Review Article

CARBON NANOTUBES PRODUCTION, CHARACTERISATION AND ITS APPLICATIONS

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ABSTRACT

Carbon nanotubes (CNTs) are allotropes of carbon with a nanostructure to revolutionize the field of nanotechnology and also pharmaceutical technology. They have unique electronic, mechanical, optical and chemical properties that make them promising candidates for a wide variety of potential biomedical applications, including drug transporters, new therapeutics, delivery systems and diagnostics. Their unique surface area, stiffness, strength and resilience have led to much excitement in the field of pharmacy. Nanotubes are categorized as single-walled nanotubes, multiple walled nanotubes and carbon nanofibres. Various techniques have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, chemical vapor deposition, silane solution method and flame synthesis method. They can pass through membranes, carrying therapeutic drugs, vaccines and nucleic acids deep into the cell to targets previously unreachable. Purification of the tubes can be divided into a couple of main techniques: oxidation, acid treatment, annealing, sonication, filtering and functionalization techniques. The main problem of insolubility in aqueous media has been solved by developing a synthetic protocol that allows highly water-soluble carbon NTs to be obtained. The modifications are done to improve efficiency of carbon nanotubes by formulating luminescent carbon nanotubes, ultrathin carbon nanoneedles, magnetically guided nanotubes. The application of carbon nanotube in tissue engineering, drug carrier release system, wound healing, in cancer treatment and as biosensor.

Keywords: Carbon nanotubes (CNTs), Single and multiple walled nanotubes.

INTRODUCTION

CNTs were discovered in October 1991 by Sumio Iijima. He studied the material deposited on the cathode during the arc-evaporation of graphite and found the cathodic deposition contained tubular structures called as nanotubes[1]. These led to an explosion of research into the physical and chemical properties of CNTs all over the world. CNTs possess various novel properties that make them useful in the field of nanotechnology and pharmaceuticals. They are tubular in shape, made of graphite and are members of the fullerene family only. They are nanometers in diameter and several millimeters in length. And, have a very broad range of electronic, thermal, and structural properties. These properties vary with kind of nanotubes defined by its diameter, length, chirality or twist and wall nature. Single walled nanotubes (SWNTs) and multiple walled nanotubes (MWNTs) are two types of nanotubes produced so far. Their unique surface area, stiffness, strength and resilience have led to much excitement in the field of pharmacy[3].

MORPHOLOGY AND STRUCTURE

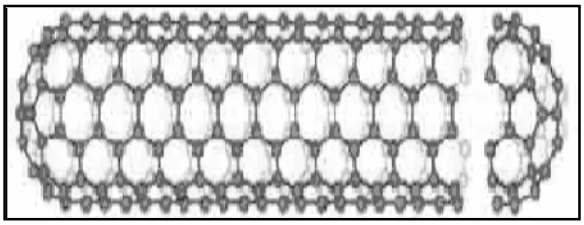


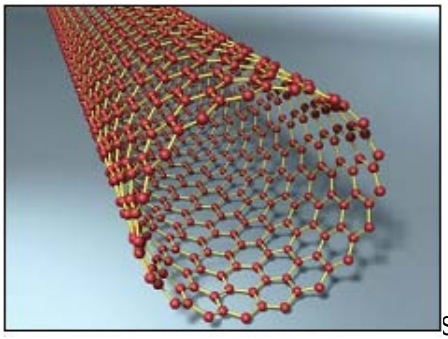
Figure 1: Structure of carbon nanotube

CNTs are sp^2 bonded, with each atom joined to three neighbours, as in graphite. Thus, tubes are considered as rolled-up graphene sheets[4].

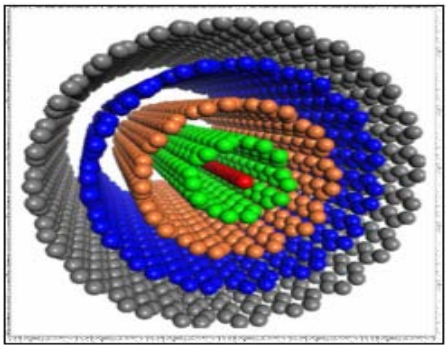
CLASSIFICATION OF CARBON NANOTUBES

Carbon nanotubes are classified in following two types:

- SWNTs- Single walled carbon nanotubes
- MWNTs- Multiple walled carbon nanotubes



SWNT



MWNT

Figure 2: Structure of SWNT and MWNT

Table 1: Comparison between SWNT and MWNT[2,5]

SWNT	MWNT
Single layer of graphene.	Multiple layer of graphene
Catalyst is required for synthesis.	Can be produced without catalyst.
Bulk synthesis is difficult as it requires proper control over growth and atmospheric condition.	Bulk synthesis is easy.
Purity is poor.	Purity is high.
A chance of defect is more during functionalization.	A chance of defect is less but once occurred it's difficult to improve.
Less accumulation in body.	More accumulation in body.
Characterization and evaluation is easy.	It has very complex structure.
It can be easily twisted and are more pliable.	It cannot be easily twisted.

PROPERTIES OF CARBON NANOTUBES[5-10]

CNTs are one of the stiffest, strongest and toughest fiber that and have huge tensile strength. They are the best conductor of electricity on a nanoscale level. And, have thermal conductivity comparable to diamond along the tube axis. Strong vandar Waals attraction operating in them leads to spontaneous roping of many nanotubes because of self assembly. Being inert, it can be reacted and manipulated with the richness and flexibility of other carbon molecules. They have great molecular perfection and are free of defects.

CHARACTERISATION OF CNTs[12]

RAMAN Spectroscopy suitable for the quick and reliable screening of the presence of SWCNT Transmission electron microscopy allowing for the assessment of detailed structures.

Scanning electron microscopy providing overviews of sample structures while less sensitive to sample preparation and homogeneity than TEM.

Thermo gravimetric analysis giving information about relative abundance of Catalyst particles, nanotubes and other carbonaceous structures.

SYNTHESIS OF CARBON NANOTUBES

A. Arc Discharge method[11-14]

Arc Discharge method has been reported for producing fullerenes. It is the most common and easiest way to produce nanotubes. In this method, nanotubes are produced through arc-vaporization of two carbon rods placed end to end with a distance of 1mm in an environment of inert gas such as helium, argon at pressure between 50 to 700 mbar. Carbon rods are evaporated by a direct current of 50 to 100 Amps driven by 20V which will create high temperature discharge between two electrodes. Due to this anode will get evaporated and rod shaped tubes will be deposited on cathode. Bulk production of CNTs depends on uniformity of plasma arc and temperature of deposition.

1. Production of SWNTs

In the synthesis SWNTs anode is dipped with a metal catalyst such as Fe, Co, Ni, Y, or Mo. It produces SWNTs with a diameter of 1.2 to 1.4nm. Efficiency of SWNT production by arc discharge method is improved with,

a) Inert Gas: Argon with a lower diffusion coefficient and thermal conductivity has given nanotube with smaller diameter (1.2nm) and 0.2nm diameter decrease with 10% increase in argon: helium ratio, when Nickel and Yttrium is used as a catalyst (4.2: 1).

b) Optical Plasma Control: As the distance between anode and cathode is increases, anode vaporization increases, due to which strong visible vortices around cathode is occurred. With a nickel and yttrium catalyst (C/Ni/Y is 94.8:4.2:1) the optimum nanotubes were produced at a pressure of 660 mbar for pure helium and 100 mbar for pure argon. The nanotubes diameter ranges from 1.27 to 1.37 nanometer.

c) Catalyst: By changing metal catalyst, the nanotubes with a diameter of 0.6 to 1.2nm are produced. Catalysts used are Co and Mo.

2. Production of MWNTs

MWNTs produced with the use of pure graphite are with an inner diameter 1-3nm and outer diameter10nm (approx.). Since catalyst is not used in this process there is no need for a heavy acidic purification. So, MWNTs can be formed with a less number of defects. Different methods used to synthesize are,

a) Synthesis in Liquid Nitrogen[12]: MWNTs are formed by generating arc- discharge in liquid nitrogen. For which low pressure and expensive inert gas are not needed. Yield is about 70% of reaction product.

b) Magnetic Field Synthesis[13]: MWNTs formed by this method are defect free and having high purity. In this arc-discharge is controlled by a magnetic field around the arc plasma. Extremely pure graphite rods (purity > 99.999 %) are used as electrodes. Highly pure MWNTs (purity > 95 %) are obtained without further purification, which disorders walls of MWNTs.

c) Plasma Rotating Arc Discharge[14]: The centrifugal force caused by the rotation generates turbulence and accelerates the carbon vapor perpendicular to the anode and the rotation distributes the micro discharges uniformly and generates stable plasma. Consequently, it increases the plasma volume and raises the plasma temperature. At the rotation speed of 5000 rpm, a yield of 60 % was found at a temperature 1025 °c without the use of a catalyst. The yield can be increased up to 90% after purification if the rotation speed is increased and the temperature is enlarged.

B. Laser Ablation method[14]

A pulsed or continuous laser is used which will vaporize a graphite target in an oven at 1200 °c. The oven is filled with helium or argon gas in order to keep the pressure at

500 torr. Since the optimum background gas and catalyst mixture is the same as in the arc discharge process, is almost similar to arc discharge. This might be due to very similar reaction conditions and mechanisms. This method is very expensive so it is mainly used for SWNTs. Laser vaporization results higher yield of SWNTs with narrower size distribution than those produced in arc discharge process. Catalyst used for SWNTs is Ni: Y (4.2: 1 at %). MWNTs can be also produced with pure graphite.

1. Production of SWNTs

a) Ultra Fast Pulses from a Free Electron Laser (FEL) Method: In this method the pulse width is ~ 400 fs. The repetition rate of the pulse is increased from 10 Hz to 75 MHz The intensity of the laser bundle ~5 x 10^{11} w/cm^2. A jet of preheated argon gas is located near the rotating graphite target. In that argon gas deflects the ablation 90away from incident beam direction, clearing carbon soot from front of target. If this system is upgraded with full power a yield of 45gm/ hr can be achieved. Catalyst used is NiCo or NiY.

b) Continuous Wave Laser-Powder Method: In this method instead of Nd: YAG laser, CO_2 laser is used in an argon stream. Laser ablation of mixture of graphite and catalyst powder is carried out, due to which thermal conductivity losses are significantly reduced. It is more economical in comparison with Nd: YAG laser system and yield is 5gm/hr.Catalyst used is Ni: Co 1: 1.

C. Chemical Vapors Deposition method[14-23]

It is carried out in two step process

1. Catalyst is deposited on substrate and then nucleation of catalyst s carried via chemical etching or thermal annealing. Ammonia is used as an etchant. Metal catalysts used are Ni, Fe or Co.

2. Carbon source is then placed in gas phase in reaction chamber. Then carbon molecule is converted to atomic level by using energy source like plasma or heated coil. This carbon will get diffuse towards substrate, which is coated with catalyst and nanotubes grow over this metal catalyst. Carbon source used is methane, carbon monoxide, acetylene. Temperature used for synthesis of nanotube is 650 – 900 C range. The typical yield is 30%. Production of nanotubes by different chemical vapor deposition can be summarized as:

D. Flame Synthesis method[23]

SWNTs are formed in controlled flame environment from hydrocarbon fuels and small aerosol metal catalyst islands. These Catalyst Island was prepared in three ways-

1. Coated mesh with catalyst

2. Burning filter paper rinsed with metal solution.

3. Metal powder was inserted in trough and evaporated.

E. Silane Solution Method[24]

Carbon nanotubes were produced using a silane solution method, in which a substrate such as carbon paper or stainless steel mesh was immersed in a silane solution of a metal catalyst, preferably Co: Ni in a 1:1 ratio; and a feedstock gas containing a carbon source such as ethylene was fed through the substrate and the catalyst deposited thereon while the substrate was heated by applying an electrical current thereto. Thus, a reaction occurs between the catalyst and the gas to yield CNTs supported on the conductive substrate.

PURIFICATION OF CNTS[25-26]

Nanotubes usually contain a large amount of impurities such as metal particles, amorphous carbon, and multishell. There are different steps in purifications of nanotube.

1) Air Oxidation: The carbon nanotubes are having less purity; the average purity is about 5-10%. So purification is needed before attachment of drugs onto CNTS. Air oxidation is useful in reducing the amount of amorphous carbon and metal catalyst particles (Ni, Y). Optimal oxidation condition is found to be at 673 k for 40 min.

2) Acid Refluxing: Refluxing the sample in strong acid is effective in reducing the amount of metal particles and amorphous carbon. Different acids used were HCl, HNO_3 and H_2SO_4, but HCl was identified to be the ideal refluxing acid.

3) Surfactant aided sonication, filtration and annealing

After acid refluxing, the CNT were purer but, tubes were entangled together, trapping most of the impurities, such as carbon particles and catalyst particles, which were difficult with filtration. So surfactant-aided sonication was carried out.

Sodium dodecyl benzene sulphonate (SDBS) aided sonication with ethanol (or methanol) as organic solvent were preferred because it took the longest time for CNTS to settle down, indicating an even suspension state was achieved. The sample was then filtered with an ultra filtration unit and annealed at 1273 k in N_2 for 4 h. annealing is effective in optimizing the CNT structures. It was proved the surfactant-aided sonication is effective to untangle CNT, thus to free the particulate impurities embedded in the entanglement. Nanotube can also be purified by multistep purification method[26].

FUNCTIONALISATION OF CNTS AND CNHS[34-37]

A wire structure itself was very strong in graphite layer and was not chemically bonded to each other but was held together by vandar Waals force. So, adsorbed molecule tends to slip easily from surface of nanotubes due to their complete graphite structure. As it was also very hydrophobic in nature, it must be modified with certain chemical or their structure must be damage partially to hold the drug on surface of nanotubes and to reduce its hydrophobicity. Chemical oxidation and functionalization process was used for these

modifications. Both this process will maintain properties like surface area, tubular shape, wettability and porosity and gave consolidation, compression, and compaction characteristics.

1. Oxidation[34]

Chemical oxidation was carried out by heating at high temperature with different acids like H_2SO_4, HNO_3 in presence of air. It causes formation of pores and nano windows. Porosity will decide extent of drug loading, smaller molecule will get fitted into small pores.

2. Functionalisation[35-37]

The functionalization of single wall carbon nanohorns was carried out by 1,3-dipolar cycloaddition of azomethinylides and the products was characterized by spectroscopy, microscopy and thermogravimetry[35].

Covalent functionalization of multiwalled CNTs(MWNT) with poly (acrylic acid) has been successfully achieved via grafting of poly (acryloyl chloride) on nanotube surface by esterification reaction of acyl chloride-bound polymer with hydroxyl functional groups present on acid-oxidized MWNT and hydrolysis of polymer attached to nanotubes[37]. Polymer-functionalized MWNT could possess remarkably high solubility in water, and their aqueous solution was very stable without any observable black deposit for a long time.

It should be noted that when functionalization is required to add new properties to the nanotubes. In the case of SWNT, covalent functionalization will break some C = C double bonds, leaving "holes" in the structure on the nanotube and thus modifying both its mechanical and electrical properties.

Various functionalized CNTs are described below[36-37]:

(a) Luminescent Carbon Nanotubes

For diagnosis, the nanotubes must be functionalized with spectroscopically characteristic fluorescent dyes. One of the novel approaches in biomarking is through targeting cancer cells with luminescent nanoparticles, such as quantum dots. Compared with traditional organic fluorophores, quantum dots have superior properties, which include a higher quantum yield and much sharper emission spectra.

(b) Ultrathin Carbon Nanoneedles (CNNS)

The nanotubes also offer a structural advantage in that they are extremely thin but very long, offering a large surface area on which to graft the required drug. This allows the amount of drug loaded onto the nanotube to be regulated. However, the mechanisms of action are still unclear and the release of the chemically conjugated drug from the nanoneedle is not always possible. Current investigations are directed to the study of reversible associations for the intracellular release of the drug.

(c) Magnetically Guided Nanotubes (Titanium Nanotubes)

The nanoscale encapsulation of ferromagnetic structures has received a great deal of attention because of the exciting possibilities to use these materials in various applications that range from novel electromagnetic to biomedical devices. For example, nanoscale magnetic entities could be transported and concentrated at pretargeted locations or organs within the human body by means of an external magnetic field in order to exert a specific function with high local and temporal precision. Therefore, functionalized magnetic nanodots, nanowires, or nanotubes have a high potential for in vivo applications such as magnetic resonance imaging or site selective drug delivery systems, if the magnetic property is combined with an appropriate drug loading and release mechanism. TiO_2 nanotubes are a highly promising encapsulating material for a magnetic core as a high degree of biocompatibility can be combined with a broad range of other functionalities. It has been established that TiO_2 is a highly active photo catalyst. This property of TiO_2 has been intensively explored in the form of photo electrodes for the decomposition of various organic pollutants in water and air, and it has been used in self-cleaning, disinfecting, and anticancer materials. The photo catalytic ability of TiO_2 can be enhanced by using nanosized TiO_2 materials because of their large specific surface area. Not only can these tubes be used as a magnetically guided photocatalyst for the decomposition of organic matter but also the photo catalytic mechanism can be exploited to release an active species (a model drug). Among the various synthetic routes used to prepare TiO_2 nanotubes, anodization approaches have gained significant attention as they lead to highly ordered nanotubular arrangements.

DISPERSION/SUSPENSION, AGGREGATION STATUS AND SEDIMENTATION OF CNTS

The lack of methods to prepare water soluble CNT particles those are homogeneous enough to ensure validity of the studies on the alleged nano size effects. The uncontrollable aggregation behavior of CNTs, for instance, bundle formation, poses a primary problem that hampers risk assessment studies[37].

Therefore; an effort to achieve a stable suspension of CNTs in water has been a familiar concern while most specific ways to solubilize CNTs i.e. by functionalization of nanotubes. Even though the use of surfactant is straight forward and simple, it may be noted that the surfactants used widely for solubilization of CNTs are toxic by

themselves and must therefore be avoided. Researchers used nontoxic surfactants, namely pluronic F127 and Tween, to see the effect on reducing aggregation of MWCNTs and achieving dispersion to confirm whether large aggregates of MWCNTs had any contribution to cytotoxicity. This study found surfactants to disperse and reduce MWCNT aggregation in the medium and thereby less sedimentation rate.

APPLICATIONS OF CNTS [38]

Various applications of CNTs are as follows:

1. Carrier for Drug delivery**:** Carbon nanohorns (CNHs) are the spherical aggregates of CNTs with irregular horn like shape. Research studies have proved CNTs and CNHs as a potential carrier for drug delivery system.

2. Functionalised carbon nanotubes are reported for targeting of Amphotericin B to Cells.

3. Cisplatin incorporated oxidized SWNHs have showed slow release of Cisplatin in aqueous environment. The released Cisplatin had been effective in terminating the growth of human lung cancer cells, while the SWNHs alone did not show anticancer activity.

4. Anticancer drug Polyphosphazene platinum given with nanotubes had enhanced permeability, distribution and retention in the brain due to controlled lipophilicity of nanotubes.

5. Antibiotic, Doxorubicin given with nanotubes is reported for enhanced intracellular penetration.

6. The gelatin CNT mixture (hydro-gel) has been used as potential carrier system for biomedicals.

7. CNT-based carrier system can offer a successful oral alternative administration of Erythropoietin (EPO), which has not been possible so far because of the denaturation of EPO by the gastric environment conditions and enzymes.

8. They can be used as lubricants or glidants in tablet manufacturing due to nanosize and sliding nature of graphite layers bound with vander waals forces.

a) Genetic engineering

In genetic engineering, CNTs and CNHs are used to manipulate genes and atoms in the development of bioimaging genomes, proteomics and tissue engineering. The unwound DNA (single stranded) winds around SWNT by connecting its specific nucleotides and causes change in its electrostatic property. This creates its potential application in diagnostics (polymerase chain reaction) mand in therapeutics. Wrapping of carbon nanotubes by single-stranded DNA was found to be sequence dependent, and hence can be used in DNA analysis. Nanotubes due to their unique cylindrical structure and properties are used as carrier for genes (gene therapy) to treat cancer and genetic disorders. Their tubular nature has proved them as a vector in gene therapy. Nanotubes complexed with DNA were found to release DNA before it was destroyed by cells defense system, boosting transfection significantly. Nanostructures have showed antiviral effect in respiratory syncytical virus (RSV), a virus with severe bronchitis and asthma. The treatment is generally done by combining nanoparticles and gene slicing technologies. Here RNA fragments capable of inhibiting a protein (which is needed for virus multiplication) is encapsulated within nanotubes and administered in the form of nasal sprays or drops. The promising results have been noted inhibiting further growth of virus. Nanotubes are reported for helical crystallization of proteins and growth of embryonic rat brain neurons. Streptavidin protein is successfully immobilized on CNT via 1-pyrene butanoic acid and succinimidyl ester. Nanotubes and nanohorns can adhere various antigens on their surface, hence act as source of antigen in vaccines. Hence, by use of nanotubes, use of dead bacteria as source for antigen which is sometimes dangerous can be avoided.

b) Biomedical applications

Bianco et al. have prepared soluble CNTs and have covalently linked biologically active peptides with them atoms in the development of bioimaging genomes, proteomics and tissue engineering. The unwound DNA (single stranded) winds around SWNT by connecting its specific neucleotides and causes change in its electrostatic property. This creates its potential application in diagnostics (polymerase chain reaction) and in therapeutics. Wrapping of carbon nanotubes by single-stranded DNA was found to be sequence-dependent, and hence can be used in DNA analysis. Nanotubes due to their unique cylindrical structure and properties are used as carrier for genes (gene therapy) to treat cancer and genetic disorders. Their tubular nature has proved them as a vector in gene therapy. Nanotubes complexed with DNA were found to release DNA before it was destroyed by cells defense system, boosting transfection significantly. Nanostructures have showed antiviral effect in respiratory syncytical virus (RSV), a virus with severe bronchitis and asthma. The treatment is generally done by combining nanoparticles and gene slicing technologies. Here RNA fragments capable of inhibiting a protein (which is needed for virus multiplication) is encapsulated within nanotubes and administered in the form of nasal sprays or drops. The promising results have been noted inhibiting further growth of virus. Nanotubes are reported for helical crystallisation of proteins and growth of embryonic rat brain neurons.

Streptavidin protein is successfully immobilized on CNT via 1-pyrene butanoic acid and succinimidyl ester. Nanotubes and nanohorns can adhere various antigens on their surface, hence act as source of antigen in vaccines. Hence, by use of nanotubes, use of dead bacteria as source for antigen which is sometimes dangerous can be avoided. In vitro studies by Kam et al. showed selective cancer cell killing obtained by hyperthermia due to the thermal conductivity of CNT internalized into those cells. The work developed regarding the use of CNT as gene therapy vectors have shown that these engineered structures can effectively transport the genes and drugs inside mammalian cells. The CNT-transported genetic material has conserved the ability to express proteins.

c) Artificial implants

Normally body shows rejection reaction for implants with the post administration pain. But, miniature sized nanotubes and nanohorns get attached with other proteins and amino acids avoiding rejection. Also, they can be used as implants in the form of artificial joints without host rejection reaction. Moreover, due to their high tensile strength, carbon nanotubes filled with calcium and arranged/grouped in the structure of bone can act as bone substitute.

d) Preservative

Carbon nanotubes and nanohorns are antioxidant in nature. Hence, they are used to preserve drugs formulations prone to oxidation. Their antioxidant property is used in antiageing cosmetics and with zinc oxide as sunscreen dermatological to prevent oxidation of important skin components.

e) Diagnostic tool

Protein-encapsulated or protein/enzyme filled nanotubes, due to their fluorescence ability in presence of specific biomolecules have been tried as implantable biosensors. Even; nanocapsules filled with magnetic materials, radioisotope enzymes can be used as biosensors. Nanosize robots and motors with nanotubes can be used in studying cells and biological systems.

f) As catalyst

Nanohorns offer large surface area and hence, 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.

g) Wound healing

The observation is that wounds or areas which have become heavily burnt are able to heal much more rapidly if they are covered with a random web of nanofibers. The web allows for an easy exchange of gases and fluids yet it restricts the access of bacteria. The nanofibers may be loaded with drugs to enhance the healing processes. We have succeeded in constructing a hand held battery operated electrospinning set-up able to deliver the nanaofibers directly to the wounds. Biodegradable synthetic polymers such as polylactides but also polymers from nature can be used for such applications.

FUTURE PROSPECTS

Carbon nanotubes are still a relatively unexplored area, and the rapidly advancing fields that they are involved in can still be pushed farther. Nanotubes are extremely versatile since they can be included in numerous different fields because of their great material properties. Any amount of improvements can be made to carbon nanotubes through various techniques. Also, it has been studied that most nanotubes are cleared from the body very quickly after being distributed throughout. This decreases the chances of higher toxicity levels in the blood. The good functionalization of carbon nanotubes allows us to attach a number of groups to the tubes for different systems. Radioactive labels could be attached for use in bioimaging. As mentioned before, fluorescence is already observed in normal carbon nanotubes, but attaching labels allows for a greater imaging window. This labeling capability can also be used for targeting drug delivery systems. It was shown that carbon nanotubes were used to deliver drugs to specific cancer cells of the epithelium, and this was accomplished efficiently. This targeted killing of cancer cells shows promise for numerous other improvements in cancer therapy and treatment as well as the treatment of various infectious diseases. With targeted nanotubes used for drug delivery, specific cells could be aimed at to take up the carbon nanotubes, as was shown with brain tumor cells. Carbon nanotubes seem to be a valuable option when considering such applications as drug delivery or bioimaging because they are readily functionalized, display excellent material properties, can be used as imaging agents or sensors, and keep the door open for many future advances.

REFERENCES

1. Discovery of all Nanos. www.engin.swarthmore.edu.
2. http://en.wikipedia.org/www/Carbon%nanotube.
3. Mike Foley. A practical guide to understanding their properties, applications, production methods, markets and utility. www.cheaptubesinc.com.
4. Peter Harris's nanotube book. www.rdg.ac.uk/ ~scsharip/tubebooks.
5. Nanotubes published by Cientifica 2004. www.cientifica.com
6. Reade advanced materials, carbon Nanohorns. Http://www.reade.com

7. Jing Fan, Masako Yudasaka, Jin Miyawaki, Sumio Iijima. Adsorption states of organic materials inside single wall carbon nanohorn.; www.fy.chalmers.se/ conferences/ nt05/ abstracts/ P158.html.
8. Peter j. F. Harris.Carbon nanotube and related structures, new materials for the twenty – first century. Published by the press syndicate of the University of Cambridge, U.K. 1999; 1-34.
9. NanoCraft, Inc at Nanotech 2004 in Boston. March, 7-12, 2004.
10. R Saito, G. Dresselhaus, M.S. Dresselhaus. Physical properties of carbon nanotube. Imperial College Press. 3, 36.
11. T. Yamaguchi, S. Bandow, S. Iijima. Synthesis of carbon nanohorn particles by simple pulsed arc discharge ignited between pre-heated carbon rods. Chemical physics letters 2004,389, 181–185.
12. Hwang1, Mchhowalla, N Sano, S Jia and g. a. j. amaratunga1. Large-scale synthesis of single-walled carbon nanohorn by submerged arc. Institute of physics publishing, nanotechnology.2004, 546-550.
13. Kazunori Anazawa, Kei Shimotani, Chikara Manabe, Hiroyuki Watanabe, and Masaaki Shimizu. High-purity carbon nanotube synthesis method by an arc discharging in magnetic field. Applied Physics Letters. 2002, 81, 739-741.
14. Wondrous world of carbon nanotubes. Http:// students. chem. tue. nl/ ifp03/ synthesis. html.
15. Xianbao wanga, Alexander volodina, Chris van haesendoncka, Nicolas moreaub, Antonio fonsecab, Janos b. Nagyb. Controllable growth of individual, uniform carbon nanotubes. By thermal chemical vapor deposition. Physica e. 2005, 25, 597–604.
16. Shen zhu1, Ching-hua su, J. C. Cochrane1, S. Gorti, S. Lehoczky, Y. Cui, and A. Burger. Orientational growth of carbon nanotube by thermal cvd. Mat. Res. Soc. Symp. Proc. 2002,706, 21.1-21.6.
17. Dr. Jun Jiao, Synthesis of single wall carbon nanotubes from alcohol. Department of Chemistry and Department of physics. Portland State University, Portland.
18. Lyu,s.c.; Kim, h.w.; Kim, s.j.; park, j. W.; lee, c.j. Synthesis and crystallinity of carbon nanotube produced by a vapor-phase growth method. Applied physics a materials science & processing, 2004.
19. B. Zheng, Y. Li, J. Liu. Cvd synthesis and purification of single-walled carbon nanotubes on aerogel-supported catalyst. Appl. Phys. A. 2002, 74, 345–348.
20. S.N.Bondi, W.J.Lackey, R.W. Johnson, X.Wang, Z.L.Wang. Laser assisted chemical vapor deposition synthesis of carbon nanotubes and their characterization. Carbon. 2006, 44, 1393-1403.
21. www.ou.edu/engineering/nanotube.Carbon Nanotubes research at the University of Oklahoma.
22. Li zhipeng, Wu xiaobin, Lin jianyi. The growth and characterization of multi-wall carbon nanotube produced by catalytic decomposition of CO. http://staff.science.nus.edu.sg/~scilooe/srp_2003/sci_paper/phy/research_paper/li_zhi_peng.pdf.
23. D.e. Resasco, W.e. Alvarez, F. Pompeo, I. Balzano, J.e. Herrera, b. Kitiyanan and A. Borgna. A scalable process for production of single-walled carbon nanotubes (swnts) by catalytic disproportionation of CO on a solid catalyst. Journal of nanoparticle research.2002, 4, 131–136.
24. Dodelet, et al. Process for preparing carbon nanotubes. United States Patent 6,887,451. www.uspto.gov.
25. Hua gao, supervisor: Professor Nkh Slater. Purification and protein immobilization of carbon nanotubes. Cambridge unit for responsive biopolymers(curb) & Cambridge unit for bioscience engineering (cube), University of Cambridge.
26. P.X. Hou, S. Bai, G.H. Yang, C. Liu, H.M. Cheng. Multi-step purification of carbon nanotubes. Carbon.2002, 40, 81-85.
27. Noriaki sano. Low-cost synthesis of single –walled carbon nanohorns using arc in water method with gas injection.J.Phys.D: Appl. Phys. 2004, 37, l17-l20.
28. N. Sano, J. Nakano, and T. Kanki. Synthesis of Single-Wall Carbon Nanohorns and Nanotubes by Arc Discharge in Water. http://materials.ipicyt.edu.mx/ ~nt04-abstracts/P25.html
29. S. Iijima , M. Yudasaka , R. Yamada , S. Bandow , K. Suenaga, F. Kokai , K. Takahashi. Nano-aggregates of single-walled graphitic carbon nanohorn. Chemical physics letters.1999, 309,165-170.
30. Kasuya, Daisuke; Yudasaka, Masako; Takahashi, Kunimitsu; Kokai, Fumio; Iijima Sumio. Selective production of single-wall carbon Nanohorns aggregates and their formation mechanism. Journal of physical chemistry b. 2002, 106(19), 4947-4951.
31. F. Kokai, k. Takahashia, d. Kasuyab, m. Yudasakac, s. Iijima. Growth dynamics of single-wall carbon nanotube and nanohorn aggregates by Co_2 laser vaporization at room temperature. Applied surface science. 2002, 197-198,650-655.
32. Goshu Tamura, Shunji Bandow, Masako Yudasaka, Sumio Iijima. Purification of single wall carbon Nanohorns by gravitational sedimentation.
33. Barroug, a., Glimcher, m. Hydroxyapatite crystals as a local delivery system for cisplatin: adsorption and release of cisplatin in vitro. J. Orthop. Res. 2002, 20, 274-280.
34. Carbon nanotube monthly November 2005.Based on NANO SPRINT Encyclopedia of carbon nanotube.
35. Carla Cioffi, Stephane Campidelli, Fulvio g., Brunetti, Moreno Meneghetti and Maurizio Prato. Functionalization of carbon nanohorns.Chemical communications,2006; (advancearticle) www.rsc.org/ publishing/ journals/ cc/ article. asp?Type = advarticle
36. Giorgia pastorin, Wei wu, Sébastien wieckowski, Jean-paul Briand, Kostas kostarelos, Maurizio Prato and Alberto bianco. Double functionalization of carbon nanotube for multimodal drug delivery. Chemical communications. 2006,79,697-700.
37. Yan-xin liu, zhong-jie du, yan li, chen zhang, hang-quan li. Covalent functionalization of multiwalled carbon nanotube with poly(acrylic acid).Chinese journal of chemistry. 2006,24, 563-568 .
38. Rajashree Hirlekar, Manohar Yamagar, Harshal Garse, Mohit Vij, Vilasrao Kadam. Carbon Nanotube and its Application: A Review. Asian Journal of Pharmaceutical and Clinical Research. 2009, 4,17-27.

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