulus and tensile strength were 4.5±0.8GPa and 150±35MPa for the “bamboo” type composites and 2±0.5GPa and 110±25MPa for the “hollow” type composites.

Figure 1.50. SEM pictures of “bamboo” and “hollow” Multi-Walled CNTs.
1.2.4.3 Hybrid Nanostructures based on Carbon Nanotubes

Recently, several research groups have focused their attention on the creation of hybrid nanostructures based on CNTs and nanoparticles like Quantum Dots (QDs) and gold nanoparticles. Building these nanostructures is of interest for creating new electronic and magnetic nanodevices, as well as nanostructures possessing new catalytic or chemical sensing properties.

Jiang et al. devise a strategy for assembling gold nanoparticles on CNTs which consisted of modifying the CNTs with sulfuric acid and nitric acid in order to obtain carboxylic groups on the surface of the CNTs, further assembling a positively charged polyelectrolyte (PDDA) on the carboxylic groups, and finally assembling negatively charged gold nanoparticles (10 nm in diameter) on the polyelectrolyte. Figure 1.52 displays a TEM picture of the resulting nanostructures that demonstrates the presence of gold nanoparticles on the surface of the treated CNTs.
Carillo et al.\textsuperscript{82} studied the attachment of gold nanoparticles to substrate grown CNTs covered with multiple layers of polymers. A layer of hydrolyzed poly(styrene-alt-maleic acid) (h-PSMA) was first attached to the CNTs surface via hydrophobic interactions, that enabled the further attachment of poly(ethyleneimine) (PEI) to the CNTs via electrostatic interaction between the carboxylic groups of h-PSMA and the amino groups of PEI. A \((\text{h-PSMA-c-PEI})_2\)-PAA-PEI multilayered film was built and gold nanoparticles (40 nm in diameter) could self-assemble on the outer PEI layer (Figure 1.53).

\textbf{Figure 1.52.} TEM picture of CNTs/gold nanoparticles hybrid structures\textsuperscript{81}.

\textbf{Figure 1.53.} SEM image of gold nanoparticles immobilized on polymer-coated SWNTs\textsuperscript{82}.
Ellis et al.\textsuperscript{83} assembled octanethiols-protected gold nanoclusters (1 to 3 nm in diameter) on acetone treated CNTs. The nanoclusters were attached to the nanotubes by mixing OT-capped nanoclusters with acetone treated MWNTs dispersed in toluene, sonicating the resulting solution and decanting the supernatant to remove unattached nanoclusters. The gold nanoclusters attached to the CNTs surface via hydrophobic interactions and interdigitation between the acetone moieties of the treated MWNTs surface and the alkyl chains of the octanethiols capped nanoclusters (Figure 1.54).

Han et al.\textsuperscript{84} developed an analogous technique to assemble decanethiolate-capped nanoparticles on CNTs. The assembly between the nanoparticles and the CNTs occured via hydrophobic interactions between the alkyl chains of the capping/linking molecules and the hydrophobic surface of the CNTs as well as via hydrogen bonding between the carboxylic groups of the capping/linking molecules and the functional groups present on the CNTs surface. 11-Mercaptoundecanoic acid (MUA) was used as the interlinking agent for gold nanoparticles having a diameter of 5 nm and 1,9-nonanedithiol as the interlinking agent for gold nanoparticles having a diameter of 2 nm. The presence of an interlinking agent enabled the assembly of well-separated gold nanoparticles. Figure 1.55 shows TEM pictures of gold nanoparticles assembled on CNTs in the presence of

**Figure 1.54.** Schematic sketch illustrating the proposed mechanism of attachment of OT-capped Au nanoclusters to acetone activated MWNTs\textsuperscript{83}.

Han et al.\textsuperscript{84} developed an analogous technique to assemble decanethiolate-capped nanoparticles on CNTs. The assembly between the nanoparticles and the CNTs occured via hydrophobic interactions between the alkyl chains of the capping/linking molecules and the hydrophobic surface of the CNTs as well as via hydrogen bonding between the carboxylic groups of the capping/linking molecules and the functional groups present on the CNTs surface. 11-Mercaptoundecanoic acid (MUA) was used as the interlinking agent for gold nanoparticles having a diameter of 5 nm and 1,9-nonanedithiol as the interlinking agent for gold nanoparticles having a diameter of 2 nm. The presence of an interlinking agent enabled the assembly of well-separated gold nanoparticles. Figure 1.55 shows TEM pictures of gold nanoparticles assembled on CNTs in the presence of
MUA (1A) and without interlinking agent (1B). In the latter case, it could be noticed that a significant amount of gold nanoparticles was not attached to the CNTs.

![Figure 1.55](image)

**Figure 1.55.** TEM micrographs for gold nanoparticles assembled on CNTs, with (A) and without (B) interlinking agent (MUA)\(^8^4\).

Quantum dots (QDs) are another type of nanoparticles that can be assembled on CNTs, in order to build new types of hybrid nanostructures. QDs are semi-conducting nanocrystals usually made of cadmium selenide (CdSe), whose electronic and optical properties can be tuned by changing their size. Building CNTs-QDs hybrid nanostructures is of great interest for the fabrication of efficient solar cells and light emitting diodes (LEDs). Placing CNTs directly in contact with QDs could provide an efficient charge transfer from or to the QDs, which is usually missing in polymer-QDs solar cells or LEDs.

Nanoclusters of CdSe-TOPO (trioctylphosphine oxide) QDs (3.2 nm in diameter) capped with different mercaptothiol derivatives (p-mercaptobenzoic acid, thioglycolic acid, and 3-mercaptopropionic acid) were attached to oxidized SWNTs using ethylenediamide or semicarbazide as intermediary linking agent in the presence of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC)\(^8^5\). EDC enabled the formation of an amide bond between the carboxylic groups of the SWNTs and the mercaptothiol derivative capping the QDs (Figure 1.56). This procedure led to the assembly of nanoclusters of CdSe QDs on the ends and sidewalls of the SWNTs as could be seen in Figure 1.57.
**Figure 1.56.** Schematic of the addition of CdSe nanocrystals to SWNTs. (a) TOPO capping was substituted by a thiol ligand to form an acid terminated CdSe nanocrystal (VI). (b) (VI) was linked to SWNTs by an ethylenediamide linker (VIII) in the presence of EDC to form the adduct (VIII)\textsuperscript{85}.

**Figure 1.57.** CdSe QDs attached to the ends and sidewalls of SWNTs\textsuperscript{85}. 
Single amino functionalized CdSe core (2.8 to 4.3 nm in diameter) and CdSe/ZnS core/shell quantum dots were attached to acid-chloride treated SWNTs via amide coupling. The number of QDs attached to the nanotubes was tailored by changing the CNTs/QDs mass ratio which was varied from 500:10 mg QDs/CNTs to 50:140 mg QDs/CNTs. The QDs passivated with trioctylphosphine oxide (TOPO) during their synthesis, were treated with 2-aminoethanethiol, in order to create amino groups on their surface. The resulting QDs were then added to a dispersion of SWNTs in ethanol, refluxed at 90°C under nitrogen for 4 days, centrifuged and decanted 3 times and finally redispersed in ethanol. AFM pictures demonstrated that QDs attached to the ends of SWNTs shorter than 200nm, and also on the sidewalls of SWNTs longer than 200 nm (Figure 1.58).

![Figure 1.58](image)

**Figure 1.58.** SWNT with QDs attached on its sidewalls.

QDs were also attached to MWNTs using a procedure similar to the one used by Banerjee at al. to attach QDs on SWNTs. Thiol capped QDs were attached on oxidized MWNTs using EDC as the coupling agent. A mild nitric acid treatment was utilized to oxidize only the ends of the MWNTs, which enabled to obtain QDs mainly attached to the extremities of the MWNTs (Figure 1.59).
Banerjee et al.\textsuperscript{88} developed a method to directly grow CdTe QDs on oxidized MWNTs. MWNTs were mixed with CdO and tetradecylphosphonic acid (TDPA) and the resulting mixture heated at 320°C in TOPO (triocylphosphine oxide) under argon. A solution of Te in triocylphosphine was added to the solution, which led to the formation of nanocrystals that could be recovered by the addition of methanol, and further filtered to remove the nanocrystals not attached to the MWNTs. Figure 1.60 displays a TEM pictures of the resulting nanostructures that shows QDs attached to the surface of the MWNTs.
1.2.5 Summary

In this chapter, a review of the literature has been provided, which described some key aspects of CNTs based research. Some theoretical background about CNTs structure and electronic properties has been provided. The different techniques used to purify and solubilize CNTs in order to process them into different types of applications have been described.

In the following chapters, the research efforts of the author involving Single-Walled Carbon Nanotubes (SWNTs) will be presented. In chapter 2 the optical limiting performances of different SWNT/conjugated polymer dispersions are described and compared. Chapter 3 involves the spontaneous assembly of dendrimer molecule patterns induced by SWNTs.
1.3 References


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