ABSTRACT

Carbon nanotubes (CNTs) are a recently discovered allotrope of carbon. They take the form of cylindrical carbon molecules and have novel properties that make them potentially useful in a wide variety of applications in nanotechnology, electronics, optics, and other fields of materials science. They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat. Inorganic nanotubes have also been synthesized. A nanotube is a member of the fullerene structural family, which also includes buckyballs. Whereas buckyballs are spherical in shape, a nanotube is cylindrical, with at least one end typically capped with a hemisphere of the buckyball structure. Their name is derived from their size, since the diameter of a nanotube is of the order of a few nanometres (approximately 50,000 times smaller than the width of a human hair), while they can be up to several millimetres in length.

There are two main types of nanotubes: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Manufacturing a nanotube is dependent on applied quantum chemistry, specifically, orbital hybridization. Nanotubes are composed entirely of sp² bonds, similar to those of graphite. This bonding structure, stronger than the sp³ bonds found in diamond, provides the molecules with their unique strength. Nanotubes naturally align themselves into "ropes" held together by Van der Waal’s forces. Under high pressure, nanotubes can merge together, trading some sp² bonds for sp³ bonds, giving great possibility for producing strong, unlimited-length wires through high-pressure nanotube linking.
CHAPTER: 1

INTRODUCTION

1.1 Carbon Nanotube

Carbon nanotubes are allotropes of carbon with nanometre diameters and lengths of many microns. They are among the stiffest and strongest fibres known, and have remarkable electronic properties and many other unique characteristics. Incorporation of a small amount of carbon nanotube into metals and ceramics leads to the formation of high performance and functional nano composites with enhanced mechanical and physical properties. Considerable attention has been applied to the development and synthesis of carbon nanotube-reinforced composites in the past decade. For these reasons they have attracted huge academic and industrial interest.

Nanotubes are members of the fullerene structural family, which also includes the spherical buckyballs. The ends of a nanotube may be capped with a hemisphere of the buckyball structure. Their name is derived from their size, since the diameter of a nanotube is on the order of a few nanometres (approximately 1/50,000th of the width of a human hair), while they can be up to a few micrometres in length. Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs).

Applied quantum chemistry, specifically, orbital hybridization best describes chemical bonding in nanotubes. The chemical bonding of nanotubes is composed entirely of sp² bonds, similar to those of graphite. These bonds, which are stronger than the sp³ bonds found in alkanes, provide nano tubules with their unique strength. Moreover, nanotubes naturally align themselves into "ropes" held together by Van der Waal’s forces.
A 2006 editorial written by Marc Monthioux and Vladimir Kuznetsov in the journal “Carbon” described the interesting and often misstated origin of the carbon nanotube. A large percentage of academic and popular literature attributes the discovery of hollow, nanometre-size tubes composed of graphitic carbon to Sumio Iijima of NEC in 1991. In 1952 L. V. Radushkevich and V. M. Lukyanovich published clear images of 50 nanometre diameter tubes made of carbon in the Soviet Journal of Physical Chemistry. This discovery was largely unnoticed, as the article was published in the Russian language, and Western scientists' access to Soviet press was limited during the Cold War. It is likely that carbon nanotubes were produced before this date, but the invention of the transmission electron microscope (TEM) allowed direct visualization of these structures. Carbon nanotubes have been produced and observed under a variety of conditions prior to 1991. A paper by Oberlin, Endo, and Koyama published in 1976 clearly showed hollow carbon fibres with nanometre-scale diameters using a vapour-growth technique. Additionally, the authors show a TEM image of a nanotube consisting of a single wall of graphene. Later, Endo has referred to this image as a single-walled nanotube.

In 1979 John Abrahamson presented evidence of carbon nanotubes at the 14th Biennial Conference of Carbon at Pennsylvania State University. The conference paper described carbon nanotubes as carbon fibers which were produced on carbon anodes during arc discharge. A characterization of these fibers was given as well as hypotheses for their growth in a nitrogen atmosphere at low pressures.

In 1981 a group of Soviet scientists published the results of chemical and structural characterization of carbon nanoparticles produced by a thermocatalytical disproportionation of carbon monoxide. Using TEM images and XRD patterns, the authors suggested that their “carbon multi-layer tubular crystals” were formed by rolling graphene layers into cylinders. They speculated that by rolling graphene layers into a cylinder, many different arrangements of graphene hexagonal nets are possible. They suggested two possibilities of such arrangements: circular arrangement (armchair nanotube) and a spiral, helical arrangement (chiral tube).
In 1987, Howard G. Tennett of Hyperion Catalysis was issued a U.S. patent for the production of "cylindrical discrete carbon fibrils" with a "constant diameter between about 3.5 and about 70 nanometers..., length 102 times the diameter, and an outer region of multiple essentially continuous layers of ordered carbon atoms and a distinct inner core...."

Fig 2.1: A picture of Professor Sumio Iijima

Iijima's discovery of multi-walled carbon nanotubes in the insoluble material of arc-burned graphite rods in 1991 and Mintmire, Dunlap, and White's independent prediction that if single-walled carbon nanotubes could be made, then they would exhibit remarkable conducting properties helped create the initial buzz that is now associated with carbon nanotubes. Nanotube research accelerated greatly following the independent discoveries by Bethune at IBM and Iijima at NEC of single-walled carbon nanotubes and methods to specifically produce them by adding transition-metal catalysts to the carbon in an arc discharge. The arc discharge technique was well-known to produce the famed Buckminster fullerene on a preparative scale, and these results appeared to extend the run of accidental discoveries relating to fullerenes. The original observation of fullerenes in mass spectrometry was not anticipated, and the first mass-production technique by Krätschmer and Huffman was used for several years before realizing that it produced fullerenes.

The discovery of nanotubes remains a contentious issue. Many believe that Iijima's report in 1991 is of particular importance because it brought carbon nanotubes into the awareness of the scientific community as a whole.
CHAPTER: 3

TYPES OF NANOTUBES

3.1 Single-walled Nanotubes

Single-walled metallic carbon nanotubes (SWNT) can be regarded to as a graphene sheet rolled up in the shape of a cylinder, with a radius of a few nm. According to the wrapping angle, one can obtain different types of nanotubes. Due to the quantization of the electron motion in the circular direction, SWNT effectively behave as one-dimensional conductors up to energies of the order of eV. Electronic correlations are therefore very important in these materials. Carbon nanotubes are formed by rolling graphene sheets of hexagonal carbon rings into hollow cylinders. Single-walled carbon nanotubes (SWNT) are composed of a single graphene cylinder with a diameter in the range of 0.4–3nm and capped at both ends by a hemisphere of fullerene. The length of nanotubes is in the range of several hundred micrometers to millimeters. These characteristics make the nanotubes exhibit very large aspect ratios. The strong van der Waals attractions that exist between the surfaces of SWNTs allow them to assemble into ropes in most cases. Nanotube ropes may have a diameter of 10–20nm and a length of 100 mm or above. Conceptually, the graphene sheets can be rolled into different structures, that is, zig-zag, armchair and chiral
Fig 3.2 Picture showing chiral vector and chiral angle

Fig 3.3: A pictorial representation of zig-zag, armchair and chiral structures
Accordingly, the nanotube structure can be described by a chiral vector \( \mathbf{C}_h \) defined by the following equation:

\[
\mathbf{C}_h = na_1 + ma_2 
\]  

\[ \ldots \text{(eqn 2.1)} \]

Where \( a_1 \) and \( a_2 \) are unit vectors in a two-dimensional hexagonal lattice, and \( n \) and \( m \) are integers. Thus, the structure of any nanotube can be expressed by the two integers \( n, m \) and chiral angle, \( \theta \) (Figure 3.2). When \( n=m \) and \( \theta=30^\circ \), an armchair structure is produced. Zig-zag nanotubes can be formed when \( m \) or \( n=0 \) and \( \theta=0^\circ \) while chiral nanotubes are formed for any other values of \( n \) and \( m \), having \( \theta \) between \( 0^\circ \) and \( 30^\circ \). The diameter of a nanotube can be calculated from its \((n, m)\) indices as follows

\[
d = \frac{a}{\pi} \sqrt{n^2 + nm + m^2}.
\]  

\[ \ldots \text{(eqn 2.2)} \]

Where \( a = 0.246 \) nm

Single-walled nanotubes are an important variety of carbon nanotube because they exhibit electric properties that are not shared by the multi-walled carbon nanotube (MWNT) variants. In particular, their band gap can vary from zero to about 2 eV and their electrical conductivity can show metallic or semiconducting behaviour, whereas MWNTs are zero-gap metals. Single-walled nanotubes are the most likely candidate for miniaturizing electronics beyond the micro electromechanical scale currently used in electronics. The most basic building block of these systems is the electric wire, and SWNTs can be excellent conductors. One useful application of SWNTs is in the development of the first intramolecular field effect transistors (FET). Production of the first intramolecular logic gate using SWNT FETs has recently become possible as well. To create a logic gate you must have both a p-FET and an n-FET. Because SWNTs are p-FETs when exposed to oxygen and n-FETs otherwise, it is possible to protect half of an SWNT from oxygen exposure, while exposing the other half to oxygen. This results in a single SWNT that acts as a NOT logic gate with both p and n type FETs within the same molecule.
3.2 Multi-walled Nanotubes

Fig 3.4: A picture of Multi-walled Nanotubes

Multi-walled nanotubes (MWNT) consist of multiple rolled layers (concentric tubes) of graphite. There are two models which can be used to describe the structures of multi-walled nanotubes. In the Russian Doll model, sheets of graphite are arranged in concentric cylinders, e.g. a (0,8) single-walled nanotube (SWNT) within a larger (0,17) single-walled nanotube. In the Parchment model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled newspaper. The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite, approximately 3.4 Å.

The special place of double-walled carbon nanotubes (DWNT) must be emphasized here because their morphology and properties are similar to SWNT but their resistance to chemicals is significantly improved. This is especially important when functionalization is required (this means grafting of chemical functions at the surface of the nanotubes) to add new properties to the CNT. In the case of SWNT, covalent functionalization will break some C=C double bonds, leaving "holes" in the structure on the nanotube and thus modifying both its mechanical and electrical properties. In the case of DWNT, only the outer wall is modified. DWNT synthesis on the gram-scale was first proposed in 2003 by the CCVD technique, from the selective reduction of oxide solutions in methane and hydrogen.
CHAPTER 4

SPECIAL TYPES

4.1 Nanotorus

In theory, a nanotorus is a carbon nanotube bent into a torus (doughnut shape). Nanotori are predicted to have many unique properties, such as magnetic moments 1000 times larger than previously expected for certain specific radii. Properties such as magnetic moment, thermal stability, etc. vary widely depending on radius of the torus and radius of the tube.

Fig 4.1: A picture of Nanotori

4.2 Nanobud

Carbon nanobuds are a newly created material combining two previously discovered allotropes of carbon: carbon nanotubes and fullerenes. In this new material, fullerene-like "buds" are covalently bonded to the outer sidewalls of the underlying carbon nanotube. This hybrid material has useful properties of both fullerenes and carbon nanotubes. In particular, they have been found to be exceptionally good field emitters. In composite materials, the attached fullerene molecules may function as molecular anchors preventing slipping of the nanotubes, thus improving the composite’s mechanical properties.

Fig 4.2: A picture of Nanobud
4.3 Cup stacked Carbon Nanotubes

Cup-stacked carbon nanotubes (CSCNTs) differ from other quasi-1D carbon structures, which normally behave as quasi-metallic conductors of electrons. CSCNTs exhibit semiconducting behaviours due to the stacking microstructure of graphene layers. The Cup Stack Carbon Nanotube overcomes the problematic stiffness of the conventional Carbon Nanotube. Nanotube is an advanced material whose structural arrangement resembles multi-layered cups uniformly stacked together in a configuration that increases durability and flexibility. Application in racket frame: Each cup in a stack has the ability to move flexibly at the point of impact. Besides generating power, positioning CS Carbon Nanotube technology at the sides of the frame increases ball dwell time, so you can depend on the racquet to hold the ball on the strings longer for shots with more finesse and more directional accuracy.

Fig 4.3: A picture of Cup stacked Carbon Nanotubes

4.4 Extreme Carbon Nanotubes

The observation of the longest carbon nanotubes (18.5 cm long) was reported in 2009. These nanotubes were grown on Si substrates using an improved chemical vapour deposition (CVD) method and represent electrically uniform arrays of single-walled carbon nanotubes. The shortest carbon nanotube is the organic compound cycloparaphenylene which was synthesized in early 2009. The thinnest carbon nanotube is armchair (2, 2) CNT with a diameter of 3 Å. This nanotube was grown inside a multi-walled carbon nanotube.
Assigning of carbon nanotube type was done by combination of high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy and density functional theory (DFT) calculations. The thinnest freestanding single-walled carbon nanotube is about 4.3 Å in diameter. Researchers suggested that it can be either (5, 1) or (4, 2) SWCNT, but exact type of carbon nanotube remains questionable. (3, 3), (4, 3) and (5, 1) carbon nanotubes (all about 4 Å in diameter) were unambiguously identified using more precise aberration-corrected high-resolution transmission electron microscopy. However, they were found inside of double-walled carbon nanotubes.

Fig 4.4: Cycloparaphenylene - the shortest carbon nanotube.
CHAPTER: 5

PROPERTIES OF CARBON NANO TUBES

5.1 Strength

Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp² bonds formed between the individual carbon atoms. In 2000, a multi-walled carbon nanotube was tested to have a tensile strength of 63 gigapascals (GPa) (This, for illustration, translates into the ability to endure tension of a weight equivalent to 6422 kg on a cable with cross-section of 1 mm².) Since carbon nanotubes have a low density for a solid of 1.3 to 1.4 g*cm⁻³, its specific strength of up to 48,000 KN*m*kg⁻¹ is the best of known materials, compared to high-carbon steel's 154 KN*m*kg⁻¹.

Under excessive tensile strain, the tubes will undergo plastic deformation, which means the deformation is permanent. This deformation begins at strains of approximately 5% and can increase the maximum strain the tubes undergo before fracture by releasing strain energy. CNTs are not nearly as strong under compression. Because of their hollow structure and high aspect ratio, they tend to undergo buckling when placed under compressive, torsional or bending stress.

The above discussion referred to axial properties of the nanotube, whereas simple geometrical considerations suggest that carbon nanotubes should be much softer in the radial direction than along the tube axis. Indeed, TEM observation of radial elasticity suggested that even the Van der Waal’s forces can deform two adjacent nanotubes. Nano indentation experiments performed by several groups on multi-walled carbon nanotubes and tapping/contact mode atomic force microscope measurement performed on single-walled carbon nanotube, indicated Young's modulus of the order of several GPa confirming that CNTs are indeed rather soft in the radial direction.
5.2. Hardness

Standard single walled carbon nanotubes can withstand a pressure up to 24GPa without deformation. They then undergo a transformation to super hard phase nanotubes. Maximum pressures measured using current experimental techniques are around 55GPa. However, these new super hard phase nanotubes collapse at an even higher, albeit unknown, pressure. The bulk modulus of super hard phase nanotubes is 462 to 546 GPa, even higher than that of diamond (420 GPa for single diamond crystal).

5.3 Kinetic

Multi-walled nanotubes are multiple concentric nanotubes precisely nested within one another. These exhibit a striking telescoping property whereby an inner nanotube core may slide, almost without friction, within its outer nanotube shell, thus creating an atomically perfect linear or rotational bearing. This is one of the first true examples of molecular nanotechnology, the precise positioning of atoms to create useful machines. Already, this property has been utilized to create the world's smallest rotational motor. Future applications such as a gigahertz mechanical oscillator are also envisaged.

5.4 Electrical

Due to the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. For a given (n, m) nanotube, if n = m, the nanotube is metallic; if n − m is a multiple of 3, then the nanotube is semiconducting with a very small band gap, otherwise the nanotube is a moderate semiconductor. Thus all armchair (n = m) nanotubes are metallic, and nanotubes (6, 4), (9, 1), etc. are semiconducting.

However, this rule has exceptions, because curvature effects in small diameter carbon nanotubes can influence strongly electrical properties. Thus, a (5, 0) SWCNT that should be semiconducting in fact is metallic according to the calculations. Likewise, vice versa— zigzag and chiral SWCNTs with small diameters that should be metallic have finite gap (armchair nanotubes remain metallic).
In theory, metallic nanotubes can carry an electric current density of $4 \times 10^9$ A/cm² which is more than 1,000 times greater than metals such as copper, where for copper interconnects current densities are limited by electro-migration. Multi-walled carbon nanotubes with interconnected inner shells show superconductivity with a relatively high transition temperature $T_c = 12$ K. In contrast, the $T_c$ value is an order of magnitude lower for ropes of single-walled carbon nanotubes or for MWNTs with usual, non-interconnected shells.

### 5.5 Optical

Within materials science, the optical properties of carbon nanotubes refer specifically to the absorption, photoluminescence, and Raman spectroscopy of carbon nanotubes. Spectroscopic methods offer the possibility of quick and non-destructive characterization of relatively large amounts of carbon nanotubes. There is a strong demand for such characterization from the industrial point of view: numerous parameters of the nanotube synthesis can be changed, intentionally or unintentionally, to alter the nanotube quality. As shown below, optical absorption, photoluminescence and Raman spectroscopies allow quick and reliable characterization of this "nanotube quality" in terms of non-tubular carbon content, structure (chirality) of the produced nanotubes, and structural defects. Those features determine nearly any other properties such as optical, mechanical, and electrical properties.

Carbon nanotubes are unique "one dimensional systems" which can be envisioned as rolled single sheets of graphite (or more precisely graphene). This rolling can be done at different angles and curvatures resulting in different nanotube properties. The diameter typically varies in the range 0.4–40 nm (i.e. "only" ~100 times), but the length can vary ~10,000 times reaching 4 cm. Thus the nanotube aspect ratio, or the length-to-diameter ratio, can be as high as 132,000,000:1, which is unequalled by any other material. Consequently, all the properties of the carbon nanotubes relative to those of typical semiconductors are extremely anisotropic (directionally dependent) and tunable.

Whereas mechanical, electrical and electrochemical (super capacitor) properties of the carbon nanotubes are well established and have immediate applications, the practical use of optical properties is yet unclear. The aforementioned tunability of properties is potentially useful in optics and photonics. In particular, light-emitting diodes (LEDs) and photo-detectors based on a single nanotube have been produced in the lab.
Their unique feature is not the efficiency, which is yet relatively low, but the narrow selectivity in the wavelength of emission and detection of light and the possibility of its fine tuning through the nanotube structure. In addition, bolometer and optoelectronic memory devices have been realised on ensembles of single-walled carbon nanotubes.

5.6 Thermal

All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction", but good insulators laterally to the tube axis. Measurements show that a SWNT has a room-temperature thermal conductivity along its axis of about 3500 W*m⁻¹*K⁻¹; compare this to copper, a metal well-known for its good thermal conductivity, which transmits 385 W*m⁻¹*K⁻¹. A SWNT has a room-temperature thermal conductivity across its axis (in the radial direction) of about 1.52 W*m⁻¹*K⁻¹, which is about as thermally conductive as soil. The temperature stability of carbon nanotubes is estimated to be up to 2800 °C in vacuum and about 750 °C in air.
CHAPTER: 6

SYNTHESIS

In this section, different techniques for nanotube synthesis and their current status are briefly explained. First, the growth mechanism is explained, as it is almost general for all techniques. However, typical conditions are stated at the sections of all the different techniques. The largest interest is in the newest methods for each technique and the possibilities of scaling up.

Carbon nanotubes are generally produced by three main techniques, arc discharge, laser ablation and chemical vapour deposition. 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 feedstock 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. The SWNTs produced with CVD have a large diameter range, which can be poorly controlled. But on the other hand, this method is very easy to scale up, what favours commercial production.

6.1 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. The actual growth of the nanotube seems to be the same for all techniques mentioned.
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 C₂-particles that are formed in the plasma.

**Figure 6.1: Visualisation of a possible carbon nanotube growth mechanism.**
6.2 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 diffusions 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 6.2. Two distinct methods of synthesis can be performed with the arc discharge apparatus.
6.2.1 Synthesis of SWNT

If SWNTs are preferable, the anode has to be doped with metal catalyst, such as Fe, Co, Ni, Y or Mo. A lot of elements and mixtures of elements have been tested by various authors and it is noted that the results vary a lot, even though they use the same elements. This is not surprising as experimental conditions differ. The quantity and quality of the nanotubes obtained depend on various parameters such as the metal concentration, inert gas pressure, kind of gas, the current and system geometry. Usually the diameter is in the range of 1.2 to 1.4 nm. A couple of ways to improve the process of arc discharge are stated below.

a) Inert gas

The most common problems with SWNT synthesis are that the product contains a lot of metal catalyst, SWNTs have defects and purification is hard to perform. On the other hand, an advantage is that the diameter can slightly be controlled by changing thermal transfer and diffusion, and hence condensation of atomic carbon and metals between the plasma and the vicinity of the cathode can control nanotube diameter in the arc process. This was shown in an experiment in which different mixtures of inert gases were used. It appeared that argon, with a lower thermal conductivity and diffusion coefficient, gave SWNTs with a smaller diameter of approximately 1.2 nm. A linear fit of the average nanotube diameter showed a 0.2 nm diameter decrease per 10 % increase in argon helium ratio, when nickel/yttrium was used (C/Ni/Y was 94.8:4.2:1) as catalyst.
b) Optical plasma control

A second way of control is plasma control by changing the anode to cathode distance (ACD). The ACD is adjusted in order to obtain strong visible vortices around the cathode. This enhances anode vaporisation, which improves nanotubes formation. Combined with controlling the argon-helium mixture, one can simultaneously control the macroscopic and microscopic parameters of the nanotubes formed. With a nickel and yttrium catalyst (C/Ni/Y is 94.8:4.2:1) the optimum nanotube yield was found at a pressure of 660 mbar for pure helium and 100 mbar for pure argon. The nanotube diameter ranges from 1.27 to 1.37 nanometre.

c) Catalyst

Knowing that chemical vapour deposition (CVD) could give SWNTs with a diameter of 0.6-1.2 nm, researchers tried the same catalyst as used in CVD on arc discharge. Not all of the catalysts used appeared to result in nanotubes for both methods. But there seemed to be a correlation of diameter of SWNTs synthesised by CVD and arc discharge. As a result, the diameter can be controllably lowered to a range of 0.6-1.2 nm with arc-discharge. Using a mixture of Co and Mo in high concentrations as catalyst resulted in this result. These diameters are considerably smaller than 1.2-1.4 nm, which is the usual size gained from arc-discharge.

e) Open air synthesis with welding arc torch

Only a couple of years ago, researchers discovered that it was possible to form MWNTs in open air. A welding arc torch was operated in open air and the process was shielded with an argon gas flow. The anode and cathode were made of graphite containing Ni and Y (Ni/Y is 4.2:1 at. %).

Fig 6.3: Experimental set-up of the torch arc method in open air.
This method was modified for preparing SWNTs. A plate target made of graphite containing metal catalyst Ni and Y (Ni/Y is 3.6:0.8 at. per cent), was fixed at the sidewall of a water-cooled, steel based electrode. The torch arc aimed at the edge of the target and the soot was deposited on the substrate behind the target (see Figure 6.3). The arc was operated at a direct current of 100 A. and shielding argon gas flowed through the torch, enhancing the arc jet formation beyond the target. In the soot, carbon Nano horns (CNHs) and bundles of SWNT with an average diameter of 1.32 nm were found. However, the yield was much lower than for the conventional low-pressure arc discharge method. There are two reasons for this fact. At first, because of the open air, the lighter soot will escape into the atmosphere. Secondly, the carbon vapour might be oxidised and emitted as carbon dioxide gas. In order to improve the yield in this method, contrivances for collecting soot and development of an appropriate target are required. This method promises to be convenient and inexpensive once the conditions for higher yield are optimised. With a Ni/Y catalyst (Ni/Y is 3.6:0.8), SWNT bundles and CNHs are formed. In this case the SWNTs have a diameter of approximately 1.32 nm.

6.2.2 Synthesis of MWNT

If both electrodes are graphite, the main product will be MWNTs. But next to MWNTs a lot of side products are formed such as fullerenes, amorphous carbon, and some graphite sheets. Purifying the MWNTs, means loss of structure and disorders the walls. However scientists are developing ways to gain pure MWNTs in a large-scale process without purification. Typical sizes for MWNTs are an inner diameter of 1-3 nm and an outer diameter of approximately 10 nm. Because no catalyst is involved in this process, there is no need for a heavy acidic purification step. This means, the MWNT, can be synthesised with a low amount of defects.

a) Synthesis in liquid nitrogen

A first, possibly economical route to highly crystalline MWNTs is the arc-discharge method in liquid nitrogen, with this route mass production is also possible. For this option low pressures and expensive inert gasses are not needed.
Fig 6.4: Schematic drawings of the arc discharge apparatus in liquid nitrogen.

The content of the MWNTs can be as high as 70 % of the reaction product. Analysis with Auger-spectroscopy revealed that no nitrogen was incorporated in the MWNTs. There is a strong possibility that SWNTs can be produced with the same apparatus under different conditions.

b) Magnetic field synthesis

Synthesis of MWNTs in a magnetic field gives defect-free and high purity MWNTs that can be applied as nano-sized electric wires for device fabrication. In this case, the arc discharge synthesis was controlled by a magnetic field around the arc plasma.

Fig 6.5: Schematic diagram of the synthesis system for MWNTs in a magnetic field.

Extremely pure graphite rods (purity > 99.999 %) were used as electrodes. Highly pure MWNTs (purity > 95 %) were obtained without further purification, which disorders walls of MWNTs.
c) Plasma rotating arc discharge

A second possibly economical route to mass production of MWNTs is synthesis by plasma rotating arc discharge technique. The centrifugal force caused by the rotation generates turbulence and accelerates the carbon vapour perpendicular to the anode. In addition, the rotation distributes the micro discharges uniformly and generates stable plasma. Consequently, it increases the plasma volume and raises the plasma temperature.

![Schematic diagram of plasma rotating electrode system.](Image)

At a rotation speed of 5000 rpm a yield of 60% was found at a formation temperature of 1025 °C without the use of a catalyst. The yield increases up to 90% after purification if the rotation speed is increased and the temperature is enlarged to 1150 °C. The diameter size was not mentioned in this publication.

### 6.3 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 6.7. 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 (100 kW/cm² compared with 12 kW/cm²). 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 van der Waals forces.

![Diagram of laser ablation apparatus](image)

Fig 6.7: Schematic drawing of a laser ablation apparatus.

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\textsubscript{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\textsubscript{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.

6.3.1 Ultra-fast pulses from a free electron laser (FEL) method

Usually the pulses in an Nd: YAG system has width of approximately 10 ns, in this FEL system the pulse width is ~ 400 fs. The repetition rate of the pulse is enormously increased from 10 Hz to 75 MHz. To give the beam the same amount of energy as the pulse in an Nd: YAG system, the pulse has to be focused.
The intensity of the laser bundle behind the lens reaches $\sim 5 \times 10^{11}$ W/cm$^2$, which is about 1000 times greater than in Nd: YAG systems. A jet of preheated (1000 °C) argon through a nozzle tip is situated close to the rotating graphite target, which contains the catalyst. The argon gas deflects the ablation plume approximately 90° away from the incident FEL beam direction, clearing away the carbon vapour from the region in front of the target. The produced SWNT soot is collected in a cold finger. This process can be seen in Figure 6.8. The yield at this moment is 1.5 g/h, which is at 20% of the maximum power of the not yet upgraded FEL. If the FEL is upgraded to full power and is working at 100% power, a yield of 45 g/h could be reached since the yield was not limited by the laser power.

![Fig 6.8: Schematic drawings of the ultra-fast-pulsed laser ablation apparatus.](image)

With this method the maximum achievable yield with the current lasers is 45 g/h, with a NiCo or NiY catalyst, in argon atmosphere at 1000 °C and a wavelength of ~3000 nm. The SWNTs produced in bundles of 8-200 nm and a length of 5-20 microns has a diameter range 1-1.4 nm.

### 6.4 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 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 nanometre 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. These different techniques will be explained more detailed in this chapter.

6.4.1 Plasma enhanced chemical vapour deposition

The plasma enhanced CVD method generates a glow discharge in a chamber or a reaction furnace by a high frequency voltage applied to both electrodes. Figure 6.9 shows a schematic diagram of a typical plasma CVD apparatus with a parallel plate electrode structure.

Fig 6.9: Schematic diagram of plasma CVD apparatus.
A substrate is placed on the grounded electrode. In order to form a uniform film, the reaction gas is supplied from the opposite plate. Catalytic metal, such as Fe, Ni and Co are used on for example a Si, SiO$_2$, or glass substrate using thermal CVD or sputtering. After nanoscopic fine metal particles are formed, carbon nanotubes will be grown on the metal particles on the substrate by glow discharge generated from high frequency power. A carbon containing reaction gas, such as C$_2$H$_2$, CH$_4$, C$_2$H$_4$, C$_2$H$_6$, CO is supplied to the chamber during the discharge. The catalyst has a strong effect on the nanotube diameter, growth rate, wall thickness, morphology and microstructure. Ni seems to be the most suitable pure-metal catalyst for the growth of aligned multi-walled carbon nanotubes (MWNTs). The diameter of the MWNTs is approximately 15 nm. The highest yield of carbon nanotubes achieved was about 50% and was obtained at relatively low temperatures (below 330°C).

### 6.4.2 Thermal chemical vapour deposition

In this method Fe, Ni, Co or an alloy of the three catalytic metals is initially deposited on a substrate. After the substrate is etched in a diluted HF solution with distilled water, the specimen is placed in a quartz boat. The boat is positioned in a CVD reaction furnace, and nanometre-sized catalytic metal particles are formed after an additional etching of the catalytic metal film using NH$_3$ gas at a temperature of 750 to 1050°C. As carbon nanotubes are grown on these fine catalytic metal particles in CVD synthesis, forming these fine catalytic metal particles is the most important process. Figure 6.10 shows a schematic diagram of thermal CVD apparatus in the synthesis of carbon nanotubes.

![Schematic diagram of thermal CVD apparatus.](image)
When growing carbon nanotubes on a Fe catalytic film by thermal CVD, the diameter range of the carbon nanotubes depends on the thickness of the catalytic film. By using a thickness of 13 nm, the diameter distribution lies between 30 and 40 nm. When a thickness of 27 nm is used, the diameter range is between 100 and 200 nm. The carbon nanotubes formed are multi-walled.

6.4.3 Alcohol catalytic chemical vapour deposition

Alcohol catalytic CVD (ACCVD) is a technique that is being intensively developed for the possibility of large-scale production of high quality single wall nanotubes SWNTs at low cost. In this technique, evaporated alcohols, methanol and ethanol, are being utilised over iron and cobalt catalytic metal particles supported with zeolite. Generation is possible at a relatively low minimum temperature of about 550 °C. It seems that hydroxyl radicals, who come from reacting alcohol on catalytic metal particles, remove carbon atoms with dangling bonds, which are obstacles in creating high-purity SWNTs. The diameter of the SWNTs is about 1 nm. Figure 6.11 shows the ACCVD experimental apparatus.

![ACCVD experimental apparatus](image)

**Fig6.11: ACCVD experimental apparatus.**

The lower reaction temperature and the high-purity features of this ACCVD technique guarantee an easy possibility to scale production up at low cost. Furthermore, the reaction temperature, which is lower than 600 °C, ensures that this technique is easily applicable for the direct growth of SWNTs on semiconductor devices already patterned with aluminium.
6.4.4 Aero gel-supported chemical vapour deposition

In this method SWNTs are synthesised by disintegration of carbon monoxide on an aero gel-supported Fe/Mo catalyst. There are many important factors that affect the yield and quality of SWNTs, including the surface area of the supporting material, reaction temperature and feeding gas. Because of the high surface area, the porosity and ultra-light density of the aero gels, the productivity of the catalyst is much higher than in other methods. After a simple acidic treatment and a oxidation process high purity (>99%) SWNTs can be obtained. When using CO as feeding gas the yield of the nanotubes is lower but the overall purity of the materials is very good. The diameter distribution of de nanotubes is between 1, 0 nm and 1, 5 nm. The optimal reaction temperature is approximately 860 °C.

6.4.5 Laser-assisted thermal chemical vapour deposition

In laser-assisted thermal CVD (LCVD) a medium power, continuous wave CO\textsubscript{2} laser, which was perpendicularly directed onto a substrate, pyrolysis sensitised mixtures of Fe (CO)\textsubscript{5} vapour and acetylene in a flow reactor. The carbon nanotubes are formed by the catalysing action of the very small iron particles. Figure 6.12 shows the experimental set-up for laser-assisted CVD. By using a reactant gas mixture of iron pentacarbonyl vapour, ethylene and acetylene both single- and multi-walled carbon nanotubes are produced. Silica is used as substrate. The diameters of the SWNTs range from 0.7 to 2.5 nm. The diameter range of the MWNTs is 30 to 80 nm.

![Experimental set-up for laser-assisted CVD.](image)

**Fig6.12:** Experimental set-up for laser-assisted CVD.
CHAPTER 7

APPLICATIONS OF CARBON NANOTUBES

Current use and application of nanotubes has mostly been limited to the use of bulk nanotubes, which is a mass of rather unorganized fragments of nanotubes. Bulk nanotube materials may never achieve a tensile strength similar to that of individual tubes, but such composites may nevertheless yield strengths sufficient for many applications. Bulk carbon nanotubes have already been used as composite fibers in polymers to improve the mechanical, thermal and electrical properties of the bulk product.

• **Paper battery:** a paper battery is a battery engineered to use a paper-thin sheet of cellulose (which is the major constituent of regular paper, among other things) infused with aligned carbon nanotubes. The nanotubes act as electrodes; allowing the storage devices to conduct electricity. The battery, which functions as both a lithium-ion battery and a supercapacitor, can provide a long, steady power output comparable to a conventional battery, as well as a supercapacitor’s quick burst of high energy—and while a conventional battery contains a number of separate components, the paper battery integrates all of the battery components in a single structure, making it more energy efficient.

• **Solar cells:** Solar cells developed at the New Jersey Institute of Technology use a carbon nanotube complex, formed by a mixture of carbon nanotubes and carbon buckyballs (known as fullerenes) to form snake-like structures. Buckyballs trap electrons, although they can't make electrons flow. Add sunlight to excite the polymers, and the buckyballs will grab the electrons. Nanotubes, behaving like copper wires, will then be able to make the electrons or current flow.

• **Nano radio:** A nanoradio, a radio receiver consisting of a single nanotube, was demonstrated in 2007. In 2008 it was shown that a sheet of nanotubes can operate as a loudspeaker if an alternating current is applied. The sound is not produced through vibration but thermo acoustically.

• **Blacker than Black?** : Black is black, right? Not so, according to a team of NASA engineers now developing a blacker-than pitch material that will help scientists gather hard-to-obtain scientific measurements or observe currently unseen astronomical objects,
like Earth-sized planets in orbit around other stars. The nanotech-based material now being developed by a team of 10 technologists at the NASA Goddard Space Flight Center in Greenbelt, Md., is a thin coating of multi-walled carbon nanotubes — tiny hollow tubes made of pure carbon about 10,000 times thinner than a strand of human hair. Nanotubes have a multitude of potential uses, particularly in electronics and advanced materials due to their unique electrical properties and extraordinary strength. But in this application, NASA is interested in using the technology to help suppress errant light that has a funny way of ricocheting off instrument components and contaminating measurements.

- **Space elevator project:** Carbon nanotube ribbons created in a University of Texas laboratory may stretch all the way into space. According to research to be published in *Science* today, Dr. Mei Zhang and his team have succeeded in creating yard-long ribbons of carbon nanotubes — just the sort of ultra-light, ultra-strong filaments needed to create the space elevator (among many other things). A space elevator is essentially a long cable that is anchored on Earth at one end and "anchored" at the other end 35,000 kilometers away by a satellite in geosynchronous orbit. Gravity and centripetal acceleration keeps the cable taut; a small elevator, or car, can crawl up the elevator at a fraction of the energy expenditure needed to actually hurl an object into orbit. Putting a satellite in orbit could cost hundreds of dollars per pound, rather than $7,000 per pound as it does on the space shuttle.

- **Energy storage:** Graphite, carbonaceous materials and carbon fibre electrodes are commonly used in fuel cells, batteries and other electrochemical applications. Advantages of considering nanotubes for energy storage are their small dimensions, smooth surface topology and perfect surface specificity. The efficiency of fuel cells is determined by the electron transfer rate at the carbon electrodes, which is the fastest on nanotubes following ideal Nernstian behaviour. Electrochemical energy storage and gas phase intercalation will be described more thoroughly in the following chapters of the report.

- **Hydrogen storage:** The advantage of hydrogen as energy source is that its combustion product is water. In addition, hydrogen can be easily regenerated. For this reason, a suitable hydrogen storage system is necessary, satisfying a combination of both volume and weight limitations. The two commonly used means to store hydrogen are gas phase and electrochemical adsorption.
Because of their cylindrical and hollow geometry, and nanometre-scale diameters, it has been predicted that carbon nanotubes can store a liquid or a gas in the inner cores through a capillary effect. As a threshold for economical storage, the Department of Energy has set storage requirements of 6.5% by weight as the minimum level for hydrogen fuel cells. It is reported that SWNTs were able to meet and sometimes exceed this level by using gas phase adsorption (physisorption). Yet, most experimental reports of high storage capacities are rather controversial so that it is difficult to assess the applications potential. What lacks, is a detailed understanding of the hydrogen storage mechanism and the effect of materials processing on this mechanism. Another possibility for hydrogen storage is electrochemical storage. In this case not a hydrogen molecule but an H atom is adsorbed. This is called chemisorption.

- **Lithium intercalation:** The basic principle of rechargeable lithium batteries is electrochemical intercalation and de-intercalation of lithium in both electrodes. An ideal battery has a high-energy capacity, fast charging time and a long cycle time. The capacity is determined by the lithium saturation concentration of the electrode materials. For Li, this is the highest in nanotubes if all the interstitial sites (inter-shell van der Waals spaces, inter-tube channels and inner cores) are accessible for Li intercalation. SWNTs have shown to possess both highly reversible and irreversible capacities. Because of the large observed voltage hysteresis, Li-intercalation in nanotubes is still unsuitable for battery application. This feature can potentially be reduced or eliminated by processing, i.e. cutting, the nanotubes to short segments.

- **Electrochemical supercapacitors:** Supercapacitors have a high capacitance and potentially applicable in electronic devices. Typically, they are comprised two electrodes separated by an insulating material that is ionically conducting in electrochemical devices. The capacity of an electrochemical supercap inversely depends on the separation between the charge on the electrode and the counter charge in the electrolyte. Because this separation is about a nanometre for nanotubes in electrodes, very large capacities result from the high nanotube surface area accessible to the electrolyte. In this way, a large amount of charge injection occurs if only a small voltage is applied. This charge injection is used for energy storage in nanotube supercapacitors. Generally speaking, there is most interest in the double-layer supercapacitors and redox supercapacitors with different charge-storage modes.
**Field emitting devices:** If a solid is subjected to a sufficiently high electric field, electrons near the Fermi level can be extracted from the solid by tunnelling through the surface potential barrier. This emission current depends on the strength of the local electric field at the emission surface and its work function (which denotes the energy necessary to extract an electron from its highest bounded state into the vacuum level). The applied electric field must be very high in order to extract an electron. This condition is fulfilled for carbon nanotubes, because their elongated shape ensures very large field amplification. For technological applications, the emissive material should have a low threshold emission field and large stability at high current density. Furthermore, an ideal emitter is required to have a nanometre size diameter, a structural integrity, a high electrical conductivity, a small energy spread and a large chemical stability. Carbon nanotubes possess all these properties.

**Transistors:** The field-effect transistor - a three-terminal switching device - can be constructed of only one semi-conducting SWNT. By applying a voltage to a gate electrode, the nanotube can be switched from a conducting to an insulating state. Such carbon nanotube transistors can be coupled together, working as a logical switch, the basic component of computers.

**Other applications:**

* Easton-Bell Sports, Inc. have been in partnership with Zyvex Performance Materials, using CNT technology in a number of their bicycle components—including flat and riser handlebars, cranks, forks, seat posts, stems and aero bars.

* Zyvex Performance Materials has also built a 54' maritime vessel, the Piranha Unmanned Surface Vessel, as a technology demonstrator for what is possible using CNT technology. CNTs help improve the structural performance of the vessel, resulting in a lightweight 8,000 lb. boat that can carry a payload of 15,000 lb. over a range of 2,500 miles.

* Amroy Europe Oy manufactures Hybtonite carbon nanoepoxy resins where carbon nanotubes have been chemically bond to epoxy, resulting composite material that is 20% to 30% stronger than other composite materials. It has been used for wind turbines, marine paints and variety of sports gear such as skis, ice hockey sticks, baseball bats, hunting arrows and surfboards.
CHAPTER 8

DRAWBACKS OF CARBON NANOTUBES

8.1 Defects

As with any material, the existence of a crystallographic defect affects the material properties. Defects can occur in the form of atomic vacancies. High levels of such defects can lower the tensile strength by up to 85%. Another form of carbon nanotube defect is the Stone Wales defect, which creates a pentagon and heptagon pair by rearrangement of the bonds. Because of the very small structure of CNTs, the tensile strength of the tube is dependent on its weakest segment in a similar manner to a chain, where the strength of the weakest link becomes the maximum strength of the chain.

Crystallographic defects also affect the tube's electrical properties. A common result is lowered conductivity through the defective region of the tube. A defect in armchair-type tubes (which can conduct electricity) can cause the surrounding region to become semiconducting, and single monoatomic vacancies induce magnetic properties.

Crystallographic defects strongly affect the tube's thermal properties. Such defects lead to phonon scattering, which in turn increases the relaxation rate of the phonons. This reduces the mean free path and reduces the thermal conductivity of nanotube structures. Phonon transport simulations indicate that substitutional defects such as nitrogen or boron will primarily lead to scattering of high-frequency optical phonons. However, larger-scale defects such as Stone Wales defects cause phonon scattering over a wide range of frequencies, leading to a greater reduction in thermal conductivity.

8.2 Toxicity

Determining the toxicity of carbon nanotubes has been one of the most pressing questions in nanotechnology. Preliminary results highlight the difficulties in evaluating the toxicity of this heterogeneous material. Parameters such as structure, size distribution, surface area, surface chemistry, surface charge, and agglomeration state as well as purity of the samples, have considerable impact on the reactivity of carbon nanotubes.
However, available data clearly show that, under some conditions, nanotubes can cross membrane barriers, which suggests that if raw materials reach the organs they can induce harmful effects such as inflammatory and fibrotic reactions. A study led by Alexandra Porter from the University of Cambridge shows that CNTs can enter human cells and accumulate in the cytoplasm, causing cell death. Results of rodent studies collectively show that regardless of the process by which CNTs were synthesized and the types and amounts of metals they contained, CNTs were capable of producing inflammation, epithelioid granulomas (microscopic nodules), fibrosis, and biochemical/toxicological changes in the lungs. Comparative toxicity studies in which mice were given equal weights of test materials showed that SWCNTs were more toxic than quartz, which is considered a serious occupational health hazard when chronically inhaled. As a control, ultrafine carbon black was shown to produce minimal lung responses.

The needle-like fiber shape of CNTs, similar to asbestos fibers, raises fears that widespread use of carbon nanotubes may lead to mesothelioma, cancer of the lining of the lungs often caused by exposure to asbestos. A recently-published pilot study supports this prediction. Scientists exposed the mesothelial lining of the body cavity of mice, as a surrogate for the mesothelial lining of the chest cavity, to long multiwalled carbon nanotubes and observed asbestos-like, length-dependent, pathogenic behavior which included inflammation and formation of lesions known as granulomas. Authors of the study conclude "This is of considerable importance, because research and business communities continue to invest heavily in carbon nanotubes for a wide range of products under the assumption that they are no more hazardous than graphite. Our results suggest the need for further research and great caution before introducing such products into the market if long-term harm is to be avoided." According to co-author Dr. Andrew Maynard "This study is exactly the kind of strategic, highly focused research needed to ensure the safe and responsible development of nanotechnology. It looks at a specific nanoscale material expected to have widespread commercial applications and asks specific questions about a specific health hazard. Even though scientists have been raising concerns about the safety of long, thin carbon nanotubes for over a decade, none of the research needs in the current U.S. federal nanotechnology environment, health and safety risk research strategy address this question." Although further research is required, results presented today clearly demonstrate that, under certain conditions, especially those involving chronic exposure, carbon nanotubes can pose a serious risk to human health.
REFERENCES


2. Carbon Nanotube Electronics; Phaedon Avouris, member, IEEE; Joerg Appenzeller, Richard Martel, and Shalom J. Wind, senior member, IEEE, proceedings of the IEEE, Vol. 91, no. 11, November 2003

3. Carbon Nanotubes: Single molecule wires, Sarah Burke, Sean Collins, David Montiel, Mikhail Sergeev


7. Carbon Nanotubes: Introduction to Nanotechnology 2003, Mads Brandbyge