Study of Carbon Nanotubes and Defect Concentration by Raman Spectroscopy Technique

By

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Abstract

CNTs are very thin materials made from carbon by rolling graphene sheets. Arc-discharge, laser ablation and chemical vapor deposition are well established techniques to prepare carbon nanotubes. Mostly purification is carried out by chemical oxidation, acid treatment and micro filtration techniques. Their nature, quality and properties examined by Scanning Electron Microscopy(SEM), Transmission Electron Microscopy(TEM), Atomic Force Microscopy (AFM), X-Ray Diffraction(XRD) and Raman Spectroscopy. CNTs have many technological applications due to their unique physical and chemical properties such as high conductivity, high strength, low weight and high aspect ratio. Carbon nanotubes (CNTs) attracts significantly attention of the scientific community because of their remarkable optical, electronic, thermal, mechanical and chemical characteristics. Raman spectroscopy is one of the most powerful tool to characterize the degree of disorder in sp^2 carbon materials with band ratio ($\frac{I_D}{I_G}$), of graphite powder, CNTs, and other allotropes of carbon. Thus, Raman spectroscopy determine the presence of crystalline, amorphus carbon and diameter of CNTs. In this project Raman spectra of graphite pristen sample is studied from available data. The result indicated that the intensity at certain frequency mode that corresponds to D-band is very large due to large amount of impurity content.

Chapter 1

Introduction

Carbon is the 4^{th} most abundant element in the universe by mass and its atomic number and atomic weight are 6 and 12 respectively. It forms many pure organic compounds with any other elements, with almost 10 millions pure organic compounds [1]. Carbon atoms can form various types of allotropes. In some representative carbon structures, diamond, graphite, fullerene, graphene, and carbon nanotubes are the allotropes of carbon [2]. Carbon nanotubes are tube shaped materials made of carbon called graphene rolled into cylinders, as shown in figure 1.1 [3]. Its diameter measuring on nanometer scale. A nanometer is one-billionth of meter or about one-ten-thousandth of the thickness of a human hair. [4]. Discovery of carbon nanotubes(CNTs) was reported for the first time by Iijima in 1991 [5], these new type of finite carbon structures consists of needle like tube as shown in the figure 1.2. The tube were produced using an arc discharge evaporation method [2].

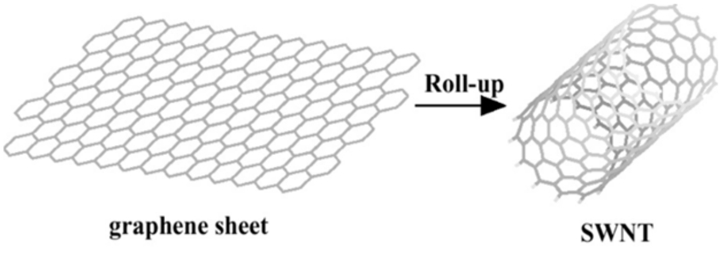

Figure 1.1: A single layer of graphite form graphene sheet that would form CNTs when rolled up [6].

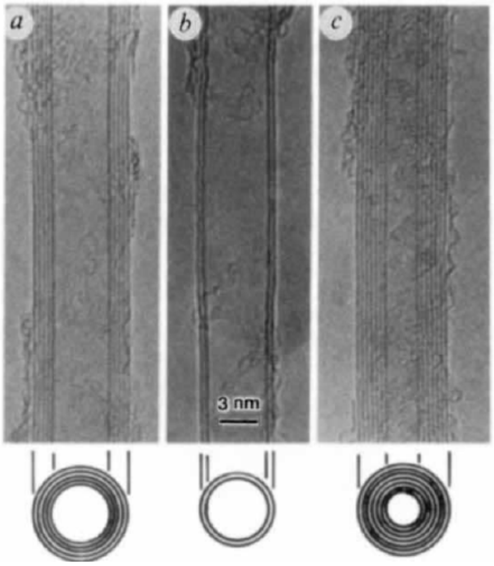

Figure 1.2: Trasmission electron microscopys (TEMs) of first observed multiwalled carbon nanotubes (MWCNTs) reported by Iijima 1991, with various inner and outer diameters, consisting of two, five and seven numbers of cylindrical shells which is (a) N=5, (b) N=2, and (c)N=7 [5]

Depending up on the number of concentrically rolled graphene sheets, carbon nanotubes are categorized as single walled carbon nanotubes(SWNTs), double walled carbon nanotubes (DWCNTs) and multi walled carbon nanotubes(MWNTs), see figure 1.3. If carbon nanotube contain one graphene layer, it is named single wall carbon nanotube and, if it contains exactly two graphene sheets, it is called double walled carbon nano tubes; where as if it contains two or more concentric layers, it is called multi wall carbon nanotubes. [7]. The structure of graphite consists of graphene layers, it is a source of CNTs production. So when these graphene sheets rolled it formed CNTs shown in figure 1.4.

According to atomic arrangement of carbon, carbon nanotubes are responsible for the unique electric, thermal and mechanical properties. The field of nanotechnology and nanoscience push their investigation forward to produce carbon nanotubes with suitable parameters for future applications. Moreover new approaches of their synthesis, purifications and characterizations need to be developed.

There are many techniques used to produce MWNTs or SWNTs, such as arc-discharge, laser ablation, electrolysis, hydro thermal and chemical vapor deposit(hot filament, water

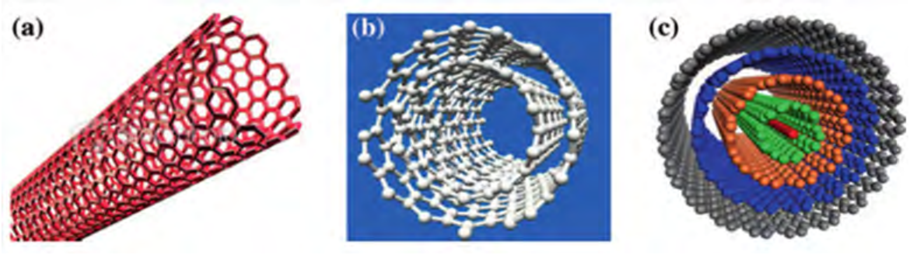

Figure 1.3: Carbon Nanotubes with exactly different layers (a) SWCNT, one layer (b) DWCNT, two layers and (c) MWCNT, four layers [7].

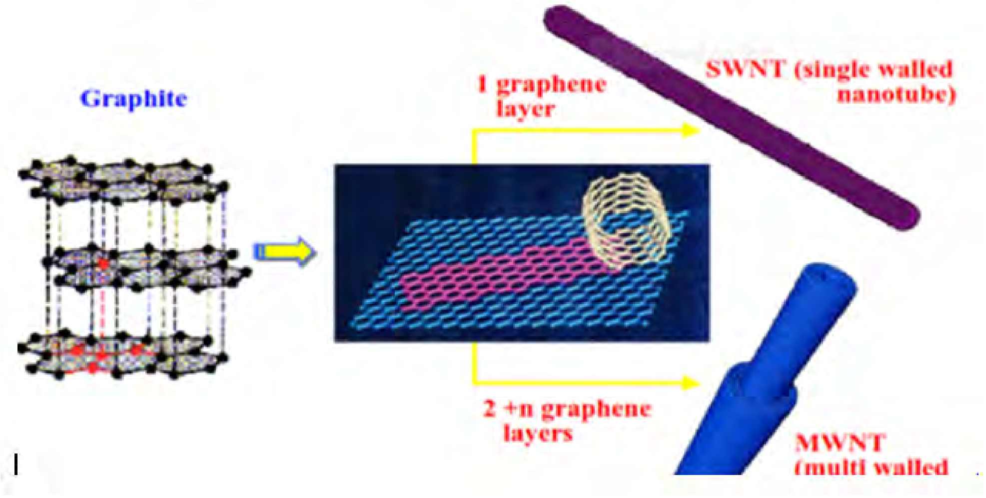

Figure 1.4: Graphite (parallel layer of graphenes),changed in to graphene(s) and then when graphene(s) rolled it forms single walled or multi-walled carbon nanotubes [8].

assisted, oxygen assisted, microwave plasma) are currently used [9, 10]. Among these techniques; arc-discharge, laser ablation and chemical vapor deposition techniques are mostly used to produce a wide Variety of CNTs.

The synthesized nanotube samples are purified by passing through several techniques such as oxidation, filtration, acid treatment, ultrasonication, annealing and thermal treatment. These mechanisms have been developed, to separate the amorphous carbons, catalysts and nano particles from the CNTs. During these purification processes a significant amount of CNTs may be destroyed [11]. To investigate the morphological and structural characterizations of the CNTs, a number of techniques can be used. Scanning Electron Microscopy(SEM), Transmission Electron Microscopy(TEM), X-ray diffraction(XRD) and

Raman spectroscopy are the most used. Various techniques have been developed, as suitable to obtain structural and quality information on carbon. In particular by Raman spectroscopy the ratio of intensity of D-band to G-band ($\frac{I_D}{I_G}$) indicate the defect concentrations, which is the degree of disorder [12]. Carbon nanotubes have unique properties that includes large current carrying capacity, small dimensions, high thermal conductivity, high electrical conductivity and mechanical strength. Due to these unique properties CNTs have many applications in the area of nanoelectronics, optics, material science and mechanics. They are used for making bridge, body armor, solar cells, batteries, filters, sensors, electrical circuits, transistors, etc. This project is organized as follows, chapter 2 focus on allotropes of carbon, and their experimental investigations (preparations, purifications and characterizations), discuss in chapter 3. In chapter 4 applications of CNTs. Detial of characterization of CNTs by Raman spectroscopy is given in chapter 5, and lastly summery of the project work is briefly written.

Chapter 2

Carbon and its Allotropes

2.1 Structures of Carbon

Carbon is the chemical element with atomic number 6 and has six electrons which occupy $1s^2$, $2s^2$ and $2p^2$ subatomic orbital. It can make single, double and triple bonds. In carbon there are three possible hybridization that occur; sp, sp^2 and sp^3 [13], and is why carbon assumes a variety of structural forms. There are several allotropes of carbon known in nature. The allotropes of carbon differ in structures. As the structures of allotropes vary, they also have different physical and chemical properties. Diamond, graphite, carbon fibers, fullerenes and carbon nanotubes are some forms of carbon [14]. But diamond, graphite and fullerene are the three main naturally occuring allotropes of carbon.

2.1.1 Diamond

Diamond (see figure 2.1) is the first form of carbon through covalent bonding, and it is one of the 3D allotropic form of carbon. By applying high temperature and pressure it is reformed from graphite, and it shows a sp^3 hybridization in its structure. It has a face centered cubic crystal structure and occurs from tetrahedral bonded carbon atoms, in which one carbon atom is covalently bonded to four other carbons [3]. Diamond transforms in to graphite the thermodynamically stable allotropes at lower pressures, and above 1500^oC temperature under vacuum or inert atmosphere [15]. It has many uses in industry because of its excellent physical properties, the naturally occurring diamond typically used for jewelery. Pure diamond is an electrical insulator but it is a thermal conductor. Due to its hardness, it is used in industrial cutting tools.

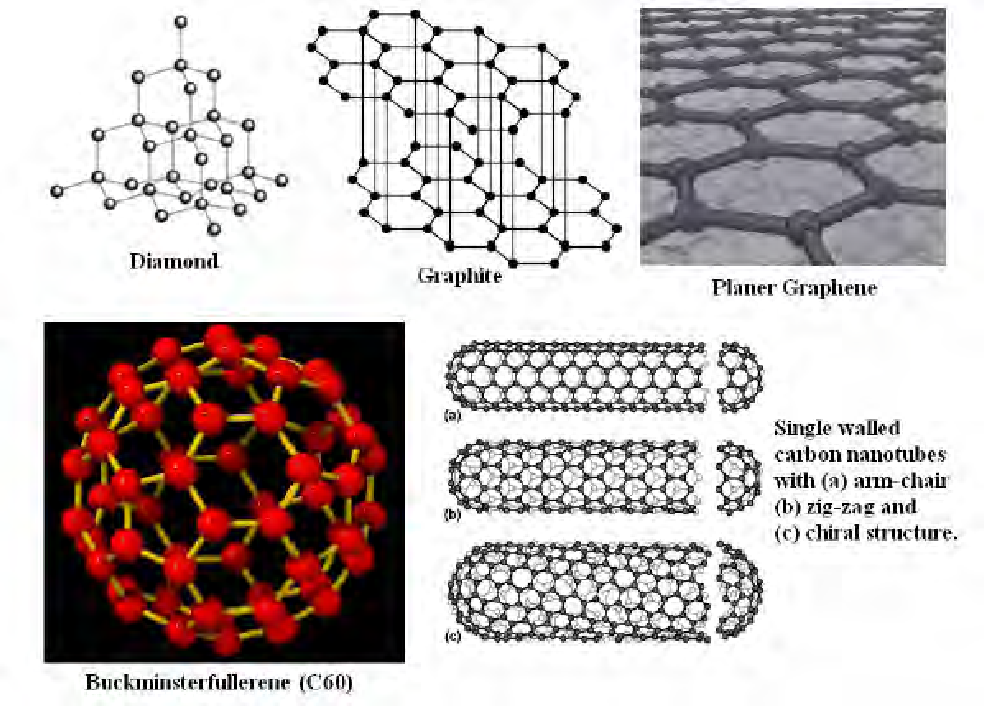

Figure 2.1: Forms or allotropes of Carbon in different structures:- Diamond, Graphite, Fullerene, Graphene, and Single walled carbon nanotubes (a) armchair b) zigzag c) chiral) [14].

2.1.2 Graphite

Graphite is one of the allotropes of carbon. Three dimensional(3D) graphite is the longest known form of pure carbon, naturally occurring on the surface of the earth as mineral. Structurally, graphite is a layered material, with individual graphene layers, in which the sp^2 bonded carbon atoms from a planar hexagonal honeycomb arrangement, as in figure 2.1. The bonding of carbon atoms in a graphene layers is weak (Vander Waals bonds) [11]. In these layers each carbon atom bonds to three coplanar neighbor atoms by strong covalent bonds [3]. Graphite is soft, light and flexible. It is an electrical conductor. High temperature break the strong bond in graphite.

2.1.3 Fullerene

Fullerene'C_{60}', is another form of carbon as shown in figure 2.1, was discovered in 1985 by Kroto, et al [16]. The fullerenes are members in the family of carbon allotropes and are carbon based nano objects in the form of hallow spheres, ellipsoids, or tubes. Spherical and ellipsoidal fullerenes are called simply "fullerenes" or "bulky balls" while tube fullerenes are called carbon nanotubes or "bucky tubes" [3]. In the fullerene structure carbon atoms bonded to one another creates both hexagon and pentagon rings. The best example being C_{60} consists of 60 $\sim sp^2$ hybridized carbon atoms arranged in 20 hexagonal rings and 12 pentagonal rings to form a spherical structure resembling a soccer ball in nano size. Because of topological restrictions the other fullerenes can be produced with exactly 12 pentagonal rings and any number of hexagonal rings. The other forms of fullerene families are C_{20} which is the smallest possible, C_{70}, C_{76} and C_{84} and others [17].

2.1.4 Graphene

Graphene as shown in figure 2.1 is a single atomic layer of sp^2 carbon derived from a honeycomb lattice . Single layer of graphene is synthesis by preparation technique, it is the source of CNT get from graphite [15].

2.1.5 Carbon Nanotubes

Carbon nanotubes are tube shaped materials made of carbon or single sheet of graphite called graphene rolled into cylinders. It's structure differing in length, thickness and number of layers. Type of carbon nanotube is determined by the number of the concentric graphene layers, and are categorized as single wall carbon nanotubes (SWNTs), double wall carbon nanotubes (DWNTs) and multi wall carbon nanotubes (MWNTs), as indicated in fig. 1.3.

Single Walled Carbon Nanotube

A single-wall carbon nanotube (SWNT) is defined by a graphene sheet rolled in to a cylindrical shape (as shown in figure 1.1), with a diameter of about 0.4-3nm and length extending up to several microns [3, 18]. Depending on wrapping to a cylinder way or based on the direction of chiral vector, there are three different forms of SWNTs such as armchair, chiral and zigzag (see figure 2.1) [19]. A SWNT's structure is characterized by a pair of indices (n, m) that describe the chiral vector and directly have an effect on electrical properties of nanotubes. In order to determine the armchair, zigzag and other structures in terms of (n,m), it is necessary to have the following conditions. For armchair CNTs the chiral indices n and m are equal ($n = m$), while for zigzag CNTs $n = 0$ or $m = 0$, i.e (0, m) or (n, 0). For other values of indices, CNTs are known as chiral, as shown in figure 2.2 below [13]. Every carbon atom on the sheet can be expressed as a function of integer (n, m). Nanotube structure can be mathematically defined in terms of chiral vector C which is given by:

$$C = na_1 + ma_2 \tag{2.1.1}$$

Where a_1 and a_2 are the lattice vector of graphene and n and m are chiral indices, which can determine the tube diameter "d". The diameter of an ideal nanotube can be calculated from its, n and m indices as follows:

$$d = \frac{a}{\pi}\sqrt{(n^2 + mn + m^2)} \tag{2.1.2}$$

Where $a = 0.246nm = 1.42\sqrt{3} \times 10^{-10}m$, and corresponds to the lattice constant in the graphene sheet [18, 20, 21]. On the other case CNTs can exhibit metallic or semi conducting proprieties. The structural design has a direct effect on the nanotube electrical property [1], by satisfying the condition $n - m = 3i$, where 'i' is an integer and when n-m is a multiple of 3, then the nanotube is described as metallic or highly conducting nanotubes, and if not, then the nanotube is a semi metallic or semi conductor see figure 2.2. At all time the armchair form metallic, where as other forms can make the nanotube metallic or semi conductor in nature [18, 21].

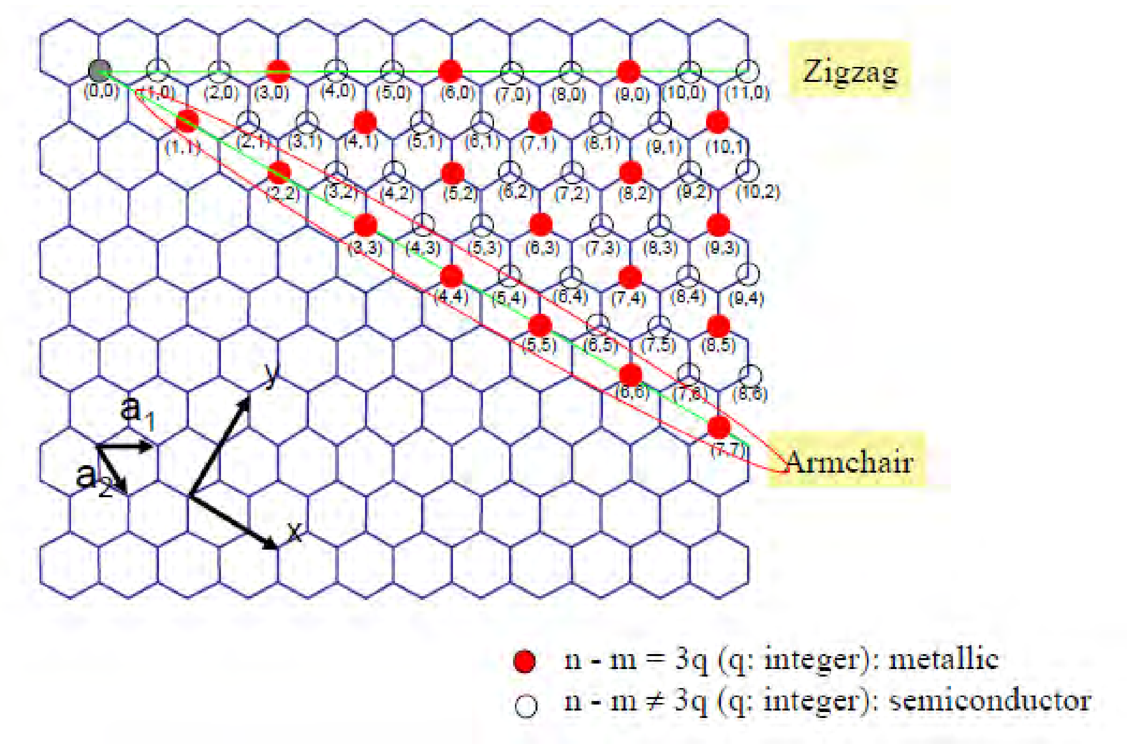

Figure 2.2: Possible vector specified by the pairs of integers(n,m) for general CNTs. The different types of carbon nanotubes; Zigzag, Armchair, and Chiral(the remaining), and Metallic and semi-conducting CNTs [3].

Multi-Walled Carbon Nanotubes

Multi walled carbon nanotubes (MWNTs) consist of multiple rolled layers (concentric tube) of graphene. Depending on the number of layers, the inner diameter of MWNTs diverges from 0.4nm up to a few nanometers and outer diameter varies characteristically from 2nm up to 20 to 30nm [19], the inter layer distance in multi-walled nanotubes is close to the distance between graphene layers approximately 0.34nm, see figure 2.3.

Both ends of MWNT usually have closed and the ends are capped by dome shaped half-fullerene molecules (pentagonal defects). The roll of the half fullerene molecules (pentagonal ring defect) is to help in closing of the tube at the two ends [13].

There are two models that can be used to describe the structure of multi-walled nanotube. These are Russian Doll model and Perchmen model. When a carbon nanotube contains another nanotube in side it and the outer nanotube has greater diameters than the inner nanotube is called the Russian Doll model. And when a single graphene sheet is wrapped

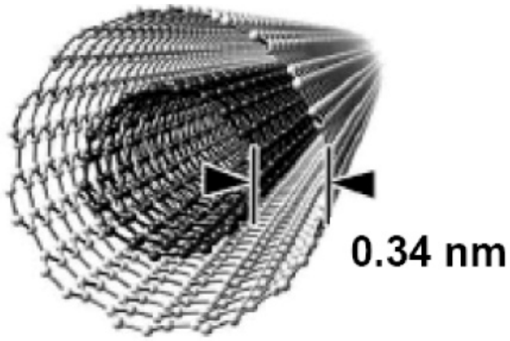

Figure 2.3: The distance between two successive graphene layers of MWCNT is approximately 0.34nm [3].

Table 2.1: Comparision between SWNT and MWNT with respect to their number of layers, catalyst used, purity, characterizations and twist ability [2]
.

No	SWCNT	MWCNT
1	single layer of graphene	multiple layer of graphene
2	catalyst is required to synthesis	can be produced with out catalyst
3	purity is poor	purity is high
4	less accumulation in body	more accumulation in body
5	characterization and evaluation is easy	it has very complex structure
6	it can be easily twisted	it can not be easily twisted

around itself manifold times, the same as a rolled up scroll of paper, it is called the Perchment model [1].

2.2 Discovery of Carbon Nanotubes

Historically, the oldest method for carbon nanotube production is the electric arc-discharge. This technique was used already in the early sixties by R. Bacon for the synthesis of carbon fibers. In early thanks to the subsequent invention of the transmission electron microscopy (TEM), the first commercial versions of which were produced by Siemens in 1939. The first TEM(transmission electron microscopy) that gives evidence for the tubular nature of some nano-sized carbon filaments is believed to have appeared in 1952 in the journal of physical chemistry of Russia. In 1952 also Radushkevich and Lukyanovich published clear images of 50nm diameter tubes made of carbon. A paper by obtain, Endo, and Koyama published in 1976 clearly showed hollow carbon fibres with nanometers scale diameters using vapor-growth technique [10, 22, 23]. Further more Harry Kroto discovered C_{60} molecule in 1985 (Kroto, et al. 1985) [16], while experimenting a laser ablation system for the vaporization of graphite by laser beams and depositing them on a copper collector and it was the beginning of a new area in carbon material science [3].

First carbon nanotube was discovered by Iijima, he experimented by an arc-discharge method in order to observe fullerene by passing large current between two graphite roads, he vaporized them and condensed them on CU tip. When he looked at the result through an electron microscopy, he noticed something unexpected, he discovered carbon nanotubes (Iijima, et.al. 1991) [5], at the negative electrode of an arc discharge. Finally in carbon nanotube history, SWCNT should be distinguished from MWCNT. It is perfectly clear that the formation of SWCNTs was first reported in the June 17^{th} issue of nature in 1993 by two papers submitted independently, one by Iijima and Ichihashi and the other by Bethune et al. [22, 23]. But now a days, different researchers prepare, purify and characterize many CNTs by different preparation, purification and characterization methods.

2.3 Properties of Carbon nanotubes

The atomic arrangement of carbon atoms are responsible for the unique electric, thermal and mechanical properties of CNTs [7]. CNTs can serve multi functional roles because their strength is at least ten times stronger and their weight is less than half of conventional copper fibers, their electrical conductivity is much higher than copper, and their thermal conductivity is high as that of diamond. The most important properties of CNTs discussed as follows:-

2.3.1 Electrical conductivity

Depending on the chiral indices and unique electric structure of a nanotube, strongly affects its electrical property for a given (n, m) nanotube If $n = m$ and $n-m$ is a multiple of 3, then the nanotubes are metallic, but if not then the nanotubes are semiconducting [18]..

The strong bond between carbon atoms also allow carbon nanotubes to with stand higher electric current than copper [1]. In theory, metallic nanotubes can carry an electrical current density of $4 \times 10^9 \frac{A}{nm^2}$, which is more than 1000 times greater than metals such as copper [19].

2.3.2 Thermal conductivity

The strength of the atomic bonds in carbon nanotubes allows them to withstand high temperature. Because of this, CNTs have been shown to be very good thermal conductors, when compared to copper wire, which are commonly used as thermal conductors. The carbon nanotubes can transmit over 15 times the amount of watt per meter per kelvin [1]. In addition, measurements show that a SWNT has a thermal conductivity is about $3500 Wm^{-1}.k^{-1}$ at room temperature; compare this to copper, a metal well known for its good thermal conductivity, which transmits $385 Wm^{-1}.k^{-1}$, which is almost ten times greater [19]. The thermal conductivity of CNT is temperature dependent which has almost linear relationship with it.

2.3.3 Mechanical

Each carbon atoms in a single sheet of graphite is connected to strong chemical bond to three neighboring atoms. Thus CNTs can exhibit the strongest elastic modulus and hence are expected to be an ultimate high strength fiber [7]. Theoretically, CNTs are the strongest and stiffest material yet known. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms [13]. SWNTs may really have a tensile strength of hundreds of times stronger than steel. A multi-walled carbon nanotube was tested to have a tensile strength of 63 Gpa, i.e. it is equivalent to a force of 62,980N on a cable with cross section of 1 sq.mm. [19]. CNTs are not only strong, but they are also elastic. You can press on the tip of nanotube and cause it to bend or twist without damaging, the nanotube will return to its original shape when the force is removed, see figure 2.4 [13]). Nanotube elasticity have limit and under very strong forces, it is possible to permanently deformed.

Figure 2.4: Simulation showing two possible ways, CNTs can deform or twist when they are loaded [24].

2.3.4 Aspect ratio

It is one of the exciting property. CNTs have high aspect ratio (length to diameter ratio) about 1000, so they can be considered as nearly one-dimensional structure. Also it indicates that a lower CNT load is required compared to other conductive additive to achieve similar electrical conductivity. The high aspect ratio of CNTs possesses unique electrical conductivity [7, 19].

Chapter 3

Experimental Study of Carbon Nanotubes

3.1 Preparation Techniques

There are many preparation techniques used to produce MWNTs or SWNTs experimentally. But now a days arc-discharge, laser ablation and chemical vapor deposition techniques are well established to produce different kind of CNTs. [11]. High temperature preparation techniques such as arc discharge or laser ablation were first used to produce CNTs but now days these methods have been replaced by low temperature chemical vapor deposition (CVD) techniques ($< 800^oC$) [10].

3.1.1 Arc Discharge Method

In 1991, Iijima [5], reported the preparation of a new type of finite carbon structures consisting of needle-like tube. The tubes were produced using an arc-discharge evaporation method similar to that used for fullerene synthesis. Also, the MWNTs were first discovered in the soot of the arc-discharge method by Iijima. The method has been used long before that in the production of carbon fibers and fullerenes [2]. Electric arc discharge method has been employed to produce CNTs. There are different approaches, an example of an electric arc reactor is shown in figure 3.1. The CNTs produced by this method were grown on the negative end of graphite electrode under inert atmosphere of helium or argon with a very high temperature needed in order to evaporate the pure graphite.

A certain potential is applied across two electrodes, which is a few millimeters in diameter, septated by a certain distance in inert atmosphere. A high current discharge (100A) passes through the opposite graphite anode and cathode, where plasma is generated, and some of the carbon atoms evaporated on the cathode and some of it on the reaction vessel [19]. In similar way direct current is passed through the chamber (arcing process), and the chamber is pressurized and heated to approximately 4,000 K. In the course of this procedure and arcing, about half of the evaporated carbon solidifies on the cathode (negative electrode) tip, whereas the anode (positive electrode) is consumed. The remaining carbon (a hard gray shell) deposited and condenses into "chamber soot" nearby the walls of the chamber and 'cathode soot' on the cathode. The inner core, cathode soot and chamber soot, which are dark and soft, yield either single-walled or multi walled carbon nanotubes and nested polyhedral graphene particles [13].

The physical and chemical factors influencing the arc discharge process are the carbon vapour concentration, the carbon vapour dispersion in inert gas, the temperature in the reactor, and the composition of catalyst. These factors affect the growth of nanotubes, the inner and outer diameter, and the type of nanotubes [25].

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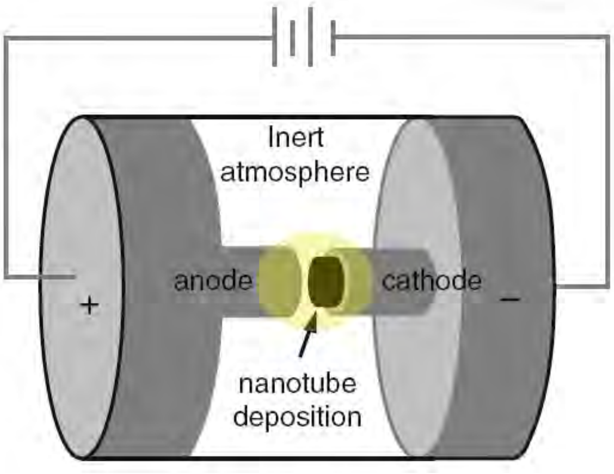

Figure 3.1: Schematic diagram for arc-discharge method, with its two electrodes (cathode and anode), a place where nanotubes deposit and source connection [11].

3.1.2 Laser-ablation Method

Both arc discharge and laser ablation methods use the condensation of carbon atoms generated from the vaporization of graphite targets. Here, the graphite target is placed in a quartz tube surrounded by a furnace (at $1200^0 C$) see schematic diagram fig. 3.2 [26]. The target is vaporized in a high temperature inert gas like argon(Ar) and formed CNTs. The CNTs are transported by the inert gas to the trap, where they are collected. Then CNTs can be found in the soot at cold end [11].

In other way, the pulse laser-ablation method for the production of single-walled carbon nanotubes was developed by Guo et al. [27]. Typically a laser shot is directed to a carbon target and vaporizes a small amount of material in side of an oven heated up to $1200^0 C$. During ablation, a uniform and smooth face for ablation is ensured by laser beam scanning across the target surface under computer control system. The soot produced by the laser vaporization is usually swept by the flowing of working gas (Ar, N_2, etc.). From the high temperature zone, and deposited on to a water-cooled collector positioned out side the furnace [25]. ‘

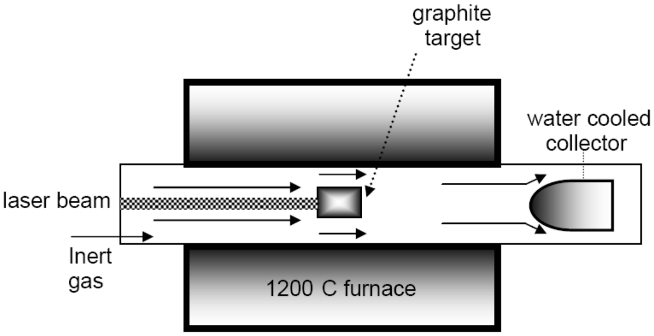

Figure 3.2: Schematic diagram for laser ablation method, with laser beam, inert gas, graphite target furnace and water cooled copper collector [11].

In recent years, the arc discharge and laser vaporization methods are used to obtain high quality CNTs in small quantity. However both methods suffer from the following three draw backs. Disadvantage of arc-discharge and laser ablation techniques are [28]

1. both are need large amount energy to produce arc or laser ablation processes.

2. both methods require carbon/graphite as target which has to be evaporated to get nanotube. It is difficult to get such large graphite to be used as target in industrial processes which limits its exploitation as large scale process.
3. both processes grow nanotubes with highly mixed unwanted form of carbon or catalysts. Thus, CNTs produced by these processes require more purification.

The studies realized until showed that the quality and the quantity of produced material can be controlled to some extent by changing [3]:

- the type of metal catalysts and their ratio.
- the kind of the ambient gas and its pressure.
- the temperature of the reaction furnace.
- the laser parameters.

3.1.3 Chemical Vapour Deposition

The chemical vapor deposition is another method for producing CNTs which produces the best quality nanotubes, in which a hydrocarbon vapor is thermally decomposed in the presence of a metal catalyst. In this method, carbon source is placed in gas phase in reaction chamber as shown in fig. 3.3. The synthesis is achieved by breaking the gaseous carbon molecules, such as methane, carbon monoxide and any acetylene, in the reactive atomic carbon in a high temperature furnace and some times helped by plasma to enhance the generation of atomic carbon. This carbon will get diffused to wards substrate, which is coated with catalyst and nanotubes grow over this metal catalyst [12]. The C_2H_2 chemical vapor deposition was carried out in a quartz tube equipped with a temperature and gas flow control. The Ar gas was passed for 30 minutes over 0.5 gr of Ni-Ce-Zr mixed oxides catalyst in quartz boat at 550^oC. Ar/C_2H_2 (4:1 v/v) mixture was then passed to the system at a flow rate of 120ml/min for 2 h. Passing Ar gas was then continued through the reaction chamber until the temperature of the furnace dropped to 200^0C. The prepared CNTs was then modified by emerging into 20% HNO_3 solution and keeping for several hours followed by washing with distilled water and drying in a vacuum oven at

120^oC. About 1 g of CNTs was obtained [29].

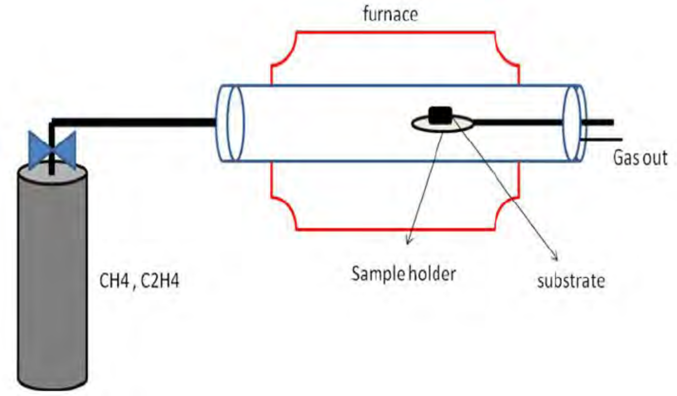

Figure 3.3: Schematic diagram of a CVD setup with furnace, sample holder, substrate and source holder [11].

3.2 Purification of CNTs

Whatever the CNT production method is applied CNTs are always produced with a number of impurities. Its type and amount depend on the type of techniques used. Most of the above mentioned production techniques produce powders which contain only a small fraction of CNTs and also other carbonaceous particles such as nano crystalline graphite, amorphous carbon, fullerenes, and different metals (typically Fe, Co, Mo, or Ni) are introduced as catalysts during synthesis [10]. The carbon nanotubes are having less purity; the average purity is about $5-10\%$, so purification is needed before we use CNTs for actual applications [30]. To increase the quality of CNTs it needs to remove these impurities, the method is known as purification. There are several approaches of purification techniques from these; oxidation, acid treatment, annealing and thermal treatment, ultrasonication, and micro-filtration are well known. During CNT purification process mostly uses a combination of two or more purification techniques to get a more pured CNTs.

3.2.1 Chemical Oxidation

The chemical oxidative purification is based on the idea of selective oxidation etching, where in carbonaceous impurities are oxidized at a fast rate than CNTs. The most common used chemical purification method involves oxidation of as-synthesized CNTs in both gas phase and liquid phase condition [31]. Oxidation is a way to remove CNTs impurities. In this way CNTs and impurities are oxidized. During oxidation time CNTs and impurities are damaged but the CNT is less damages than impurities. The efficiency and yield of the procedure are depending on a lot of factors, such as metal content, oxidation time, environment, oxidizing agent and temperature [11].

Gas-phase Oxidation

Gas phase oxidation is oxidation due to oxidant gases, it is the most successful technique for purification of nanotubes [7]. Air oxidation is useful in reducing the amount of amorphous carbon and metal catalyst particles (Ni, Y). Optimal oxidation condition is found to be at 673K for 40min [27]. In gas phase oxidative purification, CNTs are purified by oxidizing carbonaceous impurities at a temperature ranging from 225^oC to 760^oC under an oxidizing atmosphere. The most commonly used oxidants for gas phase oxidation include air, a mixture of Cl_2, H_2O and HCl, a mixture of Ar, O_2 and H_2O [31].

Liquid Phase Oxidation

Oxidation due to oxidant liquid is liquid phase oxidation. Metal particles can not be directly removed, so further acid treatment is needed. In order to over come this limitation, liquid phase purification that always simultaneously removes both amorphous carbon and metal catalyst was developed. The commonly used oxidants for liquid phase oxidation to produce high purity CNTs in a high yield, include HNO_3, H_2O_2 and $KMnO_4$ or a mixture of H_2O_2 and HCl, or a mixture of H_2SO_4 and HNO_3, or $KMnO_4$ [31].

3.2.2 Acid Treatment

Refluxing the sample in strong acid is effective in reducing the amount of metal particles and amorphous carbon. Some of the acids that are used in this treatment are hydrochloric acid (HCl), nitric acid (HNO_4) and sulphuric acid (H_2SO_4) [11]. Cherent Amente and

Keya Dharamvir applied this method hence CNTs are collected in the form of soot were purified by refluxing in a strong oxidant 8M nitric acid for the removal of catalyst metal for 24 hours. Subsequently, filteration with a 0.25μm filter membrane with the aid of a pump and thoroughly washing with distilled water until the PH value reaches neutral. Finally, the samples were dried in an oven at $100^{o}C$ followed by open air oxidizing for 15 minutes at $400^{o}C$ in a furnace for the removal of impurities [32].

3.2.3 Annealing and Thermal Treatment

High temperature has effect on the productions and paralyzes the graphitic carbon and the sort fullerenes. When high temperature is used, the metal will be melted and can also be removed [11]. Reproducible high-yield purification process of CNTs was developed by combining two step process of thermal annealing in air and acid treatment. This process involves the thermal annealing in air with the powders rotated at a temperature of $470^{o}C$ for 50 minutes, which burns out the carbonaceous particles and acid treatment with HCl for 24houres, which etches away the catalytic metals [9].

3.2.4 Micro-filteration

Micro-filtration is based on particle size or seperation of CNTs and a small amount of carbon nano particles are trapped in a filter. However the other nano particles (catalyst metal, fullerenes, and others impurities) are passing through the filter [11]. The advantage of this method is the nano capsules and amorphous carbon are removed simultaneously and nanotubes are not chemically modified [9].

3.2.5 Ultrasonication

This technique is based on the septation of particles due to ultrasonic vibrations and also mixes of different nano particles will be more dispersed by this method. When an acid is used, the purity of the CNTs depends on the sonication time. During the tubes vibration to the acid for a short time, only the metal is solvated, but in a more extended period, the CNTs are also chemically cut [11].

3.3 Characterization of CNTs

To understand properties of CNTs, it can quite necessary to characterize their structure at an atomic levels by different instrumentation tools. Some of the characterization analysis, used in the nanotechnology science are:-

- Scanning electron microscopy (SEM)
- Atomic force microscopy (AFM)
- Transmission electron microscopy (TEM)
- Raman spectroscopy
- Thermogravimetric analysis(TGA)
- X-ray diffraction (XRD)
- Optical microscopy
- Optical laser microscopy
- Energy Dispersion x-ray (EDX)
- X-ray photo emission spectroscopy (XPS)

These tools are used for answer the following characterization questions:-

- What type of CNTs are being formed: single-walled or multi-walled?
- What is the length, width and aspect ratio (length:width) of the CNTs?
- Are there any contamination or metallic catalysts such as iron or nickel?
- Are the CNTs coated with a chemical?
- What is the quantities or qualities of CNTs being formed? etc.

Even if there are different methods to characterization CNTs, we focus on the following five but more on Raman spectroscopy.

3.3.1 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) is one of the most widely used techniques in characterization of nano materials and nano structurs. The scanning electron microscopy is a microscope that uses electrons rather than light to form an image. The SEM produces images of high resolution, which means that closely spaced features can be examined at a high magnification [34]. Morphology and size of CNTs can be determined by scanning electron microscopy(SEM) with 12 and 15A accelerating voltage [35]. By sending an electron to a specimen surface, several signals can be detected. When the primary electrons are sent; electrons appear to scattered back in high energy and primary electrons can be diffracted with large angles. Secondary electrons are generated when they back scattered electrons emerge from the surface. These secondary electrons have energies between 0 and 20eV and can be attracted to a positively charged detector with high efficiency. There is a large angular detector below the final lens, facing to wards the sample and a proportion of the scattered electron signal can be collected with this detector [3].

3.3.2 Transmission Electron Microscopy (TEM)

The TEM operates on the same basic principles as the light microscope but uses electron instead of light. Due to its much lower wave length, it is possible to get a resolution about thousand times higher than a light microscope of interfaces and defects with high position accuracy [34]. There are a series of magnetic lenses in TEM after electron gun to provide a uniform illumination of the spacimen over the area of interest. The sample is mounted on a stage to provide suitable movement. The primary image is formed by the objective lens. This objective lens determines the final resolution. The final image is projected on to a viewing screen through two or more projection lenses, and can be recorded. The internal micro structure and crystal structure of samples which are thin enough to transmit electrons can be analyzed with Transmission Electron Microscopy(TEM) [3]. TEM uses a high energy electron beam (up to 300KV) to image CNTs based on electron transmission. The length and dispersion state of CNTs can be assessed by TEM at low magnification. At high magnification, TEM can be used to count the number of walls, used to measure outer and inner radius in MWCNTs [19].

3.3.3 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is device that measures the surface topography of a sample on a nanometer/micrometer scale and turn those measurements in to an image. Atomic force microscopy is a type of scanning probe microscopy, where the probe can be used, physically contact with the substrate to obtain topographical information as well as material properties [36]. The basic principle behind the AFM is based on the interaction between a probe(a sharp tip attached to a cantilever) and the atomic surface of the sample. The force on the tip can be attractive or repulsive and cause the tip to deflect due to a charge in these forces, this deflection is detected by the reflection of a laser beam reflect on the back surface of the cantilever as shown in fig. 3.4 [10].

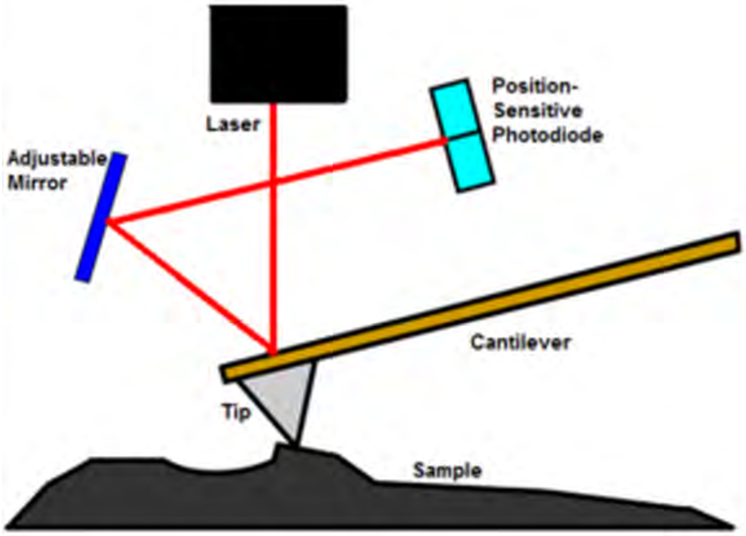

Figure 3.4: Schematic representation for AMF, with sample adjustable mirror, laser, cantilever, and position sensitive photodiod [35].

3.3.4 X-ray Diffraction (XRD)

In x-ray diffraction(XRD) system, electrons emitted from the filament(cathode) are accelerated to target(anode) and x-ray characteristic of atoms in the irradiated area are emitted. This technique is used to obtain some information on the inter layer spacing [11]. X-ray diffraction was exploited in 1913 [37], by English physicists Ser W.H. Bragg and his son Ser W.L. Bragg. On 1915, W.L. Bragg was awarded the Nobel prize in physics

[38]. Braggs' law refers to a simple equation [39], this equation explains why the facts of crystals appear to reflect (diffract) X-ray beams at a certain angle of incidence θ. This observation is an example of X-ray wave interference known as X-ray diffraction(XRD). Braggs' law easily be derived by considering the conditions necessary to make the phases of the beams coincide when the incident angle= reflected angle (fig. 3.5).

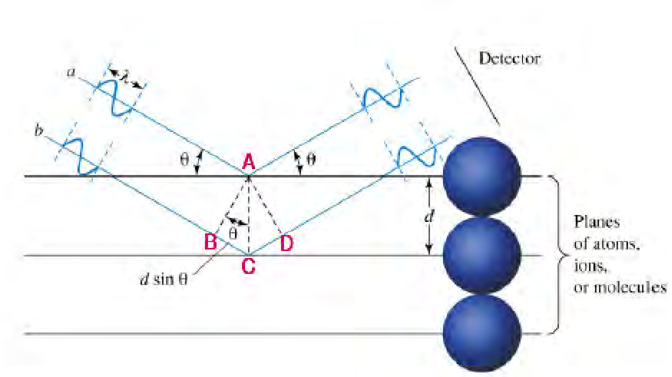

Figure 3.5: Geometry for interference of a wave scattered or reflected from two crystallographic , to derive the Bragg law X-rays (arrows) [39].

$n\lambda = BC + CD$

since $BC = CD$, We have $n\lambda = 2BC$

also $Sin\theta = \frac{BC}{d}$, then this distance BC becomes $BC = dSin\theta$

The distance in path length for the top and bottom rays is equal to one wave length λ

$$\lambda = 2dSin\theta \tag{3.3.1}$$

for n number of orders

$$n\lambda = 2dSin\theta \tag{3.3.2}$$

$$d = \frac{n\lambda}{2sin\vartheta} \tag{3.3.3}$$

where d=lattice inter planar spacing of the crystal or the distance between two successive identical plans of atoms in the crystal, θ= X-ray incidence angle (Bragg's angle) and λ= wave length of the X-ray.

3.3.5 Raman Spectroscopy

Raman spectroscopy is one of the most power full tools for characterization of CNTs. Raman spectroscopy has been extensively used as a nondestructive technique to characterize the complex microstructure of carbon-based materials; it is indeed very sensitive to structural disorder. All allotropic forms of carbon are active in Raman spectroscopy. The position, width and relative intensity of bands are modified according to the carbon forms. And also it gives qualitative and quantitative information on its diameter, electronic structure, purity, crystalline, and distinguishes metallic and semiconducting material [11]. About Raman spectroscopy we discuss more detail in chapter five.

Chapter 4

Applications of CNTs

Carbon nanotubes have unique properties that include large current carrying capacity, high thermal conductivity and high mechanical strength [7]. And also high aspect ratio, high tensile strength, low mass density, high heat conductivity, a large surface area, and a versatile electronic behavior, including high electron conductivity and metallic and semi conducting properties. These extra ordinary properties of CNTs have verity of applications in the area of nano electrons, optics, material science, mechanical and biological fields. The applications of CNTs in different fields are listed below.

4.1 Electromagnetic

1. **Bucky paper**

   Buck paper are thin nanotube sheets which are 250 times stronger and 10 times lighter than steel. Due to these reasons, they can be used as heat sink for chipboard, backlight for LCD screens or Light Faraday cage to protect electrical devices (aeroplanes) [7].

2. **Solar cell**

   CNTs are excellent materials for sun light absorption and to generate solar cells. In addition CNTs can transfer electrons or holes effectively. The most common cells in use commercially are silicon based solar cell [40].

3. **Electromagnetic antenna**

   Due to its durability light weight and conductive properties, CNTs can act as an antenna for radio and other electromagnetic devices [7]. It is quite different from thin copper antenna of the same size and shape [38].

4. **magnets**

   A strong magnetic field can be generated using multi-walled CNTs coated with magnetite [7].

4.2 Mechanical

1. **Body armor**

   Carbon nanotube is an ideal candidate material for bullate proof vests due to its unique combination of exceptionally high elastic modulus and high yield strain, due to these CNT fibers are being used as combat jackets. The jackets used to monitor the condition of the wearer and to provide protection from bullets [7].

2. **Equipments**

   Due to their strong and lighter properties, CNTs are used to make sport equipments like golf balls, tennis rackets, bicycle parts, as indicated in figure 4.1 and base ball bats. And also used to make spacecraft and aircraft body parts [7].

Figure 4.1: Winning Tour de France bicycle used carbon nanotube composite to make some parts of its body [41].

3. **Fire protection**

   Thin layers of Bucky paper can potentially protect the object from fire. The dense, compact layers of CNT or carbon fibers in the form of Bucky paper can efficiently reflect the heat [7].

4. **As catalyst**

   Nanohorns offer large surface area and hence, the catalyst at molecular level can be incorporated into nanotubes in large amount and simultaneously can be released in required rate at particular time. Hence, reduction in the frequency and amount of catalyst addition can be achieved by using CNTs [30]

4.3 Biological

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 emission [7].

2. **Water filter**

   The most important applications of CNT is to be used as a water purifier because now days there is a lot of contaminated water. We can make this contaminated water useful [42]. CNT membranes can aid in filtration. It can reduce distillation costs by 70%. 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) [7].

3. **Filter biological contaminates**

   CNT adsorption capacities in the removal of diverse range of biological contaminates including bacteria, viruses natural organic matter (NOM) and cyan bacterial toxins from water systems. The superior adsorption capacities of CNTs compared to other adsorbents is mainly attributed to their fibrous shape with high aspect ratio, provision of large external surface area that can be easily accessed by biological contaminants and presence of wall developed meso pores [42].

4. **Lubricants**

   CNTs can be used as lubricants in tablet manufacturing due to nano size and sliding nature of graphite layers bound with van der waals forces [23].

4.4 Electronically

1. **Electrical Circuits**

   CNTs are attractive materials in fundamental science and technology. They have demonstrated unique electrical properties for building electronic devices such as CNT field-effect transistors(CNTFETS) and CNT diodes. CNTs can be used to form a p-n junction diode by chemical doping and polymer coating. These types of diodes can be used to form a computer chip. CNT diodes can potentially dissipated heat out of the computer chips due to their unique thermal transmission properties [7].

2. **Inter Connects**

   CNTs have emerged as one of the most potential inter connect material solutions in current nanoscale regime. Chip manufacturers require metallic compounds to serve as a basis for interconnects between transistors on chips. With high conductivity and small dimensions, carbon nanotubes are an alternative interconnect option to copper. CNTs like copper there is no need to embed the interconnects in to trenches on the circuit board, which could make for a simpler manufacturing process [1].

3. **Transistors**

   Transistors form the basis for modern integrated circuits functioning as digital. Single walled carbon nanotubes to act as transistors. Nanotube based switch a molecule can be positioned inside a carbon tube to affect the electronic current following across it [1]. Because of low electron scattering and the suitable band gap, the SWCNTs are also well suited for field effect transistor (FET) architectures and high dielectrics. Experimental results show the current density 2.41mA/m at 0.5v for SWCNT FETs, which is greater than those from silicon device [43].

4. **Batteries**

   Most portable electronic device use rechargeable lithium-ion batteries. These batteries release charge when lithium ions move between two electrodes. Electrodes made of carbon nanotubes can be ten times thinner and lighter than amorphous carbon electrodes, their conductivity is more than one thousand times greater and supply electricity over a long period of time [1, 44]. One of which is graphite and the other is metal oxide. Researchers at the university of North Carolina have demonstrated that by replacing the graphite with SWCNT they can double storage capacity. MWCNTs are widely used in lithium ion batteries for notebook computers and mobile phones, making a major commercial success [41]. CNTs have been combined with indium-gallium zinc oxide (In-Ga-Zno) to build a more efficient hybrid computer chip which is more transparent, flexible, and more energy saving(efficient) than the typical silicon chips [43].

5. **Electron emitters**

   CNTs are emit electrons easily. In electron emission CNTs have become very popular candidate for electron emitter. Electrons are given energy to over come the potential barriers at the metal surface [45].

6. **Supper capacitor**

   Carbon nanotubes have been used in super capacitors producing a power density of 30kw/kg (compared to 4kw/kg for commercially available device). Such super capacitors could dramatically reduce the time it takes to recharge devices such as laptops and cell phones [1]. They have been recognized as potential electrode materials for energy storage device like Super capacitors for storing huge amount of energy. The most significant advantage of Super capacitors are alternative to traditional batteries due to their miniature size, high power density, long life cycle, high energy density, high efficiency, fast charging and discharging, wide operating temperature, Safe and Light weight [44].

7. **Sensors**

   CNTs based sensors can detect temperature, air pressure, chemical gases (such as carbon mono oxide, 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 carries induced in any material. This charge is typically modulated by the adsorption of a target on the CNT surface [7]. In addition, the glucose sensing application, where regular self-tests of glucose by diabetic patients are required to measure and control their sugar levels [30].

Chapter 5

Characterization by Raman Spectroscopy

5.1 History of Raman

The inelastic scattering of light is called the Raman effect in 1928 [15], commonly attributed to sir C.V. Raman (1888-1970) an Indian scientist who was award the Nobel prize in physics in 1930, for his work on the scattering of light and for the discovery of the effect named after him. For sp^2 nanocarbons, Raman spectroscopy can give information about crystalline size, clustering of the sp2 phase within a given sample, the presence of sp^3 hybridization and chemical impurities, its mass density, optical energy gap, elastic constants, doping, defects and other crystal disorder, edge structure, strain, the number of graphene layers, nanotube diameter, nanotube chirality and nanotube metallic vs. semiconductor behavior. Another important area where much work has been done is on disordered, amorphous and diamond-like carbons, as well as graphite and graphene edges [46].

5.2 Simple instrumentation of Raman spectroscopy

Raman spectroscopy is a form of molecular spectroscopy that involves the scattering of electromagnetic radiation by atoms or molecules. Thus, light as composed of particles(photons) are directed to wards a sample and collide. Instrumentation for modern Raman spectroscopy consists of three components: A laser source, a sample illumination system and a suitable spectrometer. The sources used in modern Raman spectrometry are nearly always lasers because their high intensity is necessary to produce Raman scattering of sufficient intensity to be measured with a reasonable signal-to-noise ratio. In addition, when a beam of light passes through a transparent sample of a chemical compound, a small part of the light emerges in different directions. Most of these scattered light is of unchanged wavelength. However a small part has wavelengths different from the incident light, and its presence is a result of Raman effect [3]. In Raman spectroscopy, vibrational modes are identified by measuring the energy of scattering photons generated from a sample exposed to laser light(figure 5.1). The pattern of the Raman spectrum is characteristic for every molecular spaces and the intensity is proportional to the number of scattering molecules in the path of the light. Resonance peaks are also observed in the spectrum which symbolize the presence of a particular specie type and the four dominant feature are radial breathing mode, D-band, G-band or G'- band [12].

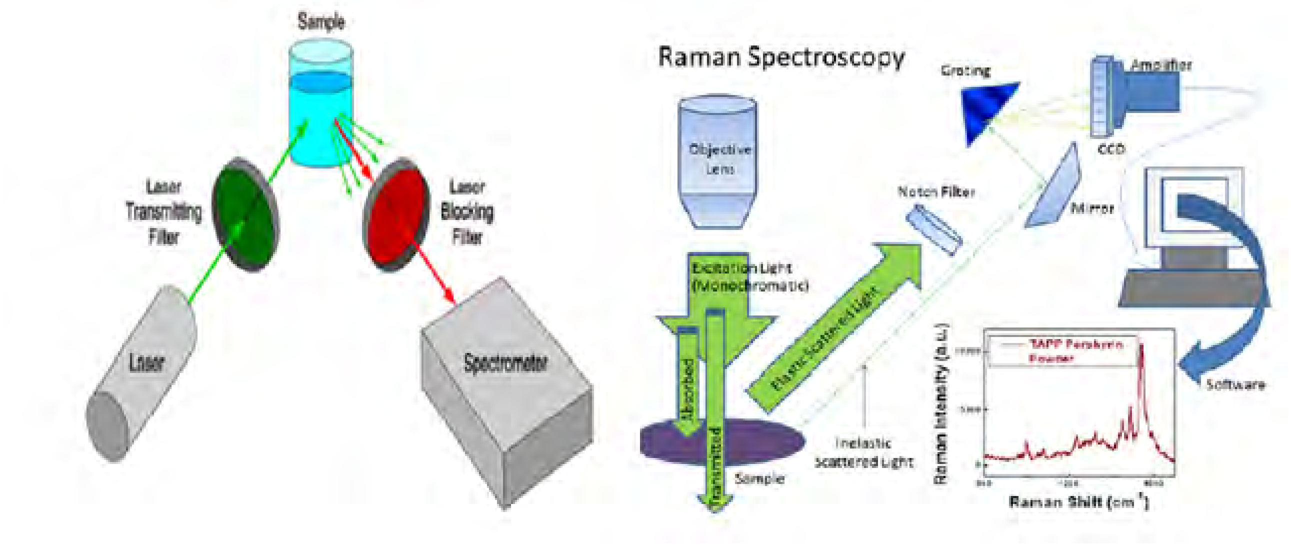

Figure 5.1: Operation of Raman spectroscopy the laser collide to the sample and the light scattered and then converge to wards the Raman spectrometer, finally we see the graph on the screen [47].

5.3 Radial breathing mode (RBM), D-band, G-band, and G'-band

The characteristic spectrum of SWCNTs includes three main zone. At low (100-250cm^{-1}), intermediate(300-1300cm^{-1}), and high(1500-1600cm^{-1}) frequencies [12]. On the other hand, for SWCNTs the four primary features ; the radial breathing mode at 160-300cm^{-1}, the D band at 1250-1450cm^{-1}, the G band at 1500-1605cm^{-1} and the G' band at 2500-2700cm^{-1} appear in these intervals. Each feature relates to the different vibration modes associated with the structure of CNTs [3].

- **Radial breathing mode (RBM)**:- The RBM bands are unique to SWCNTs and as their name suggests, corresponds to expansion and contraction of the tube. The frequency of these bands can be correlated to the diameter of SWCNTs [12]. The diameter of nanotubes, the presence of disorder in sp^2-hybridized carbon systems as well as the effect of nanotube-nanotube interactions on the vibrational modes has been assesses using Raman spectroscopy [48]. From the low frequency range if we take two peaks apper at 156 and 185 cm^{-1}. These peaks can be assigned to the RBMs corresponding to the thinnest inner tube of MWNTs . Using the formula.

  $$d(nm) = 223.9\frac{(cm^{-1}nm)}{\omega_r(cm^{-1})} \tag{5.3.1}$$

  where d is diameter of the tube and ω_r is the frequency of RBMs. We can determine inner most diameter of MWCNTs. Then the two RBMs at 156 and 185cm^{-1} corresponds to inner most diameter of 1.44 and 1.21 nm respectively [49].

- **D-band or defect mode:**- The D band originates from defects, which is a large structure assign of residual-ill organized graphite [12]. The greater the relative intensity, the more defects the CNTs possess [50].

- **G-band:**- The G band frequency related to tangential vibration of the carbon atoms, which is used to determine the diameter of nanotubes, but the information provided is less accurate than the RBM feature, and it gives information about the metallic character of the SWCNTs in resonance with laser light. G-band Raman feature consists of two main components, one peak at $1590cm^{-1}$ (G^{+}), it is independent of the nanotube diameter. And another peak at $\sim 1570cm^{-1}$ (G^{-}) which could distinguished SWCNTs, metallic or semiconducting and also measure the diameter, when the G^{-} frequency decreases the diameter also decreases [50].

- **G'-band:-** The G' band is the second strongest after the G mode and the second over tone of the defect induced D band. Determine the number of graphene layers. In general the D Raman feature and G' Raman feature of all sp^2 carbon materials are posses similar properties [50].

Measuring disorder with band ratio

The quality of a sample has often been evaluated using the $\frac{I_D}{I_G}$ band intensities. The intensity ratio is used to characterize the degree of formation of carbon materials. A small $\frac{I_D}{I_G}$ ratio, in the range of 0.1-0.2, indicates that the defect level in the atomic carbon structure is low, and it means that corresponds to higher degree of CNTs, formation, reasonable crystalline quality observed but the larger in $\frac{I_D}{I_G}$ ratio can be as indicator for structural defects of CNTs [12]. The ratio of $\frac{I_D}{I_G}$ graphite powder before arc- discharge contains large amount of defect concentration to that of graphite powder as prepared (CNT) [51]. Similar intensities of these bands has greater intensity band ratio this indicate a very high structural defects in the CNTs. The ratio between D and G band and the RBM and its relation to the diameter distribution are very important factors allowing one to distinguish between three types of nanotubes with a single analysis [52].

5.4 The Experiment

For this project we used a sample of carbon nanotubes prepared by the arc discharge method in which a d.c of 50-200A driven by 40V created a high temperature discharge between the two electrodes that are mounted with graphite rods. Crystal purity and concentration was tested by the Raman spectroscopy technique recording at room temperature using RENISHAW-Raman equipment operating with argon laser of one excitation and 514nm.

5.5 Results and discussion

The graphite powder pristen sample was annealed at 400^0C for 30 minutes. The recorded data of the Raman spectra is plotted as in figure (5.2), where the first D band is found to be at about $1355cm^{-1}$ and the second, G band at about $1578cm^{-1}$. The ratio of the intensity of D peak to the G peak is 0.85. This result shows that there is a great defect concentration, indicating the presence of large amount of impurity in the as prepared sample, corresponding to the lower degree of CNT's formation. The other peak representing $2705cm^{-1}$ the second order graphene or G' peak. The graph also shows that there are D' bands peaks including the presence of randomly distributed impurities on surface. The remaining peaks demonstrate the presence of noise due to luck of experimental safety.

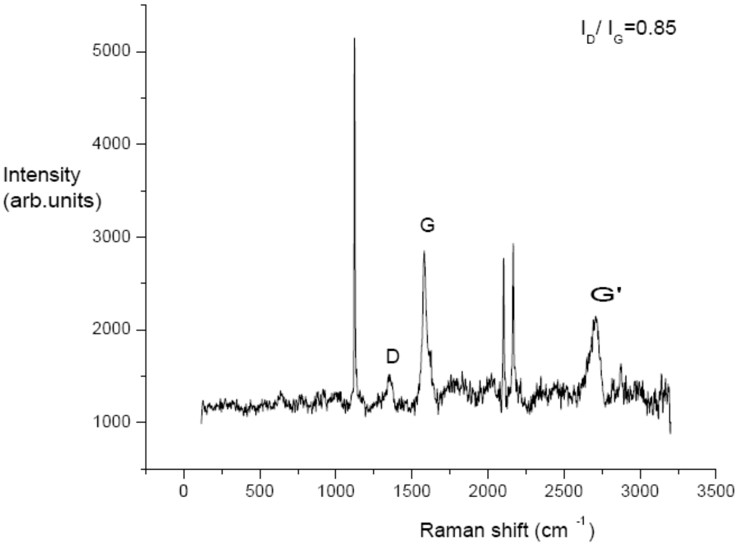

Figure 5.2: Raman spectra for CNTs pristine (as prepared) sample, with out further treatment by heating or acidic(reflexing).

Chapter 6

Summery and Conclusion

A better synthesis methods for higher yield, higher purity and low defects of produced CNTs are main points of research which are pushed forward by the successful fields of nanotechnology and nanoscience. Carbon nanotubes are clearly basic and interesting allotropes of carbon materials exhibiting a variety of novel properties. Production, Purification, and characterization are the key issue of CNTs. In this project, the different synthesis methods of CNTs have been reviewed. The CNTs are prepared by three main methods, arc discharge, laser vaporization and chemical vapor deposition methods. Many investigations in to the properties of CNTs and their potential applications require pure CNTs that contain no impurities. A number of purification methods have been developed to purify the synthesized CNTs for their unique applications. SEM, TEM, AFM, XRD and Raman spectroscopy are some of techniques used for characterization.

Raman spectroscopy is one of the most power full tool for characterization of CNTs. We have used a data from Raman spectroscopy to plot a graph as in figure 5.2 to analyzes. Accordingly to different peaks are observed indicating defects and graphite intensities, and hence the pristine sample contain large amounts of impurity.

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DECLARATION

I hereby declare that this MSc dissertation is my work and has not been presented for a degree in any other universities, and that all sources of material used for the dissertation have been duly acknowledged.

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