Chapter 7
Nano-carbon: Plant Growth Promotion and Protection

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7.1 Introduction

Carbon nanomaterials are materials of diverse structure and size such as fullerenes, nano-onions, nano-cones, nanohorns, carbon dots, carbon nanotubes, nano-beads, nano-fibers, nano-diamonds, and graphene (Sharon et al. 2010; Chai et al. 2013). Carbon-based nanomaterials were utilized by scientists in various environmental applications such as in solar cells, for the production of renewable energy, soil remediation, and contaminant degradation, and in the detection as sensors for pollutants (Mauter and Elimelech 2008; Rasool and Lee 2015). In agriculture, carbon-based nanomaterials contribute to approximately 40% of the total engineered nanoparticles used and are mainly used either as additives or as active components (Gogos et al. 2012). For example, fungicides encapsulated in multi-walled carbon nanotubes were more toxic to *Alternaria alternata* compared to bulk pesticides which were not capsulated (Sarlak et al. 2014). In the case of fertilizer application, for slow and efficient release, encapsulation with graphene oxide films was found to be effective (Zhang et al. 2014). For example, Zhang et al. (2014) reported that encapsulation of potassium nitrate in graphene oxide prolonged the release into the soil thereby making the availability of potassium nitrate more efficiently to the

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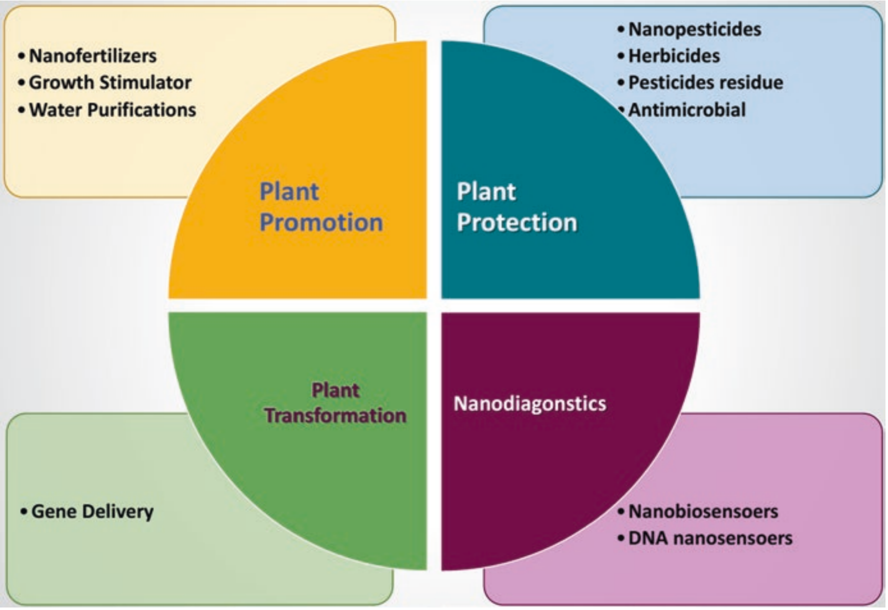

Fig. 7.1 Carbon nanomaterials applications in plant protection

plants. Carbon nanomaterials could be used as additives for the development of efficient fungicides due to antifungal properties (Wang et al. 2014a,b,c). In nano-biotechnology areas, the ability of carbon nanomaterials to penetrate and enter into cells could be used for the purpose of delivery of DNA molecules (Burlaka et al. 2015). In the past few years, it was proposed that carbon-based nanomaterials present about 40% of the total exploitation of nanotechnology in agriculture field, acting as additives as well as active components (Gogos et al. 2012). The diverse applications of carbon nanomaterials in plant crop protection are shown in Fig. 7.1.

7.2 Classification of Carbon-Based Nanomaterials

Carbon is one of the few elements known since antiquity with the ability to polymerize at the atomic level, thus forming very long carbon chains. It is nonmetallic and tetravalent—making four electrons available to form covalent chemical bonds. Carbon atoms have a valence of four due to the four electrons in the outer electron layer. The carbon atoms can bond together in different ways, termed allotropes of carbon. Until recently, only two natural carbon allotropes were known: diamond and graphite. In the meantime, various forms of new allotropic have been defined, including carbon nanomaterials. Generally, materials containing particles with at least one dimension between 1 and 100 nm in size are defined as nanomaterials (European Commission 2011). Carbon-based nanomaterials are composed of carbon atoms in their structure. Its classification is most commonly performed according to their geometrical structure. Particles of carbon nanostructures can be tube-shaped, horn-shaped, spherical, or ellipsoidal. Nanoparticles having horn-shaped particles are nanohorns and spheres or ellipsoids that belong to the group of fullerenes; the shape of tubes is termed as carbon nanotubes.

7.2.1 Fullerenes

In 1966, Harold W. Kroto, Robert F. Curl, and Richard E. Smalley have won Nobel Prize for their discovery in 1985 of fullerenes, in which the atoms are arranged in closed shells. Fullerenes consist of 20 hexagonal and 12 pentagonal rings as the basis of icosahedral symmetry closed-cage structure. Each carbon atom is bonded to three others and is sp^2 hybridized. Fullerenes are an allotropic carbon modification, often termed as a molecular form of carbon, or carbon molecules. The fullerene family includes a number of atomic Cn clusters ($n > 20$), composed of carbon atoms on a spherical surface. Carbon atoms are usually located on the surface of the sphere at the vertices of pentagons and hexagons. Fullerene C60 (is not super aromatic) is the most common and best-investigated fullerene. The spherical molecule is highly symmetric and consists of 60 carbon atoms, located at the vertices of 20 hexagons and 12 pentagons. The diameter of fullerene C60 is 0.7 nm (Yadav and Kumar 2008).

7.2.2 Carbon Nanotubes (CNTs)

In 1991, the Japanese researcher S. Iijima discovered CNTs. They are characterized by cylindrical structures with a diameter of several nanometers, consisting of rolled graphene sheets. Carbon nanotubes may vary in length, diameter, chirality (symmetry of the rolled graphite sheet), and the number of layers. CNTs may be classified into two main groups according to their structure: single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs). Some researchers additionally isolate a separate class of CNTs called double-walled carbon nanotubes (DWCNTs). Generally SWCNTs have a length of a few micrometers and a diameter around 1–3 nm. Multi-walled CNTs have a length around 10 μm and a diameter of 5–40 nm. Recently, synthesis of CNTs with a length of even 550 mm has been reported (Zhang et al. 2013). The valuable advantage of adding CNTs to polymeric membranes has been reported. These include increased oleophobicity and hydrophilicity (Zhang et al. 2016) and improved thermal, (Namasivayam and Shapter 2017) electrical, (Sarno et al. 2013) and mechanical properties of the composite membranes (Bai et al. 2017). CNTs as nanofiller in polymer matrix have attracted a great attention because of their easy functionalization, high specific surface area, proper compatibility, and chemical stability (Das et al. 2014a,b).

Bakajin et al. described a possible to modify CNTs pores to selectively rejections (Bakajin et al. 2009). Therefore, CNTs membrane can be used as a “gate keeper” for size-controlled separation of multiple pollutants. The fast and efficient method to separate emulsified oil from oily wastewater using functionalized multi-walled carbon nanotubes (F-MWCNTs) as a demulsifier was reported (Liu et al. 2016). Lately, CNTs could be covalently attached onto the surface of polymer to produce hybrid CNTs/polymer membranes for efficient separation of surfactant-stabilized oil/water emulsions (Zhang et al. 2016; Gu et al. 2016). Novel Ag/polyacrylic acid (PAA)–hybrid CNT membranes for treating oil/water/solid three-phase system have been developed (Gu et al. 2016). Also, the hybrid membranes exhibited an excellent antibacterial activity due to the carbon-based membrane that was integrated with AgNPs. Bacterial cells of *E. coli* were destroyed after incubating with the Ag/PAA–CNT membrane, indicating the antibacterial ability of the developed membrane.

7.2.3 Graphene

In 2004, the first graphene samples were defined by A. Geim (Dutch-British physicist) and K. Novoselov (Russian-British physicist), awarded with a Nobel Prize in 2010. It is a two-dimensional allotropic form of carbon, formed by single layers of carbon atoms. Carbon atoms show sp^2 hybridization linked by σ- and π-bonds in a two-dimensional hexagonal crystal lattice with a distance of 0.142 nm between carbon hexagons of closed atoms. Graphene represents a structural element of some other carbon allotropes, such as graphite, carbon nanotubes, and fullerenes. Graphene oxide (GO), the oxidation state of graphene nanosheets, could be an attractive candidate as a carbon filler because it contains epoxide, hydroxyl, and carboxylic acid groups.

7.3 Synthesis of Carbon-Based Nanomaterials

Since the discovery of carbon-based nanomaterials, their different methods for synthesis have been developed and outstanding properties have been intensively studied. The basic components for carbon nanomaterial production are carbon vapors.

7.3.1 Fullerenes

In 1990, W. Krätschmer and D.R. Huffman produced for the first time fullerenes by evaporation of graphite electrodes in a helium atmosphere (Kratschmer et al. 1990; Kratschmer 2011). Earlier, a reactor was changed by forming an electric arc between two graphite electrodes. The resulting soot condenses on the cold surface of the reactor and is collected and processed in boiling benzene, toluene, xylene, or other organic solvents. A black condensate is formed after evaporation of the solvents, having about 10–15% of C60 and C70 fullerenes, and small amounts of higher fullerenes. The ratio between the C60 and C70 fullerenes varies, depending on the synthesis parameters, but typically C60 represents the main fraction. The described method of arc discharge belongs to the large family of plasma methods which are most common and generally used compared to other techniques (Churilov 2008). However, the fullerenes are limited in practical use due to the low productivity of the methods and high costs currently available from their synthesis.

7.3.2 Carbon Nanotubes

Chemical vapor deposition (CVD), laser ablation, and arc discharge are basic techniques for CNT synthesis (Gore and Sane 2011). Presently, CVD is one of the most explored and mostly used methods for CNT production (Kumar and Ando 2010). It requires milder conditions and simpler equipment in temperature and pressure, making it more appropriate for the large-scale production of CNTs in contrast to two other methods (Zhang et al. 2011). CVD production is based on hydrocarbon decomposition to carbon, following synthesis of carbon nanostructures on various substrates having catalysts on which the nanotubes are rising. Nickel-, cobalt-, or iron-based nanoparticles are frequently utilized as catalysts. Their size strongly relates to the diameter of nanotubes synthesized on it (8–100 nm for MWCNTs, 0.5–5 nm for SWCNT synthesis).

Reactors for CVD synthesis usually consist of a reaction chamber and tubes filled with inert gas and hydrocarbon. Ethylene or acetylene is commonly used for MWCNTs, while methane for SWCNT synthesis. As a simplified method explanation, the substrate is heated up to 550–700 °C for MWCNT and up to 850–1000 °C in case of SWCNT production. Carbon is formed by thermal decomposition of hydrocarbons and dissolves in the metal nanoparticle catalyst. After reaching a certain concentration of carbon, it forms a semifullerene cap, as a starting structure for the growth of a cylindrical shell nanotube, formed by a continuous flow of carbon from the hydrocarbon source to the catalyst particle. Finally, the catalysts from the nanotubes tips are removed, and more purification is still under improvement and optimization to yield CNTs of a higher quality (Morsy et al. 2014; Matsuzawa et al. 2014).

In large scale, heterogeneous products are formed, containing impurities of amorphous carbon, carbon fiber, catalyst residuals, and other nanoparticles. So, production costs increase due to additional purification, and separation steps are needed. SWCNT production involves small metal catalyst particles to equal dispersion on the substrate and prevent aggregation. For example, when fine catalysts are sintering into larger particles, SWCNT diameter is increased or DWCNTs and MWCNTs are formed. A mixture of semiconductive and conductive SWCNTs is yielded requiring more extraction steps to get SWCNTs with defined chirality for specific applications. Vertically or horizontally aligned CNTs synthesis has numerous structural advantages as compared to bundles of agglomerated CNTs. Production of MWCNTs seems to be less complicated and expensive than SWCNTs. But, the controlled inner and outer diameters or defined numbers of walls are still major challenges.

7.3.3 Graphene

Gheim and Novoselov obtained graphene sheets using mechanical splitting of graphite with adhesive tape (Novoselov et al. 2004). Various methods for graphene production are available (Novoselov et al. 2012). These methods are based on splitting or cutting materials, such as graphite or nanotubes (Jiao et al. 2009), using a range of physical or chemical methods to obtain nanoscale graphene sheets. Graphene sheet synthesis by CVD synthesis or laser ablation methods is possible. The different methods are able to provide graphene or reduced graphene oxide sheets of different qualities, depending on the requirements of the corresponding applications. Moderate quality graphene for structural applications can be obtained in large quantities with relatively low production costs. High-quality graphene for electronic devices produced in smaller quantities is usually more expensive. The major methods suitable for mass production of graphene are liquid phase and thermal exfoliation of graphite, CVD synthesis (potentially most cost-effective), and synthesis on silicon carbide (Novoselov et al. 2012).

7.4 Chemical Functionalization of Carbon-Based Nanoparticles

Chemical functionalization can explain a wide variety of carbon-based nanomaterials. Nanoparticles are often functionalized by linking certain molecules to the nanoparticle surface, in order to modify the physical and chemical properties of the particles, which in turn greatly expands the field of applications (Hirsch and Vostrowsky 2005; Hernandez-Fernandez et al. 2010). One example for functionalization of carbon-based nanoparticles is an oxidation of CNTs. This process includes an ultrasonic treatment of nanotubes in a mixture of acids, leading to attachment of carboxylic functional groups (–COOH) on the sidewalls of the nanotubes. Oxidized CNTs attain solubility in aqueous solutions but retain their mechanical and electrical properties. Furthermore, carboxylic groups attached to the nanotube surface can serve as sites for further functionalization.

7.4.1 Properties of Carbon-Based Nanomaterials

Molecular manipulation of carbon-based nanomaterials involves controlling the conformation and structure of a material including size, length, chirality, and the number of layers.

7.4.1.1 Electronic, Optical, and Thermal Properties

CNTs possess a wide range of electrical and optical properties not only from their extended sp^2 carbon but also from their tunable physical properties (e.g., diameter, length, single-walled vs. multi-walled, surface functionalization, and chirality) (Saito et al. 1998). Diameter is a significant factor in determining the properties and applications of tube-shaped carbon nanostructures. Diameter of small single-walled carbon nanotubes is strongly related to synthesis technique (Andreas 2002). The diameter induces higher strain energies, mixing of σ and α bonds and electron orbital rehybridization. These bond structure modifications encourage essential modifications to the electronic, optical, mechanical, elastic, and thermal properties of SWCNTs.

CNTs display high thermal and electrical conductivity compared to other conductive materials. SWCNTs electrical properties depend on their chirality or hexagon orientation with respect to the tube axis. Accordingly, SWCNTs are classified into three subclasses: (1) armchair (electrical conductivity > copper), (2) zigzag (semiconductive properties), and (3) chiral (semiconductive properties). Due to variable chirality of MWCNTs, unusual mechanical properties instead of outstanding electrical characteristics can be revealed.

CNTs and graphene have similar electrical, optical, and thermal properties, but the electrical properties of graphene allotrope are basically different from the properties of three-dimensional materials due to its two-dimensional atomic sheet structure that allows more varied electronic characteristics.

The CNT structure leads to outstanding properties with a unique mixture of strength, rigidity, and elasticity compared with other fibrous materials. For example, CNTs display noticeably higher aspect ratios (length to diameter ratios) than other materials and larger aspect ratios for SWCNTs as compared with MWCNTs due to their smaller diameter. Graphene has several unique physical properties, for example, high thermal stability and extremely high mechanical rigidity.

7.4.1.2 Molecular Interaction and Sorption

The molecular interactions and sorption properties controlling carbon-based nanomaterials depend commonly on physical-chemical models and theories (electrostatics, hydrophobicity, adsorption, etc.). At the nanoscale molecular modeling can supply elucidations about physical-chemical processes. The possible energies of interaction between carbonaceous nanomaterials are already defined in the literature (Hunter 2001), considering both van der Waals attractive forces and Pauli repulsion rising from overlapping electron orbitals at short separation distances. The adsorption behavior and orientation of sorbates in microporous carbon, physic-sorption will be contributed by hydrophobicity and capillarity being the sorption dominant mechanism for not functionalized nanomaterials. Adsorption reports of high adsorption capacity, low sensitivity to pH value, rapid equilibrium rates, minimal hysteresis in dispersed nanoparticle (Hilding et al. 2001), and consistency with Langmuir were cited.

The sorptive capacity of traditional carbonaceous sorbents is limited by the surface-active site density, the slow kinetics, and the sorption nonequilibrium in heterogeneous systems. The large dimensions of conventional sorbents limit their transport through low-porosity environments and complicate the subsurface remediation. High surface area to volume ratio of carbonaceous nano-sorbent controlled pore size distribution, and their surface chemistry overcomes many of these intrinsic limitations.

7.5 Applications

7.5.1 Graphene-Based DNA Sensors

The exceptional electrical, optical, thermal, and mechanical properties of graphene oxide (GO) received worldwide attention since it was reported in 2004. Graphene with its large surface area reaching up to 2630 $m^2\ g^{-1}$ and the unique sp^2 (sp^2/sp^3)-bonded network and its other remarkable characteristics have led to its rapid development for use in the sensors making it an excellent promising candidate for biomolecule anchoring and detection (Suvarnaphaet and Pechprasarn 2017). On the other hand, the application of specific DNA sequences has been widely used for detection of bacteria, fungi, and genetically modified organisms having variety of applications such as clinical human disease detection, environmental horticulture, and food analysis. In consequence, new innovative types of nanosensor-based graphene using nucleic acid fragments as elements for pathogen detection have been developed. Although the nucleobase–graphene binding energy is slightly different via various strategies and equipments, one might be certain that ssDNA could be adsorbed on graphene sheet surface coupling crossover of several interaction forces and employing nucleobases as the anchors. This is also the root cause that ssDNA binds more strongly to graphene than dsDNA does in which nucleobases are entrapped and shielded by the phosphate–deoxyribose backbones. According to the binding affinity difference between ssDNA and dsDNA to graphene sheet, graphene oxide (GO) has been successfully adopted as a platform to discriminate DNA sequences. On the other hand and based on the specific nucleic acid hybridization of the immobilized DNA probe on the sensor and the analyte DNA sequence, DNA-based biosensor allows rapid, simple, and economical testing of genetic and infectious diseases. The most commonly adopted DNA probe is single-stranded DNA (ssDNA) on electrodes with electro-active indicators to measure hybridization between probe DNA and the complementary DNA analyte (Eun and Wong 2000).

There are four major types of DNA-based biosensors depending on their mode of transduction, namely, optical, piezoelectric, strip-type, and electrochemical DNA biosensors. Different reports revealed practically the potential effect of using this kind of nanosensors in detecting viral and bacterial pathogens due to their unique nucleic acid sequence, which can be specifically hybridized with the complementary DNA probe. The recognition of analyte DNA is dependent upon the formation of stable hydrogen bonds between the DNA probe and analyte DNA sequence. This is different from the antibody-based biosensors where hydrophobic, ionic, and hydrogen bonds play a role in the stabilization of antigen-antibody complex. Although the DNA-based nanosensors show a significant and promising rapid solutions for plant disease detection, however, polymerase chain reaction (PCR) technique may have to be performed prior to the probing process due to the small quantity of nucleic acid present in the bacterial cells (Ivnitski et al. 2000; Fang and Ramasamy 2015). We should clarify that there is still some limitations around this unique kind of sensing including the requirement for the synthesis of specific DNA probe, amplification of DNA, and high cost (DNA-based molecular beacons).

7.5.2 Graphene as a Biosensor

Construction of nanosensor-based materials for exploitation in agriculture is new and a promising direction of plant nanotechnology. Despite the material advancements, very scanty data is available where electrochemical biosensors have been applied for the detection of agricultural pathogens for their rapid and timely identification to prevent huge economic losses. The number of successful studies is still very limited, but nanosensors can be developed in the very near future. A great example is the recent building of single-walled carbon nanotubes (SWCNTs) radiometric sensors (for H_2O_2 and NO) performed by Giraldo et al. (2015) which proved the efficiency of radiometric nanosensing platform for detecting key compounds in plant tissues.

Carbon-based nanosensors were made of different types of carbon materials, metal-based nanomaterials, and screen-printed electrodes that generally utilize electrochemical mode of measurement and/or microfluidics-based system to achieve simple and compact analytical devices for detection of toxins and various applications in food, agriculture, and environmental monitoring. Use of single-walled carbon nanotubes (SWCNTs) with metal/metal oxide NPs were selected to deal agricultural by-products such as ammonia and nitrogen oxide as they are the most recent technologies in this issue. These techniques help in the development of nanosensor arrays which are of high density with a potential role in monitoring agricultural pollutants and their impact on biological and ecological health and thus in turn increasing crop productivity. On another side, the scientist Fernández-Baldo and his co-workers developed a faster screen-printed immunosensor assay modified with carbon nanotubes in a continuous-flow system for detecting the phytopathogenic fungus *Botrytis cinerea* with a detection limit reaching 0.02 μg mL^{-1} (Fernández-Baldo et al. 2009). This system was further modified by involving the use of micromagnetic beads coupled to the carbon-based screen-printed electrodes, apparently increasing in sensitivity to 0.008 μg mL^{-1} "pure" Botrytis antigen (Fernández-Baldo et al. 2010). Electrochemically functionalized single-walled carbon nanotube (SWCNT)-based nanosensors with metal/metal oxide nanoparticles or nanotubes for gases, viz., ammonia, nitrogen oxides, hydrogen sulfide, sulfur dioxide, and volatile organics have also a significant potential application in monitoring agricultural pollutants and assessment of impacts on living matter or health and in increase of crop productivity (Sekhon 2014). Also, the electrochemical DNA biosensor, graphene oxide/gold nanoparticles were also functionalized and used for rapid detection some microbial pathogens like *Helicobacter pylori* with a detection limit reaching 27 pM (Hajihosseini et al. 2016). More interestingly, a biosensor is reported for the screening of DNA-level modification and damage caused by chemotherapeutic drugs and a screen-printed gold electrode (SPGE) for the detection of *Cucumber mosaic virus* (CMV) (Ilkhani et al. 2016; Zulkifli et al. 2016).

7.5.3 Gene Delivery

Smart delivery systems of organic and inorganic agrochemicals to deliver the nucleic acids into the plant cells have a great attention recently (Zarei et al. 2018). This kind of technology is mainly based on the ability of nanomaterials to penetrate through cell walls and membranes of plant cells, solving major critical problems in agriculture sciences. Different types of nanomaterials with potential advantages were used as reliable vehicle systems to deliver therapeutic and agrochemical agents (i.e., liposomes, polymersomes, microspheres, and polymer conjugates). Carbon nanotubes are the best example showing safe interaction with biomacromolecules and a remarkable potential nano-vector to transfect plant cells with genes of interest (Wang et al. 2014a,b,c). Liu and his co-workers stated the ability of carbon-based nanomaterials particularly carbon nanotubes that showed a good potential to deliver nucleic acids (DNA or RNA) and other small molecules into tobacco plants (Liu et al. 2006a,b). Other studies also confirmed the ability of single-walled-CNTs (SWCNTs) act as nano-transporters for delivery of DNA and dye molecules into plant cells in more details (Srinivasan and Saraswathi 2010).

Different reports suggested that the multi-walled CNTs (MWCNTs) have a more magic ability to influence the seed germination and plant growth and work as a delivery system of DNA and chemicals to plant cells (Lahiani et al. 2015). On the other hand, scientists indicated that both carbon nanotubes (MWCNTs) and single-walled carbon nanohorns (SWCNHs) were documented by using Raman spectroscopy and transmission electron microscopy (TEM) (Lahiani et al. 2015). On the other hand, Serag and his research team observed that single-stranded DNA molecules wrapped around SWCNTs were able to target the cytoplasm of walled plant cells. This property could be used to introduce RNA pieces into the nucleus to activate or silence the genes of interest. Similarly, protoplast could be a target for delivering larger DNA molecules such as the delivery of plasmids into the plant cell genome. Thus, it is important to take into consideration all possible effects of carbon-based materials used as the DNA delivery machine on plant genome and proteome (Serag et al. 2015).

7.5.4 *Plant Growth Stimulators and Fertilizers*

Multi-walled carbon nanotubes (MWCNTs) are a kind of nanomaterial, and due to their unique nanostructures and extraordinary properties such as high electrical conductivity, large and special area, and significant thermal stability, they have been seriously taken into consideration in fundamental research and technological development (Milne et al. 2004).

7.5.4.1 Seed Germination

The growing consensus suggested that a high degree of the functionalized CNT leads to a dramatic reduction and toxic effects on different plant species based on CNT concentrations that have been increased daily. This may be backed up by the positive effects observed on the growth of *Cicer arietinum* L. plants after being treated by water-soluble MWCNT (wsMWCNT) (Tripathi and Shahi 2011), although some reports indicated that the germination rate of corn and rye plants treated with MWCNT was reduced, while the root length was increased (Begum and Fugetsu 2012). However, inhibitory effect of MWCNTs on plant growth has been reported by many researchers (Tiwari et al. 2014; Begum et al. 2014; Fathi et al. 2017). The MWCNTs had no effect on the germination of castor seeds and the length of plumule. But root length and wet weight in the treatment of 100 mg mL^{-1} seedlings were found improved in all factors related to the growth stage of seedlings (Fig. 7.2) (Fathi et al. 2017). Thus, the effect of NPs on plants varies from plant to plant, their growth stages, and the chemical composition of the used nanomaterial.

Other studies have also supported the positive influence of MWCNTs on seed germination and growth of six different crop species such as radish (*Raphanus sativus*), rapeseed (*Brassica napus*), rye, lettuce, maize, and cucumber (Lin and Xing 2007). Similarly, Ma et al. (2010) functionalized SWCNTs with poly-3-amino benzenesulfonic acid and studied the effects of both functionalized and non-functionalized SWCNTs on root growth of six crop plants, cabbage, carrot (*Daucus carota*), cucumber, lettuce, onion (*Allium cepa*), and tomato. Srinivasan and Saraswathi (2010) showed enhanced seed germination and growth rate in tomato seeds when exposed to CNTs. Highly maximized germination rate was observed in crop species such as tomato, hybrid Bt cotton (*Gossypium hirsutum*), Indian mustard (*Brassica juncea*), urd bean (*Vigna mungo*), and rice (*Oryza sativa*) with MWCNT treatment (Ghodake et al. 2010; Morla et al. 2011; Nalwade and Neharkar 2013). Interestingly, the effect of MWCNTs on the seed germination of *Brassica juncea* L. and *Phaseolus mungo* L. plants was 100%, which indicated their safety for seed germination (Ghodake et al. 2010).

The effects of engineered carbon nanomaterials of various dimensionalities on rice seed germination were studied, and an increase in germination rate with increased water uptake was observed for treated seeds than the control seeds. Surprisingly, the effects of MWCNTs and single-walled CNTs (SWCNTs) have

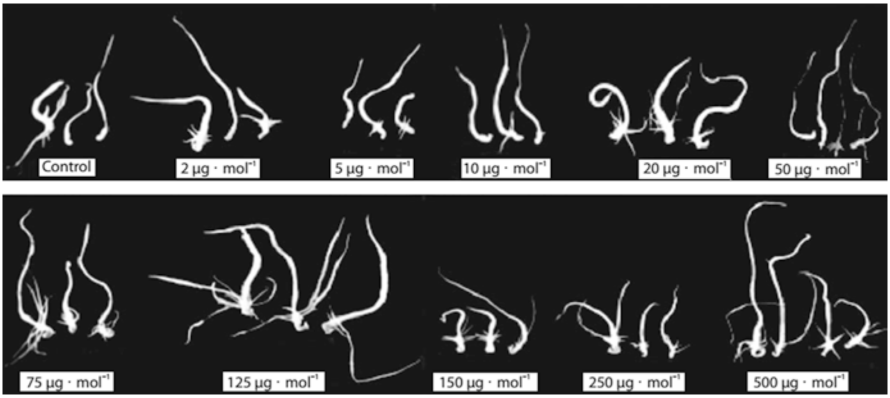

Fig. 7.2 Effects of multi-walled carbon nanotubes (MWCNTs) on root and shoot elongation of castor seedlings (Reprinted from Fathi et al. 2017)

been observed to vary. For example, zucchini plants exposed to MWCNTs did not show any detrimental effects on seed germination and root elongation, whereas a marked decrease in the biomass was recorded during further growth in the presence of SWCNTs (Stampoulis et al. 2009). Anjum et al. (2013) assessed the germinating faba bean (*Vicia faba* L.) seedling tolerance to different concentrations (0, 100, 200, 400, 800, and 1600 mgL^{-1}) of single-bilayer graphene oxide sheet (GO; size, 0.5–5 µm) and underlying potential mechanisms. Hu and Zhou (2014) reported a novel and biocompatible hydrated graphene ribbon (HGR) could promote aged (2 years) wheat seed germination, increase seed germination, and enhance resistance to oxidative stress *Onobrychis arenaria* (Kit.) DC seedlings treated with MWNTs showed an increased germination rate (Smirnova et al. 2012) that can be due to the positive role of carbon nanotubes in absorption of water (Kole et al. 2013). The growth of the roots and stems of *O. arenaria* seedlings is stimulated with MWNTs treatment (Smirnova et al. 2011). Similarly, it was observed that seed germination is activated with the sedimentation of MWCNTs on the surface of corn, barley, and soybean seeds (Lahiani et al. 2015). Synthesis of MWCNTs in low concentrations leads to increased corn seedling germination, while high concentrations lead to reduced growth. Increased growth mainly occurs via improvement of water transmission by carbon nanotubes. These compounds can be useful for the improvement of water flow, plant biomass, and essential concentrations of calcium and iron (Tiwari et al. 2014). Effects of carbon family-based nanomaterials on plant seed germination were shown in Table 7.1, Fig. 7.3.

7.5.4.2 Seedling Growth Promoters

Different studies conducted on CNMs evidently indicated their potential to enhance plant growth, nutrient uptake, seed germination, and fruit yield/quality (Khodakovskaya et al. 2009; Lahiani et al. 2015). Absorption of carbon nanotubes

Table 7.1 Effects of carbon family-based nanomaterials on the germination of plant seeds

Carbon NMs	Plant	Germination[a]	References
Graphene oxide	Faba bean	(+)	Anjum et al. (2013)
CNTs	Onion, rice, Indian mustard mung bean, tomato	(+)	Ghodake et al. (2010), Nair et al. (2010), Mondal et al. (2011), Morla et al. (2011)
	Garden cress, sorghum, tomato, radish, cucumber	(+)	Oleszczuk et al. (2011)
MWCNTs	Radish, rapeseed, rye, lettuce, maize, cucumber, zucchini	N	Lin and Xing (2007)
	Castor	N	Fathi et al. (2017)
Carbon nanohorns	Barley, maize, rice, soybean, switchgrass, tomato, and tobacco cell culture	(+)	Lahiani et al. (2015)

[a]Positive effect (+), negative effect (−), no effect (N)

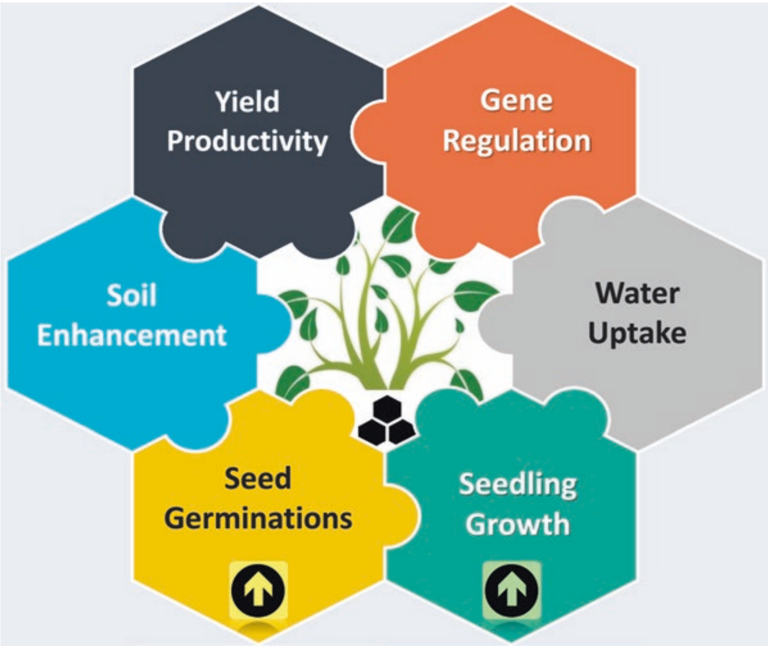

Fig. 7.3 The positive effect of nano-carbon in plants and soil

by plants is a new field in nano-agriculture. Carbon nanotubes can change the morphological and physiological properties of plant cells (Pourkhaloee et al. 2011; Lahiani et al. 2015) and are thought to regulate plant and seedling growth (Khodakovskaya et al. 2012; Haghighi and da Silva 2014). This stimulatory effect can have an important role on their application in the modeling of the plants' function. The improved root and stem growth on MWCNTs exposure may be due to the uptake and accumulation of MWCNTs by roots with their subsequent translocation to leaves (Smirnova et al. 2012). The presence of water-soluble CNTs inside wheat plants was evidenced by Tripathi and Sarkar (2015) with scanning electron and fluorescence microscope.

Furthermore, the authors linked this observation to the CNTs-induced root and shoot growth under both light and dark conditions. Interestingly, MWCNTs have been recognized to augment water retention; improve biomass, flowering, and fruit yield; and also enhance medicinal properties of plants (Khodakovskaya et al. 2013; Husen and Siddiqi 2014). In another study, it was indicated that the exposure of SWCNTs to maize seedlings promotes growth of seminal roots. Carbon-based fullerol [C60(OH)20] NPs treatment resulted in increases of up to 54% in biomass yield and 24% in water content in bitter melon (*Momordica charantia*). A 20% fruit length, 59% fruit number, and 70% fruit weight gain resulted in an overall improvement of up to 128% in fruit yield (Kole et al. 2013). The treatment of *Brassica juncea* seeds with oxidized MWCNTs increased moisture content of seeds and enhanced water absorption machinery of root tissues resulting in beneficial effect on the growth of mustard plants (Mondal et al. 2011). An interesting study published by Miralles and his co-workers indicated that root elongation due to MWCNT exposure was enhanced also in alfalfa and wheat seedlings, and it was found that carbon nanotubes were adsorbed onto the root surfaces of both plants without significant uptake or translocation (Miralles et al. 2012). Similarly, Wang et al. confirmed those findings, and their study indicated that the oxidized MWCNTs significantly promoted cell elongation in the root system of wheat (*Triticum aestivum*) and increased the dehydrogenase activity, resulting in faster root growth and higher biomass production (Wang et al. 2012). Later, the same group documented that tomato plants grown in soil supplemented with MWCNTs were able to produce two times more flowers and fruits compared to plants grown in control soil (Khodakovskaya et al. 2013). The effect of carbon nanotubes on the germination and growth of plants confirms the penetration of materials into the thick seed cover and their entrance into cellular space and participation in the processes of water absorption, leading to improved germination and growth of plants (Ghodake et al. 2010). MWCNTs, by penetrating into the seed cover, stimulated the growth of tomato and mustard seeds. It has also been demonstrated that MWCNTs can penetrate the thick cover of wheat, corn, peanut, and garlic seeds, thereby leading to absorption of water into the seeds – this was effective on growth at lower concentrations (Srivastava and Rao 2014). However, the inhibition of root elongation after application of CNTs on tomato was documented (Cañas et al. 2008). The inhibitory effects of MWCNTs on plant growth have also been reported by many researchers (Begum and Fugetsu 2012; Ikhtiar et al. 2013; Tiwari et al. 2014; Begum et al. 2014). In another study, the uptake, accumulation, and transmission of natural organic matter (NOM)-suspended MWCNTs in rice were reported (Lin et al. 2009). Some examples of CNTs influencing the yield and biomass of plants are compiled in Table 7.2.

Table 7.2 Positive and negative effects of different carbon nanomaterials on different plant species are summarized in the table

Carbon NMs	Plant	Seedling growth	References
CNTs	Alfalfa, wheat	Root elongation (+)	Miralles et al. (2012)
	Chickpea	Growth rate (+)	Tripathi and Shahi (2011)
	Tomato	Increased number of flowers and fruits (+)	Khodakovskaya et al. (2013)
	Tomato	Seedling growth (+)	Morla et al. (2011)
SWCNTs	Rice	Improved seed germination, water uptake, healthier seedlings (+)	Nair et al. (2012)
	Blackberry	Root elongations (+)	Flores et al. (2014)
	Arabidopsis, Rice protoplasts	Programmed cell death (−)	Shen et al. (2010)
	Maize	Enhanced root elongation (+)	Yan et al. (2013)
MWCNTs	Maize	Improved growth (+)	Tiwari et al. (2014)
	Rice	Improved seed germination, water uptake, healthier seedlings (+)	Nair et al. (2012)
	Red spinach	Exhibited growth inhibition, cell death (−)	Begum and Fugetsu (2012)
	Wheat	Root growth (+)	Wang et al. (2012)
	Tobacco	Growth rate (+)	Khodakovskaya et al. (2012)
	Tomato	Increase plant height and number of flowers (+)	Khodakovskaya et al. (2013)
	Castor	Improved growth (+)	Fathi et al. (2017)
	Zucchini	Reduced biomass (−)	Stampoulis et al. (2009)
	Lettuce	Reduced root length (−)	Lin and Xing (2007)
	Rye	Promoted root length	Lin and Xing (2007)
Poly-3-amino benzenesulfonic acid functionalized SWCNTs	Onion, cucumber	Enhanced root elongation (+)	Cañas et al. 2008
	Lettuce	Inhibited root elongation (−)	Cañas et al. 2008
Fullerol	Bitter melon	Increased biomass, fruit yield, and improved phytomedicines content (+)	Kole et al. (2013)
C60 fullerenes	Maize, soybean	Reduced biomass	Torre-Roche et al. (2013)

7.5.4.3 Plant Growth Promotion Mechanism

The possible mechanism for which the concentration-dependent MWCNTs affect the growth of castor seedlings needs to be clarified. Also, the mechanism behind the stimulatory effect of MWCNTs on the growth of castor seedlings is that the mentioned compounds can support the absorption of water by the seeds. Probably, carbon nanotubes can penetrate the thick seed coat and support the water uptake inside seeds. MWCNTs penetrate the cell wall and accumulate in the cells and tissues, and, via the vascular system, they are transferred from the root to the stem and to the leaf of the seedling (Srivastava and Rao 2014). MWCNTs induce the water and essential Ca and Fe nutrients uptake efficiency that could enhance the seed germination and plant growth and development (Villagarcia et al. 2012; Tiwari et al. 2014). The ability of SWCNTs to traverse across the plant cell wall and cell membrane was first reported by Liu et al. (2009). This has opened novel methods to deliver DNA and other molecules to intact plant cells. Liu and his group also studied changes in the cell wall of tobacco cells under the repression of water-soluble carboxy-fullerenes. Disruption in cell wall and cell membrane was observed on the adsorption of fullerenes which led to complete inhibition of cell growth (Liu et al. 2013a,b). Single-walled carbon nanotubes (SWCNTs) have been shown to exert adverse effects on *Arabidopsis* and rice leaf protoplasts through oxidative stress, leading to a certain amount of programmed cell death (PCD)/apoptosis, DNA damage, and chromatin condensation (Shen et al. 2010).

On the other hand, a noticeable increased glycosyl residue was observed in the cell wall of fullerene-treated plant cells with elevated levels of reactive oxygen species (ROS). Serag et al. (2011) investigated the ability of FITC-labeled MWCNTs to penetrate the cell membrane of periwinkle (*Catharanthus roseus*) protoplasts, and their internalization mechanism was studied with the help of confocal imaging and TEM techniques.

The direct penetration mode helped MWCNTs to bypass endosomes and hence opens new avenues in designing endosomes escaping nano-transporters for plant cells. MWCNTs have been shown to improve the peroxidase and dehydrogenase activity (Smirnova et al. 2012). Wang et al. (2012) reported oxidized MWCNTs significantly enhanced cell elongation in the root system and promoted dehydrogenase activity. In this regard, Zao and his co-workers noticed that graphene oxide (GO) exposure did not induce H_2O_2 production, formation of oxidative stress, increase in malondialdehyde content, or altered activities of antioxidant enzymes in *Arabidopsis* plants (Zhao et al. 2015). Although the role of CNTs in regulating cell division and plant growth and improvement of plant production is clear, however, the complex interactions of those nanomaterials with the environment and their inhabitants particularly terrestrial plant species need further investigation.

7.5.5 Nanofertilizers

Carbon-based nanomaterials significantly help in reducing losses of nutrients by leaching or evaporation caused by the classical working with common practice fertilizer application (e.g., foliar application by spraying) in conventional agriculture. On the contrary, carbon-based nanomaterials can provide a controlled-release technique for fertilizer delivery precisely functionalized to adapt the nutrient supply to the current demand of the target plant, extending the time of function, and inhibit losses by leaching with no risk of facing overdose effects. Using different cheap carbon nanomaterials like graphene oxide aids the process of commercial large-scale encapsulated fertilizer production with controlled-release technique to be possible with more economic cost (Zhang et al. 2014). Most of these fertilizers are based on amendments of mineral and organic fertilizers with nano-carbon, which in most cases acts as a fertilizer synergist with the aim of improving plant nutrient availability, reducing nutrient losses, and stimulating plant growth (Zaytseva and Neumann 2016). Several carbon-based nanomaterials have found applications in patents on nano-fertilizer formulations (Zhang and Liu 2010; Biris and Khodakovskaya 2011; Li and Guan 2011; Liu and Wangquan 2012; Xie and Liu 2012; Zhang and Chen 2012). Multi-walled carbon nanotubes (MWNTs) can be used as a carrier to improve nutrient uptake by plant cells (Torney et al. 2007; Serag et al. 2011). Upon successful delivery into the cells, the absorption and utilization of N by the plant can be increased leading to enhanced plant growth. Yatim et al. (2015) identified the significant process parameters to attach urea fertilizer (UF) onto MWNTs. The UF-MWNTs was then characterized by means of spectroscopic and microscopic analyses to confirm their bonding. Comparison study was also conducted between UF-MWNTs and UF-functionalized MWNTs on total N content bonding to the MWNTs. Their results indicated the importance of functionalization and amount of MWNTs for further optimization step in developing novel urea fertilizer and MWNTs for plant growth (Yatim et al. 2015).

On the other hand, carbon nanotubes could be used as a nutrient carrier for macro- and microelements and also as slow-release fertilizers that may reduce their higher concentrations which are usually used (Hasaneen et al. 2017). The nano-carbon is used as a coating material for slow-release fertilizer, and incorporation of nano-carbon into slow-release fertilizer is beneficial for reducing water pollution, especially the Ingzhengda slow-release fertilizer and nano-carbon (JSCU+C) (Wu 2013). To investigate the effects of combined application of nitrogen fertilizer and nano-carbon on nitrogen use of soil and rice yield, six treatments were applied by the scientist Fan and his co-workers. The utilization rate of nitrogen fertilizer increased after combined application of nano-carbon, which can save the N fertilizer in production practice. Therefore, combined treatment is suitable to application and dissemination in soda saline-alkali soil in the agriculture (Fan et al. 2012). More knowledge about nano-fertilizers in agriculture and the relationships between physicochemical characteristics of nanomaterials and biological interactions are still in need, but also more care about the risk with handling nanoparticle application in this important field is needed (Taha 2016). On the other side, much work should be done by scientists in a way to define the optimized concentrations of different types of nano-carbons in different plant species as organic fertilizer to reach for the positive impacts that are important for promoting plant growth and increasing the crop yields (Singh et al. 2017).

7.5.6 Antimicrobial

Generally, nanomaterials have an immense potential in plant disease control, providing unique novel cost-effective methodologies in crop protection with environment-friendly and ignorable limitations (Prasad et al. 2014, 2017a,b). Carbon-based nanomaterials particularly carbon nanotubes, fullerene, and graphene are best examples showing potent antimicrobial potential giving high possibility to be applied as novel fungicides and disinfection agents suitable for agricultural purposes (e.g., in plant protection) (Jung et al. 2011; Al-Hakami et al. 2013; Schmitt et al. 2015) that can be used to produce innovative nanocomposite materials. Also, Al-Hakami and his co-workers showed a good exploitation of using functionalized CNTs with the aliphatic alcohol 1-octadecanol ($C_{18}H_{38}O$) in water disinfection based on interactions of functionalized CNTs with microwaves. Based on their findings, they stated that the formed CNTs had outstanding antimicrobial properties since the long carbon chains contributed to a better absorption of the microwaves by CNTs (Al-Hakami et al. 2013). Zaytseva and Neumann reported interesting findings that revealed the broad-spectrum antifungal activity of those nanomaterials against two phytopathogenic fungi, namely, *Fusarium graminearum* and *Fusarium poae*, compared to other carbon-based nanomaterials like fullerenes and graphene oxide (Zaytseva and Neumann 2016). Also, it was indicated that CNTs displayed superior inactivation effects on the copper-resistant plant microns like *Ralstonia solanacearum*, *Fusarium graminearum*, and *F. oxysporum* (Wang et al. 2013, 2014a,b,c). Additionally, multi-walled carbon nanotubes (MWCNTs) have a noticeable strong antimicrobial activity against different microbial and viral and wastewater agents, where the MWCNTs were coated with different metallic nanomaterials like Ag NPs or Zn NPs in a good way to control the fungal growth of the phytopathogenic fungi *Aspergillus fumigatus* and *A. ochraceus* (Fosso-Kankeu et al. 2016). From the toxicological point of view, single-walled carbon nanotubes have higher antimicrobial properties than multi-walled carbon nanotubes (MWCNTs) (Oyelami and Semple 2015).

Although different published articles indicated the possible use of those nanomaterials as antimicrobial agents against bacteria and fungi (Upadhyayula et al. 2009; Das et al. 2014a,b; Pereira et al. 2014; Joshi et al. 2018), very few studies proposed the mechanism of action and suggested that the antimicrobial action may be backed up by either physical (cell wall damage and cytoplasm separation) or chemical effects (oxidative stress and ROS generation) (Wang et al. 2017). This assumption requires much more detailed investigations of the behavior of those nanomaterials, considering a wider range of phytopathogenic microbes to be tested under in vivo conditions.

7.5.7 Nano-pesticides

Nanomaterials have a great application in agriculture not only for diseases control but also for the enhancing growth effect in plants (Patel et al. 2014). Some of the nanoparticles that are widely used to control plant diseases are nanoforms of carbon, silver, silica, and aluminasilicates (Saurabh et al. 2015). Carbon nanomaterials can have different forms like hollow spheres, ellipsoids (fullerenes), or cylindrical [nanotubes such as single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT)] (Saurabh et al. 2015). Due to their antifungal properties, carbon-based nanomaterials are promising materials for the development of nano-antifungal pesticides. The effect of commercial multi-walled carbon nanotubes (MWCNTs) on conidia of the entomopathogenic fungus *Paecilomyces fumosoroseus* was investigated by Gorczyca et al. (2009). The CNTs strongly limited spore production of mycelium in applied concentrations. The polyethylene films with carbon nanotube nanocomposite base are prepared by solution casting from boiling xylene. This nanocomposite showed strong antifungal activity in packaged materials (Asgari et al. 2014). Six CNMs including SWCNTs, MWCNTs, graphene oxide (GO), reduced graphene oxide (rGO), fullerene (C60), and activated carbon (AC) were examined against two plant pathogenic fungi: *Fusarium graminearum* and *Fusarium poae* (Wang et al. 2014a,b,c).

The SWCNTs had the highest antifungal activity followed by MWCNTs, GO, and rGO. C60 and AC showed no significant antifungal activity. The antifungal activities of MWCNTs with different surface groups against *Fusarium graminearum* were explored by Wang et al. (2017). According to their findings, spore germination was remarkably inhibited by surface-modified MWCNTs, with germination rate being 18%, threefold lower than for pristine MWCNTs. Sarlak et al. (2014) have also used the multi-walled carbon nanotube (MWCNT) coated with poly(citric acid) as a carrier for the water-soluble dithiocarbamate fungicides. The encapsulation of pesticide was optimized in the pH range of 6–8 with a stirring time of 30–80 min. The pesticide loaded nanocarriers exhibited superior fungicidal activity against the leaf spot fungi *Alternaria alternata*, when compared to the bulk form of the fungicides.

7.5.8 Pesticide Monitoring Using Carbon Nanotube Sensors

Pesticides are organic compounds, which are developed to protect plant crops from pest invasion in agriculture. Although pesticides have a significant positive impact on the crop yield and food loss, however, intensification of agricultural practices can lead to an increase of the pesticide residues that can impose a serious risk to human health and the environment worldwide (Damalas and Eleftherohorinos 2011; Sangeetha et al. 2017a,b). Furthermore, their residual accumulation in the fresh and edible parts is considered a serious problem taken into account in global trade and countries particularly around the country borders in import-export exchange (Gholipour et al. 2012). On the other hand, transformation produced compounds released from the product active ingredients that may also be found in the final stage of commercial packages of pesticides which also are considered very toxic for human beings. Therefore, there is a need to develop a simple, sensitive, selective, cheap, and portable sensing platform for pesticide determination. Carbon nanotubes

(CNTs) are currently one of the most promising nanomaterials having unique properties including lightness, rigidity, high surface area, high mechanical strength in tension, good thermal conductivity, or resistance to mechanical damage. More interestingly, their unique properties put it an efficient alternative to other conventional analytical sorbents. Besides their analytical sorbent applications, carbon nanotubes are also widely enrolled in the development of different nanosensors to detect different biomolecules like drugs, dyes, ions, phenolic compounds, and also pesticide residues (Wang et al. 2014a,b,c; De Oliveira et al. 2015; Govindhan et al. 2015; Mani et al. 2015). In the past few years, electrochemical sensor-based nanotubes have been issued as a very sensitive electroanalytical method for detection of pesticide residues at very low quantities (Herrero et al. 2012).

Electrochemical sensors have been grouped into seven different carbon nanotube-based techniques including (1) carbon nanotube sensors, (2) phthalocyanine, (3) molecularly imprinted polymers (MIP), (4) ionic liquid, (5) metallic nanoparticles, (6) β-cyclodextrin, and (7) fullerene (C60)-functionalized carbon nanotubes (Wong et al. 2017). Some studies indicated that the possible combined use of carbon nanotube-based sensors showed a noticeable improvement in the detection analytical signal (Herrero et al. 2012). One of the most interesting studies in pesticide nanosensor-based electrode detection was reported by Mercan and his co-workers. They determined that the cyromazine insecticide using a multi-walled carbon nanotube paste electrode by square-wave adsorptive stripping voltammetry was assayed (Mercan et al. 2011).

Other studies used glassy carbon electrodes and a pyrolytic graphite electrode modified with multi-walled carbon nanotubes and iron (II) tetra-aminophthalocyanine (MPc) in detection of amitrole and different pesticides (Ribeiro et al. 2011). Molecularly imprinted polymers (MIP) are also used due to their biomimetic recognition of analytes similar to selective enzyme-substrate systems and/or antigen-antibody interactions and functionalized in selective sensing of certain pesticides (Yaqub et al. 2011). Also, metallic nanomaterials like gold (AU), silver (Ag), and palladium (Pd) nanoparticles combined with multi-walled carbon nanotubes show significant interesting use in the electroanalytical chemistry as electrode modifiers for a set of important advantages that can be achieved (Zhang et al. 2009). In 2013, Torre-Roche and his co-workers reported the positive impact of using such new detection technology in pesticide residue assessment in different crop plants like zucchini, corn, tomato, and soybean (Torre-Roche et al. 2013). Continually, Wong et al. reported the most recent work related to pesticide electrochemical monitoring using carbon nanotube-based electrochemical sensors and expressed that electrochemical sensors based on carbon nanotubes have an efficient potential to analyze very minute amounts of pesticide residues directly on plant surface; this for sure will have a significant great value in food production and industry (Wong et al. 2017).

7.5.9 Agricultural Wastewater Treatment

Remediation of pollutants in agricultural areas is considered one of the major global challenges up to date. Different protocols worked up in this issue either by improvement the classical and conventional methods or by introducing other innovative approaches in a way to improve the pollutant remediation strategies for environmental sustainability. In history, activated carbon (AC) has already been used as good organic sorbent in wastewater treatments due to its unique ability to adsorb a broad spectrum of organic and inorganic contaminants. However, AC has slow adsorption kinetics; it is a nonspecific adsorbent and its effectiveness against microbes is relatively low. On the other hand, in heavy wastewater that was contaminated with oils, greases, and hard solids, carbon is not well active and may often cause pore blockage in it. Furthermore, activated carbon itself is frequently removed together with the adsorbed pollutants and therefore needs to be replaced in regular intervals. In this regard, carbon-based nanomaterials offer an attractive and promising alternative tool in improving wastewater filtration systems with numerous examples in the available literature (Liu et al. 2013a,b; Das et al. 2014a,b; Smith and Rodrigues 2015). More interestingly, Husen and Siddiqi stated that carbon nanotubes and fullerene have the potential to increase the water-retaining capacity, biomass, and fruit yield in plants up to 118% (Husen and Siddiqi 2014). Carbon nanotubes (CNTs) are the best example of carbon nanomaterials that have received wide attention due to their unique properties, like large specific surface area with high absorption potential, high thermal stability, and high chemical stability. Numerous reports revealed the high adsorption capacity of CNTs toward microcystins (cyanobacterial toxins) (Yan et al. 2006), lead (Li et al. 2002), and copper (III) (Dichiara et al. 2015), which are even stronger than that of activated carbon. Furthermore, they can be used for sorption of herbicides or nitrogen (N) and phosphorus (Ph) elements in wastewater (Zheng et al. 2014). On the other hand, fullerenes as well as CNTs exhibit a mobilization potential for various organic pollutants (Mishra and Clark 2013), such as lindane (agricultural insecticide) (Srivastava et al. 2011) and persistent polychlorinated biphenyls (Wang et al. 2013). Despite the significant merits offered by carbon nanomaterials (CNMs) compared to activated carbon including the unique high surface area, mechanical and thermal stability, high chemical affinity for aromatic compounds (Yoo et al. 2011), potential antimicrobial properties, and ability to adsorb contaminants, filters based on CNMs can be recycled (Wang et al. 2014a,b,c). However, certain challenges related to the production cost, difficulties in obtaining of CNTs with certain morphological characters including the size shape, diameter distribution, uncertainties regarding the leaching potential of CNTs, as well as ecological safety and human health issues, are still limitations for commercial applications in wastewater cleanup technologies. The list of some environmental pollutants that can be remediated by different types of nano-carbon was shown in Table 7.3.

7.5.10 Effect of Carbon Nanotubes on Soil Microorganisms

Different reports indicated that fullerene NPs had no significant antimicrobial potential against microbial diversity like Eubacteria and Kinetoplastida (protozoans) community structure on DGGE profiles (20–30% of dissimilarity) (Tong et al. 2007; Johansen et al. 2008). In contrast, in 2011, Boonyanitipong and his

Table 7.3 List of some pollutants that can be removed by different types of nano-carbon

Pollutants	Initial concentration	Carbon nanotube dose	pH	Removal efficiency	References
1,2-Dichloro-benzene	20 mgL^{-1}	0.5 gL^{-1}	3–10	30.8 and 28.7 mg g^{-1} for as grown and graphitized CNT in 40 min	Peng et al. (2003)
Aniline	0.1–10,000 mgL^{-1}	/	7	114.8 mg g^{-1}	Peng et al. (2003)
Atrazine	5 mgL^{-1}	4 gL^{-1}	5	0.956 mg g^{-1}	El-Sheikh et al. (2008)
Cd^{+2}	2–15 mgL^{-1}	0.5 gL^{-1}	5	10.86 mg g^{-1}	Li et al. (2003a)
Cd^{+2}	9.5 mgL^{-1}	0.5 gL^{-1}	7	1.1 mg g^{-1}	Li et al. (2003b)
$CHBr_2$	2 mgL^{-1}	0.33 gL^{-1}	3–11	0.92 mg g^{-1}	Lu and Chiu (2006)
$CHCl_2Br$	2 mgL^{-1}	0.33 gL^{-1}	3–11	1.23 mg g^{-1}	Lu and Chiu (2006)
$CHCl_3$	2 mgL^{-1}	0.33 gL^{-1}	3–11	2.41 mg g^{-1}	Lu and Chiu (2006)
$CHClBr_2$	2 mgL^{-1}	0.33 gL^{-1}	3–11	1.08 mg g^{-1}	Lu and Chiu (2006)
Co^{+2}	10 mgL^{-1}	5 gL^{-1}	9	More than 90%	Pyrzynska and Bystrzejewski (2010)
Cu^{+2}	10 mgL^{-1}	0.5 gL^{-1}	9	Nearly 100%	Pyrzynska and Bystrzejewski (2010)
Cu^{+2}	5–30 mgL^{-1}	0.5 gL^{-1}	5	28.49 mg g^{-1}	Li et al. (2003a)
Fluoride	12 mgL^{-1}	2 gL^{-1}	5–9	14.4 mg g^{-1}	Li et al. (2003a)
Methidathion	5 mgL^{-1}	4 gL^{-1}	5	1.11 mg g^{-1}	El-Sheikh et al. (2008)
Ni^{+2}	6–20 mgL^{-1}	0.3 gL^{-1}	6.55	9.8 mg g^{-1}	Chen and Wang (2006)
Pb^{+2}	10–80 mgL^{-1}	0.5 gL^{-1}	5	97.08 mg g^{-1}	Li et al. (2003a)
Pb^{+2}	2–14 mgL^{-1}	0.5 gL^{-1}	7	1 mg g^{-1}	Li et al. (2002)
Phenol	0.1–100,000 mgL^{-1}	/	7	64.6 mg g^{-1}	Li et al. (2002)
Propoxur	5 mgL^{-1}	4 gL^{-1}	5	0.625 mg g^{-1}	El-Sheikh et al. (2008)
Th (IV)	32.32 μmol L^{-1}	0.2 gL^{-1}	1.9	65.8 μmol g^{-1}	El-Sheik et al. (2008)
U (VI)	10^{-7}–10^{-4} M	1 gL^{-1}	4	5.0 mmol g^{-1}	Schierz and Zanker (2009)
Zn^{+2}	10–80 mgL^{-1}	0.5 gL^{-1}	7	10.21–11.23	Liu et al. (2006a,b)
Zn^{+2}	60 mgL^{-1}	0.5 gL^{-1}	1–5	37.03–46.94 mg g^{-1} and 30.3–34.36 mg g^{-1} from 5 to 45 C	Lu and Chiu (2006)

co-workers revealed that about 10 g kg^{-1} soil from MWCNT have the potential to improve the degraders of recalcitrant contaminants (PAH) *Rhodococcus*. Also, their results suggested that the flourishment of their bacterial community and its diversity is passively affected by the MWCNT particularly at the highest concentrations. Interestingly, it was found that there is no observed effect on the bacterial community by MWCNT after only 1 week. The scientist attributed this early effect to the acidic nature of the MWCNT used, which caused a significant decrease in soil pH at higher exposure concentrations, and consequently the soil bacterial community and its chemistry totally changed (Boonyanitipong et al. 2011). Their studies demonstrated that the bacterial community particularly *Cellulomonas*, *Nocardioides*, and *Pseudomonas* was not changed, while the flourishment of some bacterial genera like *Derxia*, *Holophaga*, *Opitutus*, and *Waddlia* was noticeably changed and decreased (Shrestha et al. 2013).

More interestingly and by following a meta genomic comparative analysis for the bacterial populations and their diversity, Khodakovskaya et al. observed that the bacterial diversity and their richness was not significantly affected by MWCNTs, while a noticeable modification in the bacterial composition and their species was reported (Khodakovskaya et al. 2013; Jin et al. 2014). Those results are in agreement with that reported at the same year by Rodrigues and his co-workers, where a noticeable modification in the fungal community and bacterial community was reported after only 2 weeks of soil exposure to SWCNT. On the other hand, Gurunathan (2015) demonstrated the negative effect of graphene oxide nanoparticles (GO NPs) on isolated *Rhizobacteria* from the soil (five *Bacillus* species: *B. megaterium*, *B. cereus*, *B. subtilis*, *B. mycoides*, and *B. marisflavi*). They reported that after 2 weeks, the soil bacterial community composition was affected by the multi-walled carbon nanotubes at the highest concentrations (Kerfahi et al. 2015).

7.6 Phytotoxicity

An increasing number of studies outlined the environmental impacts and the safety profile of carbon nanomaterials (Lin and Xing 2007; Stampoulis et al. 2009; Shen et al. 2010; Kaphle et al. 2017). Most of the phytotoxicity studies have examined germination, cell cultures, and genetic effects (Kaphle et al. 2017). Although carbon nanomaterials were evidenced to penetrate through seed coats, enter into the plant cells, and translocate into different plant parts more efficiently, some studies indicated that exposure to carbon nanomaterials decreases seed germination and root growth and changes the root architecture (Begum and Fugetsu 2012; Kaphle et al. 2017). Carbon nanomaterials inhibit seedling growth and change morphological, physiological, biochemical, molecular, nutritional, and genetic levels in plants (Gopalakrishnan Nair 2018). Also, it was reported that carbon nanotubes and fullerene can cause damage to plants (Shen et al. 2010; Begum and Fugetsu 2012). In 2009, Lin and his co-workers revealed that blossoming of rice plants incubated with C70 fullerene was delayed by at least 1 month and their seed-setting rate was reduced by 4.6% compared to the controls (Lin et al. 2009). Also, water-soluble fullerene inhibits plant growth and causes shortening of seedling roots and loss of gravitropism. These adverse effects may be caused by auxin disruption, abnormal cell division, and microtubule disorganization. Furthermore, fullerene effect on fruit and crop production in edible plants and vegetables increases the water-retaining capacity, biomass, and fruit yield in plants up to ~118%. The internalization and accumulation of these compounds in plant roots and seedlings and their phytotoxicity have been investigated by Liu et al. (2013a,b).

Wang et al. (2016) investigated the bioaccumulation of fullerenol (water-soluble derivative of fullerene carbon nanomaterial) nanoparticles in wheat using ^{13}C-labeling methods. Also, it was revealed by Ghosh and his co-workers that the internalization of multi-walled carbon nanotubes inside the plant cells results in chromosomal aberrations, DNA fragmentation, and apoptosis in *Allium* root cells (Ghosh et al. 2015). Shen et al. (2010) found that certain amounts of single-walled carbon nanotubes can induce the production of reactive oxygen species (ROS), which eventually leads to programmed cell death, in *Arabidopsis* leaves, and protoplasts. In red spinach (*Amaranthus tricolor* L.), phytotoxicity of multi-walled carbon nanotubes causes growth inhibition and cell death; multi-walled carbon nanotubes also cause ROS production and hypersensitive response-type necrotic lesions of leaf cells and tissues (Begum and Fugetsu 2012). Although plant cells and mammalian cells have different structures, such as the thick and rigid plant cell wall, chloroplasts, and large central vacuoles, they show similar responses to fullerene. The bioaccumulation of dichloro-diphenyl-dichloro-ethylene, a persistent and estrogenic pollutant, in some food crops such as zucchini, soybean, and tomato, increased in the presence of C60 fullerene (De La Torre-Roche et al. 2012; Avanasi et al. 2014). Avanasi and his co-workers have measured plant uptake of C60 fullerene and found that ^{14}C-labeled C60 can be slowly absorbed by plants and will likely persist in soil for a long period (Avanasi et al. 2014). The modifications induced by carboxy-fullerenes to the cell wall of tobacco plants such as the mechanism of interaction and survival under repression were analyzed. The adsorption of this component led to the disruption of the cell wall and membrane with the consequent inhibition of cell growth. A further study evidenced the ability of functionalized carbon nanotubes to penetrate the plant cell wall and induce changes in specific organelles. Also, the diameter and length of single-walled carbon nanotubes are the major restraining features for their effective penetration into the plant cell wall (Serag et al. 2013). Toxicity of carbon nanomaterials was found to be largely dependent on their concentrations, growth/exposure conditions, and plant species. Due to their smaller size and altered physical, chemical, and structural properties, the absorption and translocation of different types of carbon nanomaterials raise serious concerns about their toxic effects on plants and soil microorganisms. In conclusion, different reports on CNT toxicity and safety were carried out, and it was demonstrated as a functionalization that reduces toxic effects, while pristine CNTs induce different phytotoxic effects, but further investigations are needed. Some examples on the mechanism of phytotoxic effects of different carbon nanomaterials on different plant species were shown in Table 7.4.

Table 7.4 The mechanism of phytotoxic effects of different carbon nanomaterials on different plant species

Carbon NMs	Plant	Mechanism	References
Graphene oxide (GO)	*Arabidopsis*	Fragmented nuclei, membrane damage, and mitochondrial dysfunction	Begum and Fugetsu (2012)
	Faba bean	Concentration-dependent decrease in oxidative enzyme activity	Anjum et al. (2013)
Water-soluble graphene oxide (ws-GO)	Lettuce, cabbage, red spinach, tomato	Reduced plant growth, biomass, the number and size of leaves, increased ROS along with necrotic symptoms	Anjum et al. (2013)
CNTs	Red spinach	Growth inhibition, changes to tissue structure	Begum and Fugetsu (2012)
MWCNTs	Rice cells	Increased ROS generation and decreased cell viability	Tan et al. (2009)
	Rice	Delayed flowering and seed setting. Reduced seed weight	Lin et al. (2009)
	Rice	Chromatin condensed inside the cytoplasm and caused cell death, plasma membrane detachment from cell wall and cell shrinkage	Tan et al. (2009)
	Zucchini	Negatively affected biomass production and transpiration	Stampoulis et al. (2009)
	Wheat	Enhanced the uptake of phenanthrene to the living cells	Wild and Jones (2009)
	Onion	Chromosomal aberrations, DNA fragmentation, and apoptosis in root cells	Ghosh et al. (2015)
	Onobrychis	Enhanced the POD activity	Smirnova et al. (2012)
ws-C70	Tobacco BY-2 cells	Cell boundary disruption and growth inhibition	Liu et al. (2013a,b)

7.7 Conclusion and Future Perspectives

Carbon nanotechnology has the potential to be exploited in different advanced applications in agriculture which finds use in biology, plant protection, medicine, and chemical engineering. Carbon-based nanomaterials are some of the best examples that find their application starting from increased crop yield, passing by organelle-targeted gene delivery, and ending with wastewater treatment and nanopesticide and antimicrobial pesticide extraction and detection. The antimicrobial effect of CNMs either on microbial pathogens or on soil microbiota together with the analytical-based information of the ecological interaction between those nanomaterials and organic/inorganic matter present in soil can introduce significant information in a more relevant context of a biological "realistic" scenario or will reduce the gap between experimental and environmental conditions.

On the other hand, carbon-based nanomaterials may also be helpful for the advancement of agriculture and plant protection. But in some cases, they may act a negative behavior in certain concentration that may be controlled within the permissible limit to prevent any damage. Furthermore, the insufficient information, their fate, and effects in the environment produce non-accurate assessment of their risk, which is necessary before their widespread application in agriculture generally and plant protection specifically. In some cases, carbon nanotubes were used in a modified form, by adding conductive polymers, metallic nanoparticles, phthalocyanines, porphyrins, ionic liquids, and graphene. These diverse modified nano-carbon composite electrodes are efficiently enrolled in different electroanalysis purposes, and future electrochemical investigations should be carried out on the sensing and biosensing of pesticides. As a result, more comprehensive investigations of chronic exposure under environmentally realistic scenarios will be needed at first to enable such efforts. In conclusion, we assume that carbon-based nanomaterials will find soon a fairly bright future in agriculture fields, introducing an economic solution for critical agronomic problems in a way to improve crop production and reduce the food loss.

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References

Al-Hakami SM, Khalil AB, Laoui T, Atieh MA (2013) Fast disinfection of Escherichia coli bacteria using carbon nanotubes interaction with microwave radiation. Bioinorg Chem Appl 45:8943

Andreas H (2002) Functionalization of single-walled carbon nanotubes. Angew Chem Int Ed 41:1853–1859

Anjum NA, Gill SS, Duarte AC, Pereira E, Ahmad I (2013) Silver nanoparticles in soil–plant systems. J Nanopart Res 15(9):1896

Asgari P, Moradi O, Tajeddin B (2014) The effect of nanocomposite packaging carbon nanotube base on organoleptic and fungal growth of mazafati brand dates. Int Nano Lett 4:1–5

Avanasi R, Jackson WA, Sherwin B, Mudge JF, Anderson TA (2014) C60 fullerene soil sorption, biodegradation, and plant uptake. Environ Sci Technol 48(5):2792–2797

Bai L, Bossa N, Qu F, Winglee J, Li G, Sun K, Liang H, Wiesner MR (2017) Comparison of hydrophilicity and mechanical properties of nanocomposite membranes with cellulose nanocrystals and carbon nanotubes. Environ Sci Technol 51:253–262

Bakajin O, Noy A, Fornasiero F, Grigoropoulos CP, Holt JK, In JB, Kim S, Park HG (2009) Nanofluidics carbon nanotube membranes: applications for water purification and desalination. In: Savage NF (ed) Nanotechnology applications for clean water. William Andrew Inc., Norwich, NY, pp 77–93

Begum P, Fugetsu B (2012) Phytotoxicity of multi-walled carbon nanotubes on red spinach (*Amaranthus tricolor* L.) and the role of ascorbic acid as an antioxidant. J Hazard Mater 243:212–222

Begum P, Ikhtiari R, Fugetsu B (2014) Potential impact of multi-walled carbon nanotubes exposure to the seedling stage of selected plant species. Nanomaterials 4(2):203–221

Biris AS, Khodakovskaya M (2011) Method of using carbon nanotubes to affect seed germination and plant growth. WO 2011059507

Boonyanitipong P, Kositsup B, Kumar P, Baruah S, Dutta J (2011) Toxicity of ZnO and TiO_2 nanoparticles on germinating rice seed *Oryza sativa* L. Int J Biosci Biochem Bioinforma 1:282–285

Burlaka OM, Pirko YV, Yemets AI, Blume YB (2015) Plant genetic transformation using carbon nanotubes for DNA delivery. Cytol Genet 49:349–357

Cañas JE, Long M, Nations S, Vadan R, Dai L, Luo M, Ambikapathi R, Lee H, Olszyk D (2008) Effects of functionalized and nonfunctionalized single-walled carbon nanotubes on root elongation of select crop species. Environ Toxicol Chem 27:1922–1931

Chai M, Shi F, Li R, Liu L, Liu Y, Liu F (2013) Interactive effects of cadmium and carbon nanotubes on the growth and metal accumulation in a halophyte Spartina alterniflora (Poaceae). Plant Growth Regul 71:171–179

Chen C, Wang X (2006) Adsorption of Ni (II) from aqueous solution using oxidized multiwall carbon nanotubes. Ind Eng Chem Res 45:9144–9149

Churilov GN (2008) Synthesis of fullerenes and other nanomaterials in arc discharge. Fullerenes, Nanotubes, Carbon Nanostruct 16:395–403

Damalas CA, Eleftherohorinos IG (2011) Pesticide exposure safety issues, and risk assessment indicators. Int J Environ Res Public Health 8:1402–1419

Das R, Abd Hamid SB, Ali ME, Ismail AF, Annuar MSM, Ramakrishna S (2014a) Multifunctional carbon nanotubes in water treatment: the present, past and future. Desalination 354:160–179

Das R, Ali ME, Hamid SBA, Ramakrishna S, Chowdhury ZZ (2014b) Carbon nanotube membranes for water purification: a bright future in water desalination. Desalination 336:97–109

De La Torre-Roche R, Hawthorne J, Deng Y, Xing B, Cai W, Newman LA, Wang C, Ma X, White JC (2012) Fullerene-enhanced accumulation of p,p'-DDE in agricultural crop species. Environ Sci Technol 46(17):9315–9323

De Oliveira R, Hudari F, Franco J, Zanoni MVB (2015) Carbon nanotube-based electrochemical sensor for the determination of anthraquinone hair dyes in wastewaters. Chemosensors 3:22–35

Dichiara AB, Webber MR, Gorman WR, Rogers RE (2015) Removal of copper ions from aqueous solutions via adsorption on carbon nanocomposites. ACS Appl Mater Interface 7:15674–15680

El-Sheikh AH, Sweileh JA, Al-Degs YS, Insisi AA, Al-Rabady N (2008) Critical evaluation and comparison of enrichment efficiency of multi-walled carbon nanotubes, C18 silica and activated carbon towards some pesticides from environmental waters. Talanta 74:1675–1680

Eun AJC, Wong SM (2000) Molecular beacons: a new approach to plant virus detection. Phytopathology 90(3):269–275

European Commission (2011) European commission recommendations (2011) on the definition of nanomaterial. Off J Eur Union 54:38–40

Fan LL, Wang YH, Shao XW, Geng YQ, Wang ZC, Ma Y, Liu J (2012) Effects of combined nitrogen fertilizer and nano-carbon application on yield and nitrogen use of rice grown on saline alkali soil. J Food Agric Environ 10:558–562

Fang Y, Ramasamy RP (2015) Current and prospective methods for plant disease detection. Biosensors 5(3):537–561

Fathi Z, Nejad R-AK, Mahmoodzadeh H, Satari TS (2017) Investigating of a wide range of concentrations of multi-walled carbon nanotubes on germination and growth of castor seeds (*Ricinus communis* L.). J Plant Prot Res 57:228–236

Fernández-Baldo MA, Messina GA, Sanz MI, Raba J (2009) Screen-printed immunosensor modified with carbon nanotubes in a continuous-flow system for the *Botrytis cinerea* determination in apple tissues. Talanta 79(3):681–686

Fernández-Baldo MA, Messina GA, Sanz MI, Raba J (2010) Microfluidic immunosensor with micromagnetic beads coupled to carbon-based screen-printed electrodes (SPCEs) for determination of *Botrytis cinerea* in tissue of fruits. J Agric Food Chem 58(21):1201–11206

Flores D, Chacón R, Alvarado L, Schmidt A, Alvarado C, Chaves J (2014) Effect of using two different types of carbon nanotubes for blackberry (*Rubus adenotrichos*) in vitro plant rooting, growth and histology. Am J Plant Sci 5:3510–3518

Fosso-Kankeu E, De Klerk CM, Botha TA, Waanders F, Phoku J, Pandey S (2016) The antifungal activities of multi-walled carbon nanotubes decorated with silver, copper and zinc oxide particles. In: International conference on advances in science, engineering, technology and natural resources (ICASETNR-16), Parys, South Africa, 24–25 November 2016, pp 55–59

Ghodake G, Seo YD, Park D, Lee DS (2010) Phytotoxicity of carbon nanotubes assessed by *Brassica juncea* and *Phaseolus mungo*. J Nanoelectron Optoelectron 5(2):157–160

Gholipour Y, Erra-Balsells R, Nonami H (2012) Integrative analysis of physiological phenotype of plant cells by turgor measurement and metabolomics. Eng Lett 20(4):EL01

Ghosh M, Bhadra S, Adegoke A, Bandyopadhyay M, Mukherjee A (2015) MWCNT uptake in Allium cepa root cells induces cytotoxic and genotoxic responses and results in DNA hyper methylation. Mutat Res 774:49–58

Giraldo JP, Landry MP, Kwak S, Jain RM, Wong MH, Iverson NM, Ben-Naim M, Strano MS (2015) A ratiometric sensor using single chirality near infrared fluorescent carbon nanotubes: application to in vivo monitoring. Small 32:3973–3984

Gogos A, Knauer K, Bucheli TD (2012) Nanomaterials in plant protection and fertilization: current state, foreseen applications, and research priorities. J Agric Food Chem 60:9781–9792

Gopalakrishnan Nair PM (2018) Toxicological impact of carbon nanomaterials on plants. In: Gothandam K, Ranjan S, Dasgupta N, Ramalingam C, Lichtfouse E (eds) Nanotechnology, food security and water treatment. Environmental chemistry for a sustainable world. Springer, Cham

Gorczyca A, Kasprowicz MJ, Lemek T (2009) Physiological effect of multi–walled carbon nanotubes MWCNTs on conidia of the entomopathogenic fungus, *Paecilomyces fumosoroseus* Deuteromycotina, Hyphomycetes. J Environ Sci Health A 44(14):1592–1597

Gore JP, Sane A (2011) Flame synthesis of carbon nanotubes. INTECH Open Access Publisher, Rijeka

Govindhan M, Lafleur T, Adhikari BR, Chen A (2015) Electrochemical sensor based on carbon nanotubes for the simultaneous detection of phenolic pollutants. Electroanalysis 27(4):902–909

Gu J, Xiao P, Zhang L, Lu W, Zhang G, Huang Y, Zhang J, Chen T (2016) Construction of superhydrophilic and under-water superoleophobic carbon-based membranes for water purification. RSC Adv 6:73399–73403

Gurunathan S (2015) Cytotoxicity of graphene oxide nanoparticles on plant growth promoting rhizobacteria. J Ind Eng Chem 32:282–291

Haghighi M, da Silva TJA (2014) Effect of N-TiO_2 on tomato, onion and radish seed germination. J Crop Sci Biotechnol 17:221–227

Hajihosseini S, Nasirizadeh N, Hejazi MS, Yaghmaei P (2016) A sensitive DNA biosensor fabricated from gold nanoparticles and graphene oxide on a glassy carbon electrode. Mater Sci Eng C 61:506–515

Hasaneen MNA, Abdel-Aziz HMM, Omer AM (2017) Characterization of carbon nanotubes loaded with nitrogen, phosphorus and potassium fertilizers. Am J Nano Res Appl 5(2):12–18

Hernandez-Fernandez P, Montiel M, Ocón P, de la Fuente JLG, Garcia-Rodriguez S, Rojas S, Fierro JL (2010) Functionalization of multi-walled carbon nanotubes and application as supports for electrocatalysts in proton exchange membrane fuel cell. Appl Catal B 99:343–352

Herrero M, Simó C, García-Cañas V, Ibáñez E, Cifuentes A (2012) Foodomics: MS-based strategies in modern food science and nutrition. Mass Spectrom Rev 31:49–69

Hilding J, Grulke EA, Sinnot SB, Qian D, Andrews R, Jagtoyen M (2001) Sorption of butane on carbon multiwall nanotubes at room temperature. Langmuir 17:7540–7544

Hirsch A, Vostrowsky O (2005) Functionalization of carbon nanotubes. Top Curr Chem 245:193–237

Hu X, Zhou Q (2014) Novel hydrated graphene ribbon unexpectedly promotes aged seed germination and root differentiation. Sci Rep 4:3782

Hunter RJ (2001) Foundation of colloid science, 2nd edn. Oxford University Press, Oxford; New York

Husen A, Siddiqi KS (2014) Carbon and fullerene nanomaterials in plants system. J Nanobiotechnology 12:1–10

Iijima S (1991) Helical microtubules of graphitic carbon. Nature 354:56

Ikhtiar R, Begum P, Watari F, Fugetsu B (2013) Toxic effect of multiwalled carbon nanotubes on lettuce (*Lactuca sativa*). Nano Biomed 5:18–24

Ilkhani H, Hughes T, Li J, Zhong CJ, Hepel M (2016) Nanostructured SERS electrochemical biosensors for testing of anticancer drug interactions with DNA. Biosens Bioelectron 80:257–264

Ivnitski D, Abdel-Hamid I, Atanasov P, Wilkins E, Stricker S (2000) Application of electrochemical biosensors for detection of food pathogenic bacteria. Electroanalysis 12(5):317–325

Jiao L, Zhang L, Wang X, Diankov G, Dai H (2009) Narrow graphene nanoribbons from carbon nanotubes. Nature 458:877–880

Jin L, Son Y, DeForest JL, Kang YJ, Kim W, Chung H (2014) Single-walled carbon nanotubes alter soil microbial community composition. Sci Total Environ 446:533–538

Johansen A, Pedersen AL, Jensen KA, Karlson U et al (2008) Effects of C60 fullerene nanoparticles on soil bacteria and protozoans. Environ Toxicol Chem 27:1895–1903

Joshi N, Jain N, Pathak A, Singh J, Prasad R, Upadhyaya CP (2018) Biosynthesis of silver nanoparticles using Carissa carandas berries and its potential antibacterial activities. J Sol-Gel Sci Techn. https://doi.org/10.1007/s10971-018-4666-2

Jung JH, Hwang GB, Lee JE, Bae GN (2011) Preparation of airborne Ag/CNT hybrid nanoparticles using an aerosol process and their application to antimicrobial air filtration. Langmuir 27:10256–10264

Kaphle A, Navya PN, Umapathi A, Chopra M, Daima HK (2017) Nanomaterial impact, toxicity and regulation in agriculture, food and environment. In: Ranjan S et al (eds) Nanoscience in food and agriculture 5. Sustainable agriculture reviews, vol 26. Springer International Publishing AG, Cham, pp 205–242. https://doi.org/10.1007/978-3-319-58496-6_8

Kerfahi D, Tripathi BM, Singh D, Kim H, Lee S, Lee J, Adams JM (2015) Effects of functionalized and raw multi-walled carbon nanotubes on soil bacterial community composition. PLoS One 10(3):e0123042

Khodakovskaya M, Dervishi E, Mahmood M, Xu Y, Li Z, Watanabe F, Biris AS (2009) Carbon nanotubes are able to penetrate plant seed coat and dramatically affect seed germination and plant growth. Am Chem Soc 3(10):3221–3227

Khodakovskaya MV, de Silva K, Biris AS, Dervishi E, Villagarcia H (2012) Carbon nanotubes induce growth enhancement of tobacco cells. Am Chem Soc Nano 6(3):2128–2135

Khodakovskaya MV, Kim BS, Kim JN, Alimohammadi M, Dervishi E, Mustafa T, Cernigla CE (2013) Carbon nanotubes as plant growth regulators: effects on tomato growth, reproductive system, and soil microbial community. Small 9:115–123

Kole C, Kole P, Randunu KM, Choudhary P, Podila R, Ke PC, Rao AM, Marcus RK (2013) Nanobiotechnology can boost crop production and quality: first evidence from increased plant biomass, fruit yield and phytomedicine content in bitter melon (Momordica charantia). BMC Biotechnol 13(13):37

Kratschmer W (2011) The story of making fullerenes. Nanoscale 3:2485–2489

Kratschmer W, Lamb LD, Fostiropoulos K, Huffman DR (1990) Solid C60: a new form of carbon. Nature 347:354–358

Kroto HW, Heath JR, O'Brien SC, Curl RF, Smalley RE (1985) C60: buckminsterfullerene. Nature 318:162–163

Kumar M, Ando Y (2010) Chemical vapor deposition of carbon nanotubes: a review on growth mechanism and mass production. J Nanosci Nanotechnol 10:3739–3758

Lahiani MH, Chen J, Irin F, Puretzky AA, Green MJ, Khodakovskaya MV (2015) Interaction of carbon nanohorns with plants: uptake and biological effects. Carbon 81:607–619

Li H, Guan Y (2011) Foliar fertilizer containing carbon nanoparticles for plants under stress conditions. CN 102030595

Li Y, Wang S, Wei J, Zhang X, Xu C, Luan Z, Wu D, Wei B (2002) Lead adsorption on carbon nanotubes. Chem Phys Lett 357:263–266

Li YH, Ding J, Luan Z, Di Z, Zhu Y, Xu C, Wu D, Wei B (2003a) Competitive adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from aqueous solutions by multiwalled carbon nanotubes. Carbon 41:2787–2792

Li YH, Wang S, Luan Z, Ding J, Xu C, Wu D (2003b) Adsorption of cadmium(II) from aqueous solution by surface oxidized carbon nanotubes. Carbon 41:1057–1062

Lin D, Xing B (2007) Phytotoxicity of nanoparticles: inhibition of seed germination and root growth. Environ Pollut 150(2):243–250

Lin S, Reppert J, Hu Q, Hudson JS, Reid ML, Ratnikova TA, Rao AM, Luo H, Ke PC (2009) Uptake, translocation, and transmission of carbon nanomaterials in rice plants. Small 5:1128

Liu Y, Wangquan T (2012) Special fertilizer for rapeseed base fertilizer. CN 102816021
Liu F, Wen LX, Li ZZ, Yu W, Sun HY, Chen JF (2006a) Porous hollow silica nanoparticles as controlled delivery system for water soluble pesticide. Mater Res Bull 41:2268–2275
Liu X, Feng Z, Zhang S, Zhang J, Xiao Q, Wang Y (2006b) Preparation and testing of cementing nano-subnano composites of slow- or controlled release of fertilizers. Sci Agric Sin 39:1598–1604
Liu Q, Chen B, Wang Q, Shi X, Xiao Z, Lin J, Fang X (2009) Carbon nanotubes as molecular transporters for walled plant cells. Nano Lett 9:1007–1010
Liu Q, Zhang X, Zhao Y, Lin J, Shu C, Wang C, Fang X (2013a) Fullerene-induced increase of glycosyl residue on living plant cell wall. Environ Sci Technol 47:7490–7498
Liu X, Wang M, Zhang S, Pan B (2013b) Application potential of carbon nanotubes in water treatment: a review. J Environ Sci (China) 25:1263–1280
Liu J, Li X, Jia W, Ding M, Zhang Y, Ren S (2016) Separation of emulsified oil from oily wastewater by functionalized multiwalled carbon nanotubes. J Dispers Sci Technol 37:1294–1302
Lu C, Chiu H (2006) Adsorption of zinc(II) from water with purified carbon nanotubes. Chem Eng Sci 61:1138–1145
Ma X, Geiser-Lee J, Deng Y, Kolmakov A (2010) Interactions between engineered nanoparticles (ENPs) and plants: phytotoxicity, uptake and accumulation. Sci Total Environ 408(16):3053–3061
Mani S, Cheemalapati S, Chen SM, Devadas B (2015) Anti-tuberculosis drug pyrazinamide determination at multiwalled carbon nanotubes/graphene oxide hybrid composite fabricated electrode. Int J Electrochem Sci 10:7049–7062
Matsuzawa Y, Takada Y, Kodaira T, Kihara H, Kataura H, Yoshida M (2014) Effective nondestructive purification of single-walled carbon nanotubes based on high-speed centrifugation with a photochemically removable dispersant. J Phys Chem C 118:5013–5019
Mauter M, Elimelech M (2008) Environmental applications of carbon-based nanomaterials. Environ Sci Technol 42:5843–5859
Mercan H, Inam R, Aboul-Enein HY (2011) Square wave adsorptive stripping voltammetric determination of cyromazine insecticide with multi-walled carbon nanotube paste electrode. Anal Lett 44:1392–1404
Milne WI, Teo KBK, Amaratunga GAJ, Legagneux P, Ganglof L, Schnell JP, Semet V, Binh VT, Groening O (2004) Carbon nanotubes as field emission sources. J Mater Chem 14:933–943
Miralles P, Johnson E, Church TL, Harris AT (2012) Multiwalled carbon nanotubes in alfalfa and wheat: toxicology and uptake. J R Soc Interface 9:3514–3527
Mishra A, Clark JH (2013) Green materials for sustainable water remediation and treatment. Royal Society of Chemistry, Cambridge
Mondal A, Basu R, Das S, Nandy P (2011) Beneficial role of carbon nanotubes on mustard plant growth: an agricultural prospect. J Nanopart Res 13(10):4519
Morla S, Ramachandra Rao CSV, Chakrapani R (2011) Factors affecting seed germination and seedling growth of tomato plants cultured in vitro conditions. J Chem Biol Phys Sci B 1:328
Morsy M, Helal M, El-Okr M, Ibrahim M (2014) Preparation, purification and characterization of high purity multi-wall carbon nanotube. Spectrochim Acta A Mol Biomol Spectrosc 132:594–598
Nair R, Varghese SH, Nair BG, Maekawa T, Yoshida Y, Kumar DS (2010) Nanoparticulate material delivery to plants. Plant Sci 179:154
Nair R, Mohamed SM, Gao W, Maekawa T, Yoshida Y, Ajayan PM, Kumar DS (2012) Effect of carbon nanomaterials on the germination and growth of rice plants. J Nanosci Nanotechnol 12:2212–2220
Nalwade AR, Neharkar SB (2013) Carbon nanotubes enhance the growth and yield of hybrid Bt cotton Var. ACH-177-2. Int J Adv Sci Technol Res 3:840
Namasivayam M, Shapter J (2017) Factors affecting carbon nanotube fillers towards enhancement of thermal conductivity in polymer nanocomposites: a review. J Compos Mater 51:3657–3668

Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA (2004) Electric field effect in atomically thin carbon films. Science 306:666–669
Novoselov KS, Fal'Ko VI, Colombo L, Gellert PR, Schwab MG, Kim K (2012) A roadmap for graphene. Nature 490:192–200
Oleszczuk P, Josko I, Xing BS (2011) The toxicity to plants of the sewage sludges containing multiwalled carbon nanotubes. J Hazard Mater 186:436–442
Oyelami AO, Semple KT (2015) Impact of carbon nanomaterials on microbial activity in soil. Soil Biol Biochem 86:172–180
Patel N, Desai P, Patel N, Jha A, Gautam HK (2014) Agronanotechnology for plant fungal disease management: a review. Int J Curr Microbiol Appl Sci 3(10):71–84
Peng X, Li Y, Luan Z, Di Z, Wang H, Tian B, Jia Z (2003) Adsorption of 1,2-dichlorobenzene from water to carbon nanotubes. Chem Phys Lett 376:154–158
Pereira A, Grillo R, Mello NF, Rosa AH, Fraceto LF (2014) Application of poly(epsilon-caprolactone) nanoparticles containing atrazine herbicide as an alternative technique to control weeds and reduce damage to the environment. J Hazard Mater 268:207–215
Pourkhaloee A, Haghighi M, Saharkhiz MJ, Jouzi H, Doroodmand MM (2011) Carbon nanotubes can promote seed germination via seed coat penetration. J Seed Technol 33(2):155–169
Prasad R, Kumar V, Prasad KS (2014) Nanotechnology in sustainable agriculture: present concerns and future aspects. Afr J Biotechnol 13(6):705–713
Prasad R, Bhattacharyya A, Nguyen QD (2017a) Nanotechnology in sustainable agriculture: recent developments, challenges, and perspectives. Front Microbiol 8:1014. https://doi.org/10.3389/fmicb.2017.01014
Prasad R, Gupta N, Kumar M, Kumar V, Wang S, Abd-Elsalam KA (2017b) Nanomaterials act as plant defense mechanism. In: Prasad R, Kumar V, Kumar M (eds) Nanotechnology. Springer, Singapore, pp 253–269
Pyrzyńska K, Bystrzejewski M (2010) Comparative study of heavy metal ions sorption onto activated carbon, carbon nanotubes, and carbon-encapsulated magnetic nanoparticles. Colloids Surf A 362:102–109
Rasool K, Lee DS (2015) Influence of multi-walled carbon nanotubes on anaerobic biological sulfate reduction processes. J Nanoelectron Optoelectron 10:485–489
Ribeiro WF, Selva TMG, Lopes IC, Coelho ECS, Lemos SG, de Abreu FC, do Nascimento VB, de Araújo MCU (2011) Electroanalytical determination of carbendazim by square wave adsorptive stripping voltammetry with a multiwalled carbon nanotubes modified electrode. Anal Methods 3:1202–1206
Saito R, Dresselhaus G, Dresselhaus MS (1998) Physical properties of carbon nanotubes. Imperial College Press, London
Sangeetha J, Thangadurai D, Hospet R, Purushotham P, Manowade KR, Mujeeb MA, Mundaragi AC, Jogaiah S, David M, Thimmappa SC, Prasad R, Harish ER (2017a) Production of bionanomaterials from agricultural wastes. In: Prasad R, Kumar M, Kumar V (eds) Nanotechnology. Springer Nature Singapore Pte Ltd, Singapore, pp 33–58
Sangeetha J, Thangadurai D, Hospet R, Harish ER, Purushotham P, Mujeeb MA, Shrinivas J, David M, Mundaragi AC, Thimmappa AC, Arakera SB, Prasad R (2017b) Nanoagrotechnology for soil quality, crop performance and environmental management. In: Prasad R, Kumar M, Kumar V (eds) Nanotechnology. Springer Nature Singapore Pte Ltd, Singapore, pp 73–97
Sarlak N, Taherifar A, Salehi F (2014) Synthesis of nanopesticides by encapsulating pesticide nanoparticles using functionalized carbon nanotubes and application of new nanocomposite for plant disease treatment. J Agric Food Chem 62:4833–4838
Sarno M, Tamburrano A, Arurault L, Fontorbes S, Pantani R, Datas L, Ciambelli P, Sarto MS (2013) Electrical conductivity of carbon nanotubes grown inside a mesoporous anodic aluminium oxide membrane. Carbon 55:10–22
Saurabh S, Bijendra KS, Yadav SM, Gupta AK (2015) Applications of nanotechnology in agricultural and their role in disease management. J Nanosci Nanotechnol 5:1–5

Schierz A, Zanker H (2009) Aqueous suspensions of carbon nanotubes: surface oxidation, colloidal stability and uranium sorption. Environ Pollut 157:1088–1094

Schmitt H, Creton N, Prashantha K, Soulestin J, Lacrampe MF, Krawczak P (2015) Melt-blended halloysite nanotubes/wheat starch nanocomposites as drug delivery system. Polym Eng Sci 55:573–580

Sekhon BS (2014) Nanotechnology in agri-food production: an overview. Nanotechnol Sci Appl 7:31–53

Serag MF, Kaji N, Gaillard C, Okamoto Y, Terasaka K, Jabasini M, Tokeshi M, Mizukami H, Bianco A, Baba Y (2011) Trafficking and subcellular localization of multiwalled carbon nanotubes in plant cells. ACS Nano 5:493–499

Serag MF, Kaji N, Habuchi S, Bianco A, Baba Y (2013) Nanobiotechnology meets plant cell biology: carbon nanotubes as organelle targeting nanocarriers. RSC Adv 3:4856–4862

Serag MF, Kaji N, Tokeshi M, Baba Y (2015) Carbon nanotubes and modern nanoagriculture. In: Siddiqui M, Al-Whaibi M, Mohammad F (eds) Nanotechnology and plant sciences. Springer, Cham, pp 183–201

Sharon M, Choudhary AK, Kumar R (2010) Nanotechnology in agricultural diseases and food safety. J Phytology 2(4):83–92

Shen CX, Zhang QF, Li J, Bi FC, Yao N (2010) Induction of programmed cell death in Arabidopsis and rice by single-wall carbon nanotubes. Am J Bot 97:1602–1609

Shrestha B, Acosta-Martinez V, Cox SB, Green MJ, Li S, Canas-Carrell JE (2013) An evaluation of the impact of multiwalled carbon nanotubes on soil microbial community structure and functioning. J Hazard Mater 261:188–197

Singh A, Bhati A, Gunture, Tripathi KM, Sonkar SM (2017) Nanocarbons in agricultural plants: can be a potential nanofertilizer? In: Hussain CM, Mishra AK (eds) Nanotechnology in environmental science, vol 2 Volumes. Wiley, Newark, NJ; Weinheim

Smirnova EA, Gusev AA, Zaitseva ON, Lazareva EM, Onishchenko GE, Kuznetsova EV, Tkachev AG, Feofanov AV, Kirpichnikov MP (2011) Multi-walled carbon nanotubes penetrate into plant cells and affect the growth of Onobrychis arenaria seedlings. Acta Nat 3(1):99–106

Smirnova E, Gusev A, Zaytseva O, Sheina O, Tkachev A, Kuznetsova E, Kirpichnikov M (2012) Uptake and accumulation of multiwalled carbon nanotubes change the morphometric and biochemical characteristics of *Onobrychis arenaria* seedlings. Front Chem Sci Eng 6(2):132–138

Smith SC, Rodrigues DF (2015) Carbon-based nanomaterials for removal of chemical and biological contaminants from water: a review of mechanisms and applications. Carbon 91:122–143

Srinivasan C, Saraswathi R (2010) Nano-agriculture-carbon nanotubes enhance tomato seed germination and plant growth. Curr Sci 99:273–275

Srivastava A, Rao DP (2014) Enhancement of seed germination and plant growth of whest, maize, peanut and garlic using multiwalled carbon nanotubes, enhancement of plant growth using multi-walled carbon nanotubes. Eur Chem Bull 3(5):502–504

Srivastava M, Abhilash PC, Singh N (2011) Remediation of lindane using engineered nanoparticles. J Biomed Nanotechnol 7:172–174

Stampoulis D, Sinha SK, White JC (2009) Assay dependent phytotoxicity of nanoparticles to plants. Environ Sci Technol 43:9473–9479

Suvarnaphaet P, Pechprasarn S (2017) Graphene-based materials for biosensors: a review. Sensors 17(10):2161

Taha RA (2016) Nano carbon applications for plant. Adv Plants Agric Res 5(2):00172

Tan XM, Lin C, Fugetsu B (2009) Studies on toxicity of multi-walled carbon nanotubes on suspension rice cells. Carbon 47:3479–3487

Tiwari DK, Dasgupta-Schubert N, Villasenor Cendejas LM, Villegas J, Carreto Montoya L, Borjas García SE (2014) Interfacing carbon nanotubes (CNT) with plants: enhancement of growth, water and ionic nutrient uptake in maize (Zea mays) and implications for nanoagriculture. Appl Nanosci 4(5):577–591

Tong Z, Bischoff M, Nies L, Applegate B, Turco RF (2007) Impact of fullerene (C60) on a soil microbial community. Environ Sci Technol 41:2985–2991

Torney F, Trewyn B, Lin VSY, Wang K (2007) Mesoporous silica nanoparticle deliver DNA and chemicals into plant. Nat Nanotechnol 2:295–300

Torre-Roche RDL, Hawthorne J, Deng Y, Xing B, Cai W, Newman LA, Wang Q, Ma X, Hamdi H, White JC (2013) Multiwalled carbon nanotubes and C60 fullerenes differentially impact the accumulation of weathered pesticides in four agricultural plants. Environ Sci Technol 47:12539–12547

Tripathi S, Sarkar S (2015) Influence of water soluble carbon dots on the growth of wheat plant. Appl Nanosci 5:609–619

Tripathi BP, Shahi VK (2011) Organic–inorganic nanocomposite polymer electrolyte membranes for fuel cell applications. Prog Polym Sci 36(7):945–979

Upadhyayula VKK, Deng S, Mitchell MC, Smith GB (2009) Application of carbon nanotube technology for removal of contaminants in drinking water: a review. Sci Total Environ 408:1–13

Villagarcia H, Dervishi E, de Silva K, Biris AS, Khodakovskaya MV (2012) Surface chemistry of carbon nanotubes impacts the growth and expression of water channel protein in tomato plants. Small 8(15):2328–2334

Wang YY, Hsu PK, Tsay YF (2012) Uptake, allocation and signaling of nitrate. Trends Plant Sci 17(8):458–467

Wang L, Fortner JD, Hou L, Zhang C, Kan AT, Tomson MB, Chen W (2013) Contaminant-mobilizing capability of fullerene nanoparticles (nC60): effect of solvent-exchange process in nC60 formation. Environ Toxicol Chem 32:329–336

Wang H, Ma H, Zheng W, An D, Na C (2014a) Multifunctional and recollectable carbon nanotube ponytails for water purification. ACS Appl Mater Interfaces 6:9426–9434

Wang T, Zhao D, Guo X, Correa J, Riehl BL, Heineman WR (2014b) Carbon nanotube-loaded nafion film electrochemical sensor for metal ions: europium. Anal Chem 86:4354–4361

Wang X, Liu X, Chen J, Han H, Yuan Z (2014c) Evaluation and mechanism of antifungal effects of carbon nanomaterials in controlling plant fungal pathogen. Carbon 68:798–806

Wang C, Zhang H, Ruan L, Chen L, Li H, Chang XL, Zhang X, Yang ST (2016) Bioaccumulation of 13C-fullerenol nanomaterials in wheat. Environ Sci Nano 3:799–805

Wang X, Zhou Z, Chen F (2017) Surface modification of carbon nanotubes with an enhanced antifungal activity for the control of plant fungal pathogen. Materials 10:1375. https://doi.org/10.3390/ma10121375

Wild E, Jones KC (2009) Novel method for the direct visualization of in vivo nanomaterials and chemical interactions in plants. Environ Sci Technol 43:5290–5294

Wong A, Silva TA, Caetano FR, Bergamini MF, Marcolino-Junior LH, Fatibello-Filho O, Janegitz BC (2017) An overview of pesticide monitoring at environmental samples using carbon nanotubes-based electrochemical sensors. J Carbon Res 3:8. https://doi.org/10.3390/c3010008

Wu M (2013) Effects of incorporation of nano-carbon into slow-released fertilizer on rice yield and nitrogen loss in surface water of paddy soil. Adv J Food Sci Technol 5:398–403 https://doi.org/10.1109/isdea.2012.161

Xie J, Liu J (2012) Nano-carbon synergism compound fertilizer for tobacco and preparation method thereof. CN 102718584

Yadav BC, Kumar R (2008) Structure, properties and applications of fullerenes. Int J Nanotechnol Appl 2:15–24

Yan H, Gong A, He H, Zhou J, Wei Y, Lv L (2006) Adsorption of microcystins by carbon nanotubes. Chemosphere 62:142–148

Yan S, Zhao L, Li H, Zhang Q, Tan J, Huang M, He S, Li L (2013) Single-walled carbon nanotubes selectively influence maize root tissue development accompanied by the change in the related gene expression. J Hazard Mater 246:110–118

Yaqub S, Latif U, Dickert FL (2011) Plastic antibodies as chemical sensor material for atrazine detection. Sensors Actuators B 160:227–233

Yatim NM, Azizah S, Fairuz DM, Faridah Y (2015) Statistical evaluation of the production of urea fertilizer-multiwalled carbon nanotubes using Plackett Burman experimental design. Procedia Soc Behav Sci 195:315–323

Yoo J, Ozawa H, Fujigaya T, Nakashima N (2011) Evaluation of affinity of molecules for carbon nanotubes. Nanoscale 3:2517–2522

Zarei F, Negahdari B, Eatemadi A (2018) Diabetic ulcer regeneration: stem cells, biomaterials, growth factors. Artif Cells Nanomed Biotechnol 46(1):26–32

Zaytseva O, Neumann G (2016) Carbon nanomaterials: production, impact on plant development, agricultural and environmental applications. Chem Biol Technol Agric 3:17. https://doi.org/10.1186/s40538-016-0070-8

Zhang Z, Chen J (2012) Method for preparation of compound organic fertilizer containing nanocarbon and sulfate radical organic fertilizer. CN 102816003

Zhang Z, Liu J (2010) Synergistic fertilizer containing nanometer carbon and rare earth and its preparation. CN 101633590

Zhang Y, Kang TF, Wan YW, Chen SY (2009) Gold nanoparticles-carbon nanotubes modified sensor for electrochemical determination of organophosphate pesticides. Microchim Acta 165:307–311

Zhang Q, Huang J, Zhao M, Qian W, Wei F (2011) Carbon nanotube mass production: principles and processes. ChemSusChem 4:864–889

Zhang R, Zhang Y, Zhang Q, Xie H, Qian W, Wei F (2013) Growth of half-meter long carbon nanotubes based on Schulz-Flory distribution. ACS Nano 7:6156–6161

Zhang M, Gao B, Chen J, Li Y, Creamer AE, Chen H (2014) Slow-release fertilizer encapsulated by graphene oxide films. Chem Eng J 255:107–113

Zhang L, Gu J, Song L, Chen L, Huang Y, Zhang J, Chen T (2016) Underwater superoleophobic carbon nanotubes/core–shell polystyrene@Au nanoparticles composite membrane for flow-through catalytic decomposition and oil/water separation. J Mater Chem A 4:10810–10815

Zhao S, Wang Q, Zhao Y, Rui Q, Wang D (2015) Toxicity and translocation of graphene oxide in Arabidopsis thaliana. Environ Toxicol Pharmacol 39:145

Zheng X, Su Y, Chen Y, Wei Y, Li M, Huang H (2014) The effects of carbon nanotubes on nitrogen and phosphorus removal from real wastewater in the activated sludge system. RSC Adv 4:45953–45959

Zulkifli H, Salam F, Saad SM, Rahman RA, Rani RM, Karim MSA, Ishak Z (2016) Preliminary study of electrochemical DNA sensor for cucumber mosaic virus. Procedia Chem 20:98–101