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Contrasting effects of engineered carbon nanotubes on plants: a review

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Abstract Rapid surge of interest for carbon nanotube (CNT) in the last decade has made it an imperative member of nanomaterial family. Because of the distinctive physicochemical properties, CNTs are widely used in a number of scientific applications including plant sciences. This review mainly describes the role of CNT in plant sciences. Contradictory effects of CNT on plants physiology are reported. CNT can act as plant growth inducer causing enhanced plant dry biomass and root/shoot lengths. At the same time, CNT can cause negative effects on plants by forming reactive oxygen species in plant tissues, consequently leading to cell death. Enhanced seed germination with CNT is related to the water uptake process. CNT can be positioned as micro-tubes inside the plant body to enhance the water uptake efficiency. Due to its ability to act as a slow-release fertilizer and plant growth promoter, CNT is transpiring as a novel nano-carbon fertilizer in the field of agricultural sciences. On the other hand, accumulation of CNT in soil can cause deleterious effects on soil microbial diversity, composition and population. It can further modify the balance between plant-toxic metals in soil, thereby enhancing the translocation of heavy metal (loids) into the plant system. The research gaps that need careful attention have been identified in this review.

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Introduction

Since the discovery of Buckminsterfullerene, research about carbon nanomaterials has intensively increased in the last few decades. The discovery of carbon nanotubes (CNTs) opened up a new era in materials science. CNTs are allotropes of carbon with a cylindrical nanostructure. They are arranged by carbon atoms extracted from hydrocarbon or graphite. CNTs can be 100 times stronger than steel, but only one-sixth as heavy, hence capable of strengthening any material. They are also better conductors of heat and electricity than copper (Camargo et al. 2009). There are mainly two types of CNTs, single-walled (SWCNT) and multi-walled (MWCNT). Structurally, the SWCNT is the rolled-up sheet of a graphene or graphite with several µm in length and about 1 nm in diameter. The carbon atoms in SWCNT are arranged in hexagonal and pentagonal patterns. On the other hand, MWCNT is comprised of concentrically multiple rolled-up sheets of graphene having various diameters. Because of their unique characteristics, CNTs have great potential for enhancing technology in many applications not only in material research but also in environmental sciences (De Volder et al. 2013). The involvement of CNTs in various cellular processes in plants is illustrated in Fig. 1. For example, recent attention has been focused on the application of CNT as a component of slow-release fertilizer for growing plants (Wu 2013). It was estimated that the flux of CNTs into the environment could be 0.01 µg/kg/year in a realistic scenario, whereas it could be as high as 0.02 µg/kg/year in a high exposure scenario (Servin et al. 2015; Mueller and Nowack 2008). With the development and application of CNTs, the potential hazards to biological and the environmental systems are getting more attention (Du et al. 2013).

We used SCOPUS research database to determine the number of publications related to CNTs. The SCOPUS research database showed that most of the initial work was published on the synthesis and characterization of CNTs during early 1990s. Later on, the studies on CNTs became one of the most attractive areas of innovative applied research.

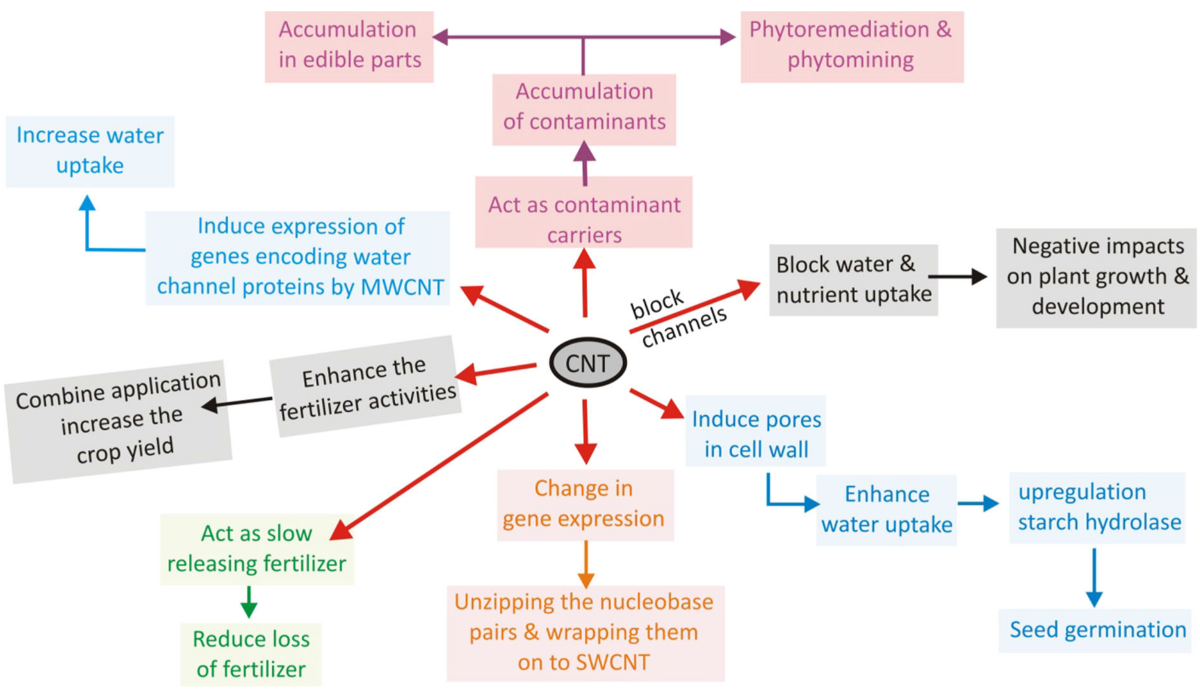

Fig. 1 The involvement of CNTs in various cellular processes in plants

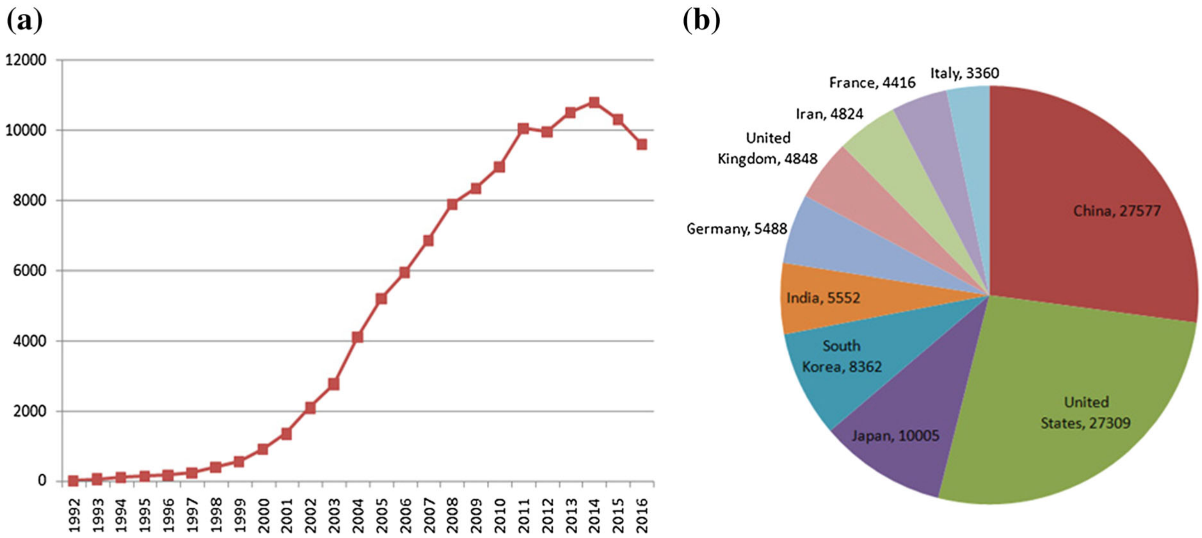

Fig. 2 **a** Publications with the keywords "carbon nanotubes" in the SCOPUS data base; and **b** Top 10 countries in the world publishing research on CNT

According to SCOPUS database, a large number of studies have been published each year with an increasing trend (Fig. 2a). In the year 2014, the maximum of 10,791 studies were published. China is leading in research publications associated with CNTs, recording over 25,000 publications to date (Fig. 2b). Altogether, over 100 thousand publications have been recorded with keyword of "carbon nanotubes" on the SCOPUS website. Of all the studies, over 15,000 are patented. Among institutions, the Tsinghua University in China holds the highest number of publications (2032) related to CNTs. To date, the top 5 countries based on number of research publications on CNTs are China, USA, Japan, South Korea and India. Considering the subject category, material science has gained the maximum attraction in CNTs research followed by physics, engineering and chemistry. However, compared to physical sciences, a limited attention has been given to CNTs in the field of biological sciences, specifically in plant sciences. Combining keywords of "nanotubes + plant" resulted only in about 787 publications; the number was further reduced to 119 when searched with the keywords of "carbon nanotubes + plant growth".

In this review, we focused on the role of CNTs in various aspects of plant sciences, such as plant growth, CNTs' potential application as slow-release fertilizer and its plausible impact on soil microorganisms. Only a few scientific studies relevant for risk assessment of CNTs have been published in recent years hence, gaps still exist on the environmental hazard identification and effects/exposure assessment of CNTs. We also discussed the advantages and limitations of using CNTs in plant sciences, and synthesized several knowledge gaps which need future research attention.

Fate of CNTs in the environment

Various types of CNTs can be obtained depending on the orientation of the tube axis relative to the carbon network. CNTs may differ in number of carbon layers on their sidewalls. Consequently, SWCNTs and MWCNTs were mainly produced commercially (Schnorr and Swager 2011). Other CNT related special structures include torus (donut shaped), nanobud (fullerene combined with CNT), graphenated CNT (graphitic foliates along the side wall of MWCNT), peapod (fullerene trapped inside CNT) and cup-stacked CNT (stacked microstructure of graphene layers) (Ren et al. 2013). Additionally, different types of functional groups can be introduced at the tips and around the sidewalls for modification of CNTs (Bianco et al. 2005; Trojanowicz 2006). For instance, CNTs could be functionalized with –OH, –COOH and –C = O groups through chemical oxidation approaches. CNTs can gain unique atomic arrangements as well as unique properties including large current carrying capacity, high thermal conductivity, long ballistic transport length, high tensile strength and capability to interact with different organic and inorganic analytes (Baughman et al. 2002; Chu et al. 2010). In recent years, the extraordinary properties of CNTs resulted in numerous applications in the area of micro- and nano-electronics, optics, separation science, medicine and mechanical fields (Chang et al. 2010; Bianco et al. 2005; Huang et al. 2010; Trojanowicz 2006; Liu and Lal 2015; De Volder et al. 2013; Schnorr and Swager 2011).

The application of CNT to plant science/agriculture is a very recent development (Mukherjee et al. 2016a; Zaytseva and Neumann 2016). It was observed that CNT in low doses was capable of stimulating physiological processes including seed germination, root elongation and plant growth in numerous plant species (Khodakovskaya et al. 2009; Cañas et al. 2008; Miralles et al. 2012b). Tiwari et al. (2014) reported an enhanced growth of maize seedlings in the presence of low concentration of CNT in soil. Moreover, CNTs were reported to penetrate into the plant cell wall and membranes (Lin et al. 2009; Mohammad et al. 2011), which might help to invent new smart-delivery systems in plants. For example, CNTs were able to deliver DNA into the plant cell via a bombardment method (Khodakovskaya et al. 2009). Taking this into account, CNT could be used to deliver herbicides to plants allowing slow and consistent release of the active ingredients. Contrasting reports also exist that despite tolerating a high concentration of MWCNTs (2560 mg/L) during germination, crop plants such as alfalfa and wheat could rarely take the nanotubes up into their body (Miralles et al. 2012b). However, CNTs could be adsorbed onto the plant root surfaces (Miralles et al. 2012a). At the same time, the recent interest is on nanofertilizers to enhance crop growth and production (Liu and Lal 2015; Yatim et al. 2015). Some of these applications are being realized in products today.

Uptake of CNTs in plants

The plant cell wall, which is a network of cellulose fibrils, can act as a protective barrier for foreign substances. The nanoparticles or nanoparticle aggregates which have a smaller diameter than the pore diameter of the cell wall are able to pass through the apoplast pathway (O'Neill and York 2003; Nair et al. 2010). Nanoparticles are able to enlarge the remaining pores and also possess the ability to induce new cell wall pores, which may enhance the uptake of nanoparticles. By endocytosis, and through carrier proteins or ion channels, the nanoparticles can enter into the cytoplasm (Jia et al. 2005). Fullerene C_{70} was reported to be taken up by roots and transported to shoots in rice plants (Lin et al. 2009). It was suggested that the translocation of C_{70} took place along with the uptake of water and nutrients. Further, it was demonstrated that C_{70} could be transported downward from leaves to roots through phloem when C_{70} entered into plants through plant leaves. However, due to the relatively larger size of MWCNT than fullerene, the penetration of CNT into the cells might be restricted. Plentiful fullerene in the form of black aggregates was reported in the seeds and roots compared to the leaves and stems of rice plants (De La Torre-Roche et al. 2013; Qiaoling Liu et al. 2013; Santos et al. 2013). A more robust translocation from the roots to the aerial parts of the plant was observed in the mature plants demonstrating the presence of fullerene aggregates in or near the stem vascular systems and leaves, not in the roots (Santos et al. 2013). Generally, fullerene follows the transmission route of nutrients and water through xylem (De La Torre-Roche et al. 2012), while it enters into the root cell walls through osmotic pressure, capillary forces, and pores by the intercellular plasmodesmata, or by means of the greatly regulated symplastic routes (Liu et al. 2010).

It was observed that MWCNT was able to pierce through the root cap cell walls in wheat plants, thereby enhancing the transport of environmental toxic chemicals into the living cells (Wild and Jones 2009). However, Miralles et al. (2012b) reported that alfalfa and wheat plants could only adsorb MWCNT on their root surfaces without significant uptake or translocation. Similar adsorption of MWCNT on rice root surface was reported by Lin et al. (2009). It was observed that about 9.8% of the initial MWCNT amount applied into the soil was translocated to the shoots in the 3 mg/kg treatment (Gogos et al. 2016). Conversely, in the higher application rate (2933 mg/kg), only 0.015% of the initial MWCNT amount was translocated to shoots, thus demonstrating the independent uptake from the applied concentration (Gogos et al. 2016). At the same time, within the MWCNT treatments, a significant reduction of flowering occurred, which was not concentration dependent (Gogos et al. 2016; Moll et al. 2016). Another study showed an uptake of SWCNTs from roots, and the nanoparticles in the stem and leaves of corn plant were observed at a minimal SWCNT concentration under drought and normal conditions, revealing independency of CNTs on their concentration, but dependant on volume and composition of soil (Cano et al. 2016).

The ability of carbon nanomaterials to penetrate the cell wall and cell membrane was reported in *Nicotiana tobacum* (Liu et al. 2009). There, the fluorescein isothiocyanate (FITC) alone was not taken up by the cells, but SWCNT-FITC was translocated effectively into the intact cells by fluid phase endocytosis. Moreover, the uptake of SWCNT-FITC was found to be time- and temperature-dependent (Liu et al. 2009). Similarly, the transport of C_{70} nanoparticles was possible in the xylem of rice plants (Lin et al. 2009). More interestingly, the C_{70} nanoparticles were transmitted even to the second generation of the rice plants, which might consequently alter plant gene expressions and related functions (Lin et al. 2009). In a molecular dynamic simulation study, it was observed that SWCNT could significantly change the conformation of rice DNA through unzipping the Watson–Crick nucleobase pairs and wrapping them onto SWCNT with time (Katti et al. 2015). Further, MWCNT entered the cells in adult broccoli plants with high accumulation under saline conditions (Martínez-Ballesta et al. 2016).

Since the plant cell wall is an effective barrier for foreign materials, plant protoplasts was previously used to study the internalization of nanomaterials. It was shown that SWCNTs were able to penetrate through various subcellular membranes of the plant cell (Serag et al. 2011).The SWCNTs were possibly passing through both the cell wall and cell membrane of tobacco and *Catharanthus* (Liu et al. 2009; Serag et al. 2011). High-resolution transmission electron microscopy (HRTEM) studies revealed that longer MWCNTs (larger than 200 nm) were accumulated in the subcellular organelles, while the shorter tubes (30–100 nm) accumulated in the vacuoles, nuclei and plastids (Serag et al. 2010, 2013). However, the viability of protoplasts and their cell division ability were strongly reduced by the applied chemicals to disorder the cell wall. Hence, a new strategy was introduced by Serag et al. (2011) to deliver cup-stacked carbon nanotubes (CSCNT) into the plant cell walls by immobilizing cellulase on their tips and walls. The immobilized cellulose was used to induce local lesions in the cell wall through which CNT could transport into the interior of the cell. This might untie a path for material transport in cell biology and plant genetic studies. CNTs can also transport through the plant body by capillary action via places where the channels are wider than their size. As they reach a narrow point, CNTs accumulate and block the passage for nutrients and other materials in the plant body. However, the ability of CNT to translocate with the plant body is still inconclusive and seems to be highly dependent on plant species (Servin et al. 2015). As a major advancement in this field, Chen et al. (2015) very recently provided an impressive evidence that MWCNTs could penetrate into the roots of mature mustard plants and then translocate into the other parts of roots and anatomical leaves. Interestingly, a study on fullerol nanoparticles resulted an increase up to 54% in biomass yield, 24% in water content, 20% in fruit length, 59% in fruit number, and 70% in fruit weight leading to an improvement up to 128% in fruit yield of bitter melon (Kole et al. 2013).

Since CNTs are potential materials for the removal of wide range of organic compounds due to the high sorption affinity, they may strongly affect bioaccumulation and translocation of pollutants in plants. However, relevant studies on plants are rather limited. De La Torre-Roche et al. (2013) reported that soil amended with MWCNT resulted in 21–80% reduction in bioaccumulation of chlordane ($C_{10}H_6C_{18}$) as well as p,p′-DDT and its metabolites p,p′-DDE and p,p′-DDD in four crop species. Although a significant uptake of MWCNT by zucchini, soybean and tomato roots was observed with increased root DDE content in plant species, no CNT was detected in shoots and the effect on shoot DDE content varied in the plant species (De La Torre-Roche et al. 2013).

Simultaneously, it was demonstrated that MWCNTs can act as contaminant carriers, influencing the accumulation of contaminants in crops (Chen et al. 2015). Although it is widely believed that CNTs in low doses are not harmful to plants (Khodakovskaya et al. 2012, 2013a, b), a study proved that MWCNTs in low doses could enhance contaminant accumulation in crops (Chen et al. 2015). Additionally, the MWCNT-adsorbed compounds could be released inside the plant, which may provide a route to effectively deliver drugs or genetic materials to specific sites of intact plants (Chen et al. 2015). At the same time, light microscopy indicated that the MWCNTs aggregated within the roots, which might cause negative effects such as potential nanotoxicity, inhibition of nutrient transport, and plant growth retardation (Chen et al. 2015). Therefore, for human safety and health, detail investigation on nanoagriculture is needed. Due to the toxic effects seen on *Lemnagibba* by decreasing chlorophylls *a* and *b* and chloroplast oxygen production, C_{60} is viewed as an environmental pollutant, potentially endangering the equilibrium of aquatic ecosystems (Santos et al. 2013).

Effect of CNT on plant growth

The CNTs are involved in both the vegetative growth (Khodakovskaya et al. 2012; Cañas et al. 2008) and reproductive induction in plants (Khodakovskaya et al. 2013a, b; Mondal et al. 2011). For example, Khodakovskaya et al. (2013b) reported that CNT applied to tomato plants during watering produced two-times more fruits per plant compared to the control plants. It indicated that the delivery of CNT activated the reproductive system of the plants and increased the production of fruits (Khodakovskaya et al. 2013a, b). This finding opens a new path on technological applications of CNT as growth regulators in plants. Similarly, MWCNT has been shown to improve the germination and growth of broccoli under salt stress, extending the applicability of the emerging nanobiotechnology field to crop science (Martínez-Ballesta et al. 2016). Concurrently, a research has demonstrated a positive effect of MWCNT on plant growth, while it induced changes in the lipid composition, rigidity and permeability of the root plasma membranes compared to the other plants under salinity stress (Martínez-Ballesta et al. 2016).

Rao and Srivastava (2014) reported an increase in shoot and root lengths and the plant biomass of wheat (*Triticum aestivum*), maize (*Zea mays*), peanut (*Arachishy pogaea*) and garlic bulb (*Allium sativum*) with the application of CNT (Table 1). In general, CNTs are considered as plant growth promoters (Mastronardi et al. 2015). They are known to stimulate growth of many plants, but their exact physiological functions, which may be dependent on the genetic trait of a particular plant species, are still largely unknown (Monreal et al. 2016; Miralles et al. 2012a). The growth stimulation of gram plants (*Cicer arietinum*) by different carbon nanostructures including SWCNTs, open-ended MWCNTs, close-ended MWCNTs and carbon nanowhiskers was found to be dependent on the materials' morphology where the best performance was recorded from SWCNTs (1D hollow nanostructures with the smallest diameters) (Tripathi et al. 2016). The difference of growth rates suggested a hypothesis that although C-dots and SWCNT can adapt the symplastic pathway to reach the root's interior, all the nanostructures are expected to prefer the apoplastic route and consequently widen the cell membrane pores due to their high potential gradient (Tripathi et al. 2016).

The difference between effects of functionalized and non-functionalized CNTs on plant growth was assessed in a study by Cañas et al. (2008). The authors observed an enhancement in root elongation of vegetable crops, and formation of nanotube sheets on cucumber root surfaces by both functionalized and non-functionalized CNTs; however, CNTs did not penetrate into the roots. It was further revealed that non-functionalized CNTs were generally more effective in increasing the root length than the functionalized CNTs. However, the influence was specifically different depending on plant type. In fact, non-functionalized CNTs inhibited root elongation in tomato and enhanced root elongation in onion and cucumber, whereas functionalized CNTs inhibited root elongation in lettuce. Cabbage and carrots were not affected by either form of the nanotubes (Cañas et al. 2008). The relationship between MWCNT and the tobacco cell growth was assessed by Khodakovskaya et al. (2012). With the addition of MWCNT, both the fresh and dry weights of the tobacco calluses increased. It indicated that the increase in cell growth with MWCNT was mainly associated with the activation of cell division. It showed a 55–64% increase of weight over the control in a wide range of CNT concentrations (5–500 µg/mL). Further, Raman spectroscopy and TEM (transmission electron microscopy) studies indicated that the interaction between CNT and tobacco cells, and the uptake of MWCNT into the tobacco plant could have the ability to induce significant responses at cellular and genetic levels (Khodakovskaya et al. 2012).

Exposure time of CNTs treatment can positively affect plant growth. Cheng et al. (2014) studied the

Table 1 Effects of CNT on plant growth

Plant	Type of CNT		Growth performances		Growth parameters			References
	SWCNT	MWCNT	Increase growth	Decrease growth	Root/shoot length	Plant dry biomass	Flowering/fruiting	
Tomato			√	–	√	√	√	Khodakovskaya et al. (2012)
Wheat, maize, peanut, garlic			√	–	–	√	–	Rao and Srivastava (2014)
Cabbage, carrot, cucumber, lettuce, onion, tomato	√	–	√	–	√	–	–	Cañas et al. (2008)
Tobacco	√	–	√	–	–	√	–	Khodakovskaya et al. (2012)
Lettuce	–	–	√	–	–	√	–	Cheng et al. (2014)
Cabbage, tomato, red spinach	–	–	–	√	–	√	–	Begum et al. (2011)
Rice	–	√	–	√	–	–	–	Tan et al. (2009)
Mustard	–	√	√	–	√	–	–	Mondal et al. (2011)
Red spinach, lettuce, rice, cucumber, chili, lady's finger, soybean	–	√	–	√	√	–	–	Begum et al. (2014)
Alfalfa, wheat	–	√	√	–	√	–	–	Miralles et al. (2012b)
Tomato	√	–	√	–	√	√	–	Mohammad et al. (2011)
Indian mustard	–	√	√	–	√	–	–	Ghodake et al. (2010)
Corn, barley, soybean	–	√	√	–	√	–	–	Lahiani et al. (2013)
Zucchini	–	√	–	√	–	√	–	Stampoulis et al. (2009)
Corn	–	√	√	–	–	√	–	De La Torre-Roche et al. (2013)

effect of nanomaterials on lettuce with varied exposure time. Lettuce plants were subjected to different treatment times (0, 2, 8 and 24 h) of nanodevices and their growth and quality were determined. The results indicated that the shoot fresh weight and dry weight in 24-h time interval increased significantly compared to the other treatments (2 and 8 h). Moreover, the number of leaves, flavonoid content, and soluble sugar content were increased significantly in the 24 h treatment.

Conversely, carbon nanomaterials were also reported to act as repressors in plant growth (Begum et al. 2011). Graphene, a two-dimensional crystalline allotrope of carbon, showed negative effects on plant growth. Cabbage, tomato, red spinach, and lettuce treated with a graphene concentration series of 500–2000 mg/L showed a significant inhibition of plant growth and biomass compared to the control (Table 1). At the same time, significant effects were detected with an increase in reactive oxygen species

(ROS), which might reflect necrotic lesions and cell death (Begum et al. 2011). Similarly, when rice seeds were grown with MWCNT, the cells interacted with the nanotubes and formed aggregates. The cell density was decreased with an increase of MWCNT concentration, indicating a self-defensive response. It, thus, suggested that MWCNT could interact directly with rice cells and influenced negatively on rice growth (Tan and Fugetsu 2007).To assess the ROS accumulation in the presence of MWCNT, rice seeds were exposed to MWCNT at a concentration of 20 mg/L. Fluorescent probe 2′,7′-dichlorofluorescin diacetate (DCFH-DA) was used to determine the intracellular ROS content. In the presence of MWCNT, the ROS content was significantly increased in a time-dependent manner. The highest level of ROS was found in the presence of sonicated MWCNT, which was almost 3.5-times higher than in the control (Tan et al. 2009).

In many instances, the CNT would act as a growth inducer at lower concentration, but become toxic as the concentration increases. When cabbage, carrot, cucumber, lettuce, onion, and tomato seeds were exposed to functionalized and non-functionalized SWCNT in the concentration range of 56 to 1750 mg/L, the root elongation was promoted by the lowest concentration of SWCNT, while it was inhibited at the highest dosage. The best results were obtained with non-functionalized SWCNT (Cañas et al. 2008). Single-walled carbon nanohorns (SWCNH) are novel carbonaceous material with unique characteristics. Since these materials are uniform in size, they can be well dispersed in solvents (Yu et al. 2010). The effect of SWCNH on six crop species (barley, corn, rice, soybean, switch grass and tomato) was observed, and tobacco cell culture showed that the growth of tobacco cells was increased by 78% (Miyawaki et al. 2004, 2008). As the crop species were exposed to a range of SWCNH concentration series, they resulted in an enhancement in plant phenotypic characters. However, the optimum concentration of SWCNH was different for each crop. Moreover, according to the phenotypic data, it was recorded that SWCNH did not cause any negative effect on the growth of seedlings of those crop species (Miyawaki et al. 2004, 2008).

The molecular mechanisms behind negative (toxicity) or positive (activation of germination and growth) effect of CNTs on plant growth are still unclear. It could be assumed that the surface properties of CNTs (e.g., functional groups) might critically influence the physiological response of plants (Villagarcia et al. 2012). Also, how well the CNTs are dispersed in the plant growth medium might make a difference in the observed effect because a single nanotube is more prone to penetrate into the plant body than an agglomerated particle. Moreover, different plant species can response differently to CNTs depending on their physiological processes.

Transportation of CNTs was detected with Raman spectroscopy. Biological tissues do not show a peak at 1568 cm, and it was considered as specific to CNTs. And also the TEM images show the presence of CNT in roots incubated with CNT. One mechanism for water uptake facilitation by CNT is creation of pores by penetration through the seed coat. Regulating gates of aquaporins in the coat of plant seeds is an another proposed mechanism (Khodakovskaya et al. 2009).

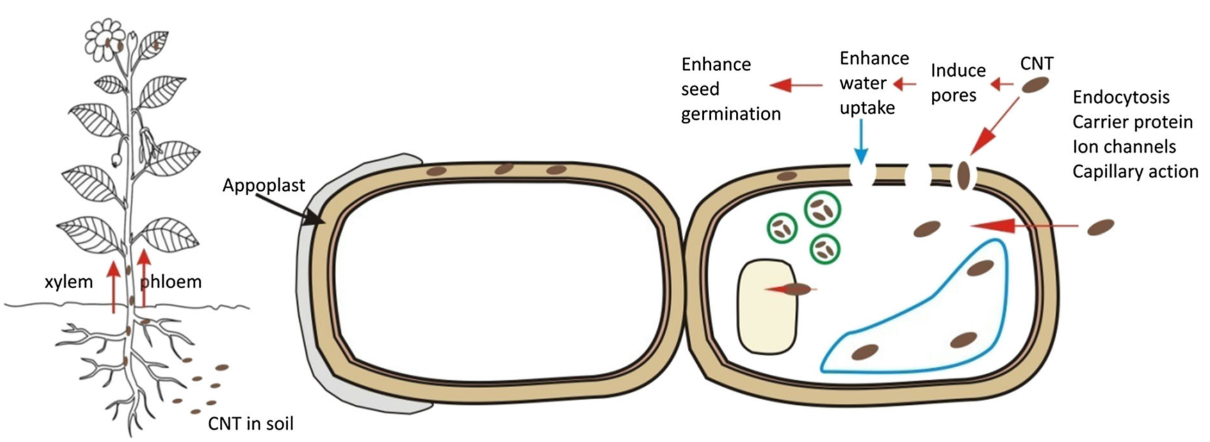

Fig. 3 Transport of CNTs via plant cells

Transport of CNTs via plant cells is illustrated in Fig. 3.

Effects of CNT on seed germination

An increase in the rate of seed germination was observed in the presence of CNT. Application of MWCNT on tomato seeds showed an enhancement in the seed germination (Khodakovskaya et al. 2009). On the 3rd day after the treatment, the seeds were germinated in a range of CNT concentrations (10, 20, 40 µg/mL), showing a positive correlation. Germinated tomato seeds exhibited a dramatic increase in the vegetative biomass too. Fresh weight of the total biomass (leaves, stems, and roots) increased by 2.5-fold in the seedlings germinated with CNT treatment in comparison with the control. The CNT-exposed tomato seedlings had longer stems and were more developed compared to the control seedlings (Khodakovskaya et al. 2009). Inclusion of SWCNTs (50–800 µg/mL) demonstrated a potential for alleviating the drought stress up to moderate levels, induced reduction in germination and growth attributes of *Hyoscya musniger* (Hatami et al. 2017). However, at the same time, high concentrations of SWCNTs (400 and 800 µg/mL) inhibited seed germination and seedling performance, increased the cellular injury indices, and changed antioxidant enzyme activities (Hatami et al. 2017). The improved plant performance was a consequence of changes in the expression of various antioxidants and also biosynthesis of proteins, phenolics, and specific metabolites such as proline (Hatami et al. 2017).

Water is one of the most essential factors for seed germination. The rate of water imbibition depends on the permeability of the seed coat and availability of water. It was found that the CNT-exposed seeds absorbed a higher level of moisture than the seeds without CNT exposure. This observation could be explained by the penetration of CNT through the seed coat by creating more number of pores, thus allowing a greater water uptake into the seeds (Khodakovskaya et al. 2009). Therefore, soaking the seeds in water containing CNT increased the water uptake and enhanced the seed germination. Similarly, Wu et al. (2010) found that the best combination of activation time and soaking time were 70 min and 9 h,

Table 2 Effect of CNT on seed germination

Plant species	Effect on seed germination	References
Tomato	Enhanced germination	Khodakovskaya et al. (2009)
Tomato, onion, reddish, turnip	CNT concentration 10–40 mg L^{-1} improved tomato and onion germination more than for radish and turnip, whereas 40 mg L^{-1} of CNT had a deleterious and toxic effect on onion and radish seed germination	Haghighi and da Silva (2014)
Salvia, pepper, tall fescue	SWCNTs increased seed germination rate compared to the control. The best SWCNT concentrations for seed germination and seedling growth for salvia and tall fescue were at 30 mg/L of SWCNT, and at 10 mg/L for pepper	Pourkhaloee et al. (2011)
Wheat, maize peanut and garlic	A positive influence on root and shoot elongation was observed for all seeds. However, low concentrations of oxidized MWCNTs were more effective	Rao and Srivastava (2014)
Rice	The seed germination and root growth were promoted with concentrations (0–100 µg/mL). However, at 150 µg/mL, the root length, root activity and stem length were decreased compared to 100 µg/mL	Jiang et al. (2014)
Barley, soybean, corn	MWCNTs activated early seed germination at 50, 100 and 200 mg/L applications	Lahiani et al. (2013)
Corn, rice, switchgrass, tomato	Early seed germination of barley (at 100 µg/mL), corn (at all concentrations), rice (at all concentrations), switchgrass (at all concentrations) and tomato (at 25 and 50 µg/mL)	Lahiani et al. (2015)
Rice	Increased rate of germination. Treated seedlings were healthier with intense development in root and shoot systems compared to control seedlings	Nair et al. (2012)
Zucchini	No significant change in seed germination with MWCNT (1000 mg/L) in water, but about 34% reduction when MWCNT was suspended in 2% sodium dodecyl sulfate	Stampoulis et al. (2009)

respectively, for an optimum germination of pepper seeds (Table 2). Even at a drought stress, SWCNT was able to activate defensive mechanisms of the plant via increasing water uptake, upregulation of mechanisms involved in starch hydrolysis, and reduction in oxidative injury indices including H_2O_2, malondialdehyde contents and electrolyte leakage (Hatami et al. 2017).

Several studies demonstrated that CNT could effectively enhance the seed germination when applied in low concentration, but might cause toxic effects at a higher concentration (Haghighi and da Silva 2014; Rao and Srivastava 2014; Pourkhaloee et al. 2011). Therefore, the concentration of CNT requires an optimization to obtain the best germination performance of various crop seeds. When treated with MWCNT, barley, soybean and corn seeds exhibited an early germination, which showed a correlation with the deposition of MWCNT on seed surfaces (Table 2). These depositions were detected by using Raman spectroscopy and TEM. Furthermore, a reverse transcription polymerase chain reaction (RT-PCR) study revealed that MWCNT induced the expression of genes encoding several types of water channel proteins (Lahiani et al. 2013). Decrease in levels of a seed protein, DcHsp17.7, during seed germination, was observed in the presence of MWCNT. Total chlorophyll content in carrot leaf tissue was increased by 25%, and the amount of the reactive oxygen species, H_2O_2, was reduced by MWCNTs at the 500 mg/L of MWCNT at 48 h (Park and Ahn 2016).

Seed coat permeability was examined using tomato (*Solanum lycopersicon*) seeds soaked in combination with carbon-based nanomaterials (CBNM) and ultrasonic irradiation (US) (Ratnikova et al. 2015). The combination enhanced tomato seed germination and seedling growth. It was suggested that CBNM or CBNM with US were able to create channels in the seed coat, which had allowed the small molecules to diffuse into the embryo (Ratnikova et al. 2015). Similarly, the expression of the tomato water channel gene in tomato seeds exposed to helical MWCNTs seemed to be upregulated, at the same time, the germination of exposed tomato seeds, as well as the growth of exposed tomato seedlings, was significantly enhanced by the addition of the morphologically different CNTs; helical MWCNTs, few-layered graphene, long MWCNTs, and short MWCNTs at the presence of 50 μg/mL in the growth medium (Mohamed et al. 2016).

Enhancement of plant water uptake by CNT

Since CNTs are tubular in structure, they are involved in water uptake in plants. Many studies revealed that CNTs could enhance water uptake in plant cells (Camargo et al. 2009). With the increasing number of surface defects, CNT was subjected to carboxylation through the high density electrophilic groups, which helped to enhance the nanotube's water dispersibility (Tripathi et al. 2011). Moreover, HRTEM images clearly showed the damage on the surface of CNT, and such damages were helpful to transport water or other ions. When SWCNT was introduced to gram seeds, it would have entered inside the lumen of tracheal elements and formed capillaries, thus enhanced the water uptake in xylem vessels (Tripathi et al. 2011). It was also recently reported that well-dispersed MWCNT, which were functionalized with stronger negative functional groups, demonstrated a better growth in tomato plants than CNT without functionalization (Villagarcia et al. 2012). The effect was ascribed to the activation of a water channel protein (aquaporin) (e.g., *LeAqp1*) in the experimental plants (Villagarcia et al. 2012; Mohamed et al. 2016). Enhanced aquaporin transduction occurred by the addition of MWCNTs under salinity stress, which improved water uptake and transport, supported to alleviate the negative effects of salt stress (Martínez-Ballesta et al. 2016). Since CNTs were able to extend optimum water uptake in plants, it might play an important role in the field of agricultural research. For instance, in temperate, arid and semi-arid water deficient areas, water loss due to evapotranspiration could be prevented, and consequently water use efficiency could be increased by using CNT-based technologies.

Plant pesticide uptake

CNTs can play an important role in the uptake and bioavailability of pesticide and other organic compounds into the plant body. A study conducted by growing lettuce in MWCNT-amended vermiculite (1000 mg/L) showed that the CNT decreased chlordane and dichlorodiphenyldichloroethylene (p,p′-DDE) uptake in root and shoot by 88 and 78%, respectively (Hamdi et al. 2015). In comparison with that, amino-functionalized MWCNT or the presence of humic acid in the growth media resulted in an increase of pesticide uptake by the lettuce plant (Hamdi et al. 2015). The pesticide uptake behavior in plants could be largely influenced by the type of crop species and CNT concentrations in soils. It was reported that chlordane and dichlorodiphenyl-trichloroethane (DDT) metabolites accumulation in zucchini, corn, tomato and soybean plants were decreased by 21–80% by the amendment of MWCNT in soil (De La Torre-Roche et al. 2013). The effect was highly dose-dependent; as the loading of MWCNT increased, the pesticide uptake in plants decreased (De La Torre-Roche et al. 2013). It was also demonstrated that MWCNT could carry a range of organic contaminants (e.g., organochlorine pesticides, organophosphorus pesticides, pyrethroid insecticides, pharmaceuticals and personal care products) from soil into mustard plants (Chen et al. 2015). By entering into the plant body, some relatively easily degradable compounds could undergo depuration, while highly persistent compounds remained unaffected (Chen et al. 2015). The strong adsorption affinity of the compounds with CNT was responsible for the co-translocation of CNT along with the organic molecules into the plant body (Shrestha et al. 2015; Chen et al. 2015). This feature of CNT-contaminant interaction might be engineered to enhance phytoremediation ability of specific plants grown in contaminated soils, which warrant future research. Alongside, care must be taken for highly persistent contaminant, e.g., DDT, because CNTs might store the harmful chemical in the edible parts of a plant. It is also noteworthy that chemical transformations of CNT under variable environmental conditions might affect their interactions with the contaminant compounds (Wang et al. 2016).

CNT as fertilizer

Nano-carbon fertilizer is a novel application of CNT in agriculture. Nano-carbon can adsorb nitrogen from ammonia and release hydrogen ions, which enhances water and nutrient absorption by plants. Thus, it would enhance the N, P and K uptake into the plant. It was suggested that the combined application of N and nano-carbon could increase the yield and quality of crops (Wu et al. 2010). By its ability to enhance the plant growth and development, CNTs are now being suggested to use as a component of fertilizer for crop production (Liu and Lal 2015). It could act as a slow-release fertilizer, thus reducing the loss of excess nutrients (Wu 2013). Few studies were performed in both laboratory level and field scale to assess the efficiency and significance of CNT in crop yield (Wu 2013). The application of nanometer carbon fertilizer to a rice variety showed an increase in the number of ears, glume flower per year, and the seed weight (yield) (QIAN et al. 2010). Furthermore, it slowed down the fertilizer release rate and reduced the fertilizer outflow. Similarly, the nano-carbon fertilizer resulted in an average yield increase of 9.5% compared to the treatment of 100% fertilizer alone (Liu et al. 2011). Moreover, the addition of nano-carbon with urea increased the dry matter accumulation of soybean, enhanced the relative growth rate in seedling stage and significantly increased soybean yield in a black soil (Li et al. 2015). Fan et al. (2012) investigated the effects of combined application of N fertilizer and nano-carbon on N use efficiency of soil. Authors indicated that with the combined application of nano-carbon, the utilization rate of N fertilizer was increased. Therefore, CNT could be used as nano-carbon fertilizer; however, its application rate in soil should be optimized to avoid possible negative effects on plants growth. The synthesis and surface engineering of CNT also require optimization to use them for slow-release fertilizer production. Appropriate surface functional groups and separation of nanotube bundles/agglomerates into individual tubes were essential to prepare a MWCNT-urea composite slow-release fertilizer (Yatim et al. 2015). Furthermore, selectively functionalized CNT products might impose a lesser level of toxicity to beneficial microorganisms, which are functioning in the natural environment (Sayes et al. 2006; Rodrigues et al. 2013; Kang et al. 2008; Kerfahi et al. 2015).

Effects of CNTs on soil microorganisms

Although recent developments in CNT research have indicated its great application potential in multiple fields, the release of CNT directly into the environment, particularly to soils, might change the microbial communities therein (Dinesh et al. 2012a, b; Mukherjee et al. 2016b). A study by Jin et al. (2014a) showed a significant negative correlation of Gram-positive and

Gram-negative bacteria, and fungal growth with the CNT concentrations in soil, while Tong et al. (2007) recorded only a little impact on the soil microbes (Table 3). Some studies also indicated that CNTs restricted the root growth of germinated plant seeds, and an application rate of 2 g/L CNT negatively affected the germination of radish, lettuce and cucumber seeds (Lin and Xing 2007). An inhibitory effect of natural catechol in soil has been observed by the presence of SWCNT, whereas vice versa was reported for MWCNT (Shan et al. 2015a). At the same time, soil microbial biomass carbon was not influenced by the presence of MWCNT in 0.2, 20 and 2000 mg/kg, while the vice versa was recorded for 2000 mg/kg of SWCNT (Shan et al. 2015a). It has been revealed that CNTs can disturb soil/plant environmental balance by modifying the fate of toxic metals in soil or their translocation to plants by diffusing through the cell membrane (Wang et al. 2014). Hence, more studies are needed to assess the biological and chemical changes in soil and plant systems including the effect on soil microorganisms. Because of the wide applications of CNT in many different fields, CNT may enter into the environment through a number of sources and tend to accumulate in the soil (Klaine et al. 2008; Jackson et al. 2013; Gardea-Torresdey et al. 2014). Hence, understanding the impact of CNT on soil biota is very important in terms of soil ecology and biogeochemical cycling of nutrient elements (Dinesh et al. 2012a, b; Zhao and Liu 2012; Vaishlya et al. 2015).

A sudden decrease of protozoan and different fast-growing bacteria by three-to four folds was observed immediately after incorporation of the C_{60} (Johansen et al. 2008a). MWCNT was reported to negatively correlate with soil microbial activity and health (Li et al. 2015). Negative effects on soil enzyme activity were also reported (Chung et al. 2011). Chung et al. (2011) showed a repression in 1,4-β-glucosidase, cellobiohydrolase, xylosidase, 1,4-β-N-acetylglucosaminidase, and phosphatase activities and microbial biomass C and Nin soils receiving MWCNT. Similar results were obtained by Jin et al. (2013), Debora F. Rodrigues et al. (2013) with SWCNT. In addition to reduction in soil enzyme activity, CNTs could also cause cytotoxic effects on both Gram-positive and Gram-negative bacteria (Jin et al. 2013). For example, SWCNT, MWCNT, aqueous phase C_{60} nanoparticles, and colloidal graphite were evaluated for their cytotoxic effects (Kang et al. 2009; Santos et al. 2013). The presence of SWCNT inactivated the highest percentage of cells in monocultures of *Escherichia coli, Pseudomonas aeruginosa, Bacillus subtilis,* and *Staphylococcus epidermis* (Kang et al. 2009).

Numerous reasons are suggested to explain the toxicity caused by CNT. They might act as "nanosyringes" and create disruptions in bacterial cell walls and membranes (Luongo and Zhang 2010; Kang et al. 2007). Moreover, CNT might generate ROS, which could damage DNA, proteins, and cellular membranes of microorganisms (Jia et al. 2005).

Interestingly, SWCNT not only influenced the microbial biomass, but also changed the microbial community composition of Gram-positive and Gram-negative bacteria, and fungi. The effects were significantly negatively correlated with SWCNT concentration (Jin et al. 2014a; Rodrigues et al. 2013). Rodrigues et al. (2013) reported some transient negative effects of SWCNT on soil bacterial community after 3 days of exposure, which were fully recovered after 14 days. But a similar effect on soil fungal community could not be recovered during the experimental period (Rodrigues et al. 2013). Similarly, MWCNT also showed negative correlations between microbial population and nanotube concentrations. Comparative metagenomic analysis of microbial communities revealed that the diversity and density of microbial communities in soil were not significantly affected, but the abundance of each bacterial group was influenced in the presence of CNT (Khodakovskaya et al. 2013a, b). Shrestha et al. (2015) observed a dramatic shift in the microbial community structure in soils amended with MWCNT and grown with alfalfa. The CNT amendment resulted in a greater abundance of some specific fatty acid methyl ester (FAME) markers (i15:0, 16:1ω5c, 10Me17:0, 10Me16:0) in a sandy loam soil (1% organic matter), but showed insignificant effects (Shrestha et al. 2015). This indicated that the effect of CNT on soil microbial community and biogeochemical functions would not only depend on the type and characteristics of CNT, but also on the physiochemical properties of the soil. The presence of co-contaminants could also influence this biotic-abiotic interaction. For example, SWCNT significantly inhibited the microbial activities (microbial biomass C), but MWCNT selectively stimulated the specific

Table 3 Published literature on the effects of engineered nanoparticles on microorganisms in the soil

Morphology	Treatment	Effect	References
MWCNT	10–10,000 mg/kg	There was no significant effect on soil microbial composition, respiration and enzymatic activities at lower concentrations (10, 100 and 1000 mg/kg)	Shrestha et al. (2013)
Graphene oxide	0.05–0.1 g/L	Enhanced activity of anaerobic ammonium-oxidation bacteria. The highest carbohydrate, protein, and total EPS contents were obtained with 0.1 g/L graphene oxide, by analysis of extracellular polymeric substances	Wang et al. (2013)
Fullerene (C_{60})	0.01, 0.10, and 1.00 mg/L	No changes in the microbial growth	Cordeiro et al. (2014)
SWNTs	1–50 μg/mL	Strong antimicrobial properties and membrane destruction	Kang et al. (2007)
Buckminsterfullerene C_{60} aggregates	0.01 mg/L	Changed the composition of membrane lipids and phase transition temperature	Fang et al. (2007)
Carboxyl-functionalized SWCNTs	0, 250, and 500 μg of SWNT/g soil	High concentrations of SWNTs caused different effects on microbial communities and biogeochemical cycling of nutrients in soils. Higher biomass loss was observed and the toxicity of SWNTs is different for different microbial groups	Rodrigues et al. (2012)
SWCNT	0.03–1 mg/g soil	Gram-positive, Gram-negative bacteria and fungal communities were adversely affected with higher SWCNT concentrations	Jin et al. (2014b)
Graphene oxide	0.5–1 mg/kg	The soil enzyme activities were lowered only for short term (reduction of xylosidase, 1,4-β-N-acetyl glucosaminidase, and phosphatase activity up to 50%) and the soil microbial biomass of the treatment was not significantly different compared to the control	Chung et al. (2015)
Raw and acid treated or functionalized MWCNTs	0, 50, 500 and 5000 μg/g	MWCNT did not affect the bacterial diversity, however, functionalized MWCNTs temporarily affected the microbial community composition	Kerfahi et al. (2015)
Fullerenes	1 μg C_{60} g^{-1} soil in aqueous suspension or 1000 μg C_{60} g^{-1} soil in granular form	Very little impact on soil respiration, enzyme activities (dehydrogenase, urease) and community structure	Tong et al. (2007)
C_{60} fullerenes (50 nm to μm-size)	0, 5, 25, and 50 mg/kg dry soil	Respiration and microbial biomass were unaffected by the fullerenes irrespectively to time; however, the counts of fast-growing bacteria was decreased after introduction of the nanomaterial	Johansen et al. (2008b)
Fullerene (C_{60})	One gram of dried sludge plated with 50 mg C_{60} was introduced to each microcosm for a final concentration of 50000 mg of C_{60} (kg of biomass)	A significant effect was not observed on the anaerobic community of biosolids and no substantial community shifts were observed	Nyberg et al. (2008)
MWCNT	0, 50, 500, and 5000 μg/g MWCNT g^{-1} soil	Enzymatic activities (1,4-β-glucosidase, cellobiohydrolase, xylosidase, 1,4-β-N-acetylglucosaminidase, and phosphatases), microbial biomass C and N were significantly lowered under high concentration of MWCNT (5000 μg MWCNT g^{-1})	Chung et al. (2011)

catechol-degrading soil microbial communities (Shan et al. 2015b). Shrestha et al. (2013) also reported that MWCNT when applied at a very high concentration (10,000 mg/kg) increased the relative abundance of *Rhodococcus*, *Cellulomonas*, *Nocardioides* and *Pseudomonas*, which could potentially degrade recalcitrant contaminants (e.g., polycyclic aromatic hydrocarbons) in soils. However, the same application rate of MWCNT decreased the abundance of *Derxia*, *Holophaga*, *Opitutus* and *Waddlia* in soils (Shrestha et al. 2013). Moreover, the difference between the effects of SWCNT and MWCNT is still poorly understood. In addition, there is a scant in information regarding the long-term impact of CNT on soil microbial activities. In a recent study, Ge et al. (2016) found that after one year of MWCNT (1 mg/g) exposure, the DNA content in a dry grassland significantly reduced and also altered the bacterial communities. However, these effects were similar to other carbonaceous soil amendments such as biochar, carbon black and graphene (Ge et al. 2016). Similarly, raw and acid functionalized MWCNT did not affect the bacterial diversity in soil, but the functionalized product when applied at high concentration altered the soil bacterial community composition (Kerfahi et al. 2015). The authors attributed this effect on the intrinsic acidic nature of the functionalized CNT, which could lower down the soil pH following application at a higher dosage (Kerfahi et al. 2015).

Remarks

This review summarizes mainly the role of CNT on plant growth and associated soil biogeochemical processes. An extensive literature evaluation revealed that CNT could play a vital role in plant growth and agriculture. Contrasting effects of CNT on plant growth and development are observed. Many instances indicated that CNT could potentially enhance seed germination, plant yield, and nutrients and water uptake. However, CNT might also accumulate in the soil and result in the inhibition of soil microbial diversity and population. The accumulation of CNT in plant tissues might also cause generation of ROS, which would result in necrotic lesions and cell death. Although many studies were conducted on CNT's effects on plant growth, there are still many knowledge gaps to be filled, such as:

- CNT plays an important role in water uptake during seed germination. However, the mechanism by which nanoparticles support water uptake inside the seed is not yet clear. Hence, more in-depth investigation on the mechanisms of the gating of water channels in plant cells is needed.
- There are experimental evidences for the positioning of CNT in the plant xylem tissue. However, the mechanism for the alignment of CNT across the xylem and its role in enhancing ionic fluid flow need further investigation.
- In comparison with MWCNTs, SWCNTs are more likely to enter into the plant system and translocate to different body parts. However, very little is known about the translocation/transmission behavior and mechanism. Plausible altered gene expression of plants due to CNT warrant further research.
- Monoculture-based studies have been carried out to determine cytotoxic effects of CNT on soil microorganisms. Nevertheless, recent studies have highlighted the need to progress beyond pure culture systems to evaluate the actual risk caused by CNT to soil ecology.
- Numerous studies have shown the positive role of CNT on plant body and their accumulation in plant cells. However, post-uptake behavior of CNT inside the plant cells should be considered.
- There is a lack of knowledge on the relationship between the physicochemical characteristics of CNT and their biological behavior. Hence, more studies should be conducted on this aspect to provide a better understanding.
- More investigations are needed on novel nanomaterials such as carbon nanohorns, about their characteristic properties and interactions on other materials and living cells.
- Since there is a negative correlation between the microbial diversity and the concentration of CNT, it is suggested to carry out detailed studies using functional genes.
- Long-term studies would be important to assess the aging effect and its relationship with soil ecology and chemistry.
- The investigation on the behavior and fate of CNT within the plant body seriously lack appropriate in vivo analytical techniques. Multiple microscopic (e.g., HRTEM) and spectroscopic (e.g., Raman spectroscopy, FTIR) techniques were used

in the past with success to some extent. However, more works are needed to develop standard high-precision analytical techniques (e.g., synchrotron-based techniques) to detect the presence of this tiny particle inside the plant system in a less invasive way.

- It seems that MWCNT has played a positive role in plants under salt stress via improving the capacity to cope with changes in the water gradient through the imposed symplastic pathway; however, this is only the starting point of a chain of biochemical changes which is to be investigated as along with the movement of MWCNTs to edible part of the plants (e.g., leaves and fruits) in different environmental conditions.
- Contrasting data have been reported on the effect of morphologically different carbon nanostructures on seed germination and growth. Hence, more attention should be given in this particular aspect.
- Abiotic stress conditions play an important role in mediating the physiological impacts of CNTs in plant systems. However, CNTs-plant cell interface under stress conditions, and more importantly managing drought tolerance of valuable crops in arid and semi-arid regions needs to be studied in detail.
- Uptake of CNTs into a plant cell depends on the fraction dispersed in water. MWCNTs are highly hydrophobic and prone to homo- as well as hetero-agglomeration which result in a very small fraction of pore water dispersed MWCNTs. At the same time, the plant surface may act as a filter that may clogged with time and hence, further experiments are needed to focus on this matter.

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