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Nanotechnology, Carbon Nanotubes (CNTs) and Applications

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Introduction

As we know that man learnt a lot from nature and natural phenomenon in the universe. With the help of natural phenomenon, man has developed the different techniques for better technology. Although his manufacturing practices and understanding abilities are primitive. Man, always tries to go close to nature by just creating the understanding abilities of the natural phenomenon occurring in the universe in one form or another form [1].

By comparing the natural phenomenon and the modern technology gives us the clear indication that how much we are away from the natural technology occurring in the natural phenomenon in the universe. In case of energy storage, modern technology has done much development but it will never get the efficiency of storing energy like Photosynthesis occurring in the nature [2].

In case of water purification, factories are unable to purify water as efficiency as it occurs in water melons and in coconut. The human brain is hundred and thousand times as efficient as today's super-fast computers. It can store much information as compared to electronic devices like super-fast computers. In case of camera industry, modern cameras are nothing in front of normal human eye. A human eye can capture more vivid images of the objects as compared to cameras with high magnification. At last but not the least, the highly sensitive sensors produced by modern technology are nothing in front of olfactory receptors of the dog. They are super sensitive and responsive as compared to sensors produced by modern technology [3,4].

Nanotechnology may be defined as the investigation, understanding and control of material in the range of 1-100nm in at least one dimension. At this dimension scale the material shows the novel applications and new physics and chemistry can be generated. At the nanoscale, the physical, chemical, and biological properties of materials differ in fundamental and valuable ways from the properties of individual atoms and molecules or bulk matter. The devices are being fabricated with in these ranges which are showing better efficiency as compared to the devices fabricated in bulk level. A nano meter is one Billionth of a meter and numerically it is written as 10^{-9}m or 10Å [5,6].

Nanometers are so small that 150,000 of them fit across the width of a strand of human hair. Generally, nanoparticles involve the range of 1-100nm. Nanotechnology is very much complex field including science (biology, chemistry & physics), information technology (computer programming), engineering (electronics & design) and mathematics. This technology is mostly directed to understand and create modified designed material, devices and systems which exhibit the new improved properties. It is also considered as the size effect technology in which different properties gets changed due to the dimension scale. With the help of nanotechnology, the same material gets different applications as per the dimension level. With the help of nanotechnology, we are fabricating different materials atom by atom [7,8].

The power of nanotechnology is rooted in its potential to transform and revolutionize multiple technology and

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industry sectors, including aerospace, agriculture, biotechnology, homeland security and national defense, energy, environmental improvement, information technology, medicine, and transportation. Discovery in some of these areas has advanced to the point where it is now possible to identify applications that will impact the world we live in. Nanotechnology is the emerging field in present time and it is believed that this will be the progressive field in future also. This technology is changing the face and structure of the world. New nanomaterials are being designed and fashioned as per the application point of view [9,10].

From these nanomaterials Carbon Nanotubes (CNTs) are one of them. It is considered as the material of 21th century and is attracting much attention of scientists and research scholars. As we know the history of scientific discoveries, fullerenes were accidently discovered. In 1985, Kroto and Smalley found strange results in mass spectra of evaporated carbon samples. From the same date fullerenes were discovered and their stability in gas phase was proven [11,12].

Fullerenes are a molecular form of carbon distinct from graphite and diamond. “Fullerenes” were named after the architectural designer, Richard Buckminster Fuller, for their resemblance to the geodesic dome. Fullerenes can be spherical, ellipsoid, or cylindrical arrangements of dozens to hundreds of carbon atoms. A spherical fullerene made of exactly sixty carbon atoms is called buckminsterfullerene (C_{60}) looks similar to a soccer ball and is often referred to as a “buckyball.” Cylindrical fullerenes are known as buckytubes or most commonly “nanotubes.” One hemisphere of a Bucky ball can be used to cap the ends of a nanotube.

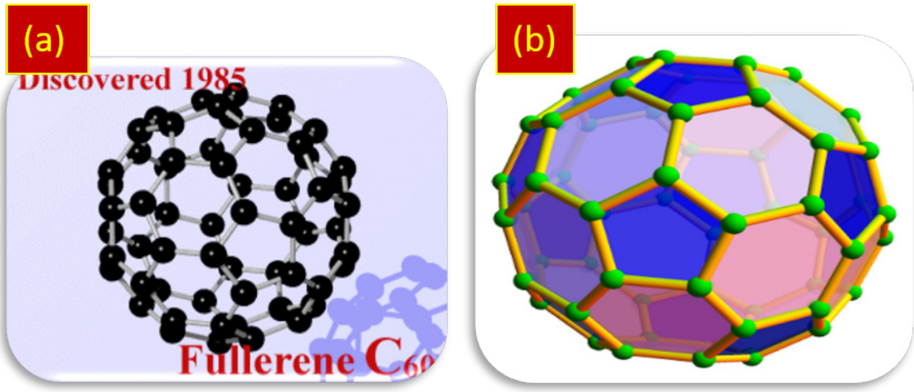

Figure 1: (a) and (b): Structures of Fullerene.

Buckyballs could be used as diagnostic tools, or drug delivery vessels. They also have potential as superconductors, catalysts, Scanning Tunneling Microscope tips, etc. The schematic diagram of fullerene has been shown in figure 1 (a) and (b) [13,14].

It is assumed that Carbon Nanotubes (CNTs) are formed by rolling the graphene sheet. The single layer of graphite is known as graphene. On the other hand, the layers of graphite are weakly bonded to each other. The interlayer distance is estimated ~0.34 nm. The graphene is also known as zero band gap semiconductors. The graphite is a soft material due to very weak interlayer coupling.

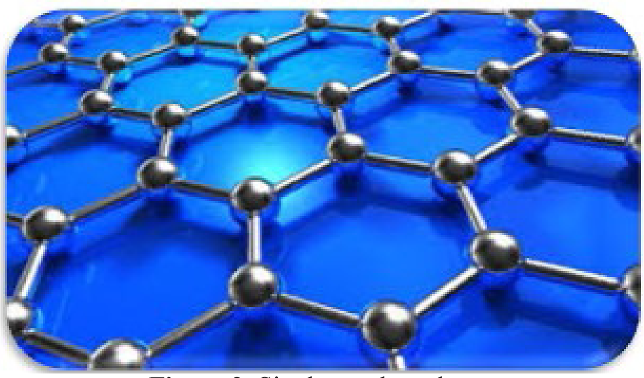

Figure 2: Single graphene layer.

Due to this the graphite is being used in writing. The graphene sheet showing the carbon atoms bonded to each other has been shown in figure 2. Iijima presented some transmission electron microscopy observations of elongated concentric layered which he named carbon nanotubes. Carbon Nanotubes (CNTs) are defined as tube shaped, hollow cylinders made of seamlessly rolled graphene. CNTs have a diameter in the range of nanometer scale.

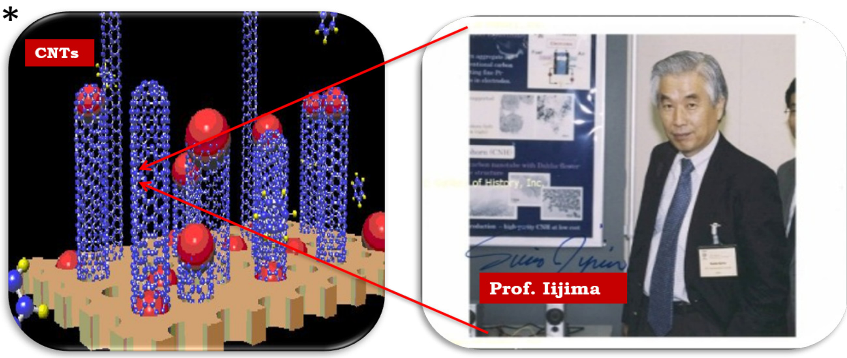

Figure 3: CNTs and their discoverer Prof. Iijima.

So structurally well–ordered CNTs were discovered and their structures were well characterized by Iijima in 1991. The CNTs with their discoverer has been shown in figure 3.

There are various ways of folding the graphene sheet. Due to the extent of variation of helacity, numerous carbon nanotube structures are possible. Carbon Nanotubes (CNTs) composed of one sheet of graphene are called Single- Walled Carbon Nanotubes (SWCNTs), and those made of more than two sheets are called Multiwall Carbon Nanotubes (MWCNTs). The electronic structure of CNTs varies on the variation of helicity [15,16].

Mostly the structure of CNTs is highly described with tube diameter (d) and a chiral angle. The chiral vector is defined as $C = na_1 + ma_2$. The a_1 and a_2 may be defined as unit vectors in the two-dimensional hexagonal lattice. All the parameters have been shown in figure 4 (a). In single sheet of graphene, the carbon atoms are hexagonally connected with each other. The graphene layer and the mechanism of rolling it have been shown in figure 4 (b).

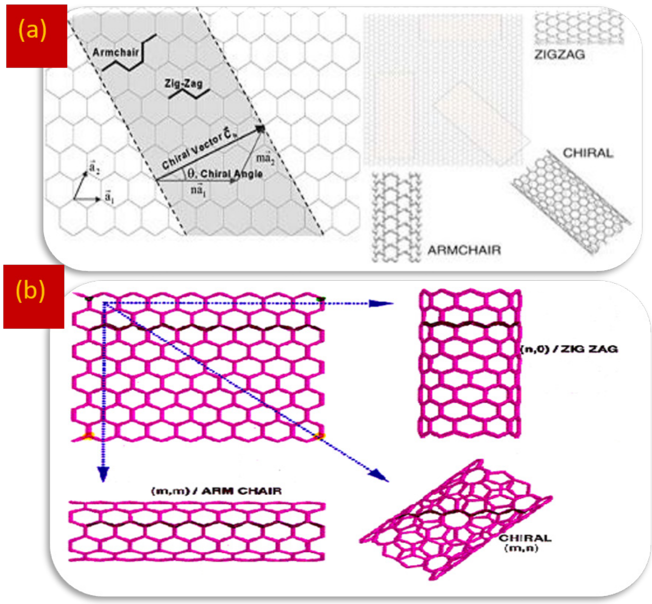

Figure 4: (a) Various parameters of CNTs (b) Helacity of graphene sheet.

The properties of CNTs usually depend on the chiral angle (θ) and the diameter d. The pair of indices represents the way of wrapping of the graphene sheet. The integer n, m represents the number of unit vectors in two directions on the graphene sheet. The CNTs are generally characterize by the pair of (n, m) indices [17,18].

The (n, m) indices specify the structure of (SWCNTs). By rolling the graphene in various ways, different CNTs structures are being obtained which depends on n, m values. The CNTs with n, n notation is called armchair and the angle (θ) is 30^0 while the CNTs with notation (n, 0) are called zigzag where angle (θ) is zero (0^0). The CNTs with notation n, m is called chiral and angle varies from 0^0 to 30^0 [19,20].

Types of carbon nanotubes

Single wall carbon nanotubes

Single-Wall Carbon Nanotubes (SWCNTs) are defined as the tubes of graphite. They are obtained by a single cylindrical wall of graphene. A single carbon atomic layer forms the wall of the tube called graphene. Mostly SWCNTs have diameter in the range between 0.6 nm and 5 nm and the length may be in micrometre. The growth of Single Wall Carbon Nanotubes (SWCNTs) is much difficult as compared to (MWCNTs). With the good flexible property CNTs can be bent, twisted, flattened without breaking [21,22].

Due to extra ordinary structure of SWCNTs, they have different electronic and mechanical properties. With these extra ordinary properties, they can be used in different advanced market applications, such as field-emission displays, nanocomposite materials, nanosensors, and logic elements. These materials may be defined as the backbone of electronic fabrication in present and future technology. They have well characterized structures and properties [23,24].

The ends of tube made from a rolled graphene remain open, but CNTs synthesis are capped by a curved graphene or by a metal particle used as catalyst in the synthesis process. Pentagons must be inserted in to a graphene sheet in order to render a positive curvature to the sheet. Six pentagons are required to form a hemi sphere dome of a curved graphene, like the half of the C_{60} fullerene, and to close one end of a Carbon Nanotube (CNT). The figure 5 shows three structures of single wall carbon nanotubes formed by the graphene sheets [25,26].

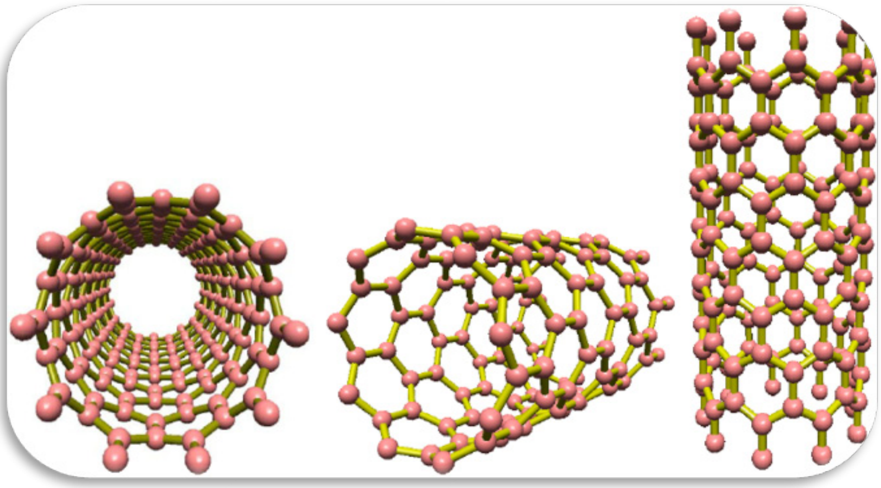

Figure 5: Three different structures of SWCNTs.

Multi wall carbon nanotubes

When a number of graphene sheets are rolled in a concentric way, Multiwall Carbon Nanotubes (MWCNTs) are obtained. The number of sheets rolled in a concentric way varies. Usually the interlayer spacing between rolled graphene sheets is 0.344 nm on average.

The diameters of Multi Wall Carbon Nanotubes (MWCNTs) usually fall in the range of 4-50 nm. The length is in micro mete (µm). MWCNTs contain narrow cavities (2-10 nm in diameter) in the center. The growth of the MWCNTs is simpler then the (SWCNTs). But to study the structures of MWCNTs is very difficult due to its greater complexity and diverse variety. Due to the large defects in MWCNTs, their properties can alter, and they can find less application in advanced technology. The CNTs can be metallic or semiconducting. Figure2.6 shows the structures of MWCNTs.

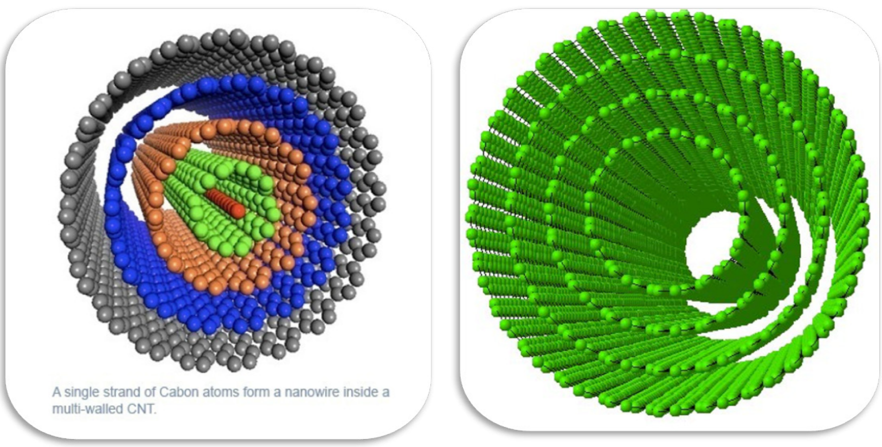

Figure 6: Multi wall carbon Nanotubes.

The Multi Wall Carbon Nanotubes (MWCNTs) have advantages over Single Wall Carbon Nanotubes (SWCNTs), they are easy to prepare. They have low product cost per unit and are also able to enhance thermal and chemical stability [27,28].

Properties of CNTs

Many scientific groups are exploring different properties and different field of applications in the nanotechnology. The CNTs has revolutionized the whole world with their extra ordinary properties and applications. In case of strength, they are 200 times stronger than best steel [29,30]. Tensile Strength of carbon nanotubes is 11- 63 GPa and high strength steel is ~ 2 Gpa.

In case of stiffness, carbon nanotubes are showing 1250 G Pa, Carbon fibers 425 GPa (max.) and high strength steel 200GPa. This strength is due to strong hexagonal carbon carbon (C-C) bond in the carbon nanotube structure. Space elevator models are being proposed on the basis of this property with carbon nanotubes.

On the other hand, many studies show that CNTs show both metallic and semiconducting nature and it depends on the chirality, twist and diameter of the tubes. The current density of metallic tube has been reported 4×10^9 A/cm^2 [31,32]. The current density value is much higher as compared to copper. This conductance is mainly due to the small-scale dimension of CNTs because every electron is capable for conductance. At this scale, all the electrons are at the surface and this conductance is known as ballistic conduction. With the both conducting and semiconducting nature of CNTs, there is wide variety of possibility for nanoelectronic devices. The chiral index n, m values of CNTs play a great role in deciding the metallic and semiconducting behavior of CNTs and this has been already discussed in section 2.1.

In case of density, CNTs are less dense then the aluminium. The reported density of carbon nanotubes is 1.33 – 1.40 gram/cm^3 while Aluminium has 2.7 gram/cm^3. Due to this low density and high strength carbon nanotubes composite find use in sport equipment and other lightweight materials [33,34]. The thermal property of CNTs is also very high. Before the invention of carbon nanotubes, diamond was considered as the best thermal conductor. CNTs are showing thermal conductivity 3000 Watts per meter-degree Kelvin.

The reported value of thermal conductivity of diamond ranges 900-2300 W/m-K, while copper is only about 400 W/m-K. In comparison of these materials, the CNTs thermal conductivity is very large. It is obvious that phonon or lattice vibrations are the exclusive carriers of heat in any kind of material. Due to the long order range (crystallinity), CNTs possess large phonon free path and this results high thermal conductivity. The thermal stability of CNTs has been reported 2800^{0}C in vacuum and 750^{0}C in air [35,36].

CNTs possess excellent field emission properties. As they have high melting point and good thermal stability with large electrical conductivity which results a high current density at low turn on field. Vertical alignment with high aspect ratio and the tip type geometry of CNTs is very favourable for electron field emission [37,38].

Since their discovery in 1991 by Iijima, they have been creating much interest among the researchers and scientists. Due to their unique geometry and morphology and enhanced properties, they can have many applications.

Due to the recent and excellent development in the nanotechnology, CNTs are being used as good chemical sensors. They are very highly sensitive, selective, low cost and portable and low power consumable sensors. The highly known gas sensing principle is the adsorption and desorption of gas molecules on sensing materials.

When CNTs are exposed to different gaseous, the electrical properties get changed and can be detected by various methods. It is well understood that by increasing the contact interface between the analyte and sensing specimen, the sensing ability can be drastically enhanced [39,40].

Methods of synthesis of carbon nanotubes

There are many methods of formation of carbon nanotubes. In all the methods for the preparation of carbon nanotubes, carbon is first generally brought into gaseous phase and then condensed. For the growth of carbon nanotubes, the source of the carbon is either solid graphite or a gaseous compound such as hydrocarbon. For the growth of single wall carbon nanotubes, a metal catalyst such as iron (Fe) or nickel is usually needed. Multi wall carbon nanotubes can be grown without catalyst.

As per the literature survey, there are three main techniques for the growth of CNTs. The main three techniques are as follows: (1) arc discharge technique [41], (2) laser ablation technique [42], (3) Chemical vapour deposition (CVD) technique [43,44].

Arc discharge technique

This is the very old and first technique for the growth of CNTs. The CNT growth processes occur in the vacuum chamber. In the vacuum chamber, two carbon electrodes are being used as carbon source. To increase the carbon deposition, inert gas like helium or argon is being used. A very high dc voltage is applied to both the electrodes. Usually a potential of 20-25v is applied across electrodes of 5-20μm diameter and separated by 1mm. A desired flow of helium at 500 torr is maintained.

A sufficient amount of plasma is generated for the evaporation of carbon atoms. Many carbon atoms are being ejected from the positive electrode and are being deposited on the negative electrode for the growth of CNTs. A good amount of cylindrical carbon nanotubes is being deposited on the cathode.

During the process of growth of carbon nanotubes, the electrode length gets decreased. The CNTs are being deposited on negative electrode. A sufficient cooling helps in more and smooth deposition of cylindrical carbon nanotubes. Usually the electrodes are water cooled. A sufficient amount of vacuum (10^{-6}) torr is being created in the chamber [45].

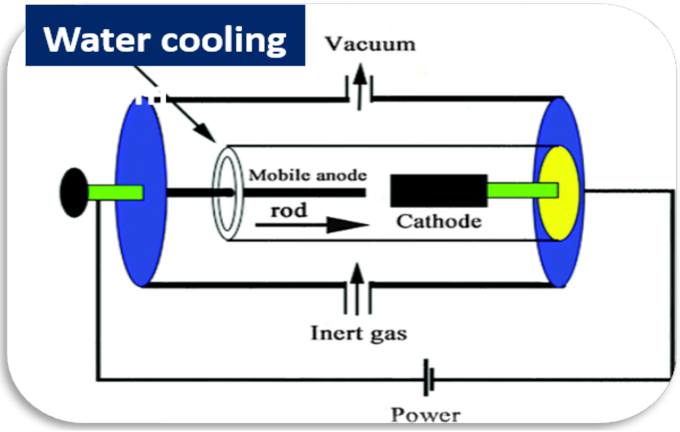

Figure 7: Arc discharge setup for CNT Growth.

The growth of CNTs increases with the increase of pressure. For the growth of single wall carbon nanotubes, a small amount of cobalt, nickel, or iron is being corporate in the central region of positive electrodes. Without catalyst, multi wall or nested carbon nanotubes are obtained. The carbon nanotubes obtained by this technique are of several nm in diameter and length may be in micrometer. The apparatus used for production of carbon nanotubes by arc discharge method is shown in figure 7.

Laser ablation technique

The second technique for the growth of CNTs is laser ablation technique. Generally, a quartz tube with argon gas and graphite target are being heated up to 1200^{0}C. But somewhere outside the furnace, a water cooled copper collector is placed. The graphitic target is being associated with some catalyst particles like iron or cobalt that provides the nucleation sites for the formation of CNTs [46].

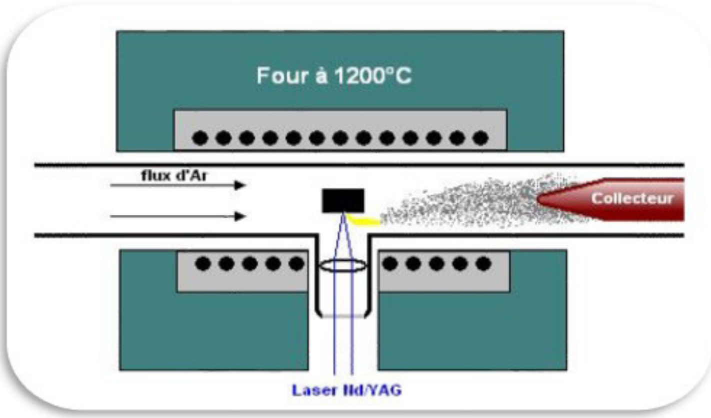

Figure 8: Laser ablation technique.

A highly intense beam of laser is being incident on the graphitic target. This intense beam evaporates some carbon atoms from the graphitic target. The argon gas than sweeps evaporated carbon atoms from the higher temperature zone to the lower temperature zone (cold copper collector) and gets condense on copper collector and hence the growth of carbon nanotubes takes place. The mechanism and diagram of apparatus of laser ablation technique is shown in figure 2.8.

Chemical vapour deposition technique

The third growth technique of CNTs is Chemical Vapour Deposition (CVD). This is considered as the best technique of CNT growth. This technique uses a carbon source in the gas form for the growth of CNTs.

Actually, chemical vapor deposition technique is a two-step process. In the first step, a thin layer of transition metal catalyst such as iron, nickel particles are being deposited by RF-Sputtering technique on the silicon substrate. The thickness of catalyst deposited layer is usually in nm range. The diameter distribution of CNTs depends on the size of catalyst particles [47].

The RF-sputtering technique consists a vacuum chamber, rotary, diffusion pumps, targets of transition metals, argon gas cylinder and radio frequency source for power supply. The schematic illustration diagram of RF-Sputtering has been shown in Figure 2.9.

The substrate is being cleaned through ultrasonic bath then it is dried at room temperature. The dried silicon or other substrate is subjected to the chamber of RF-Sputtering system [48].

A sufficient amount of vacuum is being created in the chamber for the proper deposition of catalyst particles without any contamination. The RF power is about 100w or it can vary as per the requirement. Plasma is being created by RF-frequency that acts as energy source between anode and cathode.

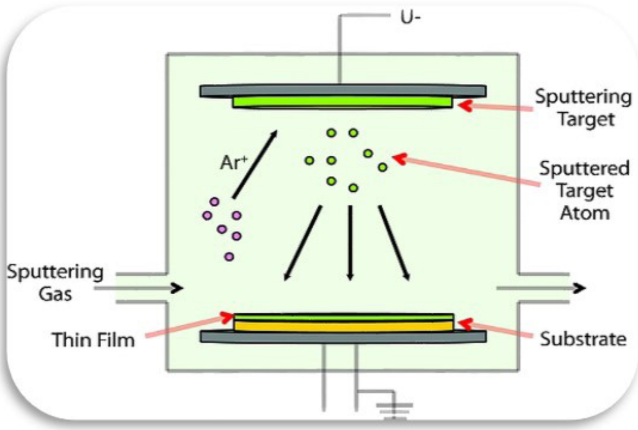

Figure 9: RF-sputtering technique.

The deposition time depends on the operator and it is usually a few min. The film thickness depends on time of sputtering, concentration of gas etc. The catalyst deposited substrate is then removed for the growth of (CNTs). The catalyst deposited substrate is then loaded into the chemical vapour deposition (CVD) chamber for the growth of CNTs. The assembly is associated with the resistive heating coil for the transfer of energy into the gas molecules and to dissociate it into its components properly [49]. The most commonly used carbon sources are C_2H_2, CH_4 and CO_2. Other gases like nitrogen and ammonia are also used during the growth processes. Nitrogen N_2 acts as the carrier gas while ammonia dilutes the source gas so that best result can be obtained.

The process temperature is being used to creak the molecule into the atomic carbon. Carbon atoms are than diffused towards the substrate which is coated with catalyst particles commonly iron (Fe), nickel (Ni) and cobalt (Co). These nano catalyst particles are helpful for providing the nucleation sites for the growth of CNTs.

Different parameters like temperature, vacuum and concentration of source gas, size of catalyst particles and time of reaction are being optimized so that best growth of CNTs takes place. The catalyst particles play a great role in the preferential growth of CNTs. Growth of MWCNTs takes place without catalyst but single wall carbon nanotubes require the presence of catalyst. The chemical vapour deposition (CVD) apparatus is shown in figure 10 [50].

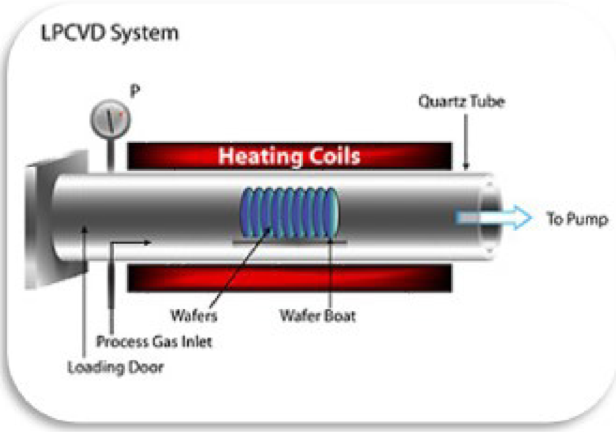

Figure 10: Schematic diagram of CVD.

Chemical vapor deposition technique involves the pumping system for the creation of vacuum in the chamber, quartz tube, electric heater for temperature growth, assembly of gas pipes and attached gas cylinders. The growth of CNTs takes place at high temperature [51].

The required temperature is raised due the resistive heater in the chamber. The most commonly source gases are C_2H_2, CH_4. The temperature of the furnace cracks the molecules into atomic carbon. The carbon then diffuses towards the catalyst-based substrate. The catalyst-based substrate is heated and the catalyst particle provides the nucleation sites for the formation of CNTs. Various parameters have to be optimized for the proper growth of (CNTs) on the substrate. The optimized parameters are temperature, concentration of source gas, size of catalyst particles, and time of the reaction etc [52].

Plasma enhanced chemical vapor deposition technique

Plasma Enhanced Chemical Vapour Deposition (PECVD) is the best alternative, excellent and most modified technique of Chemical Vapour Deposition (CVD) for the growth of CNTs. In this technique, the growth of CNTs takes place in the presence of plasma at low temperature. The technique consists two parallel plate electrodes which are generally hosted in the vacuum chamber. Both the electrodes play the important role in this technique. The upper electrode is connected with ground and the second lower electrode is used to hold the Fe deposited silicon substrate and is also connected with RF power supply [53,54].

The lower electrode is also connected with the resistive heating assembly to provide the adequate heating to substrate inspite of plasma heating. An excellent cooling arrangement is also associated beneath the substrate. For the supply of gases in the chamber, an excellent shower head is attached from the upside in the chamber. A mechanical pumping system is also associated with the PECVD reactor to create the adequate vacuum in the chamber for the operation. The operating pressure is about 10^{-3} torr in the reactor. The whole reactor/chamber assembly is shown in figure 11.

PECVD is mainly classified on the bases of plasma source. The most commonly plasma source which is used in the growth of CNTs is direct current (dc) plasma source. The dc source wastes a lot of power in accelerating the ions. One should use the power efficiently. There are many chances for the damage of substrate due to the high applied voltage. Radio frequency is other alternative source for the creation of plasma.

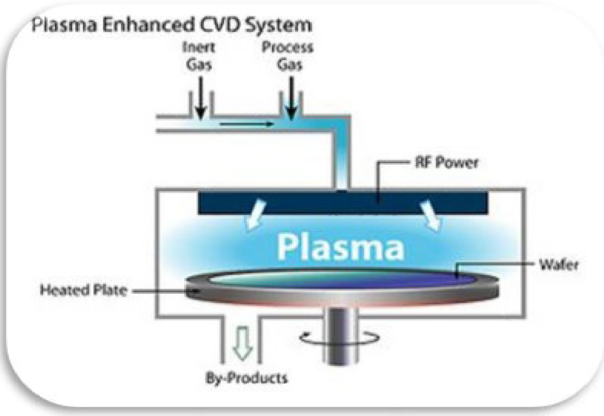

Figure 11: Schematic of PECVD technique.

The radio frequency inductively coupled plasma is also used for the growth of CNTs and it provides high density plasma at low pressure. Usually the induction coils are placed outside the vacuum chamber and are being separated from the plasma by a dielectric window (alumina or quartz). Generally, the inductive coil is the excellent and primary power source for the generation of plasma [55]. The platform of the substrate is independently connected with dc or RF power for the variation of bias. The third one plasma source is the microwave plasma (MPCVD). It is a very high-density source of plasma which uses a 2.45GHz source. It is also being used in various deposition techniques in research field.

However, the generation of plasma and deposition processes takes place in separate zones or it can be done in a single zone. In this case the substrate can be biased by using dc or RF power supply for controlling the substrate voltage. All the plasma sources discussed here require the good vacuum for the sustenance of plasma. Generally, PECVD is known as low temperature technique for CNT growth. The plasma provides the energy to the source gas and dissociates it properly into its constituents. This is the significance of plasma heating [56].

At this step when the source gas gets breakdown by the energy of plasma carbon nanotubes CNTs formation takes place. The catalyst particles help in the nucleation of carbon atoms on the substrate and the carbon atoms are being binded in a hexagonal pattern and hence the growth of CNTs takes place. Through (PECVD) or by other techniques, Single Wall Carbon Nanotubes (SWCNTs) require transition catalyst particles for their growth.

The diameter distribution of CNTs depends generally on the transition metal catalyst particles which are being deposited by RF-Sputtering technique. The growth of CNTs by PECVD is very complex phenomenon and numerous coupled phenomenon are associated with it. The phenomenon like plasma chemistry, surface chemistry, neutral and ion reactions, catalyzed growth, catalyst effect, electric field effect, effect of heat and mass flow and others [57].

The parameters which dictate the growth characteristics include source gas, dilutents like H_2, N_2, Ar etc, source gas composition and flow rate, nature of plasma power input, the nature of substrate and substrate temperature and catalyst particle size etc. All these parameters are being optimized during the growth of CNTs [58].

Role of plasma in growth of CNTs

As we know the plasma is the fourth state of matter. The other states are solid, liquid and gas. Plasma is formed by the high ionization of gaseous and it contains the similar properties to that of metals. Plasma occurs as the most abundant form of matter in the universe. Mainly plasma may be defined as the electrically neutral medium with positive and negative particles. This means that net charge of plasma may be considered as zero. The free charged particles may be ions and electrons. These particles are formed by the gas discharges. There are mainly two types of plasma specially used in CVD reactors. They are (1) arc discharge plasma (2) glow discharge plasma. Arc discharge plasma is composed of very high ion and electron densities (10^{14}-$10^{19}cm^{-3}$). In this case the electrons and ions have approximately same temperature. This means that they are in thermally equilibrium state. The temperature of electrons and ions may be 0.1-2 eV. Due to these characteristics, the arc discharge plasma may be considered as high temperature range (3000-6000K).

This cannot be used directly for direct deposition of thin films on substrates. It is commonly used for carbon nanotube growth. The arc discharge plasma generated between carbon rod electrodes induces evaporation of the carbon rods because of the high temperature of the arc discharge plasma [59].

The evaporated carbon forms a deposit or soot on the cathode in the chamber wall. The deposit and soot contain carbon nanotubes. On the other hand, glow discharge plasma is weakly ionized plasma with electron temperatures of 1-10 eV, and ion and electron densities of 10^8-10^{13} cm^{-3}. Teo et al have done a careful study to indicate the signifience of plasma heating for CNT growth.

They have achieved a substrate temperature of 700^0c without the external heating in the chamber. This study confirms that the temperature in the chamber is being created due to the plasma only and the CNT growth takes place. The high energy electrons assist in the dissociation of gas molecules. This effects substaintly lowers the growth temperature in PECVD. Another effect of plasma on CNT growth is high electric field generation in the sheath region. This electric field stems from the potential difference between the plasma and the substrate, and sheath thickness. The electric field applied to the substrate serves as a driving force for CNT directional growth toward the electric field, which results in perpendicular CNT growth on the substrate [60].

Growth mechanism of carbon nanotubes (CNTs)

Carbon nanotube growth mechanism is a very challengeable and debatable since their discovery. However, several scientific groups have proposed several growth mechanisms of carbon nanotubes which are often contradicting with each other. Therefore, it is very difficult to say the perfect growth mechanism of CNTs.

The widely accepted and most general growth mechanism of carbon nanotubes is described as under. Generally, the hydrocarbon vapors interact with hot metal nanoparticles. At first stage, the hydrocarbon gets breakdown into its constituents' carbon and hydrogen species. Carbon is being dissolved in the metal and the hydrogen flies away. At a particular temperature, the carbon gets its solubility limit in metal. Then the dissolved carbon in metal precipitate and its crystallization starts. The precipated carbon is fashioned in the form of cylindrical network and forms the CNTs [61].

The CNT network design is most stable and is without any dangling bonds. The hydrocarbon decomposition is considered as the exothermic reaction. As it releases some amount of heat to the metal exposed zone. On the other hand, carbon crystallization is endothermic process because it absorbs some amount of heat from the metal's precipitation region.

Two general cases arise here. (1) When the metal catalyst has an acute contact angle with substrate, the catalyst interaction with metal is very weak. In this case, the hydrocarbon starts growing from the top of the surface of the metal. The carbon starts diffusing down from the metal surface. The growth of carbon nanotubes starts from the metal bottom. The metal particles are being pushed up as shown in figure 12 (a).

The second growth mechanism is shown in figure 12 (b). In this case metal has a strong contact with substrate. The metal particles make obtuse contact angle with the substrate as shown in Figure 12 (b). At the first the hydrocarbon decomposes, and diffusion of carbon takes place as in tip growth. In this case the CNT precipitation gets fail in pushing the metal particle up from substrate. Generally, the precipitation takes place from metal surface [62].

Carbon atoms crystallize as the hemispherical dome. This hemispherical dome then extends into a seamless cylinder called CNTs. The hydrocarbon diffusion takes place from the lower surface of the metal. Due to the passage of time carbon diffuses upwards. The CNTs can be rooted on the base of metal particles. This growth mechanism is known as base growth.

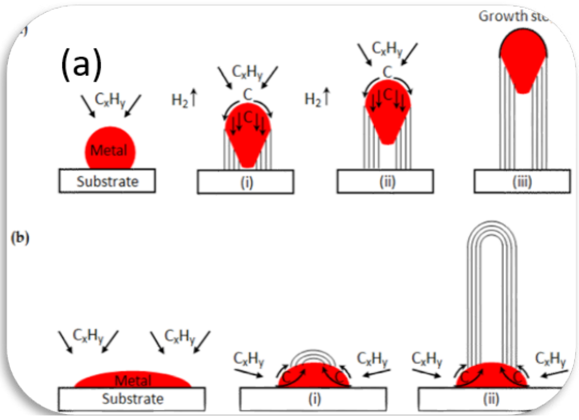

Figure 12: Growth mechanisms of CNTs: (a) Tip-Growth (b) Base Growth.

From this mechanism and the diagram, it is clear that metal particles play a great role in the growth of CNTs. The metal nanoparticles either remain at the base/bottom or at the top of the grown CNT. The other growth mechanism for the CNTs which is proposed by Baker and Harrish. They have suggested a four-step mechanism for the CNT growth. This four-step mechanism has been explained as under [63].

1. At the first stage, the source hydrocarbon gets decomposed on metal surface into its constituents' hydrogen and carbon.

2. At the second stage, the carbon gets diffuse through metal particles and its precipitation gets start. The precipitation starts from the rear face so that the body of the filament is formed.

3. At the third stage, here the supply of carbon at front face is faster that causes an accumulation of carbon at front face. To prevent the physical blocking, the accumulated should be removed. This all is done by the surface diffusion. In this way the carbon forms a skin around the main filament body.

4. In the last stage, all the catalyst particles are being covered and deactivation of catalyst particles and termination of tube growth takes place.

Potential applications of carbon nanotubes (CNTs)

Nanotechnology and nanomaterials is going to change the whole world and this technology is making the things cheaper, smaller, durable and faster.

Due to the good properties of CNTs, the highly advanced CNT nano technology can be used for a lot of market applications. On the basis of CNT size with excellent mechanical, thermal, and electrical properties, some main applications are listed and are shown in figure 13 [64].

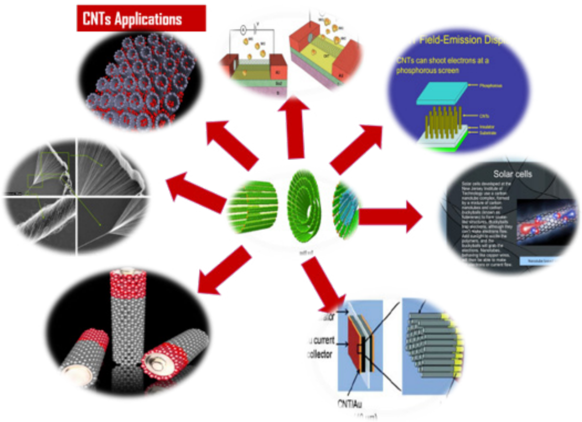

Figure 13: Market applications of CNTs.

CNTs in chemical sensors

CNTs are known as best chemical sensors. A sensor may be defined as the device that detects and respond some kind of input signals from the physical environment. The input signal may be light signal, heat, pressure, moisture, or may be any other environmental phenomenon. After processing the input signal, the output signal which is generally converted or transmitted electronically so that the observer may read or detect it accurately and get the useful information.

Generally Semiconducting CNTs show a large change in their conductance and resistance when exposed to different gaseous like NO_2, NH_3, CO_2, H_2 etc. The CNT sensor provides better results due to their small size, fast recovery and faster response as compared to other conventional sensors [65,66]. A small schematic of CNT based chemical sensor has been shown in Figure 14.

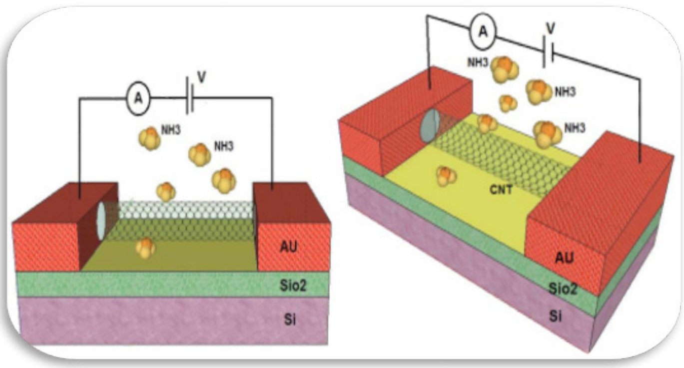

Figure 14: Schematic of CNT based Chemical sensor.

Now a day's carbon nanotubes are widely being used in chemical sensors for monitoring the outdoor and indoor environment for security reasons [67,68].

CNTs in field emission devices

As we know, field emission means the emission of electrons from the surface of the material. The current density directly depends on the electric field at the emitting surface and depends on its work function. The emission of electrons also depends on the work function of the material. In metals, the electrons occupy the energy levels which are at the top of the conduction band [69,70].

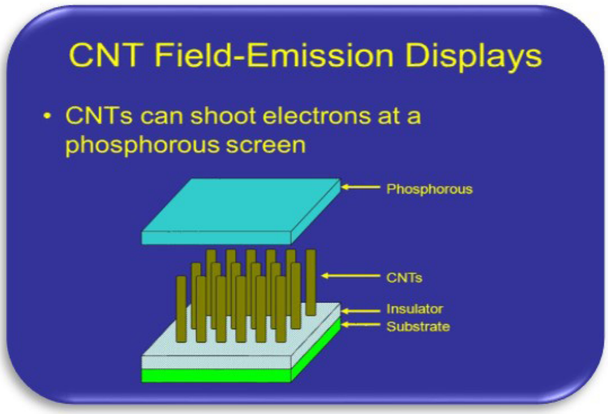

Figure 15: Market applications of CNTs.

These electrons can be easily ejected from the metal surface with the additional energy equal to or greater than the work function of the metal to electrons. The schematic diagram in Figure 15 shows how the CNTs can be used in field emissions devices [71,72].

The work function may simply be defined as the energy difference between the conduction band and vacuum level. In metals or conductors, the energy associated with the top of the conduction band is known as Fermi level. Hence the work function of most metals is defined as the energy difference between Fermi level and the vacuum level and it ranges between 2.5eV to 5.5eV.

The energy with which the emission of electrons can occur is provided by different sources. The sources may be light, heat and electric field. These emissions are called light emission, thermionic emission and field emission respectively. This external energy lowers the energy barrier between the conduction band and vacuum level and making the electrons enable to tunnel through. Many electronic devices are based on electron field emission phenomenon [73].

The material provides the intense source of electron beam for the device operation. Field emission scanning electron microscope (FESEM) is one of the best examples. Many compounds are known for their good field emission at low fields and act as field emission sources. Commonly lanthanum hexaboride is used in electron microscope.

These sources are shaped with fine tips so that intense beam of electrons can be generated. CNTs play a great role in the field emission devices with its small size, small diameter and can generate high intense beam of electrons from their tips. CNTs are associated with, high current density, high enhancement factor and good stability, low turn on electric field. Due to these factors, the CNTs can be used in many field emission display devices [74].

CNTs in solar cells

CNTs can also find applications in solar cells. They can be largely used in solar panels. CNTs have strong UV/Vis-NIR absorption characteristics which provide better help in solar use. It has been reported by different scientific groups that the use of CNTs provide better efficiency in solar cells.

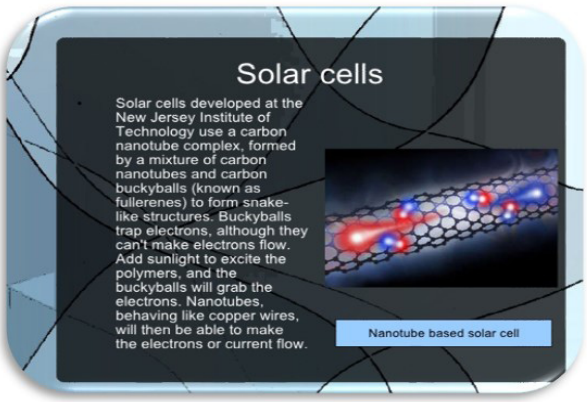

Figure 16: Market applications of CNTs.

The efficiency of solar cells can be increased drastically with the use of CNTs in solar panels. It has been reported that Solar cells have been developed at the New Jersey Institute of Technology with the use of CNTs. Snake like structures have been obtained by this mixture which are helpful in trapping the electrons. Fig 2.16 shows the use of CNTs in solar cells [75].

CNTs in super capacitors

In recent technology, the super capacitor research and efficiency has been increased very much by the use of CNTs. The charge storage capacity of super capacitor cannot be only enhanced but can be increased dramatically with the use of CNTs. Many scientific laboratories are using CNTs to increase the efficiency of super capacitors. As we know in many conventional ultra-capacitors, the activated charcoal is being used as it has many tiny hollow spaces of various sizes. These small holes are creating a large surface for storing electric charge [76].

As the charge is quantized, the elementary charges are electrons but every elementary charge requires a minimum space. The proper fraction of electrode is not available for the charge because its hollow spaces are not compatible so that it can meet with the charge's requirements. The CNT electrode is helpful in apace tailoring from few too large or too small. Due to this, the capacity of the super capacitor may be increased dramatically. According to An and co-workers, SWCNT-based super-capacitor electrodes displayed higher capacitance. Aligned CNTs are much better than the entangled CNTs. Due to the irregular network the efficiency of entangled CNTs is less than the align CNTs.

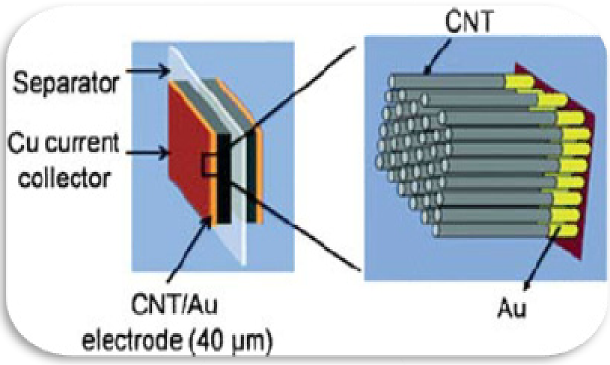

Figure 17: A super capacitor device with CNT/Au as the electrodes.

The use of aligned CNTs is beneficial in case of high power super capacitors. Figure 17 shows how some CNT/Au nanowire hybrid electrodes has been formed. From this figure it is quite clear that both the CNT and Au electrodes have been integrated into a single nanostructure resulting the enhancement in capacitance [77,78].

Hydrogen storage

It has been observed that single wall carbon nanotubes (SWCNTs) are being used to store hydrogen gas. The SWCNTs capillary effects are helpful in condensing the gas to high density. This is observed that mostly hydrogen H_2 can be stored at much higher density without condensation into liquid form. In spite of being able to store electrical energy, researchers find the use of CNTs in storing the hydrogen for fuel source. Capillary effect of carbon nanotubes is responsible for storing hydrogen like gas in high density [79].

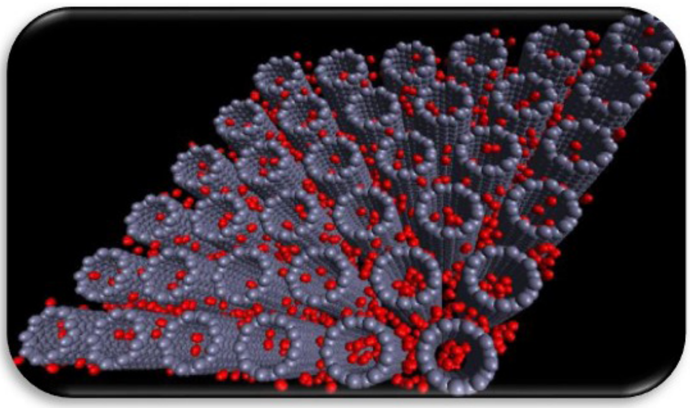

Figure 18: Hydrogen gas adsorbed in CNTs.

As per the marketing level, the storage technique/method may be used in vehicles instead of gas fuel tanks for hydrogen power car etc. By using SWCNTs one keeps the H_2 in gaseous state and the efficiency of storage goes on increasing. This may be considered as the primary source of fuel. It is observed and reported that hydrogen may contains about one fourth the energy per unit volume as gasoline. Figure 18 shows how the hydrogen is trapped in CNT cavities [80-83].

Energy storage

Electrodes are mostly used in fuel cells, batteries and so many other applications. The most advantage of CNTs in energy storage is their small dimension, highly smooth surface morphology. MWCNTs are getting applications in lithium batteries. In these lithium batteries, a small amount of MWCNTs powder is blended with a good active material and a polymer binder. CNTs are usually known to provide a high electrical connectivity. CNTs are also known for the best mechanical integrity. These factors enhance the rate capability [84-86].

CNTs can also be used in super capacitors. In super capacitors, CNTs can be bonded to the charge plates of super capacitors so that the surface area increases and hence the energy density gets enhanced. Generally, CNTs can act as catalyst support in the fuel cells. In this way the platinum usage can be reduced by 60% as compared to carbon [87,88].

Electrical cables and wires

CNTs are covering almost every corner of application in nanotechnology. In the field of electric current, CNT wires and cables are being fabricated with pure CNT and nanotube polymer composites. These cables and wires are successfully being used in the power and data transmission in the highly developed technology.

Reports shows that very small wires are being designed and fabricated with some specific conductivity that is much higher than copper and aluminum. These cables are regarded as the highest conductivity nonmetal cables. Thus, the composite obtained by CNTs and Cu possess highest current carrying density among electrical conductors. The composite of CNT and Cu can transport hundred times higher current as compared to other metals [89-92].

Textiles

As CNTs are showing excellent electrical, mechanical and thermal properties. Due to these excellent multiproperties of CNTs, they are also being used in textiles. Most of the research of CNTs is being focused on textiles and fiber spinning also. Much attention is being focused on coating of CNTs on textiles fabrics. The textiles fabrics are being modify day by day with the use of recent nanotechnology. Fig 2.19 shows how the CNTs can be used in fabrics which leads the strength of fabrics and can be used in military dresses [93-96].

As the CNTs possess highly aligned structure with negative surface charge. Now a day, various methods are being applied for coating and absorbing CNTs on fiber surface. In this way the CNT coated fiber surface becomes able for multifunctional like antibacterial, electrical conductive and flame retardant etc. With the help of CNTs, nanotechnology is able to design bullet proof suits which are useful for military purposes [98-100].

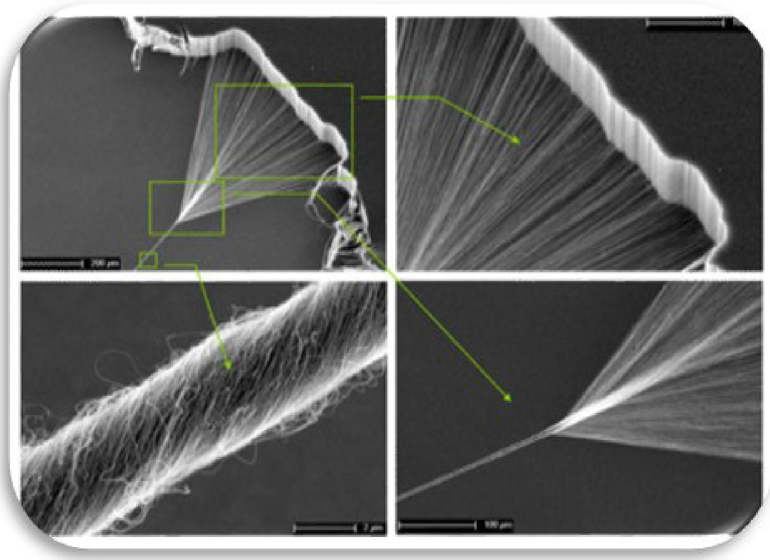

Figure 19: Threads like CNTs to reinforce in textiles.

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