

Carbon Nanotubes: Structure, Properties, Synthesis and Potential Applications

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Abstract: Carbon nanotubes are cylinders made up of rolled-up graphene sheets with diameters measurable on a nano scale and length may extend up to several millimeters. The small dimensions, strength and a wide range of electrical, thermal, and structural properties contribute to their uniqueness. Researchers believe that the carbon nanotubes have the ability to bring a sea change in the fields of automobile industry, materials science, space programs, biomedical science and a variety of activities and products associated with daily living. This article attempts to explore the structure, synthesis techniques properties and possible applications of carbon nanotubes.

Keywords: Carbon Nanotubes, CNT, SWCNT, MWCNT, Nanotechnology

1. Introduction

Nanotechnology, the science of nanoscale, has brought a revolutionary change in the field of materials. According to the U.S. Environmental Protection Agency (EPA), nanotechnology is defined as “the creation and use of structures, devices, and systems that have novel properties and functions because of their small size”.¹ Carbon nanotubes (CNTs) are one such miniature form of carbon materials with a nanostructure that can have a length-to-diameter ratio greater than 1, 000, 000^{2,3}. CNTs have been a focus of intense interest globally since their discovery by Sumio Iijima in the last decade of 1900's⁴. These nanotubes, also referred to as buckytubes, are essentially folded form of the two-dimensional graphene sheets and exhibit exceptional properties. CNTs can exist as single walled or multi walled structures. In spite of being very small and light in weight they exhibit high strength, toughness and ability to resist breakage. Their unique electrical, thermal and mechanical properties make them a material of choice in numerous fields ranging from biomedical applications to energy management, chemical processing, molecular electronics and many other areas. This article reviews the various aspects of CNTs including structure, types, properties, methods of synthesis and their applications.

Structure and Types of Carbon Nanotubes:

The unique ability of carbon to hybridize in sp , sp^2 and sp^3 forms allows it to exist in three different allotropic forms in a solid phase. The number and nature of bonds in these hybridized forms determine the geometry, structure and properties of these allotropes namely diamond, graphite and fullerenes. The tetrahedral structure of diamond is a result of the sp^3 hybridization in which one carbon atom is bonded to four other carbon atoms. In graphite, layered planar sheets of sp^2 carbon atoms are bonded together in a hexagonal network and each sp^2 hybridized carbon is bonded to only three other carbon atoms arranged at 120° in the xy plane, and a weak pi bond is present in the z axis. The sp^2 set forms

the hexagonal (honeycomb) lattice typical of a sheet of graphite. Fullerenes are the third allotropic form has all carbon atoms in sp^2 hybridized form which exist as spheroidal or cylindrical molecules in contrast to the planar arrangement that is found in graphite. The curvature thus results in the mixing of the s and p orbitals or rehybridization. The bending of the pi orbital and pyramidalization brings about a crucial change in the properties of the carbon nanotubes⁵.

A large number of potential helicities and chiralities are possible when graphene sheets roll-up in the form of seamless hollow cylindrical shells to form carbon nanotubes. The ends of these tubes are domed structures made up of six-membered rings, capped by a five-membered ring.

There are essentially two types of nanotubes: single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs), which differ in the arrangement of their graphene cylinders⁶. Nanotubes with one wall are mostly curved and are narrower in diameter than the nanotubes with multiple walls.

SWCNT:

Single-wall carbon nanotubes (SWCNTs) are infinitely long cylinders with honeycomb hexagonal lattice arrangement on surface and carbon atoms positioned at the vertices. The carbon-carbon bond length and orientation of the hexagonal ring define the properties of these nanotubes. Since the length of the carbon-carbon bonds is fairly fixed, there are constraints on the diameter of the cylinder and the arrangement of the atoms on it^{7,8}. The length of the SWCNT can be measured in micrometers and their diameters ranges from 0.4 to 2 to 3 nm. The single walled tubes can also exist in the form of bundles. The chiral vector or the direction of rolling up the graphene sheet leads to the zig, chiral or armchair pattern of the arrangement of hexagons⁴. The choice of rolling axis relative to the hexagonal network of the graphene sheet and the radius of the closing cylinder allows for these different types of SWCNTs.

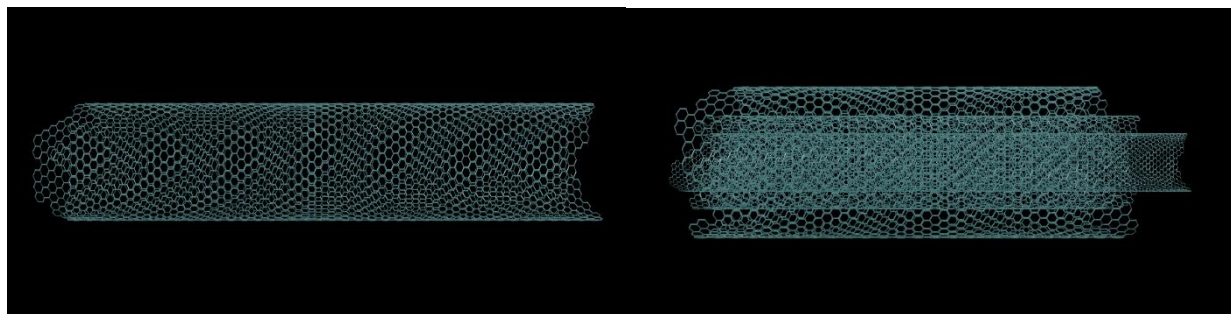


Figure 1 (a)

Figure 1 (b)

Figure 1: Diagrammatic representations of SWCNT (figure 1a) and MWCNT (figure 1b)

MWCNT: MWCNTs consist of a hollow cylinder in the center surrounded by several concentric cylinders and ends capped by dome shaped half-fullerene molecules. The interlayer spacing between these concentric cylinders can range between 0.34 to 0.39 nm. The diameter of MWCNT thus depends on the number of layers of cylinders. The inner diameter can vary from 0.4 nm up to a few nanometers and outer diameter from 2 nm up to 20 to 30 nm. The strong in plane C-C bond and a weak out of plane pi bond in sp^2 hybridized carbon atoms of graphite generates a layered structure. Multiwalled carbon nanotubes can be formed in Russian Doll model and Parchment model. The Russian Doll Model consists of a thinner nanotube contained inside an outer nanotube of larger diameter whereas the Parchment model is like a rolled-up scroll of paper in which a single graphene sheet is wrapped around itself manifold times.^{9, 10} The main differences between the single walled and multi walled nanotubes are listed in table 1.

Synthesis of carbon nanotubes:

Several procedures have been developed to manufacture nanotubes in substantial quantities, such as electrical arc discharge, laser ablation, and chemical vapor deposition (CVD).

Arc discharge method:

These methods use application of direct current (100-200 Ampere) between high-purity graphite electrodes separated by a small distance in a chamber. The arc plasma is generated between the two electrodes in an inert chamber with gas like helium or argon at sub atmospheric pressure and maintained at high temperature (3000-4000 degree) in presence of metal catalyst particles (such as nickel, yttria and cobalt and/or iron) filled in anode. The sublimated carbon from the anode (positive electrode) is deposited as

carbon soot on the cathode surface (negative electrode) as hard outer crust with cigar like structure and soft dark fibrous core¹¹. The anode rod is consumed in the process. Beside the cathode soot, a layer of soot is formed on the inner walls of the reaction chamber. The single-walled and multiwalled carbon nanotubes are now obtained from these graphite deposits on cathode and chamber wall. This method is capable of generating large number of carbon nanotubes with length ranging up to tens of micrometers however due to the presence of the metal catalyst purification process is mandatory.

Laser-ablation technique:

In this method, bulk graphite target placed inside a chamber filled with inert gas and maintained at high temperature (1200 approx) is pulsed with high-power YAG laser to ablate carbon.¹² The carbon atoms vaporize and condense and assemble at the collector to form carbon nanotubes in the presence of metallic catalyst. Laser ablation technique offers high quality yield with lesser impurities; however, the use of high-power laser increases the overall cost of production of nanotubes.

Chemical vapor deposition:

This is one of the most extensively used technique for the industrial scale production of carbon nanotubes. The reaction is initiated by introducing the gaseous phase reactant hydrocarbon (methane) and metal catalyst (iron, nickel, cobalt, ferrocene etc.) in the furnace maintained at high temperature. Metal catalyst induced decomposition of the hydrocarbon releases the carbon and hydrogen. Hydrogen is removed from the chamber along with the carrier gas. As the solubility limit of carbon in metal is achieved, the carbon precipitates on the substrate to yield carbon nanotubes by the base growth or tip growth mechanism^{13, 14}.

Table 1: Comparison between the structure and synthesis of SWCNT and MWCNT

	Single walled CNT	Multi walled CNT
Structure		
Walls/ layers	Single layered	Multiple layered
Diameter	0.4 to 2 - 3 nm	Depends on the number of layers: Inner diameter - 0.4 nm up to a few nm. Outer diameter - 2 nm up to 20 to 30 nm.
Complexity	Structure is simple	Structure is complex
Pliability	It can be easily twisted	It cannot be easily twisted.
Synthesis		
Bulk synthesis	Difficult	Easy.
Catalyst	Catalyst is required for synthesis	Can be produced without catalyst.
Purity	Less purity	Higher purity
Defects	Higher incidence	Lower incidence

Properties of Carbon nanotubes:

The exceptional structure and qualities of CNTs have opened up an unlimited potential in the field of nanotechnology. The sp^2 bonding structure, which is stronger than the sp^3 bonds and rehybridization of orbitals provides the CNTs their unique strength and properties. They are very low weight and their density is one fourth of that of steel but at the same time CNTs are much stronger. The diameter of a carbon nanotube can be 50, 000 times thinner than a human hair yet a nanotube is stronger than steel per unit weight. Carbon nanotubes have high elasticity, experimental studies have shown that carbon nanotubes are the stiffest known material^{15, 16} and buckle elastically (vs fracture) under large bending or compressive strains¹⁷. They are good conductors of heat, have good electrical conductivity, high thermal capacity and a low thermal expansion coefficient and do not expand on heating. CNTs are also chemically stable and resist corrosion

Applications of Carbon Nanotubes:

CNTs could impact broad areas of science and technology, ranging from super strong composites to nanoelectronics. They are utilized in photocatalysts, catalysts, adsorbents, membranes, sensors, conductive coatings, batteries, super capacitors, hydrogen storage devices, solar cells, and fuel cells. The exceptional mechanical properties and low weight of nanotubes make them potential filling materials in polymer composites and also ideal reinforcing fibers for composites.

Apart from these, they can also be used for aircraft and spacecraft bodies, bullet proof jackets and in sports industry. They are also used in the windmill blades because of their low weight. Carbon nanotubes are also used as nanocylinders for safe storage of gases.

They also have very promising applications in the field of biomedical science as extremely sensitive biosensors, scanning probes, drug delivery systems especially in cancer treatment. They are also used for tissue generation, as artificial implants and bone substitutes and for DNA delivery in Gene therapy.¹⁸⁻²⁰

2. Conclusion

The discovery of CNTs have opened up innumerable possibilities because of their unique structure, exciting properties and varied range of application and use. Their discovery has interested the scientists across the world and within a span of few years the researchers have made a remarkable progress. A lot still needs to be found out especially with regard to the synthesis method that allows control over the uniformity of length, diameter and properties of the nanotubes produced. The mass production of CNTs is another area that needs to be addressed. Though there are various challenges, these are being worked upon and eventually CNTs will be beneficial in a wide range of industrial and commercial applications.

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