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# A Review on: Carbon Nanotubes Are Vital for Plant Growth

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**Abstract:** Carbon Nanotubes (CNTs) are allotropes of carbon with a nanostructure that can have a length-to-diameter ratio greater than 1,000,000. These cylindrical carbon molecules have novel properties that make them potentially useful in many applications in nanotechnology. Formally derived from the grapheme sheet they exhibit unusual mechanical properties such as high toughness and high elastic moduli. Referring to their electronic structure, they exhibit semiconducting as well as metallic behavior and thus cover the full range of properties important for technology. Nanotubes are categorized as single-walled nanotubes and multiple walled nanotubes. 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. The properties and characteristics of CNTs are still being researched heavily and scientists have barely begun to tap the potential of these structures. Without doubt, carbon nanotubes represent a material that offers great potential, bringing with it the possibility of breakthroughs in a new generation of devices, electric equipment and bio fields. The main objective of this review article deals with the study of carbon nanotubes (CNTs) on the growth mechanism of plants. Multi-walled carbon nanotubes (CNTs) can affect plant phenotype and the composition of soil micro biota. Tomato plants grown in soil supplemented with CNTs produce two times more flowers and fruit compared to plants grown in control soil.

**Keywords:** Carbon Nanotube (CNT), Naohorns, Naobuds, CNT Growth Mechanism, CNT-Plant Interactions, Applications of CNT

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## 1. Introduction

A carbon nanotube (CNT) is a tubular structure made of carbon atoms, having diameter of nanometer order but length in micrometers. Although this kind of structures was synthesized, studied and reported by several researchers during 1952–1989 [1] Iijima's detailed analysis of helical arrangement of carbon atoms on seamless coaxial cylinders in 1991, proved to be a discovery report [2]. Since then, CNT has remained an exciting material ever. Its so-called extraordinary properties: many-fold stronger than steel, harder than diamond, electrical conductivity higher than copper, thermal conductivity higher than diamond, etc. Such novel nanomaterials consist of inorganic or organic matter and in most cases have never been studied in the context of pharmaceuticals. Carbon nanotubes (CNTs) are one of them. CNTs are allotropes of carbon. Elemental carbon in the

sp<sup>2</sup> hybridization can form a variety of amazing structures [3] Apart from the well-known graphite; carbon can build closed and open cages with honeycomb atomic arrangement. The first such structure to be discovered was the C<sub>60</sub> molecule by Kroto et al 1985 [4]. They 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 [5]. A graphene sheet can be rolled more than one way, producing different types of carbon Nanotubes [6]. And thus Carbon Nanotubes can be categorized by their structures [7]:

### 1.1. Single-Wall Nanotubes (SWNT)

Most Single-Walled Nanotubes (SWNT) have a diameter of close to 1 nanometer, with a tube length that can be many millions of times longer. The structure of a SWNT can be conceptualized by wrapping a one-atom-thick layer of

graphite called graphene into a seamless cylinder. The way the graphene sheet is wrapped is represented by a pair of indices (n,m) called the chiral vector. The integer's n and m denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If m = 0, the Nanotubes are called "zigzag", which is named for the pattern of hexagons as we move on circumference of the tube. If n = m, the nanotubes are called "armchair", which describes one of the two conformers of cyclohexene a hexagon of carbon atoms. Otherwise, they are called "chiral", in which the m value lies between zigzag and armchair structures. The word chiral means handedness and it indicates that the tubes may twist in either direction. [6]

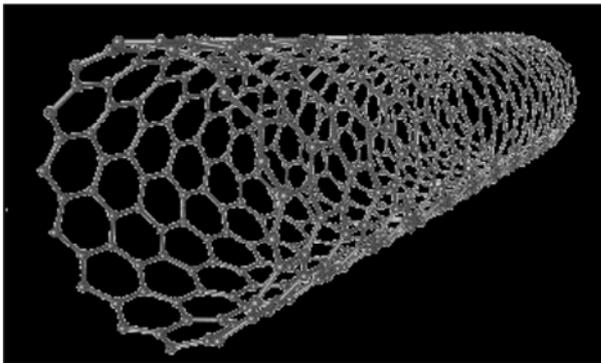


Figure 1. Single walled Carbon Nanotube.

1.2. Mwnts-Multiple Walled Carbon Nanotubes

There are two models which can be used to describe the structures of multi-walled nanotubes. In the Russian Doll

model, sheets of graphite are arranged in concentric cylinders, e.g. a single-walled nanotube (SWNT) within a larger single-walled nanotube. In the Parchment model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled newspaper. The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite, approximately 3.3 Å (330 pm). The special place of double-walled carbon nanotubes (DWNT) must be emphasized here because their morphology and properties are similar to SWNT but their resistance to chemicals is significantly improved. This is especially important when Functionalization is required (this means grafting of chemical functions at the surface of the nanotubes) to add new properties to the CNT. In the case of SWNT, covalent Fictionalization will break some C=C double bonds, leaving "holes" in the structure on the nanotube and thus modifying both its mechanical and electrical properties. In the case of DWNT, only the outer wall is modified. DWNT synthesis on the gram-scale was first proposed in 2003 by the CCVD technique, from the selective reduction of oxide solutions in methane and hydrogen. [6] [7]

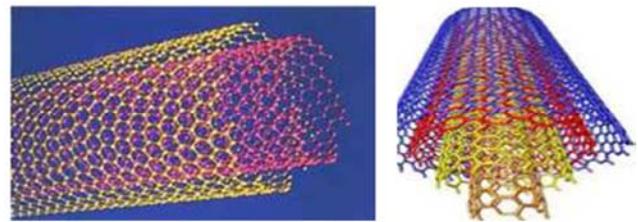


Figure 2. Double-wall Nanotubes (DWNT) Multiwalled Nanotubes.

Table 1. Comparison between SWNT and MWNT [5].

S.No.	SWNT	MWNT
1	Single layer of graphene	Multiple layer of graphene
2	Catalyst is required for synthesis	Can be produced without catalyst
3	Bulk synthesis is difficult as it requires, Bulk synthesis is difficult as it requires, atmospheric condition.	Bulk synthesis is easy
4	Purity is poor	Purity is high
5	A chance of defect is more during, Functionalization	A chance of defect is less but once occurred it's difficult to Improve
6	Less accumulation in body	More accumulation in body
7	It can be easily twisted and are more pliable	It cannot be easily twisted

1.3. Nanotorus

A nanotorus is theoretically described as carbon nano tube bent into a torus (doughnut shape). Nanotori are predicted to have many unique properties, such as magnetic moments 1000 times larger than previously expected for certain specific radii. Properties such as magnetic moment, thermal stability etc. varies widely depending on radius of the torus and radius of the tube. Nano-torus particles are promising in nano-photonics applications. [8]

1.4. Nano-Buds

Carbon Nanobuds are a newly created material combining two previously discovered allotropes of carbon; carbon nanotubes and fullerenes. In this new material fullerene-like

"buds" are covalently bonded to the outer sidewalls of the underlying carbon nanotube. This hybrid material has useful properties of both fullerenes and carbon nanotubes. In particular, they have been found to be exceptionally good field emitters. In composite materials, the attached fullerene molecules may function as molecular anchors preventing slipping of the nanotubes, thus improving the composite's mechanical properties. [9]

1.5. Nano Horns

They were first reported by Harris et al and Iijima et.al. [2]. Single-walled carbon nanohorns (SWCNHs) are horn-shaped single walled tubules with a conical tip. [10] The primary advantage of SWNHs is that no catalyst is required for synthesis so high purity materials can be produced. Their

high surface area and excellent electronic properties have led to promising results for their use as electrode material for energy storage. [11] Currently, SWCNHs have been widely studied for various applications, such as gas storage, adsorption, catalyst support, drug delivery system, magnetic resonance analysis, electrochemistry, biosensing application, photovoltaics and photoelectrochemical cells, photodynamic therapy, fuel cells, and so on. [12].

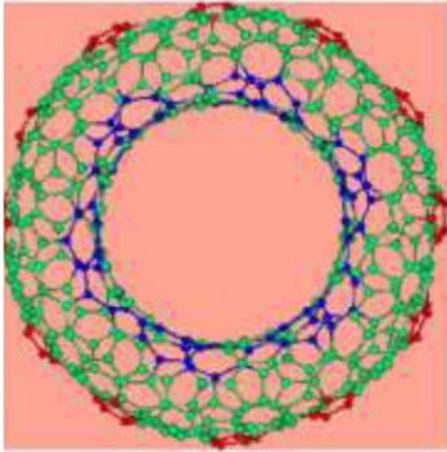


Figure 3. A complete Nanotorus Structure.

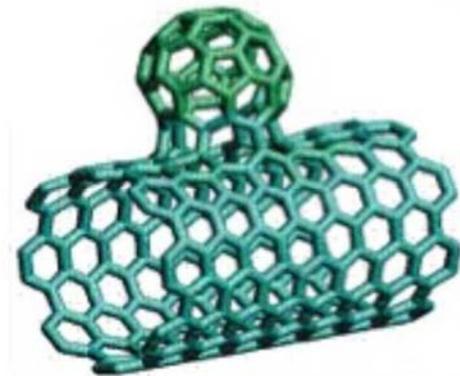


Figure 4. Nano buds.

## 2. Methods of Productions of CNTS

Historically, the oldest method for the carbon nanotube production is the electric arc discharge.

This technique was used already in the early sixties by R. Bacon for the synthesis of carbon fibres called whiskers. The same technique was adapted in 1990 by Krätschmer and Huffman to produce fullerenes in good yields, and later on this method was improved and applied for the synthesis of multiwall (MWNT) and single wall (SWNT) carbon nanotubes. Other methods such as the laser evaporation/ablation and chemical vapour deposition (CVD) were also successfully examined in the production of carbon nanotubes. The laser evaporation process is technically similar to the arc discharge method. The difference between these two methods is in the quality and purity of the obtained

products. However, the arc discharge and the different types of CVD are the most promising and utilized techniques in the large scale production of carbon nanotubes and related materials. [13].

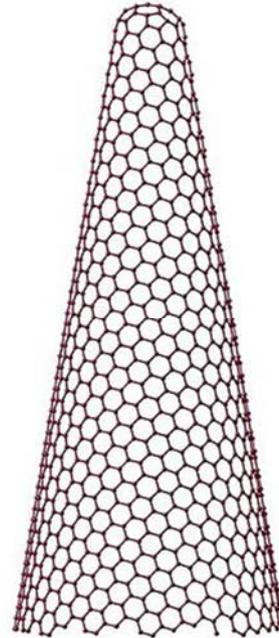


Figure 5. Carbon Nanohorns.

### 2.1. Arc Discharge Method

The arc-evaporation method, which produces the best quality nanotubes, involves passing a current of about 50 amps between two graphite electrodes in an atmosphere of helium. This causes the graphite to vaporize, some of it condensing on the walls of the reaction vessel and some of it on the cathode. It is the deposit on the cathode which contains the carbon nanotubes. Single-walled nanotubes are produced when Co and Ni or some other metal is added to the anode. It has been known since the 1950s, if not earlier, that carbon nanotubes can also be made by passing a carbon-containing gas, such as a hydrocarbon, over a catalyst. The catalyst consists of nano-sized particles of metal, usually Fe, Co or Ni. These particles catalyze the breakdown of the gaseous molecules into carbon, and a tube then begins to grow with a metal particle at the tip [14], [15]. In 1991, Iijima reported the preparation of a new type of finite carbon structures consisting of needle-like tubes [2]. The tubes were produced using an arc discharge evaporation method similar to that used for the fullerene synthesis. The carbon needles, ranging from 4 to 30 nm in diameter and up to 1 mm in length, were grown on the negative end of the carbon electrode used for the direct current (dc) arc-discharge evaporation of carbon in an argon-filled vessel (100 Torr). The perfection of carbon nanotubes produced in this way has generally been poorer than those made by arc-evaporation, but great improvements in the technique have been made in recent years. The big advantage of catalytic synthesis over arc-evaporation is that it can be scaled up for volume

production. The third important method for making carbon nanotubes involves using a powerful laser to vaporize a metal-graphite target. This can be used to produce single-walled tubes with high yield [16]. Ebbesen and Ajayan 1992

reported large-scale synthesis of MWNT by a variant of the standard arc discharge technique [17]. It was shown in 1996 that single-walled nanotubes can also be produced catalytically.

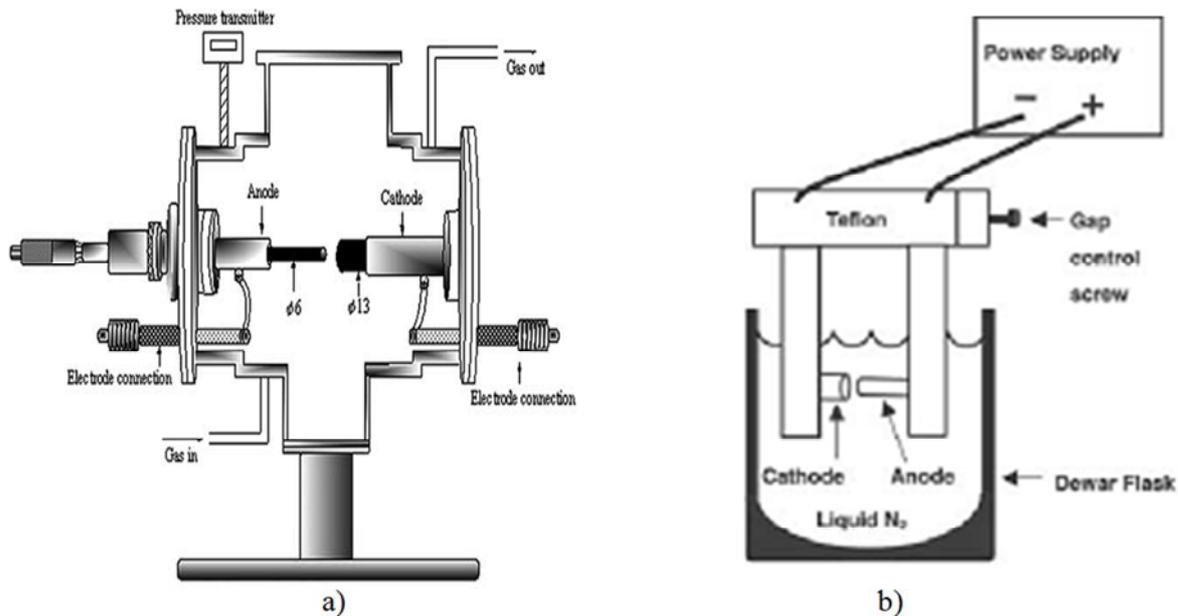


Figure 6. (a) Schematic representation of arc discharge apparatus. (b) Experimental arc discharge set-up in liquid  $N_2$ .

## 2.2. Chemical Vapor Deposition (CVD): [7]

While the arc discharges method is capable of producing large quantities of unpurified nanotubes, significant effort is being directed towards production processes that offer more controllable routes to the nanotube synthesis. A class of processes that seems to offer the best chance to obtain a controllable process for the selective production of nanotubes with predefined properties is chemical vapour deposition (CVD). In principle, chemical vapour deposition is the catalytic decomposition of hydrocarbon or carbon monoxide feedstock with the aid of supported transition metal catalysts.

It is carried out in two step process:-

- Catalyst is deposited on substrate and then nucleation of catalyst is carried via chemical etching or thermal annealing. Ammonia is used as an etchant. Metal catalysts used are Ni, Fe or Co.
- 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 diffused towards substrate, which is coated with catalyst and Nanotubes grow over this metal catalyst. Carbon source used is methane, carbon monoxide or acetylene. Temperature used for synthesis of nanotube is 650 – 9000 C range. The typical yield is 30%.[18,19,20].

Using CVD method, several structural forms of carbon are formed such as amorphous carbon layers on the surface of the catalyst, filaments of amorphous carbon, graphite layers covering metal particles, SWNTs and MWNTs made from well-crystallized graphite layers. The general nanotube

growth mechanism in the CVD process involves the dissociation of hydrocarbon molecules catalyzed by the transition metal, and the saturation of carbon atoms in the metal nanoparticle. The precipitation of carbon from the metal particle leads to the formation of tubular carbon solids in a  $sp^2$  structure. The characteristics of the carbon nanotubes produced by CVD method depend on the working conditions such as the temperature and the operation pressure, the kind, volume and concentration of hydrocarbon, the nature, size and the pretreatment of metallic catalyst, the nature of the support and the reaction time. [21].

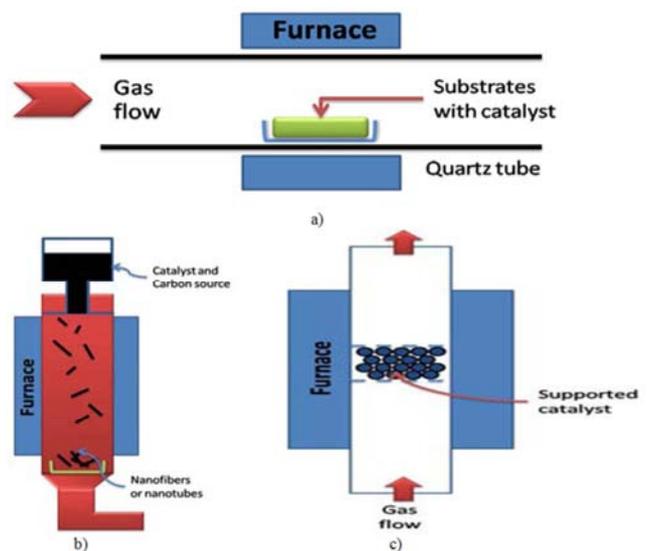


Figure 7. Schematic demonstration of CVD method. (a) Horizontal furnace. (b) Vertical furnace. (c) Fluidized bed reactor.

### 3. Purification of CNTS

Nanotubes usually contain a large amount of impurities such as metal particles, amorphous carbon, and multishell. There are different steps in purification of nanotubes. [22]

#### 3.1. 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.

#### 3.2. Acid Refluxing

Refluxing the sample in strong acid is effective in reducing the amount of metal particles and amorphous carbon. Different acids used were hydrochloric acid (HCl), nitric acid (HNO<sub>3</sub>) and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), but HCl was identified to be the ideal refluxing acid.

#### 3.3. Surfactant Aided Sonication, Filtration and Annealing

After acid refluxing, the CNTs were purer but, tubes were entangled together, trapping most of the impurities, such as carbon particles and catalyst particles, which were difficult to remove 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<sub>2</sub> for 4 h. Annealing is effective in optimizing the CNT structures. It was proved the surfactant-aided sonication is effective to untangle CNTs, thus to free the particulate impurities embedded in the entanglement. Nanotube can also be purified by multi-step purification method.

### 4. Characterisation and Properties of CNTS. [5, 23]

- a) RAMAN Spectroscopy suitable for the quick and reliable screening of the presence of SWCNT
- b) Transmission electron microscopy allowing for the assessment of detailed structures.
- c) Scanning electron microscopy providing overviews of sample structures while less sensitive to sample preparation and homogeneity than TEM.
- d) Thermogravimetric analysis giving information about relative abundance of catalyst particles, nanotubes and other carbonaceous structures.

CNTs have very interesting physicochemical properties such as ordered structure with high aspect ratio, ultralight weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semimetallic behaviour and high surface area.

### 5. Functionalisation of CNTS: [5]

For biological and biomedical applications, the lack of solubility of carbon nanotubes in aqueous media has been a major technical barrier. To overcome this problem the modification of the surface of CNT i.e. functionalisation is done. [24]. With different molecules it is achieved by adsorption, electrostatic interaction or covalent bonding of different molecules and chemistries that render them more hydrophilic. Through such modifications, the water solubility of CNT is improved and their biocompatibility profile is completely transformed. Moreover, the bundling/aggregation of individual tubes through Van der Waals forces are also reduced by the functionalisation of their surface. [25]. The recent expansion in methods to chemically modify and functionalize carbon nanotubes has made it possible to solubilize and disperse carbon nanotubes in water, thus opening the path for their facile manipulation and processing in physiological environments. Equally important is the recent demonstration that biological and bioactive species such as proteins, carbohydrates, and nucleic acids can be conjugated with carbon nanotubes.

These nanotube bioconjugates will play a significant role in the research effort toward bioapplications of carbon nanotubes. One focal point has been the development of nanoscale bioelectronics systems based on carbon nanotubes, which has been driven by the experimental evidence that biological species such as proteins and DNA can be immobilized either with the hollow cavity of or on the surface of carbon nanotubes. Concerning the intrinsic toxicity of CNT, in vitro studies had indicated that SWNT functionalised by a covalent method with phenyl-SO<sub>3</sub>H or phenyl- (COOH)<sub>2</sub> groups produced less cytotoxic effects than aqueous dispersions of pristine SWNT stabilised with a surfactant— 1% of Pluronic F108. Moreover, in the same study, the cytotoxicity of covalently modified SWNT has been reported to be further decreased with the increase in the degree of sidewall fictionalization. [26].

### 6. Applications of CNTS: [5]

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) Functionalized 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. The gelatin CNT mixture (hydrogel) has been used as potential carrier system for biomedical.

6) 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.

7) They can be used as lubricants or glidants in tablet manufacturing due to nanosize and sliding nature of graphite layers bound with Van der Waals forces.

8) In Genetic Engineering: [27, 28].

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) 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 syncytial 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.

9) Biomedical applications:

Bianco et. al. [29]. have prepared soluble CNTs and have covalently linked biologically active peptides with them. This was demonstrated for viral protein VP1 of foot mouth disease virus (FMDV) showing immunogenicity and eliciting antibody response. In chemotherapy, drug embedded nanotubes attack directly on viral ulcers and kills viruses. No antibodies were produced against the CNT backbone alone, suggesting that the nanotubes do not possess intrinsic immunogenicity. Combination of all the described features of the vaccine system with the fact that the capacities of the anti-peptide antibodies to neutralize FMDV have been enhanced has indicated that CNT can have a valuable role in

the construction of novel and effective vaccines. [5]. In vitro studies 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. [28]. Detection of cancer at early stages is a critical step in improving cancer treatment. Currently, detection and diagnosis of cancer usually depend on changes in cells and tissues that are detected by a doctor's physical touch or imaging expertise. The potential for nanostructures to enter and analyze single cells suggests they could meet this need.

10) Artificial implants:

Normally body shows rejection reaction for implants with the post administration pain. [29]. 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. [30].

11) 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 anti aging cosmetics and with zinc oxide as sunscreen dermatological to prevent oxidation of important skin components. [28]

12) Diagnostic tool.: [30, 31].

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.

13) 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 and CNHs. [31]

14) As Biosensors.: [5].

CNTs act as sensing materials in pressure, flow, thermal, gas, optical, mass, position, stress, strain, chemical, and biological sensors. Some applications of carbon nanotube based sensors are given below. Biomedical industry CNT-incorporated sensors are expected to bring about revolutionary changes in various fields and especially in the biomedical industry sector. An example is the glucose sensing application, where regular self-tests of glucose by diabetic patients are required to measure and control their sugar levels. Another example is monitoring of the exposure to hazardous radiation like in

nuclear plants/reactors or in chemical laboratories or industries. The main purpose in all these cases is to detect the exposure in different stages so that appropriate treatment may be administered. CNT-based nanosensors are highly suitable as implantable sensors. Implanted sensors can be used for monitoring pulse, temperature, blood glucose, and also for diagnosing diseases. One such example is the use of nanotubes to track glucose levels in the blood, which would allow diabetics to check their sugar levels without the need for taking samples by pricking their fingers.

## 7. Effects of CNT in Plants: [32]

A number of different CNTs have recently gained interest due to their possible applications in regulating plant growth (Khot et al., 2012). [33]. NPs with different composition, size, and concentration, physical/chemical properties have been reported to influence growth and development of various plant species with both positive and negative effects. Khodakovskaya et al., 2009, reported that multi-walled carbon nanotubes markedly influenced tomato seed germination and seedling growth by up-regulating stress-related gene expression. [34]. Importantly, the literature shows both positive and negative effects on terrestrial plant species, depending upon CNM type and concentration, growth conditions, and plant species. In this section, we present the Positive Effects.

## 8. Positive Effects

Although most studies have focused on toxicological/physiological endpoints, several early studies did attempt to evaluate CNM accumulation in plants (Table 1). In a hydroponic study, Lin and Xing (2007) found significant increase in rye grass (*Lolium perenne*) root length (17%) upon exposure to 2000 mg/L MWCNT (rye grass) as compared to untreated controls. [35]. Canas et al. (2008) evaluated the toxicity of uncoated and coated SWCNTs [poly-3-aminobenzenesulfonic acid (PABS); PABS: CNTs D 65:35 (w/w)] to six crop species; cucumber (*Cucumis sativus*), carrot (*Daucus carota*), onion (*Allium cepa*), tomato (*Lycopersicon esculentum*), cabbage (*Brassica oleracea*), and lettuce (*Lactuca sativa*). [36]. The plants were exposed hydroponically to coated (0, 160, 900, and 5,000 mg/L) and uncoated-CNTs (0, 104, 315, and 1750 mg/L) for 24 and 48 h. Upon exposure, uncoated-CNTs increased root length in onion and cucumber as compared to the coated-CNTs. Although, variability was high (0–30% for uncoated-CNTs and 5–83% for coated-CNTs), an inverse relationship between exposure time and the extent of root elongation was observed, i.e., 1-day-exposure showed more pronounced effects than 2-day-treatments. Interestingly, microscopic studies revealed no internalization of CNTs into the roots; only surface adsorption was evident. Therefore, authors hypothesized that CNTs might impose indirect effects on

plant root systems, such as impeding microbial-root interactions, causing toxicity to microbes or altering crucial biochemical processes such as nutrient acquisition. Wild and Jones (2009) noted that upon exposure to wheat, CNTs were adsorbed onto the root surface but also did appear 'pierce' the root epidermal cells and accumulate within the tissue. [37].

Conversely, Tripathi et al. (2011) investigated the impact of citrate coated water-soluble CNTs (ws-CNT) in gram (*Cicer arietinum*) after a 10-days exposure to 6.0 mg/mL and were able to visualize internalization of the CNTs by electron microscopy. [38]. The authors hypothesized that once present inside the vascular tissue, ws-CNTs formed an 'aligned network' that increased water uptake efficiency and directly resulted in the observed plant growth enhancement (Tripathi et al., 2011). There have been several other reports of plant growth enhancement upon CNT exposure. Mondal et al. (2011) studied the effect of pristine (diameter 30 nm) and oxidized-MWCNT (o-MWCNT; diameter 20 nm) on mustard (*B. juncea*) at exposures of 2.3–46.0 mg/L. The authors reported enhanced germination, as well as increased root and shoot growth. At the lowest concentrations, o-MWCNTs yielded higher rates of germination (99% in 22 days) than did the pristine form (94% in 26 days). However, the rate of germination began to decrease at higher MWCNT exposure levels. After 5–10 days of exposure at the lowest concentrations, both root and shoot lengths were increased by 2.5x and 1.6x, respectively, as compared to untreated controls. [39]. Similarly, Khodakovskaya et al. (2011) showed that in Murashige and Skoog (MS) growth medium, 50 mg/mL SWCNT and MWCNT exposure enhanced the total fresh biomass of tomato seeds by 75 and 110%, respectively, as compared to activated carbon and graphene. [40]. In a follow up study, the authors (Khodakovskaya et al., 2012) compared the effects of MWCNT and activated carbon exposure on tobacco cells and demonstrated that growth was 55–64% higher at 5–500 mg/mL MWCNT exposure as compared to untreated controls. Importantly, although activated carbon enhanced cell growth (16%) at low concentrations (5 mg/mL), growth was suppressed by 25% at the higher exposures (100–500 mg/mL). [41].

Carbon nano-horns (CNHs) have also been reported positively impact the growth of terrestrial plants (Lahiani et al., 2015). [42]. CNHs are spherical structures with "disordered single-layered graphene sheets with a lateral size of up to 10 nm and an interlayer distance of approximately 4–5 Å" (Xu et al., 2011). [43]. Lahiani et al. (2015) exposed tobacco cells to CNHs at 25, 50, and 100 mg/ml for 24 h and noted a 78% increase in growth of cultured tobacco cells at 100 mg/ml while no significant effects at 25 mg/ml, as compared to controls. Recently, Zhang et al. (2015) treated tomato seeds in cotton-cushioned glass bottles with 40 mg/ml graphene. Upon exposure, the germination rate at 2, 4, and 6 days was increased by 26.6, 43.4, and 13.5%, respectively, when compared to untreated controls. [44].

**Table 2.** Positive effects of carbon nano-materials (CNMs) in plant. [32]

Reference	CNM	Treatment	Effect
Samaj et al., 2004	CNT	-	Uptake through endocytosis.
Lin and Xing, 2007	MWCNT	2000mg/L in ryegrass ( <i>Lolium perenne</i> )	Increased root length (_17%)
Tripathi et al., 2011	Citrate coated water-soluble CNTs	10-days exposure to 6.0 mg/mL	Visualize internalization of the coated ws-CNTs by SEM and TEM.
Khodakovskaya et al., 2011	SWCNT and MWCNT	50 mg/L	enhanced the total fresh biomass
Mondal et al., 2011	Pristine (diameter 30 nm)and oxidized-MWCNT	In mustard( <i>Brassica juncea</i> ) at2.3–46.0 mg/L	Enhanced germination, increased root and shoot growth.
Wang et al., 2012	o-MWCNT	40, 80, and 160 mg/L for 3 and 7 day	Increase in root length of wheat seedlings
Tiwari et al., 2013	MWCNTs	5–60 mg/L MWCNTs for 7 days in agar gel	60 mg/L treatment; increased plant fresh biomass (43%) and higher nutrient uptake (2x calcium and 1.6x iron)
Tripathi and Sarkar, 2014	Cabon nano-dots	10 days of exposure to 150 mg/L water soluble carbon nano-dots	Enhanced root growth (10x) of wheat.
Lahiani et al., 2015	Carbon nano-horns (CNHs)	25, 50 and 100 mg/ml for 10–20 days barley, corn, rice, soybean, switchgrass, tomato) and tobacco cell culture	Growth of tobacco cells was increased 78%. Uptake confirmed by TEM

## 9. Conclusion

From the above discussion, we are only concerned with the positive effects of CNT on plants. According to literature reviews of various authors some mixed positive as well as negative effects are also observed. We had observed that CNTs introduced in soil mix through watering can affect the phenotype of tomato plants. Tomato plants grown on soil supplemented with CNTs produced the same amount of leaves but two-time more flowers and fruits than plants grown in regular soil. This observation opens new perspectives on technological applications for the introduction of CNTs as growth regulators in agricultural practices. Thus, accelerating plant growth by application of carbon nanotubes can open new perspectives for a number of avenues ranging from biofuel crops to space grown plants. Carbon/fullerene nanotechnology is a rapidly growing area of research which finds use in plant, medicine and engineering. Carbon nanotubes (single-wall carbon nanotubes and multi-wall carbon nanotubes) in many cases can penetrate the seed coat and plant cell wall which depends on their size, concentration and solubility. The size of carbon nanotubes alone is of great significance in agriculture and biotechnology. The penetration of carbon nanotubes into the plant system can bring changes in metabolic functions leading to an increase in biomass, fruit/grain yield. The nanobiotechnology may be helpful for the advancement of agriculture and plant science. The future prospect of carbon nanomaterials is fairly bright as it is a low cost solution to increase the crop production and fruit manifold.

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## References

- [1] Mukul Kumar and Yoshinori Ando Chemical Vapor Deposition of Carbon Nanotubes: A Review on Growth Mechanism and Mass Production *Journal of Nanoscience and Nanotechnology* Vol. 10, 3739– 3758, 2010.
- [2] S. Iijima, *Nature (London)* 354 56, 1991.
- [3] N. Valentin, Popov, *Mat Sci and Engg R* 43, 61, 2004.
- [4] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley, C60: Buckminsterfullerene, *Nature* 318, 162 - 163 14, November 1985.
- [5] Rajashree Hirlekar, Manohar Yamgar, Harshal Garse, Mohit Vij and Vilasrao Kadam “Carbon nanotubes and its applications: A Review” *Asian Journal of Pharmaceutical and Clinical Research*, 2009, 2 (4), 17-27.
- [6] E. N. Ganesh. Single Walled and Multi Walled Carbon Nanotube Structure, Synthesis and Applications. *International Journal of Innovative Technology and Exploring Engineering (IJITEE)* ISSN: 2278-3075, Volume-2, Issue-4, March 2013.
- [7] Kalpna Varshney., Carbon Nanotubes: A. Review on Synthesis, Properties and Applications. *International Journal of Engineering Research and General Science* Volume 2, Issue 4, June-July, 2014.
- [8] Qiang Shi, Zhongyuan Yu., Yumin Liu, Hui Gong, Haozhi Yin, Wen Zhang, Jiantao Liu, Yiwei Peng. Plasmonics properties of nano-torus: *An FEM method. Optics Communications*, Volume 285, Issues 21–22, Pages 4542–4548, 1 October 2012.
- [9] Xiaojun Wu and Xiao Cheng Zeng Periodic Graphene Nanobuds. *Nano Lett.*, December 11, 2008.
- [10] Harris P. J. F, Tsang S. C, Claridge J. B. and Green M. L. H. High resolution electron microscopy studied of a microporous carbon produced by arc evaporation *J. Chem.Soc. Faraday. Trans.*90, 2799–802, 1994.

- [11] <http://www.ee.nec.de/News/Releases/pr283-01.html> (August, 2001).
- [12] Shuyun Zhu and Guobao Xu. Single-walled carbon nanohorns and their applications. *Nanoscale*, 22538- 2549.2010.
- [13] Andrea Szabo, Caterina Perri, Anita Csato, Girolamo Giordano, Danilo Vuono and Janos B. Nagy. Synthesis Methods of Carbon Nanotubes and Related Materials. *Materials* 2010, 3, 3092-3140; doi:10.3390/ma3053092
- [14] Brenner, D. —"Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films". *Physical Review B* 42(15): 9458-9471, 1990.
- [15] Calvert, P. —'Strength in disunity'. *Nature* 357: 365-366, 1992.
- [16] Che, G., B. Lakshmi, C. Martin and E. Fisher —Chemical vapor deposition based on synthesis of carbon nanotubes and nanofibers using a template method. *Chemistry of Materials* 10: 260-267, 1998.
- [17] T. W. Ebbesen & P. M. Ajayan, Large-scale synthesis of carbon nanotubes, *Nature* 358, 220 - 222 (16 July 1992).
- [18] T. Guo, Nikolaev, P. Rinzler, A. G. Tomanek, D. Colbert, D. T.; Smalley, R.E. Self-assembly of tubular fullerenes. *J. Phys. Chem.* 99, 10694–10697, 1995.
- [19] Paradise, M.; Goswami, T. Carbon nanotubes-production and industrial application. *Mat. Design*, 28, 1477–1489, 2007.
- [20] Teo, K. B. K. Singh, Ch. Chhowalla, M.; Milne, W. I. Catalytic synthesis of carbon nanotubes and nanofibers. *In Encyclopedia of Nanoscience and Nanotechnology; Nalwa, H. S., Ed.; American Scientific Publisher: Valencia, CA, USA; Volume 1*, pp. 665–668, 2003.
- [21] <http://www.pharmainfo.net>.
- [22] Hou PX, Bai S, Yang GH, Liu C, Cheng HM. Multi-step purification of carbon nanotubes. *Carbon* 2002; 40: 81-85.
- [23] <http://www.nano-c.com/nanotubes>.
- [24] Yang W, Thordarson P, Gooding JJ, Ringer SP, Braet F. Carbon nanotubes for biological and biomedical applications. *Nanotechnology* 2007; 18: 412001.
- [25] Lacerda L, Bianco A, Prato M, Kostarelos K. Carbon nanotubes as nanomedicines: *From toxicology to Pharmacology. Adv. Drug. Deli. Rev.* 2006; 58:1460-1470.
- [26] Sayes CM, Liang F, Hudson JL, Mendez J, Guo W, Beach JM et al. Functionalization density dependence of single-walled carbon nanotubes cytotoxicity in vitro. *Toxicol. Lett.* 2006; 16: 135– 142.
- [27] 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.
- [28] Pai P, Nair K, Jamade S, Shah R, Ekshinge V, Jadhav N. Pharmaceutical applications of carbon tubes and nanohorns. *Current Pharma Research Journal* 2006; 1:11-15.
- [29] <http://www.nanotsunami.com>.
- [30] Ding R, Lu G, Yan Z, Wilson M. Recent advances in the preparation and utilization of carbon nanotubes for hydrogen storage. *Journal of Nanoscience and Nanotechnology* 2001: 17-29.
- [31] Kuznetsova A, Mawhinney D. Enhancement of adsorption inside of single-walled nanotubes: opening the entry ports. *Chem Phys Lett* 2000; 321: 292-296.
- [32] Arnab Mukherjee, Sanghamitra Majumdar, Alia D. Servin, Luca Pagano, Om Parkash Dhankher, and Jason C. White (2016). *Carbon Nanomaterials in Agriculture. A Critical Review. Front. Plant Sci.* 7:172. doi: 10.3389/fpls.2016.00172.
- [33] Khot, L. R., Sankaran, S., Maja, J. M., Ehsani, R., and Schuster, E. W.(2012). Applications of nanomaterials in agricultural production and crop protection:a review. *Crop Protect.* 35, 64–70. doi:10.1016/j.cropro.2012.01.007.
- [34] Khodakovskaya, M., Dervishi, E., Mahmood, M., Xu, Y., Li, Z., Watanabe, F., et al. (2009). Carbon nanotubes are able to penetrate plant seed coat and dramatically affect seed germination and plant growth. *ACSNano* 3, 3221–3227. doi: 10.1021/nn900887m.
- [35] Lin, D., and Xing, B. (2007). Phytotoxicity of nanoparticles: inhibition of seed germination and root growth. *Environ. Pollut.* 150, 243– 250. doi: 10.1016/j.envpol.2007.01.016.
- [36] Canas, J. E., Long, M., Nations, S., Vadan, R., Dai, L., Luo, M., et al. (2008). Effects of functionalized and nonfunctionalized single-walled carbon nanotubes on root elongation of select crop species. *Environ. Toxicol. Chem.* 27, 1922–1931. doi: 10.1897/08-117.1.
- [37] Wild, E., and Jones, K. C. (2009). Novel method for the direct visualization of in vivo nanomaterials and chemical interactions in plants. *Environ. Sci. Technol.* 43, 5290–5294. doi:10.1021/es900065h.
- [38] Tripathi, S., Sonkar, S. K., and Sarkar, S. (2011). Growth stimulation of gram (*Cicer arietinum*) plant by water soluble carbon nanotubes. *Nanoscale* 3, 1176–1181. doi: 10.1039/c0nr00722f.
- [39] Mondal, A., Basu, R., Das, S., and Nandy, P. (2011). Beneficial role of carbon nanotubes on mustard plant growth: an agricultural prospect. *J. Nanopart. Res.* 13, 4519–4528. doi:10.1007/s11051-011 0406-z.
- [40] Khodakovskaya, M. V., De Silva, K., Nedosekin, D. A., Dervishi, E., Biris, A. S., Shashkov, E. V., et al.(2011). Complex genetic, photothermal and photoacoustic analysis of nanoparticle-plant interactions. *Proc. Natl. Acad. Sci. U.S.A.* 108, 1028–1033. doi:10.1073/pnas.1008856108.
- [41] Khodakovskaya, M. V., De Silva, K., Biris, A. S., Dervishi, E., and Villagarcia, H. (2012). Carbon nanotubes induce growth enhancement of tobacco cells. *ACS Nano* 6, 2128–2135. doi:10.1021/nn204643g.
- [42] Lahiani, M. H., Chen, J., Irin, F., Poretzky, A. A., Green, M. J., and Khodakovskaya, M. V. (2015). Interaction of carbon nanohorns with plants: uptake and biological effects. *Carbon* 81, 607-619. doi:10.1016/j.carbon.2014.09.095.
- [43] Xu, J., Tomimoto, H., and Nakayama, T. (2011). What is inside carbon nanohorn aggregates? *Carbon* 49, 2074–2078. doi:10.1016/j.carbon.2011.0 1.042.
- [44] Zhang, M., Gao, B., Chen, J., and Li, Y. (2015). Effects of grapheme on seed germination and seedling growth. *J. Nanopart. Res.* 17:78. doi: 10.1007/s11051- 015-2885-9.