Carbon Nanotubes

structure, types, properties, synthesis, and applications

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1. *Introduction:*

Synthesis Nanoscience and nanotechnology refers to the control and -9 1manipulation of matter at the nanometer (10 m) dimension . CNTs are two dimensional sheets made of sp^2 hybridized carbon atoms arranged in the form of hexagons and pentagons to yield a three dimensional closed or open ended structure with the length several hundred times the width. They have been constructed with length to diameter ratio 228,000,000:1 . CNTs are produced by folding a graphene sheet just like a sheet of paper. There are infinite ways of folding the graphene sheet, resulting in tubes of different helicities. As the helicity changes, the properties of the tube also varies. In 1991, Iijma was awarded the noble prize for his discovery of single walled CNTs, he produced them by adding transition metal catalysts to carbon in an arc discharge technique. But it was Professor Tang Zikang and Wang Ning in 2000 who successfully created the smallest stable carbon nanotube in 3the world, measuring about 0.4 nm in diameter.

2. *Structure of Carbon Nanotubes*

The structure of a carbon nanotube is formed by a layer of carbon atoms that are bonded together in a hexagonal (honeycomb) mesh. This one-atom thick layer of carbon is called graphene, and it is wrapped in the shape of a cylinder and bonded together to form a carbon nanotube. Nanotubes can have a single outer wall of carbon, or they can be made of multiple walls (cylinders inside other cylinders of carbon). Carbon nanotubes have a range of electric, thermal, and structural properties that can change based on the physical design of the nanotube.

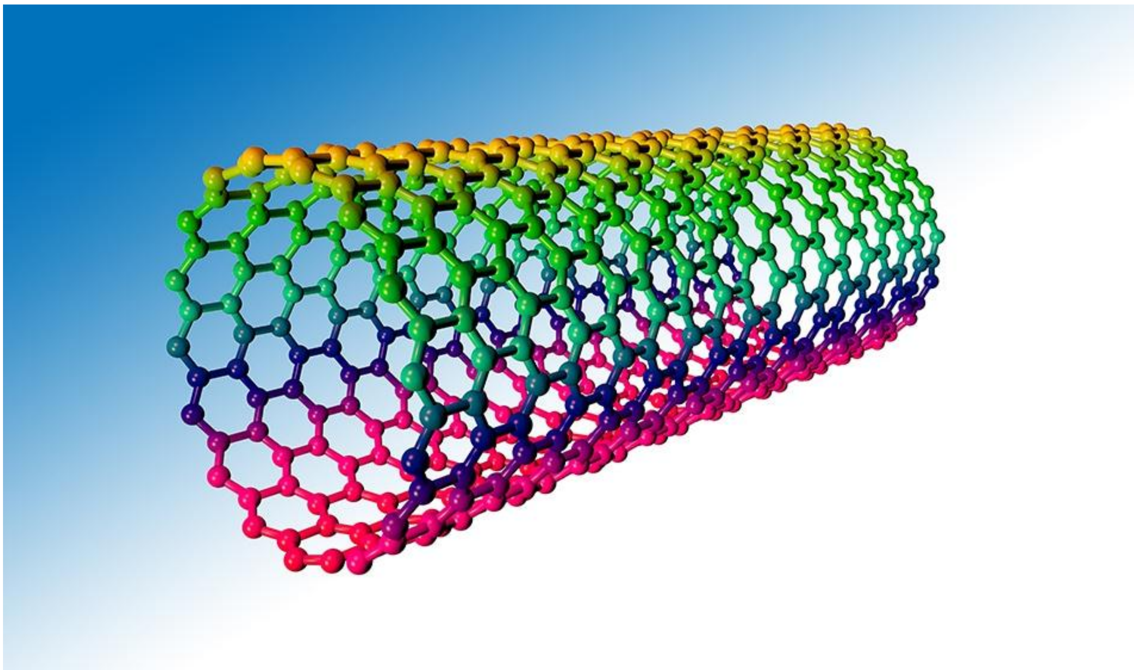
3. *Types of carbon nanotubes (CNTs):*

The carbon nanotubes are of two types namely:

- Single walled carbon nanotubes (SWCNTs)
- Multiple walled carbon nanotubes (MWCNTs)

3.1. Single-walled carbon nanotube structure

Single-walled carbon nanotubes can be formed in three different designs: Armchair, Chiral, and Zigzag. The design depends on the way the graphene is wrapped into a cylinder. For example, imagine rolling a sheet of paper from its corner, which can be considered one design, and a different design can be formed by rolling the paper from its edge. This type is shown in the figure below

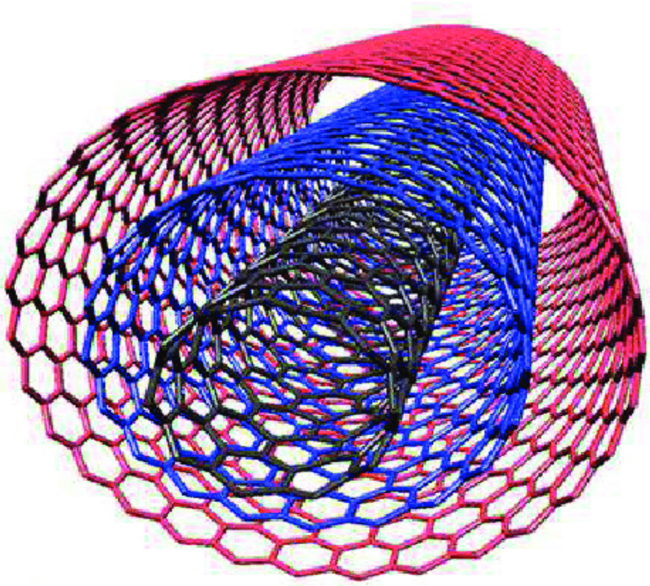


3.2.Multiple walled carbon nanotubes (MWCNTs):

MWCNTs consist of several coaxial cylinders, each made of a single graphene sheet surrounding a hollow core. The outer diameter of MWCNTs ranges from 2-100 nm, while the inner diameter is in the range of 1-3 nm, and their length is one to several micrometers [16]. The sp2 hybridization in MWCNTs, a delocalized electron cloud along the wall is generated which is responsible for the interactions between adjacent cylindrical layers in MWCNTs resulting in a less flexible and more structural defects.

MWCNTs structures can be split into two categories based on their arrangements of graphite layers: one has a parchment-like structure which consists of a graphene sheet rolled up around it and the other is known as the Russian doll model where layers of graphene sheets are arranged within a concentric structure.

Decoration of multiwall carbon nanotubes (MWCNTs) consists of depositing nanoparticles on the MWCNT walls or ends, bonded by physical interaction with potential applications in catalysis, biosensors, biomedical, magnetic data storage, and electronic devices. The various methods used for this purpose include precipitation, hydrolysis at high temperature, or chemical decomposition of a metal precursor.



4.*Carbon Nanotubes Properties*:

4.1.Strength and Elasticity

4.2.Electrical Conductivity
4.3.Thermal Conductivity And Expansion
4.4. High Aspect Ratio.

4.1.Strength and Elasticity of CNTs

Carbon nanotubes have a higher tensile strength than steel and Kevlar. Their strength comes from the sp^2 bonds between the individual carbon atoms. This bond is even stronger than the sp^3 bond found in diamond. Under high pressure, individual nanotubes can bond together, trading some sp^2 bonds for sp^3 bonds. This gives the possibility of producing long nanotube wires. Carbon nanotubes are not only strong, they are also elastic. You can press on the tip of a nanotube and cause it to bend without damaging to the nanotube, and the nanotube will return to its original shape when the force is removed. A nanotube's elasticity

does have a limit, and under very strong forces, it is possible to permanently deform to shape of a nanotube. A nanotube's strength can be weakened by defects in the structure of the nanotube. Defects occur from atomic vacancies or a rearrangement of the carbon bonds. Defects in the structure can cause a small segment of the nanotube to become weaker, which in turn causes the tensile strength of the entire nanotube to weaken. The tensile strength of a nanotube depends on the strength of the weakest segment in the tube similar to the way the strength of a chain depends on the weakest link in the chain

4.2. Electrical Conductivity of CNTs

As mentioned previously, the structure of a carbon nanotube determines how conductive the nanotube is. When the structure of atoms in a carbon nanotube minimizes the collisions between conduction electrons and atoms, a carbon nanotube is highly conductive. The strong bonds between carbon atoms also allow carbon nanotubes to withstand higher electric currents than copper. Electron transport occurs only along the axis of the tube. Single walled nanotubes can route electrical signals at speeds up to 10 GHz when used as interconnects on semi-conducting devices. Nanotubes also have a constant resistively.

4.3.Thermal Conductivity And Expansion of CNTs:

The strength of the atomic bonds in carbon nanotubes allows them to withstand high temperatures. Because of this, carbon nanotubes have been shown to be very good thermal conductors. When compared to copper wires, which are commonly used as thermal conductors, the carbon nanotubes can transmit over 15 times the amount of watts per meter per Kelvin. The thermal conductivity of carbon nanotubes is dependent on the temperature of the tubes and the outside environment

Reports of several recent experiments on the preparation and mechanical characterization of CNT-polymer composites have also appeared. These measurements suggest modest enhancements in strength characteristics of CNT-embedded matrixes as compared to bare polymer matrixes. Preliminary experiments and simulation studies on the thermal properties of CNTs show very high thermal conductivity. It is expected, therefore, that nanotube reinforcements in polymeric materials may also significantly improve the thermal and thermo-mechanical properties of the composites.

4.4. High Aspect Ratio:

CNTs represent a very small, high aspect ratio conductive additive for plastics of all types. Their high aspect ratio means that a lower loading (concentration) of CNTs is needed compared to other conductive additives to achieve the same electrical conductivity. This low loading preserves more of the polymer resins' toughness, especially at low temperatures, as well as maintaining other key performance properties of the matrix resin.

CNTs have proven to be an excellent additive to impart electrical conductivity in plastics. Their high aspect ratio (about 1000:1) imparts electrical conductivity at lower loadings, compared to conventional additive materials such as carbon black, chopped carbon fiber, or stainless steel fiber.

5. Methods of carbon nanotube synthesis

High temperature preparation techniques such as arc discharge or laser ablation were first used to produce CNTs however nowadays these methods have been replaced by low temperature chemical vapour deposition (CVD) techniques (<800 ^{0}C), since the orientation, alignment, nanotube length, diameter, purity and density of CNTs can be precisely controlled in which technique. Most of these methods require supporting gases and vacuum. However, gas-phase methods are volumetric and hence they are suitable for applications such as composite materials that require large quantities of nanotubes and industrial-scale synthesis methods to make them economically feasible. On the other hand, the disadvantages of gas-phase synthesis methods are low catalyst yields, where only a small percentage of catalysts form nanotubes, short catalyst lifetimes, and low catalyst number density.

During the CNT preparation there are always produced a number of impurities whose type and amount depend on the technique being used. The above mentioned techniques produce powders which contain only a small fraction of CNTs and also other carbonaceous particles such as nanocrystalline graphite, amorphous carbon, fullerenes and different metals (typically Fe, Co, Mo or Ni) that were introduced as catalysts during the synthesis. All these impurities interfere with most of the desired properties of CNTs and cause a serious impediment in characterization and applications. Therefore, one of the most fundamental

challenges in CNT science is the development of efficient and simple purification methods.

Most common purification methods are based on acid treatment of synthesized CNTs.

5.1. Plasma based synthesis method or Arc discharge evaporation method

In Arc discharge methods, use of higher temperatures (above 1700 ^{0}C) for CNT synthesis, which usually causes the growth of CNTs with fewer structural defects in comparison with other techniques. The electric arc method, initially used for producing C60 fullerenes, is the most common and perhaps the easiest way to produce CNTs. MWCNTs were discovered in 1991 by Iijima by the arc-discharge evaporation technique.

SWCNTs were produced subsequently in 1993 by the same. In this method, electric arc created between two graphite electrodes leads to an extremely high temperature which is sufficient to sublimate carbon. Either MWCNTs or SWCNTs can he formed when the carbon vapours cools and condenses Generally, MWCNT are formed when there is no catalyst particles between two graphite electrodes; and the SWCNT can be generated by adding Fe, Ni, or Co as catalysts. The catalysts can be introduced by packing metal powder into a hole in the anode. The metal was consumed along with the graphite and created catalyst particles favouring small-diameter SWCNTs.

In case of MWCNTs, the purity and yield depended sensitively on the gas pressure in the reaction vessel. Different atmospheres markedly influence the final morphology of CNTs. They used DC arc discharge of graphite electrodes in helium and methane. By evaporation under high pressured methane gas and high arc current, thick nanotubes embellished with many carbon nanoparticles were obtained. However, thin and long MWNTs were obtained under a methane gas pressure of 50 Torr and an arc current of 20 A for the anode with a diameter of 6 mm . Moreover, It was found that the variation of carbon nanotube morphology was more marked in the case of evaporation in methane gas than that in helium gas .

The SWNTs can be produced when the transition metal catalyst is used. The process of SWNTs growth in arc discharge utilizes a composite anode, usually in hydrogen or argon atmosphere. The anode

is made as a composition of graphite and a metal, such as Ni, Fe, Co, Pd, Ag, Pt. etc. or mixtures of Co, Fe, Ni with other elements like Co-Ni, Fe-Ni, Fe-No, Co-Cu, Ni-Cu, Ni-Ti etc. The metal catalyst plays a significant role in the process yield. To ensure high efficiency, the process also needs to be held at a constant gap distance between the electrodes which ensures stable current density and anode consumption rate. In this process, unwanted products such as MWNTs or fullerenes are usually produced too .

5.2. Laser Ablation Method

In 1995, Dr. Richard Smalley's group at Rice University reported the synthesis of carbon nanotubes by laser vaporization. A pulsed laser was used to vaporize a graphite Otarget in an oven at 1200 C. The main difference between continuous and pulsed laser, is that the pulsed laser demands a 2much higher light intensity (100 kW/cm compared with 12 2kW/cm).The oven is filled with helium or argon gas in order to keep the pressure at 500 Torr. A very hot vapour plume forms, then expands and cools rapidly. As the vaporized species cool, small carbon molecules and atoms quickly condense to form larger clusters including fullerenes.The catalysts also begin to condense, attach to carbon clusters and prevent their closing into cage structures. Catalysts may even open cage structures and grow into single-walled CNTs. The nanotubes stop growing until the catalyst particles become too large, or until conditions have cooled sufficiently that carbon no longer can diffuse through or over the surface of the catalyst particles.

The SWNTs formed in this case are 7,8bundled together by van der waals forces (Figure 5) . The laser ablation method yields nanotubes with 90% purity with a controlled diameter. However it is more expensive than either arc discharge or chemical vapour deposition techniques.

5.3. Thermal Synthesis Process

Arc discharge and laser ablation methods are fundamentally plasma based synthesis. However, in thermal synthesis, only thermal energy is relied and the hot zone of reaction never goes beyond 1200 ^{0}C, including the case of plasma enhanced CVD. In almost all cases, in the presence of active catalytic species such as Fe, Ni, and Co, carbon feedstock produce CNTs depending on the carbon feedstock; Mo and Ru are sometimes added as promoters to render the feedstock more active for the formation of CNTs. In fact, thermal synthesis is a more generic term to

represent various chemical vapor deposition methods. It includes Chemical Vapor Deposition processes, Carbon monoxide synthesis processes and flame synthesis .

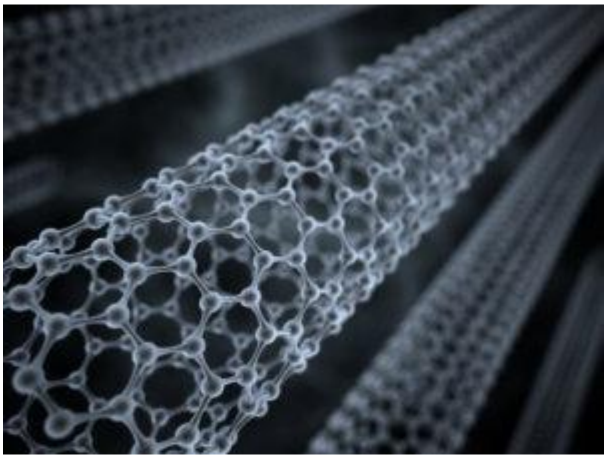
5.4. Chemical vapor deposition (CVD)

Catalytic CVD synthesis is achieved by putting a carbon source in the gas phase and using plasma or a resistively heated coil to heat the gaseous carbon containing molecules. The heat is used to "crack" the molecule into reactive atomic carbon. The most frequently used catalysts are transition metals, primarily Fe, Co, or Ni. Sometimes, the traditionally used catalysts are further doped with other metals, e.g. with Au. Concerning the carbon source, the most preferred in CVD are hydrocarbons such as methane, ethane, ethylene, acetylene, xylene, eventually their mixture, isobutane or ethanol. In the case of gaseous carbon source, the CNTs growth efficiency strongly depends on the reactivity and concentration of gas phase intermediates produced together with reactive species and free radicals as a result of hydrocarbon decomposition. These studies showed that growth efficiency strongly depends on the reactivity and concentration of gas phase intermediates produced as a result of complex gas phase reactions. On this basis, it can be expected that the most efficient intermediates, that have the potential of chemisorption or physisorption on the catalyst surface to initiate CNT growth should be produced in the gas phase. The overall kinetics of the growth process depend on the interaction, competition of gas phase and surface reaction [32]. Hydrocarbon molecules are often used as carbon sources, and ferrocene (FeCp2) as a catalyst. Yang et al., obtained SWCNTs with a mean diameter of 3.23 nm through the catalytic decomposition of a hydrocarbon with hydrogen, helium as the carrier gases [33]. Zhang et al., 2010 prepared MAVNTs with diameters of 40-60 nm by the catalytic decomposition of methane at 680 ^{0}C for 120 min using nickel oxide-silica binary aerogels as the catalyst Plasma Enhanced CVD (PECVD) Plasma-enhanced chemical vapour deposition (PECVD) systems have been used to produce both SWNTs and MWNTs. PECVD is a general term, encompassing several differing synthesis methods. In general PECVD can be direct or remote. Direct PECVD systems can be used for the production of MWNT field emitter towers and some SWNTs. A remote PECVD can also be used to produce both MWNTs and SWNTs. For SWNT synthesis in the direct PECVD system, the researchers heated the substrate up to 550-850 ^{0}C utilized a CH4-H2 gas mixture at 500 mT, and applied 900

W of plasma power as well as externally applied magnetic field. The plasma enhanced CVD method generates a glow discharge 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 as essentially a crossover between plasma-based growth and CVD synthesis. In contrast, to arc discharge, laser ablation, and solar furnace, the carbon for PECVD synthesis comes from feedstock gases such as CH4 and CO, so there is no need for a solid graphite source. The argon-assisted plasma is used to break down the feedstock gases into C2, CH, and other reactive carbon species (CxHy) to facilitate growth at low temperature and pressure.

Applications of Carbon Nanotubes

The unique nature of carbon combines with the molecular perfection of single-wall CNTs to endow them with extraordinary material properties, such as very high thermal and electrical conductivity, stiffness, strength, and toughness. It is the only element in the periodic table which bonds to itself in an extended network with the strength of the carbon-carbon bond. The delocalized pi-electron donated by each atom is free to move about the whole structure, instead of remaining with its donor atom, resulting in the first known molecule with metallic-type electrical conductivity. Moreover, an intrinsic thermal conductivity higher than even diamond is offered by the high-frequency carbon-carbon bond vibrations.



In most materials, however, due to the occurrence of defects in their structure, the actual observed material properties such as strength, electrical conductivity, and so on are degraded very significantly. For example, high-strength steel typically fails at only around 1% of its theoretical breaking strength. However, CNTs achieve values very near to their theoretical limits owing to their molecular perfection of structure.

This aspect is part of the unique story of CNTs. CNTs are examples of true nanotechnology: they are only about a nanometer in diameter, but are molecules that can be manipulated physically and chemically in very useful ways. They find an incredible range of applications in electronics, materials science, energy management, chemical processing, and many other fields.

CNTs Thermal Conductivity

CNTs have outstanding heat conductivity, electrical conductivity, and mechanical properties. They are probably the best electron field-emitter possible. They are polymers of pure carbon and can be made to and manipulated using the recognized and extremely rich chemistry of carbon. This offers the opportunity to alter their structure and to optimize their dispersion and solubility. Most notably, CNTs are molecularly perfect, in the sense that they are generally free of property-degrading flaws in the nanotube structure. Their material properties can thus reach close to the very high levels intrinsic to them. Due to these extraordinary characteristics, CNTs can be prospectively used in a number of applications.

CNTs Field Emission Applications

CNTs are the best known field emitters of any material. This is understandable, with regard to their high electrical conductivity, and the unbelievable sharpness of their tip (as the tip’s radius of curvature becomes smaller, the electric field will be more concentrated, resulting in increased field emission; this is the same reason lightning rods are sharp). In addition, the sharpness of the tip also indicates that they emit at specifically low voltage, a key fact for building low-power electrical devices that employ this feature. CNTs can carry an amazingly high

current density, probably as high as 10^{13} A/cm^2. Additionally, the current is extremely stable. Field-emission flat-panel displays are an immediate application of this behavior, receiving considerable interest. Unlike conventional cathode ray tube display where a single electron gun is used, CNT-based displays use a separate electron gun (or even many of them) for each individual pixel in the display. Their low turn-on and operating voltages, high current density, and steady, long-lived behavior make CNTs very attractive field emitters in this application. General types of low-voltage cold-cathode lighting sources, electron microscope sources, and lightning arrestors are other applications utilizing the field-emission characteristics of CNTs.

CNTs Conductive Plastics

Over the past five decades, much of the history of plastics has involved their use as a substitute for metals. For structural applications, plastics have progressed tremendously, but not where electrical conductivity is needed, since plastics are very good electrical insulators. This deficiency can be ruled out by loading plastics up with conductive fillers, such as carbon black and larger graphite fibers (the ones used to make golf clubs and tennis rackets). In order to offer the necessary conductivity using conventional fillers, the loading required is typically high, however, leading to heavy parts and, more prominently, plastic parts whose structural properties are highly degraded. It is well known that as the aspect ratio of filler particles becomes high, the loading required to achieve a given level of conductivity becomes low. For this reason, CNTs are perfect because they have the highest aspect ratio of any carbon fiber. Furthermore, their natural tendency to form ropes offers inherently very long conductive pathways even at ultra-low loadings.

This behavior of CNTs is utilized in applications such as electrostatic dissipation (ESD); EMI/RFI shielding composites; coatings for gaskets, enclosures, and other uses; radar-absorbing materials for low-observable (“stealth”) applications; and antistatic materials and (even transparent!) conductive coatings.

CNTs Energy Storage

The intrinsic properties of CNTs make them the preferred material for use as electrodes in capacitors and batteries — two technologies of fast-growing significance. CNTs possess good electrical conductivity, an extremely high surface area (~1000 m^2/g), and most importantly, their linear geometry makes their surface very accessible to the electrolyte.

Research has demonstrated that CNTs have the highest reversible capacity of any carbon material for use in lithium-ion batteries [B. Gao, Chem. Phys. Lett. 327, 69 (2000)]. Moreover, CNTs are excellent materials for supercapacitor electrodes [R.Z. Ma, et al., Science in China Series E-Technological Sciences 43 178 (2000)] and are currently being marketed for this application.

In addition, CNTs hold applications in various fuel cell components. They have several properties, such as high thermal conductivity and surface area, making them valuable as electrode catalyst supports in PEM fuel cells. Owing to their high electrical conductivity, they may also be used in gas diffusion layers, besides current collectors. The high strength and toughness-to-weight characteristics of CNTs may also prove useful as part of composite components in fuel cells that are used in transport applications, where durability is paramount.

CNTs Conductive Adhesives and Connectors

The exact properties that make CNTs desirable as conductive fillers for use in ESD materials, electromagnetic shielding, and so on make them suitable for interconnection applications and electronics packaging, including coaxial cables, potting compounds, and adhesives and other types of connectors.

CNTs Molecular Electronics

The idea of building electronic circuits out of the critical building blocks of materials — molecules — has seen growth in the past five years, and is a vital part of nanotechnology. In any electronic circuit, but specifically when dimensions reduce in size to the nanoscale, the interconnections between switches and other active devices become more

and more essential. Their ability to be precisely derived, electrical conductivity, and geometry make CNTs the most suitable candidates for the connections in molecular electronics. Furthermore, they have been shown as switches themselves.

CNTs Thermal Materials

The record-setting anisotropic thermal conductivity of CNTs is opening doors to several applications that involve heat transfer. Such an application is found in electronics, specifically advanced computing, where uncooled chips currently regularly exceed 100 °C.

The technology for creating aligned structures and ribbons of CNTs [D.Walters, et al., Chem. Phys. Lett. 338, 14 (2001)] is a step toward achieving extremely efficient heat conduits. Furthermore, composites with CNTs have been demonstrated to significantly increase their bulk thermal conductivity, even at incredibly small loadings.

CNTs Structural Composites

The superior properties of CNTs are not just restricted to thermal and electrical conductivities but also include mechanical properties, such as strength, toughness, and stiffness. These properties pave the way for use in a range of applications exploiting them, including advanced composites that need high values of one or more of these properties.

CNTs Fibers and Fabrics

Recently, fibers spun from pure CNTs have been demonstrated [R.H. Baughman, Science 290, 1310 (2000)] and are experiencing rapid development, together with CNT composite fibers. Such super strong fibers will have several applications such as woven fabrics and textiles, transmission line cables, and body and vehicle armor. CNTs are also being employed in order to make textiles stain resistant.

CNT Catalyst Supports

CNTs intrinsically possess an enormously high surface area; actually, for SWNTs, every atom is not just on one surface — but two surfaces, the

interior and exterior of the nanotube. Along with the ability to attach basically any chemical species to their sidewalls (functionalization) offers a prospect for unique catalyst supports. Their electrical conductivity may also be used propitiously in the quest for new catalysts and catalytic behavior.

CNTs Biomedical Applications

Although the exploration of CNTs in biomedical applications is just in progress, it has great potential. Since a great part of the human body is made up of carbon, it is usually considered a very biocompatible material. The growth of cells on CNTs has been demonstrated; therefore, they apparently have no toxic effect. The cells also do not adhere to the CNTs, opening doors for applications such as anti-fouling coatings for ships and coatings for prosthetics.

The ability to functionalize (chemically modify) the sidewalls of CNTs also gives rise to biomedical applications including neuron growth and regeneration, and vascular stents. It has also been demonstrated that a single strand of DNA can be bonded to a nanotube, which can subsequently be effectively inserted into a cell.

CNTs Air and Water Filtration

Several corporations and researchers have already developed CNT-based water and air filtration devices. It has been reported that these filters, apart from blocking the tiniest particles, can also destroy most bacteria. This is one more area where CNTs have already been commercialized and products are available now.

CNTs Ceramic Applications

Materials scientists at UC Davis have produced a ceramic material reinforced with carbon nanotubes. The new material is significantly tougher than traditional ceramics, conducts electricity, and can both conduct heat and function as a thermal barrier, with respect to the nanotube orientation.

Since ceramic materials are very hard and resistant to heat and chemical attack, they are valuable for applications such as coating turbine blades; however, they are also very brittle. The researchers mixed powdered alumina (aluminum oxide) with 5%–10% carbon nanotubes, in addition to 5% finely milled niobium. The mixture was treated with an electrical pulse in a process called spark-plasma sintering by the researchers. This process collates ceramic powders more rapidly and at lower temperatures than traditional processes.

The fracture toughness (resistance to cracking under stress) of the new material is up to five times of that of traditional alumina. The material exhibits electrical conductivity seven times of that of earlier ceramics made with nanotubes. It also has fascinating thermal properties, conducting heat in one direction, along the alignment of the nanotubes and, on the other hand, reflecting heat at right angles to the nanotubes, making it a preferred material for thermal barrier coatings.

Other Carbon Nanotubes Applications

There are several other potential applications for CNTs, including solar collection, nanoporous filters, catalyst supports, and all kinds of coatings. There are almost certainly several surprising applications for this excellent material that will be revealed in the future, and which may prove to be the most significant and valuable ones of all. A number of researchers have been studying the conductive and/or waterproof paper produced using CNTs. CNTs have also been demonstrated to absorb infrared light and may hold applications in the I/R optics industry.

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