Plants and Carbon Nanotubes (CNTs) Interface: Present Status and Future Prospects

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Shweta, Kanchan Vishwakarma, Shivesh Sharma, Raghvendra Pratap Narayan, Prateek Srivastava, Ambrina Sardar Khan, Nawal Kishore Dubey, Durgesh Kumar Tripathi, and Devendra Kumar Chauhan

Abstract

The unique characteristics of nanomaterials utilizing carbon have drawn great attention and interest since the breakthrough of fullerenes (in 1985), carbon nanotubes (CNTs, in 1991), and graphene (in 2004). This discovery has led to the promotion of developing methods in order to produce it at large industrial scales. Engineered nanomaterials are continuously finding its applications in medical sector, technical devices, environmental purposes, as well as agricultural sector. Despite its wide applications, there is also the unintended release of carbon-based nanostructures into the environment, thereby affecting or posing inimical

Shweta • D.K. Chauhan (✉)
D.D. Plant Interdisciplinary Research Laboratory, Department of Botany, University of Allahabad, Allahabad 211002, India
e-mail: dkchauhanau@yahoo.com

K. Vishwakarma
Department of Biotechnology, Motilal Nehru National Institute of Technology, Allahabad, India

S. Sharma
Department of Biotechnology, Motilal Nehru National Institute of Technology, Allahabad, India

Centre for Medical Diagnostic and Research, Motilal Nehru National Institute of Technology, Allahabad, India

R.P. Narayan
Government Girls Degree Collage, Lucknow, India

P. Srivastava • A.S. Khan
Amity Institute of Environmental Science, Amity University, Noida, India

N.K. Dubey
Centre of Advanced Study in Botany, Banaras Hindu University, Varanasi, India

D.K. Tripathi (✉)
Centre for Medical Diagnostic and Research, Motilal Nehru National Institute of Technology, Allahabad, India
e-mail: dktripathiau@gmail.com

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effect toward the living systems like plants. The researchers are trying to engineer such nanoparticles in a way that it may impose some advanced and beneficial applications in living systems. One of the engineered carbon-based nanomaterials includes carbon nanotubes (CNTs) which can be further classified as single-walled carbon nanotubes (SWCNTs), multiwalled carbon nanotubes (MWCNTs), water-soluble multiwalled carbon nanotubes, functionalized single-walled carbon nanotubes, double-walled carbon nanotubes etc. This chapter, therefore, focuses on all aforementioned types of carbon nanotubes, techniques utilized in synthesis, and current status of research with respect to the impact of carbon nanotubes on plant growth and development addressing relevant knowledge gap.

Keywords
Carbon nanotubes • Plants • Uptake • Translocation • Nanotechnology

16.1 Introduction

Nanotechnology and nanoscience are the science that includes the study of any particle at nanoscale level which ranges from 1 to 100 nm (Nagarjan 2008; Ju-Nam and Lead 2008; Suman et al. 2010). Moreover, the particles falling in the range of 1–100 nm are known as nanoparticles (Buzea et al. 2007). Despite their small sizes, they are being used in agriculture (Sabir et al. 2014; Parisi et al. 2015; Prasad et al. 2017a), wastewater treatment (Nassar 2013; Esakkimuthu et al. 2014; Aziz et al. 2015), drug delivery (Silva et al. 2014; Prasad et al. 2017b), electronics (Millstone et al. 2010), medicines (Shi et al. 2010; Aziz et al. 2016), etc. (Fig. 16.1). Due to the vast applications of nanoparticles in daily life, its production also increases day by day. This increasing production of nanoparticles should be analyzed in order to know whether they may be harmful for ecosystem or not because many nanoparticles possess potential to cause pollution when they interact or come in contact with atmospheric gases and living organisms (Conway et al. 2015; Tripathi et al. 2017a). The pollution created from nanoparticles in the environment is known as nanopollution (Gao et al. 2015). Plants are considered as the main part of the food web, they are under the risk of nanoparticle exposure either through soils (by using nanopesticides), atmospheric deposition, or runoff (Gottschalk and Nowack 2011; Conway et al. 2015; Tripathi et al. 2017a, b, c). A nanoparticle comes in the environment by natural processes or can be manufactured by various physical, chemical, and biological methods (Ingale and Chaudhari 2013; Iravani et al. 2014; Prasad et al. 2016), there are few examples of natural nanoparticles are dust storms, fires, volcanoes, etc. (Buzea et al. 2007; Strambeanu et al. 2015), and manufactured nanoparticles include carbon nanotubes (Eatemadi et al. 2014; Lee et al. 2016), copper oxide nanoparticles (Umer et al. 2012), etc. However, there are different functions of nanoparticles according to their size, shape, concentrations etc. from which they perform either beneficial impact or inimical impact on plants and living organisms (Tables 16.1 and 16.2; Fig. 16.2) (Ma et al. 2010; Tripathi et al. 2017a, b, c). Among

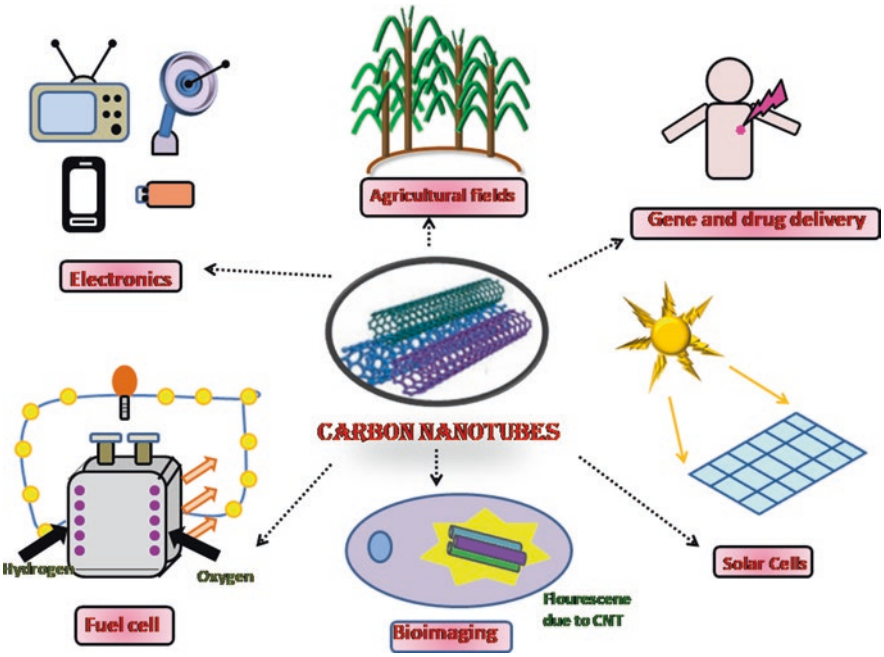

Fig. 16.1 Applications of carbon nanotubes in various sectors

all the nanoparticles, carbon nanotubes are fetching more attention due to their attractive structure, shape, size and unique physical, chemical, and biological properties (Chen et al. 2003; Kam et al. 2004; Cherukuri et al. 2004; Bianco et al. 2005; Serag et al. 2015). Carbon nanotubes are actually engineered nanoparticles whose synthesis evolved in 1985, after the discovery of Buckminster (C_{60}) fullerenes (Bergmann and Machado 2015; Hong et al. 2015; Mukherjee et al. 2016). Major classification of carbon nanotubes includes single-walled carbon nanotubes, multi-walled carbon nanotubes, fullerene, cup-stacked carbon nanotubes etc. (Serag et al. 2015). Its structure is very unique; they are engineered by folding the sheets of graphene (Iijima 1991; Dai 2002; Golberg et al. 2008; Serag et al. 2015). Its major applications occur in biological and medicinal field involving tissue engineering, drug and gene delivery and in many diagnostic areas (Panyam and Labhasetwar 2003; Zanello et al. 2006; Harrison and Atala 2007; Rao and Srivastava 2014; Prasad et al. 2016). Other than this, they are also being used in batteries, biosensors, microelectronics, and energy storages (Lee et al. 2015). Hence, there is maximum chance of interaction of nanoparticles with plants due to their extensive applications in many fields (including research) and rapidly increasing production (Fig. 16.1) (Pitsillides et al. 2003; Rao and Srivastava 2014). This also led to advances in agricultural sectors, by shaping the modern approaches in agriculture (Rao and Srivastava 2014; Sangeetha et al. 2017). Carbon nanotubes are also widely used because they can be easily penetrated in the cell wall of any plant and hence can be effectively used in agriculture by acting as direct delivery system for many fertilizers and pesticides (Rao and Srivastava 2014). Although in the field of life science,

Table 16.1 Beneficial impact of carbon nanotubes on different plants at various concentrations

Type of carbon nanotube	Size (nm)	Concentration(s)	Plant(s)	Beneficial effects	Reference(s)
MWCNTs	–	40 µg/ml	*Lycopersicum esculentum*	Increased percentage of seed germination and seedling growth	Morla et al. (2011)
	10 nm	75 wt%	*Medicago sativa*, *Triticum aestivum*	Enhanced elongation of roots and seedling growth	Miralles et al. (2012)
	Not available	25–100 µg/mL	*Hordeum vulgare*, *Glycine max*, *Zea mays*	Increased germination and growth, hence overall biomass of the plant; increased root length in *Glycine max*	Lahiani et al. (2013)
	25 nm	20, 50 mg/L	Wheat, maize, peanut, garlic	Elongated length of roots and shoots	Khodakovskaya et al. (2013)
	25	5 up to 500 µg/mL	*Nicotiana tabacum*	Flowering and fruiting increased twice as compared to control	Khodakovskaya et al. (2012)
	10–35	50 and 200 µg/mL	*Lycopersicon esculentum*	Increased overall biomass content, upregulation of stress-related genes, and penetration of MWCNTs into roots, leaves, and fruits	Khodakovskaya et al. (2011)
	Not reported	10, 20, 40 mg/L	*Lycopersicon esculentum*	Enhanced moisture contents in seed and improved rate of germination	Khodakovskaya et al. (2009)
	110–170	20 µg/mL	*Brassica juncea* and *Phaseolus mungo*	Increased root growth	Ghodake et al. (2010)
	~30	2.3×10^{-3} mg/mL	*Brassica juncea*	Improved germination and seedling growth	Mondal et al. (2011)
	< 50	25, 50, 100, 250, 500 mg/L	*Satureja*	Increased callus growth	Ghorbanpour and Hadian (2015)
	6–13	10–50 mg/L	*Zea mays*	Stimulated growth	Zhai et al. (2015)

MWCNTs, double-multiwalled carbon nanotubes	6–9	40 µg/mL	*Lycopersicon esculentum*	Increased growth, biomass, and concentration of nutrient elements	Tiwari et al. (2013)
WS-CNT	10–30	6.0 µg/mL	*Cicer arietinum*	Increased growth rate	Tripathi et al. (2011)
Pristine MWCNTs, double-multiwalled carbon nanotubes	6–9	20 mg/L	*Zea mays*	Improved water absorption, biomass of plant, and concentration of essential nutrients like Ca and Fe	Tiwari et al. (2014)
COOH- MWCNTs	10–20	50 µg/mL	*Triticum aestivum*, *Zea mays*, *Arachis hypogaea*, and *Allium sativum*	Increased root, shoot, and biomass	Rao and Srivastava (2014)
SWCNTs-COOH, SWCNTs-Fe	1.0–2.0, 3.5–4.0	4 µg/ml	*Rubus adenotrichos*	Elongated roots and shoots	Flores et al. (2014)
				Enhanced cell metabolism	
SWCNT, fSWCNT	3	9, 56, 315, and 1750 mg/L	*Allium cepa*, *Cucumis sativus*	Enhanced elongation of roots	Cañas et al. (2008)
SWCNTs	8–15	10–40 mg/L	*Lycopersicum esculentum*, *Allium cepa*	Enhanced the rate of germination	Haghighi and da Silva (2014)
	0.86–2.22	50 mg/L	Tomato	Increased fresh and dry plant biomass	Khodakovskaya et al. (2011)
CNTs	8	50, 100, 150 mg/L	*Oryza sativa*	Improved rate of germination	Jiang et al. (2014)

Table 16.2 Negative or no any significant impact of carbon nanotubes on different plants at various concentrations

Type of carbon nanotube	Size (nm)	Concentration(s)	Plant(s)	Negative effects	Reference(s)
MWCNTs	10–30	20, 40 mg/L	*Oryza sativa*	Condensed chromatin, detachment of cell membrane from cell wall, generation of ROS, and decreased cell viability, ultimately cell death	Tan et al. (2009)
	9.5	10, 60, 100, 600 mg/L	*Arabidopsis*	Reduced cell viabilities and dry weight, cell chlorophyll content, and superoxide dismutase activities	Lin et al. (2009a, b)
	–	10–50 mg/L	Soybean	Reduced growth, uptake, and translocation	Zhai et al. (2015)
	10–150	1000 mg/L	Wheat, rapeseed	No effect on development	Larue et al. (2012)
	~11	500, 1000 mg/L	*Amaranthus tricolor*	Red pigment of leaf removed, necrosis, curling, and wilting also seen in the treated leaf. Concentration-dependent reduction in root-shoot height, root-shoot weight, and leaf numbers. Enhanced electrolytic damage and generation of ROS Increased apoptosis	Begum and Fugetsu (2012)
	10	10 ppm	*Cichorium intybus*	Reduced germination percentage	Pilevar et al. (2015)
	13–16	1000 mg/L	*Zucchini*	Reduced biomass but seed germination unaffected	Stampoulis et al. (2009)
	10–20	2000 mg/L	*Lettuce*	Declined root length but no effect on germination of seeds	Lin and Xing (2007)
	110–170	100 mg/L	*Triticum aestivum*	No significant effect on growth of roots or shoots	Wild and Jones (2009)
	3 ± 4	40–2560 mg/L	*Alfalfa*, *wheat*	No effect on seed germination	Miralles et al., (2012)
	110–170	10, 20, 40 mg/L	*Mustard*, *black lentil*	No effect on seed germination	Ghodake et al., (2010)
	Not reported	100 mg/L	*Barley*, *maize*, *soybean*	No effect on seed germination	Lahiani et al., (2013)

	20	50 and 200 µg/mL	*Lycopersicon esculentum*	Elevated expression of *CycB* gene and hence plant cell divisions and growth	Khodakovskaya et al. (2013)
	7–15	5, 20, 50 mg/L	*Allium cepa*	DNA damage	Ghosh et al. (2015)
	Not reported	5 and 10 mg/L	*Allium cepa*	DNA damage	Ghosh et al. (2011)
O-MWCNTs	6–13	10, 20, 40, 80, 160 mg/L	*Triticum aestivum*	No effect on seed germination	Wang et al. (2012)
SWCNTs	8–15	10–40 mg/L	*Raphanus sativus*, *Brassica rapa*	Showed toxicity by decreasing germination rate	Haghighi and da Silva (2014)
	1.19 (major), 18, 722	400 mg/L	*Oryza sativa*	Delayed flowering, declined yield	Lin et al. (2009a, b)
	8	104, 315, 1750 mg/L	*Lycopersicum esculentum*	Reduced root length	Cañas et al. (2008)
	8	104, 315, 1750 mg/L	Cabbage, carrot, lettuce	No significant length	Cañas et al. (2008)
	1–2	20 mg/L	Maize	No any effect on germination of seeds	Yan et al. (2013)
	1–2	5–250 mg/L	*Arabidopsis*, *Oryza sativa*	Cell aggregation, condensation of chromatins, plasma membrane deposition, H_2O_2 accumulation	Shen et al. (2010)
fCNTs	8	104, 315, 1750 mg/L	*Lettuce*	Reduced length of roots	Cañas et al. (2008)
fSWCNTs	8	9, 56, 315, 1750 mg/L	*Cabbage*, *carrot*, *lettuce*, *onion*, *tomato*	No effect on development	Cañas et al. (2008)
CNTs	Not reported	Not reported	*Arabidopsis*	Declined rate of photosynthesis and transpiration. Reduced carbon gain and chlorophyll fluorescence	Voleti and Wait (2014)

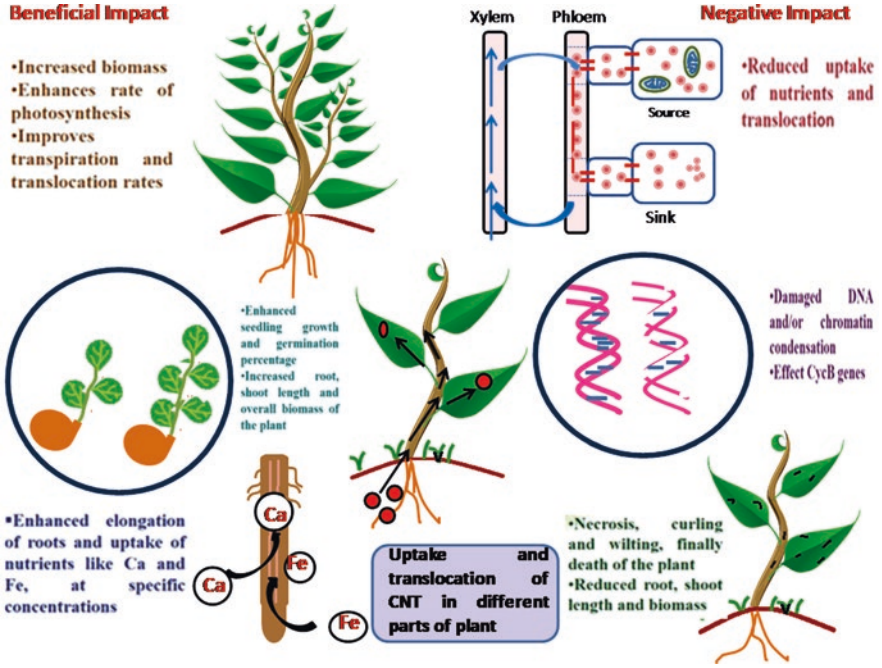

Fig. 16.2 Impact of carbon nanotubes on plants

most of the researches were performed on humans and animals, but some studies revealed the impact of carbon nanotubes on plants, especially on morphological or physiological developments because plants are thought to be geo-physico-chemical transducers. They are very necessary for life since they are the only source of oxygen and food supply and also help in sustaining life (Donaldson et al. 2006; Martinelli et al. 2012; Tiwari et al. 2013). Plants are the last receiver of carbon nanotube contamination involved or present in the environment. Hence, carbon nanotube nanoparticle-plant interaction must be assessed thoroughly from cell to organism level (Tiwari et al. 2013). From this study of interaction, one can also develop the nanoagricultural technologies, which include the area of nanobiotechnology and help in improving the biomass of the plants (Srinivasan and Saraswathi 2010). On the other hand, the toxicity of carbon nanotubes in plants is also not negligible. They exhibit high tendency to accumulate in plants and their cells (Khodakovskaya et al. 2009; Liu et al. 2009a; Begum et al. 2012). Many studies revealed the toxicity of carbon nanotubes in plants (Yang and Watts 2005; Lin and Xing et al. 2007; Tan et al. 2009; Lin et al. 2009a, b; Begum and Fugetsu 2012), and after penetration of carbon nanotubes in plants, they follow a pathway link through which carbon nanotubes enter in the biological cycles and food chain (Wierzbicka and Antosiewicz 1993; Begum and Fugetsu 2012). In addition to this, Tan and Fugetsu (2007) and Cañas et al. (2008) also reported the inimical impact of carbon nanotubes by reduced seed germination and inhibited growth percentage in selected plants and their cells (Fig. 16.2). Primary criteria by which carbon

nanotubes inhibit or alter the growth of plants include generation of ROS and oxidative stress (Tan et al. 2009, Begum et al. 2011; Begum and Fugetsu 2012). The generation of ROS and oxidative stresses causes the damaging effects on other parts or organelles of plants like mitochondria, cell membrane, DNA etc. (Apel and Hirt 2004), which ultimately cause effect on reproduction, development, and viability of organisms (Begum and Fugetsu 2012).

16.2 Properties, Synthesis, and Classification of Carbon Nanotubes

16.2.1 Properties

Carbon is the essential element having atomic number six with six electrons in their shell and electronic configuration $1s^2$, $2s^2$, $2p^2$. Moreover, discoveries revealed that similar sp^2 configurations were also found in carbon nanotubes (Chico et al. 1996), graphene (Ouyang et al. 2001), and fullerenes (Kim et al. 2003) (Eatemadi et al. 2014). Carbon nanotubes are carbon allotropes having cylindrical structures with length to diameter ratios up to 132,000,000:1 (Wang et al. 2009a). Carbon nanotubes are found in various structures like armchair, zigzag etc. Carbon nanotubes that are found in armchair tubelike structure, their diameter is found to be 1.2 nm, while their carbon bond length reported is around 1.42 Å (Ganesh 2013). Furthermore, their lattice energy, overlap energy, and density were reported to be around 17 Å, 2.5 eV, and 1.40 g/cm^3 respectively (Ganesh 2013). In addition to this, their thermal conductance and resistivity at 300 K were around 1/12.9 kW^{-1}, respectively (Ganesh 2013).

16.2.2 Synthesis of CNTs

There are a number of methods given by researchers by which carbon nanotubes can be synthesized. Some of them include laser ablation technique, carbon or electric arc discharge technique, chemical vapor deposition, pyrolysis, and electronic methods. Thess et al. (1996)reported that single-walled carbon nanotubes can be formed by condensation reaction of laser-vaporized C-Ni-Co (carbon-nickel-cobalt) mixture through laser ablation method. The process of condensation occurs at 1200 °C and the benefit of this technique is that it provides around 70% yield. Electron microscopy and XRD (X-ray diffraction) showed that they possess uniform diameter (0.2 Å) of single-walled nanotubes in ropelike structures having metallic properties. At 300 K temperature, their single-rope resistivity was observed to be $<10^{-4}$ Ω cm (Thess et al. 1996). In another method, carbon nanotubes were synthesized through arc discharge technique at very high temperature (more than 1700 °C) (Eatemadi et al. 2014). This high degree of temperature led to the expansion of carbon nanotubes with some structural defects as compared to the other processes. In this process, 6–10 nm highly pure water-cooled graphite electrodes were separated by a chamber containing helium in it at subatmospheric pressure (Grobert

2007; Eatemadi et al. 2014). The chamber contains some metal catalysts like iron, nickel, and/or cobalt, cathode and anode of graphites, and evaporated carbon molecules. However, yield of single-walled carbon nanotubes can be synthetically improved by adding either cobalt or transition elements like molybdenum, nickel, and iron with graphite (Iijima and Ichihashi 1993). Chamber was heated at 4000 K and pressurized by passing direct current through it (arcing process). This led to the evaporation and consequently solidification of half of the carbon on cathode tip, while the other remaining carbon accumulated on the periphery and condensed on the shoot of cathode. This will yield either multiwalled carbon nanotubes or single-walled carbon nanotubes (Eatemadi et al. 2014). Carbon nanotubes can also be prepared via chemical vapor deposition (CVD) and considered as one of the standard methods. It includes following types like HFCVD (hot filament chemical vapor deposition) (Ajayan et al. 1999; Dervishi et al. 2009), MPECVD (microwave plasma-enhanced chemical vapor deposition) (Ebbesen and Ajayan 1992), RF-CVD (radiofrequency chemical vapor deposition) (Bernholc et al. 1997), water-assisted CVD (Iijima et al. 1992; Journet et al. 1997; He et al. 2010), and CCVD (catalytic chemical vapor deposition) (Vander Wal et al. 2003). This process allows the expansion of carbon nanotubes and involves the breakdown of hydrocarbons. The process is somewhat similar to the arc discharge process. It also uses high temperature, i.e., 700 °C, with some metal catalyst particles like nickel, iron, and cobalt (Terrones-Maldonado 1997) or their combinations (Landi et al. 2005). First of all, the reactor was fueled with two different types of gases (the first one was process gas like ammonia, nitrogen, or hydrogen, while the second one was carbon-containing gas like ethanol, ethylene, methane, or acetylene) (Eatemadi et al. 2014). On catalyst, C-containing gas breaks down and carbon particles become visible. Hence, nanotube production takes place. However, this method is still under debate (Choudhary et al. 2014).

16.2.3 Classification of Carbon Nanotubes

Carbon nanotubes are generally made up of rolled sheets of cylindrical structures with aspect ratio of 108 (length to diameter) (Su and Cheng, 2014). On the basis of tube structure of carbon nanotubes, they are majorly classified into three groups: stacked-cup carbon nanotubes (SCCNTs), multiwalled nanotubes (MWCNTs), and single-walled nanotubes (SWCNTs) (Su and Cheng 2014). However, Jackson et al. (2013) classified carbon nanotubes in three categories: multiwalled carbon nanotubes, double-walled carbon nanotubes, and single-walled carbon nanotubes. Ganesh (2013) reported that carbon nanotubes can exist in two forms, either semiconductor or metals. Their function changes according to their structure and symmetry. Moreover, its diameter was observed to be 50,000 times thinner as compared to the hair of a human being (Ganesh 2013). In addition, they are considered to be stronger than steel also (Ganesh 2013). Structures of carbon nanotubes are so unique; they are hollow cylinders of graphite and possess hexagonally arranged carbon rings. Their end contains hexavalent arched structure while they are capped

with pentavalent ring (Ganesh 2013) They possess high tensile strength which resembles with the property of graphene (Tománek et al. 2008). Tománek et al. (2008) also reported that they remain stable even at the extreme temperatures and maximize the vibrational entropy and configuration at low energy that led to the increase in temperature to hundreds of degree Celsius and thermal contraction in length (Tománek et al. 2008).

16.2.3.1 Single-Walled Carbon Nanotubes

The diameter of single-walled carbon nanotubes varies from 0.4 to 3 nm, while their length ranges in micrometer (Eatemadi et al. 2014). Aggregation of single-walled carbon nanotubes forms ropes or bundles. Single-walled carbon nanotubes are hexagonally arranged in a bundle and form crystal-like structures (Chico et al. 1996; Eatemadi et al. 2014). Single walled carbon nanotubes are classified into different forms according to type of wrapping, with chiral, zigzag, and armchair as evidences (Eatemadi et al. 2014). Properties of single-walled carbon nanotubes are same as compared to multiwalled carbon nanotubes except in high tensile strength (Vander Wal et al. 2003).

16.2.3.2 Multiwalled Carbon Nanotubes

The arrangement of multiwalled carbon nanotubes occurs in such a way that one carbon nanotube lies inside other carbon nanotubes. Moreover, the diameter of inner carbon nanotubes is generally less than the outer one. This type of model is known as Russian doll model, while in Parchment model, one carbon nanotube (graphene sheet) is surrounded or rolled by multiple copies of another carbon nanotube. It is thought that the function of outer wall is to protect the inner wall from chemical reactions (Eatemadi et al. 2014). Multiwalled carbon nanotubes contain many concentric hollow cylinders with interlayer spacing of 0.34–0.39 nm (Ajayan and Ebbesen 1997; Eatemadi et al. 2014). Diameter of inner wall decreases depending on the wall layers, i.e., the inner one varies from 0.4 mm to few nm, while the outer one ranges from 2 to 30 nm (Eatemadi et al. 2014). Ends of the multiwalled carbon nanotubes are closed with dome-shaped half fullerene capping.

16.3 Applications of Carbon Nanotubes

Human races are attracting toward the miniature objects which are facilitated by the use of nanoparticles. These nanoparticles are now used in even small things like chip (containing silicon nanoparticles) and to the large objects, for example, in large machines or robots. Similarly, the application of carbon nanotubes is increasing at an alarming rate which is described in the following section. Inventions in the area of nanotechnologies provide many new applications in the branch of aerospace, defense, electronics, and medical sciences (Liu et al. 2006; Wang et al. 2009b; Singh 2010; Khodakovskaya et al. 2013).

It is necessary to mention that the cumulative application of electronic devices with nanotubes gives an idea of its long-term applications (Endo et al. 2007). Conversely, carbon nanotubes show a scintillating class in the field of electronics like

ballistic electronic conduction (Dekker 1999; Javey et al. 2003; Endo et al. 2007), solar cells (Huang et al. 2007), and fuel cells (Baughman et al. 2002). From year 2001 onward, progress in the field of carbon nanotubes was seen, after the invention of simple transistors to logic circuits. In addition, they are also frequently used in biological fields like imaging the live tissues and cells and detection of plaque by injecting carbon nanotubes after the microphages (Cherukuri et al. 2004). Images of photobleaching showed the affected area of plaque (Cherukuri et al. 2004). For measurement of blood count and for imaging of the tissue sections via fluorescence, single-walled carbon nanotubes were found to be useful (Cherukuri et al. 2006). Majorly the applications of carbon nanotubes are seen in the medical fields like tissue regeneration, biosensor analysis, and delivery of genes, drugs, and biomolecules (He et al. 2013). Generally, functionalized carbon nanotubes are used to fix on the surface of carbon nanotubes, which are then injected in animal cells either by targeting any specific cell or giving orally (He et al. 2013). The capsules of carbon nanotube drug are ingested by the cell, carbon nanotubes released all their contents and the drug is delivered (Liu et al. 2007; Zhang et al. 2010, 2011; Kateb et al. 2010; Singh et al. 2012; Usui et al. 2012; He et al. 2013). Functionalized carbon nanotubes are also capable to transport specific molecules across the nuclear and cytoplasmic membranes without showing any toxic effect (He et al. 2013). The drug conjugates proved very effective and safer than any other drugs (He et al. 2013). Carbon nanotubes are proved to be the promising material in context of its application in biotechnology (Wong et al. 1998; Azamian et al. 2002; Hong et al. 2010; Chen et al. 2015). They also act like transporter in animal cells (Liu et al. 2008), tumor cells (Kam et al. 2005), bacteria (Liu et al. 2009b), and plant cells (Khodakovskaya et al. 2011), which facilitates a new entry in the field of gene delivery (Chen et al. 2015). Moreover, they are also being used in agricultural fields to increase germination and promote root and shoot growth and biomass (Lin et al. 2009a, b; Liu et al. 2009a; Villagarcia et al. 2012; Khodakovskaya et al. 2013; Chen et al. 2015). In contrast, this is the era in which nanotechnology is still at its early stage in terms of development, even though they can significantly cause toxicity in plants, human health, as well as environment (Pidgeon et al. 2009). Stampoulis et al. (2009) and Khodakovskaya et al. (2011) reported that carbon nanotubes cause phytotoxicity by altering the expression of various genes. However for sampling of living biological cell, in vivo solid-phase microextraction techniques are also established (Ouyang et al. 2011; Lord et al. 2011; Chen et al. 2015). This technique is helpful because of its morphological structure, i.e., invasiveness in living organisms and smaller size, and provides the highly precise and more accurate data in very less time (Ouyang et al. 2011; Chen et al. 2015). Beside this, Lee et al. (2015) also demonstrated the application of carbon nanotubes in nanoelectronics, energy devices, and biosensors.

16.3.1 Uptake and Transportation of Carbon Nanotubes in Plants

There is a unique characteristic of plants that it contains cell wall which is a multilayered structure; that's why plant growth occurs in a fixed shape and possesses rigidity

(Serag et al. 2015). Cell wall of plants is surrounded by highly dense fibers of cellulose in which sugar polymers or glycans are embedded. This cell wall also acts as barrier for macromolecules, bacteria, and other parasites (McNeil et al. 1984; Serag et al. 2015). Crossing the barrier of cell wall of plants has now turned toward the beneficial impacts for various fields of biotechnology by applying genetic manipulation in it (Evans 1983; Serag et al. 2015). Pores of the cell wall are very narrow having a diameter of 5 nm that facilitates only the transport of selected macromolecules and allows to cross the barrier of solute materials (Meiners et al. 1991). Husen and Siddiqi (2014) also propounded that in water-suspended nanoparticles, plants either selectively absorb these nanoparticles or reject it. Carbon nanomaterials may be absorbed by the roots, but in seeds they create a hole for entry and then translocate in the shoots. After the entrance of carbon nanotubes in the plant organelles, they were shown to affect the growth and germination of plants (Khodakovskaya et al. 2012).

To overcome this problem, various enzymatic digestions were used to make it fragile so that it can be easily damaged by using any chemical and physical methods. However, there must be one precaution to look upon; osmolarity should be maintained for survival of cell or to prevent the cellular burst (Serag et al. 2015). There are several strategies that facilitate any substance or carbon nanotube to penetrate in the cell wall and plasma membranes. They are dependent on the ratio of size of carbon nanotubes to the pore size of the cell wall (Serag et al. 2015). The reported size of single-walled carbon nanotube is 1–2 nm, i.e., less than the pore size of the cell wall which is 5 nm. Thus, they are continuously leaked into the apoplastic region. Moreover, for shorter sized single-walled carbon nanotube, chemical methods like ultrasonic-assisted chemical oxidative cutting are used, and simultaneously carboxylic group is also used to introduce at the tip which increases their solubility in water (Nakayama-Ratchford et al. 2007; Serag et al. 2015). Now, the next barrier that occurs in the cell after removal of cell wall is the generation of protoplast. It was reported that the penetration of multiwalled carbon nanotubes occurs in the protoplast of *Catharanthus roseus* via nanoneedles (Pantarotto et al. 2004; Lacerda et al. 2012; Serag et al. 2015). The carbon nanotubes with large diameters have been reported to introduce in the cellulosic cell wall via hydrolysis. The cellulosic contents immobilized at the wall or tip of cup-stacked carbon nanotubes which resulted in local lesions from which carbon nanotubes could penetrate easily.

16.3.2 Cellular Uptake of Single-Walled Carbon Nanotubes

Serag et al. (2010, 2013) reported that due to the small size of single-walled carbon nanotubes, they were shown to easily penetrate in the cell wall pores of *Catharanthus roseus* and *Nicotiana tabacum*. In 2009, the first demonstration was shown about the uptake of single-walled carbon nanotubes in *Nicotiana tabacum* (Liu et al. 2009a). However, single-walled carbon nanotubes in *N. tabacum* showed temperature-dependent internalization through endocytosis. “Wortmannin” was reported as a second factor which inhibits the internalization or uptake of single-walled carbon nanotubes in plant cell. Wortmannin is a steroid metabolite that is

extracted from the fungi named as *Penicillium funiculosum*, *Talaromyces wortmannii*, which prevents endocytosis-mediated internalization of single-walled carbon nanotubes (Serag et al. 2015). Serag et al. (2015) reported that *N. tabacum* cells used molecular cargoes as a cotransporter for transport of single-walled carbon nanotubes in different cellular compartments. Further, it is also reported that free form or conjugated form of fluorescein isothiocyanate (FITC) with single-stranded DNA was used for uptake of single-walled carbon nanotubes in the cells of *N. tabacum.* Moreover, Liu et al. (2009a) demonstrated that single-walled carbon nanotubes linked with free fluorescein isothiocyanate were internalized in vacuoles, while those FITC wrapped with single-stranded DNA were internalized in cytoplasm. Furthermore, it is evidenced that the free anionic form of fluorescein isothiocyanate after internalization in cytoplasm was translocated to vacuoles of cells through protein carriers (Oparka 1991). However, this process of translocation was seen to be inhibited by the probenecid (uricosuric drug) leading to the aggregation of fluorescein isothiocyanate in cytoplasm. The accumulation of FITC in the cytoplasmic region facilitates the entry of single-walled carbon nanotubes in the nucleus of *Catharanthus roseus* demonstrated by FRAP (fluorescence recovery after photobleaching) techniques, thereby inducing the autophagy in cells of *Catharanthus roseus* (Serag et al. 2015). With the help of raster scan image correlation spectroscopy (RICS), the location of SWCNTs was quantitatively determined in various compartments of *Catharanthus roseus* cells, and it was predicted that the diffusion coefficients of FITC linked with single-walled carbon nanotubes in vacuoles to cytoplasm were almost similar. This study revealed that autophagy leaks out the vacuolar cytoplasm. Autophagy is the process of self-eating of cells, which arises as a result of stress in the eukaryotic organisms and causes severe damage to different organelles of cells (Minibayeva et al. 2012; Serag et al. 2013, 2015).

The plants possess the property to reduce the phytotoxicity by inhibiting the accumulation of single-walled carbon nanotubes. Analysis through laser scanning confocal microscopy showed that plants distribute these nanotubes in different regions of vacuoles so that they expel it toward plasma membrane by vesicle-mediated transport pathway. Therefore, the vesicles containing single-walled carbon nanotubes were fused with plasma membrane and expelled outside the cell (Serag et al. 2010).

16.3.3 Cellular Uptake of Multiwalled Carbon Nanotubes

It is reported that in protoplast of *Catharanthus roseus*, multiwalled carbon nanotubes were physically penetrated via non-endosomal pathways. After injecting multiwalled carbon nanotubes via nanoneedles, images of TEM (transmission electron microscopy) showed its subcellular location in the membrane. Further studies from electron microscopy revealed that the internalization process via endosomal organelles is poorly linked with the multiwalled carbon nanotubes. However, this process is energy independent and proceeds via declining the rate of normal endocytosis process by inclining the concentration of multiwalled carbon nanotubes in the cell.

This process creates tonicity in the cell due to increased level of multiwalled carbon nanotubes in the cell medium. This led to the hindrance in the direct uptake of multiwalled carbon nanotubes in cells (Serag et al. 2010). However, direct internalization of multiwalled carbon nanotubes led to its translocation in various organelles such as nucleus, vacuoles, and plastids. These are the primary sites of multiwalled carbon nanotube accumulation. After its direct uptake, they start accumulating in perinuclear region of nucleus. Moreover, size-dependent localization of multiwalled carbon nanotubes occurs in cells of *Catharanthus roseus*; for instance, the multiwalled carbon nanotubes ranging from 30 to 100 nm were shown to be localized in vacuole, plastid, and nucleus region, while bigger than 100 nm tubes localized most of the organelles. Short multiwalled tubes (30–100 nm) resist to accumulate in the mitochondria and endoplasmic reticulum.

16.3.4 Beneficial Impact of Carbon Nanotubes in Plants

Development in the field of agricultural sectors is very necessary because most of the living beings depend on it. So, many researchers emphasized to work out in the field of nanotechnology-based enhancement of agricultural fields. They are trying to enhance the agricultural outputs, detection of diseases, and their remediation processes. In addition to this, they are also trying to increase the efficiency of plant to uptake more nutrients from soil (Table 16.1). This will ultimately lead to enhancement in overall increase of biomass and fruit of the plants (Fig. 16.2) (Serag et al. 2015).

Morla et al. (2011) reported to enhance the percentage of seed germination and seedling growth from multiwalled carbon nanotubes at 40 μg/ml concentration in *Lycopersicum esculentum.* Similarly, in *Medicago sativa* and *Triticum aestivum*, 10 nm multiwalled carbon nanotubes of 75% weight enhanced the seedling growth and elongated roots (Miralles et al. 2012). Moreover, Lahiani et al. (2013) observed enhanced rate of growth and germination in *Hordeum vulgare*, *Zea mays*, and *Glycine max*, from 25–100 μg/mL concentrations of multiwalled carbon nanotubes. Furthermore, in *Nicotiana tabacum*, 5 nm multiwalled carbon nanotubes at concentrations of 5–500 μg/mL led to the increased flowering and fruiting (Khodakovskaya et al. 2012). Beside this, Wang et al. (2012a) also observed increased cell growth and biomass from 50 to 630 nm O-MWCNTs in *Triticum aestivum.* Similarly, Tiwari et al. (2013) also demonstrated the effect of 6–9 nm multiwalled carbon nanotubes on *Lycopersicon esculentum.* They found that at a concentration of 40 μg/mL, absorption of nutrient elements was increased that ultimately led to enhanced growth and biomass of the plant. Tiwari et al. (2014) propounded the effect of 6–9 nm pristine multiwalled carbon nanotubes on transcription and morphology which includes enhanced uptake of water and essential nutrients leading to increase in biomass of the *Zea mays* plant. Likewise, in *Brassica juncea* and *Phaseolus mungo* plants, 20 μg/mL multiwalled carbon nanotubes increased the growth of roots (Ghodake et al. 2010). Furthermore, Mondal et al. (2011) also demonstrated the morphologically increased characters in *Brassica juncea.* They reported that 2.3×10^{-3} mg/mL

concentration of 30 nm multiwalled carbon nanotubes in *Brassica juncea* showed enhanced length of roots (Table 16.1). However, Flores et al. (2014) found that single-walled carbon nanotubes also show beneficial effect on plant like *Rubus adenotrichos.* They found that at concentrations of 4 μg/ml, 1–2 nm, and 3.5–4 nm, carboxylic acid functionalized single-walled carbon nanotubes (SWCNTs-COOH); SWCNTs-Fe led to increased length of roots and shoots. In addition, improved cell metabolism was also observed. Furthermore, from 8–15 nm, SWCNTs enhanced rate of germination of plants *Lycopersicum esculentum* and *Allium cepa* (Haghighi and da Silva 2014). Additionally, Cañas et al. (2008) also observed that single-walled carbon nanotubes at concentrations of 9, 56, 315, and 1750 mg/L were shown to enhance the root elongation in *Allium cepa* and *Cucumis sativus*.

16.4 Inimical or No Significant Impact of Carbon Nanotubes in Plants

It is already discussed that the negative and positive impact of nanoparticles depends on several factors like size, concentration, ultrasonication, etc. (Ma et al. 2010). In the above section, at specific concentration(s) of carbon nanotube, some beneficial role in plants in terms of their morphology, physiology, or others was shown, while in this section, it is shown that some nanoparticles at different concentrations may cause phytotoxicity (Table 16.2).

For instance, Haghighi and da Silva (2014) demonstrated that 8–15 nm single-walled carbon nanotube at concentration of 10–40 mg/L in *Raphanus sativus* and *Brassica rapa* led to phytotoxicity by decreasing the rate of germination (Fig. 16.2). Tan et al. (2009) demonstrated that multiwalled carbon nanotubes at concentrations of 20 and 40 mg/L in *Oryza sativa* caused chromatin condensation, detachment of cell membrane from cell wall, and generation of reactive oxygen species and ultimately cause death of the cell (Table 16.2). Similarly, Begum and Fugetsu (2012) also reported that in *Amaranthus tricolor*, multiwalled carbon nanotube at concentrations of 500 and 1000 mg/L led to removal of red pigment from leaf, necrosis, curling, and wilting. In addition, they were shown to cause concentration-dependent reduction in root-shoot height, root-shoot weight, and leaf numbers which lastly causes death of the plant. It has also been demonstrated that in the plants of *Oryza sativa* and *Arabidopsis*, single-walled carbon nanotubes led to phytotoxicity by inducing cell aggregation, deposition of cell membrane, condensation of chromatins, and accumulation of H_2O_2 which ultimately causes death of the cell (Serag et al. 2015). Moreover, Shen et al. (2010) observed that 25% of death of cultured protoplasts occurs within 6 h after treatment with 25 mg/mL of single-walled carbon nanotubes. This occurs due to accumulation of ROS and finally led to the death (Shen et al. 2010; Serag et al. 2015). Similarly, hydroponic treatment of pristine multiwalled carbon nanotubes is observed to cause reduction in biomass of *Cucurbita pepo* (Serag et al. 2015). Lin and Xing (2007) and Begum et al. (2012) reported the phytotoxicity from carbon nanotubes in various plants. Begum et al. (2012) also demonstrated the reduction in root length and root fresh weight of

Cucumis sativus and *Oryza sativa* from multiwalled carbon nanotubes. It is also found that in *Cucumis sativus*, the length of roots declined in concentration-dependent manner. Furthermore, in *Hordeum vulgare* and ryegrass at 2000 mg/L multiwalled carbon nanotubes, the rate of germination decreased (Lin and Xing 2007). Chen et al. (2015) observed some black spots under light microscope and predicted its nanotoxicity by creating hindrance in transport of nutrients and also plant growth and development (Table 16.2). Cañas et al. (2008) reported the phytotoxicity of functionalized carbon nanotubes in lettuce at concentrations of 104, 315, and 1750 mg/L by decreasing the length of shoots, while functionalized single-walled carbon nanotubes at concentrations of 9, 56, 315, and 1750 mg/L showed no significant impact on phytotoxicity. Similarly, Yan et al. (2013) also observed no impact of single-walled carbon nanotubes at 20 mg/L concentrations in *Zea mays* seedlings. However, Stampoulis et al. (2009) reported that 13–16 nm multiwalled carbon nanotubes in *Zucchini* seedlings at concentration of 1000 mg/L showed reduced biomass but their seed germination remained unaffected.

16.5 Conclusion and Future Prospects

This review article discussed about carbon nanotubes, their major types and its applications in biological as well as nonbiological fields. Also, single-walled carbon nanotubes work differently from multiwalled carbon nanotubes. Although majorly positive functions of carbon nanotubes were reported in most of the studies, few carbon nanotubes at specific concentrations possess inimical or no significant impact on plant cell and their structures, because it is the characteristic of a nanoparticles that they may be toxic or beneficial depending on their concentration, size, shape, ultrasonication, etc. since each type of carbon nanotube (like oxidized multiwalled carbon nanotubes, functionalized single-walled carbon nanotubes, single-walled carbon nanotubes, multiwalled carbon nanotubes, water-soluble multiwalled carbon nanotubes, etc.) shows unique characteristic and properties and different functions on various plants at different concentrations and sizes. On seeing their highly advantageous role in plants, it can be predicted whether it can be supplemented to the plants as fertilizer or pesticide or expose their beneficial concentration on large scale in agriculture. Another method of utilizing it as a beneficial entity in agriculture is by using the biotechnological methods like gene delivery or manipulation because it is reported that carbon nanotubes can also pass from one generation to another (Tan et al. 2009). So, if they prove to be beneficial in first generation, they will exhibit positive role in second generation as well. It may enhance the quality and quantity of crops drastically, because many of the carbon nanotubes at specific concentrations change the morphology, the physiology, and even the genetic constitutions of the plant, ultimately, leading to increase in the biomass. So, it can be helpful in enhancing the biomass of agricultural fields at global scale.

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