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CARBON NANOTUBES – AN OVERVIEW

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ABSTRACT

Carbon nanotubes are the unique tubular structures with nanometer scale for measuring diameter. The nanotubes contain one up to tens and hundreds of concentric shells of carbons with adjacent shell separation. The carbon network of the shells is considered closely related to the honeycomb arrangement of the carbon atoms in graphite sheets. Amazing thermal, mechanical and electronic properties of the nanotubes appear in their structure and also in the graphite-like arrangement of the carbon atoms in shells. The carbon nanotubes have high Young's modulus and tensile strength, which makes them preferable for composite materials with extended mechanical properties. The carbon nanotubes may exhibit metallic or semiconducting nature depending on their structural parameters. These properties make a way for application of the carbon nanotubes as central elements in electronic devices including field-effect transistors (FET), single-electron transistors and rectifying diodes. These tiny structures also find their way in different applications that touch nearly every field of technology, including aerospace, electronics, medicine, defense, automotive, energy, construction, and even fashion. Carbon nanotubes are also proved to be helpful in drug delivery due to their potent drug targeting property.

Keywords: Nanotechnology, Carbon nanotubes; Synthesis, Electro-chemical properties, Thermal properties, Biosensors.

INTRODUCTION

Carbon nanotubes are of increasing interest as novel nano scale materials. Carbon nanotube which is made of carbon is a tube shaped material with nano-meter scale to measure diameter [1]. Carbon Nanotubes appear in many structures, differing in length, thickness, and in the type of helicity and number of layers [2]. The nanotubes contain one up to tens and hundreds of concentric shells of carbons with adjacent shells separated. The carbon network of the shells is considered closely related to the honeycomb arrangement of the carbon atoms in graphite sheets [3]. Depending on these structural variations carbon nano-tubes act either as metals or as semi-conductors. Carbon Nano-tubes have diameters ranging from <1 nm up to 50 nm and lengths up to several microns, Carbon Nanotubes are emerging in today's scientific field due to their unique combination of stiffness, strength, and tenacity compared to other fiber materials which usually lack one or more of these properties and are also gaining importance as their thermal and electrical conductivity are very high, and comparable to other conductive materials [4-6].

Structural Categorization

Carbon nanotubes CNTs are the allotropes of carbon obtained as single-walled (SWCNTs) or multi-walled (MWCNTs) material with a cylindrical nano structure [7]. Based on these structures, the carbon nano tubes are categorized in to:

Single-wall Nanotubes (SWNT)

Single-wall nanotubes (SWNT) are tubes made of graphite which are capped at the ends. These have a single cylindrical wall and the structure can be visualized as a layer of graphite with a single atom thick, called graphene, which is rolled into a seamless cylinder [8]. SWNT normally have a diameter close to 1 nm and longer tube length. SWNT have unique electronic and mechanical properties which are essential in numerous applications in field-emission displays, nanocomposite materials, nanosensors, and logic elements [9].

Multi-wall Nanotubes (MWNT)

Multi-wall nanotubes can appear either in the form of a coaxial assembly of SWNT or as a single sheet of graphite rolled into the shape of a scroll [10]. The diameters

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usually are in the range of 5 nm to 50 nm and the interlayer distance is close to the distance between graphene layers in graphite. MWNT are easily produced in high quantities than SWNT [11]. Because of its greater complexity and variety the structure of MWNT is less well understood.

Double-wall Nanotubes (DWNT)

Double-wall nanotubes (DWNT) which are an important sub-segment of MWNT combine similar morphology and other properties of SWNT, but significantly improving their resistance to chemicals [12]. As DWNT are synthetic blend of both SWNT and MWNT, they exhibit electrical and thermal stability of SWNT and flexibility of MWNT. In DWNT, only the outer wall is modified preserving the intrinsic properties. Studies proved that DWNT have better thermal and chemical stability than SWNT and can be applied to gas sensors and dielectrics [13].

Process of Preparation of carbon nanotubes

Carbon arc-discharge, laser ablation, high pressure carbon monoxide (HiPco), and chemical vapor deposition (CVD) are the techniques being employed to synthesize CNTs. In these techniques, the CVD method has been proven to be most promised in terms of its price/unit ratio. The method (arc-evaporation) that produces the best quality nanotubes involves applying a current of about 50 A between two graphite electrodes in a helium atmosphere [14]. In graphite evaporation, a part condenses on the walls of the reactor vessel and a part condenses on the cathode. The deposits that remain on the cathode usually contain the CNTs. SWCNTs are produced when metals like cobalt and nickel or some other metal is combined with the anode [15]. Studies reported that the synthesis of SWCNTs with diameters of around 1 nm, involves the use of a gas mixture of 10 Torr methane and 40 Torr argon at a dc current of 200 A and a voltage of 20 V. Researchers have used Co, Ni, and Fe as catalysts for the synthesis of CNTs. Researchers have also used the mixture of catalysts like NiCo, Co-Y, or Ni-Y for the synthesis of SWCNTs [16].

In the technique of laser-ablation, intense laser pulses are applied to ablate a carbon target. This pulsed laser-ablation of graphite yields CNTs in the presence of an inert gas and catalyst which exist in the form of ropes or bundles of 5 to 20 nm diameter and ten to several hundred of micrometers long [17]. Fullerenes are graphite polyhedrons with enclosed metal particles. Amorphous carbon is obtained as the by-product in arc-discharge and laser-ablation technique. Usually, the CVD technique involves the reaction of a carbon-containing gas such as methane, acetylene, ethylene, ethanol, etc., with a metallic catalyst particle like cobalt, nickel, iron, or a combination of these metals such as cobalt/iron or cobalt/molybdenum, at above 600°C temperature [18]. Both arc-discharge and laser-ablation methods produce SWCNTs more than 70%, but these methods possess disadvantages like

(i) Tangled CNTs production which make the purification and application process difficult and

(ii) These processes depend on evaporation of carbon atoms at more than 3000°C temperatures [19].

Purification of carbon nanotubes

Mostly, SWCNT sample consists of carbonaceous impurities like amorphous carbon, fullerenes, nanoparticles, and transition metals that are introduced as catalysts during the process of producing SWCNTs [20]. Potential applications of SWCNTs as nanoelectronic devices, field emitters, gas sensors, high-strength composites, and hydrogen storagers demands for pure SWCNT materials [21]. This proves that one of the greatest current demands in carbon nanotube technology research and commercialization involves the development of effective and viable methods in obtaining pure and undamaged SWCNTs. The methods which are considered include hydrothermal, gaseous, catalytic oxidation, nitric acid reflux, peroxide reflux, cross-flow filtration, chromatography, and chemical functionalization [22]. Purification based on initial selective oxidation to remove amorphous carbon followed by a reflux in concentrated nitric acid, is effective in removing metal from the reaction products, and then the refluxing in nitric acid induces wall damage in the produced nanotubes [23].

More than 90% pure SWCNTs are produced using microfiltration which is ultrasonically assisted from amorphous and crystalline carbon impurities and metal particle [24]. Purification which is 10 A scalable is possible using heating by microwave in the presence of air followed by treatment with hydrochloric acid. Microwave assisted purification is also applied for purification of MWCNTs. Now-a-days, the dissolution of SWCNTs by deoxyribonucleic acid (DNA) for purification has been reported [25]. As reported by some researchers, the solubilization of SWCNT ropes and bundles in both organic and aqueous solutions is due to noncovalent association of SWCNTs with polymers. The types of polymers which are employed in solubilization studies range from the water-soluble helical polymer amylose found in starch, to organic soluble polymers such as poly(m-phenylenevinylene)-co-(2,5-dioctoxy-p-phenylene)vinylene and various derived polymers including poly(2,6-pyridinlenevinylene)-co-(2,5-dioctoxy-p-phenylene)vinylene and poly(5-alkoxy-m-phenylenevinylene)-co-(2,5-dioctoxy-p-phenylene)vinylene [26].

Now-a-days, carboxy methylcellulose has also been employed for the purification of SWCNTs. This method also involves annealing in air and dispersing the SWCNTs in an gelatin aqueous solution [27]. The purity of the CNTs can be estimated by Raman spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), and UV-visble-near-infrared (UV-vis-NIR).

Optical properties of carbon nanotubes

Studies of the electronic properties of SWNTs reported that SWNTs could be either metallic or semiconducting in nature depending on their structural parameters. In MWNTs and in bundles of SWNTs the lower symmetry of structures when compared to the symmetry of the separate SWNTs results in the appearance or disappearance of the band gap [28]. The carbon atoms precipitated form ‘‘handles’’ migrate to the root of the nanotube where these atoms are then incorporated into the hexagonal carbon network. Mechanism involved in hexagon addition at the nanotube base is by bond formation between a pair of handles atoms at the opposite sides of a heptagon. The band structure of the ‘‘rolled-up’’ SWNTs can be studied within the tight-binding model in the zone-folding scheme [29]. The band structure of a single graphene sheet is considered as a starting point and the unit cell of the sheet contains two carbon atoms, each carbon atom consisting four valence electrons. Hence, a tight-binding model yields eight bands: four valence bands and four conduction bands in which each carbon atom are sp^2-hybridized [30].

The degeneration energy level corresponds to the Fermi energy, which proves that the graphene sheet is a zero-gap metal. By rolling-up a graphene strip into a cylindrical nanotube, the band structure of the nanotube can be derived [31]. The band structure of a nanotube is given by the zone-folding relation of grapheme. The 1D band structure of a SWNT consists of the 2D band structure of the grapheme sheet. In the case of zigzag nanotubes a singly-degenerative band was calculated lower than with the tight-binding model [32]. The structural optimization of the nanotubes had little effect on the band structure. The metallic tubes have definite density states at the Fermi surface, which is inversely proportional to tube diameter [33]. The flat parts of the tube band energies give rise to two types of absorption coefficients and the resonant Raman scattering intensity requires calculation of the matrix elements of the momentum between states in the valence and the conduction band. The optical transitions in perpendicular geometry are largely suppressed by depolarization effect [34].

Thermal properties of carbon nanotubes

Thermal properties of carbon nano-tube composites are important for both processing and applications. As a function of temperature, polymeric materials structurally transform from solid to rubbery and then to liquid states. Various intermediate processing steps are carried-out in the transformation from liquid or rubber-like state before the materials are cooled to below glass transition temperature [35]. Preliminarily carried-out experimental and simulation studies on the thermal properties of individual nanotubes conclude very high thermal conductivity of SWNTs. It also confirms that nanotube reinforcement in polymeric materials significantly change the thermal and structural properties [36]. Polyethylene is a linear chain molecule containing CH_2 as the repeating unit in the chain. The density depends on function of temperature for a pure polyethylene system. Both the polymeric materials and polyethylene systems show discontinuity in the slope of the density-temperature curve. These discontinuities represent glass transition temperatures in both the cases. The increase in the thermal expansion coefficient becaause of mixing SWNTs in the polymer sample is attributed to the increase in thermal motions of the nanotubes in the sample. We can also refer that, glass transition temperature, the self-diffusion coefficient of the polymer molecules in the composite increases to 30% above its pure polyethylene sample values. The elevation in the diffusion coefficient is larger along the axis of the added nanotube fibers and may be helpful during the processing steps due to better flow of the material above glass transition temperature [37].

Mechanical behavior of carbon nanotube-polyethylene composites

Use of fibers to elevate the mechanical ability of a composite material is considered as one of the most common practice. Its related technology has been commercialized. Materials usually used as fibers are glass, carbon black and other ceramics [38]. These materials not only add structural strength to materials but also add desired functionality in showing thermal and electrical property. The structural strength characteristics of the materials depend on the percentage of mechanical load transfer from the matrix to the fiber and also on the yield by coupling between the two [39]. Where, mechanical load from matrix to the fibers is transferred through the coupling between the two. In some cases, the coupling is carried-out through chemical interfacial bonds, which are covalent or noncovalent in nature, while in other cases the coupling will be purely physical in nature. Covalently coupled matrix and fibers are strong interacting systems while VDW coupled systems are weak interacting [40]. The ratio of fiber, which is measured as L/D, where L is the length of the fiber, and D is the diameter, are also reffered as important parameters for the efficiency of load transfers as larger surface area of the fiber is better for larger load transfers. It is expected that the limiting value of the ratio is found to be related to the interfacial shear stress and maximum strength of the fiber. Recent studies on MWNTs or SWNT ropes have proved that the strength of the nanotubes must be in the range of 50GPa [41].

Electro-chemistry of carbon nanotubes

The electronic behavior of CNTs proves that they possess the ability to promote electron-transfer when used as electrode materials. Recent investigators have explained that CNTs possess great electro-catalytic properties toward biomolecules like dopamine, epinephrine, dihydronicotinamide adenine dinucleotide (NADH), uric acid, cytochrome c and ascorbic acid. Recently, the film coated electrodes of CNTs are attracting attention of many scientific researchers [42]. Studies suggest that surfaces of carbon nanotubes exhibit enhanced electron transfer rates when applied as electrodes in electrochemical reactions.

MWCNTs play a role in the electro-catalysis of oxygen reduction, and charge transfer on CNTs is seen to occur faster compared to graphite [43]. Studies have demonstrated that MWCNT-modified electrode can be employed as amperometric oxygen sensitive electrode to construct a glucose biosensor offering better glucose determination. Functionalization or modification of CNTs within the fields of nanoscience, nanotechnology, bioengineering, and bionanotechnology, promises to be a good approach for improving the solubility and compatibility of CNTs [44].

Applications of carbon nanotubes

Carbon nanotubes are considered as the miniscule pipes of rolled up carbon atoms.. The tiny structures find their way in different applications that touch nearly every field of technology, including aerospace, electronics, medicine, defense, automotive, energy, construction, and even fashion. Indeed, NASA is developing materials using these carbon nanotubes for space applications, by taking advantage of their tremendous stiffness and strength [45].

- It can be used to sniff bombs, search for toxins in the air and water and can be used to test whether someone has skin cancer by checking for a chemical called dimethyl-sulfone.
- They are strong, elastic, and possess amazing electrical properties due to which researchers created a carbon nanotube aerogel that expands and contracts as it converts electricity into chemical energy.
- Carbon nanotubes are suitable as artificial muscles since they retain their shape after being compressed thousands of times, in similar way as that of soft tissue [46].
- Geckos climb up smooth surfaces with the help of tiny hairs on their feet exploiting the electrostatic force between themselves and the wall. Carbon nanotubes used in agecko-inspired tape sticks to dry smooth surfaces when pressed against them which make climbing up of smooth surfaces easier.
- Carbon nanotubes application can increase viewing pleasure and portability of flat screens, LEDs, flexible displays as these use tiny pipes of carbon which make excellent field emitters or conductive surfaces [47].
- Studies proved that carbon nanotubes are perfect for allowing damaged bone to restructure itself as they are strong, lightweight, and can be modified for compatibility with any part of the body.
- Carbon nanotubes may also help to reduce inflammation in broken bone.
- In medicine, modified carbon nanotubes find their use as they can enter cells to deliver drugs or knock out unwanted genes.
- Use of carbon nanotubes as electrodes in capacitors provides more current and better electrical and mechanical stability when compared to other leading materials [48].
- Addition of carbon nanotubes increases conductivity in films, also increases the organization and surface area utilization in countless materials, giving them a greater energy to protect against power surges. Addition of nanotubes (about 1 percent of the weight of the entire material) can increase products efficiency drastically.
- Carbon nanotubes are also added to strengthen materials for sports equipment, body armor, vehicles, rockets, and building materials.
- The size, surface area (500 square meter per gram), and adsorption properties of carbon nanotubes make them an ideal membrane for filtering toxic chemicals, dissolved salts and biological contaminants from water [49].
- Cup cakes made up of vertically aligned carbon nanotube arrays (VANTAs) that are grown on silicon are able to detect terahertz radiation. Using a razor blade, visible chunks of these densely packed arrays can be sliced off and placed on top of a laser power detector to detect terahertz radiation. Terahertz radiation can penetrate materials like plastic, clothing, paper and some biological tissues, making it an attractive candidate for applications such as concealed weapons detection, package inspection and imaging skin tumors [50].
- Storage of solar energy in molecules that change state in response to light could be entirely transformed by carbon nanotubes.
- Medical researchers are demonstrating carbon nanotubes as potential needles for injecting drugs or genes into sick cells. Nanotube probes may be used to test for certain substances and test certain processes beyond cell membranes [51].

Carbon nanotubes in Pharmaceutical and Medical research

Carbon nano tubes (CNTs), which are very prevalent are being medically researched in the fields of efficient drug delivery and biosensing methods for effective disease treatment. Carbon nanotube technology has been proved to possess potential benefits in drug delivery and biosensing methods [52]. CNTs possess several unique chemical, size, optical, electrical and structural properties that make them attractive as drug delivery and biosensing platforms for the treatment of various diseases. Hence, these carbon nanotubes have gained interest in medical field. Functionalization of single-walled nanotubes (SWNTs) has shown enhancement in solubility and allowed potent tumor targeting/drug delivery. This property of increased solubilization prevents cytotoxicity of SWNTs [53].

Carbon nano tubes in cancer treatment and Health monitoring

Cancer is considered as a group of diseases in which cells grow and divide abnormally. Cancer therapy involves surgery, radiation therapy and chemotherapy which are usually painful, produce adverse side effects and kill normal cells. CNTs, when used as drug delivery vehicles have proved potential activity in targeting specific cancer cells with a dose lower than conventional drugs [54]. However CNTs are proved to be effective in not harming healthy cells and significantly reduces side effects. Blood glucose monitoring methods in patients suffering from diabetes are usually invasive and often painful [55]. It was reported that 70 percent of glucose readings obtained by continuous glucose sensors differed by 10 percent or more and 7 percent differed by over 50 percent. The properties of single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) like high electrochemically accessible surface area, high electrical conductivity and useful structural properties have been reported to be potential and highly sensitive noninvasive glucose detectors [56].

Drug delivery is one of the rapidly growing medical field in which nano tube technology is applied. Systems that are in current use for drug delivery are dendrimers, polymers, and liposomes. Since, carbon nanotubes consists of effective structures that possess high drug loading capacities and good cell penetration properties, as these carbon nanotubes function with larger inner volume that can be used as the drug container and their ability to be readily taken up by the cell make these tube structures as potential sources of drug delivery [57]. Due of the tube structure of carbon nanotubes, they can be made with or without end caps and this quality of being made with-out end caps make the drug that exists inside carbon nano tube more accessible. But, carbon nanotube drug delivery systems, also give rise to some problems like the lack of solubility, clumping occurrences and half-life [58]. To overcome these problems is an essential aspect for further advancements in carbon nano tube technology. Methods to overcome include drug encapsulation which has shown to enhance water dispersibility, better bioavailability, and reduced toxicity. Encapsulation also provides a material storage application, protection and controlled release of the loaded molecules [59]. All these properties result in a better drug delivery basis from which further research and understanding could make advancements in carbon nano tube technology like increased water solubility, decreased toxicity, sustained half-life, increased cell penetration and uptake, all of these properties are currently novel but undeveloped [60].

Carbon nanotubes as biosensors

When experiencing stress or strain, this can be notified by observing the change in electrical resistance.of a single walled carbon nano tube. This effect changes flow through the nanotube, which can be measured in order to accurately quantify stress [61]. The tube network which is embedded within orthopedic plates, clamps, and screws and in bone grafts determine the state of bone healing by measuring the effect of a load on the plate, clamp, screw, or other fixation devices attached to the bone. A healed bone can bear most of the load than an unhealed bone [62]. Measurements are done wirelessly by electrical induction which allows the accurate results. Carbon nanotube of plasma polymer-based amperometric biosensors are also fabricated for ultrasensitive glucose detection. The device with single-walled CNTs showed a sensitivity higher than that of multi walled CNTs during glucose level detection [63]. The high performance of glucose biosensor activity is attributed to the fact that CNTs possess excellent electrocatalytic activity which will enhance electron transfer and that PPFs and/or the plasma process for CNTs are a suitable design of the interface between GOD and CNTs. The carbon nanotube ultrasensitive biosensor for DNA detection was developed and this fabricated biosensor is helpful in electronic detection of DNA hybridization [64].

CONCLUSION

The small dimensions, strength and the remarkable physical properties of carbon nano tubes make them a very unique material. The rapid research development and industrial application has made it necessary to summarize the current status about these carbon nano tube structures. In this review article, we have made efforts to emphasize on the structursl charecterization, preparation, purification, optical charecteristics, mechanical aspects, thermal properties and electrochemical properties as these tiny structures find their way in different applications that touch nearly every field of technology, including aerospace, electronics, medicine, defense, automotive, energy, construction, and even fashion. We have also discussed the use of these tube structures in pharmaceutical and medical fields as drug delivery equipments because of their site targeting capacity and as biosensors in glucose level and Dna hybridization determination due to their electric resistance property.

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