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Carbon Nanotubes: A Review on Synthesis, Electrical and Mechanical Properties and Applications

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ABSTRACT

Discovery of carbon Nanotubes (CNTs) by lijima in 1991 bring a revolution in the field of material physics. Carbon Nanotubes (CNTs) are allotropes of carbon having length-to-diameter ratio greater than 1,000,000. Because of such properties they exhibit unique mechanical properties such as stiffness, strength and high elastic moduli. Referring to their electrical properties, they show semiconducting as well as metallic behaviour which make them enable to explain phenomena's like thermoelectricity, superconductivity, electroluminescence and photoconductivity. Nanotubes are categorized as single-walled nanotubes (SWNTs) and multiple-walled nanotubes (MWNTs). Different techniques have been developed for synthesis like Plasma based synthesis methods, Thermal synthesis methods and Hydrothermal methods. The properties and characteristics of CNTs are still being researched heavily. Economically feasible large-scale production techniques still have to be developed. Without any doubt, CNTs represent a material which offers great potential in the field of optics, electronics, nanotechnology, bio and other fields of material science. This review has been aimed to give an outlook on the extensively studied topic of synthesis, electrical and mechanical properties and applications of CNTs in the field of technology and medicines.

Keywords: CNTs, SWNTs, MWNTs, Fullerenes and Nanosensors.

1. INTRODUCTION

In the past decade, one of the most interesting nanomaterials, carbon nanotubes (CNTs) have received significant attention in terms of fundamental properties, measurements and potential applications. Carbon nanotubes are allotropes of carbon which having tubular shape, made of graphite. They are nanometers in diameter and several millimeters in length. The graphite layer seems alike a rolled-up chicken wire with a continuous unbroken hexagonal mesh and carbon molecules at the apexes of the hexagons known as graphene. Carbon can build closed and open cages with honeycomb atomic arrangement. The first structure to be discovered was the C_{60} (fullerene) molecule by Kroto et al 1985[1].

Since various carbon cages were studied but in 1991 Iijima observed the tubular carbon structure for the first time [2]. Steady progress has been made in exploring the mechanical properties, electrical properties and potential applications of carbon nanotubes (CNTs) which vary with their diameter, length, chirality or twist and wall nature. Carbon nanotubes exist in single-walled or multi-walled structures. Single-walled nanotube (SWNT) [3] is created by rolling a single graphene sheet seamlessly to form a cylinder with a diameter of 1nm and length in centimeters. Similarly, the multi-walled nanotube (MWNT) is an array of such cylinders formed concentrically and separated by 0.35 nm with diameter from 2 to 100 nm and length of order tens of microns [4].

The measured specific tensile strength of a single layer of a multi-walled carbon nanotube (MWCNT) can be as high as 100 times that of steel, and the graphene sheet is as stiff as diamond at low strain. Composite materials reinforced by either SWCNT or MWCNT have been fabricated and significant enhancement in mechanical properties has been recently reported [5]. In supporting to electrical properties, carbon based nanoelectronics promise exhibits greater flexibility as compared to conventional silicon electronics [6].

2. SINGLE-WALLED NANOTUBES (SWNTs)

Single-walled nanotubes (SWNTs) have a diameter of close to 1 nanometer, with a tube length that can be many millions of times longer. The structure of a SWNT can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder (fig.1). It is interesting to note that graphene, by itself, can be characterized as either a zero gap semiconductor or metal and imparts these properties to nanotube. The fundamental conducting properties of a graphene tubule depend on the nature of wrapping and the way the graphene sheet is wrapped is represented by a pair of indices (n,m) called the chiral vector. The integers n and m denote the number of unit vectors along two directions in a honeycomb crystal lattice of graphene.

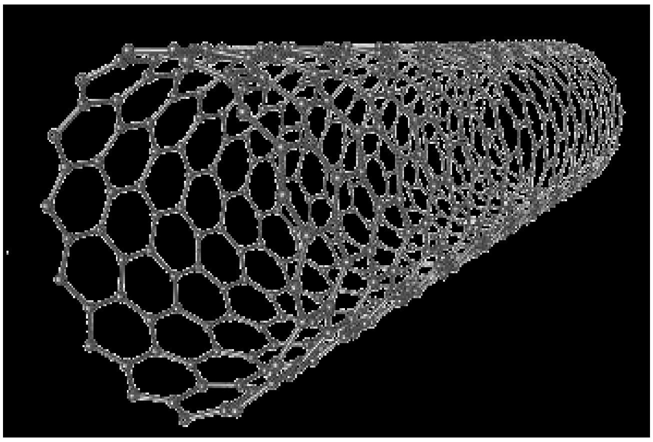

Figure 1: Single walled Carbon Nanotube

1).If m=0, the nanotubes are called ‘Zigzag’
2).If n=m, the nanotubes are called ‘Armchair’
3).Otherwise, the nanotubes are called ‘Chiral’ in which the m value lies between zigzag and armchair structures (fig.2) [7].

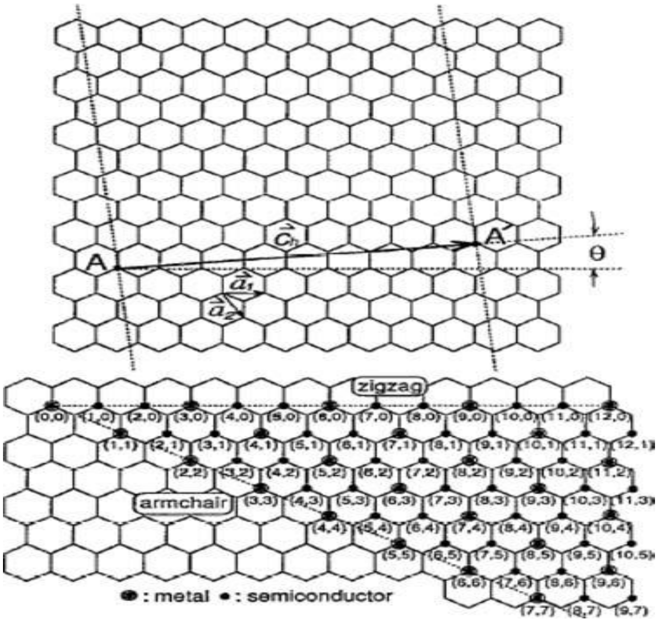

Figure 2

3. MULTI-WALLED NANOTUBES (MWNTs)

To describe the structures of multi-walled nanotubes two models can be used. According to Russian Doll model, sheets of graphite are arranged in concentric cylinders i.e. a single-walled nanotube (SWNT) within a larger single-walled nanotube.

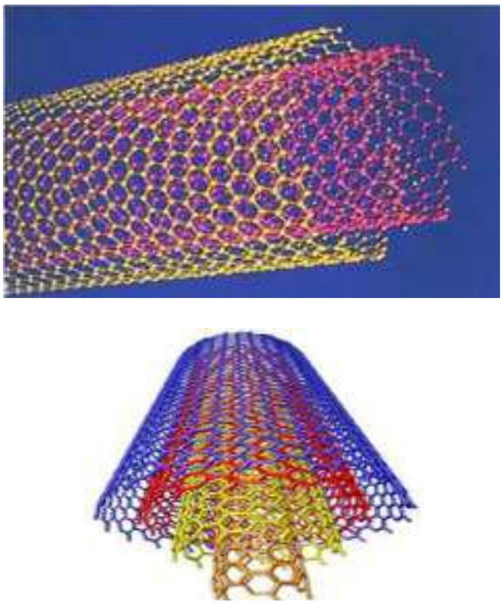

Figure-3: Double-wall Nanotubes (DWNT)

According to Parchment model, a single sheet of graphite is rolled in around itself which resembles to a scroll of parchment or a rolled newspaper. Morphology and properties of double-walled carbon nanotubes (DWNT) are similar to SWNT but their resistance to chemicals is significantly improved (fig.3). The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite ranges from 0.342nm to 0.375nm. These adjacent layers are generally non-commensurate (different chiralities) with a negligible inter-layer electronic coupling and could alternate randomly between metallic and semiconducting varieties. This effect of the curvature on the interlayer distance was reported by Kiang et al [8].

Multiwalled Nanotubes (MWNT)

The layers, constituting the individual cylinders, are found to close in pairs at the very tip of MWNT and its detailed structure plays a very important role in electronic and field emission properties of nanotubes.

4. SYNTHESIS OF CARBON NANOTUBES

Synthesis of carbon nanotubes is based on three types of methods i.e. Plasma based synthesis process, Thermal synthesis process and Hydrothermal methods, though scientists are researching more economic ways to produce such type of structures.

4.1. Plasma Based Synthesis Methods

4.1.1. Arc Discharge Method

Arc discharge method is a technique used to produce carbon nanotubes of length 1mm and diameter 4 to 30nm. When current of about 50 amps is passed between two graphite electrodes in the presence of inert gas (helium, argon). One of the carbon rods gets vapourized and forms a small rod shaped deposition on the other end which is called nanotubes. Single-walled nanotubes (SWNTs) are produced when Co and Ni or some other metal is added to the anode.

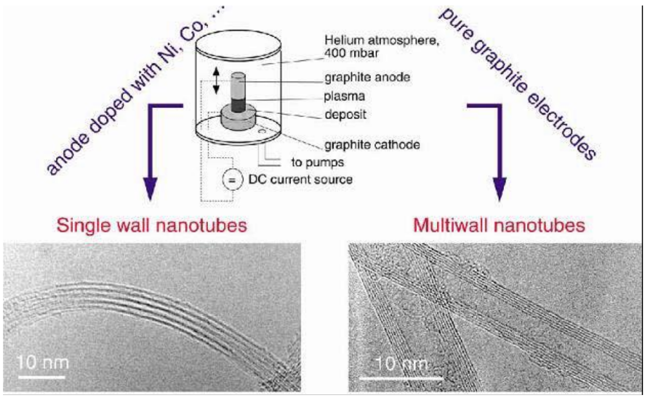

Figure 4: Arc Discharge Method

Carbon nanotubes can also be made by passing a carbon-containing gas over a catalyst such as metal, Fe, Co or Ni. These particles causes the breakdown of gaseous molecules into carbon and a tube starts growing with a metal particle at the tip [9],[10]. The big advantage of this technique over arc-evaporation is that it can be scaled up for volume production. Ebbesen and Ajayan in 1992 reported large-scale synthesis of MWNTs by arc discharge technique [11]. Temperature, carbon and metal catalyst densities affect the diameter distribution of nanotubes. Two distinct methods of synthesis can be performed with the arc-discharge apparatus as shown in fig.4 to produce SWNTs or MWNTs.

4.1.2. Laser Ablation Method

This method of synthesis of SWNTs was reported in 1996 by Smalley's group at Rice University [11],[12]. A pulsed or continuous laser is used to vaporize a 1.2 at % of Co/Ni with 98 at % of graphite composite target placed in a 1200°C quartz furnace with an inert atmosphere of 500 torr of Ar or He. At this high temperature vapour a plume form which expands and cools rapidly. As vapours cool down, small carbon molecules and atoms quickly compress to form larger clusters, including fullerenes. Also the catalysts start to condense slowly and attach to carbon clusters and obstruct their closing into cage structures. From these initial clusters, tubular molecules develop into single-wall carbon nanotubes until the catalyst particles become too huge or conditions have cooled enough such that carbon is unable to diffuse through or over the surface of the catalyst particles. But there is another possibility of enough coating with carbon layer that they cannot absorb more and the nanotube stops growing [12]. The SWNTs formed in this case are bundled together by Van-der Waals forces. The length of MWNTs produced through this method is much shorter than that produced by arc-discharge. As a result this method does not seem adequate for synthesis of MWNTs. The diameter range of SWNTs through this method lies between 1.0 to 1.6 nm. As good quality nanotubes are produced by this method, scientists are trying to scale up laser ablation. However, outcomes are not yet as good as for the arc-discharge, but they are still hopeful. Two latest achievements in this field are ultra-fast pulses from a free electron laser method and the continuous wave laser-powder method.

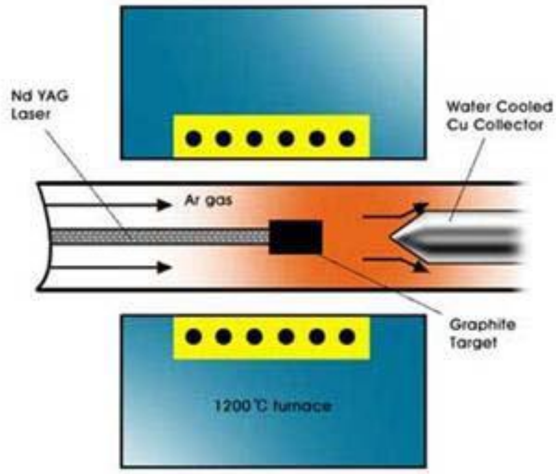

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Figure 5: Laser Ablation

4.2. Thermal Synthesis Based Methods

In thermal synthesis only thermal energy is relied and the hot zone of reaction never goes beyond 1200°C. In the presence of active catalytic species such as Fe, Ni and Co carbon feedstock produces CNTs.

4.2.1. Chemical Vapour Deposition (CVD)

In this method a carbon source is used in gaseous phase and energy is provided to it through plasma or a resistively heated coil. Commonly used gaseous carbon sources consist of methane, carbon monoxide and acetylene. The energy source is used to "fissure" the molecule into reactive atomic carbon. After that, the carbon diffuses towards the substrate, which is heated and coated with a catalyst like Ni, Fe or Co where it will bind. Carbon nanotubes are formed when the proper parameters are followed. Outstanding configuration, as well as positional control can be achieved by using CVD. The suitable metal catalyst can preferentially produce single instead of multi-walled nanotubes. CVD carbon nanotube synthesis is basically a two-step process comprised of a catalyst preparation step followed by the actual synthesis of the nanotube. The catalyst is generally prepared by sputtering a transition metal onto a substrate and then either by chemical etching or thermal annealing catalyst particle nucleation is induced. Thermal annealing results in cluster formation on the substrate, from which the nanotubes will grow. Ammonia may be used as the etchant. The temperatures for the synthesis of nanotubes by CVD lies within the 650°C –900°C. Typical yields for CVD are approximately 30% [13].

4.2.2. Plasma Enhanced CVD (PECVD)

This technique is effective for production of both SWNTs and MWNTs. PECVD can be direct or remote. Direct systems are suitable to produce MWNT field emitter towers and SWNTs. While remote systems can be used to produce both MWNTs and SWNTs. SWNTs can be synthesized in the direct PECVD system by heating the substrate upto 550°C to 850°C with CH_4/H_2 gas mixture at 500 torr using 900W of plasma power. In plasma enhanced CVD method generates a glow discharge is produced in a chamber or a reaction furnace by a high frequency voltage applied to both electrodes. A substrate is placed on the grounded electrode. In order to form a uniform film, the reaction gas is supplied from the opposite plate. Catalytic metal, such as Fe, Ni and Co are used on a Si, SiO2, or glass substrate using thermal CVD or sputtering. As such, PECVD and HWCVD is essentially a crossover between plasma-based growth and CVD synthesis. As the carbon for PECVD synthesis comes from feedstock gases such as CH4 and CO, so there is no need for a solid graphite source like arc discharge, laser ablation, and solar furnace.

4.2.3. Alcohol Catalytic CVD (ACCVD)

Alcohol catalytic CVD (ACCVD) is good method for low cost production of SWNT in large scale. Evaporated methanol and ethanol are being utilized over iron and cobalt catalytic metal particles supported with zeolite. CNT is obtained at a relatively low minimum temperature of about 550 °C. It seems that hydroxyl radicals, who come from reacting alcohol on catalytic metal particles, remove carbon atoms with dangling bonds, which are obstacles in creating high-purity SWNTs. The diameter of the SWNTs produced is about one nm.

4.3. The Hydrothermal Methods

This technique is very successful for the preparation of different carbonaceous nanoarchitectures such as nano-onions, nanorods, nanowires, nano belts, MWNTs. This process has many advantages as compared to other methods: i) the starting materials are easy to obtain and are stable in ambient temperature; ii) it is low temperature process (about 150–180 °C); iii) there is no hydrocarbon or carrier gas necessary for the operation. A mixture of polyethylene and water with a Ni catalyst is heated from 700 to 800 °C under 60–100 MPa pressure to produce MWNTs [14]. Both closed and open end multiwall carbon nanotube with outer diameter of 50–150 nm and inner diameter from 10–1000 nm can be produced [14, 15]. Typically, hydrothermal nanotubes have wall thickness of order 7–25 nm. During growth of a tube, the synthesis fluid, which is a supercritical mixture of CO, CO_2, H_2, H_2O, and CH_4 enters the tube. The hydrothermal synthesis was conducted at 150–160 °C for 24 h. The nanotubes produced in this way were about 60 nm in diameter and 2–5 μm long. Multiwall carbon nano cells and multiwall carbon nanotubes have been artificially grown in hydrothermal fluids from amorphous carbon, at temperatures below 800 °C, in the absence of metal catalysts [15]. The nano cells have diameters smaller than 100 nm with outer diameters ranging from 15 to 100 nm, and internal cavities with diameters from 10 to 80 nm. The nanotubes observed in the sample have diameters in the range of tens and length in the range of hundreds of nanometers [16].

5. ELECTRICAL PROPERTIES OF CARBON NANOTUBES

CNTs show remarkable electrical properties. Because of chiral vector, CNTs with small diameter shows properties between semiconductors and metals, therefore CNTs show resistance, capacitance and inductance properties. The differences in conducting properties are due to the molecular structure which causes different band structure and band gap. Metallic nanotubes can carry an electrical current density of 4 × 109 A/cm^2 which is 1,000 times greater than that of copper [17]. Electrical conductivity inside CNTs gets affected due to scattering defects and lattice vibrations which in turn causes resistance. In metallic CNT R= 6.45kΩ. As well as this quantum resistance there are other forms of contact resistance due to presence of Schottky barriers at metal–semiconducting nanotube interfaces. Many scattering collisions can occur in CNTs because of which CNTs mobility is as much as 1,000 times greater than in bulk silicon. The CNTs having intrinsic electronic structure leads to the capacitance of the order of 10-16 F/μm. Finally, CNTs show inductance, which is a resistance to any changes in the current flowing through them due to combined contribution of classical and quantum effects(LK ≈ 16nH /μm, LC ≈ 1 nH/μm)[18]. There is a wide scope of constructing nanoscale electronic devices from nanotubes which includes flat-panel displays, sensing devices and scanning probe microscopes.

6. MECHANICAL PROPERTIES OF CARBON NANOTUBES

Carbon nanotubes have high tensile strength and Young's modulus of elasticity because of covalent bonds between carbon atoms. The nanotubes are very flexible as they are very lengthy and large Young's modulus in their axial direction makes these compounds potentially suitable for application in composite material [19]. The value of Young's modulus for SWNT is very high approximately 1TPa to 1.8TPa which depends on diameter and chirality of tube makes it suitable like probe tips of scanning microscopy. For MWNTs, Young's modulus gets reduced due to the weak inter tube cohesion because only outer graphite shell supports stress. A SWNT is about 10 to 100 times stronger than steel per unit weight. The finest nanotubes can have Young's modulus as high as 1000GPa and tensile strength is upto 63GPa which is about 5 times and 50 times higher than steel respectively. Such properties make them suitably applicable in aerospace. Arthur C. Clarke was first who suggested using nanotubes in "Space Elevator".

7. APPLICATIONS OF CARBON NANOTUBES

7.1. Carrier for drug delivery

(a) Irregular shape of carbon nanotubes like horns is used as potential carrier in drug delivery system [20].
(b) Used for targeting of Amphotericin B to cells [21].
(c) Because of nanosize and sliding nature of graphite layers CNTs can be used as lubricants or glidants in tablet manufacturing [22].
(d)Property of controlled lipophilicity makes them useful for distribution and retention of Anticancer drug Polyphosphazene platinum in the brain [22].
(e) This carrier system based on CNTs provides a successful oral administration of Erythropoietin (EPO), which has not been possible because of the denaturation of EPO by the gastric environment conditions and enzymes [22].
(f) Antibiotic, Doxorubicin given with nanotubes is reported for enhanced intracellular penetration [22].
(g) SWNHs show slow release of Cisplatin in aqueous environment which is effective to terminate the growth of human lung cancer cells, while the SWNHs did not show any such type of anticancer activity [23].

7.2. Genetic Engineering

CNTs and CNHs are used for manipulating genes and atoms to develop bioimaging genomes, proteomics and tissue engineering. They act as a vector in gene therapy because of their tubular nature. The unwound DNA winds around SWNT by connecting its specific nucleosides and which further change in electrostatic properties. This property helps to improve its potential applications in diagnostics and therapeutics [24].

7.3. Artificial implants

Often body shows rejection for implants with the post administration pain. Because of miniature size nanotubes and nanohorns easily get attached with other amino acids and can be used for implanting artificial joints without rejection reaction by host. As carbon nanotubes consists of high tensile strength, therefore CNTs filled with calcium and arranged in the structure of bone can easily be used as bone substitute [24].

7.4. Preservative

Since carbon nanotubes and nanohorns are antioxidant in nature therefore they are used to preserve drug formulations which are prone to oxidation. Because of this property, they are used in antiaging cosmetics and as sunscreen dermatological with the help of zinc oxide to prevent oxidation of important skin components [24].

7.5. As Catalyst

As nanohorns consists of large surface area and 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 and CNHs [24].

7.6. Biomedical applications

Bianco et al. [26] have prepared soluble CNTs covalently linked with biologically active peptides. It was demonstrated for viral protein VP1 of foot mouth disease virus (FMDV) showing immunogenicity and eliciting antibody response. In chemotherapy, drug embedded nanotubes attack directly on viral ulcers and kills viruses without production of antibodies against the CNT, which shows that the nanotubes do not possess intrinsic immunogenicity [27]. Vitro studies by Kam et al. [28] showed selective cancer cell killing obtained by hyperthermia due to the thermal conductivity of CNT internalized into those cells. The use of CNT as gene therapy vectors have shown that these engineered structures can effectively transport the genes and drugs inside mammalian cells [29].

7.7. As Biosensors

CNTs based nanosensors can be used to record pulse, temperature, blood glucose and for diagnosing diseases [18]. Protein-encapsulated or protein/enzyme filled nanotubes, due to their fluorescence ability in presence of specific bio molecules have been tried as implantable biosensors. For example a glucose sensing application in which regular self-tests of glucose by diabetic patients are performed to measure and control their sugar levels. Moreover, nanocapsules filled with magnetic materials, radioisotope enzymes can also be used as biosensors. Nanosize robots and motors with nanotubes can be used in studying cells and biological systems [25].

8. LIMITATIONS OF CARBON NANOTUBES [30]

1. Lack of solubility in most of solvents which are compatible with the biological milieu (aqueous based).
2. The production of structurally and chemically reproducible batches of CNTs with identical characteristics.
3. Difficulty to maintain high quality and minimal impurities.

9. CONCLUSION

This review on carbon nanotubes results an overview on the structure, synthesis methods along with their properties and applications. Carbon nanotubes having a striking feature of controlled drug delivery allow easy functionalization on side walls and in the core, thus drugs can easily be located on them. The remarkable physical properties of CNTs make them useful in conventional carbon fiber applications along with the new possibilities based on the novel electronic and mechanical behaviour of nanotubes. Nanotubes bridge the gap between the molecular and the macro-word. In contrast of gene therapy, cancer treatments and new innovative techniques for threatening diseases, Nano medicines have become a growing field with an incredible ability to overcome barriers. The properties and characteristics of CNTs are still under research. SWNTs and MWNTs are more safer and effective alternatives to prior drug delivery methods. This review suggests the CVD method is the best one for large scale production of MWNTs. However, the production of SWNTs is still in grams and the helical CNTs are only obtained together with linear CNTs.

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