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CARBON NANOTUBES AN ADVANCED DRUG DELIVERY SYSTEM – A REVIEW

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ABSTRACT: In today's 21st century, Carbon nanotubes (CNTs) are the most researched material by world investigation of the growing industry due to their various reasons properties for use in many applications either in medical or other potential applications. Carbon nanotubes become increasingly popular in various fields simply because of their small size and amazing optical, electric, and magnetic properties when used alone or with additions of metals. Carbon nanotubes are described as a cylindrical rolled graphene sheet. They are cap with end containing the pentagonal ring and also cylindrical of graphene with a diameter of 12 nm. Carbon nanotubes have potential therapeutic applications in various fields like drug delivery for API, diagnostics, and biosensing. Functionalized carbon nanotubes can also act as vaccine delivery systems. The basic principle involved in this to link the antigen to carbon nanotubes while retaining its conformation, thereby inducing antibody response with the right specificity. With the increasing interest shown by the nanotechnology research community during this field, it's expected that a lot of applications of carbon nanotubes are going to be explored in the future for medical as well as other file.

INTRODUCTION: Carbon nanotubes have generated vast activity in most areas of science and engineering because of their outstanding physical and chemical properties. No previous materials have displayed the mix of superlative mechanical, thermal, and electronic properties attributed to them. These properties make nanotubes ideal, not only for a wide range of applications but as a testbed for fundamental science [1]. Researchers have envisaged taking advantage of their conductivity and high aspect ratio to produce conductive plastics with exceedingly low percolation thresholds.

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Carbon nanotubes tend to have impressive mechanical properties with Young's modulus in the range of 100-1000 GPa and strengths between 2.5 and 3.5 GPa. Nanotubes have a diameter ranging from 1 to 100nm and lengths of up to millimeters **Fig. 1**. Their densities can be as low as ~1.3 g / $cm^{3,}$ and their Young's moduli are superior to all carbon fibers with valves greater than 1 TPa [2]. The highest measured strength for a carbon nanotube was 63 GPaand, even the weakest of type of CNT has the strength of several GPa. CNTs have received much attention from scientific communities up to this date mainly because of their superior properties such as having a wide bandgap, high melting point, high tensile strength, and high thermal conductivity.

Its (CNTs) attractiveness comes from its unique properties like physical, chemical, mechanical, and thermal properties originating from the small size, cylindrical structure, and high aspect ratio of length to diameter. According to the wall of monotubes, it divides mainly into two types. A single-walled carbon nanotube (SWCNT) consists of a single graphene sheet wrapped around to form a cylinder. A multi-walled carbon nanotube (MWCNT) is concentrically nested cylinders of grapheme sheets. CNTs have extremely high tensile strength (≈150 GPa, more than 100 times that of the stainless steel), high modulus (≈1 TPa), large aspect ratio, low density (1100–1300 kg/m^3, one-sixth of that of stainless steel), good chemical and environmental stability, high thermal conductivity (3000 W/m/K, comparable to diamond) and high electrical conductivity (comparable to copper) [3]. Carbon nanotubes have various applications, like electrodes for electrochemical double-layer capacitors, field emitters, nanoelectronic devices, and hydrogen storage, as functional polymers, *etc*.

Researchers have also reported making of conductive, electromagnetic, and microwave absorbing and high-strength composites, fibers, sensors, inks, energy storage,, and energy conversion devices, radiation sources and nanometer-sized semiconductor devices, probes, and interconnect using carbon nanotubes [4].

Recently, strong and stretchable CNT fibers were spun from 0.65-mm-long CNT forests, which have the strength and Young's modulus of 1.91 GPa and 330 GPa, respectively. SWCNT/PVA composite fibers are tougher than any natural or synthetic organic fiber described so far. Carbon nanotubes bulk production in an economical way is the route for the feasibility of these applications. CNTs are generally synthesized by electric arc discharge method, laser ablation method, catalytic chemical vapor deposition (CVD), flame synthesis, solar energy route, *etc*. The common feature of arc discharge and laser ablation methods is the need or high amount of energy, which is supplied by means of an arc discharge or laser for inducing the reorganization of carbon atom into CNTs. In CNTs better crystallization temperature used is more than 3000 °C, this gives good graphite alignment to products. However, the main important requirements of these systems are continuous graphite target replacement, vacuum conditions, pose difficulties to the large-scale production of CNTs. For large scale production of carbon nanotubes contrast chemical vapor deposition (CVD) has been proven to be a preferred route [1, 5].

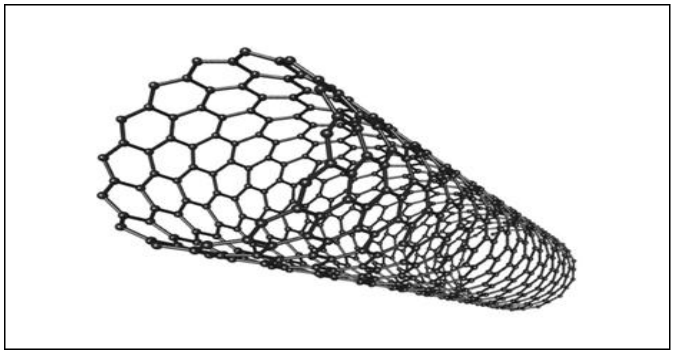

FIG. 1: STRUCTURE OF CARBON NANOTUBES

Here the carbon is deposited from a hydrocarbon (or any other carbon-bearing source) in the presence of a catalyst at temperatures lower than 1200 °C. During the CVD process, the CNT structure, such as its wall number, diameter, length, and alignment, can be well controlled. Thus, the CVD method has the advantages of mild operation, low cost, and controllable process, and is the most promising method for the mass production of CNTs. Various scalable processes have been reported with CVD methods, including "Carbon Multiwall Nanotubes" of Hyperion Company [6], "CoMoCATTM Process at SWCNT" of the University of Oklahoma, "HiPCO Process" of Rice university and "Nano Agglomerate Fluidized Bed" process of Tsinghua University [7-8]. Though the fluidized bed technique is the most promising route for the mass production of carbon nanotubes, the fluidization of nano-sized particles is itself a challenge. The published literature contains four good reviews on the present subject matter. Due to hollow and much smaller than the blood cells, CNTs are the potential to carry the drug. The way was developed for attaching proteins and DNA molecules to the inside and outside of the nanotubes. This gives one the ability to target and destroy individual cells that may be cancerous or infected by a virus [9-10].

Types of CNTs: [11-13] There are two types of Carbon nanotubes.

- Single-walled carbon nanotubes (SWCNTs) **Fig. 2**.
- Multiwalled carbon nanotubes (MWCNTs) **Fig. 3**.

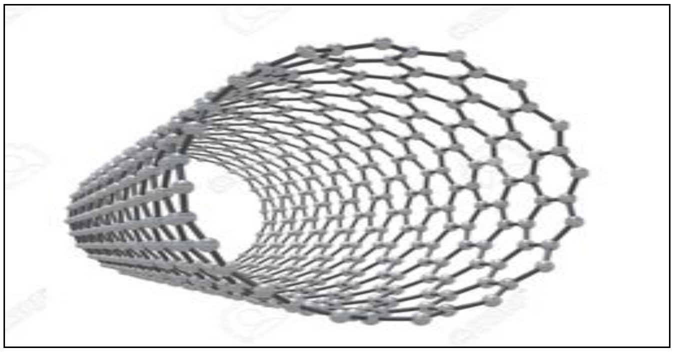

FIG. 2: SINGLE-WALLED CNT's

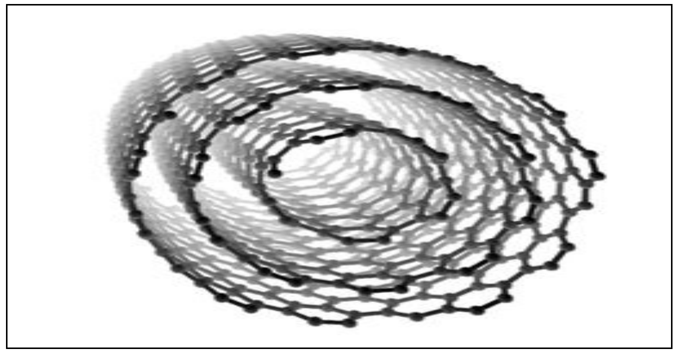

FIG. 3: MULTI-WALLED CNT's

Differences between types of CNTs shown in **Table 1**.

TABLE 1: DIFFERENCE BETWEEN SINGLE WALLED CARBON NANOTUBES (SWCNTs)

Single-Walled Carbon Nanotubes	Multiwalled Carbon Nanotubes
Single-layer of graphene	Multiple graphene layer
Catalyst is necessary for the synthesis	Can be produced without catalyst
Bulk synthesis is hard because it requires proper control overgrowth and atmospheric conditions.	Bulk synthesis is easy
Purity is poor	Purity is high
A chance of defect is more than MWNT	A chance of defect is less but once occurred it is difficult to improve
Less accumulation in the body	More accumulation in the body
Evaluation & characterization is easy in SWNT.	It has a very complex structure
It can be easily twisted & are more liable	It cannot be easily twisted

Method of Preparation: [1, 14-15] There are three types of methods generally used

- ARC Discharge Method
- Laser Ablation Method
- CVD (Chemical Vapour Deposition) Method

1. ARC Discharge Method: This method applicable for the preparation of a large amount of CNTs. This method is used for producing C60 fullerene; it is the most common and the easiest way to produce carbon nanotubes. This technique produces a mixture of components and requires separating nanotubes from the sooth and the catalytic metals present in the crude product. This is regarding ARC-vaporization of 2 carbon rods which placed end to the end site, separated by about a 1mm, in an enclosure filled with inert gas (helium or argon) at low pressures, i.e., between 50 to 700 mbar. A direct current of 50 to 100A driven by approximately 20V creates a high-temperature discharge between two electrodes. The discharge vaporizes one of the carbon rods and forms a small shaped deposit on the opposite rod. Then, the carbon diffuses towards the substrate. Depending on the exact technique, it is possible to selectively grow SWCNTs or MWCNTs, and the typical yield is up to 30 to 90% [1].

2. Laser Ablation Method: This synthesis was first reported in 1995, by Smalley's group at Rice University. A periodic or continuous laser is employed to vaporize a graphite target in an oven at 1200 °C. The main distinction between continuous and periodic laser is that the periodic laser demands a way higher intensity (100KW/cm^2 compared with 12KW/cm^2). The oven is stuffed with helium or argon gas to stay the pressure at five hundred Tor. A very hot vapor plume forms then expand and cool quickly. As the gaseous species cool, small carbon molecules and atoms rapidly condense to form larger clusters, possibly including fullerenes. The catalysts also begin to condense and attach to carbon clusters and prevent their closing into cage structure. (Catalysts may even open cage structures when they attach to them) and the typical yield is up to 70%. The SWCNTs formed in this case are bundled together by Van der walls forces [14].

3. Chemical Vapour Deposition (CVD): It is achieved by putt a carbon supply (methane, carbon monoxide, and acetylene) in the gas phase and using an energy source, such as plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule. The energy supply is employed to crack the molecule into reactive atomic carbon. Then, the carbon diffused towards the substrate, which is heated and coated with a catalyst (Ni, Fe & CO) where it will bind. CVD synthesis is a two-step process consisting of a catalyst preparation followed by the actual synthesis of CNT.

The catalyst is usually prepared by chemical etching or thermal annealing to induce catalyst particle nucleation. Thermal annealing leads to cluster formation on the substrate, from which the nanotube will grow. Ammonia may be used as the etchant. The temperature ranges maintained at 650 to 900 °C, and also the typical yield is 20 to 100% [15].

Properties of Carbon Nanotubes: [16-19]

- Carbon nanotubes are cylindrical tubes of nanoscopic dimensions. There are two types of nanotubes: CNT-SW (single-walled nanotubes) and CNT-MW (multiwalled nanotubes).
- Typical diameters range from a few nanometers (approx. 5 – 30 nm, and even <1nm for single-walled nanotubes); typical lengths are in the range of a few millimeters [16].
- The substructure of carbon nanotubes (“armchair”, “zigzag”) is derived from the type of process used during synthesis and affects features such as the existence of semiconductor properties. The electric and thermal properties of the raw materials are greatly superior to those of conventional materials. In particular, correct insertion of the carbon nanotubes into a material matrix will cause a significant shift of the percolation curve towards reduced material concentrations [17]. These promising properties are based on the emergence of a network that takes advantage of the high aspect ratio between the length and the diameter. The formation of networks also supports the improvement of mechanical properties within the matrices, particularly as the basic material has a tensile strength (11 – 63GPa) 20 times that of steel.
- Another interesting property of carbon nanotube is that their electrical resistance changes significantly when other molecules attach themselves to the carbon atoms [18].
- Another property of nanotubes is that they can easily penetrate membranes such as cell walls. In fact, nanotube's long, narrow shape makes them look like miniature needles, so it makes sense that they can function as a needle at the cellular level. Medical researchers are using this property by attaching molecules that are attracted to cancer cells to nanotubes to deliver drugs directly to diseased cells [19].

Filling Up of Nanotube: The Nanotube obtained in processes closes on both the ends. The ends can be opened by suitable chemistry [1]. One of the ways used is an acid treatment that oxidizes the ends and leaves behind the oxide-containing functionalities. The common functional groups are –COOH and –OH [20].

Drug Delivery: In general drug delivery system is designed to improve the physiological and therapeutic profile of a drug molecule. The large inner volume of CNTs permits encapsulation of both low as well as high molecules APIs [1]. It also permits the encapsulation of both hydrophilic and lipophilic drugs. More than one drug can even be loaded in CNTs within the case of multi-drug treatment. Ligands and diagnostic materials may also be conjugated to the surface of CNTs by fictionalization to focus on the medicine to specific sit of action. The CNTs can act as a controlled release system for the drug by releasing the loaded drugs for a long period of time [21].

The Purpose of Using Nanotubes in the Human Body: [1, 22] In today’s world of medical research CNTs are very prevalent and are being highly researched in the fields of efficient drug delivery and biosensing methods for various diseases treatment and health monitoring. CNTs have recently garnered interest in the field of medicine due to their potential to alter drug delivery and biosensing methods for the better effect. The use of CNT’s in drug delivery and biosensing technology has the potential to revolutionizes medicine. The fictionalization of SWNT’s has proved to increase solubility as well as allow for effective tumor targeting/drug delivery. It prevents SWNT’s from being cytotoxic and altering the function of immune cells. Cancer is a group of diseases in which cells divide and grow abnormally, which is the main disease being looked at with regards to how it responds to CNTs drug delivery [1]. Current cancer treatment primarily involves radiation therapy, surgery, and chemotherapy. These ways of treatment are mostly painful, and they destroy healthy cells in addition to producing more hazardous adverse side effects. CNTs as drug delivery vehicles have shown potential in targeting specific cancer cells with a dose below standard medicine, which is just as effective in killing the cancerous cells, however, does not harm healthy cells and significantly reduces side effect. Current blood glucose monitoring methods by patients suffering from diabetics are normally invasive and often painful. For example, one method, in which needle is inserted under the skin to monitor glucose level, in this needle contains an integrated small glucose sensor inside the needle. Another method of glucose monitoring strips to which blood must be applied [22]. These methods are not only invasive, but they can also yield inaccurate results. This reading mainly varies and shown error in this 70 percent glucose reading shown error by 10 percent more and 7 percent differed by more than 50 percent. In this, the potential use of single-walled nanotubes and multi-walled nanotubes used in highly sensitive non-invasive glucose detectors due to their various properties like high electrochemical accessible surface area, high electrical conductivity, and helpful structural properties.

CNTs in Drug Delivery and Cancer Therapy: The advantages of nanotubes technology taken as drug delivery which is rapidly growing area. Currently various system used for drug delivery which includes cubosomes, dendrimers, niosomes, liposomes, phytosomes but all of this carbon nanotubes has superior drug loading capacities and good cell penetration capability. These nanotubes function with a larger inner volume to be used as the drug container, large aspect ratios for numerous functionalization attachments, and the ability to be readily taken up by the cell**.** Due to their tube structure, CNTs can be made with or without endcaps, useful for the drug is held would be more accessible. At present in CNTs mainly some problem arises which includes lack of solubility, half-life issue, clumping occurrences, *etc*. However, these are all issues that are currently being addressed and altered for further advancements in the field of Carbon nanotubes. The advantages of CNTs as nano-vectors in the field of drug delivery system remain where cell uptake of these structures was demonstrated efficiently where the effects were prominent, showing the particular nanotubes can be less harmful as nano-vehicles for drug delivery [21].

In CNTs drug encapsulation shown various improved properties which involve enhance water dispersibility, improve the bioavailability of drug with minimizing toxicity. An encapsulated drug molecule gives controlled release in CNTs; it also provides material storage application for drugs. All of these result in a good drug delivery basis where further research and understanding could improve upon numerous other advancements, like increased water solubility, decreased toxicity, sustained half-life, increased cell penetration, and uptake.

This all results of CNTs gives good drug delivery where further research and understanding could improve upon numerous other advancements, which involve increased water solubility, minimizing toxicity, sustained or controlled half-life, increased cell permeation, and uptake [22].

Selective Cancer Cell Destruction: CNTs can be used in various biological transporters and near-infrared agents for selective cancer cell destruction in cancer treatment. In 700- to 1,100nm near-infrared (NIR) light biological system are highly transparent.

In special spectral range, single-walled carbon nanotubes (SWNTs) shown strong absorbance; this is an intrinsic property of SWNTs, which can be used for optical stimulation of CNTs within the living cells to afford multifunctional nanotube biological transporters. CNTs used oligo-nucleotides transported inside living Hela cells. Cancerous cell distraction gets occur by translocation of an oligonucleotide into a cell nucleus by rupturing the endosomal, which is triggered by NIR radiation pulses.

Cell destroy due to excessive local heating SWN. This cannot harm a healthy cells. Thus, a combination of CNTs with an appropriate drug gives a new class of drug delivery for cancer therapy [23].

Mode of Breakdown of CNTs in the Body: Carbon nanotubes did not break down in body tissue or in nature. In recent few years, scientists exposed animals to CNTs *via* injection or through inhalation into the abdominal cavity develop serve inflammation. This tissue changes (fibrosis) that exposure causes lead to impaired lung function and perhaps even to cancer. For example, in the previous two to three years ago, scientist publishes an alarming report which shows CNTs are very similar to asbestos, themselves biopersisten and it creates lung cancer (mesothelioma) in humans a considerable time after exposure [24].

Their discoveries presented in nature nanotechnology and contradict what was believed in the past, that the CNTs couldn't breakdown in body and in nature. Now scientist finds out how MPO convert CNTs into water and carbon dioxide.

CNTs can be broken down by an enzyme -- Myeloperoxidase (MPO) -- found in white blood cells this mechanism first discovered by America and Swedish Scientists. This discovery presented in nature nanotechnology and contradict what was previously believed or published, that CTNs are not broken down by nature or in the body. This current study thus represents a breakthrough in nanotechnology and nanotoxicology, since it clearly shows that endogenous MPO can break down carbon nanotubes. MPO enzyme found in a specific type of white blood cell (WBC) *i.e.*, neutrophils, whose role is to neutralize harmful bacteria. Now scientists found that this enzyme also works on CNTs, breaking them into water and carbon dioxide. The researchers also showed that carbon nanotubes that have been broken down by MPO no longer give rise to inflammation in mice [25].

Medical Applications:

1. Nanotubes bind to an antibody produced by chickens, mainly used in laboratory tests to kill breast cancer cells. In this antigen carrying nanotubes bind to the protein produced by breast cancer cells. After these nanotubes absorb light from an infrared laser after inserting the nanotubes and then therapy carrying out [26].

2. Nanotubes are used to deliver protein to cancer cells also, and it used to improve the healing process for broken bones [27].

3. In the field of diagnostics and disease management combining of carbon nanotubes with biological system are used [28].

4. Fully developed and finalized is not done till, but we see progress every day. As an example, we'll take anti-cancer treatment [29].

5. A combination of carbon nanotubes with biological systems can be improved medical science – mainly in disease treatment and diagnosis of disease. And in this, we progress day by day. *e.g.*, anti-cancer treatment [28].

6. Another application of carbon nanotube in medicine is for sensing the molecules or species.

7. CNTs are also used as a blood vessel to deliver the drug to their specific site of action. This minimizes drug wastage and avoids the adverse effect.

There are two types, both equally effective —

1. The drug can be attached to the side or behind.
2. The drug can actually be placed inside the nanotube.

8. Synthetic muscles: Due to their high contraction/extension ratio given an electric current CNTs are ideal for synthetic muscle.

9. Artificial muscles: CNTs have sufficient contractility to make them candidates to replace muscle tissue.

10. Osteoblastic and proliferation and bone formation.

11. As the nanotubes function like a needle at the cellular level. This property is used in attaching molecules that are attracted to cancer cells to nanotubes to deliver drugs directly to diseased cells [29].

12. The attachment of ethylene glycol molecules to nanoparticles of nanotubes stops WBCs from recognizing the nanoparticles as foreign materials, allowing them to circulate in the bloodstreams long enough to attach to cancer tumor therapy [28-29].

13. Used to stimulate an immune response to fight respiratory viruses when inhaled.

14. CNTs promote blood cell maturation of bone marrow transplant recipients.

1**5.** A loaded drug in CNTs is used as nanovector for the delivery of therapeutics.

16. CNTs are used as nanomedicines in pharmacology.

17. Functionalization of SWCNTs enhances solubility and allows for efficient tumor-targeting drug delivery [26, 28].

18. CNTs are work with lipids, which are highly water-soluble, which would make their movement through the human body easier, which reduces blockage, thus making them more attractive as drug delivery vehicles.

19. CNTs used as drug delivery vehicles they shown potentially targeting specific cancer cells with a dosage lower than conventional drugs used [21-23, 29, 30].

- For selective cancer treatment and in multifunctional biological transporters, CNTs are used.
- An aligned CNT with an ultra-sensitive biosensor for DNA detection was developed.

Non-Medical Applications:

1. Structural
2. Electromagnetic
3. Electroacoustic
4. Chemical
5. Mechanical

1. Structural: They are used for various purposes.

- ❖ **Textiles:** We make waterproof and tear-resistant fabrics with the help of CNTs.
- ❖ **Body Armor:** Using CNTs fibers, MIT was able to stop bullets and monitor the condition of the wearer.
- ❖ **Concrete:** CNTs in concrete increase the tensile strength and stops the crack propagation.
- ❖ **Sports Equipment:** Stronger and lighter tennis rackets, bicycle parts, golf balls, golf clubs, and baseball bats can be made.
- ❖ **Bridges:** CNTs are also able to replace steel in suspension.
- ❖ Uses of CNTs in Aircraft increase its strength and flexibility in highly stressed component [31].

2. Electromagnetic:

- ❖ **Optical Ignition:** A layer of twenty-nine percentage of iron-enriched single-walled nanotubes (SWNT) is placed on prime of a layer of explosive material like PETN and can be ignited with a regular camera flash.
- ❖ **Superconductor:** Nanotubes have been shown to be superconducting at low temperatures.
- ❖ **Ultra Capacitors:** MIT is researching the utilization of nanotubes bounding with the charge plates of capacitors so as to dramatically will increase the area and energy storage ability.
- ❖ **Electromagnetic Antenna:** CNTs can act as antennas for radios and other electromagnetic devices [32].

3. Chemical

- ❖ **Desalination:** Separation of salt from water is get done by forcing water from CNTs network, and this process required less pressure than the conventional reverse osmosis method.
- ❖ **Air Pollution Filter:** CNTs filter used in industry to purified and plant carbon dioxide.
- ❖ **Hydrogen Storage:** CNTs have the potential to store between 4.2 and 65% hydrogen by weight. If they can be mass-produced economically, 13.2 liters (2.9 imp gal; 3.5 US gal) of CNT could contain the same amount of energy as a 50 liters (11 imp gal; 13 US gal) gasoline tank [31-32].

4. Electro-Acoustic: In Beijing 2008, Tsinghua-Foxconn Nanotechnology Research Centre declared that loudspeakers are prepared from CNTs, generating sound similar to how lightning produces thunder. Near term, commercial uses include replacing piezoelectric speakers in greeting cards [32].

5. Mechanical

- **Oscillator:** Oscillators supported on CNT have achieved higher speeds than other technologies (> 50 GHz).

- For reflectivity of the buckypaper which is made up of "super growth," the chemical vapor deposition technique is 0.03 or less, which mainly gained in the performance of pyroelectric infrared detector, which is important in IR-analysis.

- **Thermal Radiation:** For thermal emission in space such as space satellites [31-33].

CONCLUSION: Due to the long-lasting life of carbon nanotubes makes it more reliable for use. CNTs can treat cancer with guarantee 85% of the other treatment that cannot afford and having site target with its body-friendly nature adds to it advantage. The versatile properties of CNTs have made them stand high in all fields, especially in medicine it has become a boon to the mankind, but the lack of technology for mass production and the costs of the production is what is holding them back. Until now the accumulation of Carbon nanotubes and its harmfulness has taken pave among the researchers but not until the discovery of the enzyme MPO (Myeloperoxidase) expressed in a certain type of white blood cells (neutrophils) which can breakdown Carbon Nanotubes into water and carbon dioxide thus declaring it as body-friendly.

However, despite many surprising results of CNTs obtained during the beginning of this research field, there are still tremendous opportunities to be explored and significant challenges and risks to be solved. Therefore, a lot of imagination and innovation required to elaborate totally different new types of CNTs and their conjugates with high effectualness and safety for health use within the future.

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