



A REVIEW : CARBON NANOTUBES

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Accepted on: 02-12-2011; Finalized on: 25-02-2012.

ABSTRACT

Since the discovery of carbon nanotubes in 1991 by Iijima, they have been of great interest, both from a fundamental point of view and for future applications. The eye-catching features of these structures are their electronic, mechanical, optical and chemical characteristics, which open a way to future applications. These properties can even be measured on single nanotubes. For commercial application, large quantities of purified nanotubes are needed. Different types of carbon nanotubes can be produced in various ways. The most common techniques used nowadays are: arc discharge, laser ablation and chemical vapour deposition. Purification of the tubes can be divided into a couple of main techniques: oxidation, acid treatment, annealing, sonication, filtering and functionalisation techniques. Economically feasible large-scale production and purification techniques still have to be developed. Fundamental and practical nanotube researches have shown possible applications in various fields. Real applications are still under development. This report provides an overview of current nanotube technology, with a special focus on synthesis and purification, properties, benefits and applications.

Keywords: Carbon nanotubes, Fullerenes, Dispersions, Functionalisation, Nanomedicines.

1. INTRODUCTION

Fullerenes are molecules composed entirely of carbon in the form of a hollow sphere, ellipsoid, or tube. Spherical C_{60} (Figure 1, A) is composed of 60 carbon atoms arranged in a series of interlocking hexagons and pentagons (truncated icosahedron); however, less spherical fullerene configurations, such as C_{20} , C_{36} , C_{70} , and C_{78} , have also been described. CNHs are horn-shaped sheaths composed of single-walled graphene sheets, 2 to 3 nm in diameter, that cluster into aggregates with a diameter around 80 nm. Individual CNHs are cone shaped graphitic carbon structures, with their tips capped by five-membered rings (Figure 1, B). CNTs have relatively well-defined diameters with controllable lengths, whereas CNHs increase in diameter as their length increases, because as length increases so does the base of the nanocone.¹

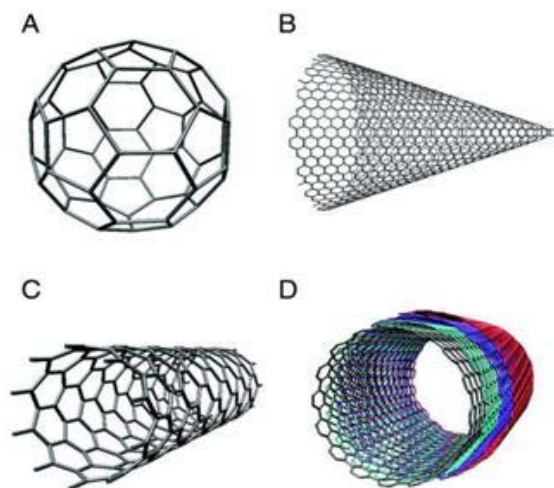


Figure 1: Fullerene molecules

1.1. Fullerenes

Fullerenes are large, closed-cage, carbon clusters and have several special properties that were not found in any other compound before. Therefore, fullerenes in general form an interesting class of compounds that surely will be used in future technologies and applications. Before the first synthesis and detection of the smaller fullerenes C_{60} and C_{70} , it was generally accepted that these large spherical molecules were unstable. However, some Russian scientists already had calculated that C_{60} in the gas phase was stable and had a relatively large band gap. As is the case with numerous, important scientific discoveries, fullerenes were accidentally discovered. In 1985, Kroto and Smalley found strange results in mass spectra of evaporated carbon samples. Herewith, fullerenes were discovered and their stability in the gas phase was proven. The search for other fullerenes had started.²

2. HISTORY OF CARBON NANOTUBES

Since their discovery in 1991 by Iijima and coworkers⁴, carbon nanotubes have been investigated by many researchers all over the world. Their large length (up to several microns) and small diameter (a few nanometres) result in a large aspect ratio. They can be seen as the nearly one-dimensional form of fullerenes. Therefore, these materials are expected to possess additional interesting electronic, mechanic and molecular properties. Especially in the beginning, all theoretical studies on carbon nanotubes focused on the influence of the nearly one-dimensional structure on molecular and electronic properties.³

3. CNT MORPHOLOGY

CNTs belong to the fullerene family of carbon allotropes. They are cylindrical molecules consisting of a hexagonal arrangement of sp^2 -hybridized carbon atoms (C-C distance of 1.4 Å). They are described as hollow cylinders formed by rolling single or multiple layers of graphene sheets into seamless cylinders. These cylindrical structures have two forms (SWNTs) and multi walled carbon nanotubes (MWNTs). SWNTs are composed of a single cylindrical graphene layer capped at both ends in a hemispherical arrangement of carbon networks. The closure of the cylinder results from the inclusion of pentagonal and heptagonal C-C structures during the growth process. MWNTs comprise several to tens of concentric cylinders of graphitic shells, each one forming a SWNT. MWNTs generally have a larger outer diameter (2.5–100 nm) than SWNTs (0.6–2.4 nm) and consist of a varying number of concentric SWNT layers, with an interlayer separation of about 0.3 nm. SWNTs have a better defined diameter, whereas MWNTs are more likely to have structural defects, resulting in a less stable nanostructure.⁴

4. CARBON NANOTUBE STRUCTURE

Many exotic structures of fullerenes exist: regular spheres, cones, tubes and also more complicated and strange shapes. Here we will describe some of the most important and best-known structures. Single Walled Nanotubes (SWNT) can be considered as long wrapped graphene sheets. As stated before, nanotubes generally have a length to diameter ratio of about 1000 so they can be considered as nearly one-dimensional structures. More detailed, a SWNT consists of two separate regions with different physical and chemical properties. The first is the sidewall of the tube and the second is the end cap of the tube. The end cap structure is similar to or derived from a smaller fullerene, such as C_{60} . C-atoms placed in hexagons and pentagons form the end cap structures. It can be easily derived from Euler's theorem that twelve pentagons are needed in order to obtain a closed cage structure which consists of only pentagons and hexagons. The combination of a pentagon and five surrounding hexagons results in the desired curvature of the surface to enclose a volume. A second rule is the isolated pentagon rule that states that the distance between pentagons on the fullerene shell is maximised in order to obtain a minimal local curvature and surface stress, resulting in a more stable structure. The smallest stable structure that can be made this way is C_{60} the one just larger is C_{70} . Another property is that all fullerenes are composed of an even number of C-atoms because adding one hexagon to an existing structure means adding two C-atoms. The other structure of which a SWNT is composed is a cylinder. It is generated when a graphene sheet of a certain size that is wrapped in a certain direction. As the result is cylinder symmetric we can only roll in a discrete set of directions in order to form a closed cylinder. (Two atoms in the graphene sheet are chosen, one of which

serves the role as origin. The sheet is rolled until the two atoms coincide. The vector pointing from the first atom towards the other is called the chiral vector and its length is equal to the circumference of the nanotube. The direction of the nano tube axis is perpendicular to the chiral vector. SWNTs with different chiral vectors have dissimilar properties such as optical activity, mechanical strength and electrical conductivity. Multi Walled Nanotubes (MWNT) can be considered as a collection of concentric SWNTs with different diameters. The length and diameter of these structures differ a lot from those of SWNTs and, of course, their properties are also very different.⁵

5. CHIRALITY OF CARBON NANOTUBES

Chirality of a SWNT is obtained from its chiral vector C , defined by a pair of integers (n, m) obtained from the arrangement of the graphite hexagons with respect to the SWNT axis. The armchair configuration (Figure 2, A) with chiral vectors (n, n) is characterized by the perpendicular shape of the chair to the tube axis, whereas the zigzag conformation (Figure 2, B) is characterized by vectors $(n, 0)$ and has a V-shape perpendicular to the tube axis. All other vector compositions (i.e., neither armchair nor zigzag) are described as chiral or helical. The chirality of SWNTs determines their conductivity, allowing for their potential development into a wide variety of SWNT-based electronic switching devices.⁴

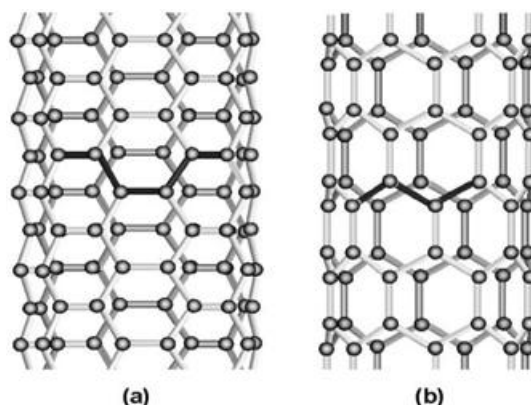


Figure 2: Chirality of CNT

6. CNT DISPERSION AND SOLUBILITY

The solubility of CNTs in aqueous solvents is a prerequisite for biocompatibility; hence, CNT composites in therapeutic delivery should meet this basic requirement. Similarly, it is important that such CNT dispersions be uniform and stable to obtain accurate concentration data. In this regard, the solubilization of pristine CNTs in aqueous solvents remains an obstacle to realizing their potential as pharmaceutical excipients because of the rather hydrophobic character of the graphene sidewalls, coupled with the strong p-p interactions between the individual tubes, which causes CNTs to assemble as bundles. To successfully disperse CNTs the dispersing medium should be capable of both wetting the hydrophobic tube surfaces and modifying the tube surfaces to decrease tube aggregation.⁶

Four basic approaches have been used to obtain dispersion:

- (1) Surfactant-assisted dispersion,
- (2) Solvent dispersion,
- (3) Functionalization of CNT side walls, and
- (4) Biomolecular dispersion.

As part of the characterization of the degree of dispersibility, CNT dispersion can be assigned to three different categories: dispersed, swollen, and sedimented. In the dispersed state CNTs show no signs of aggregation and phase separation for several months after dispersion by sonication, resulting in a stable brown or black uniform suspension. Swollen describes the partial dispersion of CNTs, with aggregation, precipitation, and phase separation of the CNT solution within several days after sonication. The separated dispersion typically has a hazy brown or black supernatant, with visible “fluffy” sediment of CNTs in the medium. In sedimented dispersions CNT aggregates form sediment within minutes of sonication, have a low sedimentation volume, and a clear supernatant.⁶

Surfactants in general can be useful for dispersing CNTs, although the chemical structure of the surfactant is important. Ham and Moore et al independently showed that dispersibility by nonionic surfactants is a function of the hydrophobic alkyl chain length of the surfactant. Ham et al determined that if adequate dispersibility is to be achieved an alkyl chain length greater than 10 was required, and that dispersibility increased with increasing alkyl chain length. The higher molecular weight surfactants and polymers increased the solubility of CNTs through steric stabilization by adsorbed surfactant/polymer onto the walls of the CNTs, thereby impeding aggregation. Vaisman *et al.*, determined that the controlling factor for dispersion seems to be the charge of the head group, rather than the hydrophobic alkyl chain length. As the charge (zeta potential) increases, the dispersion is stabilized by the increased electrostatic repulsion. The current limitations of surfactant-based solubilization are the relatively low levels of solubility and that the surfactant often remains as an impurity in downstream processes. Nevertheless, this approach could be potentially useful in pharmaceutical applications, where surfactants are routinely incorporated in formulations for improved delivery.⁶

The chemistry behind the dispersion of CNTs in solvents is under investigation, and it is not clear what forces drive dispersion. Some of the organic solvents used to achieve dispersion are N,N'-dimethylformamide, methyl pyrrolidone, chloroform, and dimethyl sulfoxide (DMSO). However, these suspensions are stable only over a timescale of days. Irrespective of the dispersion approach, the “dissolution” process is aided by prolonged sonication, because sonication provides the mechanical energy to overcome the inter tube vander Waals forces, resulting in exfoliation into individual CNTs.⁶

Various modifications to CNT side walls have been used to improve solubility and dispersion in polar solvents by introducing polar functional groups on CNT surfaces. Dispersion is achieved by eliminating the vander Waals forces between individual or bundles of CNTs by introducing functional groups on their surfaces. The most common functionalization approach is carboxylation by itself and the subsequent functionalization of the carboxylated intermediate into other soluble biocompatible products. Some of the relevant functionalization techniques used include the 1,3-dipolar cyclo addition reaction and functionalization with polyethylene glycol moieties, a process known as PEGylation.⁷

The use of biomolecules to disperse CNTs in solution has been described in several reports. Dieckmann *et al.*, reported the dispersion of CNTs in solution using nonspecific binding of an α -helix amphiphilic peptide to CNTs. Both single-stranded (ss) and double-stranded (ds) DNA have been used to disperse CNTs. Initial reports suggested that ssDNA-assisted dispersion of CNTs in solution depended on a nucleotide sequence rich in guanine and thymine. However, this dispersion is not necessarily a function of nucleotide sequence but primarily a result of p-stacking of the ssDNA on the CNT sidewalls. The stability of DNA dispersions results from the electrostatic repulsion of the negatively charged phosphate backbone of the DNA, giving rise to a stable CNT dispersion.⁸

Covalent sidewall functionalization is expected to produce the most stable dispersion, because the dispersion becomes a function of the bound functional groups and the density of the bound groups. Surfactant and biomolecular dispersion, on the other hand, are controlled by the efficiency of the physical wrapping of molecular units around the CNTs, which involves forces that are relatively weaker than those involved in covalent functionalization. The chemistry of solvent dispersion, however, is not clear.⁶

7. SYNTHESIS OF CARBON NANOTUBES

Carbon nanotubes are generally produced by three main techniques, arc discharge, laser ablation and chemical vapour deposition, though scientists are researching more economic ways to produce these structures. In arc discharge, a vapour is created by an arc discharge between two carbon electrodes with or without catalyst. Nanotubes self-assemble from the resulting carbon vapour. In the laser ablation technique, a high-power laser beam impinges on a volume of carbon containing feed stock gas (methane or carbon monoxide). At the moment, laser ablation produces a small amount of clean nanotubes, whereas arc discharge methods generally produce large quantities of impure material. In general, chemical vapour deposition (CVD) results in MWNTs or poor quality SWNTs.⁹



7.1. Growth mechanism

The way in which nanotubes are formed is not exactly known. The growth mechanism is still a subject of controversy, and more than one mechanism might be operative during the formation of CNTs. One of the mechanisms consists out of three steps. First a precursor to the formation of nanotubes and fullerenes, C_2 , is formed on the surface of the metal catalyst particle. From this metastable carbide particle, a rod like carbon is formed rapidly. Secondly there is a slow graphitisation of its wall. This mechanism is based on in-situ TEM observations. The exact atmospheric conditions depend on the technique used, later on, these will be explained for each technique as they are specific for a technique.⁹

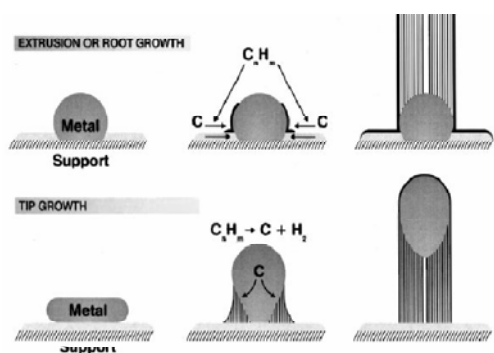


Figure 3: Growth mechanism of carbon nanotubes

There are several theories on the exact growth mechanism for nanotubes. One theory postulates that metal catalyst particles are floating or are supported on graphite or another substrate. It presumes that the catalyst particles are spherical or pear-shaped, in which case the deposition will take place on only one half of the surface (this is the lower curvature side for the pear shaped particles). The carbon diffuses along the concentration gradient and precipitates on the opposite half, around and below the bisecting diameter. However, it does not precipitate from the apex of the hemisphere, which accounts for the hollow core that is characteristic of these filaments. For supported metals, filaments can form either by 'extrusion (also known as base growth)' in which the nanotube grows upwards from the metal particles that remain attached to the substrate, or the particles detach and move at the head of the growing nanotube, labelled 'tip-growth'. Depending on the size of the catalyst particles, SWNT or MWNT are grown. In arc discharge, if no catalyst is present in the graphite, MWNT will be grown on the C_2 -particles that are formed in the plasma.

7.2. Arc Discharge

The carbon arc discharge method, initially used for producing C_{60} fullerenes, is the most common and perhaps easiest way to produce carbon nanotubes as it is rather simple to undertake. However, it is a technique that produces a mixture of components and requires separating nanotubes from the soot and the catalytic metals present in the crude product. This method creates

nanotubes through arc-vaporisation of two carbon rods placed end to end, separated by approximately 1mm, in an enclosure that is usually filled with inert gas (helium, argon) at low pressure (between 50 and 700 mbar). Recent investigations have shown that it is also possible to create nanotubes with the arc method in liquid nitrogen. A direct current of 50 to 100 A driven by approximately 20 V creates a high temperature discharge between the two electrodes. The discharge vaporises one of the carbon rods and forms a small rod shaped deposit on the other rod. Producing nanotubes in high yield depends on the uniformity of the plasma arc and the temperature of the deposit form on the carbon electrode.

Insight in the growth mechanism is increasing and measurements have shown that different diameter distributions have been found depending on the mixture of helium and argon. These mixtures have different diffusion coefficients and thermal conductivities. These properties affect the speed with which the carbon and catalyst molecules diffuse and cool., affecting nanotube diameter in the arc process. This implies that single-layer tubules nucleate and grow on metal particles in different sizes depending on the quenching rate in the plasma and it suggests that temperature and carbon and metal catalyst densities affect the diameter distribution of nanotubes. Depending on the exact technique, it is possible to selectively grow SWNTs or MWNTs, which is shown in Figure 4. Two distinct methods of synthesis can be performed with the arc discharge apparatus.¹⁰

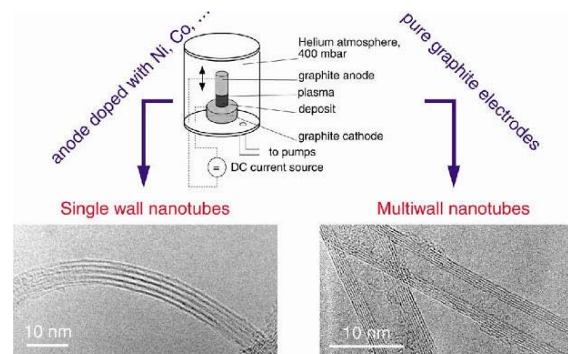


Figure 4: Arc Discharge Method

7.3. Laser ablation

In 1995, Smalley's group at Rice University reported the synthesis of carbon nanotubes by laser vaporisation. The laser vaporisation apparatus used by Smalley's group is shown in Figure 5. A pulsed or continuous laser is used to vaporise a graphite target in an oven at 1200°C. The main difference between continuous and pulsed laser, is that the pulsed laser demands a much higher light intensity. The oven is filled with helium or argon gas in order to keep the pressure at 500 Torr. A very hot vapour plume forms, then expands and cools rapidly. As the vaporised species cool, small carbon molecules and atoms quickly condense to form larger clusters, possibly including fullerenes. The catalysts also begin to condense, but more slowly at first, and attach to carbon clusters and prevent their closing into cage structures. Catalysts may even

open cage structures when they attach to them. From these initial clusters, tubular molecules grow into single-wall carbon nanotubes until the catalyst particles become too large, or until conditions have cooled sufficiently that carbon no longer can diffuse through or over the surface of the catalyst particles. It is also possible that the particles become that much coated with a carbon layer that they cannot absorb more and the nanotube stops growing. The SWNTs formed in this case are bundled together by vander Waals forces.¹¹

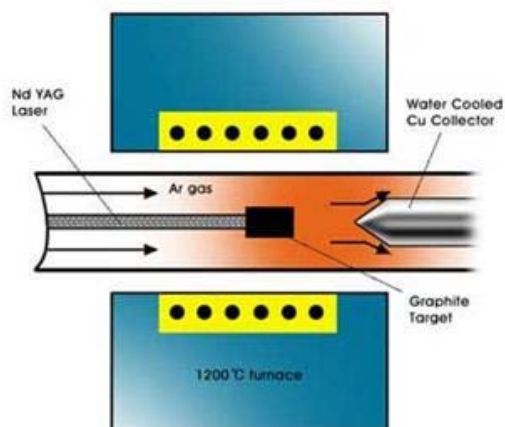


Figure 5: Laser Ablation

There are some striking, but not exact similarities, in the comparison of the spectral emission of excited species in laser ablation of a composite graphite target with that of laser-irradiated C_{60} vapour. This suggests that fullerenes are also produced by laser ablation of catalyst-filled graphite, as is the case when no catalysts are included in the target. However, subsequent laser pulses excite fullerenes to emit C_2 that adsorbs on catalyst particles and feeds SWNT growth. However, there is insufficient evidence to conclude this with certainty. Laser ablation is almost similar to arc discharge, since the optimum background gas and catalyst mix is the same as in the arc discharge process. This might be due to very similar reaction conditions needed, and the reactions probably occur with the same mechanism.¹¹

7.4. Chemical vapour deposition

Chemical vapour deposition (CVD) synthesis is achieved by putting a carbon source in the gas phase and using an energy source, such as a plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule. Commonly used gaseous carbon sources include methane, carbon monoxide and acetylene. The energy source is used to “crack” the molecule into reactive atomic carbon. Then, the carbon diffuses towards the substrate, which is heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) where it will bind. Carbon nanotubes will be formed if the proper parameters are maintained. Excellent alignment, as well as positional control on nanometer scale, can be achieved by using CVD. Control over the diameter, as well as the growth rate of the nanotubes can also be maintained. The appropriate metal catalyst can

preferentially grow single rather than multi-walled nanotubes. CVD carbon nanotube synthesis is essentially a two-step process consisting of a catalyst preparation step followed by the actual synthesis of the nanotube. The catalyst is generally prepared by sputtering a transition metal onto a substrate and then using either chemical etching or thermal annealing to induce catalyst particle nucleation. Thermal annealing results in cluster formation on the substrate, from which the nanotubes will grow. Ammonia may be used as the etchant. The temperatures for the synthesis of nanotubes by CVD are generally within the 650–900°C range. Typical yields for CVD are approximately 30%. These are the basic principles of the CVD process. In the last decennia, different techniques for the carbon nanotubes synthesis with CVD have been developed, such as plasma enhanced CVD, thermal chemical CVD, alcohol catalytic CVD, vapour phase growth, aero gel-supported CVD and laser assisted CVD.¹²

8. PURIFICATION

The as-produced SWNT soot contains a lot of impurities. The main impurities in the soot are graphite (wrapped up) sheets, amorphous carbon, metalcatalyst and the smaller fullerenes. These impurities will interfere with most of the desired properties of the SWNTs. Also in the fundamental research, it is preferred to obtain SWNTs or the impurities, as pure as possible without changing them. In order to understand the measurements better, the SWNT samples also have to be as homogeneous as possible. The common industrial techniques use strong oxidation and acid refluxing techniques, which have an effect on the structure of the tubes. Basically, these techniques can be divided into two main streams, structure selective and size selective separations. The first one will separate the SWNTs from the impurities; the second one will give a more homogeneous diameter or size distribution. The techniques will be briefly explained in this chapter and if possible, the selectivity will be discussed. The techniques that will be discussed are oxidation, acid treatment, annealing, ultrasonication, micro filtration, ferromagnetic separation, cutting, functionalisation and chromatography techniques.¹³

8.1. Oxidation

Oxidative treatment of the SWNTs is a good way to remove carbonaceous impurities or to clear the metal surface. The main disadvantages of oxidation are that not only the impurities are oxidised, but also the SWNTs. Luckily the damage to SWNTs is less than the damage to the impurities. These impurities have relatively more defects or a more open structure. Another reason why impurity oxidation is preferred, is that these impurities are most commonly attached to the metal catalyst, which also acts as oxidising catalyst. Altogether, the efficiency and the yield of the procedure are highly dependable on a lot of factors, such as metal content, oxidation time, environment, oxidising agent and temperature.¹³

8.2. Acid Treatment

In general the acid treatment will remove the metal catalyst. First of all, the surface of the metal must be exposed by oxidation or sonication. The metal catalyst is then exposed to acid and solvated. The SWNTs remain in suspended form. When using a treatment in HNO_3 , the acid only has an effect on the metal catalyst. It has no effect on the SWNTs and other carbon particles. If a treatment in HCl is used, the acid has also a little effect on the SWNTs and other carbon particles. The mild acid treatment (4 M HCl reflux) is basically the same as the HNO_3 reflux, but here the metal has to be totally exposed to the acid to solvate it.¹⁴

8.3. Annealing

Due to high temperatures (873 – 1873 K) the nanotubes will be rearranged and defects will be consumed. The high temperature also causes the graphitic carbon and the short fullerenes to pyrolyse. When using high temperature vacuum treatment (1873 K) the metal will be melted and can also be removed.¹⁴

8.4. Ultrasonication

In this technique particles are separated due to ultrasonic vibrations. Agglomerates of different nanoparticles will be forced to vibrate and will become more dispersed. The separation of the particles is highly dependant on the surfactant, solvent and reagent used. The solvent influences the stability of the dispersed tubes in the system. In poor solvents the SWNTs are more stable if they are still attached to the metal. But in some solvents, such as alcohols, monodispersed particles are relatively stable. When an acid is used, the purity of the SWNTs depends on the exposure time. When the tubes are exposed to the acid for a short time, only the metal solvates, but for a longer exposure time, the tubes will also be chemically cut.¹⁴

8.5. Magnetic Purification

In this method ferromagnetic (catalytic) particles are mechanically removed from their graphitic shells. The SWNTs suspension is mixed with inorganic nanoparticles (mainly ZrO_2 or CaCO_3) in an ultrasonic bath to remove the ferromagnetic particles. Then, the particles are trapped with permanent magnetic poles. After a subsequent chemical treatment, a high purity SWNT material will be obtained.¹⁴

8.6. Micro Filtration

Micro filtration is based on size or particle separation. SWNTs and a small amount of carbon nanoparticles are trapped in a filter. The other nanoparticles (catalyst metal, fullerenes and carbon nanoparticles) are passing through the filter. One way of separating fullerenes from the SWNTs by micro filtration is to soak the as-produced SWNTs first in a CS_2 solution. The CS_2 insolubles are then trapped in a filter. The fullerenes which are solvated in the CS_2 , pass through the filter.¹⁴

8.7. Cutting

Cutting of the SWNTs can either be induced chemically, mechanically or as a combination of these. SWNTs can be chemically cut by partially functionalising the tubes, for example with fluor. Then, the fluorinated carbon will be driven off the sidewall with pyrolysis in the form of CF_4 or COF_2 . This will leave behind the chemically cut nanotubes. Mechanical cutting of the nanotubes can be induced by ball-milling. Here, the bonds will break due to the high friction between the nanoparticles and the nanotubes will be disordered. A combination of mechanical and chemical cutting of the nanotubes, is ultrasonic induced cutting in an acid solution. In this way the ultrasonic vibration will give the nanotubes sufficient energy to leave the catalyst surface. Then, in combination with acid the nanotubes will rupture at the defect sites.¹⁴

8.8. Functionalisation

Functionalisation is based on making SWNTs more soluble than the impurities by attaching other groups to the tubes. Now it is easy to separate them from insoluble impurities, such as metal, with filtration. Another functionalisation technique also leaves the SWNT structure intact and makes them soluble for chromatographic size separation. For recovery of the purified SWNTs, the functional groups can be simply removed by thermal treatment, such as annealing.¹⁴

8.9. Chromatography

This technique is mainly used to separate small quantities of SWNTs into fractions with small length and diameter distribution. The SWNTs are run over a column with a porous material, through which the SWNTs will flow. The columns used are GPC (Gel Permeation Chromatography) and HPLC-SEC (High Performance Liquid Chromatography - Size Exclusion Chromatography) columns. The number of pores the SWNTs will flow through, depends on their size. This means that, the smaller the molecule, the longer the pathway to the end of the column will be and that the larger molecules will come off first. The pore size will control what size distribution can be separated. However, a problem is that the SWNTs have to be either dispersed or solvated. This can be done by ultrasonication or functionalisation with soluble groups.¹⁴

9. PROPERTIES OF CARBON NANOTUBES

Electronic, molecular and structural properties of carbon nanotubes are determined to a large extent by their nearly one dimensional structure. The most important properties of CNTs and their molecular background are stated below.¹⁵

9.1. Chemical Reactivity

The chemical reactivity of a CNT is, compared with a graphene sheet, enhanced as a direct result of the curvature of the CNT surface. Carbon nanotube reactivity is directly related to the pi-orbital mismatch caused by an increased curvature. Therefore, a distinction must



bemaded between the sidewall and the end caps of a nanotube. For the same reason, a smaller nanotube diameter results in increased reactivity. Covalent chemical modification of either sidewalls or end caps has shown to be possible. For example, the solubility of CNTs in different solvents can be controlled this way. Though, direct investigation of chemical modifications on nanotube behaviour is difficult as the crude nanotube samples are still not pure enough.¹⁵

9.2. Electrical Conductivity

Depending on their chiral vector, carbon nanotubes with a small diameter are either semi-conducting or metallic. The differences in conducting properties are caused by the molecular structure that results in a different band structure and thus a different band gap. The differences in conductivity can easily be derived from the graphene sheet properties. It was shown that a (n,m) nanotube is metallic as accounts that: $n=m$ or $(n-m) = 3i$, where i is an integer and n and m are defining the nanotube. The resistance to conduction is determined by quantum mechanical aspects and was proved to be independent of the nanotube length.¹⁵

9.3. Optical Activity

Theoretical studies have revealed that the optical activity of chiral nanotube disappears if the nanotubes become larger. Therefore, it is expected that other physical properties are influenced by these parameters too. Use of the optical activity might result in optical devices in which CNTs play an important role.¹⁵

9.4. Mechanical Strength

Carbon nanotubes have a very large Young modulus in their axial direction. The nanotube as a whole is very flexible because of the great length. Therefore, these compounds are potentially suitable for applications in composite materials that need anisotropic properties.¹⁵

10. ANALYTICAL TECHNIQUES FOR CARBON NANOTUBES

Thermogravimetric analysis is used to quantitatively determine the amount of carbon and non carbon materials in bulk CNT samples, as well as CNT homogeneity and thermal stability. This is a nonselective method for assessing CNT quality, because the technique does not differentiate CNTs from metallic impurities present in the sample. It is therefore The most extensively used techniques are thermogravimetric analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), Raman spectroscopy, infrared (IR) spectroscopy, and nuclear magnetic resonance (NMR). Whereas TEM, SEM, and AFM have been used predominantly to qualitatively establish the general morphology of CNTs, IR spectroscopy, Raman spectroscopy, and NMR have been used to confirm the presence of functional groups on CNTs. Each technique has advantages used in conjunction with other techniques.¹⁶

10.1. TEM

It is used to determine the morphology and to give qualitative insight into the purity of produced CNTs. TEM uniquely provides qualitative information on the size, shape, and structure of carbonaceous materials, as well as non-CNT structured impurities in a sample. However, it is unable to identify metallic impurities, and does not differentiate from MWNTs. TEM has also been used to image cellular uptake of CNT-drug composites and to determine the fate of the CNT component after cellular uptake.¹⁷

10.2. SEM

It is used in the preliminary evaluation of CNT morphology. In its conventional setting the technique is limited by its inability to differentiate catalyst and carbonaceous impurities from CNTs. However, the metallic content of CNT samples are routinely estimated by SEM coupled with an energy dispersive x-ray analysis detector (SEM-EDX). Regardless, SEM is probably the only technique that can provide information on both CNT morphology and the metallic impurity content.¹⁸

10.3. Raman Spectroscopy

It has been used to evaluate the synthesis and purification processes of SWNTs. Carbonaceous impurities (graphite, fullerenes, amorphous carbon, etc.) present a major obstacle in interpreting Raman spectra of SWNTs, because these impurities have characteristic Raman features (D- and G-bands) identical to that of SWNTs.¹⁹

10.4. Proton NMR

It has been used to monitor the progress of CNT functionalisation. The presence of functional groups can be predicted by characteristic peaks arising from the difference in the magnetic environment. H-NMR of functionalized CNTs is characterized by broad bands for protons close to the CNT, becoming sharper with distance. H-NMR has been used to monitor the synthesis and attachment of functional groups to CNTs.⁽²⁰⁾

10.5. IR Spectroscopy

It is primarily a qualitative tool used to identify functional groups and the nature of their attachment to CNT sidewalls. Different functional groups absorb characteristic frequencies of IR radiation, giving rise to a fingerprint identification of bonds. It is a complementary technique to NMR, to confirm the presence of bonds between CNTs and of attached moieties.²⁰

11. FUNCTIONALISATION OF CNT

CNT are materials practically insoluble, or hardly dispersed, in any kind of solvent. To integrate the nanotube technology with the biological milieu, the solubility of the tubes especially in aqueous solutions must be improved. Several ways of dispersion and solubilization have been explored and can be basically divided in two main approaches. One procedure consists



on the noncovalent functionalization of CNT with surfactants, nucleic acids, peptides, polymers and oligomer. The advantage of this process is the preservation of the electronic structure of the nanotube aromatic surface. This property is of fundamental importance for the use of nanotubes as biosensors. The second methodology is based on CNT covalent functionalization. First, CNT are cut and oxidized to generate a certain number of carbon nanotubes and subsequently derivatized with different types of molecules. Alternatively, CNT sidewalls can be directly functionalized by addition reactions. The introduction of moieties on the tube external surface creates repulsion between the single tubes allowing them to easily disperse into the solvent.¹

11.1. Noncovalent functionalization of carbon nanotubes

The noncovalent dispersion of CNT in solution allows preservation of their aromatic structure and thus their electronic characteristics. The dispersion procedures usually involving ultrasonication, centrifugation and filtration are quick and easy. Hydrophobic or k-k interactions are often evoked as likely responsible for noncovalent stabilization. Nowadays, three classes of molecules are mainly used for CNT dispersion. Surfactants are used because they are easily available and low cost. Polymers and biopolymers (nucleic acids and peptides) are also very efficient in the dispersion process.¹

11.1.1. Surfactants

A series of anionic, cationic and nonionic surfactants have been already proposed to disperse nanotubes. Sodium dodecylsulfate (SDS) and Triton X-100 were used to obtain CNT suspensions up to 0.1 and 0.5 mg/mL, respectively. However, the stability of this suspension was no longer than 1 week. A better result was obtained by using sodium dodecylbenzenesulfonate (SDBS), which was able to provide stability over one month reaching 10 mg/mL concentration of the suspension. The combination of k-k interactions of aromatic moieties between CNT and SDBS and the long lipid chains of the SDBS increases the stability of the complex. Atomic force microscopy (AFM) and electronic transmission microscopy (TEM) studies of SDS/CNT dispersions showed that CNT are mainly present as individual tubes uniformly covered by the surfactant. The types of amphiphilic molecules with long lipid chains are able to form a half-cylinder perpendicular or tilted around the tubes in a micelle-like arrangement. Triton-X instead mainly interacts by k-stacking. Another approach for the adsorption/dispersion of CNT via k interaction resides on the use of 1-pyrene butanoic acid activated a succinimidyl ester, which promptly reacts with the amino groups present in the proteins like ferritin or streptavidin. The solubility of CNT was between 0.1 and 0.7 mg/mL, which is rather low but acceptable for biological use. Although surfactants may be efficient in the solubilization of CNT, they are known to permeabilize plasma membranes and have a toxicity profile of their own. Therefore, the implications stemming from use of

surfactants interacting with biological systems can limit the possible biomedical applications of such surfactant-stabilized CNT complexes.¹

11.1.2. Polymers

Polymers are widely used for example as molecular carriers for drug delivery. In the solubilization of CNT they represent a good alternative to surfactants although they do not have a better dispersion efficiency. The mechanism of dispersion is based in this case on wrapping of the polymer around the tubes. In the case of nonionic polymers, based on poly(oxyethylene) copolymers, the efficiency of the dispersion is instead due to their hydrophilic counterpart. For particularly high molecular weight polymers, the suspendability is enhanced as the steric stabilization is increased by a wider coverage of the surface. In a similar approach, CNT were dispersed by using cationic copolymers. The nanotubes were covered by the hydrophobic backbone of the polymer while the positive tetraalkylammonium groups were exposed at the surface to display water solubility. These types of fluorescent polymers have also been employed to study the interaction with mammalian cells. Poly(vinylpyrrolidone) was conjugated with various fluorescent dyes. CNT were suspended in 1% SDS and mixed with the fluorescent polymers to form supramolecular complexes, which were found to have potential applications as new molecular probes.¹

11.1.3. Biopolymers

Self-assembly processes similar to k-k interactions typical of double-stranded DNA can be exploited to disperse the nanotubes. Nucleic acids are certainly ideal candidates to form supramolecular complexes based on k-stacking between the aromatic bases and the CNT surface. Indeed, Zeng *et al.*, have described an easy way to solubilize carbon nanotubes by simple sonication in the presence of a single-strand DNA. A molecular modeling study was performed to explain the formation of the hybrids exerted by DNA wrapping and subsequent CNT debundling. The DNA-nanotube complexes displayed solubility in the range of mg/ml, and their good stability permitted the purification using ion-exchange chromatography. Amphiphilic peptides belong to another class of biopolymers that efficiently disperse CNT. The presence of amino acids like tryptophan, phenylalanine, tyrosine and histidine into the peptide sequence plays a key role on the solubilization process in water. These peptides could be selected from phage-display peptide libraries or by design. The design of highly specific peptides able to wrap around the nanotubes represent an interesting way to assure solubility and may even provide a useful tool for size separation. More recently, cyclic peptides were also proven to have similar capabilities.¹

11.2. Covalent functionalization of carbon nanotubes

The alternative way to render CNT soluble into a wide range of solvents is the modification of their sidewalls and tips by organic functionalization can be assured for



example by a covalent attachment of hydrophilic moieties. Two main strategies are currently used to attach functional groups to CNT.¹

11.2.1. Oxidative treatment using strong acid solutions

The variation of the type of acid, its concentration and the reaction conditions (temperature, sonication) generated carbon nanotubes are covered by carboxylic functions at their tips and at the defect points. The carboxylates were then used to incorporate a variety of other groups to improve CNT solubility. The introduction occurred via COOH activation using thionyl chloride or carbodiimide. Similarly, oxidized CNT were solubilized by direct heating in the presence of amino polymer.¹

11.2.2. Addition reactions to CNT

By exploiting the chemistry of fullerenes, 1,3-dipolar cyclo addition of azomethine ylides, aryl diazonium salt addition or reductive alkylation using lithium and alkyl halides have been successfully employed to CNT. Such direct sidewall modification of CNT permitted the incorporation of different functional groups on the nanotube which could be further derivatized. The covalent bond presents the advantage of being more robust during manipulation and processing in comparison to the noncovalent dispersion. Nevertheless, both covalent and noncovalent functionalization of CNT have been exploited for the application of such materials in the field of drug delivery.¹

12. APPLICATIONS OF CNTS

12.1. Carrier for drug delivery

Research studies have proved CNTs and CNHs as a potential carrier for drug delivery system.

- 1) Functionalised carbon nanotubes are reported for targeting of Amphotericin B to Cells.
- 2) Cisplatin incorporated oxidized SWNHs have showed slow release of Cisplatin in aqueous environment. The released Cisplatin had been effective in terminating the growth of human lung cancer cells, while the SWNHs alone did not show anticancer activity.
- 3) Anticancer drug Polyphosphazene platinum given with nanotubes had enhanced permeability, distribution and retention in the brain due to controlled lipophilicity of nanotubes.
- 4) Antibiotic, Doxorubicin given with nanotubes is reported for enhanced intracellular penetration.
- 5) The gelatin CNT mixture (hydro-gel) has been used as potential carrier system for biomedical.
- 6) CNT-based carrier system can offer a successful oral alternative administration of Erythropoietin (EPO), which has not been possible so far because of the denaturation of EPO by the gastric environment conditions and enzymes.
- 7) They can be used as lubricants or glidants in tablet manufacturing due to nanosize and sliding nature of graphite layers bound with vander waals forces.²¹

12.2. Genetic Engineering

In genetic engineering, CNTs and CNHs are used to manipulate genomes and atoms in the development of bioimaging genomes, proteomics and tissue engineering. Their tubular nature has proved them as a vector in gene therapy. The unwound DNA winds around SWNT by connecting its specific nucleosides and causes change in its electrostatic properties. This creates its potential application in diagnostics (polymerase chain reactions) and therapeutics.²¹

12.3. Artificial Implants

Normally body shows rejection reaction for implants with the post administration pain. But, miniature sized nanotubes and nanohorns get attached with other proteins and amino acids avoiding rejection. Also, they can be used as implants in the form of artificial joints without host rejection reaction. Moreover, due to their high tensile strength, carbon nano tubes filled with calcium and arranged/grouped in the structure of bone can act as bone substitute.²¹

12.4. Preservative

Carbon nanotubes and nanohorns are antioxidant in nature. Hence, they are used to preserve drugs formulations prone to oxidation. Their antioxidant property is used in antiaging cosmetics and with zinc oxide as sunscreen dermatological to prevent oxidation of important skin components.⁽²¹⁾

12.5. Diagnostic Tool

Protein-encapsulated or protein/enzyme filled nanotubes, due to their fluorescence ability in presence of specific biomolecules have been tried as implantable biosensors. Even, nanocapsules filled with magnetic materials, radioisotope enzymes can be used as biosensors. Nanosize robots and motors with nanotubes can be used in studying cells and biological systems.²¹

12.6. As Catalyst

Nanohorns offer large surface area and hence, the catalyst at molecular level can be incorporated into nanotubes in large amount and simultaneously can be released in required rate at particular time. Hence, reduction in the frequency and amount of catalyst addition can be achieved by using CNTs and CNHs.²¹

13. LIMITATIONS OF CNT

- Lack of solubility in most solvents compatible with the biological milieu (aqueous based).
- The production of structurally and chemically reproducible batches of CNTs with identical characteristics.
- Difficulty in maintaining high quality and minimal impurities.²¹



14. CONCLUSION

This review on carbon nanotubes reveals the overview on structure, morphology, synthesis and purification methods of carbon nanotubes along with their properties, benefits and applications. The distinct structural properties of carbon nanoparticles, in particular their high aspect ratio and propensity to functional modification and subsequent use as carrier vectors, make them useful for pharmaceutical nanodelivery. Carbon nanotubes have the added advantage of being potential nanodevices for controlled drug delivery. As the carbon nanotubes allow the easy functionalization on their sidewall and also in the core, many drugs can easily be sited on them, thus giving them the property as targets in drug delivery systems. The remarkable physical properties of nanotubes create a host of application possibilities, some derived as an extension of traditional carbon fiber applications, but many are new possibilities, based on the novel electronic and mechanical behaviour of nanotubes. It needs to be said that the excitement in this field arises due to the versatility of this material and the possibility to predict properties based on its well-defined perfect crystal lattice. Nanotubes truly bridge the gap between the molecular realm and the macro-world, and are destined to be a star in future technology. With the prospect of gene therapy, cancer treatments, and innovative new answers for life-threatening diseases on the horizon, the science of nanomedicine has become an ever-growing field that has an incredible ability to bypass barriers. The properties and characteristics of CNTs are still being researched heavily and scientists have barely begun to tap the potential of these structures. Single and multiple walled carbon nanotubes have already proven to serve as safer and more effective alternatives to previous drug delivery methods. They can pass through membranes, carrying therapeutic drugs, vaccines, and nucleic acids deep into the cell to targets previously unreachable. They also serve as ideal non-toxic vehicles which, in some cases, increase the solubility of the drug attached, resulting in greater efficacy and safety. Overall, recent studies regarding CNTs have shown a very promising glimpse of what lies ahead in the future of medicine.

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