



## **CARBON NANOTUBES & THEIR APPLICATIONS**

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# Abstract

The desire to know the internal composition and structure of matter and to unfold the hidden secret behind the formation of universe is universal quality of human being. The new and hot technology which encompasses many areas such as Physics, Biology, Chemistry, Engineering, etc. is called nanotechnology which is big issues for big brains though it is small. Do you ever wonder about our future? Do you ever imagine how discoveries could make the impossible a reality? Do you ever wish you had cures for threatening diseases at hand?

Nanotechnology, the ability to inexpensively arrange atoms in most of the patterns permitted by physical law – often called the manufacturing technology of the 21st century – is expected to revolutionize essentially all manufactured products, from computers to medical instruments, from cars to solar cells to batteries to planes and rockets. Carbon nanotubes, nanotechnology's dream materials and the corner stone of nanotechnology because of their superior electrical, mechanical, and thermal properties which have novel applications in every day to day life. CNTs may become the first applications to truly transform nanotechnology from an exciting science with great potential to a real technology or products.

The main objective of this project works are to focus on some relevant issues :

- What is Fullerene and Carbon nanotubes?
- What is the structure and unusual properties of CNTs?
- How CNTS synthesised, Some potential applications and potential risks

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# Chapter 1

## Introduction

### 1.1 The Element Carbon and Its Properties

Many of the things we use in our day-to-day lives like wheat, rice, vegetables, fruits, clothes, baking soda etc. all contain carbon. Carbon is in the pencils we use, the diamond rings we wear and the drill tips industries use. Carbon is everywhere present in the universe. Carbon not only makes our lives convenient but, in the form of hydrocarbons, is a crucial component of living organisms. Hence it is important for us to know something about this invaluable element [1], particularly its allotropic forms and diverse applications.

Without the element carbon, life as we know it would not exist. Carbon provides the framework for all tissues of plants and animals. These tissues are built of elements grouped around chains or rings made of carbon atoms. Carbon also provides common fuels such as coal, coke, oil, gasoline, and natural gas. Sugar, starch, and paper are compounds of carbon with hydrogen and oxygen. Proteins such as hair, meat, and silk contain carbon and other elements such as nitrogen, phosphorus, and sulfur [2].

Carbon is the sixth most abundant element in the cosmos, yet its abundance in the earth's crust does not even make it among the top ten elements on our planet.

There are more known chemical compounds of carbon than any other element except for oxygen and hydrogen. Carbon composes compounds with diverse properties such as graphite and diamond, as well as the recently discovered Buckminster Fullerenes (buckyballs) and carbon nanotubes. Carbon plays a critical role on Earth as the "stuff" that Life is made from. Every living cell, plant or animal contains carbon. Even in its pure, elemental form carbon is very versatile [2].

Carbon is without doubt one of the most versatile elements known to man, as can be seen by the fact that it is the basis of life on this planet. Carbon forms the basic building block of virtually all organic chemistry and of the 20 million known molecules, about 79% are classified as organic. Carbon in its ground state has an electronic structure of  $1s^2 2s^2 2p^2$ , but the 2s and 2p wavefunctions are normally hybridised to form 4 degenerate orbitals in a now  $sp^3$  hybridised atom. This allows the carbon atom to form 4 identical covalent bonds to other atoms and gives the atom a tetrahedral geometry. The reasons why carbon is such a diverse element is that it can form bonds to a huge range of other compounds, such as N, S, O, Cl, Br and P which crucially, are all thermodynamically stable. In addition to this, carbon can form single, double or triple bonds to other atoms and crucially, can also form these bonds to other carbon atoms. These carbon - carbon bonds have a very high intrinsic strength compared to similar bonds between other elements, for example, the bond strength of a C-C single bond has a value of  $356 \text{ kJ mol}^{-1}$  compared to a value of  $226 \text{ kJ mol}^{-1}$  for the equivalent Si-Si bond. As a result of this, it is possible to form

carbon chains of phenomenal lengths, which is a property that allows materials such as carbon fibres to be produced. In addition to the wide range of organic molecules which contain carbon, there are several very important allotropes of carbon [3].

### 1.1.1 Allotropes of Carbon

Allotropy is a behavior exhibited by certain chemical elements: these elements can exist in two or more different forms, known as allotropes of that element. In each different allotrope, the element's atoms are bonded together in a different manner [4].

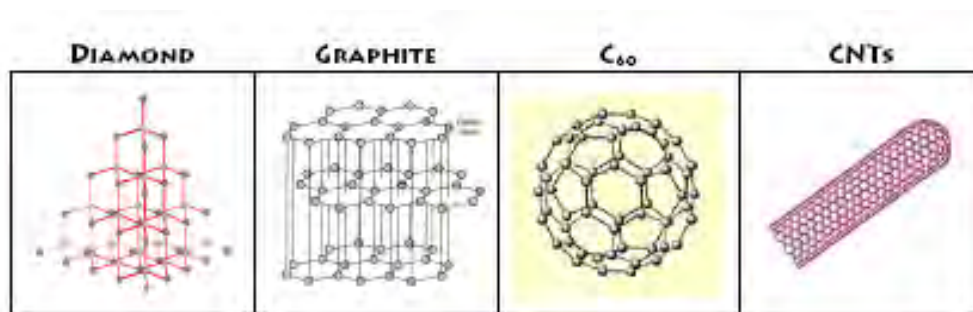


Figure 1.1: Schematic of carbon allotropes

The phenomenon of an element existing in two or more physical forms is said to be allotropy. Sometime it is called allotropism. The element carbon exist in different allotropic forms including the known forms diamond, graphite, fullerenes, the main issues of this project i.e carbon nanotubes (CNTS) and others. Molecular modeling for known alotropic forms of carbon are given in figure1.1 above [5]. Some

other common examples of allotropes are phosphorus (“white” or “yellow”, “red”, and “black / purple”), oxygen (O<sub>2</sub> and O<sub>3</sub>).

The specific hybridization of carbon, and its bonding to surrounding atoms will determine which allotrope carbon will assume. Carbon with sp<sup>3</sup> hybridization will form a tetrahedral lattice, thus giving rise to diamond. Carbon with sp<sup>2</sup> hybridization will form either graphite (arranged in hexagonal sheets), buckminsterfullerene (60 carbon atoms forming a sphere), or carbon nanotubes (long hollow tubes of carbon) depending on the conditions in which it is formed [6].

### **1.1.2 Isotopes of Carbon**

An isotope is a form of a chemical element whose atomic nucleus contains a specific number of neutrons, in addition to the number of protons that uniquely defines the element. The nuclei of most atoms contain neutrons as well as protons. (An exception is the common form of hydrogen, whose nucleus consists of a lone proton.) Every chemical element has more than one isotope. For any element, one of the isotopes is more abundant in nature than any of the others, although often multiple isotopes of a single element are mixed [7].

Every carbon atom contains six positively charged particles called protons in its nucleus and six or more neutral particles called neutrons. The carbon atom's nucleus is surrounded by six negatively charged electrons. The number of neutrons in a carbon atom's nucleus determines which isotope it is. Isotopes are atoms of the

same element that have different numbers of neutrons in the nucleus. Three different isotopes of carbon exist in nature. The important isotopes of carbon are carbon-12, carbon-13, and carbon-14. Scientists identify them by their mass number, which is the sum of the number of protons and neutrons in an atom. Carbon-12 contains six protons and six neutrons, carbon-13 contains six protons and seven neutrons, and carbon-14 contains six protons and eight neutrons [7].

### 1.1.3 Types of Hybridization in Carbon

The phenomenon of mixing up of different orbitals of same energy level of an atom to produce equal number of hybrid-orbitals of same energy and identical properties is known as hybridization. A hybrid orbital contains maximum two electrons with opposite spin. In hybridization, only those orbital take part that have very little difference of energy [8].

There are three types of hybridization  $sp^3$ -hybridization,  $sp^2$ - hybridization and  $sp$ - hybridization. To give the the properties like bonding, hybrid orbitals, structure and other properties of each of them in carbon atom as follows.

The  $sp^3$  hybridization results from the combination of the s orbital and all three p orbitals in the second energy level of carbon. It results in four hybrid orbitals and occurs when a carbon atom is bonded to four other atoms. The geometric arrangement of those four hybrid orbitals is called tetrahedral.

Another kind of hybridization uses the s orbital and two of the p orbitals from the second energy level of carbon to form three hybrid orbitals. This kind of hybridization is called  $sp^2$  hybridization. The geometric arrangement of these three  $sp^2$  hybrid orbitals is in a flat plane with 120 degree angles between them. The leftover p orbital lies at a 90 degree angle to the hybrid orbitals. This kind of hybridization occurs when a carbon atom is bonded to three other atoms. If it is a very simple molecule with just the carbon atom and the other three atoms, it would be a flat triangular molecule. If this is part of a larger molecule, this part would have a flat triangular shape.

Similarly in sp hybridization the s orbital and one of the p orbitals from carbon's second energy level are combined together to make two hybrid orbitals. Those hybrid orbitals form a straight line. There is a 180 degree angle between one orbital and the other orbital. They are exactly opposite one another from the center of the carbon atom. Because this type of sp hybridization only uses one of the p orbitals, there are still two p orbitals left which the carbon can use. Those p orbitals are at right angles to one another and to the line formed by the hybrid orbitals. This kind of hybridization occurs when a carbon atom is bonded to two other atoms [22]. In the next section we try to give some concepts about the new and novel technology nanotechnology and nanoscience other related issues.

## 1.2 Nanoscience

The pursue for the understanding of the composition and structure of matter in terms of atoms dates back to ancient Greek philosophers. Since then to explain matter interms of atoms and atoms interms of subatomic particles in a number of philosophical, experimental and theoretical periods have been gone. Recently a new dimension of thought, interpreting matter by assembling atoms into their correct, precise and right position at a nanoscale has begun.

Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale [10].

Nanoscience is a new emerginig area of science that involves studying and working with matter that have very very small dimentions.[16]. The word “nano” means dewarf in Greek [15] but “ nano” now refers to dimensions that are one-billionth times smaller than a meter or simply  $0.000000001(10^{-9}m)$ .An average single human hair is about  $100 \mu m (10^{-4})$ . Thus if a segment of human hair is longitudinally divided into 100,000 parts, then the diameter of one part will be one nanometer. For example, the bohr’s radius of hydrogen atom is 0.0529nm which is approximately 0.1nm [23]. Thus one nanometer equals alength covered by ten hydrogen atoms in the same row. In general,the average size of an atom is on the order of 0.1 to 0.2 nm in radius. Therefore, in one nanometer there may be 3-5 atoms de-

pending on the atomic radii. “Nano” dimension is smaller than the usual meaning of small [17].

Nanoscience is shaping and understanding how to assemble nanoscale materials and how to understand their properties [18]. The fundamental building blocks of nature, atoms and molecules, have dimensions in the nanometer domain (i.e., the nanoscale). Many water molecules can easily occupy a sphere 1 nm in diameter. The DNA double helix is approximately 2 nm wide [19]. Nanoscience can not be called Physics, Biology, or Chemistry or Engineering. However, sorts of scientists are studying very small things in order to better understand the world rather it involves the integrated principles of the whole fields of science and mathematics. Thus, nanotechnology is an interdisciplinary subject [20].

### **1.2.1 The Difference Between Nanoscience and Nanotechnology**

We should distinguish between nanoscience, which is here now and flourishing, and nanotechnology, which is still in its infancy. Nanoscience is a convergence of physics, chemistry, materials science and biology, which deals with the manipulation and characterisation of matter on length scales between the molecular and the micron size. Nanotechnology is an emerging engineering discipline that applies methods from nanoscience to create products [6].

## 1.3 Nanomaterials

A key driver in the development of new and improved materials, from the steels of the 19th century to the advanced materials of today, has been the ability to control their structure at smaller and smaller scales. The overall properties of materials as diverse as paints and silicon chips are determined by their structure at the micro- and nanoscales. As our understanding of materials at the nanoscale and our ability to control their structure improves, there will be great potential to create a range of materials with novel characteristics, functions and applications [16].

Natural or man-made particles often have qualities and capabilities quite different from their microscopic counterparts. The reason why so many nanosolids look different from their larger counter parts is primarily due to their edges. A tiny piece of graphite would have many of its atoms at its edges, which are unstable. For example, gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales [1]. Nanoscaled devices will bear much stronger resemblance to nature's nanodevices. Proteins, DNA, membranes etc. falls in that category [15].

### 1.3.1 The Importance of Nanoscale

Nanoscale is a magical point on the dimensional scale: Structures in nanoscale (called nanostructures) are considered at the borderline of the smallest of human-made devices and the largest molecules of living systems. Our ability to control and manipulate nanostructures will make it possible to exploit new physical, biolog-

ical and chemical properties of systems that are intermediate in size, between single atoms, molecules and bulk materials.

There are many specific reasons why nanoscale has become so important some of which are as the following [15]:

(i). The quantum mechanical (wavelike) properties of electrons inside matter are influenced by variations on the nanoscale. By nanoscale design of materials it is possible to vary their micro and macroscopic properties, such as charge capacity, magnetization and melting temperature, without changing their chemical composition.

(ii). A key feature of biological entities is the systematic organization of matter on the nanoscale. Developments in nanotechnology would allow us to place man-made nanoscale things inside living cells. It would also make it possible to make new materials using the self-assembly features of nature. This certainly will be a powerful combination of biology with materials science.

(iii). Nanoscale components have very high surface to volume ratio, making them ideal for use in composite materials, reacting systems, drug delivery, and chemical energy storage (such as hydrogen and natural gas).

(iv). Macroscopic systems made up of nanostructures can have much higher density than those made up of microstructures. They can also be better conductors of electricity. This can result in new electronic device concepts, smaller and faster

circuits, more sophisticated functions, and greatly reduced power consumption simultaneously by controlling nanostructure interactions and complexity [15]

## 1.4 Nanotechnology

Nanotechnology is a field of applied science and technology covering a broad range of topics [9]. Nanoscience and nanotechnologies involve studying and working with matter on an ultra-small scale. One nanometre is one-millionth of a millimetre and a single human hair is around 80,000 nanometres in width. The technology stretches across the whole spectrum of science, touching medicine, physics, engineering and chemistry [10].

Nanotechnology is the engineering of functional systems at the molecular scale. This covers both current work and concepts that are more advanced. In its original sense, 'nanotechnology' refers to the projected ability to construct items from the bottom up, using techniques and tools being developed today to make complete, high performance products [11].

The term "nanotechnology" has evolved over the years via terminology drift to mean "anything smaller than microtechnology," such as nano powders, and other things that are nanoscale in size, but not referring to mechanisms that have been purposefully built from nanoscale component. This evolve version of the term is more properly labeled "nanoscale bulk technology," while the original meaning is now

more properly labeled "molecular nanotechnology" (MNT), or "nanoscale engineering," or "molecular mechanics," or " or "molecular manufacturing [12] .

Nanotechnology describes many diverse technologies and tools, which dont always appear to have much in common! Therefore it is better to talk about nanotechnologies, in the plural.

Properties of materials can be very different at this level; for instance, they can be more chemically reactive, have greater strength or conduct electricity more effectively. Take the differences between graphite, which is used in the lead of pencils, and diamond -although both are made up of the same element (carbon), the way in which the atoms are arranged in each is slightly different, giving the dramatic differences between the two. While in the case of graphite and diamond this happens naturally, nanotechnology offers the opportunity for us to make such differences by design [13] .

### **1.4.1 Self-Assembly**

Self-assembly is a branch of nanotechnology in which objects, devices, and systems form structures without external prodding [6]. Self-assembly is the fundamental principle which generates structural organization on all scales from molecules to galaxies. It is defined as reversible processes in which pre-existing parts or disordered components of a preexisting system form structures of patterns [9]. The fundamental characteristic of nanotechnology is that nanodevices self-assembled; they build

themselves from bottom-up atom by atom. In the microscopic world, self-assembly occurs all the time, such as when proteins fold into complicated structures. The problem is that scientists still do not understand how such biological systems achieve self-assembly, so they have no blueprint to use in their quest of self-assembly. It is defined as processes in which pre-existing parts or disordered components of a pre-existing system form structures of patterns [14].

### **1.4.2 Self-assembly and Nanotechnology**

Molecular self-assembly is a strategy for nanofabrication that involves designing molecules and supramolecular entities so that shape-complementarity causes them to aggregate into desired structures. Self-assembly has a number of advantages as a strategy: First, it carries out many of the most difficult steps in nanofabrication—those involving atomic-level modification of structure—using the very highly developed techniques of synthetic chemistry. Second, it draws from the enormous wealth of examples in biology for inspiration: self-assembly is one of the most important strategies used in biology for the development of complex, functional structures. Third, it can incorporate biological structures directly as components in the final systems. Fourth, because it requires that the target structures be the thermodynamically most stable ones open to the system, it tends to produce structures that are relatively defect-free and self-healing [6].

Self-assembly also poses a number of substantial intellectual challenges. The brief summary of these challenges is that we do not yet know how to do it, and cannot even mimic those processes known to occur in biological systems at other than quite elementary levels. Although there are countless examples of self-assembly all around us—from molecular crystals to mammals—the basic rules that govern these assemblies are not understood in useful detail, and self-assembling processes cannot, in general, be designed and carried out "to order". Many of the ideas that are crucial to the development of this area—"molecular shape", the interplay between enthalpy and entropy, the nature of non-covalent forces that connect the particles in self-assembled molecular aggregates—are simply not yet under the control of investigators.

In addition, there are issues of function in self-assembled aggregates that need solution. The most promising avenues for self-assembly are presently those based on organic compounds, and organic compounds, as a group (although with exceptions), are electrical insulators; thus, many ideas for information processing and electrical/mechanical transduction will require either fundamental redesign in going from the macroscopic systems presently used to self-assembled systems, or the development of new types of organic molecules that show appropriate properties [6].

## **1.5 Typical Length scales in Nanotechnology**

In physics, length scale is a particular length or distance determined with the precision of one order (or a few orders) of magnitude. The concept of length scale is

particularly important because physical phenomena of different length scales can not affect each other and are said to decouple. The decoupling of different length scales makes it possible to have a self-consistent theory that only describes the relevant length scales for a given problem. Scientific reductionism says that the physical laws on the shortest length scales can be used to derive the effective description at larger length scales [21].

When we come back to the length scale of nanotechnology we want to compare and justify with justification with micro,macro (bulk), micro scales. A nanometer is one billionth of a metre, but let's try to put this in context. We could call our everyday world the macroscale. This is the world in which we can manipulate things with our bare hands, and in rough terms it covers about a factor of a thousand. The biggest things I can move about are about half a meter big (if they're not too dense), and my clumsy fingers can't do very much with things smaller than half a millimeter.

We've long had the tools to extend the range of human abilities to manipulate matter on smaller scales than this. Most important is the light microscope, which has opened up a new realm of matter - the microscale. Like the macroscale, this also embraces roughly another factor of a thousand in length scales. At the upper end, objects half a millimeter or so in size provide the link with the macroscale; still visible to the naked eye, handling them becomes much more convenient with the help of a simple microscope or even a magnifying glass. At the lower end, the wavelength of light itself, around half a micrometer, gives a lower limit on the size of

objects which can be discriminated even with the most sophisticated laboratory light microscope.

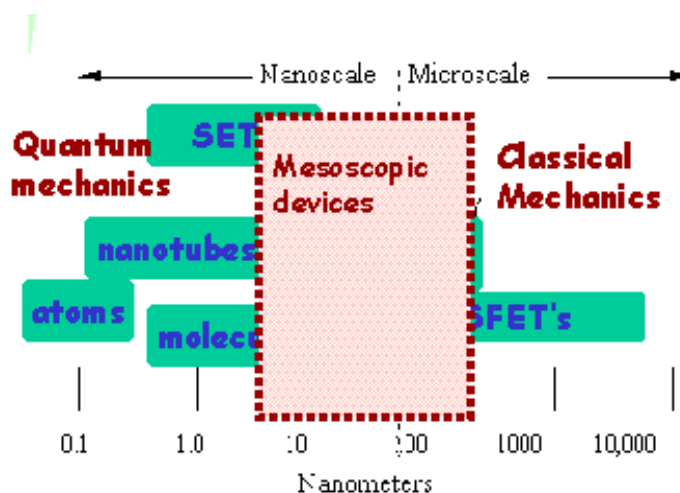


Figure 1.2: Typical length scales

If we take as the upper limit of the nanoscale the half-micron or so that represents the smallest object that can be resolved in a light microscope, then another factor of one thousand takes us to half a nanometer. This is a very natural lower limit for the nanoscale, because it is a typical size for a small molecule. The nanoscale domain, then, in which nanotechnology operates, is one in which individual molecules are the building blocks of useful structures and devices [24]. In general nanoscale is defined as it's the nanoscale if it's too small to resolve in an ordinary light microscope, and if it's bigger than your typical small molecule. The project is organised as follows: **Discovery, structure and properties, synthesis, and some applications of Carbon nanotubes will be dealt in the following chapters.**

## Chapter 2

# Discovery of Fullerene and Carbon Nanotubes

### 2.1 The origins of Nanotechnology and Nanoscience

Up to 1959 most scientists and engineers were primarily concerned with the theory of breaking very small things. But in 1959 the thought of nanotechnology forwarded in the talk that Richard Feynman on December 29th 1959 at the annual meeting of the American Physical Society at the California Institute of Technology entitled "There is Plenty of Room at the Bottom" [15, 25–28]. But he never used this term nanotechnology that time. In his talk Feynman described how the laws of nature do not limit our ability to maneuver things at the molecular level atom by atom. Instead, he said, it was our lack of equipment and techniques for doing so. Feynman in his lecture talked about "How do we write small?" "Why not we write the entire 24 volumes of the Encyclopedia Britannica on the head of a pin?" "Information in small scale", the possibility to have "better electron microscope" that could take the image of atom, doing things small scale through 'the marvelous biological system', 'miniaturizing the computer', 'rearranging the atoms' to build various nanostructures and nanodevices and behavior of 'atoms in the small world' which include atomic scale fabrication as a bottom-up approach opposed to the top-down approach that we are

accustomed to. Bottom-up approach is self-assembly machines from basic chemical building blocks, which is considered to be the ideal through which nanotechnology is ultimately implemented. Top-down approach is assembly by manipulating components with much larger devices, which is more readily achievable using the current technology [15, 27]. Feynman suggested a means to develop the ability to manipulate atoms and molecules directly by developing a set of one-tenth-scale machine tools analogous to those found in any machine shop. These small tools would then help to develop and operate a next generation of one-hundredth scale machine tools, and so forth. As the size gets smaller, we would have to redesign some tools because the relative strength of various forces would change. Gravity would become less important, quantum effect become more prominent, such as surface tension would become more important; van der Waals attraction would become important etc. Due to the small size at which nanotechnology operates, physical phenomena not observed at the macroscopic scale. These nanoscale phenomena include quantum size effects and short-range forces. Furthermore, the vastly increased ratio of surface area-to-volume ratio promotes surface phenomena. Feynman's 1959 lecture initiated a number of research activities among the scientists at the time.

The term "nanotechnology" was defined by Tokyo Science University Professor Norio Taniguchi in a 1974 paper (N. Taniguchi, "On the Basic Concept of 'Nanotechnology'," Proc. Intl. Conf. Prod. Eng. Tokyo, Part II, Japan Society of Precision Engineering, 1974.) As follows: "'Nano-technology' mainly consists of the process-

ing of, separation, consolidation, and deformation of materials by one atom or one molecule." In the 1980s the basic idea of this definition was explored in much more depth by Dr. Eric Drexler, who promoted the technological significance of nanoscale phenomena and devices through speeches and the books *Engines of Creation: The Coming Era of Nanotechnology* and *Nanosystems: Molecular Machinery, Manufacturing, and Computation*, and so the term acquired its current sense [9].

## 2.2 The Discovery of Fullerenes

The discovery of  $C_{60}$  has a long and very interesting history [27]. The structure of truncated icosahedron was already known in about more than 500 years. Archimedes is credited for discovering the structure and Leonardo da Vinci included it in one of his drawings. At the end of 1960's, scientists were increasingly interested in non-planar aromatic structure, and thereafter the saucer-shaped corannulene was synthesized [28]. In 1970, Eiji Osawa realized that a molecule made up of  $sp^2$  hybridized carbons could have the soccer structure. He therefore made the first proposal for  $C_{60}$ . But this prediction turned out to be incorrect later.

Then, a group of Russian scientists independently proposed the  $C_{60}$  structure, the paper published by Bochvar and Gal'pern in 1973 not only predicted some properties of  $C_{60}$ , but also of  $C_{20}$  (the smallest fullerene) as well [29]. The first spectroscopic evidence for  $C_{60}$  and other fullerenes was published in 1984 by Rohfing and coworkers [30].

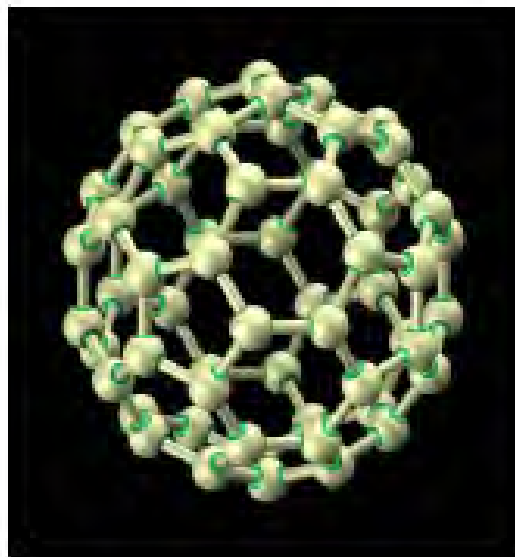


Figure 2.1: C<sub>60</sub>, Buckminsterfullerene (bucky ball)

In 1985, Professor Kroto, from University of Sussex, UK, met Professor Curl, from Rice University, at a conference on molecular structure in Austin, Texas. Kroto went back to Houston with Curl, who introduced him to Smalley and showed him around the lab. They arranged to examine a special kind of carbon produced in a cluster beam apparatus of Smalley. They soon reproduced the earlier work of Rohlfing and coworkers. What is more important is that research student James Heath, now professor at CalTech., found conditions whereby C<sub>60</sub> was formed exclusively, showing it to be a particularly stable species. After discounting various highly improbable structures, they concluded that the molecule must be a cage, and Smalley succeeded in building it out of his paper and tape. The paper including describing this work was submitted to Nature, on September 12th, 1985 [27]. They named C<sub>60</sub> as Buck-

minsterfullerene, because of the similarity of the structure to be geodesic structures widely credited to R. Buckminster Fuller. Because of this work, Kroto, Smalley, and Curl were awarded the Nobel Prize in Chemistry in 1996. However, the fullerenes would be interesting only to a small number of scientists if the major breakthrough was made by Wolfgang Kratschmer of Heidelberg University and Donald [27].  $C_{60}$  shown in the figure above.

### **2.3 The Discovery of Carbon Nanotubes**

In 1991, the Japanese electron microscopist, Sumio Iijima (a researcher at the NEC laboratory in Tsukuba, Japan) discovered that carbon could be made to a form of tubular structures while he was studying the material deposited on the cathode during the arc-evaporation synthesis of fullerenes. By using transmission electron microscope (TEM) to magnify carbon ash, he found that the cathode deposit contained a variety of closed graphitic structure. In that ash he found tiny cylinders made of carbon atoms with the diameters in the order of nanometers and he called the cylinders nanotubes. The graphite layer appears somewhat like "a rolled-up chicken wire" with a continuous unbroken hexagonal mesh and carbon at the apexes of the hexagons. Therefore, it was found that when an electric arc struck between two carbon electrodes in inert gas atmosphere carbon nanotubes are synthesized. Therefore, it can be thought that the newly discovered carbon variety as an elongated fullerene type and

spherical fullerenes are sometimes called buckyballs, while cylindrical fullerenes are called buckytubes or nanotubes [12, 31, 32]

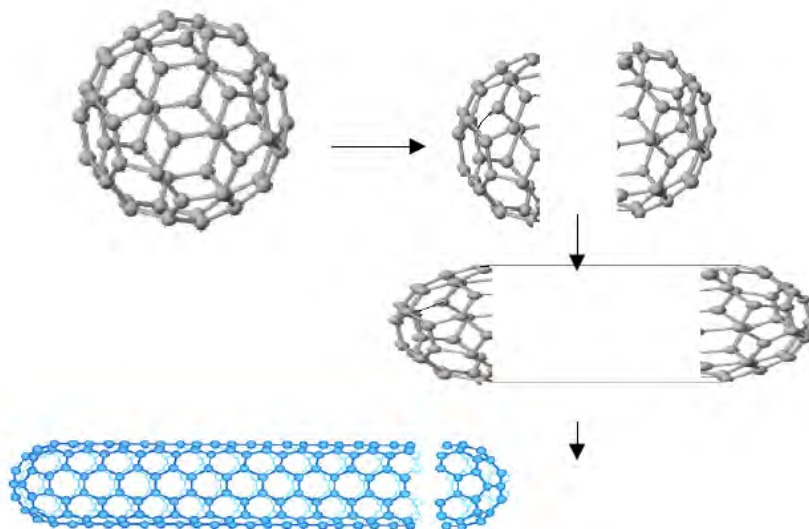


Figure 2.2: From fullerene to carbon nanotube

A "carbon nanotube" is a tube-shaped material made up of carbon that has a diameter of measuring on the nanometer scale. Their name derives from their size; nanotubes are on the order of only a few nanometers wide (on the order of one ten-thousandth the width of a human hair), and their length can be millions of times greater than their width. They can also be thought as of narrow sheets of a million or more carbon atoms linked together in a hexagonal rings connected as in graphite, but rolled in to a very long cylinder that is 1-2 nm in diameter internally. By comparison, a hair is about 100,000 nanometers across. To illustrate how narrow the nanotubes

are, a carbon nanotube long enough to reach from earth to the moon could be rolled to in a ball of the size of poppy seed [25].

## 2.4 Types of Carbon Nanotubes

Carbon is unique among chemical elements in its ability to assume a wide variety of different structures and forms. In addition to the  $sp^3$ -bonded diamond,  $sp^3$ -bonded graphite, and fullerenes the fourth form of carbon, the  $sp^3$ -bonded carbon nanotubes were first discovered in 1991 by Iijima, in the form of multiple coaxial carbon fullerene shells (multi-wall carbon nanotubes: mwCN). Later, in 1993 single fullerene shells (single-wall carbon nanotubes: swCN) were synthesized using transitional metal catalysts. Carbon nanotubes possess remarkable structural, mechanical, thermal and electrical properties that derive from the special properties of carbon bonds, their unique quasi-1D nature, and their cylindrical symmetry.

A nanotube is a member of the fullerene structural family, which also includes buckyball. 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 on the order of a few nanometers (approximately 100,000 times smaller than the width of a human hair), while they can be up to several micrometers in length. There are two main types of nanotubes:



The vector pointing from the first atom towards the other (from 'A' to 'B', in the Figure) is called the chiral vector  $R$  and its length is equal to the circumference of the nanotube. The direction of the nanotube axis is perpendicular to the chiral vector. SWNTs with different chiral vectors have dissimilar properties such as optical activity, mechanical strength and electrical conductivity.

The way the graphene sheet is wraps represented by a pair of indices of chiral vector  $(n, m)$ . The integer's  $n$  and  $m$  denote the number of unit along two directions in the honeycomb lattice of graphene. This is often thought of as representing the number of carbon atoms around.

Draw two parallel lines along the tube axis where the separation takes place. In other words, if you cut along the two lines and then match their ends together in a cylinder, you get a nanotube. Now, find any point on one of the tube axes that intersects one of the carbon atoms (say point A). Next, draw the Armchair line which travels across each hexagon, separating them into two equal halves. Now that you have the armchair line drawn, find a point along the other tube axis that intersects a carbon atom nearest to the Armchair line (say point B). Now connect A and B with your chiral vector,  $R$ . The wrapping angle is formed between  $R$  and the armchair line [31, 15].

There are a large variety of forms of each of the nanotubes identified by a two-digit sequence such as  $(4,0)$ ,  $(4,1)$ ,  $(4,2)$ ,  $(4,3)$ ,  $(4,4)$ , etc.

- The first digit indicates how many carbon atoms around the tube.

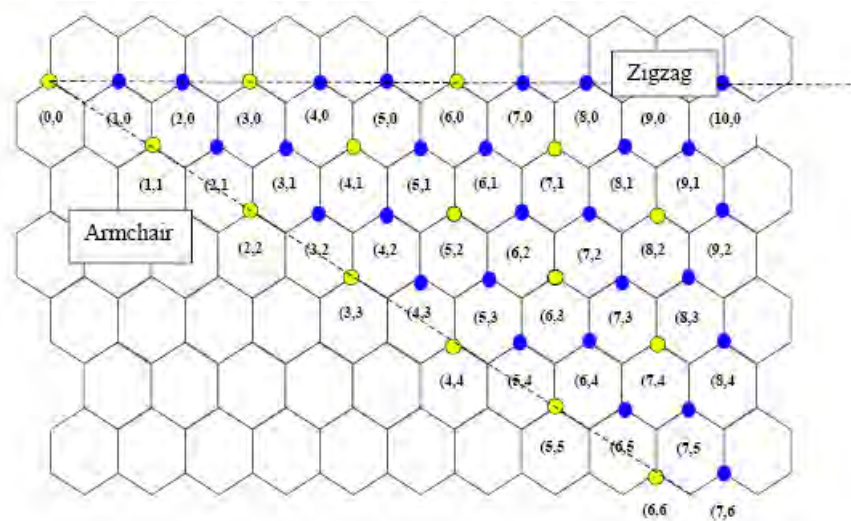


Figure 2.4: All possible structures of SWNTs can be formed from chiral vectors lying in the range given by this figure.

- The second digit determines the offset where the nanotubes wrap around.

If the second digit is zero ( $m = 0$ ), and the chiral angle  $\theta = 30^\circ$  then the nanotube is called zigzag nanotube.

If both digits are the same ( $n = m$ ) and ( $\theta = 0^\circ$ ), then it is called an "Armchair" nanotube.

If  $0 < \theta < 30^\circ$  then it is called a "chiral" nanotube.

Depending on details of their synthesis, carbon nanotubes can act like conducting metals or semiconductors, and have found use in elementary transistors and chemical sensors.

The structure of the nanotube (zigzag, armchair or chiral) affects its electric conducting properties. For example, (6, 0), (6, 6), (9, 0) and (9, 9) nanotubes are all excellent conductors. Carbon nanotube is seamless, with either open or capped ends.

The diameter of single-wall carbon nanotubes is 0.7 to 2 nm, 100,000 times thinner than a human hair. Buckytube lengths are 100 to 1,000 times their diameters [37, 15]. Their large length (up to several millimeters) and small diameter (a few nanometers) result in a large aspect ratio. Nanotubes generally have a length to diameter ratio of about 1000 so they can be considered as nearly one-dimensional structures [31, 15]. The SWNT can exist as bundles of many single walled nanotubes held together by Vander Waals force.

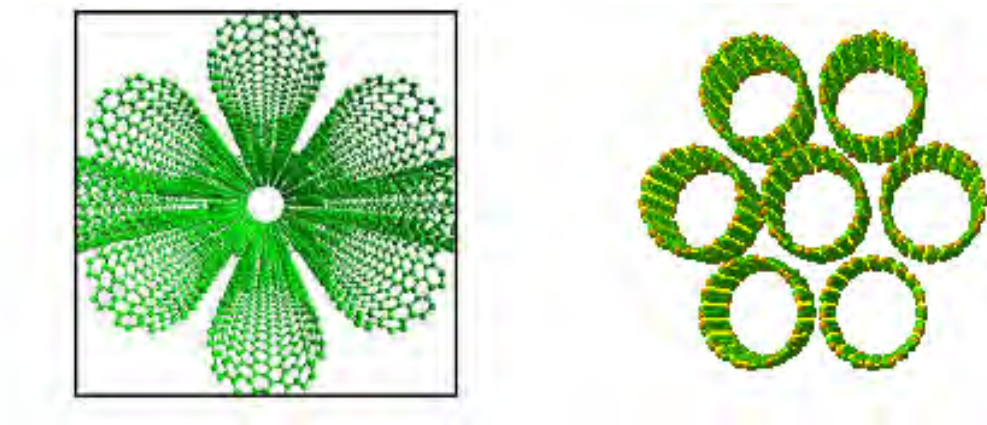


Figure 2.5: Bundles of many single walled nanotubes held by together by Vander wall forces

### 2.4.2 Multi-walled Carbon Nanotubes

Multi-walled carbon nanotubes are concentric cylindrical graphitic tubes [12, 15]. They contain atomic layer planes of carbon, which form a nested series of concentric cylinders, much like the growth rings of on a tree. MWNTs have several characteristics: wall thickness, number of concentric cylinders, cylinder radius, and cylinder length [37].

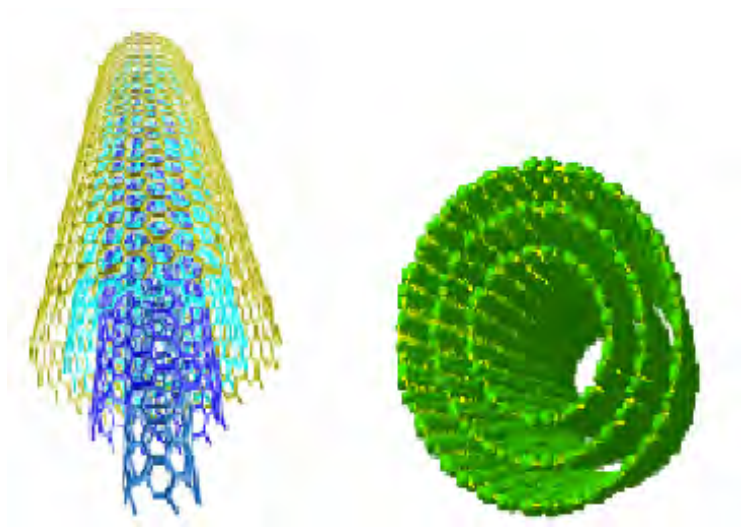


Figure 2.6: Schematic of Multi-walled CNT

Multi-walled nanotubes are invariably produced with a high frequency of structural defects that they frequently contain regions of structural imperfection and the occurrence of defects that inevitably degrade the material properties of a substance, such as strength.

# Chapter 3

## Structure & Unusual Properties of Carbon Nanotubes

### 3.1 Carbon Nanotube Structure and Defects

There are many exotic structures of fullerenes, e.g. regular spheres, cones, tubes and other more complicated and strange shapes. Here, we will describe some of the most important and best-known structures, useful for potential applications.

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 (called aspect ratio) so they can be considered as nearly one-dimensional structures or quasi one dimensional structure [37].

Carbon nanotubes (CNTs) are hollow cylinders of carbon atoms. Their appearance is that of rolled tubes of graphite, such that their walls are hexagonal carbon rings, and they are often formed in large bundles. The ends of CNTs are domed structures of six-membered rings, capped by a five-membered ring [12]. There are two main types of Carbon Nanotubes, Multi-Walled Nanotubes and Single-Walled Nanotubes. MWNTs contain overlapping cylindrical tubes, like a coaxial cable. Their diameters range from a few nanometers to around 40nm, depending on the number

of concentric tubes. SWNTs, on the other hand, consist of one tube with a diameter of approximately 1.4nm [33].

The structure of a SWNT can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder. The way the graphene sheet is wrapped is represented by a pair of indices  $(n,m)$  called the chiral vector. The integers  $n$  and  $m$  denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If  $m=0$ , the nanotubes are called "zigzag". If  $n=m$ , the nanotubes are called "armchair". Otherwise, they are called "chiral" [34].

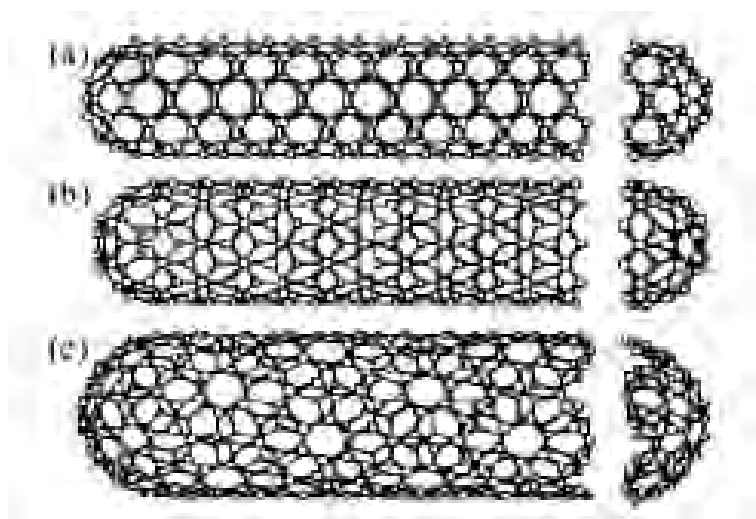


Figure 3.1: The tubes. a) Armchair structure b) Zigzag structure c) Chiral structure

In more detailed way, 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 12 pentagons and 20 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  $C_{70}$  and so on. 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 nanotube axis is perpendicular to the chiral vector [38]. The schematic of angle  $\theta$ , the vector  $a_1$  and  $a_2$  are shown in chapter 2.

After presenting ideal structures without flaws, we discuss the possible desirable or undesirable defects. Deformations, such as bends and nanotube junctions, are introduced by replacing a hexagon with a heptagon or pentagon. Deformations can be inward or outward and, among others, electrical properties are drastically changed by these deformations. Another class of defects is caused by impurities that are built in during or after the nanotube growth process; Compounds that can be incorporated into the structure are for example catalyst particles.

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 [34].

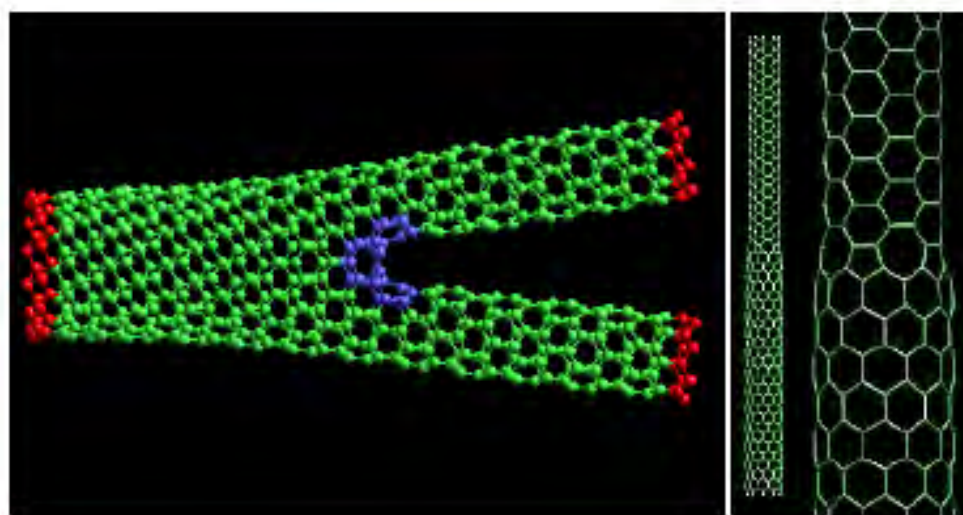


Figure 3.2: Left: A Y-branch structure. Right: A transition from a metallic to a semi-conducting SWNT. The change is made by insertion of pentagons and heptagons.

Introduction of defects can also result in various new structures such as Y-branches, T-branches or SWNT junctions (Figure 3.2). Under certain circumstances, these defects can be introduced in a 'controlled' way.

## 3.2 The Properties of Carbon Nanotubes

The wide range of electronic, thermal, magnetic and structural properties of carbon nanotubes vary according to the different diameter, length, and direction of 'twist' of the nanotube. Many applications arise from the surprising and desirable properties they exhibit, some of which are already being used in new and improved products. For example, carbon nanotubes are highly conductive both to electricity and heat - they exhibit an electrical conductivity higher than copper, and thermal conductivity greater than diamond.

Nanotubes can be either metallic or semiconducting, leading to the potential for developing nanowires, nanoscale electrical components and nanoelectromechanical systems. They, therefore, offer amazing possibilities for creating future nanoelectronic devices, circuits and computers. Carbon nanotubes also have extraordinary mechanical properties - they are 100 times stronger than steel, while only one sixth of the weight. These mechanical properties offer huge possibilities - for example, in creating nanocomposites for a variety of application scenarios ranging from military to aerospace to medicine [39].

As mentioned in chapter two that carbon nanotubes were first isolated and characterized by Ijima in 1991. Since then, tones of research articles have been published, and new applications for CNTs have been proposed every year. The unique physical and chemical properties of CNTs, such as structural rigidity and flexibility continue to generate considerable interest. CNTs can also act as either conductors or semiconductors depending on their chirality, possess an intrinsic superconductivity, are ideal thermal conductors, and can also behave as field emitters [37].

Electronic, molecular and structural properties of carbon nanotubes are determined to a large extent by their nearly one dimensional structure [34].

The very important properties of carbon nanotubes have exceptionally high material properties such as extremely very high tensile strength, lightweight, thermal stability, chemical inertness, field emission, electrical conductivity have potential applications [35]. In the following sections some of the special properties of carbon nanotubes are defined in detail.

### **3.2.1 Mechanical Properties of Carbon Nanotubes**

The strength of the  $sp^2$  carbon-carbon bonds gives carbon nanotubes amazing mechanical properties. The stiffness of a material is measured in terms of its Young's modulus, the rate of change of stress with applied strain. The Young's modulus of the best nanotubes can be as high as 1000 GPa which is approximately 5x higher than steel. The tensile strength, or breaking strain of nanotubes can be up to 63

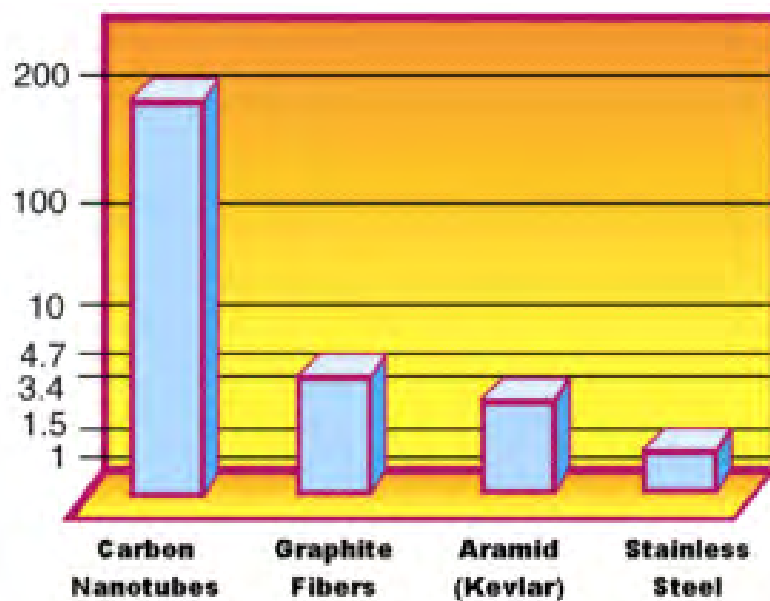


Figure 3.3: The chart compares the tensile strength of SWNT's to some common high-strength materials.

GPa, around 50x higher than steel. These properties, coupled with the lightness of carbon nanotubes, gives them great potential in applications such as aerospace engineering. It has even been suggested that nanotubes could be used in the space elevator, an Earth-to-space cable first proposed by Arthur C. Clarke. The electronic properties of carbon nanotubes are also extraordinary. Especially notable is the fact that nanotubes can be metallic or semiconducting depending on their structure. Thus, some nanotubes have conductivities higher than that of copper, while others behave more like silicon [36, 37].

There is great interest in the possibility of constructing nanoscale electronic devices from nanotubes, and some progress is being made in this area [37]. However, in

order to construct a useful device we would need to arrange many thousands of nanotubes in a defined pattern, and we do not yet have the degree of control necessary to achieve this. There are several areas of technology where carbon nanotubes are already being used. These include flat-panel displays, scanning probe microscopes and sensing devices [36]. The unique properties of carbon nanotubes will undoubtedly lead to many more applications.

### **3.2.2 Electrical Characteristics of Carbon Nanotubes**

The unique electronic properties of carbon nanotubes are due to the quantum confinement of electrons normal to the nanotube axis. In the radial direction, electrons are confined by the monolayer thickness of the graphene sheet. Around the circumference of the nanotube, periodic boundary conditions come into play. For example, if a zigzag or armchair nanotube has 10 hexagons around its circumference, the 11th hexagon will coincide with the first. Going around the cylinder once introduces a phase difference of  $2\pi$ . Because of this quantum confinement, electrons can only propagate along the nanotube axis, and so their wavevectors point in this direction. The resulting number of one-dimensional conduction and valence bands effectively depend on the standing waves that are set up around the circumference of the nanotube. These simple ideas can be used to calculate the dispersion relations of the one-dimensional bands, which link wavevector to energy, from the well known dispersion relation in a graphene sheet [40].

The electronic properties of SWNTs have been studied in a large number of theoretical works. All models show that the electronic properties vary in a predictable way from metallic to semiconducting with diameter and chirality. This is due to the very peculiar band structure of graphene and is absent in systems that can be described with usual free electron theory. Graphene is a zero-gap semiconductor with Basically, all armchair tubes are metallic. One out of three zigzag and chiral tubes show a small very small bandgap due to the curvature of the graphene sheet, while all other tubes are semi-conducting with a bandgap that scales approximately with the inverse of the tube radius. Bandgaps of 0.4 – 1 eV can be expected for SWNTs [15].

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  $2n + m = 3q$  (where  $q$  is an integer), then the nanotube is metallic, otherwise the nanotube is a semiconductor. Thus all armchair ( $n=m$ ) nanotubes are metallic, and nanotubes  $(5, 0)$ ,  $(6, 4)$ ,  $(9, 1)$ , etc. are semiconducting. In theory, metallic nanotubes can have an electrical current density more than 1,000 times larger than metals such as silver and copper [12, 34, 37].

One can view carbon nanotubes as giant conjugated molecular wires with a conjugation length corresponding to the whole length of the tube. In order to understand their electronic structure, we have to start with graphene, a single sheet of graphite. Carbon has four valence electrons of which three are strongly bound to neighbor atoms giving graphene its very high in-plane rigidity. The fourth electron

is delocalised and shared by all the atoms, thus allowing for electronic current transport. However, because of its particular structure, graphene is electronically between semiconductor and metal. It is a semimetal or a "zero-gap" semiconductor.

A perfect metallic nanotube with uncorrelated electrons, is supposed to be a ballistic conductor, i.e. the best (normal electron) conductor an engineer can dream of, only surpassed by a superconductor. If an electron is injected from a contact into a ballistic wire with ideal contacts, the electron will emerge with certainty at the drain contact. There is no backscattering in the wire, which is the source of intrinsic electric resistance and leads to Ohm's law. For a perfect ballistic tube theory predicts not one, but the existence of two propagating eigenmodes independent of the diameter. The electric conductance (the inverse of the resistance) is then expected to be twice the fundamental conductance unit  $G_0 = \frac{2e^2}{h} = \frac{1}{13} \text{ k}\Omega^{-1}$ . Note, the resistance is not zero, as it would be for a superconductor but in contrast to classical resistors and to Ohm's law, the resistance is independent of the length of the wire. Data suggesting that MWNTs are indeed ballistic conductors even at room temperature as depicted in figure 3.4, although the observed conductance quantum appears to be at  $G_0$ .

### **3.2.3 Thermal Properties of Carbon Nanotubes**

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. Prior to Carbon nanotubes, diamond was the best thermal conduc-

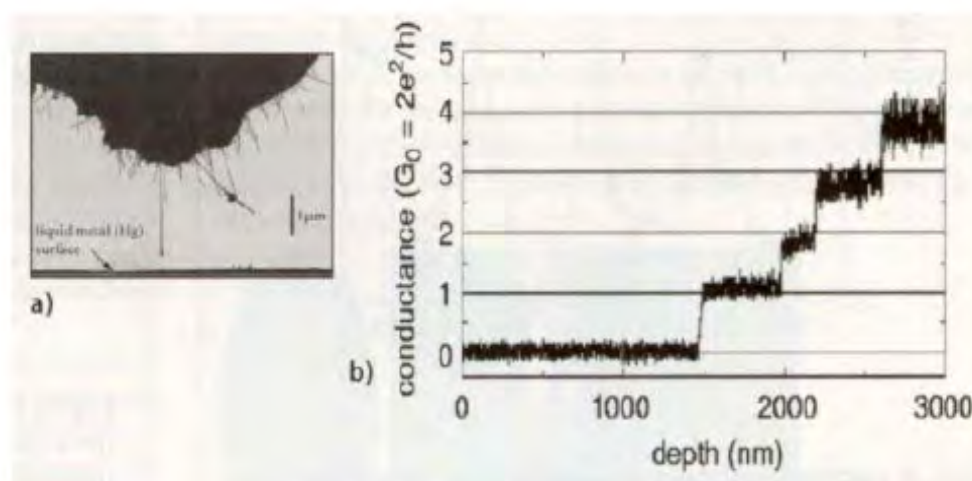


Figure 3.4: a) Electron microscope image of an ensemble of MWNTs mounted on a motion stage realized by de Heer and coworkers at Georgia Tech. The MWNT sticking out most is progressively dipped into liquid mercury, which serves as a second electrode. (b) As the individual nanotubes enter the metal, they contribute  $G_0 = \frac{2e^2}{h}$  to the overall quantum conductance, which appears to be ballistic, i.e. independent of length on each plateau.

tor. Carbon nanotubes have now been shown to have a thermal conductivity at least twice that of diamond. The high-frequency carbon-carbon bond vibrations provide an intrinsic thermal conductivity higher than even diamond. Unlike bulk diamond, however, whose thermal conductivity is the same in all directions, buckytubes conduct heat far better down the tube axis than sideways from tube to tube.

Carbon based nanotechnology is predicted to spark a series of industrial revolutions in the next two decades that will transform our lives to a far greater extent than silicon microelectronics did in the 20th century. Carbon nanotubes could play a pivotal role in this upcoming revolution if their remarkable electrical and mechanical properties can be exploited.

Since the first measurements were made in 1997, these rolled up sheets of graphite have captured the imagination of researchers around the world. Progress in understanding the basic physics and chemistry of nanotubes has advanced at a phenomenal rate - and shows no signs of slowing.

Nanotubes have an impressive list of attributes. They can behave like metals or semiconductors, can conduct electricity better than copper, can transmit heat better than diamond, and they rank among the strongest materials known - not bad for structures that are just a few nanometers across. Several decades from now we may see integrated circuits with components and wires made from nanotubes, and may be even buildings that can snap back into shape after an earthquake [12, 34]. The thermal conductivity of carbon nanotubes is dependent on the temperature and the large phonon mean free paths [35]. The graph of thermal conductivity vs length is shown in figure 3.5.

To summarize all the properties below in the tables are a compilation of research results from scientists all over the world. All values are for Single Wall Carbon Nanotubes (SWNT's) unless otherwise stated.

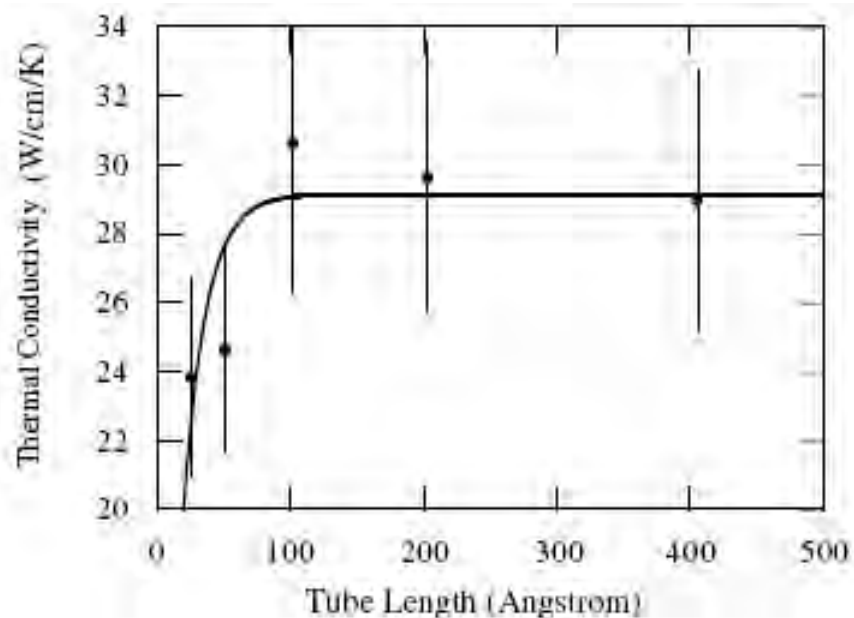


Figure 3.5: Convergence of thermal conductivity.

Equilibrium Structure	
Average Diameter of SWNT's	1.2-1.4nm
Distance from opposite Carbon Atoms (Line 1)	0.283nm
Analogous Carbon Atom Separation (Line 2)	0.246nm
Parallel Carbon Bond Separation (Line 3)	0.245nm
Carbon Bond Length (Line 4)	1.42nm
C - C Tight Bonding Overlap Energy	2.45eV
Group Symmetry (10, 10)	$C_{5v}$
Lattice: Bundles of Ropes of Nanotubes	Triangular Lattice (2D)
Lattice Constant	17 Å
Lattice Parameter	
(10, 10) Armchair	16.78 Å
(17, 0) Zigzag	16.52 Å
(12, 6) Chiral	16.52 Å
Density:	
(10, 10) Armchair	1.33 g/cm <sup>3</sup>
(17, 0) Zigzag	1.34 g/cm <sup>3</sup>
(12, 6) Chiral	1.40 g/cm <sup>3</sup>
Interlayer Spacing:	
(n, n) Armchair	3.38 Å
(n, 0) Zigzag	3.41 Å
(2n, n) Chiral	

Optical Properties	
Fundamental Gap:	
For (n, m); n-m is divisible by 3 [Metallic]	0 eV
For (n, m); n-m is not divisible by 3 [Semi-Conducting]	~0.5 eV
Electrical Transport	
Conductance Quantization	$(12.9 \text{ k}\Omega)^{-1}$
Resistivity	$10^{-4} \Omega\text{-cm}$
Maximum Current Density	$10^{13} \text{ A/m}^2$
Thermal Transport	
Thermal Conductivity	~2000 W/m/K
Phonon Mean Free Path	~100 nm
Relaxation Time	~ $10^{-11}$ s
Elastic Behavior	
Young's Modulus (SWNT)	~1 TPa
Young's Modulus (MWNT)	1.28 TPa
Maximum Tensile Strength	~100 GPa

Table 3:1 Electrical, thermal, optical and elastic properties of CNTs [35]

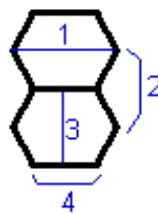


Figure 3.6: Bonding in graphite structure

In the next chapter we will see some growth methods of carbon nanotubes. Synthesis & characterization is obviously an important issue.

# Chapter 4

## Techniques for Synthesis of Carbon Nanotubes

### 4.1 Techniques for Synthesis of Carbon Nanotubes

Since the discovery of MWNTs in 1991 and subsequent production of SWNTs, research studies on carbon nanotubes have acquired the important status as one of the most active fields of nanoscience and nanotechnology. Nanotubes, are closed allotropes of carbon and are made in the same way with the the conditions altered slightly [41]. Here we focus on some of the techniques for CNT synthesis.

Fullerene and carbon nanotubes are not necessarily products of high-tech laboratories, and are also formed in such ordinary places as in candle soot. However, these naturally occurring varieties are highly irregular in size and quality, and attempting to ensure the high degree of uniformity is necessary to meet the needs of research and industrial applications are impossible in such uncontrolled environment [10, 42].

Synthesis of CNTs is a rapidly advancing field, but there is a lot that researchers don't know about how nanotubes form and grow. Synthesis, while rapidly developing, is currently the weakest link for most nanotube applications, with high yield and high precision diameter and chirality control being important goals. Ideally one would like to detect individual nanotubes and ensembles as they grow and mea-

sure their physical properties while imposing minimal constraints on the synthesis method. In other words, with a good understanding of the synthesis process we would be better able to control the product. It is feasible that by actually observing nanotubes as they grow one will gain a better understanding of the growth process and also better characterize the grown product. Greater control over the physical characteristics of the nanotube product is essential to enable many applications, as well as many fundamental studies. Although chemical vapor deposition (CVD) is now a very standard method to synthesize CNTs [43].

Methodes have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, chemical vapor deposition (CVD), water-assisted synthesis, and catalytic decomposition of hydrocarbons, electrolysis method and thermal pyrolysis of organometallic. Of these, the CVD method has shown the most promise in terms of its price/unit ratio.

Here some of synthesis methodes of carbon nanotubes such as arc-discharge, laser vaporization, chemical vapor deposition (CVD) will be discussed in detail.

#### **4.1.1 Arc Discharge Method**

The carbon arc discharge method, initially used for producing  $C_{60}$  fullerenes, is the most common and perhaps easiest way to produce CNTs, as it is rather simple. However, it is a technique that produces a complex mixture of components, and

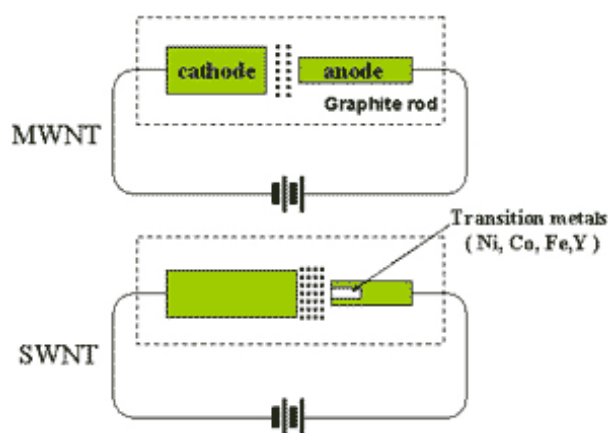


Figure 4.1: Schematic diagram of arc-discharge apparatus

requires further purification - to separate the CNTs from the soot and the residual catalytic metals present in the crude product.

This method creates CNTs through arc-vaporization of two carbon rods placed end to end, separated by approximately 1mm, in an enclosure that is usually filled with inert gas at low pressure (between 50 and 700 mbar). Recent investigations have shown that it is also possible to create CNTs with the arc method in liquid nitrogen. A direct current of 50 to 100A, driven by a potential difference of approximately 20 V, creates a high temperature discharge between the two electrodes shown in figure 4.1. The discharge vaporizes the surface of one of the carbon electrodes, and forms a small rod-shaped deposit on the other electrode. Producing CNTs in high yield depends on the uniformity of the plasma arc, and the temperature of the deposit forming on the carbon electrode [12].

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, carbon and metalcatalyst densities affect the diameter distribution of nanotubes.

Depending on the exact technique, it is possible to selectively grow SWNTs or MWNTs. Two distinct methods of synthesis can be performed with the arc discharge

### A) 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.

### B) 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 scientist are developing ways to gain pure MWNTs in a large-scale process without purification. Figure 4.1 shows schematic diagram of the process.

Typical sizes for MWNTs with inner diameter of 1-3 nm and an outer diameter of approximately 10nm. 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 [38].

#### **4.1.2 Laser Ablation Method**

In 1996 CNTs were first synthesized using a dual-pulsed laser and achieved yields of more than 70wt% purity. Samples were prepared by laser vaporization of graphite rods with a 50:50 catalyst mixture of Cobalt and Nickel at 1200°C in flowing argon, followed by heat treatment in a vacuum at 1000°C to remove the C<sub>60</sub> and other fullerenes. The initial laser vaporization pulse was followed by a second pulse, to vaporize the target more uniformly. The use of two successive laser pulses minimizes the amount of carbon deposited as soot. The second laser pulse breaks up the larger particles ablated by the first one, and feeds them into the growing nanotube structure. The material produced by this method appears as a mat of “ropes”, 10-20nm in diameter and up to 100μm or more in length. Each rope is found to consist primarily of a bundle of single walled nanotubes, aligned along a common axis. By varying

the growth temperature, the catalyst composition, and other process parameters, the average nanotube diameter and size distribution can be varied. The arrangement is shown in the figure 4.2.

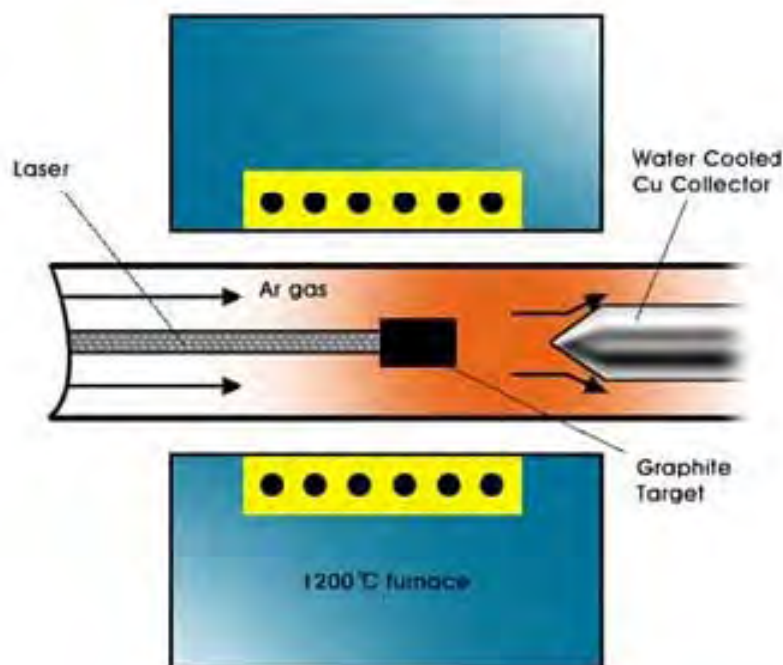


Figure 4.2: Schematic diagram of laser vaporization apparatus for the synthesis multi-walled nanotubes

Arc-discharge and laser vaporization are currently the principal methods for obtaining small quantities of high quality CNTs. However, both methods suffer from drawbacks. The first is that both methods involve evaporating the carbon source, so it has been unclear how to scale up production to the industrial level using these

approaches. The second issue relates to the fact that vaporization methods grow CNTs in highly tangled forms, mixed with unwanted forms of carbon and/or metal species. The CNTs thus produced are difficult to purify, manipulate, and assemble for building nanotube-device architectures for practical applications [12].

### **4.1.3 Chemical Vapor Deposition**

Chemical vapor deposition of hydrocarbons over a metal catalyst is a classical method that has been used to produce various carbon materials such as carbon fibers and filaments for over twenty years (Figure 4.3). Large amounts of CNTs can be formed by catalytic CVD of acetylene over Co and Fe catalysts supported on silica or zeolite. The carbon deposition activity seems to relate to the Co content of the catalyst, whereas the CNTs' selectivity seems to be a function of the pH in catalyst preparation. Fullerenes and bundles of single walled nanotubes were also found among the multi walled nanotubes produced on the carbon/zeolite catalyst.

Some researchers are experimenting with the formation of CNTs from ethylene. Supported catalysts such as Fe, Co, and Ni, containing either a single metal or a mixture of metals, seem to induce the growth of isolated single walled nanotubes or single walled nanotubes bundles in the ethylene atmosphere. The production of single walled nanotubes, as well as double-walled CNTs, on molybdenum and Mo-Fe alloy catalysts has also been demonstrated. CVD of carbon within the pores of a thin alumina template with or without a Ni catalyst has been achieved. Ethylene was used

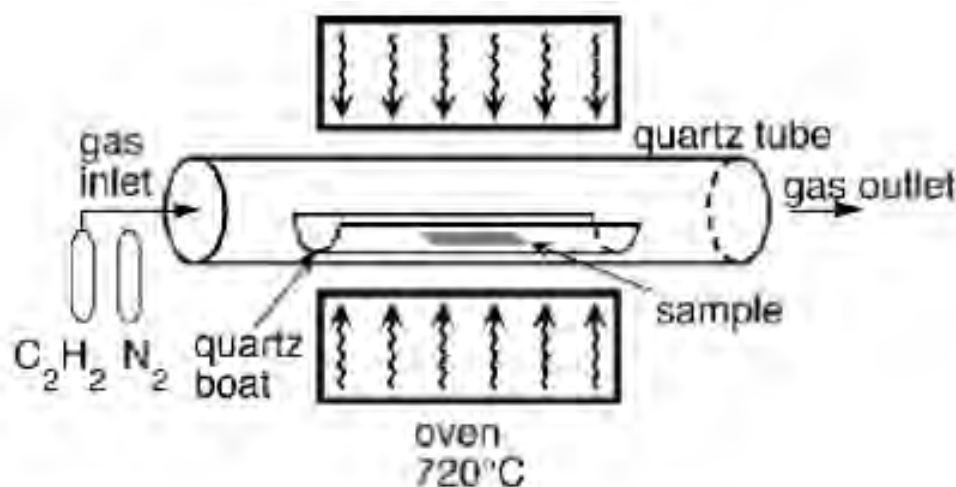


Figure 4.3: Schematic of CVD method

with reaction temperatures of  $545^\circ C$  for Nickel-catalyzed CVD, and  $900^\circ C$  for an uncatalyzed process. The resultant carbon nanostructures have open ends, with no caps. Methane has also been used as a carbon source. In particular it has been used to obtain 'nanotube chips' containing isolated single walled nanotubes at controlled locations. High yields of single walled nanotubes have been obtained by catalytic decomposition of an  $H_2/CH_4$  mixture over well-dispersed metal particles such as Cobalt, Nickel, and Iron on magnesium oxide at  $1000^\circ C$ . It has been reported that the synthesis of composite powders containing well-dispersed CNTs can be achieved by selective reduction in an  $H_2/CH_4$  atmosphere of oxide solid solutions between a non-reducible oxide such as  $Al_2O_3$  or  $MgAl_2O_4$  and one or more transition metal oxides. The reduction produces very small transition metal particles at a temperature of usually more than  $800^\circ C$ . The decomposition of  $CH_4$  over the freshly formed

nanoparticles prevents their further growth, and thus results in a very high proportion of single walled nanotubes and fewer multi-walled nanotubes [12].

To summarize the synthesis methods of CNTs in short: Arc discharge method was first used by Ebbesen and Ajayan (NEC, Japan 1992) which is used in connecting two graphite rods to a power supply place them a few millimetres apart, and throw the switch. At 100 amps, carbon vaporises and forms a hot plasma. It's typical yields is about 30% to 90% and the diameter of SWNT produce in this way is 0.6 to 1.4 nm which is short tube but MWNT has inner diameter of 1 to 3 nm and outer diameter of approximately 10 nm. This method can easily produce SWNT, MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis possible. The draw back of arc discharge method is that tubes tend to be short with random sizes and directions; often needs a lot of purification. CVD (Endo, Shinshu University, Nagano, Japan) method is used by placing substrate in oven, heat to 600°C, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of NTs. It's typical yields is about 20% to 100% ,and the diameter of long tubes with diameters ranging from 0.6 to 4 nm and MWNT about 10 240 nm. This method is easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure. The draw back of this method is that NTs are usually MWNTs and often riddled with defects. The third technique is that of Laser ablation (Smalley, Rice, 1995) how it is used is by blasting graphite with intense laser pulses, use the

laser pulses rather than electricity to generate carbon gas from which the NTs form and trying various conditions until hit on one that produces prodigious amounts of SWNTs. Which gives typical yield of up to 70%, the product SWNT is long bundles of tubes (5-20 microns), with individual diameter from 1-2 nm, and MWNT is not very much interest in this technique, as it is too expensive, but MWNT synthesis is possible. The advantage of this method is that primarily SWNTs, with good diameter control and few defects. The reaction product is quite pure and its draw back is that Costly technique, because it requires expensive lasers and high power requirement, but is improving.

In the next chapter we will discuss the marvelous potential applications of CNTs. Application is the main target of every science.

## Chapter 5

# Applications of Carbon Nanotubes

In recent years many potential applications have been proposed for carbon nanotubes - including nanometer-sized semiconductor devices, probes, and interconnects; conductive and high-strength specialist composites; devices for energy storage and energy conversion; sensors; field emission displays and radiation sources; and hydrogen storage media. Research is expected to lead to new materials, lubricants, coatings, catalysts, electro-optical devices, and medical applications [39, 49, 52].

The cost, purification, separation of nanotube type (SWNTs from MWNTs), constraints in processing and scaling up, and assembly methods are still hurdles for some applications which are in the process of being overcome. However, some applications are already manifest in products in the market place, others are under development. For example, tennis racquets containing carbon nanotubes are already in the market. The nanotubes are used to reinforce the frame and improve the racquet's ability to absorb shocks. Reinforced tennis racquets are only one of many potential applications. Some Carbon nanotubes can be mixed with many different materials such as plastics and textiles for lightweight bullet-proof vests [49, 52].

According to engineers at the Fraunhofer Technology Development Group TEG in Stuttgart the greatest potential for creating new products at the present time lies in harnessing the electrical properties of light and robust nanotubes to generate heat.

Potential applications range from electric blankets and heatable aircraft wings that no longer ice up, through to wallpaper heating for cold walls.

Not to be outdone by their nanotube cousins, the bucky ball, the only molecule composed of a single element, forms a hollow spheroid which is already a focus of attention by medical researchers for its potential for in novel drug delivery systems [39].

Nanoscale technologies include many diverse applied fields. This installment will give a flavor of what the technology is about and how it works. Nanoscale features are used in a variety of applications including computers, disinfectants, self-cleaning surfaces, stronger plastics, medicines, solar cells, biological research, and materials science. These applications depend on a surprising variety of physical principles and means of manufacture.

One way to make nanoscale particles is simply to vary existing manufacturing processes. Grinding bulk materials finer, or condensing gases more quickly, can create smaller particles. Nanoscale structures can also be made chemically. Chemists have learned to make large, precise, branching molecules called dendrimers. Some chemicals can self-assemble into larger patterns, sticking together as regions of the chemical attract each other in particular ways. Non-molecular particles can also stack up, forming quasicrystalline arrays. Then there are a variety of ways, collectively called lithography, to form nanoscale features on an existing surface.

New physical and chemical structures can display novel features. For example, smaller particles of a catalyst can be more active, not just because of increased surface area, but because of increased strain between the atoms. Other particles may trap electrons in ways that make them glow in specific colors or make them useful for new computer circuit designs.

Sometimes, simply arranging nanoscale objects more precisely can be helpful. New techniques for making single layers of molecules can be used for better semiconductors, sensors, surface characteristics, structural properties, and displays.

Tools to deal with the nanoscale also are called nanotechnology, because they sense or manipulate on the nanometer scale. These tools may not actually incorporate many nanoscale components. For example, the only nanoscale part of a scanning tunneling microscope (other than in the computer chips) is the scanning probe tip, which is sometimes made by the low-tech technique of cutting a wire with an ordinary pair of scissors.

Carbon nanotubes are a hot issue in nanotechnology. Conceptually, a carbon nanotube is formed by a thin strip of graphite rolled into a tube and chemically stitching the edges together. Carbon nanotubes are extremely strong. Depending on how the graphite is twisted, they may be excellent conductors, semiconductors, or insulators. They are unusual in that they are single molecules, with precise chemical formulas, but may be thousands of nanometers long. Carbon nanotubes are being

investigated for use in electronics as well as for reinforcing plastic and making it conductive.

Tiny particles of gold absorb certain colors of infrared light, heating up as they do. If attached to a chemical that seeks out cancer cells, the particles will cluster around even tiny tumors. Shining infrared light on the patient will then overheat and kill the tumors without damaging the healthy cells of the body.

Nanoscale technology does not build complete products, only components. The wide diversity of applications means that substantial research is necessary to develop the new applications. But small size, new structures, and greater precision can improve performance in a variety of ways. Less material may be needed; stronger components can be made; new optical and electronic elements promise to shrink computers by a hundredfold; hybrids of molecules and nanoparticles can have significant medical uses including destroying tumors without harming surrounding tissue. This combination of improved performance and new applications makes nanoscale technologies well worth investigating, and a wide variety of large and small companies, as well as academic research institutions, already are doing so [44].

One of the most exciting aspects of carbon nanotubes for applications is due to their unique structure, outstanding physical and chemical properties. Carbon nanotubes are an example of true nanotechnology: only a nanometer in diameter, but molecules that can be manipulated chemically and physically. They open incredible applications in materials, electronics, chemical processing and energy management.

However, practical applications are still limited by the complicated process of synthesis and the inability of present manufacturing methods to provide large-scale production of carbon nanotubes [12].

Carbon nanotubes are expected to become a key material in ultrafine devices of the future, because of their unique electrical characteristics, and their extraordinarily fine structure on a nanometer scale. Other merits offered by carbon nanotubes are light weight, extremely high mechanical strength (they have larger tensile strength than steel), their ability to withstand extreme heat of 2000°C in the absence of oxygen, and the fact that they emit electrons efficiently when subjected to electrical field. Currently, research is being conducted throughout the world targeting the application of carbon nanotubes as materials for use in transistors and fuel cells, big television screen, ultra-sensitive sensors, high-resolution AFM probes, supercapacitor, transparent conducting film, drug carrier (nanomedicine), catalysts, and composite materials [45].

Some of the applications will be discussed in this chapter including field emission, nanomedicine, energy storage and others.

## **5.1 Carbon Nanotubes in Field Emission Applications**

Buckytubes are the best known field emitters of any material. This is understandable, given their high electrical conductivity, and the unbeatable sharpness of their tip (the sharper the tip, the more concentrated will be an electric field, leading

to field emission; this is the same reason lightening rods are sharp). The sharpness of the tip also means that they emit at especially low voltage, an important fact for building electrical devices that utilize this feature. Buckytubes can carry an astonishingly high current density, possibly as high as  $10^{13}$  A/cm<sup>2</sup>. Furthermore, the current is extremely stable.

An immediate application of this behaviour receiving considerable interest is in field-emission flat-panel displays. Instead of a single electron gun, as in a traditional cathode ray tube display, here there is a separate electron gun (or many) for each pixel in the display. The high current density, low turn-on and operating voltage, and steady, long-lived behaviour make Buckytubes attract field emitters to enable this application [37].

## **5.2 Carbon Nanotubes in Hydrogen Storage**

The revolution in science and technology during the last century has brought tremendous changes in our lives, in such diverse areas as traffic, communication, daily work routines and entertainment. The constantly improving standard of living the world over is based on energy consumption, which is increasing rapidly in proportion to the growth in the economy as well as in the global population. Rapid depletion of fossil energy sources and increasing environmental pollution caused by high fossil energy consumption have contributed to making this problem a world-

wide concern and therefore a new and tough challenge that human beings are having to face.

Many researchers and policy analysts see hydrogen as the fuel of the future because it is readily available in water and, unlike fossil fuels, it is a non-polluting source of energy. However, there are a number of significant barriers to adopting a new source of fuel. Nanotechnology may help to overcome these barriers through the development of nanocatalysts that can derive hydrogen from water at low cost. Carbon nanotubes could also be used to make light but strong storage containers for gaseous hydrogen, so vehicles could be operated safely using liquid hydrogen.

Hydrogen is considered to be among the best solutions available, although technical barriers, in particular effective hydrogen storage, need to be dealt with. Quasi-one-dimensional carbon nanotubes (CNTs) with rich nanosized pore structures are considered to be a potential hydrogen storage medium [46].

### **5.3 The Impact of Carbon Nanotubes on The Use of Solar Energy**

With an increased focus on alternative sources of cheap, abundant, clean energy, solar cells are receiving lots of attention. Harnessing the power of the sun to replace the use of fossil fuels holds tremendous promise. One way to do this is through the use of solar or photovoltaic cells. Until now, solar cells that convert sunlight to electric power have been dominated by solid state junction devices, often made of silicon

wafers. Thanks to nanotechnology, this is now being challenged by the development of a new generation of solar cells based on thin film materials, nanocrystalline materials and conducting polymeric films. These offer the prospects of cheaper materials, higher efficiency and flexible features. This has opened up new opportunities in solar cell research and development and, consequently, there is considerable investor interest in solar nanotechnology startups. Both inventors and investors are betting that flexible sheets of solar cells used to harness the sun's strength will ultimately provide a cheap and efficient source of energy [43].

## **5.4 Carbon Nanotubes in Medical Sector**

Disease and ill health are caused largely by damage at the molecular and cellular level. Today's surgical tools are, at this scale, large and crude. From the viewpoint of a cell, even a fine scalpel is a blunt instrument more suited to tear and injure than heal and cure. Modern surgery works only because cells have a remarkable ability to regroup, bury their dead and heal over the injury [26].

In the near future, advancement in nanomedicine will deliver a valuable set of research tools and clinically helpful devices. The National Nanotechnology Initiative expects new commercial applications in the pharmaceutical industry that will include advanced drug delivery systems, new therapies, and in vivo imaging. Farther down the line, neuro-electronic interfaces and cell repair machines could revolutionize medicine and the medical field, but now nanomedicine is becoming one

of the biggest industries in the world. In 2004, nanomedicine sales reached 6.8 billion dollars, and with over 200 companies and 38 products worldwide, a minimum of 3.8 billion dollars in nanotechnology R&D is being invested every year. As the nanomedicine industry continues to grow, there is no doubt that it will have a significant impact on the economy. The most important innovations are taking place in drug delivery which involves developing nanoscale particles or molecules to improve bioavailability. Bioavailability refers to the presence of drug molecules where they are needed in the body and where they will do the most good. Drug delivery focuses on maximizing bioavailability both at specific places in the body and over a period of time. Over 65 billion dollars is wasted every year because of poor bioavailability. In vivo imaging is another area where tools and devices are being developed. Using nanoparticle contrast agents, images such as ultrasound and MRI have a favorable distribution and improved contrast. The new therapies and surgeries that are being developed might be effective in treating illnesses and diseases such as cancer. Finally, a shift from the possible to the potential will be made when nanorobots such as neuro-electronic interfaces and cell repair machines are discussed. Nanoparticles are a great source of vitamins and minerals.

Nanomedicine is the medical application of nanotechnology. It covers areas such as nanoparticle drug delivery and possible future applications of molecular nanotechnology (MNT) and nanovaccinology. Current problems for nanomedicine

cine involve understanding the issues related to toxicity and environmental impact of nanoscale materials [47].

Nanomedicine is the application of nanotechnology (the engineering of tiny machines) to the prevention and treatment of disease in the human body. This discipline is in its infancy. It has the potential to change medical science dramatically in the 21st century.

The biological and medical research communities have exploited the unique properties of nanomaterials for various applications (e.g., contrast agents for cell imaging and therapeutics for treating cancer). Terms such as biomedical nanotechnology, bionanotechnology, and nanomedicine are used to describe this hybrid field.

Functionalities can be added to nanomaterials by interfacing them with biological molecules or structures. The size of nanomaterials is similar to that of most biological molecules and structures; therefore, nanomaterials can be useful for both in-vivo and in-vitro biomedical research and applications.

The integration of nanomaterials with biology has led to the development of diagnostic devices, contrast agents, analytical tools, physical therapy applications, and drug-delivery vehicles [47].

The most elementary nanomedical devices will be used to diagnose illness. Chemical tests exist for this purpose; nanomachines could be employed to monitor the internal chemistry of the body. Mobile nanorobots, equipped with wireless transmitters, might circulate in the blood and lymph systems, and send out warnings when

chemical imbalances occur or worsen. Similar fixed nanomachines could be planted in the nervous system to monitor pulse, brain-wave activity, and other functions.

A more advanced use of nanotechnology might involve implanted devices to dispense drugs or hormones as needed in people with chronic imbalance or deficiency states. Heart defibrillators and pacemakers have been around for some time; nanomedicine carries this to the next level down in terms of physical dimension, with the potential to affect the behavior of individual cells. Ultimately, artificial antibodies, artificial white and red blood cells, and antiviral nanorobots might be devised.

The most advanced nanomedicine involves the use of nanorobots as miniature surgeons. Such machines might repair damaged cells, or get inside cells and replace or assist damaged intracellular structures. At the extreme, nanomachines might replicate themselves, or correct genetic deficiencies by altering or replacing DNA (deoxyribonucleic acid) molecules.

#### **5.4.1 Carbon Nanotubes Versus HIV**

Nanotubes can transport RNA into the human immune system's white blood cells, making the cells less vulnerable to attack by the HIV virus.

Researchers at Stanford University have added one more trick to carbon nanotubes' repertoire of accomplishments: a way to fight the human immunodeficiency virus (HIV). Chemistry professor Hongjie Dai and his colleagues have used carbon

nanotubes to transport RNA into human white blood cells that defend the body from disease, making the cells less susceptible to HIV attack [48, 15].

The recently discovered technique of RNA interference (RNAi)—using snippets of RNA to shut down disease-causing genes—could be an important weapon against diseases such as cancer and AIDS. Researchers have shown that one way to combat HIV with RNAi is to switch off a gene that controls the expression of receptor proteins on the surface of white blood cells known as T cells; the virus binds to this receptor and then enters and infects the T cells. If interfering RNA could turn off the receptors, the virus would have no point of entry into the cells. However, RNA can't easily cross cell membranes and enter cells on its own, and researchers are trying to find a way to get the RNA into cells more efficiently [48].

## **5.5 Carbon nanotubes in Electrical Circuits**

Carbon nanotubes have many properties from their unique dimensions to an unusual current conduction mechanism that make them ideal components of electrical circuits. Currently, there is no reliable way to arrange carbon nanotubes into a circuit.

The major hurdles that must be jumped for carbon nanotubes to find prominent places in circuits relate to fabrication difficulties. The production of electrical circuits with carbon nanotubes are very different from the traditional IC fabrication process. The IC fabrication process is somewhat like sculpture - films are deposited

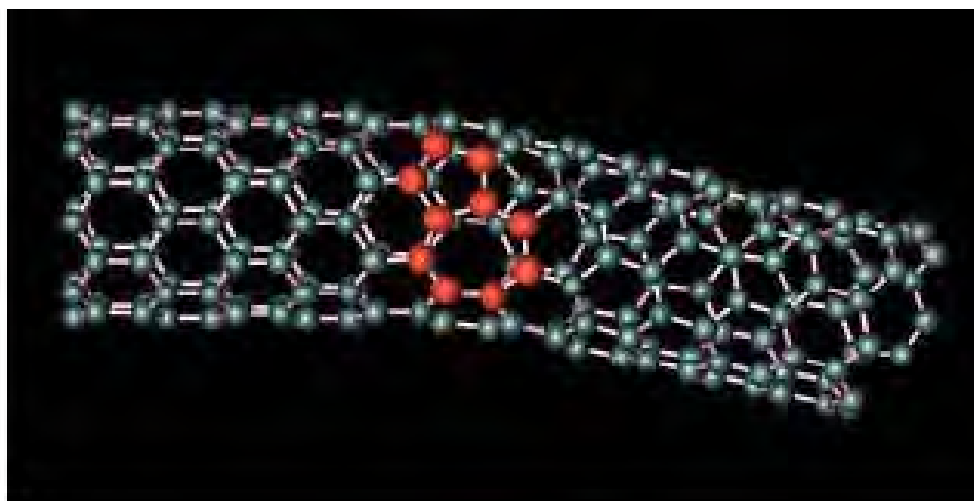


Figure 5.1: Making of a diode by joining hexagonal and pentagonal ends of CNT

onto a wafer and pattern-etched away. Because carbon nanotubes are fundamentally different from films, carbon nanotube circuits can so far not be mass produced [49, 15, 53].

Researchers sometimes resort to manipulating nanotubes one-by-one with the tip of an atomic force microscope is a painstaking, time-consuming process. Perhaps the best hope is that carbon nanotubes can be grown through a chemical vapor deposition process from patterned catalyst material on a wafer, which serve as growth sites and allow designers to position one end of the nanotube. During the deposition process, an electric field can be applied to direct the growth of the nanotubes, which tend to grow along the field lines from negative to positive polarity. Another way for the self assembly of the carbon nanotube transistors consist in using chemical or bi-

ological techniques to place the nanotubes from solution to determinate place on a substrate [49].

Even if nanotubes could be precisely positioned, there remains the problem that, to this date, engineers have been unable to control the types of nanotubes metallic, semiconducting, single-walled and multi-walled produced. A chemical engineering solution is needed if nanotubes are to become feasible for commercial circuits.

### **5.5.1 Metallic and Semiconducting nanotubes**

Most experimentally observed CNTs are multi-walled structures with outer most shell diameters exceeding 10 nm. Since current conduction in a MWCNT is known to be mostly confined to the outer most single-walled nanotube and since band gap of a SWCNT varies inversely with its diameter, MWCNTs are metallic in nature. SWCNTs can be either metallic or semiconducting depending on the way the roll-up of the graphene sheet occurs - an aspect termed as Chirality, and if all the roll-up types are realized with equal probability, 1/3 of the SWCNTs end up being metallic and 2/3 semiconducting. Thus, when CNTs are fabricated either by arc discharge growth, laser ablation or chemical vapor deposition (CVD), a mixture of metallic and semiconducting nanotubes are always formed [49, 37].

### **5.5.2 Carbon Nanotube Interconnects**

Metallic CNTs have aroused a lot of research interest in their applicability as very-large-scale integration (VLSI) interconnects of the future because of their

desirable properties of high thermal stability, high thermal conductivity and large current carrying capacity. An isolated CNT can carry current densities in excess of 1000 MA/sq-cm without any signs of damage even at an elevated temperature of 250 °C, thereby eliminating electromigration reliability concerns that plague Cu interconnects. Recent modeling work comparing the performance, power dissipation and thermal/reliability aspects of CNT interconnect to scaled copper interconnects have shown that CNT bundle interconnects can potentially offer advantages over copper. Additionally, the concept of hybrid CNT/Cu interconnects-employing CNT vias in tandem with copper interconnects has been shown to offer advantages from a reliability/thermal-management perspective. More information on state-of-the-art of CNT interconnects (including their fabrication) can be found in the literature [39].

### **5.5.3 Carbon Nanotube Transistors**

Semiconducting CNTs have been used to fabricate field effect transistors (CNT-FETs), which show promise due to their superior electrical characteristics over silicon based MOSFETs. Since the electron mean free path in SWCNTs can exceed 1 micrometer, long channel CNTFETs exhibit near-ballistic transport characteristics, resulting in high speed devices. In fact, CNT devices are projected to be operational in the frequency range of hundreds of GHz. Recent work detailing the advantages and disadvantages of various forms of CNTFETs have also shown that the tunneling based CNTFET offers better characteristics compared to other CNTFET structures.

This device has been found to be superior in terms of subthreshold slope - a very important property for low power applications [49, 15].

#### **5.5.4 Challenges in Electronic Design and Design Automation**

Although CNT devices and interconnects have been separately shown to be promising in their own respects, there have been few efforts to successfully combine them in a realistic circuit. Most CNTFET structures employ the silicon substrate as a back gate. Applying different back gate voltages might become a concern when designing large circuits out of these devices. Several top-gated structures have also been demonstrated, which can alleviate this concern. Recently, a fully integrated logic circuit built on a single nanotube has been reported [49, 52]. However, this circuit also employs a back-gate. Additionally, there are still several process related challenges that need to be addressed before CNT-based devices and interconnects can enter mainstream VLSI process. This makes it an exciting and open field for research. Problems like purification, separation of carbon nanotubes, control over nanotube length, chirality and desired alignment, low thermal budget as well as high contact resistance are yet to be fully resolved. Although these are serious technological challenges, innovative ideas have been proposed to build practical transistors out of nano-networks. Since lack of control on chirality produces a mix of metallic as well as semi-conducting CNTs from any fabrication process and it is difficult to control the growth direction of the CNTs, random arrays of SWCNTs (that are easily

produced) have been proposed to build thin film transistors. This idea can be further exploited to build practical CNT based transistors and circuits without the need for precise growth and assembly [49].

## 5.6 Some General Applications of Carbon Nanotubes

As mentioned before CNTs offer significant advantages over many existing materials due to their exceptional mechanical, electronic and chemical properties. While unprecedented interest in a variety of possible commercial applications has accelerated research and development, a key obstacle to commercialization remains the need for cost-effective, large-scale production methods.

Some more applications includes: Electrochemical and Gas Phase Hydrogen Storage, Nanotube Composite Materials, Supercapacitors, Lithium Ion Batteries, Field Emission Displays, Proton Exchange Membrane (PEM) Fuel Cells, Nanoelectronics, AFM Tips, and Nanotube Actuators [49, 15, 52].

**Structural applications** are: clothes: waterproof tear-resistant cloth fibers; combat jackets: MIT is working on combat jackets that use carbon nanotubes as ultrastrong fibers and to monitor the condition of the wearer; concrete: In concrete, they increase the tensile strength, and halt crack propagation; polyethylene: Researchers have found that adding them to polyethylene increases the polymer's elastic modulus by 30%; sports equipment: Stronger and lighter tennis rackets, bike parts, golf balls, golf clubs, golf shaft and baseball bats; space elevator: This will be possible only if

tensile strengths of more than about 70 GPa can be achieved. Monoatomic oxygen in the Earth's upper atmosphere would erode carbon nanotubes at some altitudes, so a space elevator constructed of nanotubes would need to be protected (by some kind of coating). Carbon nanotubes in other applications would generally not need such surface protection; ultrahigh-speed flywheels: The high strength/weight ratio enables very high speeds to be achieved. Bridges: For instance in suspension bridges (where they will be able to replace steel), or bridges built as a "horizontal space elevator" .

The **Electromagnetic Applications** ranges from: artificial muscles; buckypaper - a thin sheet made from nanotubes that are 250 times stronger than steel and 10 times lighter that could be used as a heat sink for chipboards, a backlight for LCD screens or as a faraday cage to protect electrical devices/aeroplanes. chemical nanowires: Carbon nanotubes additionally can also be used to produce nanowires of other chemicals, such as gold or zinc oxide. These nanowires in turn can be used to cast nanotubes of other chemicals, such as gallium nitride. These can have very different properties from CNTs - for example, gallium nitride nanotubes are hydrophilic, while CNTs are hydrophobic, giving them possible uses in organic chemistry that CNTs could not be used for. computer circuits: A nanotube formed by joining nanotubes of two different diameters end to end can act as a diode, suggesting the possibility of constructing electronic computer circuits entirely out of nanotubes. Because of their good thermal properties, CNTs can also be used to dissipate heat from tiny

computer chips. The longest electricity conducting circuit is a fraction of an inch long. (Source: June 2006 National Geographic).

- **Conductive films:** A 2005 paper in Science notes that drawing transparent high strength swathes of SWNT is a functional production technique. Additionally, Eikos Inc of Franklin, Massachusetts and Unidym Inc. of Silicon Valley, California are developing transparent, electrically conductive films of carbon nanotubes to replace indium tin oxide (ITO) in LCDs, touch screens, and photovoltaic devices. Carbon nanotube films are substantially more mechanically robust than ITO films, making them ideal for high reliability touch screens and flexible displays. Nanotube films show promise for use in displays for computers, cell phones, PDAs, and ATMs.

- **Electric motor brushes:** Conductive carbon nanotubes have been used for several years in brushes for commercial electric motors. They replace traditional carbon black, which is mostly impure spherical carbon fullerenes. The nanotubes improve electrical and thermal conductivity because they stretch through the plastic matrix of the brush. This permits the carbon filler to be reduced from 30% down to 3.6%, so that more matrix is present in the brush. Nanotube composite motor brushes are better-lubricated (from the matrix), cooler-running (both from better lubrication and superior thermal conductivity), less brittle (more matrix, and fiber reinforcement), stronger and more accurately moldable (more matrix). Since brushes are a critical failure point in electric motors, and also don't need much material, they became economical before almost any other application.

The other electromagnetic applications of carbon nanotubes includes:

- **Light bulb filament** which is alternative to tungsten in candescent lamps,
- **Magnets** (MWNTs coated with magnetite),
- **Optical ignition:** A layer of 29% iron enriched SWNT is placed on top of a layer of explosive material such as PETN, and can be ignited with a regular camera flash,
- **Solar cells:** GE's carbon nanotube diode has a photovoltaic effect. Nanotubes can replace ITO in some solar cells to act as a transparent conductive film in solar cells to allow light to pass to the active layers and generate photocurrent.
- **Superconductor:** Nanotubes have been shown to be superconducting at low temperatures.
- **Ultracapacitors:** MIT is researching the use of nanotubes bound to the charge plates of capacitors in order to dramatically increase the surface area and therefore energy storage ability.
- **Displays:** One use for nanotubes that has already been developed is as extremely fine electron guns, which could be used as miniature cathode ray tubes in thin high-brightness low-energy low-weight displays. This type of display would consist of a group of many tiny CRTs, each providing the electrons to hit the phosphor of one pixel, instead of having one giant CRT whose electrons are aimed using electric and magnetic fields. These displays are known as field emission displays (FEDs).
- **Transistor:** developed at Delft, IBM, and NEC [49, 15, 37].

**Chemical applications** of carbon nanotubes includes:

- **Air pollution filter:** Future applications of nanotube membranes include filtering carbon dioxide from power plant emissions.

- **Biotech container:** Nanotubes can be opened and filled with materials such as biological molecules, raising the possibility of applications in biotechnology.

- **Hydrogen storage:** Research is currently being undertaken into the potential use of carbon nanotubes for hydrogen storage. They have the potential to store between 4.2 and 65% hydrogen by weight. This is an important area of research, since if they can be mass produced economically there is potential to contain the same quantity of energy as a 50l gasoline tank in 13.2l of nanotubes.

- **Water filter:** Recently nanotube membranes have been developed for use in filtration. This technique can purportedly reduce desalination costs by 75%. The tubes are so thin that small particles (like water molecules) can pass through them, while larger particles (such as the chloride ions in salt) are blocked [49].

In addition to the above mechanical applications are also sounded such as fastest known;

- **Oscillators, liquid flow array:** Liquid flows up to five orders of magnitude faster than predicted through array,

- **Slick surface:** slicker than Teflon and waterproof [49, 15, 52].

## **5.7 Carbon Nanotubes (CNT) in Space Technology**

CNT, with diameters of a few nanometers, as fullerene derivatives represent pure carbon compounds and occur in different modifications, e.g. SWCNT or MWCNT. CNT possess unusual mechanical characteristics (on molecular level approximately 50 times stronger than steel and outstanding thermal and electrical conductivity). Due to their special properties, CNT possess numerous application potentials in space, among other things, within the ranges of space structures, thermal control devices, sensor technology, electronics and biomedicine.

A substantial part of the nanotechnology programme of NASA is based on the development and application of CNT based materials, sensors and electronics. In particular, the huge potential for mass savings in space structures makes CNT very interesting for space applications. A further advantage of CNT composites is that the changes of the mechanical properties of the material can be indicated through changes of the electrical resistance and so possible damages could in principle be easily detected by simply monitoring the electric conductance of the material.

If it should succeed in the future to manufacture favourably-priced CNT with defined characteristics on industrial scale and to transfer the outstanding molecular properties into macroscopic materials, not only improved conventional spacecraft will be possible, but also the type of space applications which sound very visionary at present. Conceivable, for example, is a space elevator, consisting of a self-supporting CNT rope, which is connected from earth to a geostationary object in space.

At present, however, technical applications of CNT based materials for structures are still far away. This is, on the one hand, due to the very high price, particularly for SWCNT, which amounts to approximately 500\$ per gram, depending on the purity and quality of the product. The high price is due to the fact that CNT can be produced so far only on a laboratory scale, with quantities up to 100 g per day through different gas-phase processes (flame synthesis, catalytic CVD, electrical arc discharge, laser ablation, etc), and require a complex cleaning procedure. On the other hand, problems concerning the transfer of the molecular properties to macroscopic materials are also still unsolved, e.g the dispersion of CNT in composite matrices or spinning of CNT to macroscopic fibers.

While applications of CNT materials for structure applications are to be expected rather in a long-term time horizon, due to their high price and problems with the scalability of production processes, other applications of CNT, such as fillers for electrically conductive polymer composites, e.g. for antistatic insulating materials, could be realized earlier. Such materials are developed, among other things, in the context of a SBIR project of NASA by the US-American companies Triton-Systems and Foster-Miller. In addition, a multiplicity of further space relevant applications of CNT is conceivable, for example, in the sensor technology or in molecular electronics [12].

## 5.8 Future Prediction and Outlook

A crucial objective of nanotechnology is to make products inexpensive. While the ability to make a few very small, very precise molecular machines very expensive would clearly be a major scientific achievement, it would not fundamentally change how we make most products.

The discovery of fullerenes and carbon nanotubes have opened a new chapter on the physics and chemistry of carbon. So far, the physical and chemical properties of fullerenes and carbon nanotubes are still under investigation. More research are needed to be done to confirm the suitability of some important application. Some potential applications will need more time for them to become reality.

Carbon nanotubes exhibit a wealth of properties and phenomena as mentioned previously. While many of these are understood, others remain controversial, and nanotubes are sure to remain an exciting area of condensed-matter physics for years to come. Like any new technology, however, nanotubes will have to outperform current technology to gain a foothold in commercial markets. All these challenges will keep nanotube researchers busy for a long time to come [49].

There is no doubt that carbon-based nanotechnology will continue to infiltrate our lives. As with most advanced materials they will initially find uses in somewhat more exotic applications. With increasing commercial production and more efficient production techniques, prices will come down and these amazing materials

will quietly find their way into our homes with the aid of recent developments in high resolution microscopy & material processing technologies.

Will carbon nanotubes be used to build a space elevator? Unlikely to happen in this lifetime, but beyond that, only time will tell.

As the electronic circuits on computer chips become smaller and smaller, conventional transistors run into physical limitations caused by extreme miniaturization. Nanotubes hold the promise of creating novel devices, such as carbon-based single-electron transistors, that will allow the miniaturization to continue beyond the limits of current silicon-based device technology. IBM scientists are now examining the basic properties of carbon Nanotubes and the feasibility of using them as the basis for a new class of nanoelectronic devices [50].

## Chapter 6

# Potential Risks of Nanotechnology

Almost any technology can be abused, and nanotechnology will be no exception, there are dangers from both accidents and deliberate misuse. The promise of nanotechnology to accelerate technological change has prompted some to advise caution about pursuing rapid innovation without some understanding of where it might lead us. The research community should be able to respond to questions about the consequences of new products based on nanotechnology [26, 49].

Carbon nanotubes sound like a product designer's dream. But like many technologies that offer benefits, there are risks which have to be addressed sensibly in order that the full benefits can be realized. We have all learned how to handle electricity, gas, steam and even cars and aeroplanes in a safe manner because we need their benefits. The same goes for carbon nanotubes. Mostly they will be perfectly safe, embedded within other materials, such as polymers. There is some possibility that free carbon nanotubes of a specific length scales may pose health threats if inhaled, particularly at the manufacturing stage. Industry is very conscious of this possibility, and is endeavouring to ensure that any potential hazard is minimised, so that we can all reap the benefits and promise of this new wonderful materia [39].

Ready or not, here it comes. In the next 20 years, nanotechnology will touch the life of nearly every person on the planet. The potential benefits are mind boggling

and brain enhancing. But like many of the great advancements in earth's history, it is not without risk. Here are some of the risks posed to society by nanotechnology. We can classify the risks as real risks, potential risks and far-fetched risks.

**Real Risk** such as Nanopollutants; nanopollutants are nanoparticles small enough to enter lungs or be absorbed by skin. Studies are ongoing as to the toxicity of nanoparticles and it is unknown how the body's immune system will react to invaders this small. Nanoparticles are used in some of the products found on shelves today, like anti-aging cosmetics and sunscreen. The highest risk is to the workers in nano-technology research and manufacturing processes.

**Potential risk** include Privacy Invasions (5 to 15 years), virtually undetectable surveillance devices could dramatically increase spying on governments, corporations and private citizens, **Economic upheaval** (10 to 20 years); Molecular manufacturing is the assembly of products one molecule at a time. It could make the same products you see today, but far more precisely and at a very low cost. It is unclear whether this would bring boom or bust to the global economy. **Nanotech weapons** (10 to 20 years): Untraceable weapons made with nanotechnology could be smaller than an insect with the intelligence of a supercomputer. Possible nano and bio technology arms race.

**Far-fetched (unbelievable) risks** such as Gray Goo (30+ years): Free range, self-replicating robots that consume all living matter. However unlikely, experts say this scenario is theoretically possible, but not for some time.

We have just scratched the surface of carbon nanotechnology. There are many areas of nanotechnology science that hold potential dangers to society. Bio-engineering and artificial intelligence for example, have their own set of risks. As we enter an era of unprecedented understanding, it is important that society takes a proactive role in the responsible development of nanotechnology. As with any new technology, nanotechnology raises ethical concerns, some of which are common to other technological fields and others more specific [51].

## Conclusion

The idea of this dissertation was to give a thumbnail-sketch of the applications of carbon-based nanotechnology for 21<sup>st</sup> century.

Carbon nanotubes are one of the most important materials under investigation for nanotechnology applications. Their unique properties, ranging from ultra high strength through unusual electronic behaviour and high thermal conductivity to an ability to store nanoparticles inside the tubes themselves has suggested potential applications in many different fields of scientific and engineering endeavour. As was the case with silicon transistor technology, these applications will grow in time as the capacity for industrial production and manipulation of CNT is created and as understanding of the physics of CNT continues to improve.

A scientific and technological revolution has begun, which enables human being to systematically manipulate and organize matter on a bottom-up fashion starting from atomic level This will lead to the next industrial revolution. Carbon nanotube has unique dimension and properties at nanoscale that can be exploited to develop nanodevices that will contribute to the advancement of present technologies.

If nanotechnology is practised as predicted, then nanoscience and nanotechnology revolution will change the nature of almost every human objects and activities. The societal impacts of this technology will be greater than that of the first industrial revolution.

From a solid state physics perspective, CNTs are wonderful materials, however, their growth & control over separation of metallic from semiconducting nanotubes remains the biggest challenge. From an electrical engineering perspective, CNTs are also wonderful materials, however, their applications to novel device structures and ultimately integrated circuits is hindered by several fundamental and practical difficulties.

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