Carbon Nanotubes(CNTs): Origin, Application, Preparation and Characterization by Transmission Electron Microscopy (TEM).

By

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Dedication

This Work is dedicated to :
My Father: **Thanks for always being here for me.**
and

My Mother: **I lost you my Great! You left fingerprints of grace on my life. You shan't be forgotten.**

and

My Wife: **Yirgalem Anagaw, I lost you my beloved! You are in my heart forever.**

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Abstract

Carbon nanotubes (CNTs) are allotropes of carbon with a nanostructure that can have a length-to-diameter ratio greater than 1,000,000. These cylindrical carbon molecules have novel properties that make them potentially useful in many nanotechnology applications. Their unique surface area, stiffness, strength and resilience have led to much excitement in the field of pharmacy. Carbon nanotubes are categorized as single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). Techniques have been developed to prepare nanotubes in sizeable quantities, such as: arc-discharge, laser-ablation, chemical vapor-deposition, silane-solution and flame-synthesis methods. The properties of CNTs are still being researched heavily and scientists have barely begun to tap the potential of these structures. They can pass through membranes, carrying therapeutic drugs, vaccines and nucleic acids deep into the cell to targets previously unreachable. Overall, recent studies regarding CNTs have shown a very promising glimpse of what lies ahead in the future of nano-medicines. This project presents the unique atomic structure, properties, application and problems of carbon nanotubes (CNTs). The electronic band structure of carbon nanotubes along with their small size and low dimension are responsible for their unique electrical, mechanical and thermal properties. More over the project focuses on the preparation, purification and characterization of CNTs by Transmission Electron Microscope (TEM).

Chapter 1

Introduction

The last 20 years have witnessed the discovery, development, large scale manufacturing and production of novel materials that lie within the nanometer scale. Such novel materials consist of inorganic or organic matter and in most cases have never been studied in the context of pharmaceuticals. Carbon nanotubes (CNTs) are one of them. They are made of allotropes of carbon (graphite), tubular in shape, nanometers in diameter and several millimeters in length. CNTs possess various novel properties that make them useful in the field of nanotechnology and pharmaceuticals. They have a very broad range of electronic, thermal and structural properties. These properties vary with kind of nanotubes defined by its diameter, length, chirality or twist and wall nature. Their unique surface area, stiffness, strength and resilience have led to match excitement in the field of pharmacy [1].

Carbon nanotubes (CNTs) have received significant attention in terms of fundamental properties of measurements and potential application. This is largely due to the impressive physical properties as revealed from both theoretical and experimental studies. For example, the electrical properties of CNTs may be tuned by mechanical deformation. Such properties are of great interest for applications such as sensors or smart materials. The study of these properties is multi-disciplinary and involves various branches of science and engineering.

Steady progress has been made in exploring the mechanical properties and potential applications of two types of CNTs, formed by rolling graphene layers in to cylinders [2]. These are single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes

(MWNTs). The measured specific tensile strength of a single layer of a multi-walled carbon nanotube can be as high as 100 times that of steel and the graphene sheet (in-plane) is as stiff as diamond at low strain. These mechanical properties motivate further study of possible applications for light-weight and high strength materials [3].

Since CNTs are made from allotropes of carbon, graphite, it is basic to discuss about the properties of carbon and graphite. In this project the properties of carbon and graphite, a brief explanation, properties, application, problems, preparation and characterization of CNTs is presented.

Chapter 2

Carbon and its Allotropes

2.1 Carbon

The word carbon is derived from the Latin word ”carbo” which to the Romans meant charcoal (or ember). Carbon is the most abundant element next to (nitrogen, hydrogen and oxygen) and it is self evident. All elements are unique, but carbon especially so.

Carbon’s polymorph ranges from the highest-strength and transparent diamond to the soft black graphite, with a host of semi-crystalline and amorphous forms also available such as the best gas adsorbers (activated charcoal), an essentially non-crystalline product and the best helium gas barriers (vitreous carbon). To describe a ”carbon” material, the term is used with a qualifier such as carbon fiber, pyrolytic carbon, vitreous carbon and others. A great deal is yet to be learned and new forms of carbon are still being discovered such as the fullerence molecules, lonsdalite and the hexagonal poly types of diamond. These allotropes of carbon are composed of entirely carbon but have different physical structures [3].

2.1.1 The Structure of Carbon Atom

All atoms have positively charged nucleus composed of one or more protons, each with a positive electrical charge +1 and neutrons which are electrically neutral. Each proton and neutron has a mass of 1amu (atomic mass unit) and together account for practically the entire mass of the atom. The nucleus is surrounded by electrons, moving around the nucleus, each with a negative electrical charge of -1. The number of electrons is the same as the number of protons so that the positive charge of the nucleus is balanced by the negative charge of the electrons and the atom is electrically neutral.

As determined by Schrodinger, the behavior of the electrons in their movement around the nucleus is governed by the specific rules of standing waves. These rules state that, in any given atom, the electrons are found in series of energy levels called orbitals, which are distributed around the nucleus. These orbitals are well defined and in between them, large ranges of intermediate energy levels are not available (or forbidden) to the electrons since the corresponding frequencies do not allow a standing wave. In any orbital, no more than two electrons can be present and these must have opposite spins as stated in the Pauli's exclusion principle [4].

The element carbon has the symbol C and an atomic number (Z) of 6, i.e., the neutral atom has six protons in the nucleus and correspondingly six electrons. The electrons configuration, that is, the arrangement of the electrons in each orbital, is described as:

$$1s^2 2s^2 2p^2 \tag{2.1.1}$$

Where the notation $1s^2$ refers to the three quantum numbers necessary to define an orbital, the number "1" referring to the K or first shell (principal quantum number). The letter "s" refers to the sub-shell s (angular momentum quantum number) and the superscript number "2" refers to the number of atoms in that sub-shell. There is only one orbital (the s orbital) in the K shell which can never have more than two electrons. These two electrons, which have opposite spin, are the closest to the nucleus and have the lowest possible energy. The filled K shell is completely stable and its two electrons do not take part in any bonding.

The next two terms, $2s^2$ and $2p^2$, refer to the four electrons in the L shell. The L shell when filled can never have more than eight electrons. The L shell electrons belong to two different sub-shells, the s and the p. The 2s and the 2p electrons have different energy levels. The number "2" referring to the L or second shell and the letters "s" and "p" to the orbital or sub-shells. The two 2s electrons have opposite spin and the two 2p electrons have parallel spin.

The configuration of the carbon atom described above refers to the configuration in

Table 2.1: Electron configuration of carbon atom

Symbol	Atomic number(Z)	K-shell	L-shell	M-shell
C	6	2	2, 2	–

its ground state. That is, the state where its electrons are in their minimum orbits, as close to the nucleus as they can be and with their lowest energy level.

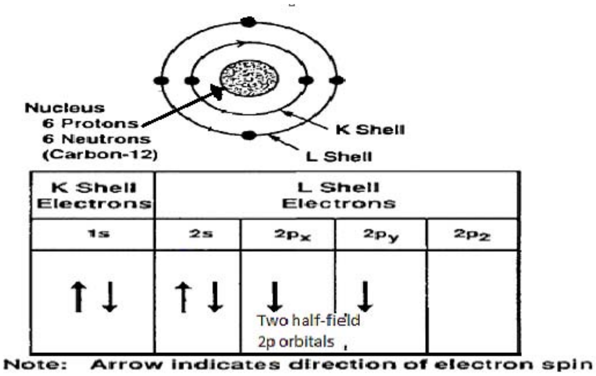


Figure 2.1: Schematic of the electronic structure of the carbon atom in the ground state.

2.1.2 Valence Electrons of Carbon Atom

In any given atom, the electrons located in the outer orbital are the only ones available for bonding to other atoms. These electrons are called the valence electrons. In the case of carbon atom, the valence electrons are the two in the 2p orbital. Carbon in this state would then be divalent, since only these two electrons are available for bonding. Divalent carbon does indeed exist and is found in some highly reactive transient-organic intermediates such as the carbenes (for instance methylene). However, the carbon allotropes and the stable carbon compounds are not divalent but tetravalent (four valence electrons) [5].

2.1.3 Hybridization of the Carbon Atom

Electron Orbital

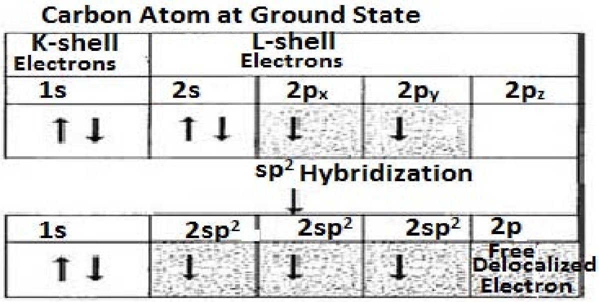
The electron configuration of the six electrons of the carbon atom in the ground state is $1s^2 2s^2 2p^2$, that is, two electrons are in the K shell (1s) and four in the L shell (2s and 2p orbital) as shown in Figure 2.1.

At the electron configuration stage, no electron in an atom or a molecule can be accurately located. The electron wave function, establishes the probability of an electron being located in a given volume with the nucleus being the origin of the coordinate system. Mathematically speaking, this function has a finite value anywhere in space, but the value of the function becomes negligible at a distance of a few angstroms from the nucleus. For all practical purposes, the volume where the electron has the highest probability of being located is well defined and is usually represented as a small shaded volume, what is uncertain is the precise location within this volume [5].

The Trigonal (sp^2) Orbital

The sp^2 and the sp orbital are the series of electronic building blocks of all carbon allotropes and compounds. The sp^2 (or trigonal) orbital is the basis of all graphitic structures.

The mechanism of the sp^2 hybridization is somewhat different from that of the sp^3 hybridization. The arrangement of the electrons of the L shell of the atom in the ground state is modified as one of the 2s electrons is promoted and combined with two of the 2p orbital (hence the designation sp^2), to form three sp^2 orbital and an un hybridized free (or delocalized) p orbital electron as shown in Figure 2.2. The valence state is then four (V_4). The calculated electron-density contour of the sp^2 orbital is similar in shape to that of the sp^3 orbital as shown in Figure 2.2. These three identical sp^2 orbitals are in the same plane and their orientation of maximum probability forms a 120° angle from



Carbon Atom at Ground State

K-shell Electrons	L-shell Electrons			
1s	2s	$2p_x$	$2p_y$	$2p_z$
↑ ↓	↑ ↓	↓	↓	

sp^2 Hybridization ↓

1s	$2sp^2$	$2sp^2$	$2sp^2$	2p
↑ ↓	↓	↓	↓	Free Delocalized Electron

Figure 2.2: The sp^2 hybridization of carbon orbitals; Shaded electrons are valence electrons (divalent for ground state and tetravalent for hybrid state).

each other as shown in Figure 2.3. The fourth orbital, i.e., the delocalized non-hybridized p electron, is directed perpendicularly to the plane of the three sp^2 orbital and becomes available to form the subsidiary π bond with other atoms [5].

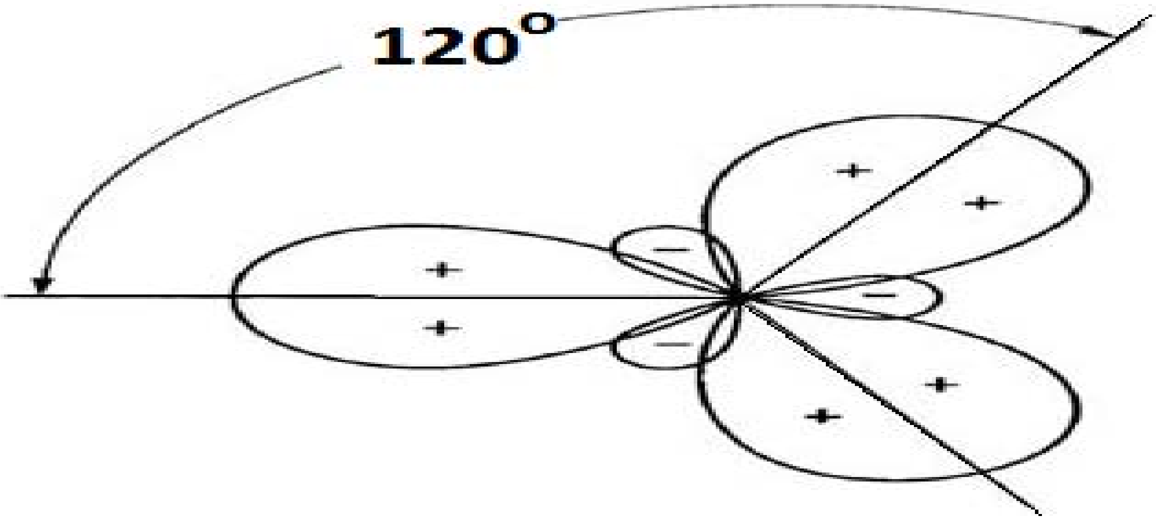


Figure 2.3: Planar section of the sp^2 hybrid orbitals of the carbon atom.

The Carbon Hybridized (sp^3) Orbital

In order to have an electron configuration that would account for this symmetry, the structure of the carbon atom must be altered to a state with four valence electrons instead of two, each in a separate orbital and each with its spin uncoupled from the other electrons. This alteration occurs as a result of the formation of hybrid atomic orbital, in which the arrangement of the electrons of the L shell of the atom in the ground state is modified as one of the 2s electron is promoted (or lifted) to the higher orbital 2p as shown in Figure 2.4. These new orbital is called hybrid since they combine the 2s and the 2p orbital. They are labeled sp^3 since they are formed from one s orbital and three p orbital [6].

In this hybrid sp^3 state, the carbon atom has four $2sp^3$ orbital, instead of two-2s and two-2p of the ground-state atom and the valence state is raised from two to four.

The energy required to accomplish the sp^3 hybridization and raise the carbon atom from the ground state to the corresponding valence state V_4 is 230 $KJmol^{-1}$. This

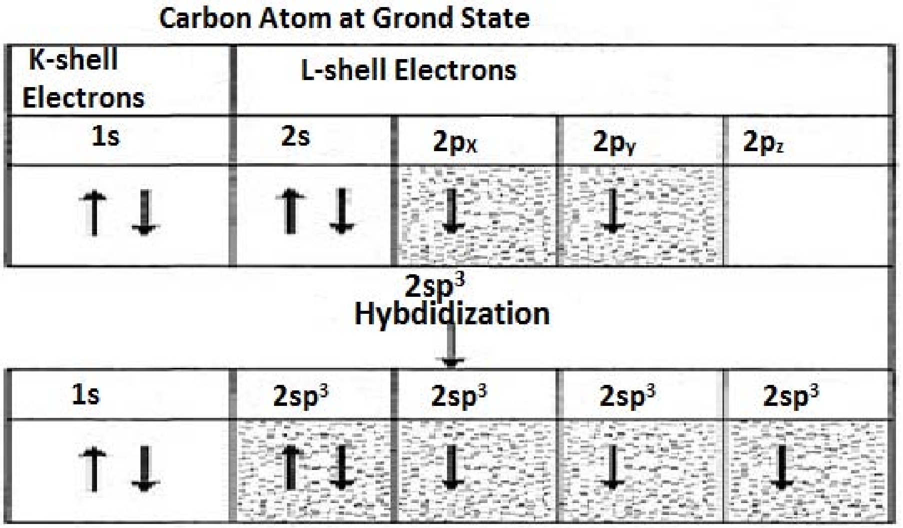


Figure 2.4: The sp^3 hybridization of carbon orbitals, Shaded electrons are valence electrons (divalent for ground state, tetravalent for hybrid state). Arrow indicates direction of electron spin.

hybridization is possible only because the required energy is more than compensated by the energy decrease associated with forming bonds with other atoms.

The hybridized atom is now ready to form a set of bonds with other carbon atoms. It should be stressed that these hybrid orbital (and indeed all hybrid orbital) are formed only in the bonding process with other atoms and are not representative of an actual structure of a free carbon atom.

2.2 Allotropes of Carbon, Graphite

2.2.1 Definition of Graphite

Materials with an atomic structure of $2sp^3$ are called by the name of their allotropic form, i.e., diamond, lonsdalite, etc and not commonly referred to as "carbon" material although speaking they are. But graphite is with an atomic structure of $2sp^2$. The properties of various carbon allotropes can be vary widely. For instance, diamond is the hardest, transparent to the visible spectrum and an electrical insulator while graphite is the softest, opaque and a conductor; the fullerenes are different from either one. Yet these materials are made of the same carbon atoms; the disparity is the result of different

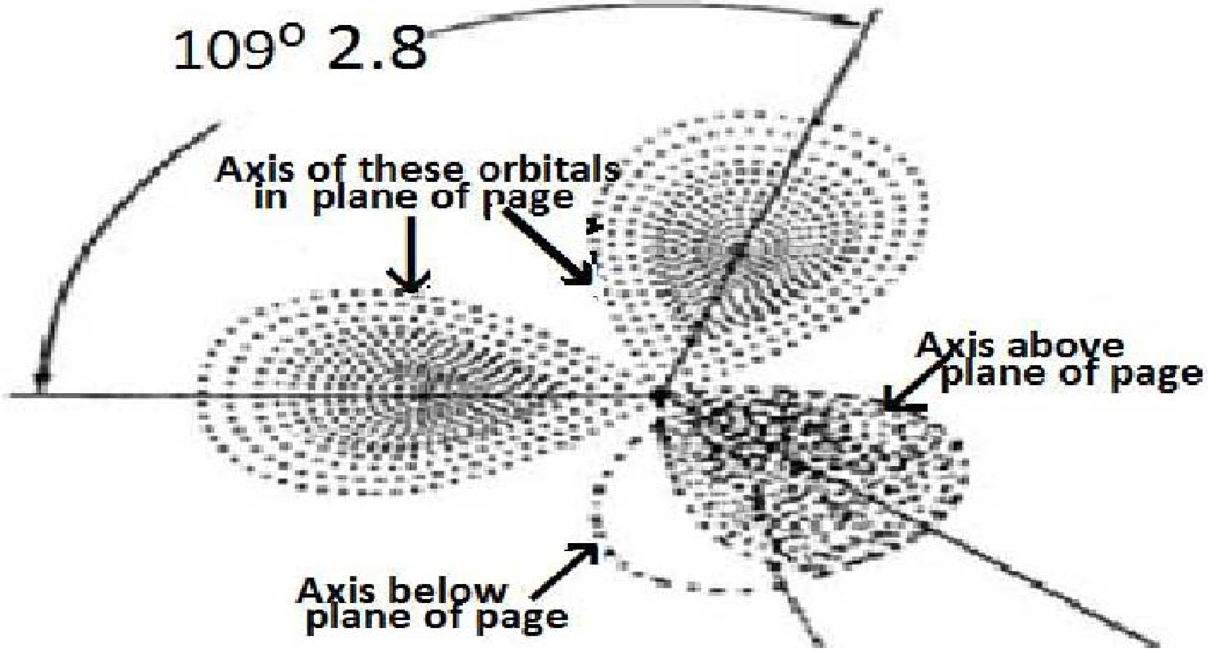


Figure 2.5: Tetrahedral hybridization axes of the four sp^3 orbital. Negative lobes omitted for clarity.

arrangement of their atomic structure.

The origin of the word "graphite" is the Greek word "graphein" which means "to write". Indeed, graphite has been used to write (and draw) since the dawn of history and the first pencils were manufactured in England in the 15^{th} century. In the 18^{th} century, it was demonstrated that graphite actually is an allotrope of carbon.

There are limited numbers of ways in which carbon atoms can combine in molecules that do not contain other elements. One way is to form graphite, which chemically are the most stable allotropes of carbon. Graphite consists of flat planes of six-membered rings of carbon. The planes slip easily over each other making graphite an excellent lubricant [6]. Each carbon atom in the planes of the graphite structure is bonded to three other carbon atoms that lie at the corners of the equilateral single and double bonds, in which two electrons are shared and double bonds in which four electrons are shared. All the bond angles in a graphite molecule measure 120°. Chemists say that the bond exists because the electrons in adjacent carbon atoms form hybrid sp^2 orbital (as in Figure 2.3

2.2.2 Structure of the Graphite Crystal

Graphite is composed of series of stacked parallel layer planes shown schematically in Figure 2.6 below, with the trigonal sp^2 bonding described before. The circles showing the position of the carbon atoms. Each atom contacts its neighbors [7].

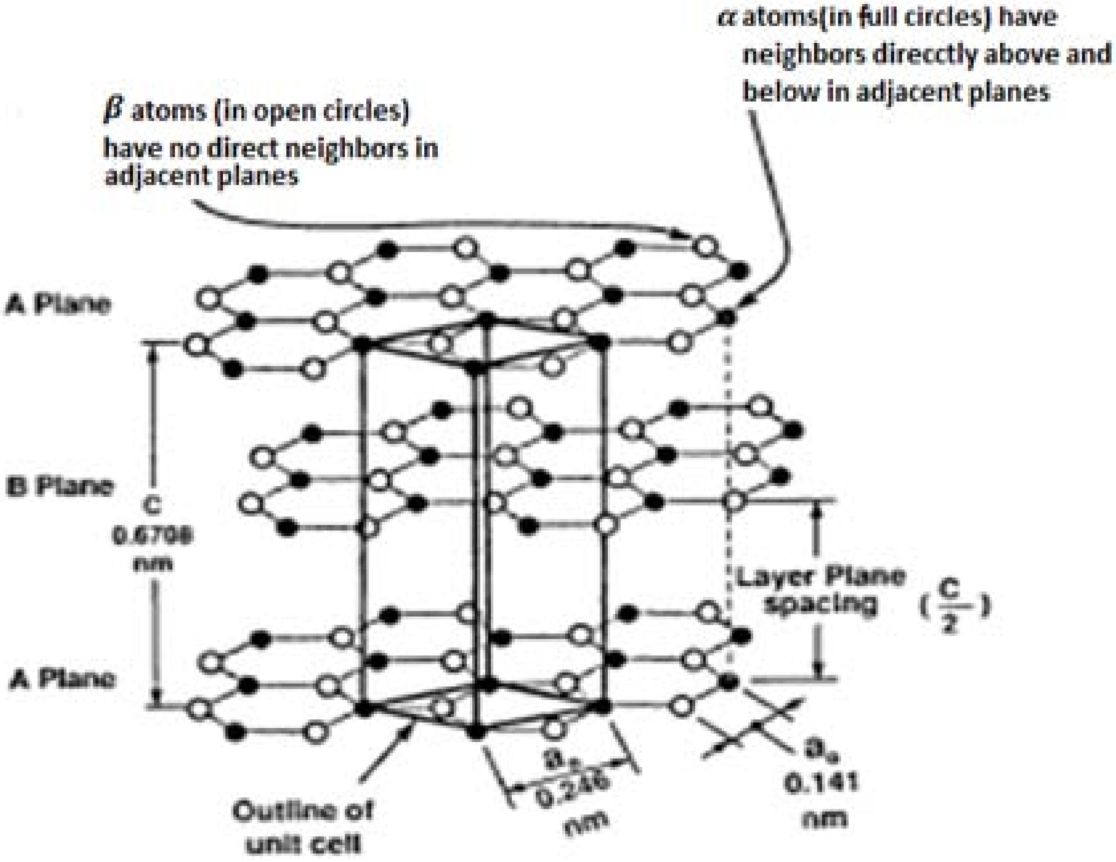


Figure 2.6: Crystal structures of graphite showing ABAB stacking sequence and unit cell.

Within each layer plane, the carbon atom is bonded to three others, forming a series of continuous hexagons in what can be considered as an essentially infinite two-dimensional molecule. The bond is covalent (sigma) and has a short length (0.141 nm) and high strength (524 KJ/mole). The hybridized fourth valence electron is paired with another delocalized electron of the adjacent plane by a much weaker Vander Waals, (πbond), of only 7 KJ/mol. Carbon is the only element to have this particular layered hexagonal structure.

The spacing between the layer planes is relatively large (0.335 nm) or more than twice the spacing between atoms within the basal plane and approximately twice the Vander Waals radius of carbon. The stacking of these layer planes occurs in two slightly different ways: hexagonal and rhombohedral [6].

Hexagonal Graphite:

The most common stacking sequence of the graphite crystal is hexagonal (alpha) with a -ABABAB- stacking order, where the carbon atoms in every other layer are superimposed over each other as shown in Figure 2.6 above.

Atoms of the alpha type, which have neighbor atoms in the adjacent planes directly above and below, are shown with open circles. Atoms of the beta type, with no corresponding atoms in these planes, are shown with full circles. A view of the stacking sequence perpendicular to the basal plane is given in Figure 2.7 below [6].

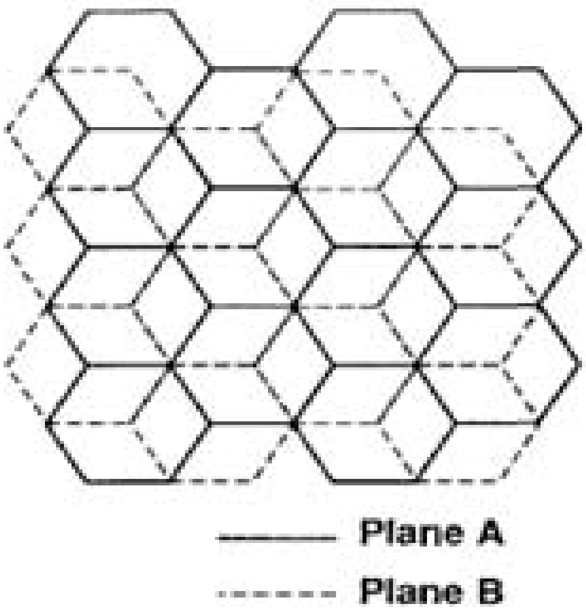


Figure 2.7: Schematic of hexagonal graphite crystal, view is perpendicular to basal plane.

Other characteristics of the graphite crystal are the following:

- The crystal lattice parameters, i.e., the relative position of its carbon atoms along the ortho-hexagonal axes are: $a_0 = 0.245\ nm$ and $c_0 = 0.6708\ nm$.

- The common crystal faces are {0002}, {1010}, {1011} and {1012}.
- The crystal is black and gives a black streak.
- Hexagonal graphite is the thermodynamically stable form of graphite and is found in all synthetic materials.

Rhombohedral Graphite:

The other graphite structure is rhombohedral with the stacking order -ABCABCABC-. The carbon atoms in every third layer are superimposed. The crystal lattice parameters are: $a_0 = 0.2256\ nm$ and $c_0 = 1.006\ nm$. A view of the stacking sequence perpendicular to the basal plane is given in Figure 2.8 below [6].

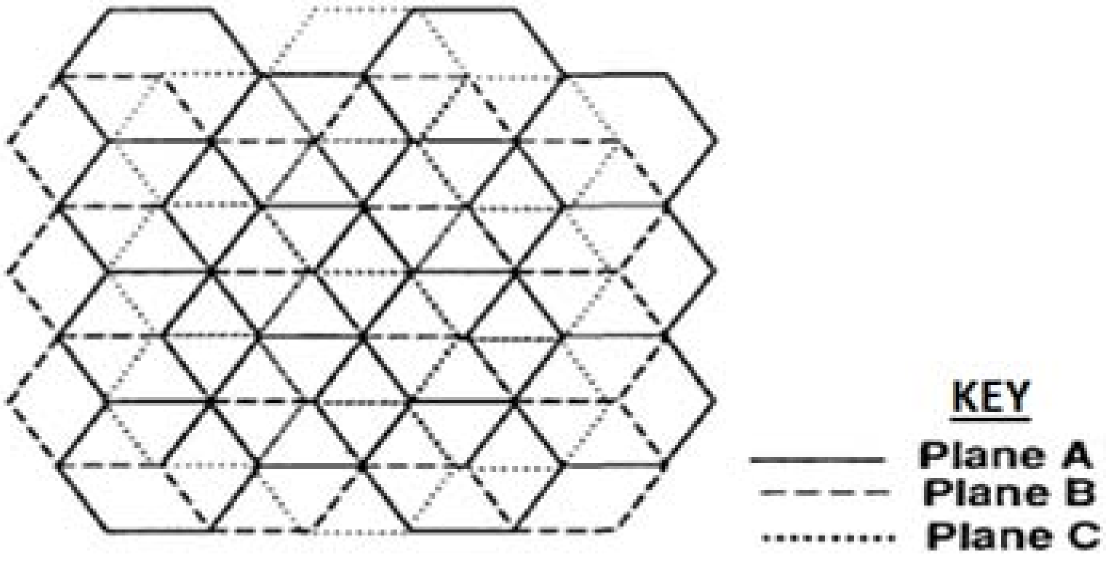


Figure 2.8: Schematic of rhombohedral graphite crystal, view is perpendicular to basal plane.

Rhombohedral graphite is never found in pure form but always in combination with hexagonal graphite, up to 40 % in some natural and synthetic materials. It usually reverts to the hexagonal form during heat treatment above $1300^{\circ}C$. It should be noted that in both structures, hexagonal and rhombohedral, no basal plane lies directly over another one.

2.2.3 Physical Properties of Graphite

An Isotropy of the Graphite Crystal

The peculiar crystal structure of graphite results in a considerable an isotropy. That is, the properties of the material may vary considerably when measured along the ab directions (within the plane) or the c direction (perpendicular to the planes). Such an isotropy, especially in electrical and thermal properties, can often be put to good use.

Table 2.2: Physical Properties of Graphite

Roll NO.	Property	description
1	Crystalline form	Hexagonal
2	Lattice parameters	a_0=0.246 nm, c_0= 0.671 nm
3	Color	Black
4	Density at 300 K, 1 atm	2.26 $g(cm)^{-3}$
5	Atomic volume	5.315 $cm^3(mol)^{-1}$
6	Sublimation point at 1atm (estimated)	4000 K
7	Triple point at 1atm (estimated)	4200 K
8	Boiling point at 1atm (estimated)	4560 K
9	Heat of fusion	46.84 KJ$(mol)^{-1}$
10	Heat of vaporization to mono atomic gas (estimated)	716.9 KJ$(mol)^{-1}$
11	Pauling electro negativity	2.5
12	Molar heat capacity (specific heat) at 25 $°C$	8.033 - 8.635 J$(mol.K)^{-1}$

Thermal Conductivity of Graphite

The thermal conductivity and expansion of graphite are strongly influenced by the isotropy of the graphite crystal. The thermal conductivity (K) is the time rate of transfer of heat by conduction. In graphite, it occurs essentially by lattice vibration and is represented by the following relationship (Debye equation) [7]:

$$K = bC_pvL \tag{2.2.1}$$

where:

- b is a constant,
- C_P is specific heat per unit volume of the crystal,

- v is speed of heat-transporting acoustic wave (phonon),
- L is mean free path for wave scattering.

The thermal conductivity of a graphite crystal has been reported as high as 4180 W$(mK)^{-1}$ in the ab directions for highly crystalline, stress-annealed pyrolytic graphite [7]. However, the average value for commercial pyrolytic graphite is considerably smaller, (390 W$(mK)^{-1}$). Still, this is a high value and graphite in the ab directions, can be considered a good thermal conductor comparable to high-conductivity metals and ceramics as shown in Table 2.3 [8].

Table 2.3: Thermal Conductivity of Selected Materials

Roll number	Material	W$(mK)^{-1}$ at 25 °C
1	Pyrolytic graphite: ab directions	390
2	Pyrolytic graphite: c direction	2
3	Graphite fiber (pitch-based)	1180
4	Diamond (Type II)	2000–2100
5	Silver	420
6	Copper	385
7	Beryllium oxide	260
8	Aluminum nitride	200
9	Alumina	25

The thermal conductivity in the c direction is approximately 2.0 $W(mK)^{-1}$. In this direction, graphite is a good thermal insulator, comparable to phenolic plastic [9].

The thermal conductivity of graphite decreases with temperature as shown in Figure 2.9. In the Debye equation, K is directly proportional to the mean free path, L, which in turn is inversely proportional to temperature due to the increase in vibration amplitude of the thermally excited carbon atoms. L becomes the dominant factor above room temperature, more than offsetting the increase in specific heat, Cp, shown in Figure 2.9 [9].

Thermal Expansion

The interatomic spacing between the carbon atoms of graphite (as with any other material) is a function of temperature. At 0 K ($-273°C$), these atoms have their lowest

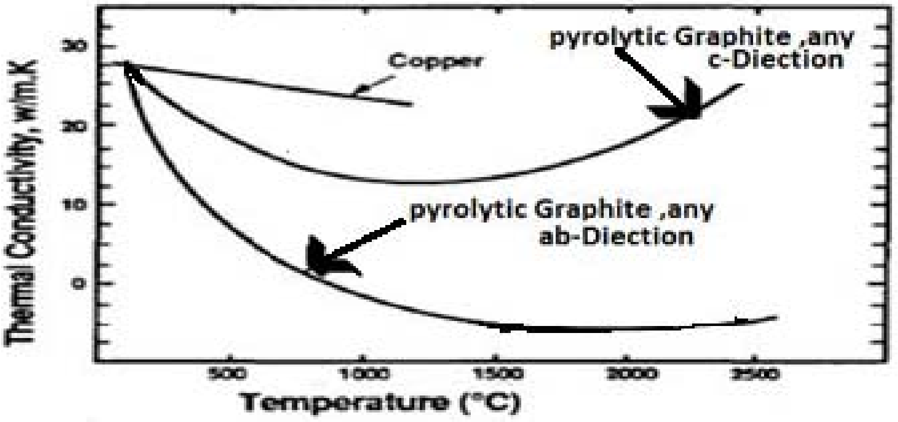


Figure 2.9: Thermal conductivity of graphite crystal in the ab and c directions.

energy position or ground state. The increased energy resulting from increasing temperature causes the atoms to vibrate and move further apart. In other words, the mean inter atomic spacing increases and the result is thermal expansion.

As seen in Figure 2.10, the graphic relationship between interatomic spacing and energy has the configuration of a trough. This configuration changes with the strength of the atomic bond. In a strongly bonded solid such as graphite in the ab directions, the trough is deep and the amplitude of the vibrations is small. During the outward motion of the atoms, the atomic bonds are not overstretched. Consequently, the dimensional changes remain small. When the atomic bond is weak such as in graphite in the c direction, the energy trough is shallow, the vibration amplitude and the dimensional changes are large [10].

As a result, the thermal expansion of the graphite crystal has a marked an isotropy. It is low in the ab directions (lower than most materials) but higher by an order of magnitude in the c direction [11], as shown in Figure 2.10. The increase with temperature is not linear. In the c direction, it increases slowly and gradually. At $0°C$, the coefficient of thermal expansion averages $25 \times 10^{-6}/°C$ and at $400°C$, it reaches $28 \times 10^{-6}/°C$ [12].

In the ab direction, the thermal expansion is actually negative up to approximately $400°C$ with a minimum at $0°C$. It is possible that this observed negative expansion is due to internal stress (Poisson effect) associated with the large expansion in the c direction

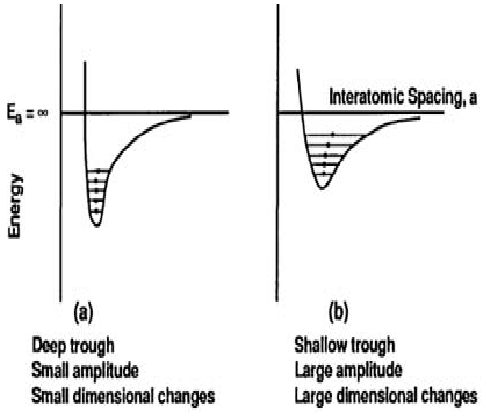


Figure 2.10: The energy trough of graphite: in (a) ab directions and (b) c direction.

and it has been suggested that, if it were possible to measure the ab thermal expansion of a single atomic plane, this expansion would be positive [13].

The large thermal expansion and an isotropy often results in large internal stresses and structural problems such as delamination between planes.

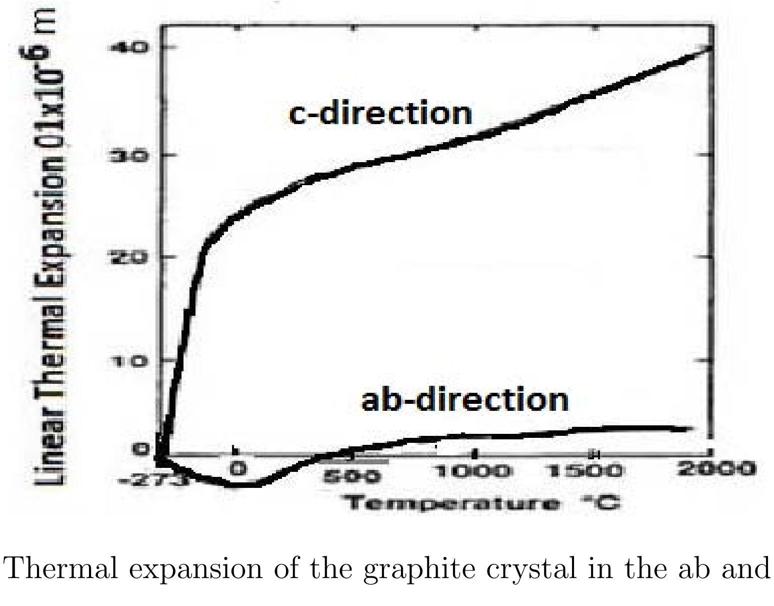


Figure 2.11: Thermal expansion of the graphite crystal in the ab and c directions.

Electrical Resistivity of Graphite

In electrical conductors such as metals, the attraction between the outer electrons and the nucleus of the atom is weak. The outer electrons can move readily and since an electric current is essentially a flow of electrons. In electrical insulators (or dielectrics), electrons are strongly bonded to the nucleus and are not free to move [14]. Electrically, graphite can be considered as a semi-metal, that is a conductor in the basal plane and an insulator normal to the basal plane. Its atomic structure is such that the highest-filled valence band overlaps the lowest-empty conduction band by approximately 36 meV. The delocalized fourth-valence electrons form a partially-filled conduction band between the basal planes where they can moved readily in a wave pattern as they respond to electric fields. Consequently, the electrical resistivity of graphite parallel to the basal planes (ab directions) is low and the material is a relatively good conductor of electricity [15].

In the c direction, the spacing between planes is comparatively large, and there is no comparable mechanism for the electrons to move from one plane to another, in other words, normal to the basal plane. As a result the electrical resistivity in the c direction is high and the material is considered as an electrical insulator. In some cases, it may be 10000 times higher than in the ab directions. Often quoted resistivity values are $3000 \times 10^{-6}\ \Omega m$ in the c direction and $2.5 - 5.0 \times 10^{-8}\ \Omega m$ in the ab directions [16].

The electrical resistivity of the graphite crystal in the ab directions increases with temperature, as does that of metals. This increase is the result of the decrease in the electron mean free path, in a mechanism similar to the increase in thermal conductivity reviewed above.

The electrical resistivity in the c direction, however, decreases slightly with increasing temperature, possibly because electrons can jump or tunnel from one plane to another due to increased thermal activation [17].

Mechanical Properties of Graphite

The bond between atoms within the basal plane of a graphite crystal is considerably stronger than the bond between the planes with an anisotropy ratio of approximately 75.

This means that, while the strength in the ab directions is considerable high, that in the c direction (interlaminar strength) is low and graphite shears easily between basal planes [18]. The elastic constants are:

$$ab - direction = 1060\ GPa$$

$$c - direction = 36.5\ GPac$$

$$parallel - to - the - planes = 4.5\ GPa$$

Chemical Properties of Graphite

Pure graphite is one of the most chemically inert materials. It is resistant to most acids, alkalies and corrosive gases. However impurities are almost always present to some degree in both natural and artificial graphites and often have an important catalytic effect with resulting increase in the chemical reactivity.

The anisotropy of the graphite crystal is reflected in its chemical behavior. Reaction with gases or vapors occurs preferentially at "active sites", i.e., the end of the basal planes. Reaction with the basal plane surfaces is far slower. The reason is that the graphite crystal exhibits large differences in surface energy in the different crystallographic directions; these energies amount to 5 J/m^2 in the prismatic plane but only 0.11 J/m^2 in the basal plane [19]. Consequently, graphite materials with large crystals and few defects have the best chemical resistance.

The chemical reactivity is also appreciably affected by the degree of porosity, since high porosity leads to large increase in surface area with resulting increase in reactivity. Obviously, high surface area materials such as activated carbon are far more reactive than dense, pore free or closed-pore materials such as glassy carbon.

Reactivity also generally increases with increasing temperature and, at high temperatures, graphite becomes far more reactive. For instance, above $450°C$, it oxidizes readily with water, oxygen, some oxides and other substances.

Chapter 3

Carbon Nanotubes (CNTs)

3.1 Definition of Carbon Nanotubes (CNTs)

The discovery of carbon nanotubes (CNTs) in 1991 opened up a new era in material science. These incredible structures have an array of fascinating electronic, alternate randomly between metallic and semiconducting varieties, magnetic and chemical properties.

A carbon nanotube is a tube-shaped material made of allotropes of carbon, sheet of graphite, rolled into seamless cylinders of one or more layers of graphene. A two dimension (2D) single layer of graphite is called graphene. CNTs having a diameter measuring on the nanometer scale, about 10000 times smaller than a human hair.

CNTs are unique because the bonding between the atoms, sp^2, is very strong and the tubes can have extreme aspect ratios. A carbon nanotube is as thin as a few nanometers, yet has been as long as hundreds of microns, holding the record for the mechanically strongest material and making them useful for the reinforcement of polymers in composite materials. To put this into perspective, if your hair had the same aspect ratio, a single strand would be over 40 m long.

3.2 Classification of Carbon Nanotubes

Carbon nanotubes are classified in to two:

- Single walled carbon nanotubes (SWNTs) and,
- Multi walled carbon nanotubes (MWNTs)

3.2.1 Single-Walled Carbon Nanotubes (SWNTs)

A single-walled carbon nanotube (SWNT) is formed by wrapping a single sheet of graphite (graphene) seamlessly in to tubular form. Graphene by itself can be characterized as either a zero gap semiconductor or a metal, since the density of states (DOS) is zero at the Fermi energy (E_F) and imparts those properties to a nanotube. The fundamental conducting properties of a graphene tubule depends on the nature of wrapping (chirality) and the diameter, which is in the range 0.4 nm–2 nm in SWNTs [20].

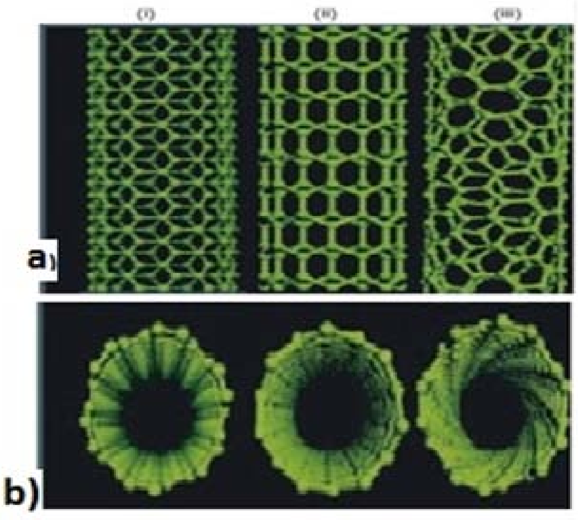


Figure 3.1: Illustrations of the structures of: (i) Arm-chair, (ii) zigzag, and (iii) chiral SWNTs.

Single-walled carbon nanotubes can be formed in three different designs: Armchair, Chiral and Zigzag. The design depends on the way the graphene is wrapped into a cylinder. For example, imagine rolling a sheet of paper from its corner, which can be considered one design and a different design can be formed by rolling the paper from its edge. A single-walled nanotube's structure is represented by a pair of indices (n, m) called the chiral vector as shown in Figure 3.2 [21].

The structural design has a direct effect on the nanotube's electrical properties. When n-m is a multiple of 3, then the nanotube is described as ”metallic” (highly conducting), otherwise the nanotube is a semiconductor. The Armchair design is always metallic while other designs can make the nanotube a semiconductor.

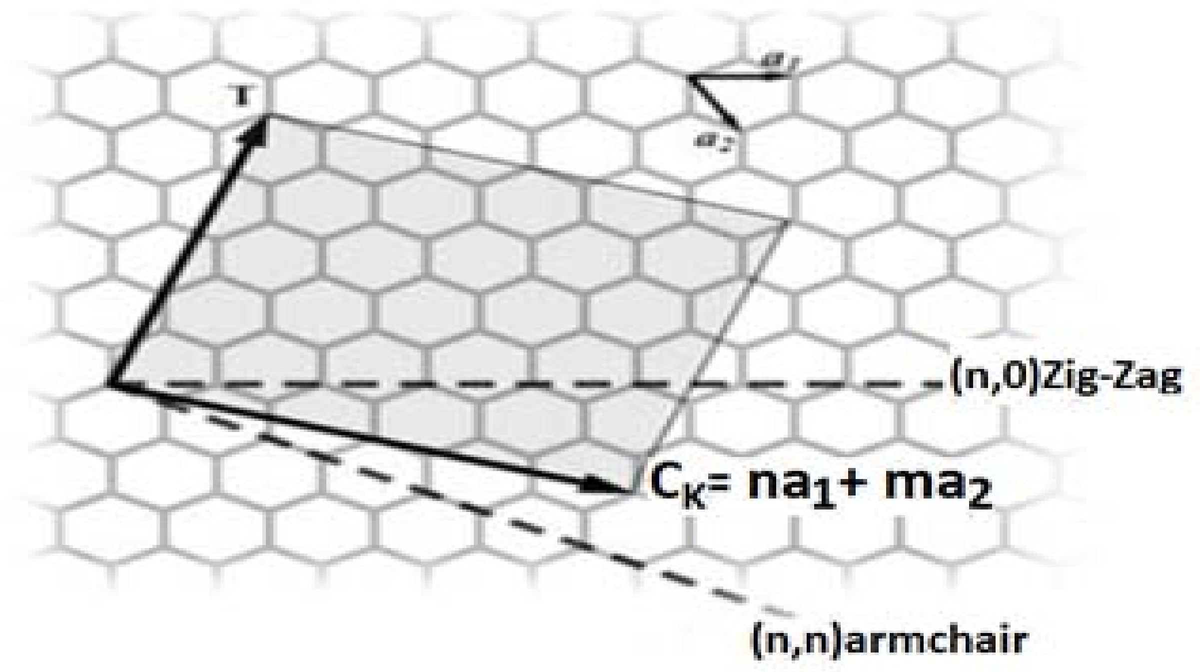


Figure 3.2: The structure of single-walled carbon nanotubes.

It is then possible to associate a particular integer pair (n, m) with each SWNT. The rotation between n and m also defines three categories of SWNTs:

- $m = 0$, 'Zigzag' ,
- $n = m$, 'Armchair',
- $other$, 'Chiral'.

SWNTs can have either open ends or closed ends. The shapes of the ends are not unique for SWNTs with the same radius. For instance, a 'Bill' like or a semi-toroidal end cap can occur. SWNTs with open ends can be found as shown below in Figure 3.3.

3.2.2 Multi-Walled Carbon Nanotubes (MWNTs)

MWNTs are composed of coaxial nanotubes, cylinders of different helicities, with a typical spacing of $\sim 0.34\ nm$ [22], which corresponds closely to the inter-layer distance in graphite of 0.335 nm [23]. MWNTs diameters' grown by the arc discharge method

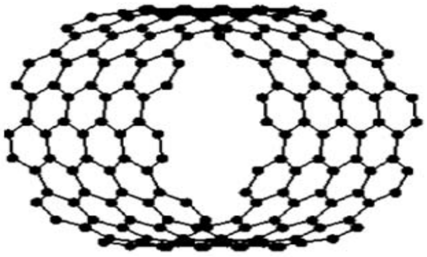


Figure 3.3: Molecular structure of an open end SWNT, each node shown is a carbon atom and lines are the chemical bonds.

are $\sim 20\ nm$ while CVD grown nanotubes can have much larger diameters of up to 100 nm. Larger diameter tubes are found to have a greater density of defects, i.e., vacancies or interstitials [24].

There are two structural models of multi-walled carbon nanotubes. In the Russian Doll model, a carbon nanotube contains another nanotube inside it. In the Parchment model, a single graphene sheet is rolled around itself multiple times. Multi-walled carbon nanotubes have similar properties to single-walled nanotubes, yet the outer walls on multi-walled nanotubes can protect the inner carbon nanotubes from chemical interactions with outside materials [25]. Multi-walled carbon nanotubes also have a higher tensile strength than single-walled carbon nanotubes [26].

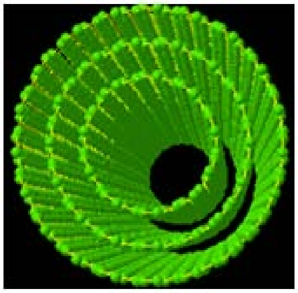


Figure 3.4: Structure of multi-walled carbon nanotubes (MWNTs).

3.3 Properties of CNTs

The atomic arrangements of carbon atoms are responsible for the unique electrical, thermal and mechanical properties of CNTs. Some of the properties of CNTs are the following:

3.3.1 Electrical conductivity

The structure of the CNTs determines how conductive the nanotube is. The structure of the atoms in a carbon nanotube minimizes the collisions between conduction electrons and atoms, to withstand higher electric current than copper. Electron transport occurs only along the axis of the tubes. Nanotubes also have a constant resistivity [15].

3.3.2 Thermal Conductivity and Expansion

The strength of atomic bonds in CNTs allows them to withstand high temperature. Because of this, carbon nanotube have been shown to be very good thermal conductors. When compared to copper wires, which are commonly used as thermal conductors, the carbon nanotubes can transmit over 15 times the amount of watt per meter per Kelvin [8].

The thermal conductivity of CNTs is dependent on the temperature of the tubes and the outside environment [27]. CNTs can exhibit superconductivity below 20 K due to the strong in-plane C-C bond of graphene. The strong C-C bond provides the exceptional strength and stiffness against axial strains. Moreover the longer inter plane and zero in-plane thermal expansion of SWNTs results in high flexibility against non-axial strains.

3.3.3 Strength and Elasticity of CNTs

Carbon nanotubes have a higher tensile-strength than Steel and Kevlar [18]. Their strength comes from the sp^2 bonds between the individual carbon atoms. This bond is even stronger than the sp^3 bond found in diamond. Under high pressure, individual nanotubes can bond together, trading some sp^2 bonds for sp^3 bonds. This gives the possibility of producing strong nanotube wires.

By using tensile load on SWNTs bundles, tensile strength values ranging from 13 to 52 GPa. Similarly, the tensile strength corresponding to MWNTs ranges from 11 to 63

GPa [28]. There are factors which have effect on the strength of CNTs, such as: defects, loading rate and temperature [29].

3.3.4 Field Emission of CNTs

Under the applications of strong electric field, tunneling of electrons from metal-tip to vacuum, results in the field emission phenomenon. Field emission results from the high aspect ratio and small diameter of CNTs. The field emitters are suitable for the application in flat-panel displays. For MWNTs, the field emission properties occur due to the emission of electrons and light. Without applied potential, the luminescence and light emission occurs through the electron field emission and visible part of the spectrum respectively [30].

3.4 APPLICATIONS OF CNTs

There are many applications of CNTs: from water proof and tear resistant cloth fabrics, concrete and steel like applications, a space elevator has been proposed based on the property of thermal conductivity, vacuum proof food packaging and even as a vessel for delivering drugs.

3.4.1 Nanoelectronics

CNTs are in the domain of nanoelectronics. This is as a result of CNT's being highly conductive. Conductivity in nanotube is based on the degree of chirality. i.e., the degree of twist and size of the diameter of the actual nanotube, which results in a nanotube that is actually extremely conductive or non conductive [31].

Interconnect

With high conductivity and small dimensions, CNTs may provide an alternative interconnect option to copper, they can also be used along-side existing IC manufacturing process.

Transistors

Transistors form the basis for modern integrated circuits functioning as digital switches. Alternative configurations of CNTs result in defects being present that allow SWNTs to act as transistors. In such a switch molecule can be positioned inside a CNT to affect the electronic current flowing across it. The result is a molecular scare gate in which the position of the molecule controls the flow of the electronical current. In this method, the gate is about one nanometer in size or three orders of magnitudes smaller than a silicon chip.

Flat Panel Display Screens

When a nanotube is put into an electric field, it will emit electrons from the end of the nanotube like small cannon. If those electrons are allowed to bombard a phosphor screen then an image can be created [30].

Electromagnetic

CNTs can be fabricated as electrical conductors, semiconductors and insulators. Such applications include:

1. **Bucky paper**–Thin nanotube sheets which are 250 times stronger and 10 times lighter than steel, can be used as heat sink for chipboards, backlight for LCD screens and Faraday cage to protect electrical devices/aeroplanes.

2. **Light Bulb Filament**–CNTs can be used as alternative to tungsten filaments in incandescent lamps.

3. **Magnets**-A strong magnetic field can be generated using MWNTs coated with magnetite.

4. **Electromagnetic Antenna**–CNTs can act as an antenna for radio and other electromagnetic devices due to its durability, light weight and conductive properties.

3.4.2 Actuators (Artificial muscles and Artificial implants)

An actuator is a device that can induce motion. In the case of a carbon nanotube actuator, electrical energy is converted to mechanical energy causing the nanotubes to move. Two small pieces of "buckypaper" papers, made from CNTs, are put on either side of a piece of double-sided tape and attached to either a positive or a negative electrode. When current is applied and electrons are pumped into one piece of buckypaper and the nanotubes on that side expand, causing the tape to curl in one direction. This has been called an artificial muscle and it can produce 50 to 100 times the force of a human muscle in the same size [32].

Normally, body shows rejection reaction for implants with the post administration pain. But, miniature sized nanotubes get attached with other proteins and amino acids avoiding rejection. Also, they can be used as implants in the form of artificial joints without host rejection reaction. Moreover, due to their high tensile strength, carbon nanotubes filled with calcium and arranged in the structure of bone can act as bone substitute [33].

3.4.3 Genetic Engineering

In genetic engineering, CNTs are used to manipulate genes and atoms in the development of bioimaging genomes, proteomics and tissue engineering [34]. The unwound DNA (single stranded) winds around SWNTs by connecting its specific neucleotides and causes change in its electrostatic property. This creates its potential application in diagnostics (polymerase chain reaction) and in therapeutics. Wrapping of carbon nanotubes by single-stranded DNA was found to be sequence-dependent and hence can be used in DNA analysis. Nanotubes due to their unique cylindrical structure and properties are used as carrier for genes (gene therapy) to treat cancer and genetic disorders. Nanostructures have showed antiviral effect in respiratory syncytical virus (RSV), a virus with severe bronchitis and asthma [35]. The treatment is generally done by combining nanoparticles and gene slicing technologies [36]. Nanotubes can adhere various antigens on their surface, hence act as source of antigen in vaccines. Hence, by use of nanotubes, dead bacteria as source for antigen which is sometimes dangerous can be avoided.

3.4.4 Biomedical Applications

In chemotherapy, drug embedded nanotubes attack directly on viral ulcers and kills viruses. No antibodies were produced against the CNTs backbone alone, suggesting that the nanotubes do not possess intrinsic immunogenicity. CNTs can have a valuable role in the construction of novel and effective vaccines [37].

3.4.5 Chemical

CNTs finds tremendous applications in the chemical fields, such as [37]:

1. **Air pollution Filter**–CNTs are one of the best materials for air filters. Because they possess high adsorption capacity and large specific area. The conductance of CNTs changes when polluted gas comes in its contact. This helps in detecting and filtering the polluted air. CNTs membranes can successfully filter carbon dioxide from power plant emissions.

2. **Water Filter**–CNTs membranes can aid in filtration. It can reduce distillation costs by 75%. These tubes are so thin that small particles (like water molecules) can pass through them, while blocking larger particles (such as the chloride ions in salt). CNTs have high active site and controlled distribution of pore size on their surface. This increases not only its sorption capabilities, but also its sorption efficiency. CNTs have effective sorption capacity over broad pH range (particularly for 7 to 10 pH).

3. **Sensors/biosensors**

    - CNTs based sensors can detect temperature, air pressure, chemical gases (such as carbon monoxide, ammonia), molecular pressure, strain, etc. The operation of a CNT based sensor is primarily dependent on the generation of current/voltage. The electric current is generated by the flow of free charged carrier induced in any material. This charge is typically modulated by the adsorption of a target on the CNT surface. When compared to conventional sensors, carbon nanotubes provide the advantages of a smaller size, an increased sensitivity and a faster response [38].

- Protein-encapsulated or protein/enzyme filled nanotubes, due to their fluorescence ability in presence of specific bio-molecules have been tried as implantable biosensors. Even, nanocapsules filled with magnetic materials, radioisotope enzymes can be used as biosensors [33]. Nanosize robots and motors with nanotubes can be used in studying cells and biological systems.

4. **Preservative**–Carbon nanotubes are antioxidant in nature. Hence, they are used to preserve drugs formulations prone to oxidation. Their antioxidant property is used in anti-aging cosmetics and with zinc oxide as sun-screen dermatological to prevent oxidation of important skin components [39]

3.4.6 Structural

CNTs possess remarkable properties and qualities as structural materials. Their potential applications include [40]:

1. **Textiles**–CNTs can produce waterproof and tear-resistant fabrics.
2. **Body Armour**–CNT fibers are being used as combat jackets. The jackets are used to monitor the condition of the wearer and to provide protection from bullets.
3. **Concrete**–CNTs in concrete increases its tensile strength and halt crack propagation.
4. **Sports Equipment**–Golf balls, golf clubs, stronger and lighter tennis rackets, bicycle parts and base ball bats can be made from CNTs.
5. **Bridges**– CNTs may be able to replace steel in suspension and bridges.
6. **Flywheels**– the high strength-weight ratios of CNTs enable very high rotational speeds.

7. **Fire Protection**–thin layers of buckypaper can potentially protect the object from fire. The dense, compact layer of CNTs or carbon fibers in the form of buckypaper can efficiently reflect the heat.

8. **Loud Speaker**–Loudspeakers can be manufactured from sheets of parallel CNTs. Such a loudspeaker can generate sound similar to the sound of lightening producing thunder.

3.4.7 Energy Production and Storage

Carbon Nanotubes technology also holds promise for a wide range of energy-related applications.

1. **Batteries**
    - Most portable electronic devices use rechargeable lithium-ion batteries. These batteries release charge when lithium ions move between graphite and metal oxide electrodes.
    - Electrodes made of carbon nanotubes can be ten times thinner and lighter than amorphous carbon electrodes and their conductivity is more than 1000 times greater.
    - Ultra-thin flexible batteries have been made with CNTs infused paper. Ionic liquid is soaked into the paper as the battery's electrolyte. Electrolytes in human blood, sweat, and urine can also help to power the battery which may be useful in implantable medical devices [41].
2. **Solar Cells**
    - Unlike typical solar cells that have peak efficiency when the sun is at 90°, these cells have two peaks at 45° and operate with relatively high efficiency during most of the day. This makes them particularly appropriate for applications in space because it eliminates the requirement of having a mechanical means of orienting the cells to face the sun [42].

   - Germanium CNT diode exploits the photovoltaic effect. In some solar cells, nanotubes are used to replace the ITO (indium tin-oxide) to allow the light to pass to the active layers and generate photocurrent.

3. **Optical**–When a particle of light bounces between the nanotubes, light is completely absorbed and it is converted to heat. Therefore, the absorbance of CNTs is extremely high in wide ranges from FUV (Far Ultraviolet, $100 - 200\ nm$) to FIR (Far Infrared, $50 - 1000\ \mu m$).

4. **Hydrogen Storage**–When oxygen and hydrogen react in a fuel cell, electricity is produced and water is formed as a byproduct. Carbon nanotubes are able to store hydrogen and could provide the safe, efficient, and cost-effective means to achieve this goal [43].

3.5 Problems of CNTs

3.5.1 Electronic Heterogeneity

CNTs are heterogeneous mixtures of metallic and semiconducting tube types. Electrical devices typically require these types to be separated, but so far it has been difficult to tune production in this regard [44]. There also remain issues with doping or tuning conductivity and electrical behavior at contact points.

3.5.2 Toxicity and Environmental Impact of CNTs

As the number of industrial applications of CNTs increases constantly with the production capacity at the worldwide level, its toxicity increases [44]. CNTs are mostly found as bundles rather than as individual objects or more likely as large micrometric agglomerates. All samples contain different levels of residual catalyst(s), depending on the synthesis route and purification steps that they may have undergone. Usual purification treatments involve the combination of acids and oxidizing agents, which leads to partial functionalization of the outer wall, making the treated samples more hydrophilic. SWNTs usually form long and flexible bundles (typically hundreds of micrometers long) whereas MWNTs are generally shorter (tens of micrometers) and more rigid. MWNTs also have generally more surface defects, which enhances their chemical reactivity. The specific surface area can range from a few tens of squared meters per gram in the case of densely packed MWNTs to just below 1000 m^2/g in the case of SWNTs (the theoretical limit being 1300 m^2/g in the case of individual closed SWNTs). Generally, the harmful effects of CNTs arise from the combination of various factors. Two of which are:

1. The high surface area and
2. The intrinsic toxicity of the surface [45].

In contrast with conventional particles of larger mean diameter, CNTs under 100 nm can potentially be more toxic to the lung (portal of entry), can redistribute from their site of deposition, can escape from the normal phagocytic defenses and can modify the structure of proteins. Therefore, CNTs can activate inflammatory and immunological responses and may affect the normal tissue function [46].

Chapter 4

Preparation & Characterization of CNTs by Transmission Electron Microscopy(TEM)

4.1 Methods of Preparation of CNTs

4.1.1 Arc Discharge Method:

Carbon nanotubes are prepared through arc vaporization of two carbon rods placed end to end with a distance of 1 mm in an environment of inert gas such as helium or argon at pressure between 50 to 700 mbar. Carbon rods are evaporated by a direct current of 50 to 100 A driven by 20 V which will create high temperature discharge between two electrodes. Due to this, anode will get evaporated and rod shaped tubes will be deposited on the cathode. Bulk production of CNTs depends on uniformity of plasma arc and temperature of deposition [47].

In the course of this procedure, about half of the evaporated carbon solidifies on the cathode tip in to a ”cylindrical hard deposit.” The remaining carbon condenses in to ”chamber soot” around the walls of the chamber and ”cathode soot” on the cathode. The cathode soot and the chamber soot yield either single-walled or MWNTs. The choice of buffer gas, the pressure of the chamber and the metallic catalyst added to the chamber determine the shape and where they are single or multi-walled. Apparently the CNTs grown from the surface of the metallic catalyst particles.

The advantage of this method is that it produces a large quantity of CNTs. But the main advantage is that there is relatively little control over the alignment (i.e., chirality) of the produced CNTs, which critical to their characterization and role. Furthermore, due to the metallic catalyst, include in the reaction, the products need to be purified afterwards such as oxidation, centrifugation, filtration and acid treatment have been used [47].

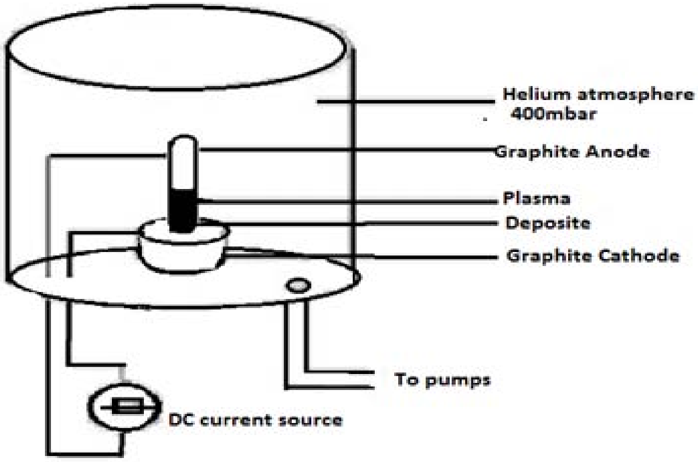


Figure 4.1: Arc Discharge Method.

4.1.2 Laser Ablation Method.

A pulsed or continuous laser is used to vaporize a graphite target in an oven at 1200°C. The oven is filled with helium or argon gas in order to keep the pressure at 500 torr. This method is very expensive so it is mainly used for SWNTs. Laser vaporization results in higher yield of SWNTs with narrower size distribution than those produced in arc discharge process. Catalyst used for SWNTs is Ni:Y (4.2:1 at%) [48].

4.1.3 Chemical Vapors Deposition Method

It is carried out in two steps process:

1. Catalyst is deposited on substrate and then nucleation of catalyst is carried via chemical etching or thermal annealing. Ammonia is used as an etchant. Metal catalysts used are Ni, Fe or Co.

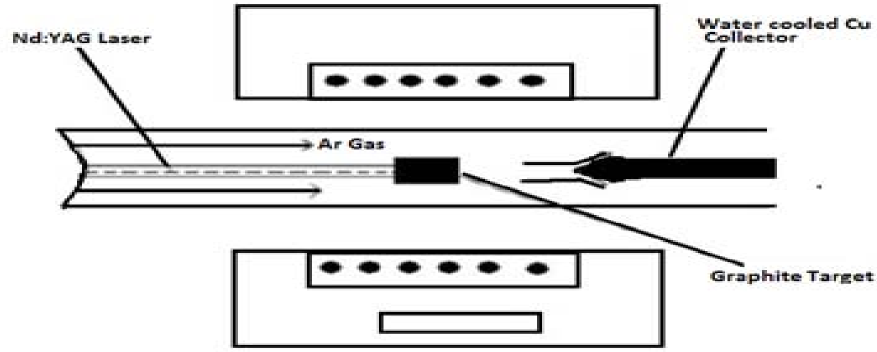


Figure 4.2: Laser ablation method.

2. Carbon source is then placed in gas phase in reaction chamber. Then carbon molecule is converted to atomic level by using energy source like plasma or heated coil. This carbon will get diffused towards substrate, which is coated with catalyst and nanotubes grow over this metal catalyst. Carbon sources used are methane, carbon monoxide or acetylene. Temperature used for synthesis of nanotube is $650 - 9000°C$ range. The typical yield is 30 % [49].

4.1.4 Flame Synthesis Method:

SWNTs are formed in controlled flame environment from hydrocarbon fuels and small aerosol metal catalyst. SWNTs have been observed in the post-flame region of a premixed acetylene/oxygen/argon flame operated at 50 Torr (6.7 kPa) with iron penta carbonyl vapor used as a source of metallic catalyst. Between 40 and 70 mm heights above burner($\sim$ 30 ms), CNTs are observed to form and coalesce into clusters [50].

4.1.5 Silane Solution Method:

CNTs can be produced using a silane solution method, in which a substrate such as carbon paper or stainless steel mesh is immersed in a silane solution of a metal catalyst, preferably Co:Ni in a 1:1 ratio; and a feedstock gas containing a carbon source such as ethylene fed through the substrate and the catalyst deposited there on while the substrate is heated by applying an electrical current there too. Thus, a reaction occurs between the catalyst and the gas to yield CNTs supported on the conductive substrate [51].

4.2 Purification of CNTs

The CNTs are having less purity, about 5-10 %, usually contain a large amount of impurities such as metal particles, amorphous carbon and multi-shell. There are different steps in purification of CNTs [52]:

1. **Air Oxidation**–is useful in reducing the amount of amorphous carbon and metal catalyst particles (Ni, Y) at 673 K for 40 min.

2. **Acid Refluxing**–is effective in reducing the amount of metal particles and amorphous carbon. Different acids used are: HCl, HNO_3 and H_2SO_4.

3. **Surfactant aided sonication, filtration and annealing**–After acid refluxing, the CNTs are purer but, tubes are entangled together, trapping most of the impurities, such as carbon particles and catalyst particles, which are difficult to remove with filtration. So surfactant aided sonication is carried out. Sodium dodecyl benzene sulphonate (SDBS) aided sonication with ethanol (or methanol) as organic-solvent are preferred because it took the longest time for CNTs to settle down, indicating an even suspension state is achieved. The sample is then filtered with an ultra filtration unit and annealed at 1273 K in N_2 for 4 h. Annealing is effective in optimizing the CNTs structures. The surfactant-aided sonication is effective to untangle CNTs. Thus to free the particulate impurities, embedded in the entanglement.

4.3 Characterization of Carbon Nanotubes

CNTs have at least one dimension smaller than 100 nm, which makes their characterization complicated and requires sophisticated instruments [53].

Carbon nanotubes can be characterized by Transmission Electron Microscopy (TEM), Raman Spectroscopy, X-Ray Diffractogram (XRD), Energy Dispersion X-Ray (EDX), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Scanning Tunneling Microscopy (STM), etc [54].

4.3.1 Transmission Electron Microscopy(TEM)

TEM is a type of electron microscope operating at 200 KeV and standard magnification from 1000 to 800000 times. Illuminating system consisted of cool beam electron gun with pre-centered lab filaments. There are three-stage condenser lenses and five apertures. A beam total angle is 2°.

Each sample is directly pulled onto the membrane for observations. The carbon membrane is drilled with holes in order to get more accurate observations. TEM micrographs clearly illustrate that CNTs obtained, display and control widely different morphologies according to some variable parameters. Within the medium value of the plasma power, CNTs are yet grown. These samples however display different mutual orientations. The highly oriented films are obtained under optimized conditions and poorly and medium oriented films are also obtained and show more defects [55].

High resolution Transmission Electron Microscopy (HRTEM) is the most powerful instrument that reveals the diameters, the number of walls and the distance between the walls of the CNTs. In addition, the electron diffraction mode of the TEM helps to identify the nature of the cap on top of CNTs [56].

The TEM examination can yield:

- The topographical information: the surface features of an object or ”how it looks”, its texture.
- The morphological information: the shape and size of the particles making up the object.
- The composition information: the elements and compounds that the object is composed of and the relative amounts of them.
- The crystallographic information: itemizes how the atoms are arranged in the object and provides direct relation between these arrangements and material’s properties.

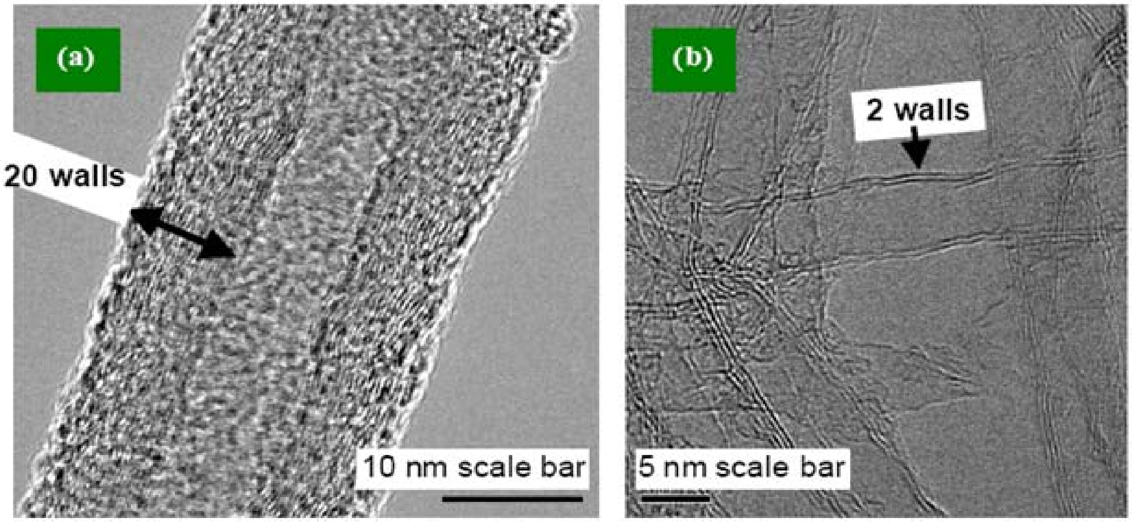


Figure 4.3: High Resolution TEM images of CNTs: (a) MWCNT with 15-20 nm outer diameter and 7 nm inner diameter; (b) Double wall CNT found with about 5 nm diameter [56].

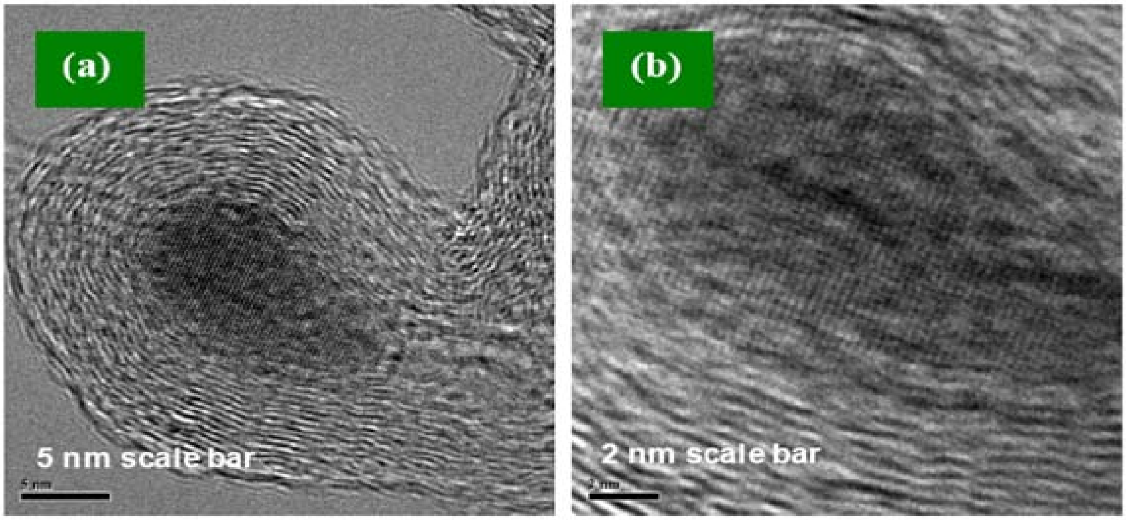


Figure 4.4: Internal structure of the CNT by TEM: (a) Multi-Wall CNTs with encapsulated catalyst particle; (b) Lattice structure of the catalyst particle is visible [56].

The TEM observations show at the same time that, the surface of the CNTs exhibits an amorphous structure due to wall surface defects. The outer diameters of the CNTs are directly determined from TEM images with high accuracy. Thus the mean outer diameter is 20 nm to MWNTs and 10 nm to SWNTs as shown in the Figure 4.3 and Figure 4.4 above.

4.4 TEM Characterization of CNTs

4.4.1 Our Observation from Experiment

In this section we give analysis to a experimental result that was done at the Department of Physics Punjab University, India.

Procedure

During sample preparation, drilled and one end open pieces of carbon-graphite rod, stuffed with a mixture of graphite and nickel powder were mounted horizontally on the fixed electrodes. The rods/electrodes were kept few millimeter away in a glass chamber filled with deionized water. A high temperature discharge was created between two electrodes, through a direct current (DC) of 50–200 A driven by 40 V. The chamber was removed after frequent discharging and the product soot along with water was transferred to a bigger beaker. The beaker was kept for about 6 h, until the crude formation took place at the bottom, and then the water was decanted off. Subsequently, the crude was dried in air at $100°C$ for about 12 h, and was collected for further analysis. The collected CNTs in the form of soot were also purified, by refluxing it in a strong oxidant, i.e. 8 M Nitric acid (HNO_3) for 24 h at $100°C$. Subsequently, the filtration was carried out through a 0.25 mm filter membrane with the aid of a pump. The filtered product was thoroughly was held with distilled water until the pH value reaches neutral. Finally, the samples were dried in an oven at $100°C$, followed by open air annealing at $400°C$ for 15 min, for the removal of un-reacted reagents and impurities [57].

4.4.2 Results and Discussion

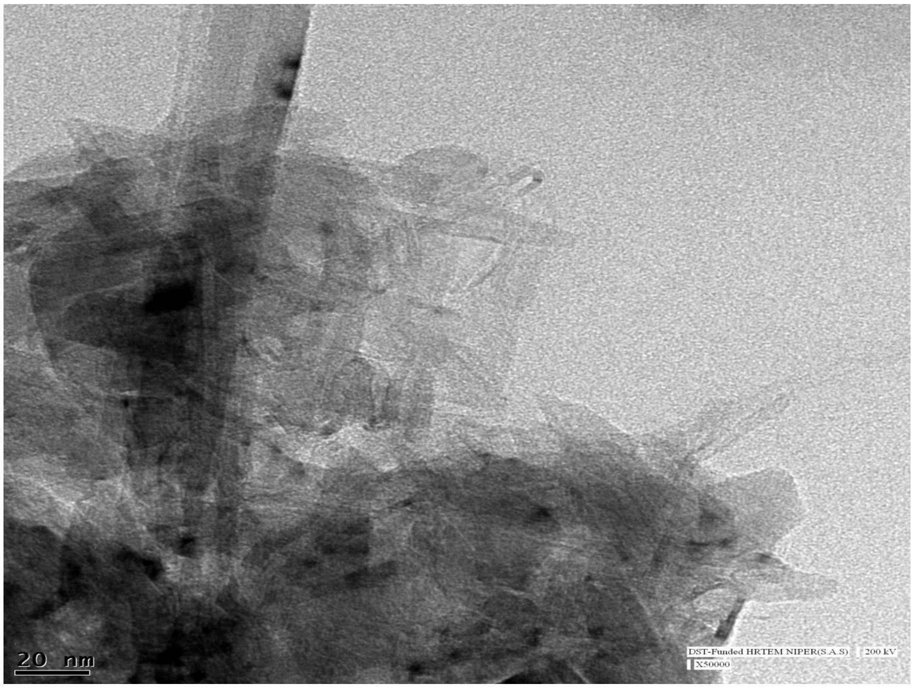


Figure 4.5: TEM Image of CNTs in the Lateral view .

Based on the experiment, the TEM images of the products were captured from different positions after sonication of samples in ethanol for 3 h, placing a droplet of the suspension onto a TEM Carbon coated grid and dried in air, using a HITACHI 7500 device with maximum magnification 6×10^6 times and resolution of 0.2 . The TEM images obtained for Ni:C, 1:24 M ratio mixture, after annealing at $400°C$ for 30 min are collected. Transmitted electrons formed images from small regions of the sample that contained contrast, due to several scattering mechanisms associated with interactions between electrons and the atomic constituents of the sample as shown in Figure 4.5 and Figure 4.6 above.

Figure 4.6 shows the TEM image of the lateral side view of CNTs. As it is shown many layers have overlapped, layers laying over one another in irregular order. It is also observed that the layers have skeining around longer tubes. The layers' length is very mach greater than relative to the tubes diameter. They are black in colors. Their lateral dimension scale is 20 nm as it is indicated in the figure above.

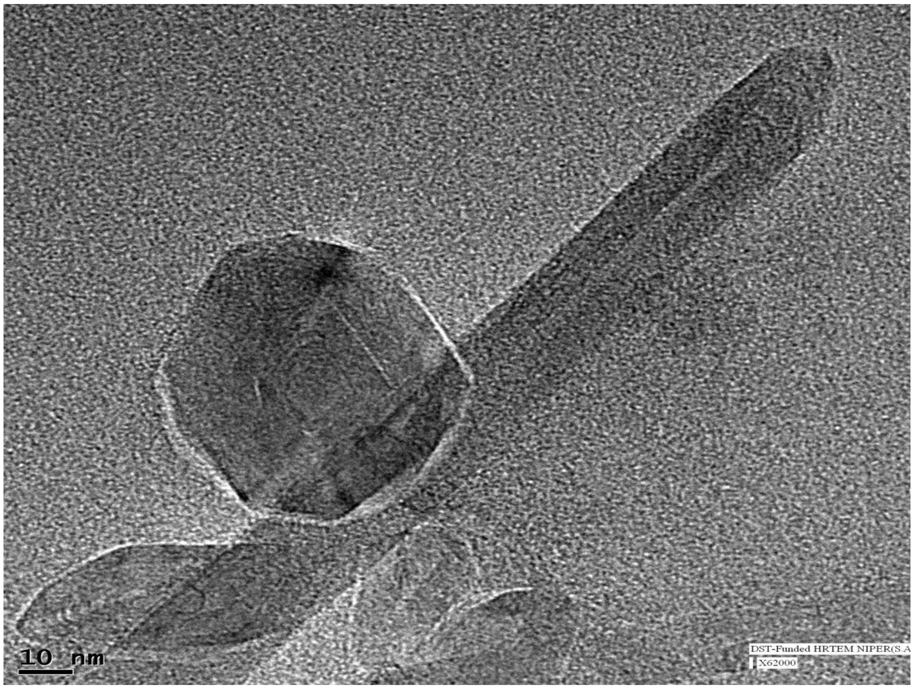


Figure 4.6: TEM Image of CNTs, Top or bottom edge view.

Figure 4.6 also shows the TEM image of CNTs at the top edge view. As it is shown, there are many concentric circular edges. These concentric circles are the tubes which are concentric one inside/outside the other. The inner tubes are narrower in diameter, the outer tubes' diameter increases consecutively. It indicates a multi-walled CNTs. Their edge dimension scale is 10 nm. The lateral length is longer than the diameter of the top edge. It is thin, long, black colored and needle like shaped.

Chapter 5

Conclusion

CNTs are molecular/nano-scale tubes of graphitic carbon with outstanding properties. The simplest CNT is composed of a single sheet of a honeycomb network of carbon atoms, called graphene. When it is rolled up seamlessly into a tubular form gives CNTS. It can be SWNTs or MWNTs based on the number of tubes rolled up.

Due to their spectacular electronic, thermal, mechanical and chemical properties; CNTS are expected to offer an exceptional choice. CNTs have attracted wide interest in many areas of science, technology and medicine. With the prospect of gene therapy, cancer treatments and innovative new answers for life-threatening diseases; the science of nanomedicine has become an ever-growing field that has an incredible ability to bypass barriers. CNTs have already proven to serve as safer and more effective alternatives to previous drug delivery methods. They can pass through membranes, carrying therapeutic-drugs, vaccines and nucleic acids deep into the cell to targets previously unreachable.

CNTs basic parameters can be measured using TEM. It is evident that, the TEM is used for detail analysis of CNTs. Analysis of transmitted electron microscopy images yield information both about the atomic structure, shape, dimensions and defects of the material in the sample. TEM gives direct insight into the structure of CNTs and can help to identify the material or the phase correctly. It used to identify the type of CNTs (SWNTs or MWNTs), to know the size of the dimensions of CNTs (diameter and length). It is the most important and most reliable technique for correctly identifying the nature and the form of CNTs.

CNTs can give a large opportunity for future technological advancement. Not only will they help create sophisticated technology gadgets, they may also help to solve the world's energy problem. CNTs will play a significant role in a wide range of commercial applications in the very near future

There is much about CNTs that is still unknown. The properties of CNTs are yet to be fully identified. The history of CNTs has only just begun.

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