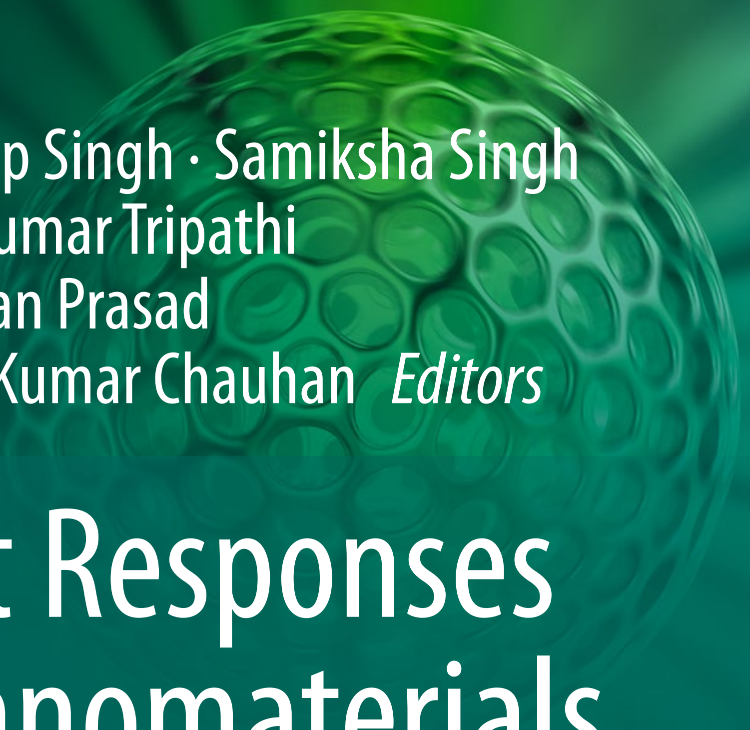
Nanotechnology in the Life Sciences



Vijay Pratap Singh · Samiksha Singh
Durgesh Kumar Tripathi
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Devendra Kumar Chauhan *Editors*

Plant Responses to Nanomaterials

Recent Interventions, and Physiological and Biochemical Responses

Springer

Nanotechnology in the Life Sciences

Series Editor

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Nano and biotechnology are two of the 21st century's most promising technologies. Nanotechnology is demarcated as the design, development, and application of materials and devices whose least functional make up is on a nanometer scale (1 to 100 nm). Meanwhile, biotechnology deals with metabolic and other physiological developments of biological subjects including microorganisms. These microbial processes have opened up new opportunities to explore novel applications, for example, the biosynthesis of metal nanomaterials, with the implication that these two technologies (i.e., thus nanobiotechnology) can play a vital role in developing and executing many valuable tools in the study of life. Nanotechnology is very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale, to investigating whether we can directly control matters on/in the atomic scale level. This idea entails its application to diverse fields of science such as plant biology, organic chemistry, agriculture, the food industry, and more.

Nanobiotechnology offers a wide range of uses in medicine, agriculture, and the environment. Many diseases that do not have cures today may be cured by nanotechnology in the future. Use of nanotechnology in medical therapeutics needs adequate evaluation of its risk and safety factors. Scientists who are against the use of nanotechnology also agree that advancement in nanotechnology should continue because this field promises great benefits, but testing should be carried out to ensure its safety in people. It is possible that nanomedicine in the future will play a crucial role in the treatment of human and plant diseases, and also in the enhancement of normal human physiology and plant systems, respectively. If everything proceeds as expected, nanobiotechnology will, one day, become an inevitable part of our everyday life and will help save many lives.

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Preface

Technology of synthesis of materials in the size of less than 100 nm comes in the form of nanotechnology, a new and emerging branch of materials science. In recent years, nanotechnology has occupied a central position in science because of its wider applications in plant and animal science. For instance, nanoparticles have increasingly been used as agents in enhancing crop productivity, abiotic and biotic stress tolerance in plants, nano-fertilizers, biosensors, cancer therapy, nano-medicines, cosmetics, electronics, and waste water treatments. Thus, at present, the use of nanotechnology is increasingly being enhanced in nearly every dimension of plant and human life. Global investment in nanotechnology has increased from $10 billion (in 2005) to almost $1 trillion (in 2015), indicating wider acceptability and application of nanotechnology in every domain of plant and human life.

Concentration and size dependent impacts of nanoparticles have been reported in plants. Nevertheless, when nanoparticles are excessively being released in the environment, they get accumulated in biotic components (plants and animals) and thus they adversely affect plant productivity as well as human health. In controlled conditions, nanoparticles of some essential metals are generally beneficial for plant yields even at higher concentrations, but after a threshold concentration they pose toxicity. Interestingly, nanoparticles of toxic metals sometimes show beneficial impact on plant growth, which has been ascribed to their surface to volume ratio. Nanoparticles may affect plants at morphological, anatomical, physiological, biochemical, and molecular levels. Thus, differential regulation of these plant processes collectively decide the fate of plants which were exposed to nanotoxicity. In this book, we have compiled various aspects of nanoparticles ranging from plant protection to agricultural production.

In total, 13 chapters have been compiled in this book. The contents of the chapters range from sources to toxicity of nanoparticles in the environment and their impacts on plant systems. For instance, topics ranging from regulation of seed germination by nanoparticles to the response of the whole plant are covered in this book. Special emphasis has also been given on the role of nanoparticles in boosting crop productivity. Overall, we believe that this book will serve as an important repository for students and researchers for understanding the behavior of nanoparticles in plants and their potential use in agriculture.

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Applications of Nanomaterials to Enhance Plant Health and Agricultural Production

Bhumika Yadu, Roseline Xalxo, Jipsi Chandra, Meetul Kumar, Vibhuti Chandrakar, and S. Keshavkant

1 Introduction

Agriculture is the most fundamental and stable sector as it is the producer which provides raw materials to the food and feed industries. Therefore, the development of agricultural sector is very necessary to clean up the hunger and poverty from our society (Manjunatha et al. 2016). The increasing growth of population and limitations in the natural resources (productive land and water) in the world make researchers to think for the agricultural development economically, environmentally, and efficiently (Prasad et al. 2017).

In this text, nanotechnology has been described as the next great frontier in the agricultural science that focuses on getting better agricultural production and occupies a prominent position in transforming agriculture, development of soil fertility, and food production through efficient management of soil nutrients (Fig. 1) (Jhanzab et al. 2015; Venkatachalam et al. 2017). Nowadays, the devices based on nanotechnology are widely used in the field of genetic transformation and plant breeding (Torney et al. 2007). The development of nanomaterials could open up the novel applications in the field of soil science and food nutrition (Duhan et al. 2017; Shweta et al. 2018). Moreover, agriculture could also serve as a good source of bio-nanocomposites with improved physical-mechanical properties based on traditionally harvested materials such as soy hulls and wheat straw for bio-industrial purposes (Parisi et al. 2015).

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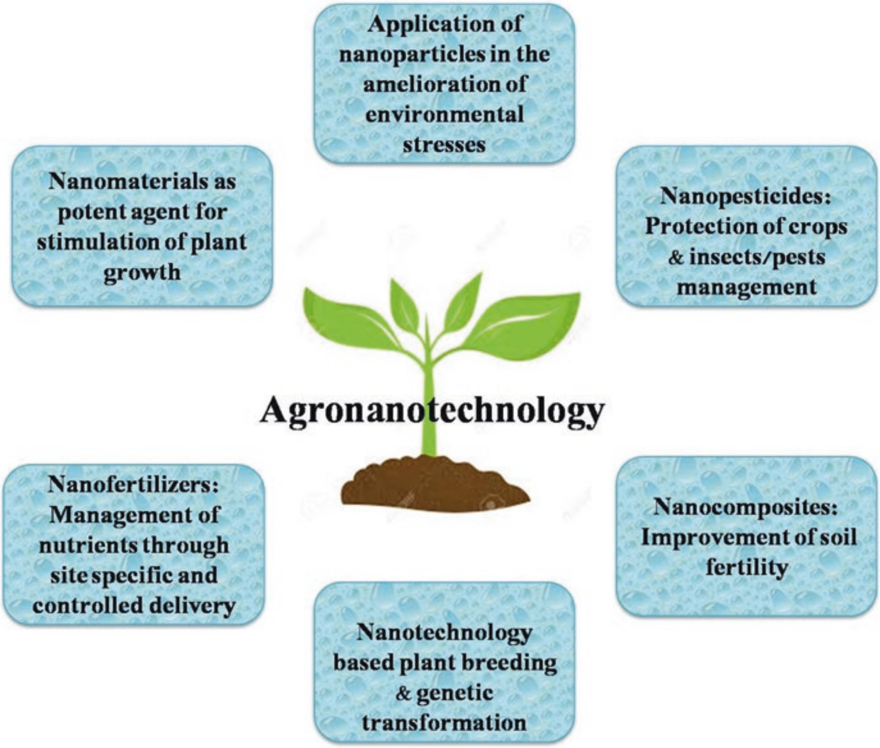

Fig. 1 Perspectives of nanotechnology in the sustainable agriculture

In the field of agriculture, benefits of nanotechnology are directly improving crop productivity by increasing water use efficiency; uptake of nutrition from the soil or irrigating water; precision farming; plant protection against insects and pests, fungal infections, and diseases; and innovative tools for pathogen detection, molecular biology, and environmental protection (Parisi et al. 2015; Duhan et al. 2017; Tripathi et al. 2017a, b; Ojha et al. 2018). The use of nanomaterial-based pesticides and insecticides can resist the plants against predators, and nanoparticles (NPs)-encapsulated fertilizers increased the absorption and transportation of nitrogen (N), phosphorus (P), and potassium (K) to seed; therefore, nanotechnology has great influence in strengthening the agricultural practices (Ojha et al. 2018). Use of nanofertilizers revealed better catalytic ability with enhanced surface area; hence, they are highly dispersible with high water-adsorbing properties. Therefore, nanofertilizers can increase the efficiency of nutrient, ions, and water uptake, ultimately improving the yield and nutrient content in the edible parts of the crop plants (Venkatachalam et al. 2017; Vishwakarma et al. 2018).

Moreover, exogenous application of nanoparticles (NPs) for the growth augmentation of plants and also for the amelioration of several types of environmental stresses is one of the recent and effective approaches and has attracted attention of the researchers worldwide (Tripathi et al. 2015, 2016; Venkatachalam et al. 2017;

Yadu et al. 2018). Due to the high volume and surface effect, NPs can interact with cellular biomolecules and stimulate various biochemical pathways in the cell. Some NPs have the ability to protect the protein oxidation and membrane damage of the cells caused due to oxidative stress imposed by the exposure of plants to various environmental factors such as heavy metals, salinity, high temperature, ultraviolet (UV), etc. (Tripathi et al. 2017c; Venkatachalam et al. 2017).

In agriculture, the chief concern of using nanotechnology consists of specific applications like use of nanofertilizers and nanopesticides for the augmentation of plant growth and productivity without causing harm to the environment and also protection against several insects, pests, and microbial diseases. Here, we briefly discuss various nano-based materials and their properties and functions in plant growth intensification, pest management, and delivery vehicles for nutrients and fertilizers.

2 Nanoparticles: General Properties and Functions

2.1 Silver Nanoparticles

As silver nanoparticles (AgNPs) have a high surface area, fraction of surface atoms, and high microbial effect, they can be used as an antimicrobial agent for crop protection (Saber et al. 2017). Therefore, there is a mounting interest to utilize this property of AgNP to diminish the burden of insects from crops and for the management of plant diseases. Like other nanomaterials, AgNP can also be synthesized by biological, chemical, electrochemical, photochemical, and physical methods (Banerjee et al. 2014; Salem et al. 2015). Owing to prerequisition of extreme conditions and toxic chemicals used in other methods, biological methods are nontoxic, eco-friendly, and widely accepted (Duhan et al. 2017).

Due to higher antifungal activity of silver than that of other metals, it inactivates the sulfhydryl groups of fungal cell walls, thereby disrupting the transmembrane, electron transport chain, and energy metabolism (Duhan et al. 2017). The biosynthesized AgNP has a strong antibacterial activity and is effective against both gram-negative and gram-positive bacteria. Moreover, AgNP neutralizes the electric charge of the surface of bacterial cell membranes, which changes its permeability and consequently leads to cell death (Prasad et al. 2017). This crucial property of silver metal makes it an ideal alternative for different aims in the medical and biotechnological fields (Salem et al. 2015). The efficacy of AgNP is dependent on particle size and shape, surface coating, concentration and duration of exposure, and species and developmental stage of plant and decreases with increasing size of the particles (Jhanzab et al. 2015). Pal et al. (2007) reported that truncated triangular AgNP showed higher "cidal" effect than that revealed by spherical and rod-shaped particles. This property of AgNP is a boon against a variety of harmful microorganisms. This AgNP sequesters the free radicals formed in the cells when exposed to various environmental stresses and facilitates the stabilization of cellular macromolecules

(Kim et al. 2007; Yadu et al. 2018). Also, AgNP has great influence on plant growth and development such as germination, root growth, root elongation, root-shoot ratio, and senescence inhibition (Jhanzab et al. 2015). The possible reason for this enhancement might be attributed to high specific surface area of AgNP which may be responsible for sequestering nutrient ions on their surfaces hence serving as a nutrient supplier to the germinating seeds and give support in their growth (Banerjee et al. 2014). In agriculture, its application of AgNP might be a feasible, effective, and safer mode as it possesses ability to reform the field by enhancing the efficiencies of plants to uptake and translocate more nutrients, and boosting antioxidant defense system thereby withstanding against various environmental stresses and consequently improving crop yield (Yadu et al. 2018).

2.2 Zinc Nanoparticles

Zinc (Zn) is one of the important micronutrients for plant and human diet. In human, its deficiency is considered to be one of the leading risk factors as it causes severe health disorders in infants and also leads to development of chronic diseases in the youngsters (Rameshraddy et al. 2017). In plants, its deficiency is the most widespread micronutrient crisis that adversely affects the agricultural production in highly alkaline soils with calcium carbonate (Duhan et al. 2017). The parameter that restricts the availability of Zn to plants in calcium carbonate-loaded soils of agricultural field is the alkaline pH, which decreases solubility of Zn and increases calcium carbonate content which can absorb and precipitate Zn (Rashid and Ryan 2004). Although the oxides and sulfates of Zn are commonly used as Zn fertilizers to overcome its deficiency in soils, yet their applications are limited due to the nonavailability of Zn to plants. Therefore, global challenge for food and nutrition security is to increase the agricultural crop production without negotiating their nutritional content (Quasem et al. 2009).

Therefore, use of zinc nanoparticles (ZnNPs) is the easiest, simplest, and sustainable way to achieve the target by supplying more soluble and available form of Zn to plants due to their higher reactivity (Duhan et al. 2017). The use of this NP as Zn fertilizers may augment Zn dissolution and its bioavailability even in soils with calcium carbonate. With these NP dissolved, Zn can easily diffuse from fertilizer to plant tissues and thereby fills the Zn crisis (Gangloff et al. 2006). Due to small size as less than 100 nm and high surface-to-volume ratio of ZnNP, it shows much better antimicrobial activity and allows better interaction with bacteria (Xie et al. 2011). Synthesis of ZnNP from plants is more cost-effective and eco-friendly as compared to chemically synthesized NP (Duhan et al. 2017). Usually, plant leaf extract dissolved in solvents such as water, ethanol, or methanol has been used for its synthesis, which was mixed with appropriate aqueous solutions of either zinc sulfate heptahydrate or zinc acetate dehydrate at desired pH. This NP has been tested in the laboratory and was proved to be a good antifungal agent, bactericide, and environment friendly (Rajiv et al. 2013). Elumalai et al. (2015) has reported the antimicrobial activity of 16- to 20-nm-sized ZnNP, synthesized from leaf extract of *Moringa oleifera*, which was effective against a number of bacterial strains such as *Escherichia coli*, *Bacillus subtilis*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa* and fungal strains like *Candida albicans* and *Candida tropicalis*. Moreover, according to the reports of Rajiv et al. (2013), ZnNP synthesized from the leaves of *Parthenium hysterophorus* showed antifungal activity against plant pathogens like *Aspergillus flavus* and *Aspergillus niger*. Thus, the use of ZnNP in the agricultural field has given promising results against diseases and enhanced plant growth and nutrition.

2.3 Silicon Nanoparticles

In the composition of the Earth's crust, after oxygen, there is 28.8% silicon (Si) based on dry weight. The biological role of Si was firstly well known for improving the growth and development of cells in diatoms, sponges, and corals (Alsaeedi et al. 2017). It is ubiquitous in nature and exists in all forms of life including humans and plants. Higher plants absorb Si from the aqueous solution more easily than the other essential nutrients. Due to having ability of regulating the defense mechanisms of plants, its amelioration potential has been well reported in several studies against varied biotic stresses such as insects and diseases and abiotic stresses including salinity, metal, and drought (Mateos-Naranjo et al. 2013; Farooq and Dietz 2015; Tripathi et al. 2015). Application of Si in plants reduces their sensitivity for toxic organisms, enhances water use efficiency by lowering evapotranspiration, and strengthens the activities of antioxidant enzymes (Roohizadeh et al. 2015). Therefore, Si has popularly been used in nanotechnology to form silicon nanoparticles (SiNPs) to expand crop productivity and improve its quality (Lu et al. 2002; Siddiqui and Al-Whaibi 2014). Thus, engineering silica in nanosize makes silica more easy to pass the cell wall passively which plays a key role in improving the plant's tolerance to abiotic stresses (Alsaeedi et al. 2017). A bird's-eye view of the literature survey indicates that exogenous application of SiNP played a greater role in the alleviation of abiotic stress-induced toxicity in crop plants (Tantawy et al. 2015; Tripathi et al. 2015, 2016).

Under stressed conditions, use of SiNP improved the rate of seed germination and growth and biomass accumulation of crop plants (Alsaeedi et al. 2017). This alleviation of stressed conditions may be assigned due to more than one mechanism(s): (i) SiNP-mediated decrease in heavy metals uptake and accumulation, (ii) elevated levels of macro- as well as micronutrients, (iii) decreased accumulations of free radicals, (iv) stabilization of photosynthetic apparatus, (v) reduced markers of oxidative damage, (vi) as a plasma membrane and protein stabilizer, (vii) enhanced enzymatic antioxidant defense system, (viii) adjusting the levels of non-enzymatic antioxidants, etc. (Tripathi et al. 2015, 2016). Also, SiNP releases Si which gets deposited underneath the cuticle layer of leaves, thereby reducing the rate of transpiration and thus maintaining a higher relative water content in leaves which makes the plant to withstand the stressed conditions. According to Alsaeedi et al. (2017), use of SiNP in agriculture is expected to improve the crop production by boosting the uptake of plant nutrition, water use efficiency, precision farming, and crop protection against insects and diseases. Thus, exogenous use of SiNP in agricultural fields emerged as an innovative tool for pathogen detection, amelioration of various biotic and abiotic stress-induced toxicities in crop plants, and environmental management.

2.4 Carbon Nanotubes

Carbon nanotubes (CNTs) are a new form of cylindrical-structured carbon and a two-dimensional graphene sheet rolled into a tubelike configuration (Zaytseva and Neumann 2016). Depending on the number of concentric layers of rolled graphene sheets, it is categorized as single-walled nanotubes with outer diameter of 0.8–2 nm and multiwalled nanotubes with outer diameter of 5–20 nm (De Volder et al. 2013). Lengths of CNT range from 100 nm to several centimeters, depending on its desired application in various fields such as optics, nanomedicines, electronics, biosensors, etc. (Mukherjee et al. 2016). This CNT soaks the water-containing contaminants such as toxic organic solvent dichlorobenzene, oil, fertilizers, pesticides, and pharmaceuticals (Camilli et al. 2014). Agrochemicals or any potential compounds can be targeted to hosts by CNT-based delivery systems; therefore, it can cut down the level of chemicals discharged into the environment and hence can reduce the damage caused to other parts of the plants (Hajirostamlo et al. 2015).

Due to the extraordinary unique optical, electric, and magnetic properties and tiny size, these CNTs are gaining much attention in recent decade from scientists in the field of plant genetic engineering too (Akhter et al. 2011). According to Lin et al. (2009), when the *Arabidopsis thaliana* cell cultures were exposed to CNT, it provoked hypersensitive signals that lead to defense responses in the cells causing cell death. Applications of nanosensors with metal/metal oxide NP based on electrochemically functionalized single-walled CNT for gases, viz., sulfur dioxide, nitrogen oxides, ammonia, hydrogen sulfide, and volatile organics, are very effective in monitoring agricultural pollutants and also for assessment of their effects on living matter or health and in increase of crop productivity and yield (Sekhon 2014).

Silver-coated CNT hybrid NPs have shown antimicrobial activity. More particularly, single-walled CNT showed the strongest antifungal activity (Zaytseva and Neumann 2016). Tripathi et al. (2011) reported that in *Cicer arietinum*, citrate-coated water-soluble CNT created an aligned network that enhanced the water uptake capacity and consequently improved the plant growth and development. An increased rate of germination, root length, biomass accumulation, shoot growth, and nutrient and water uptake in response to CNT have been well reported (Tripathi et al. 2011; Khodakovskaya et al. 2012; Mukherjee et al. 2016). An upregulation in the aquaporin genes upon CNT exposure was reported by Khodakovskaya et al. (2012); thus, CNT has also proven to be involved in water transport, cell division, and cell wall formation.

2.5 Quantum Dots

In the field of nanotechnology, quantum dots (QDs) have been commenced as a promising innovative tool for basic and applied life sciences (Muller et al. 2006; Chakravarty et al. 2015). Due to having unique optical properties, QDs are far better and rapid than organic fluorescent dyes because of more efficient luminescence, small characteristic emission spectra, outstanding photostability, and tenability according to the particle sizes and material composition and can be applied more effectively in bioimaging and biosensing (Jaiswal and Simon 2004). Recently, QDs have been used for labeling the plant proteins and hence are widely used in the detection of pathogens related with several diseases (Chahine et al. 2014). Use of QDs has been proven a boon in the field of food technology also. For the chemical conversion of water molecules into hydrogen, QDs have been utilized as a photocatalyst in the solar fuel pathway (Jaiswal and Simon 2004). The layer-by-layer assembly technique comprising the optical transducer of highly sensitive biosensors based on nanostructured films of acetylcholinesterase and cadmium telluride QDs has been used in the detection of pesticides (organophosphorus) present in the vegetables and fruits (Zheng et al. 2011).

The exogenous application of QDs at a very low concentration revealed no any toxic effects and also proved to be a plant growth regulator (Chakravarty et al. 2015). Therefore, QDs can be applied as smart treatment delivery systems for the regulation of seed germination and seedling development and can easily enter the plant's cell walls due to the smaller size than that of pores of the cell wall. Also, QDs can be used for bioimaging in plant root systems for the verification of known physiological processes (Duhan et al. 2017). Chakravarty et al. (2015) reported that exogenous application of graphene QDs enhanced the growth rate of *Coriandrum sativum* and was involved in the production of proteins that are essential for the development of plants. Also, their study on QDs has revealed that application of QDs increased the average length and weight of the roots with the enhancement in the size, strength, and green color of leaves as compared with untreated *Coriandrum sativum* plants.

3 Nanoparticles as an Agent In

3.1 Plant Protection

Plants are continuously exposed to various types of stresses which include both biotic and abiotic (Chandrakar et al. 2016). These stresses induce oxidative injury in the plant cell which causes damage to the important cellular macromolecules such as nucleic acids, protein, enzymes, and lipid. In the extreme conditions, the plant's inbuilt tolerance mechanisms become slower or inhibited to withstand against this condition (Yadu et al. 2019). Therefore, exogenous applications of some of the compounds are needed to enhance the tolerance against environmental stresses

(Chandrakar et al. 2018). Since the last decade, exogenous application of NPs has come into limelight to protect the plants from various abiotic stresses such as heavy metal (Venkatachalam et al. 2017), arsenic (Praveen et al. 2018), fluoride (Yadu et al. 2018), etc.

Nanoparticles have been proved to be a very promising compound because of its unique properties and important roles in integrating the environmental and intrinsic cues that help the plants to withstand under growth-limiting conditions. This has significance in agronomy because NPs represent a novel means of providing tolerance to important crops against biotic and abiotic stresses, thereby promoting sustainable agriculture (Yadu et al. 2018). In plants, exogenous application of NPs may act as a powerful tool against various abiotic stresses by inducing a wide range of processes involved in their tolerance mechanisms (Praveen et al. 2018).

Rameshraddy et al. (2017) reported that application of zinc oxide nanoparticles (ZnNPs) plays an important role in protecting the plants against oxidative damage catalyzed by reactive oxygen species (ROS) by increasing the activities and gene expressions of antioxidant enzymes. Their results revealed that because of having higher surface area, the NPs can deliver higher Zn content to the plants. According to Abdel Latef et al. (2008), titanium dioxide NPs have the ability to boost photosynthesis, biomass accumulation, and antioxidant defense, which help plants to enhance their growth potential and tolerance under salinity stress.

3.2 Plant Growth Augmentation

Application of NPs in the crop plants enhances their growth and development due to the high surface-to-volume ratio that increases the reactivity of NPs and possible biochemical activity. The NP-mediated plant growth augmentation may probably be the resultant of several mechanism(s) such as i) NP-mediated decrease in accumulation of toxic metals present in the soil/water that reduces the plant growth, (ii) decreased level of free radicals and oxidative damage caused by several environmental factors, (iii) activated antioxidant defense system, and (iv) enhanced level of macro- as well as micronutrients available for the plants (Tripathi et al. 2016).

Also, nanomaterials upregulate the expression of water channel genes (aquaporins) and thus play a crucial role in the permeability and enhancement of water, and nutrient uptake during seed germination (Lahiani et al. 2016; Singh et al. 2016). Thus, the application of engineered NPs in the agricultural land should always be a beneficial step to sustain an eco-friendly approach for the agricultural sector. The origin of these NPs can be either chemically or green synthesized. More efficient and eco-friendly is the green synthesis of NPs using extracts of some of the other potential plants, which can be applied to protect the crops from the adverse effects of several abiotic stresses. Green synthesis provides advance technique over chemical method as it is cost-effective, nontoxic, and environment friendly. Moreover, in the agricultural field, the application of polymeric NPs loaded with insecticides of plant origin (green synthesized) is a distinctive and widely accepted technique.

4 Nanotechnology and Agricultural Development

Without the use of agrochemicals like pesticides and fertilizers, better production and efficiency in modern agriculture are inconceivable these days. Although there are some potential issues related with every agrochemical that can negatively affect both the human being and environmental health, this risk needs to be reduced up to safer level by putting control in the inputs and precise management (Fraceto et al. 2016; Prasad et al. 2017). Therefore, to bring a revolution in agricultural practices, the development of high-tech agricultural system could be an excellent strategy, following the use of engineered smart nanotools. The influence of agrochemicals on the environment could lessen and/or be eliminated by exploiting the nanotools that can enhance both the quantity and quality of crops (Sekhon 2014; Parisi et al. 2015; Prasad et al. 2017). Nowadays, for site-specific and controlled delivery of fertilizers and pesticides to the plants, nanoencapsulation, nanoformulation, and functionalized nanomaterial of next-generation fertilizers and pesticides are exploited for reducing the risk of excess runoff (Gogos et al. 2012; Chowdappa and Gowda 2013). Therefore, for sustainability of agrisector, the development and utilization of smart delivery system as nanocomposites, nanosensor, nanofertilizer, nanopesticide, and nanoherbicide have been inaugurated as a new mode of applications (Manjunatha et al. 2016; Chhipa 2017).

4.1 Nanofertilizers

Today, half of the agricultural productivity relies on the chemical fertilizers. However, increasing the doses of fertilizers does not provide assurance of the improvement in the crop yield; rather, it leads to serious environmental problems like soil degradation and pollution of surface and groundwater resources (Chowdappa and Gowda 2013; Chhipa 2017; Duhan et al. 2017). Nitrogen, P, and K are the main constituents of chemical fertilizers, and it is estimated that about 40–70% of N, 80–90% of P, and 50–70% of K of the applied fertilizers cannot be absorbed by the plants and are lost in the atmosphere. So the major portion of fertilizer added resides in soils, thereby causing eutrophication by entering into the aquatic system (Oosterhuis and Howard 2008; Liu and Lal 2015). Therefore, to overcome the problems like imbalanced fertilization and low fertilizer use efficiency, nanofertilizer technology is a modern approach (Duhan et al. 2017; Anjum and Pradhan 2018). Nanofertilizers have several advantages over the conventional chemical fertilizers and are as follows: (a) they increase the fertility of soil, (b) improve the quality and yield of crops, (c) are nontoxic and eco-efficient, and (d) minimize cost and maximize profit (Sekhon 2014; Liu and Lal 2015; Prasad et al. 2017).

Slow release of fertilizers can be achieved by the use of nanomaterials. Nanocoatings or surface coating of the fertilizer particles by nanomaterials has the potential to hold not only the fertilizer material but also plant roots more strongly due to the higher surface tension than the conventional surfaces (Oosterhuis and Howard 2008; Manjunatha et al. 2016). The stability of nanocoating reduces the rate of dissolution of the fertilizer and allows slow, sustained release of coated fertilizers so that all the available/required nutrients are absorbed by the plants and restore the energy due to which the productivity and yield increase drastically (Wilson et al. 2008; Anjum and Pradhan 2018). Nanofertilizers balance the release of N and P with the absorption by the plant, thereby averting the loss of nutrients and avoiding their interaction with microorganisms, water, and air. To meet the demand of soil fertility and crop productivity, nanocoated urea and phosphate and their sustained release will be beneficial. For the sustained release of fertilizers, several natural and synthetic polymers have been used (DeRosa et al. 2010; Chen and Yada 2011). Corradini et al. (2010) have reported that biodegradable polymeric chitosan nanoparticles (approx. 78 nm) showed good results for the slow release of NPK fertilizer. A study on nanofertilizer-encapsulated nanosilica was performed by Wang et al. (2002) which revealed that after absorption of nutrients, nanosilica formed a binary film on the cell wall of fungi or bacteria and prevented infections, hence perking up the growth of the plant under high temperature and humidity and improving plant's resistance to diseases. Titanium (TiO_2) is a nontoxic material and hence can be used as additives in fertilizers for increasing the food production and water retention capacity of the plants. In *Spinacia oleracea*, increase in total N, protein, and chlorophyll was observed after the application of TiO_2 as an additive (Gao et al. 2006). Srinivasan and Saraswathi (2010) have reported that CNT can be used as nanofertilizer which promotes water uptake capacity and growth by entering into the germinating seeds of *Lycopersicon esculentum*.

To achieve slow release of nutrients in the environments, another nanomaterial, i.e., zeolites, can be used. These are group of naturally occurring minerals having a honeycomb-like layered crystal structure. The N and K can be loaded in its network of interconnected tunnels and cages which can combine with other slowly dissolving ingredients containing P, calcium (Ca), and other trace elements (Manjunatha et al. 2016). For slow and controlled release of N, and for longer time length, urea-coated zeolite chips have been synthesized and utilized (Millan et al. 2008; Kottegoda et al. 2011). An alternative of conventional Ca macronutrients, Liu et al. (2004) synthesized Ca NP and observed increment in the nutrient content in shoot and root of *Arachis hypogaea*. Likewise, Delfani et al. (2014) used iron oxide (FeO) and magnesium (Mg) NP fertilizer as alternate of Fe and Mg, and increments in seed weight and chlorophyll content of *Vigna unguiculata* were observed. Similarly, nanoforms of micronutrients are synthesized as micronutrients are also essential for different metabolic processes of plants, although they are required in minute amounts. Pradhan et al. (2013) have recorded that use of manganese (Mn) NP on *Vigna radiata* increased the root and shoot lengths, biomass, and chlorophyll content in comparison with bulk manganese sulfate. Zinc is another essential micronutrient which regulates the different enzymatic activities in plants. Enhancement in the plant growth and root-shoot dry mass was registered in *Vigna radiata* and *Cicer arietinum* by Mahajan et al. (2011) after addition of zinc oxide (ZnO) NP.

4.2 Nanopesticides

To control pests and insects, nowadays, biopesticides occupy a unique position in the agrimarket as an alternative of synthetic pesticides (Chhipa 2017; Duhan et al. 2017). The deployment of engineered nanomaterials is an efficient and novel technology in the field of biopesticides. In the agronomic sector, it is well known that insects and pests are the predominant destroyers which affect growth and productivity of crops adversely, in general (Nair et al. 2010; Ghormade et al. 2011). Therefore, in order to control insects/pests and host pathogens, nanopesticides may have key role due to their typical properties like enhanced solubility, specificity, stability, and permeability (Prasad et al. 2017; Thakur et al. 2018). Hence, for increasing agriculture production, syntheses and exploitation of nontoxic and environment-friendly nanopesticide delivery systems are urgently required, which will not only be better substitute of chemical pesticides but also helpful in reducing destructive impacts of toxic chemicals on the ecosystem (Agrawal and Rathore 2014; Duhan et al. 2017). Due to the electrostatic interaction of NPs with cell membranes of bacteria and their accumulation in cytoplasm, most of the metal NPs exhibit good antibacterial, antifungal, and antipathogenic activities (Chinnamuthu and Boopathi 2009; Bansal et al. 2014).

Nanomaterials including silver, silver oxide, gold, ZnO, TiO_2, magnesium oxide (MgO), and copper oxide (CuO) NPs possess antimicrobial activity due to which these are popularly explored for their insecticidal, bactericidal, and fungicidal activities against phytopathogens, alone or in combination with other metallic NPs (Khot et al. 2012; Agrawal and Rathore 2014). Because of their diverse mode of inhibition, these NPs inhibit or delay the growth of a number of pathogens. Therefore, these NPs can be used as new antimicrobial agents and as an alternative to synthetic pesticides (Li et al. 2008; Ghormade et al. 2011). Reports suggested that AgNPs are toxic against a broad range of plant pathogens. Alghuthaymi et al. (2015) demonstrated that AgNP not only inhibited the nutrient uptake phenomenon of *Raffaelea sp*. hyphae but also hindered their growth and conidia formation activity. Silver NPs are considered as a potent nanopesticide as they obstruct microbial growth by inhibiting germination of their spores. Mondal and Mani (2012) have reported that CuNP showed antibacterial activity against *Xanthomonas axonopodis* pv. *punicae* in *Punica granatum*. These CuNPs can bind with nucleic acids inside the bacterial cells and cause intermolecular cross-linking. These are also shown to damage the proteins by binding with their sulfhydryl groups and/or carboxyl groups of amino acids so that the biological processes of bacteria are hampered. Debnath et al. (2011) tested the entomotoxicity of SiNP against *Sitophilus oryzae* in *Oryza sativa* and compared its efficiency with bulk-sized silica. These authors found SiNP to be highly effective against this pest, which indicated the effectiveness of SiNP toward insects/pests control.

Further, to improve efficiency and stability, and reduce effective concentration of a pesticide, nanoformulation was developed such as nanoformulations of insecticide-coated liposome, *Azadirachta indica* oil, *Eucalyptus globulus* oil, pyridalyl, *Allium sativum* essential oil, *Syzygium aromaticum* oil, carbofuran, thiram, atrazine, and simazine (Nuruzzaman et al. 2016; Chhipa 2017). A significant insecticidal activity of *Allium sativum* essential oil was observed by Yang et al. (2009) against *Tribolium castaneum* following the use of polyethylene glycol (PEG)-coated NPs. Anjali et al. (2012) reported that nanoemulsion of *Azadirachta indica* oil was an effective larvicidal agent against *Culex quinquefasciatus*.

Hence, formulation of nano-encapsulated pesticide is quite effective than the normal agrochemical due to its slow and sustained release, allowing proper absorption of the chemical into the plants, and has a long-lasting and persistent effect (Nuruzzaman et al. 2016; Ojha et al. 2018). The specificity of synthetic pesticides toward the targeted pests is high, but they have detrimental impacts on human health and environment too. So there is an urgent need to expand the frontiers for nanomaterial-based technologies in insect/pest management (Ghormade et al. 2011; Prasad et al. 2017).

4.3 Nanocomposites

Nanocomposites are composites in which at least one of the phases has dimensions in the range of nanometer. Just like conventional composites, nanocomposites are comprised of at least two components: (i) matrix or continuous phase, in which nanosized particles are dispersed and (ii) the nanosized particles/nanoparticles constituting the second phase, i.e., dispersed phase (Othman 2014; Ojha et al. 2018).

Nanocomposite can be classified, depending on the matrix materials, into three groups: (1) metal matrix composites [Ni/Al_2O_3,Fe-Cr/Al_2O_3, Co/Cr, Fe/MgO, Al/CNT], (2) ceramic matrix composites (Al_2O_3/SiO_2, Al_2O_3/CNT, SiO_2/Ni, Al_2O_3/TiO_2, Al_2O_3/SiC), and (3) polymer matrix composites (polymer/CNT, polyester/TiO_2, polymer/layered silicates) (Camargo et al. 2009; Gupta 2018).

Nanocomposites have potential applications in growth and development of plants and insect/pest management. Metal matrix nanocomposites consist of an alloy metal reinforced with nanosized materials. Metal nanocomposites, like AgNP, CuNP, and TiNP possess antimicrobial activity due to which they can modify the properties of bacterial cell membranes by adhering on their surfaces (Navarro et al. 2008; Rai and Ingle 2012; Ojha et al. 2018). Metal nanocomposites having positive charge interact with the negatively charged cell wall/membranes of bacteria or fungus via electrostatic interactions. This interaction can result into destruction of cell structure and increase in membrane permeability leading to the leakage of intracellular stuffs. After entering into microbial cells, these metal nanocomposites bind with various cellular organelles, start disturbing the metabolic processes of the cells, and ultimately lead to death of the microbe (Navarro et al. 2008; Tripathi et al. 2017a). One of the study performed by Tejeda et al. (2009) observed that soda lime glass powder containing Cu nanocomposites possesses antibacterial activity against *Escherichia coli* and *Micrococcus luteus*. Likewise, Pallavi et al. (2016) have reported that Ag nanocomposite showed antibacterial activity against rhizospheric bacterial diversity and enhanced the root-shoot lengths and dry mass of *Triticum aestivum*, *Vigna sinensis,* and *Brassica juncea*.

Due to the multifunctional structure and property, polymer/CNT has also been used as a nanocomposite (Peigney et al. 2000; Thostenson et al. 2001). Sarlak et al. (2014) have encapsulated the pesticides zineb and mancozeb into the multiwalled CNT-grafted poly-citric acid hybrid which showed a marked effect against *Alternaria alternata* as compared to the bulk ones. In some other experiments, chitosan/CNT nanocomposite has been applied for the controlled and improved delivery of a broad-range insecticide azinphosmethyl and was used to protect fruits like *Citrus limon*, *Pyrus malus*, and *Prunus persica* from various insects (Bibi et al. 2016).

5 Future Perspectives of Nanotechnology in the Field of Agriculture

To maximize the production and yield of various crops in agronomic sector, new technologies, approaches, innovative ideas, increased use of nano-chemicals, and policies of the government should be adapted. It is mandatory to exploit the new technology in the food industry to overcome the problems occurring due to the usage of agrochemical products. After few years, without the use of pesticides and fertilizers, the viable production and efficacy of crops are unconceivable in the agriculture as these pesticides and fertilizers have some prospective issues like contamination of water with toxic chemicals or their residues in food chain that affects the human health and atmosphere. Thus, the alternative eco-friendly and controlled delivery system can diminish these risks. Therefore, the main motives of using nanomaterials/NPs in the agrisector are to reduce the amount of hazardous chemicals, curtail the loss of nutrients in fertilization, and increase the productivity and yield of crops via insect/pest and nutrient management.

Nanoparticles are usually manufactured by using chemical methods, and studies have illustrated that the use of a chemical-reducing agent consumes more energy and generates larger-sized particles. Additionally, the chemically synthesized NPs are accounted to show less stability and more agglomeration. Hence, alternate eco-friendly protocols should be adopted which can utilize bacteria, fungi, and plant extracts as reducing agents, which is considered as “bio-nanotechnology/green nanotechnology.” These biological/green syntheses methods can produce stable and dispersible NPs of desired size by consuming comparatively less energy. Moreover, these are not only environment friendly but also cost-effective, rapid, and less arduous, generate less waste, and are more proficient than the conventional chemical procedures. Hence, the development of smart “nanotools” with high-tech agricultural system makes a revolution in agricultural practices. The nanotechnology-based delivery of NPs has improved the crops production and yield via site-specific delivery and controlled release of nanofertilizers and nanopesticides.

In the near future, more attention and research toward some of the focused areas are required in the field of agro-nanotechnology or nanofoods:

(a) Nanotechnology may provide green, efficient, and eco-friendly strategy for insects/pests management in agriculture, so main emphasis should be on green nanotechnology: a new environmentally safer delivery system.
(b) The biosensor-based nanotechnology can have an effective role in pests/insects control and cross contamination of agriculture and food products.
(c) Some reliable and analytical methods are required to identify, characterize, and quantify different forms of NPs and for the assessment of their impacts on both the human being and environment prior to their delivery in the field.

6 Conclusions

Currently, in the field of agriculture, we are facing varied challenges due to the growing global population and climatic change. In such situation, the application of modern nanotechnologies as well as the introduction of potential nanomaterials in agriculture can greatly contribute in the sustainable growth of this very important sector. Nanotechnology has the potential to provide a great and promising future with the use of nanomaterials in agronomic sector and food industry through rapid and precise disease diagnosis and desired delivery of fertilizers and nutrients to the plants. Although ample of information are available about individual NPs, the level of toxicity of many of them is yet to be diagnosed. Therefore, due to the inadequate knowledge of risk assessment and effects on human health and environment, its application in agriculture and food industry is still at the inceptive phase. So for better acceptance of this emerging and modern technology, public awareness regarding the advantages and challenges of nanotechnology is must.

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Nanoparticles and Their Impacts on Seed Germination

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1 Introduction

Nanoparticles (NPs) have attracted great interests due to their enhanced physicochemical properties and biological activities compared to their bulk parent materials. With high volume of production, the wide spread of NPs in the environment can be anticipated. Despite the desired properties as commercial products, the toxicity of NPs has raised significant environmental concerns. Seed germination test is a common cost-effective method to evaluate phytotoxicity of NPs (Wang et al. 2001). Germination is defined as a physiological process which begins with water imbibition by air-dry seeds and culminates in the emergence of the rootlet (Bewley 1997). The mobilization of reserved chemicals (proteins, carbohydrates, lipids) following germination is essential for an embryo to complete seeding establishment.

NPs have shown both positive and negative effects on seed germination (Tables 1 and 2). Typical negative effects are related to the generation of harmful reactive oxygen species (ROS), thus increasing cellular oxidative stress and possibly attacking DNA, proteins, and membranes resulting in cellular injury (Moore 2006). Nanoparticles also have positive impacts on seed germination mainly by inducing α-amylase and protease enzymes activity, increasing the total amount of protein in germinating seeds, as well as increasing water uptake inside the seed (Rossi et al. 2016; Saharan et al. 2016; Singh et al. 2016).

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Table 1 Nanoparticles-enhanced seed germination

Nano-particles	Size (nm)	Concentration	Growth media	Plant(s)	References
Au	10	62 μg mL^{-1}		Cucumber and lettuce	Barrena et al. (2009)
	24	10 and 80 μg mL^{-1}		*Arabidopsis thaliana*	Kumar et al. (2013)
Ag	30–40	10–30 μg mL^{-1}	Murashige and Skoog basal medium	Boswellia ovalifoliolata	Savithramma et al. (2012)
	6–36	5 and 10 ppm	Aqueous suspension	Rice	Mahakham et al. (2017)
TiO_2		60 ppm		Fennel	Feizi et al. (2013)
	21	10 ppm	Aqueous suspension	Wheat	Feizi et al. (2012)
	20	2000 ppm	Aqueous suspension	Canola	Mahmoodzadeh et al. (2013)
ZnO	25	1000 ppm	Aqueous suspension	Peanut	Prasad et al. (2012)
	20	20 μg L^{-1}	Aqueous suspension	Onion	Raskar and Laware (2014)
		1600 mg L^{-1}	Aqueous suspension	Cucumber	de la Rosa et al. (2013)
SiO_2	12	8 g L^{-1}	Aqueous suspension	Tomato	Siddiqui et al. (2014)
γ-Fe_2O_3		20 mg L^{-1}	Aqueous suspension	Corn	Li et al. (2016)
MWCNTs		10–40 μg mL^{-1}	Murashige and Skoog medium	Tomato	Khodakovskaya et al. (2009)
		25, 50, and 100 μg mL^{-1}	Sterile agar	Barley, soybean, and corn	Lahiani et al. (2015)
	Diameter: 15–18; length: 1–12 μm	50 μg mL^{-1} and 200 μg mL^{-1}	Murashige and Skoog medium	Switchgrass	Pandey et al. (2018)
	Diameter: 12.8 ± 3.8	40, 80, 160, 320, 640, 1280, and 2540 mg L^{-1}	Agar media	Wheat	Miralles et al. (2012)
	Length: 0.5–200 μm	50 mg L^{-1}	Murashige and Skoog medium	Rice	Nair et al. (2012)
SWCNTs	Diameter: 1.1; length: 0.5–100 μm	50 mg L^{-1}	Murashige and Skoog medium	Rice	Nair et al. (2012)
	50–100	25, 50, and 100 μg mL^{-1}	Murashige and Skoog medium	Barley, tomato, corn, rice, and switchgrass	Lahiani et al. (2015)

(continued)

Table 1 (continued)

Nano-particles	Size (nm)	Concentration	Growth media	Plant(s)	References
$C_{60}(OH)_{20}$ (fullerol)		50 mg L^{-1}	Agarose gel	Tomato	Ratnikova et al. (2015)
Fullerene		50 mg L^{-1}	Murashige and Skoog medium	Rice	Nair et al. (2012)
Graphene		40 μg mL^{-1}	Aqueous suspension	Tomato	Zhang et al. (2015)

2 Carbon-Based Nanoparticles

2.1 Single-Walled Carbon Nanotubes

Single-walled carbon nanotubes (SWCNTs) are promising nanomaterial often showing positive effect on seed germination and plant growth. Their effectiveness on germination varies with plant species and applied SWCNTs concentration. Study with seeds of barley, corn, rice, soybean, switchgrass, tomato, and tobacco showed that SWCNTs can activate seed germination of selected crops and enhance growth of different organs of corn, tomato, rice, soybean, etc. (Lahiani et al. 2015; Shweta et al. 2017). For tomato, SWCNTs were able to affect the expression of a number of tomato genes that are involved in stress responses, cellular responses, and metabolism (Lahiani et al. 2015). Besides, *Hyoscyamus niger* seeds treated with low concentration of SWCNTs (50 μg mL^{-1}) showed tolerance to moderate level of drought stress during germination through improved water uptake and regulation of plant defense system (Hatami et al. 2017). However, a study conducted by Cañas et al. (2008) has shown that SWCNTs had negative effect on germination with root length being more affected by nonfunctionalized carbon nanotubes compared to functionalized nanotubes (Cañas et al. 2008). While nonfunctionalized nanotubes inhibited root elongation in tomato and enhanced root elongation in onion and cucumber, functionalized nanotubes inhibited root elongation in lettuce (Cañas et al. 2008).

2.2 Multiwalled Carbon Nanotube

In general, multiwalled carbon nanotubes (MWCNTs) showed toxic effect on plants including germination. Begum et al. (2012) evaluated the possible phytotoxicity of MWCNTs (0, 20, 200, 1000, and 2000 mg L^{-1}) with red spinach, lettuce, rice, cucumber, chili, lady's finger, and soybean based on root and shoot growth, cell death, and electrolyte leakage at the seedling stage. Their result indicated that high concentration of MWCNTs (1000 and 2000 mg L^{-1}) significantly reduced the root and shoot lengths of red spinach, lettuce, and cucumber, with red

Table 2 Nanoparticles-inhibited seed germination

Nanoparticles	Size (nm)	Concentration	Growth media	Plant	References
CuO		600 ppm		Cucumber	Moon et al. (2014)
				Spring barley	Rajput et al. (2018)
Zero-valent iron	1–20	1000–2000 mg L^{-1}	Aqueous suspension	Flax, barley, and ryegrass	El-Temsah and Joner (2012)
		750 and 1500 mg L^{-1}	Sandy soil	Flax and ryegrass	
Fe_3O_4	7	116 µg mL^{-1}	Aqueous suspension	Cucumber and lettuce	Barrena et al. (2009)
Ag	1–20	10 mg L^{-1}	Aqueous suspension	Flax, barley, and ryegrass	El-Temsah and Joner (2012)
	2	100 µg mL^{-1}	Aqueous suspension	Cucumber and lettuce	Barrena et al. (2009)
ZnO	20 ± 5	2000 mg L^{-1}	Aqueous suspension	Corn	Lin and Xing (2007)
	44.4 ± 6.7	400, 2000, and 4000 mg L^{-1}	Aqueous suspension	Arabidopsis thaliana (mouse-ear cress)	Lee et al. (2010)
	20	40 µg L^{-1}	Aqueous suspension	Onion	Raskar and Laware (2014)
		1600 mg L^{-1}	Aqueous suspension	Tomato and alfa	de la Rosa et al. (2013)
Zn		2000 mg L^{-1}	Aqueous suspension	Corn	Lin and Xing (2007)
CeO_2	7	500, 1000, and 2000 mg L^{-1}	Aqueous suspension	Corn	López-Moreno et al. (2010)
		2000 mg L^{-1}		Tomato and cucumber	
		2000 mg L^{-1}	Aqueous suspension	Glycine max (soybean)	
Graphene		50 mg L^{-1}	Murashige and Skoog medium	Rice	Nair et al. (2012)

spinach and lettuce being the most sensitive. Ghodake et al. (2010) studied the effects of the varying concentrations of MWCNTs (10, 20, and 40 mg L^{-1}) on the growth and development of *Brassica juncea* and *Phaseolus mungo* seedlings. Although *Phaseolus mungo* has only shown a slight decrease in the shoot and root length with MWCNTs, seedlings of *Brassica juncea* showed dramatic increase in vegetative biomass at varying MWCNTs concentrations. Overall, it is clear that different plant species respond differently to different concentrations of MWCNTs.

2.3 Graphene

Graphene often has shown enhanced effect on seed germination and seedling growth. The concentration of graphene plays a major role in the effectiveness of seed germination. Tomato seeds treated with low concentration of graphene showed higher seed germination and seedling growth (Zhang et al. 2015). Graphene can penetrate seed coat, promoting higher water imbibition and resulting in faster germination and higher germination rate. Rice seed treated with different concentration of graphene showed positive effect on seed germination at low concentration of 5 mg L^{-1} but negative effect at concentration above 50 mg L^{-1} (Liu et al. 2015). Pandey et al. (2018) reported graphene at 200 mg L^{-1} helps eliminate salt stress by desalination of saline growth medium and facilitates seed germination of bioenergy crops like sorghum and switchgrass. However, research on high-concentration graphene (500–2000 mg L^{-1}) showed inhibition of root and shoot growth of cabbage, tomato, and red spinach due to concentration-dependent increase in ROS and cell death (Begum et al. 2011).

3 Metal-Based Nanoparticles

3.1 Copper-Based Nanoparticles

CuO NPs often have shown toxic effects on seed germination, which depends on both CuO NPs concentration and the species of plant used for germination test (Arif et al. 2018). Moon et al. (2014) tested the toxicity of CuO NPs on cucumber germination at 200 and 600 mg L^{-1}, and CuO NPs effectively inhibited germination rate at 600 mg L^{-1}. Research conducted by Rajput et al. (2018) also has shown that CuO NPs can inhibit *spring barley (Hordeum sativum distichum) growth* by affecting the germination rate, root and shoot lengths, maximal quantum yield of photosystem II, and transpiration rate. However, study using CuO NPs at 100 mg L^{-1} has shown no effect on seed germination of maize, indicating the toxic effect of CuO NPs on germination may be concentration dependent (Wang et al. 2012). Different plant species also respond to CuO NPs toxicity differently. The different response of different plant species may be due to the variations in the lipid content/the wax of the seed coat, since the seed coat constituents can affect nanoparticles aggregation on seed surface (Wu et al. 2012). Even at high concentration (2000 mg L^{-1}), CuO NPs had no effect on soybean, chickpea, rice, and maize (Adhikari et al. 2012; Yang et al. 2015).

Different from CuO nanoparticles, Cu-chitosan nanoparticles showed positive effect on seed germination. Saharan et al. (2016) investigated the impact of Cu-chitosan nanoparticles (NPs) on physiological and biochemical changes during maize seedling growth, and the results showed that Cu-Chitosan nanoparticles significantly enhanced the germination rate by enhancing α-amylase and protease enzyme activity and starch and protein mobilization.

3.2 Silver Nanoparticles

Due to their antimicrobial properties, silver nanoparticles (AgNPs) are one of the most applied nanoparticles. Studies of AgNPs showed they have positive and negative effects on seed germination and also on plant growth and development (Savithramma et al. 2012; Yin et al. 2012; Tripathi et al. 2017a, b; Vishwakarma et al. 2017). Mahakham et al. (2017) reported that nanopriming seed with AgNPs enhanced α-amylase and antioxidant enzyme activity, resulting in higher soluble sugar content for supporting seedlings growth, thereby enhancing seed germination. Besides, increased ROS stress in AgNPs-treated seeds has also been observed, indicating ROS/antioxidant systems rebooting, generation of hydroxyl radicals for cell wall loosening, and nanocatalyst for fastening starch hydrolysis (Mahakham et al. 2017). However, El-Temsah and Joner (2012) observed that AgNPs can inhibit barley, flax, and ryegrass seed germination. No effect on seed germination has been observed for *Cucurbita pepo* (zucchini), *Bacopa monnieri*, and castor seed germination (Krishnaraj et al. 2012; Stampoulis et al. 2009; Yasur and Rani 2013). The ineffectiveness on seed germination may be due to the increased thickness of the seed coating, since generally thicker seed coating lessens nanoparticles penetration.

Besides, particle size, surface coating, and germination medium all play important roles in the effectiveness of AgNPs on seed germination. In general, smaller AgNPs are more effective on seed germination due to the increased specific surface area. Yin et al. (2011) reported that at similar concentration, smaller size Ag NPs (6 nm) affected seed growth more effectively than larger Ag NPs (25 nm), probably because smaller size nanoparticles with larger surface area to volume ratio are more reactive. Thuesombat et al. (2014) also observed smaller AgNPs (20 nm) have higher uptake in rice (*Oryza sativa* L. cv. KDML 105) seed germination compared to larger AgNPs (150 nm). Surface coating of AgNPs also affects its effect on seed germination. Gum Arabic-coated silver nanoparticles showed significant effect on seed germination of wetland plants, whereas polyvinylpyrrolidone-coated silver nanoparticles did not (Yin et al. 2012). Yin et al. (2012) also observed that AgNPs effect on germination defers with growth medium. Seeds growing in pure culture medium are more affected by AgNPs compared to those in soil medium.

3.3 Titanium Dioxide Nanoparticles

TiO_2NPs have various effects on seed germination and depend on factors such as plant species, particle size, and particle concentration. Although TiO_2NPs showed no effect on the germination of rice and maize, enhanced germination by TiO_2NPs was observed in fennel wheat and soybean (Feizi et al. 2012, 2013; Lu et al. 2002; Yang et al. 2015). However, Zheng et al. (2005) also reported that nanosized TiO_2 accelerated spinach seeds germination by improved water adsorption. In addition, Laware and Raskar (2014) reported that for onion seeds with suitable concentration, TiO_2NPs can increase hydrolytic enzymes (amylase and protease) and antioxidant enzymes (catalase, peroxidase, and superoxide dismutase) activity than promote seed germination. However, the activity of enzymes decreased at higher concentration (Laware and Raskar 2014).

3.4 Silicon Oxide Nanoparticles

SiO_2NPs were often reported to enhance seed germination, and the effect is concentration dependent (Siddiqui et al. 2015). In the experiment conducted by Siddiqui et al. (2014), SiO_2NPs (2, 4, 6, 8, 10, 12, 14 g L^{-1}) were used to investigate the germination rate of tomatoes. The results showed that the percent of tomato germination increased before SiO_2NPs reached 8 g L^{-1} and then the percent of germination declined with further increase in concentration. Suriyaprabha et al. (2012) reported that TiO_2NPs can increase maize seed germination by proving better nutrient availability. Study conducted by Lu et al. (2002) indicated that a mixture of nanosized SiO_2 and TiO_2 could increase the nitrate reductase enzyme and facilitate its antioxidant system in soybean (glycine max), thus increasing its abilities to absorb and utilize water and fertilizer which accelerate its germination and growth. However, limited effect of SiO_2NPs on *Arabidopsis thaliana*, rice, and maize has also been reported (Lee et al. 2010; Yang et al. 2015). This suggests that SiO_2NPs effects on seed germination are also dependent on plant species.

3.5 Zinc Oxide Nanoparticles

The effect of ZnO NPs on seed germination depends on NPs concentration, size, morphology, and plant species. Raskar and Laware (2014) reported that up to 20 μg mL^{-1} ZnO NPs enhanced onion seed germination but inhibited germination as ZnO NPs concentration increased to 40 μg mL^{-1}. Study on peanuts indicated positive effect of nanoscale ZnO on germination (Prasad et al. 2012). In contrast, significant inhibition effect on corn germination was observed for ZnO NPs at 2000 mg L^{-1} (Lin and Xing 2007). However, at same concentration of 2000 mg L^{-1}, ZnO NPs showed no effect on soybean germination (López-Moreno et al. 2010). Pokhrel and Dubey (2013) examined the difference of ZnO NPs on cabbage seed and maize seed germination, and the results showed that cabbage with smaller seeds and more surface area-to-volume ratio was more vulnerable to the negative effect of ZnO NPs. A study conducted by Xiang et al. (2015) found that both particle size and morphology affected the toxicity of ZnO nanoparticles on the germination of Chinese cabbage seeds.

4 Conclusions and Future Perspective

Due to the unique physiochemical and biological properties, NPs are highly reactive in soil and plant system. Factors such as particle size, surface coating, and germination medium all play important roles in determining the effectiveness of NPs on seed germination. Although some NPs have shown positive effect on plant growth, unwanted NPs translocation to edible part of the plants may be harmful to human health (Rico et al. 2011). A group of NPs (e.g., AgNPs, CuO NPs) has shown germination and root elongation inhibition in certain plants (Ma et al. 2013; Peng et al. 2015). Little is currently known about plant interaction with NPs or about how factors are affecting the effects of NPs. Till now, most studies focus on the effect of NPs in lab or greenhouse condition, and little field experiment data is available on agricultural soil matrix, especially after interaction with different soil components (e.g., soil minerals, soil organic matter, colloids, etc.). The interactions may result in a shift of NPs' toxicity or bioavailability. In the future, long-term studies are necessary to identify the interactions between NPs and plants for safe NPs application or NPs disposal.

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Synthesis and Characterization of Zinc Oxide Nanoparticles and Their Impact on Plants

Alireza Iranbakhsh, Zahra Oraghi Ardebili, and Narges Oraghi Ardebili

1 Introduction

Nowadays, great attention has been paid on the synthesis of diverse nano-products (size 1–100 nm) and potential advantage and risk associated with their utilization in different industries, especially food, medicine, and agriculture. It has been estimated that the worldwide application of nanoparticles would be an increase from 225,060 metric tons to approximately 585,000 metric tons during 2014–2019 (Rajput et al. 2018). Interestingly, nano-products possess remarkable exclusive properties, like small size ranging 1–100 nm diameters, specific surface properties, large surface areas, and high reactivity, affecting their interactions with biomolecules and structures (Asgari-Targhi et al. 2018). It is worth noting that different living organisms may respond to nano-compounds different from their bulk counterparts due to their specific properties (Bandyopadhyay et al. 2015; Asgari-Targhi et al. 2018; Vishwakarma et al. 2017; Shweta et al. 2018). Moreover, differential behavior, availability, and reactivity of nano-compounds may occur in various conditions (Moghanloo et al. 2019; Seddighinia et al. 2019). Nanoparticles can be classified into two main divisions:

1. Inorganic nanoparticles: metals, metal oxides, and quantum dots
2. Organic nanoparticles: fullerenes and carbon nanotubes

Nano-based compounds possess potency to be functionalized as sensors, elicitors, protectants, and delivery systems to improve crop production and protection (DeRosa et al. 2010; Ghormade et al. 2011; Khot et al. 2012; Sekhon 2014; Grillo

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et al. 2016; Wang et al. 2016a, b; Tripathi et al. 2016; Tripathi et al. 2017a; Asgari-Targhi et al. 2018; Yadav and Yadav 2018; Babajani et al. 2019a; Singh et al. 2019). Moreover, the utilization of various nano-products in agricultural industries as nanofertilizers and nanopesticides is rapidly growing worldwide (Tripathi et al. 2017a; Asgari-Targhi et al. 2018). Taking agriculture into account, different strategies have been employed to provide an efficient nano-based pesticide delivery, thereby decreasing the high consumption of conventional pesticides (Babajani et al. 2019a). Furthermore, it has become evident that nanoparticles may enter cells and trigger varieties of inter- and intracellular signaling cascades through which influencing primary and secondary metabolism in plants (Javed et al. 2017; Asgari-Targhi et al. 2018). It is obvious that different aspects of the potential risks associated with the utilization of nanometal-based products should be explored to provide a theoretical basis for exploitation in agriculture. Metal and metal oxide nanomaterials display specific physicochemical traits, including their surface, electrical, thermal, and optical characteristics. The current evidence points to this fact that metal oxide nanoparticles may be formulated as fertilizers or pesticide for exploitation in agriculture.

Zinc oxide (ZnO) as a semiconductor oxide possesses remarkable physical and chemical characteristics including a wide energy band (3.37 eV), high exciton binding energy (60 meV), high photostability, a wide range of violet/ultraviolet absorption, and chemical stability, making it a potential candidate for use in technology (Kołodziejczak-Radzimska and Jesionowski 2014). In addition, it contains considerable properties such as antifouling and antimicrobial properties, as well as photocatalytic activities (Ong et al. 2018; Slama et al. 2016). ZnO nanoparticles (nZnO), on the other hand, have received more attention owing to their unique properties differing from those in the bulk counterpart (Mohan and Renjanadevi 2016). Because of their different properties, which include efficient UV absorption, anti-inflammatory, microbial, and wound healing (Ramesh et al. 2015) characteristics, it makes nZnO extensively applicable to various fields including optics, electronics (Tripathi et al. 2017a), food, cosmetic (Ramesh et al. 2015), and pharmaceutical industries (Mirzaei and Darroudi 2017). Besides, due to cost-effective production (compared to other photocatalysts such as TiO2), the broad range of solar spectrum absorption, and nontoxicity, nZnO can be therefore employed as a photocatalyst for photodegradation of persistent organic compounds (Ong et al. 2018). It should be noted that nZnO have been ranked as the third most commonly applied metal-based nano-compound (Jiang et al. 2018) in various industries. Hence, an inevitable entry of nZnO to the environment due to the intensive application, production, and disposal process has provoked tremendous concerns on the ecosystem, especially plants as a key initiator agent of a food chain.

As zinc (Zn) deficiency in soil is a worldwide common issue, the plant−/seed-originated foods have a low Zn content which is an important characteristic considering human health and nutrition. Hence, various attempts have been employed to develop methods for biofortification of cultivating crops with essential nutrients like Fe, Zn, and Se (Babajani et al. 2019a, b). It is worth mentioning that Zn deficiency in human nutrition (nearly 30% of the world's population) associates with a disturbance in various body systems, especially nervous, reproduction, and immunity (Anderson et al. 2017). Furthermore, Zn is known as a key essential micronutrient which plays vital roles in plant growth, metabolism, development, reproduction, yield, and protection (Babajani et al. 2019a, b). Interestingly, it plays critical roles in cellular metabolism as contributed to protein interaction domains, many transcription factors, and enzymes. On the other hand, Zn is toxic to plant cell at excess contents, provoking phytotoxicity signs, including chlorosis, halting plant growth and development, and making physiological disturbances (Babajani et al. 2019a, b). In plants, there are several homeostatic mechanisms and a modulated network of metal acquisition, transport, chelation, trafficking, and sequestration activities through which regulating the levels of essential nutrient ions in intracellular compartments and protecting cells against toxic metal ions (Clemens 2001). It is important to note that diverse proteins contribute to Zn uptake, translocation, and localization within plant cell (Clemens 2001) among which three following groups are the most well-known transporter proteins (Nair and Chung 2017):

1. ZIP (ZRT, IRT-like proteins)
2. HMA (heavy metal ATPases)
3. MTP (metal tolerance protein)

In this chapter, the literature indicates various methods of nZnO synthesis (chemical, physical, and biogenic methods). Bio-uptake, translocation, accumulation, and phytotoxicity of this nano-compound also will be presented. Furthermore, some references to its impact on plant microbiome are exhibited. Moreover, we discuss the morphological, anatomical, biochemical, physiological, and molecular basis of plant responses to nZnO. In particular, we mainly focus on the effects of nZnO on seed germination, nutrition, photosynthesis, secondary metabolism, antioxidant system, defense-responsive genes, transcriptome, and soil microbiome. In addition, behaviors of seed, cell, and tissue following supplementations of culture medium with nZnO in in vitro condition will be focused. Herein, we try to provide a theoretical foundation for contributing to possible future exploitation in diverse agricultural activities.

2 Synthesis

2.1 Biological, Chemical, and Physical Approaches

Biological, chemical, and physical procedures have been proposed for the synthesis of nanoparticles. There are various procedures for physical methods of nanomaterial fabrication including the arc discharge method, condensation, spray pyrolysis, evaporation, laser beam ablation, inert gas condensation, and vapor phase synthesis (Sharma et al. 2018; Tiwari et al. 2019). Taking nZnO synthesis into account, a rich variety of physical methods are used for synthesis of nZnO, namely, molecular beam epitaxy (Ong et al. 2018; Diallo et al. 2015), pulsed laser deposition (Thema et al. 2015), chemical vapor deposition, thermal evaporation, metal–organic chemical vapor deposition, and infrared irradiation (Diallo et al. 2015). Likewise, the chemical methods, including sol–gel (Jiang et al. 2018), hydrothermal (Jamdagni et al. 2018), solvothermal, sonochemical, electrodeposition, and spray pyrolysis processes (Thema et al. 2015), are employed to fabricate nZnO. Chemical synthesis strategy suffers varied disadvantages owing to the usage of some poisonous chemical or organic solvents as reducing agents (Sharma et al. 2018; Jamdagni et al. 2018) leading to the production of noxious by-products which are harmful to the environment and human health (Jamdagni et al. 2018), whereas physical procedures are energy consuming and need high vacuum (Thema et al. 2015). As a result, the greener method is being developed. Various metal and metal oxide nanoparticles, including nZnO, gold, silver, iron, aluminum, and copper, have been successfully synthesized from a green method (Iravani 2011; Hulkoti and Taranath 2014). Through these synthesis methods, the morphology and size of the nanomaterials can be easily modified by manipulating reaction conditions (Ong et al. 2018).

2.2 Green Synthesis

As highlighted above, the biological methods provide advancement over chemical and physical approaches because of its renewable nature, simplicity, environment friendly, low production cost, and free of noxious by-product (Fatimah et al. 2016). For the biogenic method for synthesis of nanomaterial, plant, algae, and microorganisms have been utilized as reducing and stabilizing agents (Koul et al. 2018). To synthesize nZnO and other metal nanoparticles in the industrial scale, two key issues, including production rate and yield, need to be regarded (Iravani 2011). Therefore, biosynthesis conditions in the reaction medium need to be optimized. Bio-reduction conditions can be controlled by altering different parameters, including metal concentrations, the different plant extract quantities, mixing speed, reaction time, pH, buffer strength, temperature, and light (Iravani 2011; Dubey et al. 2010; Kuppusamy et al. 2016). For example, it was demonstrated that pH was the key parameter in determination of the gold nanoparticles formed by *Rhodopseudomonas capsulata* (Hulkoti and Taranath 2014). Moreover, other complementary factors like incubation temperature could affect the accumulation of the nanoparticles (Hulkoti and Taranath 2014). Agarwal et al. (2017) also showed that the size of the synthesized nanoparticle is dependent on the concentration of plant extract. The changes in these critical factors could, therefore, alter the properties of biosynthesis of nanoparticles.

2.2.1 Biosynthesis of nZnO Using Plant Extract

Plant extracts are used as reducing and stabilizing agents due to the presence of a different combination of organic reducing agents in the fabrication of nanoparticles (Geetha et al. 2016). Plants consist of phytochemicals (such as flavones, polyphenols, ketones, carboxylic acids, amides, and aldehydes) which involve in the reduction of metal and metal oxide ions to synthesize nanoparticles (Sharma et al. 2018). Different parts of the plant as a mediator have been studied. Various parts of plants (flower, leaf, root, peel, seed, stem, and callus) are washed several times using tap water and subsequently with double distilled water. The plant part is dried or ground to yield a powder. The plant powder is then mixed in a different solvent (water or ethanol) and heated under continuous stirring to form the extract. Next, the mixture is filtered to achieve clear solution and used as an aqueous plant extract. To synthesize nZnO, different concentrations of zinc salts (zinc nitrate, zinc acetate dehydrate, etc.) are used and dissolved in the aqueous plant extract at different pH, temperature, and time. Detailed processes of biosynthesis of nZnO by aqueous flower extract of *Nyctanthes arbor-tristis* are described by Jamdagni et al. (2018). The synthesized nZnO can be found in two forms (suspended in the liquid or solid form) and have different morphology such as nanoflowers, nanoflakes, nanobelts, and nanorods as well as nanowires (Kumar and Rajeshkumar 2018). Further, the properties of synthesized nanomaterial are characterized by two main methods: spectroscopic analysis and microscopic imaging. The imaging technique involves various kinds of microscopy including electron microscopy (scanning electron microscopy (SEM), transmission electron microscopy (TEM), and field emission scanning electron microscopy (FE-SEM)), ion microscopy, and atomic force microscopy (AFM). Besides, spectroscopic technique is employed to determine the physicochemical characteristics of nanomaterial (Sharma et al. 2018).

Diallo et al. (2015) investigated a cost-effective and biosafe method of synthesis of nZnO by using flower of *Aspalathus linearis* which acts as reducing and stabilizing agents to form nanoparticles. This experiment elucidated the involvement of proteins of pollen grains in the formation of nZnO. Moreover, the solution of Zn ions when subjected to the aqueous shoot extract of *Physalis alkekengi* was reduced and led to biosynthesis of nZnO with triangle and elongated morphologies ranging from 50 to 200 nm (Qu et al. 2011). Furthermore, green synthesis of nZnO using an aqueous extract of *Artocarpus gomezianus* fruit was reported. Flavonoids as a part of plant secondary metabolite were believed to be responsible for the reduction of Zn ions (Suresh et al. 2015c). Many other flower, fruits, and seed extracts including *Cassia auriculata* (flower) (Ramesh et al. 2014), *Rosa indica* (petal) (Tiwari et al. 2016), *Jacaranda mimosifolia* (flower) (Sharma et al. 2016), *Anchusa italica* (flower) (Azizi et al. 2016), *Trifolium pratense* (flower) (Dobrucka and Długaszewska 2016), *Vitex negundo* (dried flowers) (Ambika and Sundrarajan 2015), *Poncirus trifoliata* (fruit extract) (Nagajyothi et al. 2013), *Citrus aurantifolia* (fruit) (Rafaie et al. 2014), *Citrus maxima* (fruit) (Pavithra et al. 2017), *Borassus flabellifer* (fruit) (Vimala et al. 2014), *Terminalia chebula* (fruit) (Rana et al. 2016), *Rosa canina* (fruit) (Jafarirad et al. 2016), *Lemon juice* (fruit) (Hinge and Pandit 2017; Krishna et al. 2017), *Nephelium lappaceum* (fruit Peel) (Yuvakkumar et al. 2014), *Nephelium lappaceum* (fruit peel) (Yuvakkumar et al. 2015; Karnan and Selvakumar 2016), pomegranate peel (Kaviya and Prasad 2016), *Punica granatum* (fruit peel) (Prashanth et al. 2015), *Citrus aurantifolia* (fruit peel) (Çolak and Karaköse 2017), avacado fruit (Veluswamy et al. 2017), *Garcinia xanthochymus* (fruit) (Nethravathi et al. 2015), *Vitis labrusca* (skin extract) (Nagaraju et al. 2017), *Peganum harmala* (seed) (Fazlzadeh et al. 2017), *Nigella sativa* (seed) (Kavyashree et al. 2015a), *Guizotia abyssinica* (seed) (Kavyashree et al. 2015b), *Garcinia gummi* (seed) (Raghavendra et al. 2017) were successfully used for the green synthesis of nZnO.

Apart from flower, fruits, and seed extracts, Elumalai et al. (2015) explored the green synthesis of nZnO by *Vitex trifolia* leaf extract. They introduced vitrifolin A, 20-hydroxyecdysone, 5-thio D-glucose, 1,1-bicyclopropyl-2-octanoic acid, 20-hexyl, and methyl ester in *V. trifolia* leaf extract as the major contributing chemical compounds. It was concluded that nZnO size and morphology are clearly affected by the concentration of *V. trifolia* leaf extract so that leaf extract concentration of 40 ml was able to synthesize the smallest crystallite size of the fabricated nanoparticles (14 nm). *V. trifolia* extract contains different biochemicals such as phenols, alcohols, amines, aliphatic amines, and aromatics which are responsible for the fabrication of nZnO. Considering temperature-dependent synthesis of nZnO using *Hibiscus sabdariffa* leaf extract, plant extract carries reducing sugar, starch, phenolics, flavonoids, and ascorbic acid which may attach to the surface of zinc ions, thus triggering the synthesis of nanoparticles and controlling the size of the fabricated nZnO. Moreover, $C=O$, $C=O-C$, and $C=C$ groups of heterocyclic compounds and amide from proteins may behave as stabilizing agents (Bala et al. 2015). Agarwal et al. (2017) also showed that carbonate moieties, alkane, alcohol, carboxylic acid, amine, and amide present in leaves of *Azadirachta indica* play vital role in the fabrication of nanoparticles confirmed by FTIR. *Aspalathus linearis* extract acts as an effective reduction chemical agent for nZnO synthesis containing phenolic compounds among which aspalathin and aspalalinin are the most bioactive material (Diallo et al. 2015). Similarly, nZnO was synthesized via the green approach from leaf extract of *Agathosma betulina* (Thema et al. 2015); *Buchanania lanzan* (Suresh et al. 2015b); *Aloe vera* (Qian et al. 2015; Das et al. 2016); *Aloe barbadensis* (Sangeetha et al. 2011); *Cassia fistula* (Suresh et al. 2015a); *Ocimum basilicum* benth (Salam et al. 2014); *Coriandrum sativum* (Hassan et al. 2015); *Tabernaemontana divaricata* (Sivaraj et al. 2014); *Prunus x yedoensis matsumura* (Velmurugan et al. 2016); *Allium sativum* (Stan et al. 2015); *Azadirachta indica* (Bhuyan et al. 2015); *Eclipta prostrata* (Chung et al. 2015); *Olea europaea* (Hashemi et al. 2016); *Justicia adhatoda* (Taranath et al. 2015); *Melia dubia* (Prabhu et al. 2016); *Bougainvillea glabra* (Samzadeh-Kermani et al. 2016); *Artocarpus heterophyllus* (Vidya et al. 2016); *Eclipta prostrata* (Chung et al. 2015); *Pongamia pinnata* (Sundrarajan et al. 2015); *Camellia japonica* (Maruthupandy et al. 2017); *Moringa oleifera* (Matinise et al. 2017); *Camellia japonica* (Murali et al. 2017); *Lagerstroemia speciosa* (Saraswathi et al. 2017); *Carica papaya* (Rathnasamy et al. 2017); *Acalypha indica* (Karthik et al. 2017); *Calotropis procera* (Gawade et al. 2017); *Sageretia thea* (Khalil et al. 2017); *Hibiscus sabdariffa* (Mahendiran et al.

2017); *Calotropis gigantea* (Chaudhuri and Malodia 2017); *Azadirachta indica*, *Moringa oleifera, Hibiscus rosa-sinensis, Tamarindus indica,* and *Murraya koenigii* (Rehana et al. 2017); and *Solanum nigrum* (Ramesh et al. 2015).

2.2.2 Biosynthesis of nZnO Using Microbes and Other Green Sources

Due to the use of noxious chemical and costly equipment employed in the chemical and physical method, green approach exploiting the use of bacteria, algae, and fungi has been adopted (Agarwal et al. 2017). The synthesis of nanoparticles by microorganisms such as bacteria is due to their abilities to reduce metal ions or form water-insoluble materials to survive in toxic environment (Hulkoti and Taranath 2014). Jayaseelan et al. (2012) worked on *Aeromonas hydrophila* as to synthesize nZnO. The atomic force microscopy (AFM) confirms the formation of spherical nanoparticles with average particle size of 57.72 nm. The synthesized nZnO showed antimicrobial activity against *Aspergillus flavus* and *Pseudomonas aeruginosa* with maximum inhibition zone at the concentration of 25 μg mL^{-1} nZnO (Jayaseelan et al. 2012). Another article reported the fabrication of nZnO from zinc chloride solution using probiotic bacteria *Lactobacillus sporogenes*. The synthesized nZnO mentioned in this research were found to be hexagonal shaped with the average particle size in the range of 5–15 nm as showed by data (Prasad and Jha 2009). Synthesis of stable nZnO (RL@ZnO) using *Pseudomonas aeruginosa* rhamnolipids (RLs) as stabilizing agent with zinc nitrate aqueous solution as a precursor was described by (Singh et al. 2014). *Pseudomonas aeruginosa* is thought to be as a capping agent because of a long carbon chain. The evaluation of their antioxidant potential revealed the decrease in antiradical capacity of RL@ZnO nanoparticles by 6.9% compared to roughly 88% in bare nZnO at the same concentration up to 15 months. Thus, the synthesized nZnO can be utilized as a promising antioxidant in biological system. The marine biological resources are other abundant green sources for fabrication of nanoparticles. They are not only cost-effective but also can be exploited for large-scale production due to cosmopolitan distribution (Sharma et al. 2018). Besides, microalgae gain more attention due to its ability to convert toxic metals to less toxic forms (Agarwal et al. 2017). However, the application of algae to synthesize nZnO is limited (Agarwal et al. 2017). The marine source-based seaweeds including brown *Sargassum myriocystum*, red *Hypnea valencia,* and *Caulerpa peltata* were used in the fabrication of nZnO among which *S. myriocystum* was able to synthesize spherical-shaped nanoparticles with average size of 36 nm. Its characteristics were monitored through various techniques such as AFM, TEM, SEM–EDX, DLS, FTIR, and XRD. The synthesized nZnO was proved to be effective antimicrobial agent against gram-positive than the gram-negative bacteria. They demonstrated that fucoidan pigments present in the extract behave as reduction and stabilization of nZnO (Nagarajan and Kuppusamy 2013). The hexagonal-shaped nZnO ranging from 30 to 57 nm were synthesized using brown marine macroalgae *Sargassum muticum*. The phyto-synthesis of nZnO is dependent on bioactive materials such as sulfate and hydroxyl moieties of polysaccharide (Azizi et al. 2014). The nZnO compound fabricated from *Ulva lactuca* seaweed extract with average crystallite size of 10–50 nm (confirmed by TEM) exhibited photocatalytic activity against methylene blue dye and also showed bactericidal activity against *Bacillus licheniformis* and *Bacillus pumilus* (gram-positive) and *Escherichia coli* and *Proteus vulgaris* (gram-negative). *Ulva lactuca*-synthesized nZnO with such properties can therefore be used as eco-friendly antimicrobials and mosquito larvicides and be more effective than the conventional antibiotics against gram-positive and gram-negative bacteria (Ishwarya et al. 2018). Fungal strains are the more preferred source of nanoparticles than bacteria because of the presence of different enzymes such as reductase, secretion of a large amount of protein (Hulkoti and Taranath 2014), large-scale production (Sharma et al. 2018), and metal bioaccumulation property (Agarwal et al. 2017). This is because the protein and enzymes secreted from fungi behave as stabilizing/capping agents which makes them better potential candidate for nanoparticles synthesis (Ahmed et al. 2017). For example, *Candida albicans* was used as capping and reducing agent to synthesize nZnO. The prepared nZnO showed good catalytic activities for the efficient formation of steroidal pyrazolines from a,b-unsaturated steroidal ketones (Mashrai et al. 2017). The nZnO fabrication using mycelia of *Aspergillus fumigatus* with the average particle size of 3.8 nm was reported. In the formation of metal and metal oxide nanoparticles such as nZnO by *Aspergillus fumigatus*, extracellular secreting enzymes produced by fungus are responsible for the reduction of metal salt to metal nanoparticles. Such biologically synthesized nZnO are eco-friendly, cost-effective, and biocompatible, since fungal proteins encapsulate metal ions and act as capping factors. Therefore, they can be used in various industries such as pharmaceutical and cosmetic sectors (Raliya and Tarafdar 2013). The extracellular mycosynthesis of highly stable nZnO by *Alternaria alternata* was also reported. Spherical-, triangular-, and hexagonal-shaped nZnO had a size range of 45 to 150 nm and the average size of 75 nm proved by DLS and TEM analysis. Sarkar et al. (2014) showed the presence of protein outside of formed nZnO confirmed by FTIR, which act as a stabilizing agent. Biocompatible and eco-friendly chemicals like protein are regarded as alternative green sources for fabrication of nanoparticles. The extracellular fungal proteins were mixed with an aqueous zinc acetate solution to synthesize nZnO. It was believed that extracellular proteins coated the produced nanoparticles, thereby stabilizing them. Furthermore, the photocatalytic performance of protein-capped nZnO revealed its more increased activity (approximately 90% degradation) than bare nZnO (approximately 40% degradation) against methylene blue under the same conditions. Such remarkable photocatalytic activity results from the presence of protein on the surface of nZnO facilitating dye absorption (Jain et al. 2014).

3 Soil Microbiome

Among the various factors determining soil productivity and sustainability, soil microbiome has been found to play pivotal roles, mainly owing to their fundamental contributions to the cycling of nutrients and decomposition processes of soil organic materials. Therefore, any factor which influences microbiome would necessarily alter soil productivity and sustainability (Dinesh et al. 2012). Moreover, community, biodiversity, biomass, and metabolic activities of soil microbiome are considered as vital indexes which directly and indirectly contribute to soil productivity and sustainability. It is important to note that nanoparticles can contaminate the soil through two main routes, including sewage sludge and industrial wastes (Rajput et al. 2018). The fate, transport, and reactions of nanoparticles in soil, and the likelihood of entering into the groundwater, are controlled by the occurring interactions between these particles and soil constituents, colloids (Zhao et al. 2012). Various environmental factors determine adsorption, transportation, and mobility of nanoparticles in soil (Ben-Moshe et al. 2013). Zhao et al. (2012) showed that nZnO strongly adsorbed to soil colloids and displayed low mobility. It has been hypothesized that the soil contamination with nanoparticles can affect soil properties, microbiome, and biotic reactions (Fig. 1). Moreover, Rajput et al. (2018) stated that nanoparticles can alter the physicochemical characteristics of soil and mobilize soil minerals. Several factors play critical roles in bioavailability of nanoparticles and soil changes which can be divided into the following main sections:

1. Physicochemical traits of nanoparticles
2. Soil microbiome (microbial diversity and community)
3. Soil characteristics: soil texture, structure, clay level, dissolved organic matter, ionic strength, cation exchange capacity (CEC), and pH (Ben-Moshe et al. 2013)

The nZnO-associated alterations in soil microbiome are represented in Table 1. Seed priming with *Pseudomonas chlororaphis* O6 (PcO6) improved the resistance of the colonized wheat against drought stress where these beneficial bacteria were not impaired by the presence of nZnO in soil (Yang et al. 2017). On the other hand, Shen et al. (2015) explored the possible ecotoxicological effects of nZnO presence (1, 5, and 10 mgg^{-1} soil) on soil microbiome based on changes in diverse biochemical process and enzyme activities (respiration, fluorescent diacetate hydrolase ammonification, and dehydrogenase activity). They found that nZnO inhibited the most of the evaluated traits, especially when the soil pH was acidic. The highest toxicity was found in the acidic, followed by the neutral, and the lowest was recorded in the alkaline condition. Interestingly, the toxicity caused by nZnO on various microbial biochemical processes was dependent on soil type. Moreover, Ge et al. (2011) evaluated the effect of soil contamination with different concentrations of nZnO (0.05, 0.1, and 0.5 mgg^{-1} soil over 60 days) on soil microbial biomass and community using total extractable DNA, substrate-induced respiration (SIR), and terminal restriction fragment length polymorphism (T-RFLP) analyses. The nZnO presence changed the microbial biomass, community, and diversity. They concluded

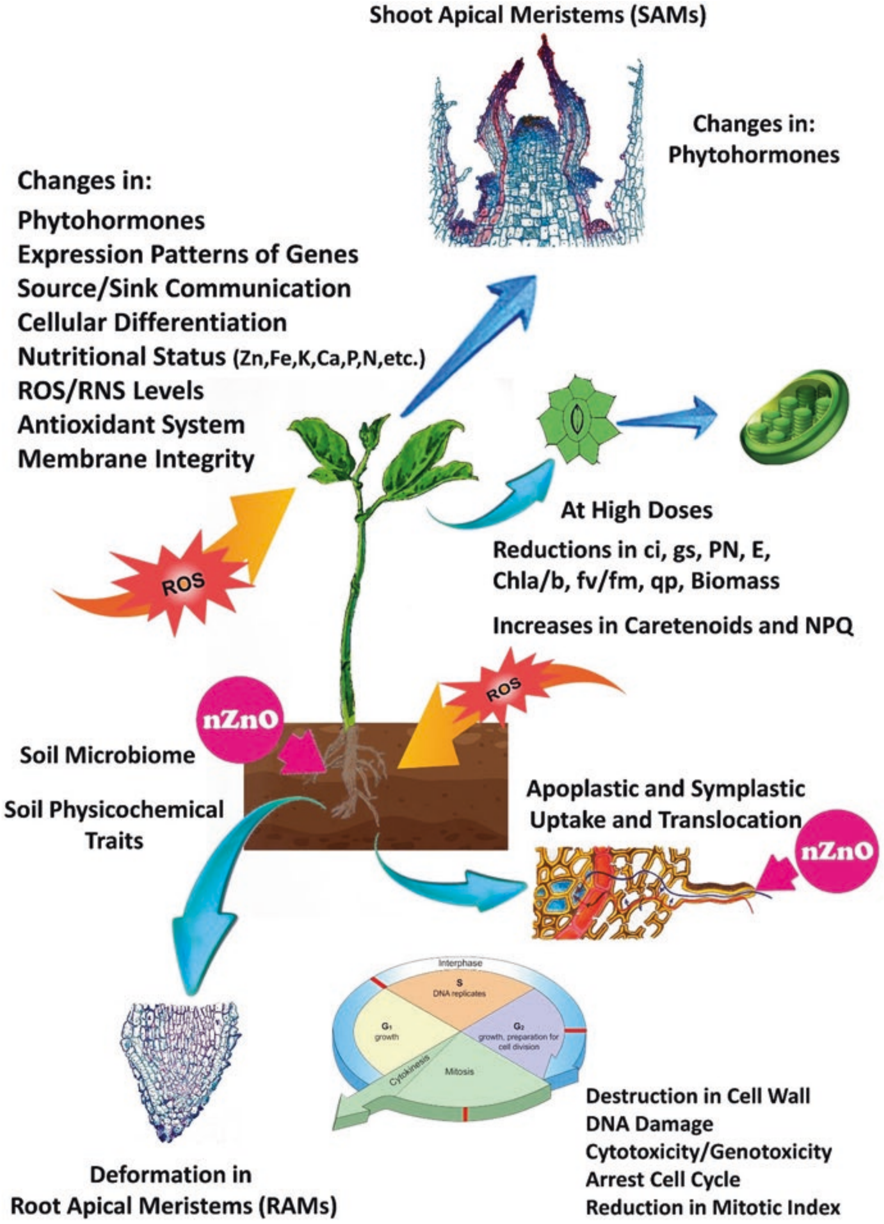

Fig. 1 The schematic design on the nZnO-mediated changes in plant

Table 1 The nZnO-mediated changes in soil microbiome

Concentrations	Evaluated parameter	Findings	References
500 $mgkg^{-1}$ soil	*Pseudomonas chlororaphis*	No adverse effect	Yang et al. (2017)
0.05, 0.1, and 0.5 mgg^{-1}	Soil microbiome	Changes in microbial biomass, community, and diversity	Ge et al. (2011)
1, 5, and 10 mgg^{-1} soil	Soil microbiome	Inhibition in biochemical process and enzyme activities (respiration, ammonification, and dehydrogenase) Higher toxicity in acidic pH	Shen et al. (2015)
1 mgg^{-1} soil	Azotobacter and P- and K-solubilizing bacteria	Inhibiting thermogenic metabolism and enzymatic activities	Chai et al. (2015)
0–1000 $mgkg^{-1}$soil	Microbial activity	Reductions in C transformation, phosphatase, and dehydrogenase at 1000 $mgkg^{-1}$ No adverse effect on N transformation Lower toxicity of nZnO relative to $ZnCl_2$	García-Gómez et al. (2015)

that the nanometal oxides, especially nZnO, can negatively affect soil microbiome. Chai et al. (2015) also examined the ecotoxicological effect of different engineered nanoparticles by monitoring changes in thermal metabolism, the abundance of functional bacteria, and enzymatic activity following supplementation of agricultural soil with ZnO, SiO_2, TiO_2, and CeO_2 nanoparticles at the level of 1 mgg^{-1} soil. The nZnO and CeO_2 nanoparticles exhibited the inhibiting roles on the abundance of Azotobacter and P- and K-solubilizing bacteria. A similar trend was found for thermogenic metabolism and enzymatic activities, including fluorescein diacetate hydrolysis, urease, and catalase (Chai et al. 2015). Moreover, the ecotoxicological risk associated with the utilization of sewage sludge containing nZnO (0–1000 $mgkg^{-1}$soil) was reported (García-Gómez et al. 2015). Except for N transformation, the soil supplementation with nZnO at 1000 $mgkg^{-1}$ diminished the microbial activity, including C transformation, phosphatase, and dehydrogenase activities. However, $ZnCl_2$ of 1000 exhibited the highest toxicity rate. García-Gómez et al. (2015) concluded that the ionic forms possessed a higher availability, and the risk of nZnO toxicity toward soil and aquatic organisms may be low. It is worth mentioning that the results represented by Watson et al. (2015) clearly indicate that soil pH plays a crucial role in plant responses upon the nZnO exposure. Besides, sorption of nZnO to soil colloids enhanced with increasing soil pH (Waalewijn-Kool et al. 2013). However, the size parameter (30 and 200 nm) of the nanoparticles made little difference in the nZnO toxicity toward *Folsomia candida* as a model in soil biology (Waalewijn-Kool et al. 2013). Metal oxides may, therefore, provoke changes in enzymatic reactions made by soil microbiome. It is important to note that the direct interactions of nZnO with biological targets have been accounted as a key mechanism through which the nZnO caused toxicity in soil microbiome and inhibited different microbial biochemical processes (Shen et al. 2015). Further investigations in particular at molecular levels are needed to clarify the exact implicated mechanisms. Hence, the pH factor and soil type should be regarded for future exploitation in agriculture. These findings could also contribute to improving our understanding of the nZnO-mediated changes in soil productivity and plant–microbe interactions.

4 Uptake and Translocation

The diverse techniques, like confocal microscopy (Zhao et al. 2012), Zinpyr-1 fluorescence imaging method (Nair and Chung 2017), light microscopy (Rao and Shekhawat 2014), scanning electron microscopy (SEM) (Rao and Shekhawat 2014), transmission electron microscopy (TEM) (Kim et al. 2012; Lee et al. 2013; Chen et al. 2015; Raliya et al. 2015; Zhang et al. 2015; Moghaddasi et al. 2017), X-ray fluorescence microscopy (μ-XRF) (Wang et al. 2013), ICP method (Nair and Chung 2017), X-ray absorption spectroscopy (XAS) (De La Rosa et al. 2011; De la Rosa et al. 2013; Hernandez-Viezcas et al. 2013; Wang et al. 2013; Bandyopadhyay et al. 2015; Lv et al. 2015), and STEM-EDX imaging technique (Bandyopadhyay et al. 2015), have been employed to trace the nZnO uptake, up- and downward translocations, and biotransformation in plant tissues. The current evidence indicates that there are several factors, including the physicochemical traits of nZnO (especially size, shape, surface charge, and concentration of nZnO), plant species, and soil characteristics (in particular pH, organic materials, and cation exchange capacity) contributing to uptake, translocation, and bioaccumulation of nZnO in plants. The uptake and translocation of nZnO mediate through both symplastic and apoplastic routes (Fig. 1). Ma et al. (2007) provide evidence on penetration and nZnO entry in both root endoderm region and vascular cylinder of ryegrass. The confocal microscope images revealed that the nZnO uptake and translocation from the root to shoot occurred through both apoplastic and symplastic routes (Lin and Xing 2008). Likewise, the nZnO was detected in the root tip cells, epidermis, cortex, and vascular system in the exposed maize plant (Lv et al. 2015). It entered the xylem through the junction sites of lateral primary roots, although nZnO was not detected in shoot, probably owing to its dissolution and transformation. The results of Lv et al. (2015) reflected the uptaken Zn^{2+} released from nZnO and bioaccumulated in the form of Zn phosphate. Using Zinpyr-1 fluorescence imaging method, the uptake and translocation of nZnO were also traced in the *Arabidopsis* seedlings exposed to nZnO at the level of 100 mgl^{-1} level for 2 weeks (Nair and Chung 2017). No alteration in Zinpyr-1 fluorescence as a sign of upward translocation of nZnO was recorded in shoots, while strong green fluorescence in the shoot–root junction, the primary lateral root junction, and the main root apex was confirmed by ICP assessment. Zhao et al. (2012) evaluated the uptake and transport of Zn/nZnO in corn seedlings cultured in sandy loam, showing low mobility. Similarly, translocation factors of Zn originated from the nZnO source from root to shoot were much lower than that of

Zn^{2+} controls, referring low potency of upward translocation in the ryegrass (Lin and Xing 2008). No translocation of nZnO from roots to above ground tissues was also evident in cowpea (*Vigna unguiculata*) in either solution or soil culture (Wang et al. 2013). However, Raliya et al. (2015) provided evidence on uptake and both up- and downward transportation through xylem- and phloem-conducting tissue. Besides, the TEM analysis reflected that nZnO maintained its size and morphology despite interaction with tissues and up to the fruiting reproductive stage. Both ICP-MS and TEM observations confirmed that nZnO bioaccumulate in stems, leaves, and roots and bio-distribute through vascular system independent of the foliar or soil application modes (Raliya et al. 2015). In TEM image, nZnO was detected in root cells and cell wall of *Cucumis sativus* (Kim et al. 2012). However, X-ray absorption spectroscopy (XAS) confirmed the biotransformation of nZnO within the root in three desert plant species, including *Salsola tragus* (tumbleweed), *Prosopis juliflora*-velutina (velvet mesquite), and *Parkinsonia florida* (blue palo verde), while nanoparticles were not detected (De La Rosa et al. 2011). Furthermore, a TEM analysis revealed that the nZnO (1000 mgL^{-1}) can pass through cellular membrane and formed agglomerates with other intracellular materials in root tissue of *Fagopyrum esculentum* depicted by the presence of the dark dots in the cytoplasm (Lee et al. 2013). Similarly, the presence of dark dots in both shoot and roots confirmed the uptake and translocation (Chen et al. 2015). Moreover, Zn bioaccumulation and upward translocation in *Fagopyrum esculentum* treated with nZnO were higher than that with the ZnO microparticle (Lee et al. 2013). Furthermore, the results represented by Tripathi et al. (2017b) revealed that Zn concentrations in xylem and phloem sap of plants subjected to nZnO (100 and 200 μM) were higher by approximately twofold relative to the control which was lowered by the NO. Interestingly, the higher bioaccumulation factor in the soybean pods was found for 100 $mgkg^{-1}$ dose relative to 500 $mgkg^{-1}$ attributed to the higher solubility at lower dose (Peralta-Videa et al. 2014). The penetration of nZnO (dark dots) into the root and shoot cells, the sedimentation on cell wall, the accumulation adjacent to the cellular membrane, and the aggregation of the nanoparticles in the cytoplasm were also depicted in the TEM images recorded by Moghaddasi et al. (2017) in cucumber. Based on the bulk XAS analysis, De la Rosa et al. (2013) concluded that nZnO are biotransformed in alfalfa (*Medicago sativa*), tomato (*Solanum lycopersicum*), and cucumber (*Cucumis sativus*). Moreover, results represented by Bradfield et al. (2017) indicated that Zn bioaccumulated in both flesh and peel parts of the tubers of sweet potato. Furthermore, the root uptake of Zn originated from nZnO (1000 mgl^{-1}) was substantially higher than that of equivalent Zn^{2+} (Zhang et al. 2015). However, the translocation rates were low for nZnO, and Zn^{2+} groups indicated that the translocation capacity from root to shoot was limited. The recorded SEM and TEM images manifested the distribution of nZnO within the root. Zhang et al. (2015) also represented convincing evidence on nanoparticle pass through cell walls and intracellular presences of nanoparticle in the exposed *Schoenoplectus tabernaemontani*. TEM images provided by Zhang et al. (2015) confirmed the uptake of nZnO into the root of *Zea mays*. It has been also reported that seed coats of corn alleviated the nZnO toxicity on root longitudinal growth and prevented Zn entering into root and endosperm (Zhang et al. 2015). In addition, Bandyopadhyay et al. (2015) found that the bulk form had higher dissolution rates in comparison with nZnO, attributed to agglomeration of nZnO, and hinders the dissolution kinetics under their experimental procedures. The presence of nZnO in the leaf, stem, root, and nodule tissues, nuclear membrane, and inside nucleus in alfalfa is depicted by STEM-EDX imaging technique. However, no visual sign of toxicity in spite of higher Zn accumulation in leaves was observed in alfalfa. The results represented by Bandyopadhyay et al. (2015) revealed that the translocation factor for ionic treatments was lower than the nZnO, probably due to compartmentation in root vacuoles. The X-ray absorption spectroscopy analysis conducted by Hernandez-Viezcas et al. (2013) exhibited no presence of nZnO throughout of soybean (*Glycine max*) seeds cultivated under nZnO at 500 $mgkg^{-1}$ soil. Also, the μ-XANES data confirmed the formation of oxygen-bound Zn complex (resembling Zn-citrate) in the reproductive/edible portion of soybean. The apparent shining dots in the nZnO-treated plants were speculated in SEM images of a transverse section of leaf in *Brassica juncea* (Rao and Shekhawat 2014). The light microscopic analysis also confirmed the adsorption and aggregation of nanoparticles on the root surface of *Brassica juncea* exposed to nZnO of 1500 mgl^{-1} (Rao and Shekhawat 2014). The supplementation of culture medium with nZnO (10, 20, 50, and 100 mgL^{-1}) increased Zn concentrations in both shoot and root of tomato (Li et al. 2016).

5 Plant Responses to nZnO

5.1 Seed Germination, Biomass, and Plant Early Growth

There are numerous studies dealing with advantages or toxicity of nZnO. The main factors contributing to the differential behaviors of plants to nZnO are as follows:

1. Physicochemical characteristics of nanoparticle: purity, morphology, size, size distribution, crystallinity, surface charge (estimating based on zeta potential index), agglomeration status, catalytic activity, redox potential, and porosity (Rajput et al. 2018)
2. Plant species
3. Plant developmental stage
4. Treatment method: foliar, soil amendment, hydroponic, in vitro solid culture medium, etc.
5. Exposure time
6. Continuous or pulse treatment
7. Physicochemical traits of in vitro culture medium, soil, or culture matrix
8. The nZnO bioavailability

The nZnO-mediated changes in seed germination, seedling morphology, and early growth and performance are noticed in Table 2. It should be noted that the majority

Table 2 The nZnO-mediated changes in seed germination, seedling morphology, and early growth

Plant species	Size (nm)	Treatments	Main findings	Reference
Cucumber	75–100	10, 100, 1000 mgkg^{-1} soil	Increases in shoot and root biomass at 10 and 100 mgkg^{-1} contrasted with 1000 mgkg^{-1}	Moghaddasi et al. (2017)
Melissa officinalis	10–30	50 and 250 mgL^{-1}	No effect on seed germination Increases in biomass	Babajani et al. (2019b)
Parkinsonia florida *Prosopis juliflora* *Salsola tragus*	≤100	500, 1000, 2000, and 4000 mgL^{-1}	No significant effect on germination Limitations in root elongation in *P. florida* (16% at 4000 mgL^{-1}) and *S. tragus* (16% at 2000 mgL^{-1}) IC50 of 1000 mgL^{-1} for *P. juliflora*	De La Rosa et al. (2011)
Rice (*Oryza sativa*)	50	10, 100, 500, and 1000 mgL^{-1}	No effect on seed germination percentage Reduction in root length and lateral roots above 100 mgL^{-1}	Boonyanitipong et al. (2011)
Wheat	70	500 mgkg^{-1}	Increase in lateral root formation	Yang et al. (2017)
Arabidopsis thaliana	20–45	20, 50, 100, and200 mgL^{-1} for 14 days	Chlorosis Reduction in leaf size and root elongation at high doses Increase in lateral root formation at low doses Changes in root architecture	Nair and Chung (2017)
Sweet potato (*Ipomoea batatas*)	30–40	100, 500,or 1000 mgkg^{-1}	Adverse effect on tuber biomass only for 1000 mgkg^{-1} No signs of stress or toxicity in the aboveground tissues Zn bioaccumulations in both the flesh and peel of the tubers No difference between the nanoparticle and ionic type	Bradfield et al. (2017)
Arabidopsis	<50	50, 100, 200, 250, and 300 mgL^{-1}	Decrease in biomass above 200 mgl^{-1} Reduction in water contents in 300 mgL^{-1} Reduction in root/shoot ratio	Wang et al. (2016a, b)
Cowpea	<35	38.2 μM	No effects on growth in soil, while reductions in solution culture	Wang et al. (2013)
Soybean (*Glycine max*)	≤100	0.05, 0.1, or 0.5 gkg^{-1} soil	At reproductive stage, evidence on uptake and distribution throughout edible tissues	Priester et al. (2012)
Cucurbita pepo	5–10	1000 mgL^{-1}	No significant change in germination and early growth	Stampoulis et al. (2009)

(continued)

Table 2 (continued)

Plant species	Size (nm)	Treatments	Main findings	Reference
Wheat	5–20	100 and 200 µM	Decline in fresh weight by mean 23%	Tripathi et al. (2017b)
Wheat (*Triticum aestivum*)	22	100, 500, and 1000 mgL^{-1}	Higher effectiveness of nZnO than the Zn^{+2} for bioaccumulation No effect on germination Promotions in both Zn nutrition and plant growth	Elhaj Baddar and Unrine (2018)
Alfalfa Cucumber Tomato	10	50, 100, 200, 400, 800, and 1600 mgL^{-1}	Differential responses in a plant species and/or dose-dependent manner	De la Rosa et al. (2013)
Maize Cabbage	10–20	0.01, 0.1, 1, 10, 100, 500, and 1000 mgL^{-1}	Alterations in germination, root apical meristem, cellular morphology, and differentiation of xylem tissue in plant species and dose-specific manners	Pokhrel and Dubey (2013)
Chickpea	≤100	1.5 or 10 mgL^{-1}	Increase in biomass accumulation	Burman et al. (2013)
Pisum sativum	10	125, 250, and 500 mgkg^{-1} soil	Increase in root length	Mukherjee et al. (2014)
Pearl millet	15–25		Increase in shoot length (15.1%), root length (4.2%), and area (24.2%), dry biomass (12.5%), and grain yield by 37.7%	Tarafdar et al. (2014)
Banana	40–50	50, 100, and 200 mgL^{-1}	No marked negative effects on explants regeneration	Helaly et al. (2014)
Soybean	≤50	50 and 500 mgkg^{-1}	Impairment in plant growth, development, and reproduction	Yoon et al. (2014)
Wheat Radish Vetch	≤100	250 and 1000 mgkg^{-1} soil	nZnO was more effective than the bulk Advantage or toxicity in a plant species-specific response Risk associated with the nZnO was similar to bulk	García-Gómez et al. (2015)
Wheat	100	125, 250, and 500 mgL^{-1}	Critical role of soil pH in plant responses	Watson et al. (2015)
Corn Cucumber	30	10, 100, and 1000 mgL^{-1}	Plant species-specific behaviors Differential uptake mechanisms in two species at 1000 mgl^{-1} Reductions in root length	Zhang et al. (2015)
Daucus carota	≤100	50, 100, and 150 mgL^{-1}	Increase in plant height, number of leaves, petiole length, leaf area, root diameter, root length, and yield/hectare	Elizabath et al. (2017)

(continued)

Table 2 (continued)

Plant species	Size (nm)	Treatments	Main findings	Reference
Soybean (*Glycine max*)	8	500, 1000, 2000, and 4000 mgL^{-1}	No effect on seed germination Differential effect on growth and uptake in a dose-dependent	López-Moreno et al. (2010)
Buckwheat	$\leq$100	50, 500, 2000, and 4000 mgL^{-1}	Reduction in root length at 4000 mgl^{-1}	Lee et al. (2013)
Tomato (*Solanum lycopersicum*)	28	10, 100, 250, 500, 750, and 1000 mgkg^{-1}	No effect on germination up to 750 (reduction at 1000 mgkg^{-1}) Increase in plant height and root length up to 250 mgkg^{-1} Increase in number of flowers Promotion in fruit yield Increase in biomass, shoot, and root growth	Raliya et al. (2015)
Vigna radiata *Cicer arietinum*	20	10, 20, 50, 100, 500, 1000, and 2000 mgL^{-1}	Increase in growth up to 20 mgl^{-1} Growth inhibiting above 50 mgl^{-1}	Mahajan et al. (2011)
Pepper	10–30	100 mgL^{-1}	Delay in germination and plant early growth and performance Decrease in the total fresh mass and leaf area	Iranbakhsh et al. (2018b)
Tomato	35	2,4, 8, or 16 mgL^{-1}	Increase in growth indexes, biomass, and leaf area	Faizan et al. (2018)
Leucaena leucocephala	2–64	25 mgL^{-1}	Promotion in growth indexes and biomass The ameliorating effect of heavy metal stress (Pb and Cd)	Venkatachalam et al. (2017a)
Cotton	2–54	25, 50, 75, 100, and 200 mgL^{-1}	Increase in root and shoot length Increase in total biomass	Venkatachalam et al. (2017b)
Alfalfa (*Medicago sativa*)	10	250, 500, and 750 mgkg^{-1}	Decrease in root and shoot biomass, contrasted with the bulk No effect on germination rates up to 750 mgkg^{-1} Acceleration in the early flowering	Bandyopadhyay et al. (2015)
Rice	$\leq$100	50, 100, 250, 500, and 1000 mgL^{-1}	Reduction in root length, shoot height, and biomass Toxicity above 250	Chen et al. (2015)
Brassica juncea	50–100	200, 500, 1000, and 1500 mgL^{-1}	Decrease in plant biomass and root and shoot length Stunted growth and leaf chlorosis with increasing the doses	Rao and Shekhawat (2014)
Duckweed	25	1, 10, and 50 mgL^{-1}	Restricting growth rate at 50 mgL^{-1} The released Zn^{2+} as the main agent of toxicity	Hu et al. (2013)

(continued)

Table 2 (continued)

Plant species	Size (nm)	Treatments	Main findings	Reference
Soybean	<50	500 mgL^{-1}	No effect on shoot height and shoot fresh mass Decrease in root length, fresh mass, and leaf fresh weight	Hossain et al. (2016)
Lactuca sativa	5–80	5–30 mgL^{-1}	Reductions in seed germination	Kong et al. (2018)
Tomato	20–30	10, 20, 50, and 100 mgL^{-1}	Growth inhibition above 50 mgL^{-1}	Li et al. (2016)

of studies have been focused on germinating or newly germinated seedlings, and data regarding other developmental stages are rare and needs to be further explored in the future. There are contradictory reports on the potential advantages or toxicity of nZnO in different plant species. The nZnO at the concentration of 1000 mgl^{-1} enhanced seed germination, shoot and root lengths, and vigor index (Prasad et al. 2012). Interestingly, the coated and uncoated nZnO were found to be more bioaccessible than the bulk (Moghaddasi et al. 2017). Moreover, the applications of coated and uncoated nZnO (10 or 100 $mgkg^{-1}$) in soil enhanced the biomass accumulations in both shoot and root in cucumber, whereas higher concentrations made no significant change or even declined seedling growth. In addition, the bulk ZnO at 1000 $mgkg^{-1}$ increased dry mass by 21%, in contrast to nZnO. The coated and uncoated nZnO at low concentration ($\leq$100 $mgkg^{-1}$) exhibited more positive effects than the bulk while more phytotoxic at high dose (1000 $mgkg^{-1}$) in the soil (Moghaddasi et al. 2017). Venkatachalam et al. (2017b) also conducted an experiment to explore the effects of nZnO-carrying phycomolecule ligands at 25, 50, 75, 100, and 200 mgL^{-1} on the growth rate in cotton (*Gossypium hirsutum*). The nZnO treatments exhibited the growth-promoting roles and considerably enhanced root length, shoot length, and total biomass accumulation. Similarly, the experiment conducted by Tarafdar et al. (2014) revealed that the nZnO application as a fertilizer improved growth indexes, biomass accumulation, and grain yield by nearly 40% in pearl millet (*Pennisetum americanum*). Furthermore, the effects of different pulse transient treatments of nZnO (root dipping into 2, 4, 8, or 16 mgL^{-1} for 15, 30, and 45 min) on 20-day-old seedlings of tomato were investigated by Faizan et al. (2018). Interestingly, these treatments effectively led to increases in the growth indexes, including the length of shoot and root, fresh and dry mass of shoots and roots, and leaf area, by approximately 30%. Moreover, seed priming with nZnO (100, 500, and 1000 mgL^{-1}) was found to promote Zn nutrition and growth rate in wheat, and the nanoform exhibited higher effectiveness relative to the ionic form (Elhaj Baddar and Unrine 2018). Also, the growth-promoting role of nZnO (25 mgL^{-1}) and the nZnO-mediated mitigation of Cd- or Pb-associated toxicity have been reported in *Leucaena leucocephala* (Venkatachalam et al. 2017a). Likewise, growing the green pea (*Pisum sativum*) plants in the organic-enriched soil with nZnO at 0, 125, 250, and 500 $mgkg^{-1}$ enhanced the root elongation while having no effect on shoot length (Mukherjee et al. 2014). Babajani et al. (2019b) investigated the effects of the nZnO treatments (50 and 250 mgL^{-1}) on the early growth of *Melissa officinalis.* The nZnO treatments had no effect on the germination and promoted biomass accumulation in the exposed *Melissa officinalis* (Babajani et al. 2019b). The nZnO exposure in alfalfa had no effect on germination rate at 250 and 500 mgkg^{-1} soil where ionic Zn represented higher toxicity (Bandyopadhyay et al. 2015). The accelerations in the flowering also occurred upon treatment of bulk form at 500 mgkg^{-1} levels which was different from the nZnO counterpart (Bandyopadhyay et al. 2015). Similarly, the nZnO applications (both foliar and soil amendment) exhibited potential benefits on the biomass accumulation, the number of flowers, and fruit yield in tomato plants (Raliya et al. 2015). Developments of lateral roots in wheat plants were also enhanced upon the nZnO exposure in wheat (Yang et al. 2017). Moreover, the field experiment conducted by Elizabath et al. (2017) revealed that the foliar utilization of nZnO improved various vegetative growth, yield, and biochemical traits. In addition, the biogenic nZnO treatment (600 mgl^{-1} for 3 h) enhanced vigor index and germination in *Vigna mungo* (Raja et al. 2019).

One critical determining factor is the plant species which is highlighted in several reports. For example, De La Rosa et al. (2011) investigated the effect of nZnO at concentrations ranging between 0 and 4000 mgL^{-1} on the early growth of three desert plant species (*Salsola tragus* (tumbleweed), *Prosopis juliflora*-velutina (velvet mesquite), and *Parkinsonia florida* (blue palo verde). The observed responses were dependent on the plant species and the nZnO doses. Even at the highest dose (4000), only the slight reduction in root lengths in blue palo verde and tumbleweed were observed, whereas the 50% inhibitory dose (IC50) in velvet mesquite was found to be 1000 mgL^{-1}. This report provides evidence that resistant plant species adapted for the desert condition may tolerate high doses of nanoparticles, implying the contribution of common defense mechanisms. Likewise, De la Rosa et al. (2013) evaluated the effect of plant species and dose factors on seed germination and seedling early performance. Seeds of three plant species, including alfalfa (*Medicago sativa*), tomato (*Solanum lycopersicum*), and cucumber (*Cucumis sativus*), were exposed to different doses of nZnO (0, 50, 100, 200, 400, 800, and 1600 mgL^{-1}). The results indicated that plant behaviors at the germination stage were dependent on the plant species and the applied concentrations. Inhibitory levels of 50% (IC50) were found in tomato and alfalfa plants exposed to 800 and 1600 mgL^{-1} of nZnO. Interestingly, the nZnO presence at 200 mgL^{-1} reinforced root system in cucumber by 2.7-fold relative to the control. The results represented by Pokhrel and Dubey (2013) also confirmed the importance of plant species as a key factor contributed to the differential plant behaviors to nanoparticles. In germinating maize, the nZnO exposure at concentrations ranging 0.01–1000 μgmL^{-1} did not make significant alteration, while inhibition of germination was found in a concentration-dependent way in cabbage (Pokhrel and Dubey 2013). Moreover, the evidence provided by Pokhrel and Dubey (2013) declares that nanoparticles may provoke specific responses differential from the corresponding ionic solution. Moreover, root anatomy and cellular morphology were altered in maize seedlings following the nZnO exposure ranging 0.01–1000 μgmL^{-1} which were partially different from their corresponding ionic controls (Pokhrel and Dubey 2013). Furthermore, the experiment carried out by Zhang et al. (2015) on corn (*Zea mays*) and cucumber (*Cucumis sativus*) confirmed plant species-specific behaviors. The nZnO of 1000 mgL^{-1} decreased root length in cucumber by 51% while this rate declined to 17% for corn seedlings. However, this high dose of nZnO did not make a significant change in the seed germination rate (Zhang et al. 2015).

Another key factor contributing to the nZnO advantage or toxicity is a soil characteristic or growth matrix which has been considered in several studies. For intense, Watson et al. (2015) explored the role of soil characteristics on Zn bioavailability and toxicity by conducting an experiment in a calcareous alkaline and acidic soil. Root elongation rate of the wheat seedlings cultured in soil supplemented by nZnO was curbed in a concentration-dependent manner in acidic soil, while the nZnO toxicity on wheat root system was alleviated in the calcareous alkaline soil. In addition, sand amendment with humic acid did not find a method for mitigating the nZnO toxicity based on changes in the growth, shoot uptake, and solubility of Zn. These results imply that variation in humic acid level may not be a key factor contributing to plant behaviors to the nanoparticles (Watson et al. 2015). The close correlation was also found to be between soluble Zn in the soil, Zn shoot content, and phytotoxicity pointing to the critical role of soil pH in plant responses to nZnO. Watson et al. (2015) concluded that formulations of nZnO as a soil amendment to improve plant Zn content require to be tuned to soil traits, especially pH, to exploit in agriculture. Also, Wang et al. (2013) highlighted the importance of the growth matrix (solution culture vs. soil culture) in plant experiments. In solution culture, $ZnCl_2$ was found to be more toxic than the nZnO with respect to the growth of cowpea, whereas there was no difference between ionic and nanoforms in a plant grown in soil (Wang et al. 2013). The fate and possible toxicity of different nZnO levels (10, 100, and 1000 mgL^{-1}) on *Schoenoplectus tabernaemontani* were evaluated by Zhang et al. (2015). The supplementation of nZnO at 1000 mgL^{-1} under the hydroponic condition inhibited the growth of *S. tabernaemontani*. Interestingly, seed priming with *Pseudomonas chlororaphis* O6 (PcO6) improved the resistance of the colonized wheat against drought stress, where these beneficial bacteria were not impaired by the presence of nZnO in soil (Yang et al. 2017). Yang et al. (2017) concluded that nZnO bioavailability plays critical roles in governing root morphology and function.

The nZnO-mediated toxicities have been reported in diverse plant species. Wang et al. (2016a, b) monitored the responses of *Arabidopsis* to different doses of nZnO, including 50, 100, 200, 250, and 300 mgL^{-1}. Decreases in biomass occurred above 200 mgL^{-1} doses. In addition, reductions in water contents and root/shoot ratio were found upon the nZnO treatment at 300 mgL^{-1} level. They concluded that the root organ is more sensitive than the shoot to nZnO. Nair and Chung (2017) also investigated the morphological changes of *Arabidopsis thaliana* seedlings in response to the different nZnO doses (20, 50, 100, and 200 mgL^{-1}) for 14 days. Except for the 20 mgL^{-1} treatment, the fresh weight of seedlings and primary root lengths were diminished. On the other hand, the formation of lateral roots was accelerated upon the nZnO exposures at 20 and 50 mgL^{-1} levels. Chlorosis and reduction in leaf size were found at high concentrations. The root architecture was altered with increases in lateral roots at 20 and 50 mgL^{-1} doses contrasted to the higher levels of nZnO (Nair and Chung 2017). The adverse effects of nZnO (250–1000 mgL^{-1}) on the root length, shoot height, and biomass were also addressed in rice (Chen et al. 2015). Moreover, Bradfield et al. (2017) reported that the nZnO application at 1000 $mgkg^{-1}$ made an adverse effect on tuber biomass. The soil supplementation with nZnO posed no higher risk to food safety or crop productivity than do the ionic counterpart. Therefore, they reported dissolution of the nanoparticles to ionic type. Furthermore, the high dose of nZnO (500 mgL^{-1}) at germinating stage diminished leaf fresh weight, root length, and biomass in soybean seedlings, while it did not make a significant change in shoot height and fresh weight (Hossain et al. 2016). In addition, the nZnO treatments (200, 400, and 800 mgL^{-1}) restricted the shoot and root growth in tomato plants (Wang et al. 2018). Iranbakhsh et al. (2018b) explored the effects of seed priming with nZnO (100 mgL^{-1}) on the germination and early growth and performance of pepper (*Capsicum annuum*) in both *in vitro* and pot conditions. The nZnO treatment exhibited a growth-delaying impact and reduced biomass accumulation in both root and leaves (Iranbakhsh et al. 2018b). Furthermore, Yoon et al. (2014) carried out an experiment to evaluate the long-term effects of nZnO on vegetative growth, development, and reproduction of *Glycine max*. The soil was amended with 0, 50, or 500 $mgkg^{-1}$ soil. The high dose of nZnO severely impaired soybean growth and development as well as inhibited seed formation. Moreover, the nZnO (10, 100, 500, and 1000 mgL^{-1}) treatments displayed no effect on seed germination percentage (Boonyanitipong et al. 2011). However, reduction in root length and lateral root formations at concentrations above 100 mgL^{-1} doses were observed (Boonyanitipong et al. 2011). Similarly, the growth-inhibiting roles of nZnO at high doses (200, 500, 1000, and 1500 mgL^{-1}) were observed in *Brassica juncea* (Rao and Shekhawat 2014). Interestingly, Tripathi et al. (2017b) explored the ameliorating effects of exogenous nitric oxide (NO) in wheat plants counteracted with nZnO (100 and 200 μM). The nZnO exposure caused decreases in biomass accumulation which were partially mitigated by the NO application.

Several reasons may consider as key predominant mechanisms through which nanoparticles affect seed germination and seedling early performance. These mechanisms are as follows (Pokhrel and Dubey 2013; Tripathi et al. 2017a; Iranbakhsh et al. 2018b):

1. Specific ion effect
2. Osmotically induced change and water content
3. Changes in phytohormonal balance
4. Plant species
5. Triggered signaling by reactive oxygen/nitrogen species (ROS/RNS)
6. Changes in ROS/RNS inter- and intracellular accumulations
7. Differential activity of enzymes, like amylase
8. Alterations in nutritional status
9. Molecular-based modifications
10. Modulations in the cell cycle

11. Modifications in primary and secondary metabolism
12. Changes in organ–communications and source/sink relationship

As highlighted above, nZnO exposure may influence root architecture, especially the development of the lateral root. In this regard, the close correlation was found between the Zn homeostasis and root developmental pattern in *Arabidopsis* (Jain et al. 2013). It should be also noted that the contrasting results are recorded for nZnO in comparison to ionic salts, reflecting the possible implications of differential uptake, the mechanism(s), and/or toxicity pattern in different plant species. It is noteworthy that there are limitations in studies focusing on the effects of the nZnO treatment at the higher developmental stage and plant reproductive system which needs to be further explored in upcoming studies.

5.2 Anatomical and Morphological Changes

In plants, cell identity and differentiation process are regulated and progressed through a complicated interplay between time, position, and internal and external cues. Phytohormones, transcription factors, small peptide signaling, and miRNAs construct modulatory networks determining cell fate and mediating communication between organs (Pierre-Jerome et al. 2018). Plant reactions to stress conditions are firmly adjusted with the developmental program (Iyer-Pascuzzi et al. 2011). However, there is a gap of knowledge in the cross talk between stress and development routes. There are several limited studies to address how nZnO exposure may affect plant anatomy. Pokhrel and Dubey (2013) provided the anatomical and histological evidence on the nZnO-associated changes at a wide range (0.01–1000 μgmL^{-1}). Interestingly, the tunneling-like effect in apical meristem and differential cellular growth and morphology at the root elongation zone were observed in the nZnO-exposed maize seedlings. The nZnO treatment of 1000 mgL^{-1} in *Zea mays* led to an increase in metaxylem vessel count relative to the untreated and equivalent ionic controls. Moreover, Mahajan et al. (2011) monitored behaviors of mung (*Vigna radiata*) and gram (*Cicer arietinum*) seedlings upon different doses of nZnO (10, 20, 50, 100, 500, 1000, and 2000 mgL^{-1}). The toxicity signs of high doses were observed in the epidermis, cortex region, and vascular system in the exposed roots of both plant species. The high concentrations of nZnO resulted in the vacuolated and collapsed cortical cells, whereas vascular cylinder was found to be shrunk. Using SEM-EDEX analysis, the adsorption and aggregation of nZnO on root surface were also evident (Mahajan et al. 2011). The seed incubation in nZnO delayed growth changed morphology and restricted a differentiation process of vascular-conducting tissue, xylem, in pepper (Iranbakhsh et al. 2018b). It is worth mentioning that the contribution of specific transcription factors, including VASCULAR-RELATED NAC-DOMAIN6 (VND6) and VND7, in conductance of cellular differentiation into metaxylem vessel elements has been manifested (Kubo et al. 2005). These findings are consistent with the fact that nanomaterials may interact with biological systems in the way different from their bulk counterparts. Water deficiency, phytohormonal modifications (in particular auxin and cytokinin), osmotically induced alterations, and/or molecular changes have been mentioned as key mechanisms contributing to the nZnO-provoked anatomical changes, especially xylem-conducting tissue (Pokhrel and Dubey 2013; Iranbakhsh et al. 2018b). It is important to note that there is a gap of knowledge in the nZnO-mediated changes in cellular differentiation process and plant anatomy, especially at different developmental stages like reproduction which need to be further figured out.

5.3 Antioxidant System

To counteract with oxidative burst, plants activate defense antioxidant machinery. The antioxidant system in plants consists of two main subgroups, including enzymatic and nonenzymatic low-molecular-weight antioxidants. These antioxidants function in quenching, scavenging, and detoxification of intracellular accumulated ROS. The most common antioxidant enzymes are peroxidase (POX), ascorbate peroxidase (APX), catalase (CAT), superoxide dismutase (SOD), and glutathione reductase (GR). Moreover, glutathione and ascorbates are the most important low-molecular-weight antioxidants. It is worth mentioning that the ROS production is mediated through reactions occurring in different organelles, including peroxisomes, chloroplast, mitochondria, membrane, and apoplast. When plants are exposed to diverse biotic or abiotic stress conditions, the disturbance in the balance between the scavenging antioxidants and ROS production occurs. It is well known that ROS are not only destructive toxic molecules but can also act as a critical inter- and intracellular signaling factor. Furthermore, ROS at sublethal concentrations triggers specific signaling cascades through which defense machinery is activated (Iranbakhsh et al. 2018a). Interestingly, the steady-state intracellular status of ROS is tightly modulated through a highly dynamic complicated network of genes (over 150 genes in *Arabidopsis*) (Mittler et al. 2004). Besides, the transduction process of various extra-, inter-, and intracellular signals is mediated through mitogen-activated protein kinase (MAPK) cascades which are highly conserved signaling units and play pivotal roles in mediating stress tolerance in plants. Furthermore, MAPK cascades contribute to diverse processes, like ROS generation, the biosynthesis/signaling of phytohormones, stomatal conductance, cell wall strengthening, activations of defense-responsive genes, and hypersensitive response cell death (Pitzschke et al. 2009). Interestingly, ROS (in particular H_2O_2) activates several components of MAPK cascade. Signal transduction and ROS accumulation may induce multiple signaling cascades by which gene expression pattern changes at the transcriptional level. Protein phosphorylation modulated by specific MAP kinases, heterotrimeric G-proteins, and protein Tyr phosphatases involves in ROS signaling (Ahmad et al. 2008). Modulation of gene expression through various oxidants and antioxidants is an important mechanism in regulating plant growth and development (Ahmad et al. 2008; Iranbakhsh et al. 2018a). It should be noted that ROS via modifying the activity of transcription factors may influence the cellular pattern of gene expression (Ahmad et al. 2008). Owing to specific physicochemical characteristics, an especially high ratio of surface area to volume, small size, along with specific surface traits (Ghosh et al. 2016), nanoparticles possess highly penetration into cellular compartments and intensive reactivity. There are several ways to explore whether nanoparticle presence is inducing an oxidative burst:

1. Detecting and quantifying intracellular accumulations of ROS, especially H_2O_2
2. Investigating the activation of enzymatic or nonenzymatic antioxidant machinery
3. Detecting transcriptional upregulation or downregulation genes involved in the antioxidant machinery
4. Evaluating membrane integrity via determining the lipid peroxidation rates (malondialdehyde (MDA) method) or utilizing markers like Evans blue dye

Findings of various reviewed reports point to the nZnO-induced overaccumulation of ROS/RNS and associated oxidative stress (especially toward membrane integrity) as the main mechanism contributing to its phytotoxicity. It has been hypothesized that inductions in enzymatic and nonenzymatic antioxidants may indirectly reflect the ROS overaccumulation in the counteracted cells. The oxidative damages mediated by the excessive intracellular production and accumulation of ROS are oxidative impairments in biomolecules, including DNA, proteins, and lipids and ultimately cell death. The nZnO-mediated alterations in the antioxidant system are represented in Table 3. The results represented by Tripathi et al. (2017b) indicated that the nZnO treatments (100 and 200 μM) posed the oxidative stress confirmed by increases in H_2O_2 and lipid peroxidation levels which is relieved by the nitric oxide (NO) utilization. Moreover, the activities of enzymes implicated in the ascorbate–glutathione cycle (APX, GR, dehydroascorbate reductase (DHAR), and monodehydroascorbate reductase (MDHAR)) were restricted under the nZnO presence at 100 and 200 μM doses by nearly 30% which these inhibiting signs were declined by NO supplementation in wheat seedlings. Furthermore, the concentrations of dehydroascorbate and ascorbate were found to be enhanced under the nZnO treatments, whereas ascorbate/dehydroascorbate ratio severely declined following the nZnO exposures. The nZnO treatments also improved the concentrations of GSH + GSSG, GSH, and GSSG, while the content of GSH/GSSG ratio was declined (Tripathi et al. 2017b). Similarly, the nZnO treatments ranging from 250 to 1000 mgL^{-1} augmented the accumulation of superoxide and H_2O_2 and lipid peroxidation levels which is partially mitigated with an exogenous NO (Chen et al. 2015). The concentrations of GSH in both root and shoot were also increased in rice plants counteracted with high doses of nZnO (Chen et al. 2015). The high concentrations of nZnO induced the SOD activity in both shoot and root but declined the activities of CAT, APX, and POX activity (Chen et al. 2015). Interestingly, these results were supported with molecular analysis at transcriptional levels. The results represented by Venkatachalam et al. (2017b) showed that the nZnO presences (25–200 mgL^{-1}) in the culture medium caused inductions in activities of SOD and POX enzymes while decreased CAT activity in *Gossypium hirsutum*. The levels of lipid peroxidation in leaves were also found to be reduced in the plants supplemented with nZnO. Moreover,

Table 3 The nZnO-mediated alterations in oxidative burst, membrane integrity, ROS accumulation, and antioxidant system

Plant	Dose	Main findings	Reference
Allium cepa	25, 50, 75, and 100 mgl^{-1}	Increases in lipid peroxidation in a dose-dependent manner	Kumari et al. (2011)
Buckwheat	0, 1, 5, 100, 1000, and 2000 mgL^{-1}	Increases in GSH Inductions in CAT activity	Lee et al. (2013)
Tomato	10, 20, 50, and 100 mgL^{-1}	Increases in H_2O_2, and lipid peroxidation Augmentation in GSH and decrease in GSSG Increase in GSH:GSSG ratio Inductions in SOD, CAT, APX, and GR	Li et al. (2016)
Corn	100, 200, 400, and 800 mgkg^{-1} soil	Reductions in CAT activity	Zhao et al. (2013)
Wheat	500 mgkg^{-1} sand matrix	Increases in root lipid peroxidation and shoot GSSG Inductions in root POX and CAT activities	Dimkpa et al. (2012)
Cucumis sativus	10, 50, 100, 500, and 1000 mgL^{-1}	Increases in POX, SOD, and CAT	Kim et al. (2012)
Duckweed	1, 10, and 50 mgL^{-1}	Inductions in SOD and CAT activity Differential POX activity dependent on the dose and exposure time	Hu et al. (2013)
Velvet mesquite	500 to 4000 mgL^{-1}	Promotion in CAT activity in roots, stems, and leaves inductions in APX in stems and leaves	Hernandez-Viezcas et al. (2011)
Green pea	125, 250, and 500 mgkg^{-1}soil	Reductions in leaf CAT activity while unaffected in root Downregulation in root and leaf APX Increases in leaf H_2O_2 (61%) and lipid peroxidation (twofold) at 500 mgkg^{-1}	Mukherjee et al. (2014)
Allium cepa *Vicia faba* *Nicotiana tabacum*	0.2, 0.4, and 0.8 gL^{-1}	Differential sensitivity dependent on plant species Loss of membrane integrity	Gosh et al. (2016)
Bean Tomato	3, 20, and 225 mgkg^{-1} soil	Oxidative burst Increases in lipid peroxidation level Changes in enzymatic antioxidants dependent on plant species, exposure time, dose, and soil pH	García-Gómez et al. (2017)

(continued)

Table 3 (continued)

Plant	Dose	Main findings	Reference
Oryza sativa	500 and 750 mgl^{-1}	Increase in electrolyte leakage Augmentations in H2O2 and superoxide radical Severe oxidative burst Inductions in SOD, CAT, POX, DHAR, and MDAR	Sheteiwy et al. (2017)
Rice	250, 500, and 750	Inductions in antioxidant enzymes SOD, POX, and CAT Increases in lipid peroxidation levels Stimulations in transcription of genes of antioxidant enzymes	Salah et al. (2015)
Rice	250, 500, and 750 mgl^{-1}	Inductions in GR activity ROS accumulation Expression of *GR1* and *GR2* genes in both shoots and roots	Sheteiwy et al. (2016)
Tomato	200, 400, or 800 mgdm^{-3}	Inductions in SOD, CAT, and APX activities in a dose-dependent manner Upregulation of genes contributed to an antioxidant enzymes.	Wang et al. (2018)
Salvinia natans	1–50 mgL^{-1}	Inductions in SOD and CAT activities at 50 mgl^{-1}	Hu et al. (2014)
Rice	50, 100, 250, 500, and 1000 mgL^{-1}	Increase in superoxide and H2O2 Increases in lipid peroxidation in leaves contrasted to root. Increase in GSH in both root and shoot Inductions in SOD Decline in CAT, APX, and POX activity in roots and shoots Increase in NO in root and shoot Changes in expression of several related genes	Chen et al. (2015)
Wheat	100 and 200 μM	Decreases in NO content by mean 36% Increases in H_2O_2 and lipid peroxidation Restriction in enzyme activities of the AsA–GSH cycle (APX, GR, DHAR, and MDHAR) Augmentations in the AsA + DHAsA and AsA Decline in AsA/DHAsA ratio Improvement in GSH + GSSG, GSH, and GSSG Reduction in GSH/GSSG ratio	Tripathi et al. (2017b)

(continued)

Table 3 (continued)

Plant	Dose	Main findings	Reference
Leucaena leucocephala	25 mgL^{-1}	Decrease in lipid peroxidation Inductions in activities of SOD, CAT, and POX The ameliorating effect of heavy metal stress Alterations in isoenzyme patterns	Venkatachalam et al. (2017a)
Cotton	25, 50, 75, 100, and 200 mgL^{-1}	Reduction in the level of lipid peroxidation in leaves Inductions in SOD and POX Decrease in the CAT activity Differential isoenzyme patterns of POX, CAT, and SOD	Venkatachalam et al. (2017b)
Brassica juncea	200, 500, 1000, and 1500 mgl^{-1}	Changes in antioxidant enzymes in dose- and organ-dependent Inductions in APX and SOD Downregulation in GR and CAT Increase in lipid peroxidation at 1000 mgl^{-1} Acceleration in ROS generation	Rao and Shekhawat (2014)
Tomato	0, 2, 4, 8, or 16 mgL^{-1}	Inductions in CAT, POX, and SOD activities	Faizan et al. (2018)
Banana	50, 100, and 200 mgL^{-1}	Inductions in SOD, CAT, and POX activities	Helaly et al. (2014)
Alfalfa	250, 500, and 750 $mgkg^{-1}$	No alteration in CAT activity	Bandyopadhyay et al. (2015)
Soybean	500 mgl^{-1}	H_2O_2 accumulation in leaves	Hossain et al. (2016)

Venkatachalam et al. (2017b) conducted an electrophoresis analysis to evaluate the possible nZnO-mediated changes in the isoenzyme expression patterns of several key antioxidant enzymes (SOD, CAT, and POX). They observed that the nZnO applications differentiated the isoenzyme expression patterns and intensity of the appeared bands. Interestingly, five SOD isoforms appeared in the plants exposed to nZnO ranging from 25 to 200 mgL^{-1} levels, while only one isoform was detected in the control plants. Also, the nZnO treatments mediated the presence of new CAT isoform in the exposed plants. Furthermore, the higher intensities of the two POX isoforms were recorded in the nZnO-supplemented plants. Venkatachalam et al. (2017b) concluded that nZnO exposure may upregulate the expression rate of POX, CAT, and SOD isoenzymes in lower concentrations and slightly downregulate upon higher doses. In another study, the nZnO presences (500 and 750 mgL^{-1}) in hydroponic conditions for 2 weeks triggered oxidative burst (accumulations of H_2O_2 and superoxide radical) and impaired membrane integrity in rice (Sheteiwy et al. 2017). Also, the inductions in SOD, CAT, POX, DHAR, and MDAR were recorded in the rice plants counteracted with nZnO (Sheteiwy et al. 2017). Furthermore, the molecular evidence provided by Salah et al. (2015) manifested the upregulations in transcription of several genes involved in the enzymatic antioxidants which will be explained later in more details in this chapter. Moreover, the GR activity and expression of the related genes (GR1, GR2) were found to be induced in rice challenged with the high concentrations of nZnO (Sheteiwy et al. 2016). Kumari et al. (2011) explored the effects of different concentrations of nZnO (25, 50, 75, and 100 g mL^{-1}) in *Allium cepa*. They found that the lipid peroxidation rates were enhanced at 50 mgL^{-1} dose and above. Similarly, the nZnO toxicity at 200–800 mgL^{-1}, relatively high concentrations, in 7-day-old onion (*Allium cepa*) seedlings was estimated by Gosh et al. (2016). Interestingly, the intracellular accumulation of ROS following the nZnO treatments at concentrations of 400 mgL^{-1} and above was recorded using DCFH-DA (2,7-dichlorofluorescin diacetate) staining method and evaluating fluorescence intensity of DCF (Gosh et al. 2016). The nZnO presence inhibited the catalase activity in *A. cepa* root cells while increased peroxidase activity and GSH levels. Total thiols and GSH were also enhanced by the nZnO treatments at 0.2 and 0.4 gL^{-1} levels. Moreover, the close correlations were found to be between the H_2O_2 production, lipid peroxidation, enzymatic (peroxidase and catalase) and nonenzymatic (thiols and glutathione) antioxidants, and DNA damage (Gosh et al. 2016). Likewise, the utilization of nZnO above 50 mgL^{-1} levels in tomato augmented the accumulations of hydrogen peroxide (H_2O_2) and lipid peroxidation in roots, implying the occurrence of oxidative stress (Li et al. 2016). The activities of SOD, CAT, APX, and GR were induced upon the nZnO exposure. Furthermore, reduced glutathione (GSH) contents were also enhanced, while the oxidized glutathione (GSSG) levels were decreased (Li et al. 2016). Mukherjee et al. (2014) investigated the phytotoxicity on green pea (*Pisum sativum*) under nZnO treatments (125, 250, and 500 $mgkg^{-1}$ organic-enriched soil) for 25 days. At all nZnO doses, CAT activity was declined in leaves whereas unaffected in the root. APX activities in both roots and leaves were also diminished. In the case of bulk ZnO, APX activity was downregulated in the root and leaf, and CAT was unaffected. With a similar trend, the CAT activity was declined in leaves whereas remained unchanged in the root. In addition, the nZnO presence at 500 $mgkg^{-1}$ soil augmented the H_2O_2 accumulations in leaves by 61% and lipid peroxidation by twofold (Mukherjee et al. 2014). Moreover, the induction of oxidative stress following the nZnO treatments was confirmed by the stimulations in the accumulations of H_2O_2 and other ROS/RNS in *Spirodela punctata*, an aquatic plant (Thwala et al. 2013). Furthermore, the augmentation in GSH content and induction in CAT activity were recorded in buckwheat seedling subjected to nZnO (Lee et al. 2013). The corn cultivations in soil amended with nZnO at 400 $mgkg^{-1}$ level declined the activities of CAT and APX (Zhao et al. 2013). Hernandez-Viezcas et al. (2011) reported that the nZnO treatments at the concentrations ranging from 500 to 4000 mgL^{-1} induced CAT and APX in different plant organs of the exposed *Juliflora velutina* (velvet mesquite). As mesquite plants displayed tolerance to the nZnO exposure and exhibited no sign of toxicity, like necrosis, chlorosis, or wilting, even after 30 days, an existence of efficient antioxidant machinery in this plant may be responsible for its resistance. The presence of nZnO in the culture medium led to inductions in activities of SOD and CAT in duckweed (*Spirodela polyrhiza*) (Hu et al. 2013). The nZnO treatments (10, 50, 100, 500, and 1000 mgL^{-1}) provoked stimulations in POX, CAT, and SOD activities in the exposed root of *Cucumis sativus* (Kim et al. 2012). The inactivation of the enzyme protein associated with excessive ROS, alterations in the assembly of the enzyme subunits, or downregulation in enzyme synthesis may be responsible for the observed decline in catalase activity following the nZnO exposure (Gosh et al. 2016). The activities of several antioxidant enzymes (SOD, CAT, and APX) were stimulated upon the nZnO (200, 400, and 800 mgL^{-1}) treatments in tomato plants in a dose-dependent manner (Wang et al. 2018). Consistent with these findings, the genes contributing to an enzymatic antioxidant system (Cu/Zn2-SOD, Fe-SOD, APX2, and CAT1) were upregulated in tomato seedlings exposed to nZnO above 400 mgL^{-1} doses (Wang et al. 2018). Interestingly, the transient pulse treatments of 20-day-old tomato seedlings with nZnO (2, 4, 8, or 16 mgL^{-1} for 15, 30, and 45 min) induced the activities of key antioxidant enzymes, including CAT, POX, and SOD (Faizan et al. 2018). The nZnO (25 mgL^{-1}) improved activities of important antioxidant enzymes (CAT, POX, and SOD) in *Leucaena leucocephala* challenged by heavy metals (Cd or Pb) (Venkatachalam et al. 2017a). In addition, Venkatachalam et al. (2017a) provide data on the nZnO-mediated changes in POX isoenzyme pattern in the *L. leucocephala* exposed to Pb and Cd heavy metals. Moreover, the nZnO application declined the ROS accumulation and lipid peroxidation levels. The nZnO treatment (50 mgL^{-1}) also induced the CAT and SOD activities in *Salvinia natans*, an aquatic plant (Hu et al. 2014). Furthermore, the nZnO exposure (200, 500, 1000, 1500 mgL^{-1}) in *Brassica juncea* mediated the alterations in enzymatic antioxidants, including CAT, GR, APX, and SOD in the dose- and organ-dependent manner (inductions in APX and SOD and downregulation in GR and CAT) (Rao and Shekhawat 2014). Interestingly, the supplementation of acidic soils with high concentrations of nZnO provoked an augmentation in the ROS accumulation and lipid peroxidation (the most prominent symptom of oxidative stress) in the counteracted bean (García-Gómez et al. 2017). The experiment conducted by García-Gómez et al. (2017) proved that the nZnO presence can alter the oxidative burst biomarkers and activities of antioxidant enzymes dependent on plant species, applied doses, exposure time, and pH of soil or exposure media.

5.4 Photosynthesis

Photosynthesis processes, including the electron transport chain and carbon assimilation, get influenced by different internal and environmental cues. To avoid photoinhibition phenomenon during stress conditions, plants activate non-photochemical quenching (NPQ) through which the excess energy is dissipated in the form of heat. Diverse attempts have been employed to improve the productivity of cultivating crops by manipulating their biochemical processes. It has been stated that the efficiency of chemical energy production in photosynthetic systems may be induced by metal nanoparticles (Govorov and Carmeli 2007). Both potential benefits and

Table 4 The nZnO-mediated changes in different traits related to photosynthesis performance

Plant	Dose	Main findings	Reference
Tomato	2, 4, 8, or 16 mgL^{-1}	Increases in the photosynthetic pigments Promotion in leaf gas-exchange traits (Ci, gs, PN, E) by 38% Inductions in carbonic anhydrase activity by 38.5%	Faizan et al. (2018)
Leucaena leucocephala	25 mgL^{-1}	Augmentations in photosynthetic pigments	Venkatachalam et al. (2017a)
Cotton (*Gossypium hirsutum*)	25, 50, 75, 100, and 200 mgL^{-1}	Increases in the Chl a, Chl b, and carotenoids	Venkatachalam et al. (2017b)
Salvinia natans	1–50 mgL^{-1}	Decreases in photosynthetic pigments at 50 mgl^{-1}	Hu et al. (2014)
Tomato	200, 400, or 800 mgL^{-1}	Reductions in Chl a (60%) and b (70%) at the highest dose Increases in carotenoid contents Upregulation of carotenoid synthesis genes Downregulation of diverse photosynthesis genes	Wang et al. (2018)
Arabidopsis	50, 100, 200, 250, and 300 mgl^{-1}	Changes in chlorophyll synthesis and transcriptions of genes contributed to photosystem. Little effects on Chl at low doses Increases in Chl a/b ratio at high doses Increases in carotenoid Decreases in the net rate of photosynthesis, with an about 60% decrease observed in 300 mgL^{-1}	Wang et al. (2016a, b)
Wheat	100 and 200 μM	Decline in Chl content by mean 22.5% Reduction in Fv/Fm and qP Elevation in NPQ	Tripathi et al. (2017b)
Capsicum annuum	100 mgl^{-1}	Reduction in Chl a Increase in carotenoid	Iranbakhsh et al. (2018b)
Pearl millet		Increases in Chl (24.4%)	Tarafdar et al. (2014)
Brassica juncea	200, 500, 1000, and 1500 mgl^{-1}	Decrease in Chl contents	Rao and Shekhawat (2014)
Phaseolus vulgaris *Solanum lycopersicon*	3, 20, and 225 mg kg^{-1} soil	Changes in photosynthetic pigments dependent on plant species, exposure time, dose, and soil pH	García-Gómez et al. (2017)

toxicity of nZnO have been evident. The nZnO-associated changes in photosynthesis pigments and performance are represented in Table 4. Faizan et al. (2018) conducted an experiment to explore the effect of pulse treatments of nZnO on photosynthesis performance in tomato. Interestingly, root dipping of 20-day-old seedlings into solution containing nZnO of 2, 4, 8, or 16 mgL^{-1} for different duration (15, 30, and 45 min) led to the increases in chlorophyll (Chl) contents; promotions in leaf gas-exchange traits, including intercellular CO_2 concentration (Ci), leaf stomatal conductance (gs), net photosynthetic rate (PN), and transpiration rate (E) by mean 38%; and inductions in carbonic anhydrase activity by approximately 38.5%. The nZnO treatment at 25 mgL^{-1} enhanced the concentrations of photosynthetic pigments, including Chl a, Chl b, and carotenoids in *Leucaena leucocephala* (Venkatachalam et al. 2017a). Similarly, the photosynthesis pigments, including Chl a, Chl b, and carotenoids, were found to be enhanced in the cotton plants subjected to the nZnO treatments ranging 25–200 mgL^{-1}(Venkatachalam et al. 2017a). The increases in carotenoids were also observed in the nZnO-treated pepper seedlings (Iranbakhsh et al. 2018b). The enhancing roles of nZnO on photosynthetic pigments were also reported by Tarafdar et al. (2014) in *Pennisetum americanum*. Furthermore, the increases in Chl and carotenoid contents occurred in bean or tomato plants grown in the calcareous soil supplemented with nZnO, whereas decrease or no change in photosynthetic pigments was recorded in acidic soil (García-Gómez et al. 2017). On the other hand, there are several reports implying the potential toxicity of nZnO application on the photosynthesis performance. Wang et al. (2016a, b) explored the effects of nZnO at 100, 200, and 300 mgL^{-1} doses on the transcription rates of diverse genes implicated in Chl synthesis, including CHLOROPHYLL A OXYGENASE (CAO), COPPER RESPONSE DEFECT 1 (CRD1), CHLOROPHYLL SYNTHASE (CHLG), MG-CHELATASE SUBUNIT D (CHLD), and MAGNESIUM-PROTOPORPHYRIN IX METHYL TRANSFERASE (CHLM) in *Arabidopsis*. Also, they monitored the nZnO-mediated changes in the expression of several genes involved in carotenoid metabolism (PHYTOENE SYNTHASE (PSY), GERANYL GERANYL PYROPHOSPHATE SYNTHASE 6 (GGPS6), ZETA-CAROTENE DESATURASE (ZDS), and PHYTOENE DESATURASE (PDS)) and photosystem structure (PHOTOSYSTEM I SUBUNIT K (PSAN), PHOTOSYSTEM ISUBUNIT E-2 (PSAE2), PHOTOSYSTEM ISUBUNIT D-2 (PSAD2), and PHOTOSYSTEM ISUBUNIT K (PSAK)). Interestingly, the expression of CRD1, CHLM, CAO, CHLG, and CHLD was declined in response to the nZnO treatments at all doses (100, 200, and 300 mgL^{-1}). In plants exposed to the supernatant solution of 300 mgL^{-1}, the slight increase in the transcription of CHLG and CAO was recorded, whereas the expression of CHLM, CHLD, and CRD1 remained unchanged. In addition, the nZnO treatments exhibited enhancing effects on the expression of PDS, PSY, GGPS6, and ZDS. The reductions in stomatal conductance, intercellular CO_2 levels, transpiration rate, and consequently net photosynthesis were recorded in the *Arabidopsis* plants counteracted with the high doses of nZnO (Wang et al. 2016a, b). In another experiment, the nZnO (200, 400, or 800 mgL^{-1}) treatments in a dose-dependent manner reduced the Chl a and Chl b concentrations, Chl fluorescence traits, and photosynthetic efficiency in tomato (Wang et al. 2018). Moreover, impairment in the photochemical system and decreases in Chl contents upon exposure to high doses of nZnO may limit photosynthesis and consequently lead to the reduction in biomass accumulation. Wang et al. (2018) reported that the lower doses of nZnO made little or no changes in Chl a and Chl b concentrations, whereas severe decreases (mean 65%) occurred in the seedlings counteracted with nZnO of 800 $mgdm^{-3}$. The nZnO treatments exhibited an enhancing role in carotenoid contents. Consistently, the transcription rates of genes contributing to chlorophyll synthesis (CHLG, CRD1, CAO, CHLI, HEMB, HEMG, and HEMC) were declined in the seedlings challenged with the high doses of nZnO (Wang et al. 2018). Moreover, the transcriptions of genes implicated in carotenoid synthesis (PSY and LYCB) enhanced upon the nZnO treatments. The high level of nZnO (800) diminished the PN, gs, E, and ci in the tomato seedlings, referring decrease in photosynthesis performance. The transcription rates of genes involved in photosynthesis (SBPASE and FBPASE) were also restricted in the plant treated with the high levels of nZnO (Wang et al. 2018). With the increasing nZnO concentrations, the Chl fluorescence characteristics, including Fv/Fm (maximum efficiency of PS II photochemistry), ΦPSII (quantum yield of PS II photochemistry), qP (photochemical quenching), and ETR (apparent electron transport rate), were reduced by approximately 25%, implying some damages to the photochemical system. Furthermore, the high dose of nZnO restricted the expression of photosystem structure genes (PSBH, PSBD, PSAA, and PSBF) (Wang et al. 2018). Interestingly, the nZnO treatments (100 and 200 μM) declined total Chl levels by a mean 23% in the wheat, which was alleviated by the NO application (Tripathi et al. 2017b). Also, the nZnO treatments at 100 and 200 μM led to reductions in Fv/Fm (by 8% and 24%) and qP (by 11% and 31%), while NPQ was enhanced in wheat plants challenged with nZnO. Interestingly, Tripathi et al. (2017b) found that the exogenously applied NO mitigated the nZnO-mediated increases in NPQ. The adverse impacts of the nZnO exposure at high doses on the photosynthetic pigments were also observed in *Brassica juncea* (Rao and Shekhawat 2014).

5.5 Phytohormones

(IAA), cytokinin, gibberellin (GA), abscisic acid (ABA), ethylene, polyamines, salicylic acid (SA), and jasmonic acid (JA), modulate cellular division and differentiation process, cell cycle, growth, development, metabolism, and protection. Moreover, there is intensive cross talk between the developmental signals, environmental cues, signaling pathways, and phytohormonal balances, thereby regulating plant growth, development, and metabolism. Furthermore, different environmental stresses may change the hormonal profiles through which plants may regulate growth, development, and metabolism and activate the defense system. It is worth mentioning that downregulation of growth-promoting hormones (especially cytokinin and auxin) results in growth suppression. It is well known that cytokinins

Table 5 The nZnO-mediated change in hormonal balances

Plant	Dose	Main findings	Reference
Rice	500 and 750 mgL^{-1}	Increase in ABA Upregulations in genes involved in ABA biosynthesis and catabolism Decreases in GA and expressions of related genes	Sheteiwy et al. (2017)
Arabidopsis	0.16, 0.8, 4, 20, and 100 mgL^{-1}	Improvements in cytokinin at low doses, contrasted to high doses Decline in the cytokinin ribosides Reduction in auxin in apices, no change in leaf level Augmentation in ABA in leaf and apices Increases in SA in leaves, root, and meristem at low doses, contrasted with high Decrease in JA levels in apices, roots, and leaves	Vankova et al. (2017)
Cicer arietinum	2000 mgL^{-1}	Increases in auxin (IAA) in root	Pandey et al. (2010)
Rice	50, 100, 250, 500, and 1000 mgL^{-1}	Increase in NO in root and shoot	Chen et al. (2015)
Wheat	100 and 200 μM	Decrease in NO content by mean 36%	Tripathi et al. (2017b)
Arabidopsis	20, 50, 100, and 200 mgL^{-1}	Modifications in transcription of genes contributed to hormone regulation	Nair and Chung (2017)

stimulate cellular division. Moreover, signaling cascades triggered by various phytohormones as ubiquitous mechanisms contribute to the integration within cross-communicating signaling networks through which transcription factors, growth, development, and defense system are regulated and interconnected (Allahverdiyeva et al. 2015). Furthermore, they are involved in the modulation of the cell cycle. It is important to note that hormones act as key signals for two checkpoints (G1/S and G2/M) of cell cycle progression (Vankova et al. 2017). Plants respond to diverse environmental factors via differential distributions of hormones within different organs (Wang et al. 2015). It has been well documented that there is a close cross-link between ROS-, NO-, and phytohormones-mediated signaling network (Iranbakhsh et al. 2020) through which plant growth, physiology, development, and stress adaptation are modulated. The current findings point to this fact that nanoparticles may influence phytohormonal balances at both signal transduction and metabolite levels. Hence, the nZnO-mediated modifications in hormonal balances are of crucial importance and need to be further explored (Table 5). It is worth mentioning that the nZnO-mediated alterations in hormonal status have been illustrated in rice (Sheteiwy et al. 2017). The high doses of nZnO (500 and 750 mgL^{-1}; hydroponic; exposure time of 14 days) augmented the ABA contents while decreased GA concentrations in the exposed rice plants (Sheteiwy et al. 2017). Interestingly, these results were supported by the molecular assessments at transcriptional levels (explained in more details later). Moreover, the upregulation in OsABA8ox2 and OsNCED1 (two key genes contributing to ABA biosynthesis and catabolism) was triggered in rice plants hydroponically grown under the high doses of nZnO (500 and 750 mgl^{-1}) nutrient solution (Sheteiwy et al. 2017). However, the transcriptions of OsGA20ox2 and OsGA3ox1 genes were found to be downregulated upon the nZnO treatments (Sheteiwy et al. 2017). Vankova et al. (2017) monitored changes in phytohormones upon exposure to the different doses of nZnO (0.16, 0.8, 4, 20, and 100 mgL^{-1}; for 2 weeks; hydroponic condition) in *Arabidopsis*. The supplementation of nutrient solution with nZnO affected the cytokinin contents in the meristem zone located in the apices. The nZnO application at 0.8 and 4 mgL^{-1} doses enhanced the cytokinin levels while decreased at higher concentrations (20 and 100 mgL^{-1}). As the cytokinin deactivation process (N- and O-glycosylation and making a conjugative form) in the apical meristem was influenced in a dose-dependent manner by the high doses of nZnO, the reduction in the cytokinin ribosides (the transport forms) occurred. The close correlation was found to be between the plant growth suppression (at 20 and 100 mgL^{-1}) and reduction of cytokinin content in the meristem zone. Moreover, the nZnO presence in the culture medium at high levels inhibited the accumulation of indole-3-acetic acid (the active auxin) in the apices, while auxin level in leaf organ remained unchanged, with the exception of the highest nZnO dose (100 mgL^{-1}) which downregulates. Abscisic acid content was, on the other hand, augmented in leaves and apices at the high nZnO (20 and 100 mgL^{-1}). Vankova et al. (2017) hypothesized that apical meristems are the most sensitive tissue to nZnO. In another study, the nZnO treatment (500 mgkg^{-1} sand matrix) induced the IAA oxidase activity in the shoot while unchanged in the root, implying changes in auxin (Dimkpa et al. 2012). It should be noted that changes in the concentrations of dihydrozeatin riboside, trans-zeatin riboside, auxin, and the auxin/cytokinin ratio were observed upon Zn^{+2} exposures in *Arabidopsis* (Sofo et al. 2013). The Zn-upregulated transcription of two genes involved in the synthesis of auxin and cytokinin (AtNIT and AtIPT) has been reported in *Arabidopsis* (Sofo et al. 2013). Sofo et al. (2013) concluded that changes in phytohormonal balance, especially the auxin/cytokinin ratio, is responsible for alteration in root morphology. Moreover, plants counteracted with excessive Zn^{+2} could dynamically and differentially adjust the transcription pattern of auxin-related genes, a mechanism through which acclimation or adaptation to stress may occur (Wang et al. 2015). On the other hand, the transient exposure to the nZnO (2000 mgL^{-1} for 2–5 hours) led to the increases in root auxin concentrations in *Cicer arietinum* (Pandey et al. 2010). Another important phytohormone is abscisic acid (ABA) which contributed to activation of the plant defense system against stress condition. At high nZnO doses (20 and 100 mgL^{-1}), ABA accumulation in apical meristem zones and leaves occurred in *Arabidopsis* (Vankova et al. 2017). Likewise, the ABA concentrations were also increased in leaves and roots of the plant exposed to ZnSO4 (Sofo et al. 2013). It is noteworthy that ABA may increase the ROS accumulation, change the intracellular Ca^{2+} concentration, induce ABRE (ABA-responsive element) binding transcription factor, and modulate the transcription process (Shukla et al. 2014). Furthermore, ABA contribution in improving plant resistance against heavy metal stress has been attributed to the presence of ABRE in the promoter region of varieties of metal-responsive genes (Shukla et al. 2014). The next evaluated hormonelike compounds by Vankova et al. (2017) are SA and JA. Interestingly, SA was strongly increased in leaves, root, and apical meristem zone at low and moderate doses while decreased in apical meristem and leaves at high doses. Moreover, the shoot apical meristem was found to be the most sensitive to nZnO exposure. With increasing doses of nZnO, JA levels were decreased in apices, roots, and leaves (Vankova et al. 2017). Furthermore, Chen et al. (2015) provided evidence on augmentation in NO, a vital multitask signaling agent, in rice upon the nZnO exposure. However, the nZnO treatment in wheat was observed to decrease the NO contents (Tripathi et al. 2017b). It is worth mentioning that the nZnO-mediated changes in transcriptions of genes involved in hormone regulation have been reported in *Arabidopsis* (Nair and Chung 2017). Taken collectively, it appears that the presence of nZnO associates with increases in plant growth-promoting hormones (especially cytokinin), whereas it induces stress at moderate and high concentrations, enhances the accumulations of growth-inhibiting phytohormones, and activates defense responses.

5.6 Nutritional Status

Both Zn deficiency and excess led to the reductions in primary root length and increases in the development of lateral roots in *Arabidopsis thaliana* (Jain et al. 2013). It is worth mentioning that changes in expression of ZIP4, ZIP9, and ZIP12 as members of the ZIP family occurred under different Zn regimes, underscoring their involvements in the maintenance of Zn homeostasis (Jain et al. 2013). Interestingly, the transcription of HMA2 (involved in Zn movements into xylem) in roots was modulated in response to exogenous Zn status (Jain et al. 2013). Inductions in the expression of Fe-responsive FRO2 and IRT1 in Zn^{+2}-exposed roots pointed to the prevalence of cross talk between Fe and Zn homeostasis (Jain et al. 2013). The current molecular evidence declares the existence of cross talk between Zn and Fe nutritional status, especially at the transcriptional level (Fukao et al. 2011; Shanmugam et al. 2011; Jain et al. 2013; Nair and Chung 2017). Furthermore, Jain et al. (2013) provided convincing evidence on the existence of cross talk between the Zn sensing and signaling cascades and macronutrients, especially potassium, phosphate, and sulfur, based on the transcriptional modifications. There is limited evidence on the nZnO-mediated changes in plant nutritional status (Table 6). Peralta-Videa et al. (2014) explored changes of the several macro- and micronutrients in soybean plants grown in the soil amended with different doses of nZnO (50, 100, and 500 $mgkg^{-1}$). They found that the nZnO exposure exhibited some interference with the accumulations of several macronutrients (K and Mg) or micronutrients (Mo, Cu, and Fe) in the dose- and organ-dependent manners. The nZnO utilization (50, 100, and 500 $mgkg^{-1}$ soil) enhanced molybdenum (Mo) concentrations in nodules (mean 2.5-fold) and stem (80%) (Peralta-Videa et al. 2014). It has been well illustrated that Mo contributes to the nitrogen and sulfur metabolism

Table 6 The nZnO- mediated changes in nutritional status

Plants	Doses	Main finding	Reference
Soybean	50, 100, and 500 mg kg^{-1}	Higher Zn bioaccumulation factor at 100 mgkg^{-1} than 500 Increases in Mo in nodules (about 2.5-fold) and stem (80%) Decrease in Fe Reductions in root Cu at high dose Increases in Cu in pods by 3.8-fold Reductions in root K and Mg at high dose High Ca/P ratio in pods at 50 mgkg^{-1}	Peralta-Videa et al. (2014)
Cucumber	400 and 800 mgkg^{-1}	Increases in Zn levels in fruit by mean twofold Reduction in Mo and Cu concentration No effect on macronutrients in fruit	Zhao et al. (2014)
Tomato	2, 4, 8, or 16 mgL^{-1}	Induction in nitrate reductase activity Increase in proline	Faizan et al. (2018)
Arabidopsis	20, 50, 100, and 200 mgL^{-1}	Adverse effects on P, S, K, Cu, and Fe Changes in transcription of genes involved in Zn, microelement, and micronutrient homeostasis Changes in root architecture	Nair and Chung (2017)
Rice	250, 500, and 750 mgL^{-1}	Increase in proline	Sheteiwy et al. (2016)
Banana	50, 100, and 200 mgL^{-1}	Increase in proline	Helaly et al. (2014)
Duckweed	1, 10, and 50 mgL^{-1}	Inductions in ATPase activity at low doses	Hu et al. (2013)

regarding its fundamental roles in sulfite oxidase, nitrate reductase, and nitrogenase (responsible enzyme for nitrogen fixation in the specific symbiosis between legumes and rhizobium bacteria) (Peralta-Videa et al. 2014). The Ca/P ratio in soybean was found to be doubled with the nZnO application at 50 mgkg^{-1} soil, while the other treatments did not make significant changes in this ratio. Peralta-Videa et al. (2014) concluded that the nZnO presence may enhance plant nutrition at low doses, thereby improving the nitrogen assimilation and photosynthesis, but at the high doses, the nutritional balances, biochemical processes, and fruit quality may be disturbed in the exposed plants. Moreover, the nZnO treatments (400 or 800 mgkg^{-1}) did not change contents and/or distribution of macronutrients within cucumber fruit (Zhao et al. 2014). Interestingly, the soil supplementations with nZnO of 400 or 800 mgkg^{-1} increased Zn contents in cucumber fruit by 1.7- and 2.5-fold which may be considered for biofortification regarding human diet. However, Zhao et al. (2014) reported that the nZnO exposure reduced Cu and Mo contents in cucumber fruit which may restrict seedling growth on next plant generation.

Interestingly, the transient exposures of 20-day-old tomato seedlings to different doses of nZnO (2, 4, 8, or 16 mgL^{-1} for 15, 30, and 45 min) induced the activity of nitrate reductase (key enzyme contribute to nitrogen assimilation) by 31.2% and in parallel increased proline content, implying the change in the nitrogen metabolism (Faizan et al. 2018). The nZnO-associated increases in proline contents were also found in rice (Sheteiwy et al. 2016) and banana (Helaly et al. 2014) which may indirectly reflect the possible changes in the nitrogen metabolism. Also, there is evidence on the inductions in ATPase activity at low doses of nZnO in duckweed, which indirectly implies the possible changes in intracellular uptake of nutrients through cotransporters (symporters and antiporters; secondary active transport) located into the plasma membrane. On the other hand, the supplementation of semi-solid half-strength MS medium with different nZnO doses (20, 50, 100, and 200 mgL^{-1}) exhibited the negative effects on the nutritional status of both macro- and microelements (P, S, K, Cu, and Fe) in *Arabidopsis* (Nair and Chung 2017). The molecular evidence provided by Nair and Chung (2017) confirmed that nZnO exposure influenced transcription of several genes implicated in the homeostasis of Zn, macronutrients, and micronutrients. The expressions of the ZIP genes in *Arabidopsis* were declined in both shoot and root following supplementation of MS medium with nZnO ranging from 20 to 200 mgL^{-1} as a strategy to maintain Zn homeostasis (Nair and Chung 2017). It has been stated that the excess Zn acts as an inhibiting role on ZIP gene (Jain et al. 2013). As highlighted above, nZnO exposure may change the transpiration rate in the exposed plants. There is a close correlation between the transpiration rate and nutrient uptake from the soil. Therefore, it seems that the nZnO-mediated changes in transpiration should be also considered in plant nutritional status.

It is important to note that the phytohormones and their balances contribute to communication and cross talk between source (producer or exporter of photo-assimilates, amino acids, and mobile nutrients) and sink organs (importers of sugar, amino acids, and nutrients) through phloem-conducting tissue during plant growth, development, and adaptations to stress condition. Plant hormones, nutrients, and diverse environmental factors modulate source metabolism and sink strength through a complicated signaling network (Moghanloo et al. 2019). As mentioned above, nZnO exposure may alter hormonal balances through which cross talk between organs and nutritional status may be influenced. It is obvious that further molecular and physiological studies are required to clarify cross talk between nZnO/Zn^{+2} signaling and other macro−/micronutrients. These studies improve our knowledge on the nZnO-associated benefits or risk on the plant nutrition.

5.7 *Molecular Basis Responses*

Specific receptors in plants perceive environmental signals, thereby triggering various signaling cascades and transmitting the perceived signals to modulatory systems through secondary messengers, signaling proteins, and ion channels (Gururani et al. 2015). Hormones, mitogen-activated protein kinases (MAPKs), transcription factors, protein kinases, and phosphatases are the main components of the plant regulatory system contributing to modulation of the expression pattern of diverse

Table 7 The molecular evidence on the nZnO-mediated changes

Plant species	Doses	Main findings	References
Lactuca sativa	2.8 $cm^2\ L^{-1}$	Upregulations in 223 and 844 genes in leaf and root Downregulations in 286 and 2822 genes in leaves and root	Wang et al. (2017)
Leucaena leucocephala	25 mgL^{-1}	Alterations in isoenzyme patterns Protective genomic alteration	Venkatachalam et al. (2017a)
Arabidopsis	100 mgL^{-1}	Upregulations of 660 genes (particularly stress responsive) Downregulation of 826 genes	Landa et al. (2012)
Soybean	500 mgL^{-1}	910 and 182 differentially abundant proteins in roots and leaves	Hossain et al. (2016)
Wheat	500 $mgkg^{-1}$	Upregulations in transcriptions of genes involved in cross protections against metal and drought stresses	Yang et al. (2017)
Arabidopsis	20, 50, 100, and 200 mgL^{-1}	*Specific response to Zn ion exposure:* Decreases in AtZIP4, AtZIP9, and AtZIP12 Increases in AtHMA3 and AtHMA4 expression *Specific response to nZnO:* Inductions in AtHMA3 and AtHMA4 expression in shoot Reductions in the AtHMA4 expression in roots only at 100 mgL^{-1} Downregulation of AtMTP1 and AtMTP3 expressions *In response to Zn ions and nZnO:* Inductions in AtKC1 and AtCHX17 expressions Modifications in AtPS1 and AtSultr1, AtIRT1, AtIRT2, and AtFRO2 Upregulation of the AtHMA5 and AtCOPT5 Upregulations of AtNAC1 and AtASA1 expressions in roots Downregulation of AtNAC1 and AtASA1in shoots	Nair and Chung (2017)
Five tomato cultivars	15 and 30 mgL^{-1}	Improve in plant metabolism under salt stress Inductions in transcription of SOD and GPX genes	Alharby et al. (2016)
Tomato	10, 20, 50, and 100 mgL^{-1}	Inductions in transcription of Cu/Zn-SOD, CAT1, GSH1, and GR1	Li et al. (2016)
Oryza sativa	500 and 750 mgL^{-1}	Upregulations in OsABA8ox2 and OsNCED1 Downregulations in OsGA20ox2 and OsGA3ox1	Sheteiwy et al. (2017)

(continued)

Table 7 (continued)

Plant species	Doses	Main findings	References
Rice	250, 500, and 750 mgL^{-1}	Inductions in expression of APXa, APXb, CATa, CATb, CATc, SOD1, SOD2, and SOD3 genes	Salah et al. (2015)
Rice	50, 100, 250, 500, and 1000 mgL^{-1}	Stimulations in the expression of Cu/Zn-SOD and Mn-SOD Decline in the gene expression of CATa, CATb, APX, and POD	Chen et al. (2015)
Rice	250, 500, and 750 mgL^{-1}	Increases in expressions of GR1, GR2, Amy2A, and Amy3A genes	Sheteiwy et al. (2016)

stress-responsive genes (Gururani et al. 2015). The intracellular concentrations of ROS are modulated by the expression of genes encoding nonenzymatic (like glutathione and ascorbate) and/or enzymatic antioxidants. It is worth noting that the ROS/RNS levels act as pivotal signaling agents and second messenger. The nZnO-mediated modifications in the transcription of various genes are addressed in Table 7. Interestingly, the results of transcriptome analysis in lettuce subjected to nZnO suggested that the genes involved in the nitrogen metabolism (especially ammonium transporter genes), photosynthesis, enzymatic antioxidant system, and sucrose/starch metabolic route play critical roles in the plant responses to nanoparticles (Wang et al. 2017). The nZnO-associated alterations in the transcriptions of genes implicated in the phytohormonal metabolism have also become evident. In rice, the nZnO treatments at high doses led to the upregulation in OsABA8ox2 and OsNCED1 (ABA metabolism genes), while the transcriptions of OsGA20ox2 and OsGA3ox1 (GA metabolism genes) were declined (Sheteiwy et al. 2017). Moreover, the transcriptions of Amy2A and Amy3A genes (related to amylases) were changed by the nZnO application at high doses (Sheteiwy et al. 2016). Amylases are important enzymes which play pivotal roles in the seed germination process and seedling early performance. Using a gel-free proteomic method, 910 and 182 differentially abundant proteins were, respectively, detected in roots and leaves of soybean exposed to nZnO (Hossain et al. 2016). The nZnO (500 mgL^{-1})-altered proteins in roots were found to be predominately implicated in the varieties of biological process, including cellular organization, protein synthesis, hormone metabolism, lipid metabolism, secondary metabolism, and stress-responsive proteins (Hossain et al. 2016). However, the most differential proteins in leaves contributed to tricarboxylic acid cycle (TCA; an important part of respiration phenomenon), Calvin cycle (CO_2 fixation and assimilation), carbohydrate metabolism, lipid metabolism, amino acid metabolism, protein degradation, and tetrapyrrole synthesis (Hossain et al. 2016). The nZnO treatment upregulated 223 genes in lettuce leaves, while 286 genes were downregulated (Wang et al. 2017). In addition, the transcriptions of 844 genes were induced in roots of lettuce plants exposed to nZnO, whereas 2822 genes were found to be downregulated (Wang et al. 2017). Nair and Chung (2017) explored the effect of nZnO (20, 50, 100, and 200 mgL^{-1} for 14 days) and Zn^{+2} ions in *Arabidopsis thaliana* to compare their molecular toxicity mechanisms. They monitored the transcriptional modulations of genes involved in hormone regulation (AtNAC1, AtASA1), Zn homeostasis (AtZIP4, AtZIP9, AtZIP12, AtHMA3, AtHMA4, AtMTP1, AtMTP3), and macro- and micronutrient homoeostasis (AtIPS1, AtCHX17, AtKC1, AtSultr1, AtFRO2, AtIRT1 AtIRT2, AtHMA5, AtCOPT5) in response to nZnO or Zn^{+2} ions. Interestingly, several specific and nonspecific changes in the gene expression patterns were recorded in response to the nZnO or Zn ions. Decreases in AtZIP4, AtZIP9, and AtZIP12 (in both shoots and roots) and increases in AtHMA3 and AtHMA4 expression in both shoots and roots were found in the Zn^{+2}-treated plants. Inductions in AtHMA3 and AtHMA4 expression in the shoot, reductions in the AtHMA4 expression in roots (only at 100 mgL^{-1}), and downregulation of AtMTP1 and AtMTP3 expressions in roots and shoots (contrasted with Zn^{+2} control) were observed in response to the nZnO exposure. In addition, inductions in AtKC1 and AtCHX17 expressions (in both shoot and root); modifications in AtPS1 and AtSultr1, AtIRT1, AtIRT2, and AtFRO2 expression (in both root and shoot); upregulation of the AtHMA5 and AtCOPT5 (in shoots and roots); stimulations in AtNAC1 and AtASA1 expressions in roots; and downregulation of AtNAC1 and AtASA1 in shoots were found in the nZnO- or Zn^{+2}-exposed seedlings. Interestingly, Nair and Chung (2017) provided the convincing molecular evidence on the differential expression of genes contributing to Zn uptake, distribution, translocation, and detoxification in response to the different doses of nZnO in *Arabidopsis thaliana*. They monitored the nZnO-induced changes in expression pattern of three main groups of genes involved in Zn uptake and subsequent mobilization (AtZIP4, AtZIP9, and AtZIP12), root-to-shoot Zn translocation (the AtHMA3 and AtHMA4), and detoxification and partitioning of excessive Zn (the AtMTP1 and AtMTP3) in *Arabidopsis* seedlings. It should be noted that nZnO exposure influences the expression of diverse genes implicated in cellular respiration, cytoskeletal transport, and reproduction (Poynton et al. 2010). The specific nZnO expressions of three biomarker genes (a C1q-, ferritin-, and multicystatin-containing gene in *Daphnia magna* (small planktonic crustacean)) have been reported by Poynton et al. (2010). Moreover, microarray analysis revealed that the nZnO at the concentration of 100 mgL^{-1} upregulated 660 genes (stress responsive) whereas downregulated 826 genes involved in cellular organization and biogenesis (Landa et al. 2012). The transcriptions of genes implicated in detoxification of heavy metals and intracellular metallic ion homeostasis were augmented in *A. thaliana* counteracted with nZnO (Landa et al. 2012). Moreover, the nZnO treatment rectified the transcription of Fe-uptake genes (AtFRO2, AtIRT1, and AtIRT2) in *Arabidopsis* seedlings. The current molecular evidence declares the existence of cross talk between Zn and Fe nutritional status, especially at the transcriptional level (Fukao et al. 2011; Shanmugam et al. 2011; Jain et al. 2013; Nair and Chung 2017). Interestingly, the nZnO-associated transcriptional modifications represented by Landa et al. (2012) manifested that the toxicity mechanisms are highly specific to nanoform rather than ionic despite a limit overlap in gene expression pattern. Furthermore, the downregulation of the ZIP genes (ZIP4, ZIP9, and ZIP12) in *Arabidopsis* counteracted with nZnO (100 mgL^{-1}) for 7 days was recorded based on the microarray analysis (Landa et al. 2012). It has been reported that the Zn nutritional status in *Arabidopsis thaliana* transcriptionally modified the expression pattern of several genes, including AtHMA3, AtHMA4, AtMTP1, and AtMTP3 which are related to Zn homeostasis (Jain et al. 2013). In *Melissa officinalis*, rosmarinic acid synthase (RAS) and hydroxy phenyl pyruvate reductase (HPPR) genes were also upregulated in response of nZnO at 100 and 300 mgL^{-1} (Babajani et al. 2019a), implying its regulatory roles on secondary metabolism.

There are several reports on the potential benefits of nZnO application to improve plant protection against stress condition, implying the specific signaling and activation of defense-responsive genes. For example, the results represented by Venkatachalam et al. (2017a) proved that the nZnO-mediated modifications in isoenzyme patterns and genomic levels contributed to overcoming genotoxicity associated with Cd or Pb in *Leucaena leucocephala*. The modified DNA bands in the RAPD profile were recorded upon the nZnO exposure in combination with Cd and Pb in *L. leucocephala* (Venkatachalam et al. 2017a). The findings of Venkatachalam et al. (2017a) pointed to the protective effect of the nZnO-mediated activation of specific molecular mechanisms for detoxification of Cd and Pb. Similarly, the nZnO exposure enhanced plant resistance against salt stress via inductions in the transcription of SOD and glutathione peroxidase (GPX) genes (Alharby et al. 2016). In addition, it has become evident that the nZnO presence upregulated transcriptions of diverse genes involved in protections of wheat against drought stress (Yang et al. 2017). The modifications in the transcription rates of several genes implicated in the enzymatic antioxidant system, including Cu/Zn-SOD, CAT1, GSH1, and GR1, resulted from the nZnO treatments (10, 20, 50, and 100 mgL^{-1}) for 15 days in tomato seedlings (Li et al. 2016). Moreover, the nZnO treatments stimulated the expression of Cu/Zn-SOD and Mn-SOD genes, whereas the transcription of CATa, CATb, APX, and POD genes were downregulated in rice (Chen et al. 2015). Inductions in expressions of several antioxidant genes, including APXa, APXb, CATa, CATb, CATc, SOD1, SOD2, and SOD3, were also addressed in rice seedlings at high doses of nZnO (Salah et al. 2015). Furthermore, the expressions of GR1 and GR2 were found to be induced in rice in response to the high concentrations of nZnO (Sheteiwy et al. 2016).

5.8 Cytotoxicity, Genotoxicity, and Cell Cycle

During multicellular development, the cell cycle transition is mediated through conserved machinery (especially regarding cyclin-dependent kinase (CDK)) and tightly coordinated in both space and time. It is important to note that there is close cross talk between cell cycle machinery, developmental signals, and environmental cues. Diverse cyclin types contribute to modulating transitions of various phases of the cell cycle (G1–S–G2–M). Majority of the phytohormones have direct or indirect interaction with the cell elongation, expansion, and/or cycle, particularly through transcriptional regulation.

Table 8 The nZnO-mediated cytotoxicity/genotoxicity and induced changes in cell cycle

Plant species	Doses	Main findings	References
Cucumber	1000 mgkg^{-1}	Deformation in the root tip	Moghaddasi et al. (2017)
Ryegrass	100 mgl^{-1}	Shrink in root tips High vacuolization or collapse in epidermal and cortical cells of root	Lin and Xing (2008)
Allium cepa	100 mgl^{-1}	Reductions in mitotic index but not arrest Increase in chromosomal aberration	Kumari et al. (2011)
Rice	750 mgl^{-1}	Damages in leaf mesophyll and root cells in two cultivars	Salah et al. (2015)
Garlic		Decreases in mitosis index in a concentration- and time-dependent manner Occurrence of chromosome bridges, breakages, stickiness, and laggings	Shaymurat et al. (2012)
Allium cepa *Vicia faba* *Nicotiana tabacum*	0.8 gl^{-1}	Differential sensitivity to nZnO dependent on plant species DNA damage Loss of membrane integrity Chromosome aberrations Micronucleus formation (a mutagenic role)	Ghosh et al. (2016)
Allium cepa	1000 mgL^{-1}	DNA damage in cells (% DNA tail) above 100	Demir et al. (2014)
Alfalfa	750 mgkg^{-1}	No sign of apoptosis, DNA condensation, damaged cellular membrane, or impaired organelles	Bandyopadhyay et al. (2015)

There are several determining factors involved in the cellular sensitivity to nZnO exposure which are as follows:

1. Developmental stage
2. Plant species
3. Physicochemical characteristics of nZnO
4. Doses
5. Exposure time and method (transient or continuous)
6. Culture medium or matrix traits

The nZnO-mediated cytotoxicity/genotoxicity and induced changes in the cell cycle are addressed in Table 8.

The intensive accumulation of nZnO in the intracellular and the chromosomal modules of the exposed *Allium cepa* have been reported (Ghodake et al. 2011). Shaymurat et al. (2012) provided evidence on genotoxic impacts of nZnO in garlic (*Allium sativum* L.). The nZnO exposure reduced the mitosis index in a dose- and time-dependent way. Moreover, several mitotic aberrations, including chromosome bridges, breakages, stickiness, and laggings, occurred. As the nZnO concentrations and exposure times increased, the frequencies of abnormal cells also enhanced (Shaymurat et al. 2012). Gosh et al. (2016) monitored the behaviors of three newly germinated plant species (*Allium cepa*, *Vicia faba*, and *Nicotiana tabacum*) to nZnO exposure to address the possible differential responses in different plant species. The nZnO exposure exhibited cytotoxic effects in root cells of *A. cepa*, where nanoform had higher toxicity than the bulk type. This cytotoxicity was manifested based on the Evans blue dye (a marker of membrane integrity) (Gosh et al. 2016). The cytotoxicity and comet assays confirmed the greater sensitivity of *A. cepa* to nZnO exposure relative to *Nicotiana tabacum* (Gosh et al. 2016). Mitotic index in correlation with cytotoxicity of nZnO diminished in cells located in the root meristematic zone in *A. cepa* and *V. faba*. The chromosome aberrations also occurred probably due to spindle impairment. In the *A. cepa* (7-day-old plant), the loss of membrane integrity and increases in micronucleus formation, chromosome aberrations, and DNA strand breaks occurred following exposure of root meristem to nZnO ranging from 200 to 800 mgL^{-1} (Gosh et al. 2016). The cells in control group exhibited regular cellular structures and organization, whereas vast vacuolation, interrupted plasma membrane, loss of nuclear conformation, and protoplast shrinkage were recorded as phytotoxicity signs of nZnO in *A. cepa* root cells. These alterations in cellular ultrastructure upon the nZnO exposure at high doses could be associated with cellular death (Gosh et al. 2016). An arrest of the cellular cycle at G2/M checkpoint is a key mechanism to counteract with DNA impairment and provide time for relieving or activating the apoptosis-like program. Moreover, cell cycle dynamics in the root meristem of *A. cepa* was changed and arrested at the G2/M checkpoint following the nZnO treatments (200–800 mgL^{-1}) (Gosh et al. 2016). It should be noted that Gosh et al. (2016) investigated the nZnO toxicity at 800 mgL^{-1}, relatively high concentration, in 7-day-old seedlings. Similarly, using the comet assay, the DNA damage in root meristem cells was detected in *A. cepa* counteracted with nZnO of 100 and 1000 µgmL^{-1} (Demir et al. 2014). In another study, the high concentration of nZnO (1000 mgkg^{-1} soil) caused deformation in the root tip which in turn restricts plant growth and nutrition (Moghaddasi et al. 2017). Lin and Xing (2008) using SEM and TEM analysis examined cellular uptake, transportation, and toxicity of nZnO in ryegrass in a hydroponic culture system. They found that the nZnO exposure in ryegrass led to the reduction in biomass accumulation, shrink in root tips, and high vacuolization or collapse in epidermal and cortical cells of root organ. Kumari et al. (2011) examined the genotoxic and cytogenetic impacts of different doses of nZnO (25, 50, 75, and 100 mgL^{-1}) on the root cells based on membrane integrity, the micronuclei index, mitotic index, and chromosomal aberration through the hydroponic culturing of *A. cepa*. The mitotic index was reduced in response to the increasing concentrations of nZnO, while the chromosomal aberration rate was increased. However, even the highest applied nZnO dose (100 mgL^{-1}), the mitotic index did not arrest. The ultrastructure analysis (TEM) in *Oryza sativa* confirmed the destructions in cellular morphology and cell wall, accumulation of starch grain, and vacuolated calls in root tip and mesophyll upon exposure to the high dose of nZnO (750 mgL^{-1}; hydroponic culture for 2 weeks) (Sheteiwy et al. 2017). Similar results (damages in leaf mesophyll and root cells) have been reported in rice (Salah et al. 2015). On the other hand, no sign of apoptosis, DNA condensation, damaged cellular membrane, or impaired organelles was recorded in alfalfa upon the nZnO exposure at 500 mgkg^{-1} level (Bandyopadhyay et al. 2015).

5.9 Secondary Metabolism

As highlighted and discussed above, it has become evident that the nZnO exposure in manners dependent on the dose, plant species, exposure time, and developmental stages may alter hormones or like-hormones among which ABA, JA, SA, and NO efficiently may trigger specific signaling cascades and systemic response through which secondary metabolism may be modulated. Direct or indirect interfering of nanoparticles with various signaling routes may modify secondary metabolism (Marslin et al. 2017). Moreover, ROS/RNS can serve as signals and have cross-link with other messengers like NO, SA, JA, and ethylene, each capable of regulating secondary metabolism directly or indirectly (Marslin et al. 2017; Tripathi et al. 2017c; Babajani et al. 2019a, b). It appears that the intracellular accumulation and signaling of ROS/RNS, antioxidant machinery, calcium spikes, and upregulation of MAPK cascades (downstream of transcription factors) are the initial reactions to the nanoparticles, similar to other physicochemical stresses. Consequently, modification in MAPK signaling cascades and transcription factors in response to the nanoparticles may provoke the transcriptional reprogramming of secondary metabolism in plants (Marslin et al. 2017; Iranbakhsh et al. 2018a; Safari et al. 2018). However, there is a gap of knowledge on the nZnO interfering with MAPK cascades and transcription factors which need to be further figured out. The nZnO may act as an epigenetic factor and elicitor to trigger specific signaling and stimulate secondary metabolism which could be exploited for pharmaceutical industries, metabolite engineering, and agricultural industries, mainly owing to the outstanding properties of secondary natural metabolites originated from plants (antimicroorganism, antiherbivore, medicinal roles, etc.). The phenylpropanoid pathway in plants is transcriptionally modulated by diverse agents like inter- or intracellular redox status, developmental stages, and environmental factors (Cavallini et al. 2015). This route is tightly influenced by transcription factors. Phenylpropanoids derived from phenylpropanoid route play critical roles such as regulators of developmental signaling cascades, pigments, free radical scavenger, UV-absorbing compounds, and antimicrobes (Cavallini et al. 2015; Babajani et al. 2019a). Moreover, phenylalanine ammonia-lyase (PAL) which catalyzes the deamination process of phenylalanine amino acid to cinnamate is known as a key enzyme in the phenylpropanoid pathway. The changes in the activity of this enzyme and transcription of the related genes may be considered as an index for evaluation of secondary metabolism. Therefore, the nZnO-mediated changes in ROS/RNS and phytohormones may act as inductive signals for reprogramming of secondary metabolism (Babajani et al. 2019a). The nZnO-mediated changes in secondary metabolism are exhibited in Table 9. Interestingly, the nZnO (500 $\mathrm{mgL^{-1}}$) treatment in soybean modified protein patterns involved in secondary metabolism (Hossain et al. 2016). The nZnO treatments at 100 $\mathrm{mgL^{-1}}$ level induced the activity of PAL enzymes in both shoot and root of pepper seedlings (Iranbakhsh et al. 2018b). The supplementation of rooting culture medium with nZnO at 1 $\mathrm{mgL^{-1}}$ during regeneration process was found to be the best treatment to promote the production of secondary metabolites (steviol glycosides,

Table 9 The nZnO-mediated changes in secondary metabolism

Plant species	Concentrations	Main findings	References
Stevia rebaudiana	0.1, 1.0, 10, 100, or 1000 mgL^{-1}	Enhancement in steviol glycosides by twofold at 1 mgl^{-1} Promotions in total antioxidant capacity Increases in total flavonoid and total phenolic contents	Javed et al. (2017)
Cucumis sativus	400 and 800 mgkg^{-1}	No impact on flavonoid content	Zhao et al. (2014)
Capsicum annuum	100, 200, and 500 mgL^{-1}	Increases in total phenols contents and flavonoids Increases in condensed tannins Promotions in antioxidant capacity	García-López et al. (2018)
Glycine max	500 mgl^{-1}	Modifications in proteins contributed to secondary metabolism.	Hossain et al. (2016)
Capsicum annuum	100 mgL^{-1}	Inductions in PAL activity Increases in soluble phenols	Iranbakhsh et al. (2018b)

flavonoids, and soluble phenols) in *Stevia rebaudiana* (Javed et al. 2017). The nZnO applications (10, 25, 50, 75, and 100 mgL^{-1}) altered the concentrations of diverse secondary metabolites, including total phenol, flavonoid, and anthocyanin in *Lilium ledebourii* (Chamani et al. 2015). However, the nZnO treatments (400 or 800 mgkg^{-1}) did not change the flavonoid contents in cucumber fruit (Zhao et al. 2014). It is worth mentioning that flavonoids are considered important secondary metabolites involved in plant protection and human nutrition.

5.10 *Toxicity Mechanisms*

Owing to the release of metal ions along with the possible phytotoxic impact of the nanoparticles themselves, clarification of the exact mechanisms contributing to the phytotoxicity of nZnO is partly complicated. Wang et al. (2013) highlighted the importance of the growth matrix (solution culture vs. soil culture) in plant experiments. In solution culture, $ZnCl_2$ was found to be more toxic than the nZnO with respect to the growth of cowpea, whereas there was no difference between ionic and nanoforms in a plant grown in soil. Findings of Wang et al. (2013) suggested that risks associated with soil presence of nZnO or $ZnCl_2$ was almost equal, and particle dissolution in solubilized Zn^{2+} and adhesion of nanoparticles onto the root surface could be accounted for toxicity rather than the uptake of nanoparticles. LCF results represented by Wang et al. (2013) indicated that Zn was predominantly coordinated with histidine and cysteine amino acids, while a smaller proportion precipitated with phosphate. These results emphasize on crucial contributions of histidine and the cell wall in Zn homeostasis and detoxification. Moreover, the soil pH and plant species are two key factors affecting nZnO bioavailability and toxicity (García-Gómez et al. 2017). Zn bioaccumulation rate in the leaves proved that the nZnO was highly bioavailable in the acidic soil. García-Gómez et al. (2017) also showed that the nZnO dissolution may not be the only toxicity mechanism, particularly at low doses. Likewise, based on the experiments conducted by Zhang et al. (2015) in *Schoenoplectus tabernaemontani* grown under the controlled hydroponic condition, it appears that the concentration of dissolved Zn^{2+} released from nZnO may not consider as the main factor contributing to significant toxicity of the nano-compound. In another study, Zhang et al. (2015) concluded that the mechanism contributing to the toxicity of nZnO (1000 mgL^{-1}) in corn (*Zea mays* L.) and cucumber (*Cucumis sativus* L.) seems to be different. It appears that specific effects of nanoparticles caused toxicity in corn, while the released Zn^{2+} ion was the main reason in cucumber (Zhang et al. 2015). Corn seedlings exposed to nZnO exhibited a higher uptake rate of Zn relative to the corresponding level of Zn^{2+} solution, whereas there was a correlation between Zn uptake and soluble Zn suspension in cucumber. This evidence points to this matter that differential uptake mechanisms may be involved in a plant species-specific way (Zhang et al. 2015). Lee et al. (2010) investigated the developmental behaviors of *Arabidopsis thaliana* in response to the nZnO exposure at three concentrations (400, 2000, and 4000 mgL^{-1}). Soluble Zn levels released from the nZnO suspensions were found to be much lower (33-fold) than the minimum inhibitory dose of Zn^{+2}, implying that this factor could not solely be responsible for the associated toxicity. The Zn^{2+} fraction did not contribute to the toxicity of nZnO toward *Daphnia magna* and showed the differential action mode (Poynton et al. 2010). Monitoring changes in the gene expression patterns in *D. magna* upon sublethal doses of nZnO or $ZnSO_4$ pointed to the distinct modes of toxicity (Poynton et al. 2010).

Both the morphology and particle size are the determining factors involved in the nZnO toxicity (Xiang et al. 2015). Zn bioaccumulation in roots and shoots and overproduction of free hydroxyl groups have been mentioned as the main toxicity mechanisms associated with nZnO exposure in Chinese cabbage seedlings (Xiang et al. 2015). Therefore, current evidence underscores the ecological impact of the disposed wastes and sludge containing nZnO.

6 The nZnO-Mediated Protection Against Stress Condition

Varieties of environmental perturbations restrict crop productivity. Hence, different strategies have been employed to develop methods improving tolerance of cultivating crops. The cross talk and integration between different signaling networks provoke complex plant reactions to the various stress conditions. The activations of common and specific defense mechanisms at the expense of growth and productivity protect plants against various biotic and abiotic stresses. Progress toward understanding how plants respond to nZnO and switch between growth and defense mechanism is required for the future formulation and exploitation in agricultural fertilizers, protectant, pesticides, etc. ROS/RNS serve as signaling agents and act as a secondary messenger in the plant cells. These bioactive signaling factors are mostly responsible for communicating between cells and modulating the plant responses to stress conditions. ROS accumulation at specific concentrations may improve plant protection mainly via activating stress-responsive agents, including transcription factors, MAPKs, antioxidant system, pathogenesis-related (PR) proteins, and heat-shock proteins (Rejeb et al. 2014). Various exogenous and priming treatments, like NO (Tripathi et al. 2017b, c), cold plasma (Iranbakhsh et al. 2018a, b; Babajani et al. 2019b), have been introduced to improve plant protection against stress conditions, the majority of them mediated through the specific modifications in ROS signaling. Another important factor contributing to the protection of plants counteracted with various abiotic stress conditions is hormone signaling. As focused above, the nZnO may change hormones and hormonelike compounds in the dose- and plant species-dependent manners. Furthermore, following the perception of external factors, transcription factors serve to modulate and reprogram the molecular machinery in the plant cell. It is important to note that varieties of genes play multifunctional roles and contribute to plant protection against several different stresses. In this chapter, the evidence on the nZnO-mediated changes in the molecular machinery was also focused. Hence, the optimized application of nZnO is a good candidate to improve plant protection against stresses. There is limited evidence on the ameliorating roles of nZnO toward plant tolerance to stress conditions and need to be further explored. It has become evident that the nZnO presence upregulated transcriptions of diverse genes implicated in protections of wheat counteracted with drought conditions (Yang et al. 2017). Interestingly, Cd- or Pb-associated toxicities in *Leucaena leucocephala* were mitigated by the nZnO (25 mgL^{-1}) treatment (Venkatachalam et al. 2017a).

7 In Vitro Application

The soil complexity and the existence of different involved factors, including texture, organics, pH, and microbiome, make it difficult to explore the plant interactions with nano-products in natural soil environments. Hence, in vitro setup under controlled laboratory conditions provides a theoretical basis for improving our knowledge and clarifying the implicated mechanisms (Asgari-Targhi et al. 2018). It is worth mentioning that plant tissue culture as a key component of plant science and technology may be applied to explore a theoretical scientific basis for potential benefits or toxicity of diverse physical, chemical, or biological agents (Asgari-Targhi et al. 2018). Moreover, this technique possesses great importance in genetic manipulation, generation of pathogen-free plants, micropropagation, germplasm conservation, and production of various pharmaceutical secondary metabolites (Ghasempour et al. 2019). The nZnO-triggered responses in the exposed plants grown in in vitro condition are represented in Table 10. It has been proved that different nano-compounds have considerable antimicrobial potencies which may be

Table 10 The nZnO-mediated changes in plants grown in culture medium in in vitro sterile conditions

Plant species	Doses	Main findings	References
Banana	50, 100, and 200 mgL^{-1}	Antibacterial effects No marked negative effects on explant regeneration Promotions in somatic embryogenesis (the highest at 100 mgl^{-1})	Helaly et al. (2014)
Stevia rebaudiana	0, 0.1, 1.0, 10, 100, or 1000 mgL^{-1}	Maximum biomass, shoot formation and length, and numbers of nodes and leaves at 1 mgL^{-1} followed by ten The lowest shoot formation and number of nodes and leaves at 1000 mgL^{-1} Improving the contents of secondary metabolites	Javed et al. (2017)
Brassica nigra	1–20 mgL^{-1}	Accelerations in root formation	Zafar et al. (2016)
Lilium ledebourii	10–100 mgL^{-1}	Increases in secondary metabolites (flavonoids and phenolics)	Chamani et al. (2015)
Capsicum annuum	100 mgL^{-1}	Delay in growth Increases in secondary metabolites	Iranbakhsh et al. (2018b)

exploited in the plant tissue cultures to eliminate the various microbial contaminants from explants. Furthermore, the supplementation of culture media with different nanoparticles in a dose-, type-, and size-dependent manners may modify cell proliferation, differentiation processes, organogenesis, embryogenesis, secondary metabolism, and genetic transformation (Kim et al. 2017). Several crucial internal and external factors contribute to the success of plant cell and tissue cultures in in vitro-controlled sterile condition. Plant species; genetic and epigenetic agents; developmental stage; hormonal, physiological, and differentiation status in the selected explant; and microbial decontamination methods are among the most important internal factors, while temperature, photoperiod, light spectrum, intensity, and the ingredients of rooting culture medium (especially exogenous hormonal balances) are the environmental external factors. Nano-products like nanoparticles, and nano-hybrid composites have exhibited specific traits different from their bulk counterparts (Asgari-Targhi et al. 2018). Numerous scientific convincing reports indicate potential advantages of the application of nanomaterials in plant tissue culture. Microbial contamination is known as an important restricting factor in plant tissue culture, while surface decontamination of explant with the utilization of nano-compounds instead of common antibiotics decreases microbial infection, thereby improving culture efficiency. Moreover, the presence of nanoparticles in the culture medium may lead to somaclonal variation (Kim et al. 2017). The current evidence points to this fact that a wide range of metal and metal oxide nanoparticles have considerable potency to eliminate different microorganisms. The supplementation of Murashige and Skoog (MS) medium with nZnO of 100 and 200 mgL^{-1} doses in bananas led to the bacterial- and fungal-free cultures with no negative impact on regeneration process (Helaly et al. 2014). The utilization of nZn or nZnO at 100 mgL^{-1} improved somatic embryogenesis in banana (Helaly et al. 2014). With increasing concentrations of nZnO ranging from 50, 100, to 200 mgL^{-1}, the growth rate of callus inhibited whereas biomass accumulation, proline content, and activities of antioxidant enzymes, including superoxide dismutase, catalase, and peroxidase, were enhanced (Helaly et al. 2014). Furthermore, the enhancing roles of nZnO incorporation (100 mgL^{-1}) with MS medium on the shoot and root system have been reported during banana in vitro regeneration (Helaly et al. 2014). Incorporation of nZnO (500, 1000, and 1500 mgL^{-1}) into the MS culture medium exhibited inhibiting roles toward seed germination of *Brassica nigra* (Zafar et al. 2016). However, root formation from stem explants of micropropagated *B. nigra* was accelerated in MS medium containing nZnO ranging from 1 to 20 mgL^{-1} (Zafar et al. 2016). Interestingly, the shoot formation from nodal explants of *Stevia rebaudiana* was augmented about twofold when MS medium was supplemented with 1 mgL^{-1} (Javed et al. 2017). The presence of nZnO at 1 mgL^{-1} during regeneration process promoted the production of secondary metabolites (steviol glycosides, flavonoids, and soluble phenols) in *S. rebaudiana*, in contrast with the phytotoxic high doses (Javed et al. 2017). Furthermore, the nZnO (100 mgL^{-1}) treatment led to a delay in the growth of pepper seedlings and change in the differentiation process in in vitro culture (Iranbakhsh et al. 2018b). Moreover, amending MS culture medium with nZnO (10, 25, 50, 75, and 100 mgL^{-1}) in a dose-dependent manner changed the accumulation of various secondary metabolites, including total phenol, flavonoid, and anthocyanin in *Lilium ledebourii* (Chamani et al. 2015).

8 Knowledge Gaps, Exploitation, and Future Perspective

Majority of the current studies exploring the nZnO toxicity have evaluated the early growth and performance of germinating or newly germinated seedlings, uptake and translocation of nanoparticles, and antioxidant system. Hence, there is a gap of knowledge on the nZnO-mediated specific changes at different signaling, biochemical, and molecular levels during different vegetative and reproductive developmental stages. It should be noted that the plant–nZnO interaction is extensively complicated and depends on diverse internal and external factors, especially physicochemical traits, concentrations, exposure time, treatment method, plant species, developmental stage, physicochemical properties of soil or culture medium, etc. While the nZnO exposure at high doses exhibited phytotoxicity, it may improve plant growth, tissue differentiation, senescence, nutrition, primary and secondary metabolism, productivity, and protection at suitable concentrations, declaring its possible exploitations in agriculture (as nanofertilizers, pesticides, and protectant), medicine (as an elicitor), and postharvest life of flowers, fruits, and seeds. Taking nZnO into account, researchers in their future studies should focus on how this compound or its nanocomposite interferes with various inter- and intracellular structures and biomolecules, how it triggers specific signaling and affects transcription, how it may improve plant productivity and yield, how it may act as an elicitor to increase specific secondary metabolites, how it may improve plant protection against stress conditions, and how it may be cytotoxic and exhibit genotoxicity.

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Physiology of Zinc Oxide Nanoparticles in Plants

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1 Introduction

Zinc oxide (ZnO) is a multifunctional material with unique physical and chemical properties, for example, broad range of radiation absorption, high chemical and photostability and high electrochemical coupling coefficient (Segets et al. 2009; Lou 1991). The covalence of ZnO is between ionic and covalent semiconductors and it is classified as a semiconductor in group II–VI. It has a high bond energy of 60 meV and a broad energy band of 3.37 eV. The thermal and mechanical stability makes it useful in laser technology, electronics and optoelectronics (Bacaksiz et al. 2008; Wang et al. 2005). It has multiple uses in hydrogen production, ceramic industry, biomedicine, pro-ecological systems or plant disease management (Wang 2008; Chaari and Matoussi 2012; Özgür et al. 2005; Bhattacharyya and Gedanken 2007; Ludi and Niederberger 2013; Elmer et al. 2018). ZnO has three crystal structures in nanoparticles: wurtzite, zinc-blende and rock salt (Özgür et al. 2005; Moezzi et al. 2012). Similar to other metallic engineered nanoparticles, its size range is within 1–100 nm (Marslin et al. 2017). ZnO crystals can appear as 1 D, 2 D or 3 D structures with a large variety of morphology (Kołodziejczak-Radzimska and Jesionowski 2014), which affects the toxicity and influences of the nanoparticles (Stanković et al. 2013). It was estimated that nearly 30,000 tons of ZnO NPs is used per year in various products, such as textiles, pigments, semiconductors, industrial coatings, medicines, food additives and sunscreens (Mukherjee et al. 2016; Mishra et al. 2017; The Global Market for Metal and Metal Oxide Nanoparticles 2010–2027). ZnO NPs are often used as a nanofertiliser; however, they can increase the Zn ion levels in the soil in excess of expected concentrations (Watson et al. 2015).

Many factors have an impact on the exact outcome of the ZnO NP–plant interactions, including the investigated plant species, the size of the applied particles, the

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duration or existence of pre-cultivation, the concentration and duration of ZnO exposure or the applied growth conditions, namely germination test in Petri dishes or hydroponics or pot experiment. Up to now, it has been well reviewed that how the metallic nanoparticles (including ZnO NPs) may influence the development, the photosynthetic activity or other processes there is still much lack of our knowledge (Marslin et al. 2017; Hou et al. 2018; Pullagurala et al. 2018b).

2 The Uptake and Transport of ZnO NPs in Higher Plants

The uptake and accumulation of ZnO NPs is not fully understood up to this date, but it consists of two major pathways: zinc ion release and direct nanoparticle accumulation (Poynton et al. 2011). Zinc homeostasis is regulated in plants through transporter proteins, which control the intake, mobilisation and compartmentalisation of the ion (Clemens 2001). Well-known zinc transporter protein families are as follows: ZIP (ZRT, zinc transporter proteins; IRT-like protein) are tasked with zinc uptake in the root system, root to shoot translocation is realised via HMA (heavy metal ATPases) proteins, and MTP (metal tolerance protein) is used for compartmentalisation and detoxification (Pence et al. 2000). The uptake and translocation of ZnO NPs is much less investigated. In soil, the interactions between soil grain, clay minerals and nanoparticles determine the transport, the fate and the behaviour of nanoparticles (Darlington et al. 2009). García-Gómez et al. (2018b) presented in case of several vegetables and crops that pH values or other characteristics of the soil may determine the impact of ZnO NPs on plants (Table 1c). ZnO NPs are absorbed on kaolin surfaces, followed by a dissolution (Scheckel et al. 2010). Accumulation of ZnO NPs on root surface areas is supported by multiple sources. Lin and Xing (2008) detected large amounts of nanoparticles adhered to the root epidermis in ryegrass applying scanning electron microscopy. In *Schoenoplectus tabernaemontani* ZnO NPs were observed on the root surface (Zhang et al. 2015), as well as in case of maize roots where nanoparticles were absorbed on the surface (Lv et al. 2015). The accumulation of zinc was examined in ZnO NP-treated sweet potato tubers and large amounts of Zn accumulated in the outer layers (namely the peel) of the tubers, which could have been nanoparticles (Bradfield et al. 2017; Table 1d). There are some reports of ZnO NPs invading tissues or even cells in ryegrass (Lin and Xing 2008), onion (Kumari et al. 2011), maize (Zhao et al. 2012; Lv et al. 2015), rice (Chen et al. 2018a) and *Schoenoplectus tabernaemontani* (Zhang et al. 2015). Since plants in natural conditions usually grow in the soil, the root tissues and cells are the first targets of ZnO NP "invasion", mainly at higher doses. The main symptoms of ZnO NP toxicity are reduced root length and consequently higher root diameter, sometimes fewer root hairs (Lee et al. 2013; Balážová et al. 2018; Table 1d). Some reports showed that ZnO NPs may be transported until the endodermis using both apoplastic and symplastic pathway then they can enter the vascular cylinder (Lin and Xing 2008; reviewed by Lee et al. 2013; Lv et al. 2015) but there is not much evidence of translocation to shoot as nanoparticles. Chen et al.

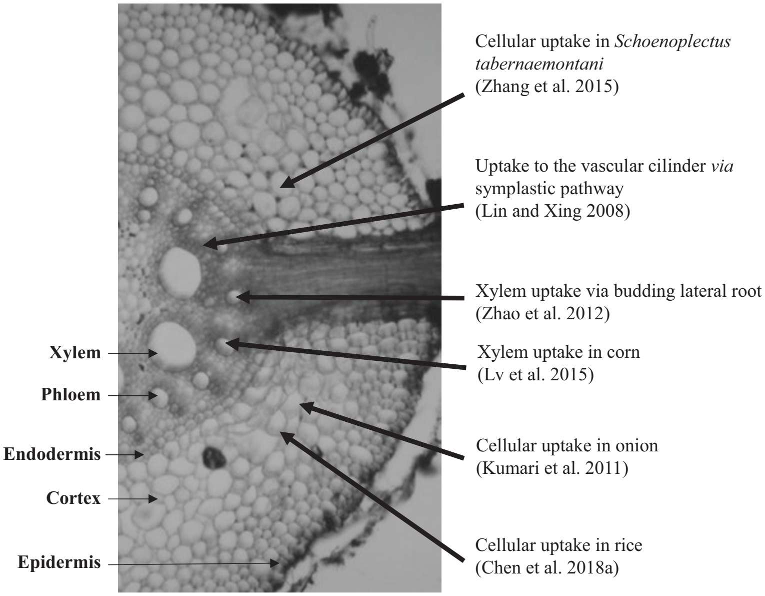

Fig. 1 Comparison of ZnO NP uptake by different plant species at the tissue level

(2018a) demonstrated the presence of ZnO NPs as dark dots both in the intercellular space and in the cytoplasm of the root cortical cells in the elongation zone which supports the dual (symplastic and apoplastic) transport theory. Besides, it was exhibited that cell organelles can be also influenced, Lin and Xing (2008) detected ZnO NPs in the nuclei and cytoplasm, as well. The root uptake and the potential transport mechanisms of ZnO NPs are depicted in Fig. 1.

Raliya et al. (2015) detected ZnO NPs with TEM in the shoot and leaves of tomato plants but only after foliar application and not soil amendment. In Indian mustard, ZnO NPs were translocated to the leaves (Rao and Shekhawat 2014). At the same time, in soybean (López-Moreno et al. 2010) and mesquite roots (Hernandez-Viezcas et al. 2011), there were no detectable ZnO NPs, which indicates that nanoparticles entering the tissues is not a common phenomenon across all species.

It is well known that plant cell wall has pores that measure up to several nanometres (Carpita et al. 1979), which should filter out nanoparticles and prevent them from entering the cell. It has been reported that, in bacteria, ZnO NPs may increase the permeability generating "holes" in cell walls to reach the plasma membrane (Stoimenov et al. 2002; Brayner et al. 2006). Between cells, nanoparticles are most likely transported via plasmodesmata, which have a reported diameter of ~40 nm (Tilney et al. 1991). To enter the cortex, there are two possible ways: (1) entering it through the plasmodesmata as previously mentioned, or (2) potentially entering it via budding lateral roots which temporarily allow nutrients to pass the Casparian strip (Bell et al. 2003; Lv et al. 2015).

It seems that ZnO NPs may influence living cells via three distinct pathways: (1) biotransformation and release of Zn (II) ions, (2) surface interaction of nanoparticles resulting in harmful molecules such as reactive oxygen species (ROS) and (3) direct interaction of nanoparticles with cell metabolism, like photosynthesis and nutrient homeostasis (Brunner et al. 2006). ZnO NPs undergo biotransformation due to humic acid and other organic root exudates then they penetrate the root through the root pores and it is accompanied by the uptake processes, as it has been described in many studies and accumulate in tissues of plants, mainly in ionic form (Chen et al. 2018a; López-Moreno et al. 2010; Raliya et al. 2015; Balážová et al. 2018). In rice, Chen et al. (2018a) demonstrated that the plants can accelerate the degradation process of ZnO NPs, resulting in a higher Zn ion concentration. Similar results were obtained by Lv et al. (2015) in maize, proving the importance of this pathway. It is important to note that the effects of nanoparticles are more than just the release or effects of Zn ions, which has been described by numerous studies (Lin and Xing 2008; Chen et al. 2018a; Poynton et al. 2011; Zhang et al. 2015; Bradfield et al. 2017). Zn accumulation triggered by ZnO NP treatment has a lower translocation factor to shoot when compared to direct Zn ion treatment in cilantro (Pullagurala et al. 2018a, b; Table 1a), ryegrass (Lin and Xing 2008), *Schoenoplectus tabernaemontani* (Zhang et al. 2015), unlike previous examples in maize (Zhao et al. 2012) translocation factors were between 0.8 and 2.

3 ZnO NPs and Oxidative Stress

Metal oxide nanoparticles have distinct antimicrobial properties, which are well examined (Sirelkhatim et al. 2015), and one of the proposed mechanisms is the generation of ROS (Huang et al. 2008; Xia et al. 2008; Lipovsky et al. 2009). ZnO NPs will produce ROS under visible or UV light, like superoxide anion or hydrogen peroxide (Sawai et al. 1998; Padmavathy and Vijayaraghavan 2008; Zhang et al. 2008; Jalal et al. 2010) and there are even reports of ROS generation in darkness, as well (Zhou et al. 2008; Adams et al. 2015). Since the electronic band structure of ZnO immediately absorbs photons with greater energy than 3.3 eV and as a result h^+ positive holes and free electrons in conduction band are created (Seven et al. 2004). This positive hole is a strong oxidant and it will create reactive hydroxyl radicals (Zhang et al. 2012). It is also documented that nanoparticles can enhance ROS generation in plants (Wang et al. 2014; Barhoumi et al. 2015). The effect on ZnO NPs on the homeostasis of ROS seems to be dose dependent, as described by Javed et al. 2017, where lower (0.1, 1.0 and 10 mg/L) ZnO concentrations had beneficial effects in *Stevia* plants such as increased antioxidant activity, but in contrast, at higher doses ZnO had toxic effect due to oxidative burst (Table 1a).

Positively, ZnO can stimulate the enzymatic antioxidants, e.g. superoxide dismutase (SOD), catalase (CAT) or peroxidase (POX), as it has been determined by Rizwan et al. (2019) (Table 1a), wherein treated wheat SOD and POX activities increased compared to control, similarly, in cotton lipid peroxidation (LP) decreased

Table 1a Positive effects of ZnO NPs in higher plants

	Plant name	Size of ZnO NP	Duration of pre-cultivation	Concentration of the ZnO exposure	Time of exposure	Growth conditions	Plant organ investigated	Main effects (physiological/ biochemical/ morphological)^{a}	Reference
Positive effect	*Allium cepa* L.	~18 nm	nd	10, 20, 30 or 40 µg/ml	Sprayed three times with 15 days interval	Six month rested bulbs planted in pots	Aboveground parts	Plant growth ↑ and earlier flowering after 20 and 30 µg/ml ZnO; seed number per umbel and 1000 seed weight ↑	Laware and Raskar (2014)
	Arachis hypogea L. var. 'K-134'	25 nm	–	100, 1000 and 2000 ppm for seed priming; 2 or 30 g/15 L for foliar spraying	3 hours seed priming; two foliar spraying	Pot and field experiment	Whole plant	Germination % ↑, seedling vigour ↑, root and shoot length ↑, plant height ↑, earlier flowering, chlorophyll content ↑, productivity ↑; foliar spraying with ZnO NPs increased pod yield	Prasad et al. (2012)
	Capsicum annuum L.	nd	14 day-long growing	0.25, 0.5 and 0.75 g	6 h	Moistened blotter paper (in Petri dishes)	Whole seedling	Concentration-dependent ↑ of seed germination, root length ↑, seedling length ↑; shoot length ↓ at the lowest concentration	Afrayeem and Chaurasia (2017)
	Caspicum annuum L. var. California	nd	29 days (?)	50 mg/L	21 days (foliar spraying once a week)	Hydroponics	Whole plant	No change in plant height, root length ↑ ns, chlorophyll content ↑ ns	Méndez-Argüello et al. (2016)
	Cicer arietinum L. var. HC-1	16–30 nm	10 days	1.5 or 10 ppm	15 days	Pot experiment (vermiculite, irrigated with nutrient solution)	Whole plant	Shoot DW ↑ at lower ZnO concentration, root growth ↓ at higher ZnO concentration, total biomass ↑; SOD and peroxidase activity↓ in shoot	Burman et al. (2013)

(continued)

Table 1a (continued)

	Plant name	Size of ZnO NP	Duration of pre-cultivation	Concentration of the ZnO exposure	Time of exposure	Growth conditions	Plant organ investigated	Main effects (physiological/ biochemical/ morphological)[a]	Reference
	Cucumis sativus L. 'Poinsett 76'	8 nm	–	50, 100, 200, 400, 800 and 1600 mg/L	Until 65% of the seeds were germinated	Petri dishes (germination test)	Whole plant	Germination % ↑ at 400–1600 mg/L concentration, root length ↑ at 200–800 mg/L ZnO NP	de la Rosa et al. (2013)
	Coriandrum sativum L.	24 ± 3 nm	–	100, 200 and 400 mg/kg (soil)	35 days	Pot experiment (soil)	Leaves	Photosynthetic pigment content ↑; lipid peroxidation ↓ at 400 mg/kg ZnO NP	Pullagurala et al. (2018a)
	Daucus carota L. cv. Pusa Rudhira	nd	nd	50, 100 and 150 ppm	nd	Field experiment with foliar ZnO NP spraying	Whole plant	Number of leaves ↑, root length and root diameter ↑ at 100 ppm ZnO combined with 50 ppm FeO NP	Elizabath et al. (2017)
	Fagopyrum esculentum Moench	<50 nm	–	50, 500, 2000 and 4000 ml/L	1 week or 3 days (?)	Petri dishes with wet filter paper (germination test)	Whole plant	Biomass ↑at low Zn NP but ↓ ns at higher conc., root growth and the number of root hairs ↓ at high ZnO NP; MDA content ↓, SOD and peroxidase activity ↓	Lee et al. (2013)
	Fragaria x ananassa Duch. cv. Chandler	nd	–	50, 100 or 150 ppm	135 days	Field experiment	Shoot	Plant height ↑; 150 ppm ZnO + 150 ppm FeO had a positive effect on the growth parameters and fruit yield	Kumar et al. (2017)
	Gossypium hirsutum L.	2–54 nm	7 days	0, 25, 50, 75, 100 and 200 mg/L	21 days	Hydroponics	Whole plants	Root length and shoot length ↑; photosynthetic pigment level and total soluble protein content ↑, SOD and POX activity ↑; MDA level and CAT activity ↓	Venkatachalam et al. (2017b)

	Hordeum vulgare L.	30 nm	–	0, 5, 10, 20, 40 and 80 mg/kg	7 days germination then 21 days cultivation	Petri dishes (germination) then pot experiment	Whole plant	No effect on seed germination and root elongation; SOD activity ↓, CAT activity ↑	Doğaroğlu and Köleli (2017)
	Lactuca sativa L.	90 ± 10 nm	–	0, 1, 10 and 100 mg/kg (soil)	7 weeks	Pot experiment (soil)	Whole plants	Biomass and photosynthetic rate ↑ at 10 mg/kg ZnO NP	Xu et al. (2018)
	Phaseolus vulgaris L. var. red hawk kidney	93.8 or 84.1 nm	–	62.5, 125, 250 and 500 mg/kg (soil)	45 days	Soil (pot experiment)	Whole plant	No effect on germination, pod production and chlorophyll content. Coated ZnO NPs increased root and leaf length	Medina-Velo et al. (2017)
	Phaseolus vulgaris L. var. Valentino	nd	33 or 44 days	25, 50, 100 and 200 ppm	nd	Field experiment with foliar ZnO NP spraying at 33 and/or 44 days after sowing	Whole plant	Shoot length and root length ↑; chlorophyll a + b content ↑ and ↑ ns at higher ZnO concentration	Ewais et al. (2017)
	Sesamum indicum L.	12 ± 3 nm and 18 ± 2 nm	–	0.1, 0.25, 0.5, 1 and 2 g/L	nd	Soil (pot experiment)	Whole plant	Root length and shoot length ↑, photosynthetic pigment content ↑ mainly at lower concentration	Narendhran et al. (2016)
	Solanum lycopersicum L. cv. PKM-1	35 nm	20 days	2, 4, 8 or 16 mg/L	15, 30 or 45 minutes	Sand then sandy loam	Whole plant	Shoot length and root length ↑ and ↑ ns; photosynthetic activity, carbonic anhydrase activity and antioxidant enzyme activities ↑ in a dose- and duration-dependent way	Faizan et al. (2018)

(continued)

Table 1a (continued)

	Plant name	Size of ZnO NP	Duration of pre-cultivation	Concentration of the ZnO exposure	Time of exposure	Growth conditions	Plant organ investigated	Main effects (physiological/ biochemical/ morphological)[a]	Reference
	Solanum lycopersicum L. hybr. 'tomato cherry super sweet 100'	25 ± 3.5 nm	Seed priming for 1 h	0, 10, 100, 250, 500, 750 and 1000 mg/L	5 days	Petri dishes (germination test)	Whole plant	Germination % ↓ at 1000 mg/kg concentration	Raliya et al. (2015)
			14 days before foliar or soil application of ZnO NP	0, 10, 100, 250, 500, 750 and 1000 mg/L or /kg (soil)	Foliar spraying or soil exposure on 14-day-old plants, then analysis on the 28th, 40th and 66th day	Pot experiment (soil)	Whole plant	Foliar application: plant height ↑ ns and ↓ ns, root length ↑ at 100–250 mg/kg but ↓ ns at higher concentration, chlorophyll content ↑ at 1000 mg/kg; soil exposure: plant height ↑ at 250–500 mg/kg, root length ↓ at higher concentration, chlorophyll content ↑ and ↑ ns	
	Stevia rebaudiana Bertoni	34 nm	–	0, 0.1, 1.0, 10, 100 or 1000 mg/L	4 weeks	Culture medium	Shoots formed from nodal regions	Highest percentage of shoot formation at 1 mg/L ZnO; steviol glycoside content ↑ and oxidative stress ↑; concentration-dependent phytotoxic effects at higher ZnO concentration	Javed et al. (2017)

	Triticum aestivum L.	34.4 nm	–	25, 50, 75 and 100 ppm	24 h seed priming	Soil (pot experiment)	Whole plant	Plant height ↑, biomass ↑, photosynthetic pigment content and activity ↑, Zn content ↑ concentration-dependently	Munir et al. (2018)
	Vigna radiata L.	~18 nm	–	0, 20, 40, 60, 80 and 100 mg/L	3 h then germinating for 7 days	Germination test	Whole plant	Germination % ↑; root and shoot length ↑ and ↑ ns	Jayarambabu et al. (2014)
	Vigna unguiculata L.	30 nm	–	250, 500 and 750 ppm	6 hours seed treatment	Soil (pot experiment)	Whole plant	Seedling length ↑, germination % ↑, seedling fresh weight ↑ and vigour index↑, shoot and root length ↑, productivity ↑	Srinivasan et al. (2017)
	Vigna unguiculata L.	75 nm	–	0, 100, 500, 1000 and 2000 ppm	Overnight seed soaking	Wet filter paper (Petri dishes) and pot experiment	Whole seedling	High ZnO NP uptake, positive effects on plant growth	Suriyaprabha et al. (2018)

[a] ↑ indicates significant and ↑ ns indicates non-significant increase, while ↓ refers to significant decrease and ↓ ns to non-significant reduction

Table 1b Stress alleviating effects of ZnO NPs in higher plants

	Plant name	Size of ZnO NP	Duration of pre-cultivation	Concentration of the ZnO exposure	Time of exposure	Growth conditions	Plant organ investigated	Main effects (physiological/biochemical/morphological)[a]	Reference
Stress alleviation	*Triticum aestivum* L. ecotype 'Stolichna' and 'Acveduc'	nd	–	1:100	Seed pretreatment for 4 hours	Sand culture	Leaves	Negative effects of drought ↓; antioxidant enzyme activity and water content of the leaves ↑, stabilised photosynthetic pigments	Taran et al. (2017)
	Leucaena leucocephala (Lam.) de Wit	2–64 nm	5 days	25 mg/L	15 days	Hydroponics	Whole plants	Alleviation of Cd- and Pb-induced stress: total soluble protein and photosynthetic pigment content ↑, lipid peroxidation ↓ in leaves; antioxidant enzyme (SOD, CAT, POX) activities ↑	Venkatachalam et al. (2017a)
	Oryza sativa L.	15–137 nm (68.1 avg)	50 days	100 mg/L	6 days	Hydroponics	Whole plants	As(III) and As(V) accumulation of the roots ↓ after ZnO NP treatment, but had no effect on As(V) content in the shoots	Wang et al. (2018b)
	Triticum aestivum L.	20–30 nm	15 days	0, 25, 50, 75 and 100 mg/kg	Four foliar spraying: 2, 4, 6 and 8 weeks after sowing	Soil from a polluted field (pot experiment)	Whole plant	Plant growth ↑, photosynthesis ↑ and grain yield ↑; Cd content ↓; electrolyte leakage ↓; SOD and POD activity ↑ in leaves; generally Cd toxicity ↓	Hussain et al. (2018)
	Triticum asestivum L. var. Lassani-2008	20–30 nm	Seed priming for 1 h	0, 25, 50, 75 and 100 mg/L	124 days	Pot experiment (soil contaminated with Cd)	Whole plant	Plant height ↑, spike length ↑, photosynthetic pigment content ↑, Cd content of root and shoot↓; POD and SOD activity ↑ in leaves	Rizwan et al. (2019)

[a] ↑ indicates significant and ↑ ns indicates non-significant increase, while ↓ refers to significant decrease and ↓ ns to non-significant reduction

Table 1c Mixed or concentration-dependent effects of ZnO NPs in higher plants

	Plant name	Size of ZnO NP	Duration of pre-cultivation	Concentration of the ZnO exposure	Time of exposure	Growth conditions	Plant organ investigated	Main effects (physiological/ biochemical/ morphological)[a]	Reference
Mixed or concentration-dependent effect	*Allium cepa* L.	<35 and 50 nm	Until the roots reached 2–3 cm in length	10, 100 and 1000 μg/ml	18 h	Glass beaker, darkness, watered	Root	Dose-dependent genotoxicity of meristematic cells	Demir et al. (2014)
	Allium cepa L.	~50 nm	3 days	5, 10 and 20 μg/ml	3 days	Hydroponics	Root	Root growth ↓ concentration-dependently	Ghodake et al. (2011)
	Allium cepa L.	20 nm	–	10, 20, 30 and 40 mg/L	10 days	Wet filter paper (germination test)	Whole seedling	Mitotic index ↓ and number of chromosomal abnormalities ↑ at 30–40 mg/L ZnO NP, germination % and seedling growth ↑ns at lower concentration	Raskar and Laware (2014)
	Allium sativum L.	4 nm	Until roots of the bulbs reached 2 cm length	0, 10, 20, 30, 40 and 50 mg/L	24 h	Beakers with water	Roots	Concentration-dependent root growth and mitosis inhibition. Mitotic aberrations	Shaymurat et al. (2012)
	Arabidopsis thaliana	20–45 nm	–	20, 50, 100 and 200 mg/L	14 days	1/2 MS media	Whole plant	Lateral root number ↑, imbalance in nutrient homeostasis	Nair and Chung (2017)
	Avena sativa L.	nd	–	750, 1000 and 1250 mg/kg seed	10 min priming	Wet paper and field experiment	Whole plant	Germination %, seedling vigour and yield ↑ at low concentration, root and shoot length ↓ at higher doses; however, no toxicity was observed	Maity et al. (2018)

(continued)

Table 1c (continued)

	Plant name	Size of ZnO NP	Duration of pre-cultivation	Concentration of the ZnO exposure	Time of exposure	Growth conditions	Plant organ investigated	Main effects (physiological/ biochemical/ morphological)[a]	Reference
	Beta vulgaris L.	<100 nm	–	0.075, 0.84, 1.68 or 3.36 g ZnO NP/ kg (soil) which was equivalent to 20, 225, 450 and 900 mg Zn/kg (soil)	7–10 + 35 days	Calcareous or acidic soil (pot experiment)	Whole plant	Biomass ↓ ns at 900 mg/kg Zn (calcareous soil); oxidative enzyme activities ↓ (calcareous soil)	García-Gómez et al. (2018b)
	Brassica oleracea var. capitata L. cv. Golden Acre	17.4 ± 4.9 nm	–	0.001, 0.1, 1, 10, 100, 500 and 1000 µg/ml	6 days	Wet filter paper (germination test)	Root	Germination and root elongation is less sensitive to NPs than to free ions	Pokhrel and Dubey (2013)
	Cucumis sativus L.	<100 nm	–	0.075, 0.84, 1.68 or 3.36 g ZnO NP/ kg (soil) which was equivalent to 20, 225, 450 and 900 mg Zn/kg (soil)	7–10 + 35 days	Calcareous or acidic soil (pot experiment)	Whole plant	Biomass ↓ ns at 900 mg/kg Zn (calcareous soil); oxidative enzyme activities ↓ (calcareous soil)	García-Gómez et al. (2018b)
	Daucus carota L. cv. Danvers Half Long	30–40 nm	16 weeks	0.5, 5, 50 and 500 mg/kg DW (soil)	13 weeks	Pot experiment (sand)	Whole plant	Root and total biomass ↓ dose-dependently; Zn accumulation in the taproot periderm	Ebbs et al. (2016)
	Glycine max L.	8 nm	–	500, 1000, 2000 and 4000 mg/L	Until 65% of control roots were 5 mm long	Petri dishes with wet filter paper (germination test)	Whole plant	Germination was not affected; root elongation ↑at 500 mg/L but ↓ at 2000 mg/L ZnO NP	López-Moreno et al. (2010)

	Glycine max L.	10 nm	18 days	50, 100 and 500 mg/kg (soil)	48 days	Soil (pot experiment)	Whole plant	Altered nutritional values of soybean	Peralta-Videa et al. (2014)
	Lactuca sativa L.	<100 nm	–	0.075, 0.84, 1.68 or 3.36 g ZnO NP/kg (soil) which was equivalent to 20, 225, 450 and 900 mg Zn/kg (soil)	7–10 + 35 days	Calcareous or acidic soil (pot experiment)	Whole plant	Germination % (acidic soil); oxidative enzyme activities ↓ (calcareous soil)	García-Gómez et al. (2018b)
	Pennisetum glaucum L.	<50 nm	–	0, 100, 250, 500, 750 and 1000 mg/L	7 days	Petri dishes (germination test)	Whole plant	Germination % ↓; root length ↑ but ↓ at 500–1000 mg/L. concentration; shoot length ↑ ns and ↓ ns	Jain et al. (2017)
	Phaseolus vulgaris L. cv. Contender	<100 nm	–	0.075, 0.84, 1.68 or 3.36 g ZnO NP/kg (soil) which was equivalent to 20, 225, 450 and 900 mg Zn/kg (soil)	7–10 + 35 days	Calcareous or acidic soil (pot experiment)	Whole plant	Germination % ↓ (acidic soil); photosynthetic pigments ↓ (acidic soil); oxidative enzyme activities ↓ (calcareous soil)	García-Gómez et al. (2018b)
	Phaseolus vulgaris L. var. Pinto Saltillo	<50 nm	–	1, 3 and 6 mg/L	120 days	Pot experiment with irrigation of ZnO NP	Whole plant	No change in root length; shoot length ↓ ns; no change in chlorophyll content	Medina-Pérez et al. (2018)
	Phaseolus vulgaris L. var. red hawk	93.8 or 84.1 nm	–	125, 250 and 500 mg/kg (soil)	87 ± 11 days (until maturity)	Soil (pot experiment)	Produced seeds	ZnO NPs have low residual transgenerational effects on the properties of produced seeds	Medina-Velo et al. (2018)

(continued)

Table 1c (continued)

	Plant name	Size of ZnO NP	Duration of pre-cultivation	Concentration of the ZnO exposure	Time of exposure	Growth conditions	Plant organ investigated	Main effects (physiological/ biochemical/ morphological)[a]	Reference
	Pisum sativum L.	<100 nm	–	0.075, 0.84, 1.68 or 3.36 g ZnO NP/ kg (soil) which was equivalent to 20, 225, 450 and 900 mg Zn/kg (soil)	7–10 + 35 days	Calcareous or acidic soil (pot experiment)	Whole plant	Photosynthetic pigments ↓ (acidic soil); oxidative enzyme activities ↓ (calcareous soil) but ROS ↑ (acidic soil)	García-Gómez et al. (2018b)
	Raphanus sativus L.	<100 nm	–	0.075, 0.84, 1.68 or 3.36 g ZnO NP/ kg (soil) which was equivalent to 20, 225, 450 and 900 mg Zn/kg (soil)	7–10 + 35 days	Calcareous or acidic soil (pot experiment)	Whole plant	Germination % ↑ (acidic soil); oxidative enzyme activities ↓(calcareous soil)	García-Gómez et al. (2018b)
	Salicornia persica 'Akhani' ecotype	50 nm particle size, 677,450, Sigma–Aldrich	10 days	100 and 1000 mg/L	14 days	1/2 MS medium	Whole plant	Concentration-dependent inhibition of plant growth: shoot length ↓, root length ↓ and root diameter ↑ at 1000 mg/L concentration. Loss of root tip viability, RNS and ROS ↑, oxidative stress	Balážová et al. (2018)
	Solanum lycopersicum L. cv. cerasiforme	<100 nm	–	0.075, 0.84, 1.68 or 3.36 g ZnO NP/ kg (soil) which was equivalent to 20, 225, 450 and 900 mg Zn/kg (soil)	7–10 + 35 days	Calcareous or acidic soil (pot experiment)	Whole plant	Germination % ↓ (acidic soil); oxidative enzyme activities ↓ (calcareous soil)	García-Gómez et al. (2018b)

	Solanum lycopersicum L. cv. Moneymaker	nd	3 weeks	0, 200, 400 and 800 mg/L	2 weeks	Pot experiment (soil)	Whole plant	Plant growth ↓ at 400–800 mg/L concentration, and photosynthetic rate ↓, chlorophyll content ↓ but carotenoid content ↑ at 400–800 mg/L concentration, SOD, CAT and APX activity ↑ concentration-dependently	Wang et al. (2018a)
	Trifolium alexandrium L.	nd	–	750, 1000 and 1250 mg/kg seed	10 min priming	Wet paper and field experiment	Whole plant	Germination %, seedling vigour and yield ↑ at low conc., root and shoot length ↓ at higher doses; however no toxicity was observed	Maity et al. (2018)
	Triticum aestivum L.	<100 nm	–	0.075, 0.84, 1.68 or 3.36 g ZnO NP/kg (soil) which was equivalent to 20, 225, 450 and 900 mg Zn/kg (soil)	7–10 + 35 days	Calcareous or acidic soil (pot experiment)	Whole plant	Biomass ↓ ns at 900 mg/kg Zn (calcareous soil); oxidative enzyme activities ↓ (calcareous soil)	García-Gómez et al. (2018b)
	Zea mays L.	<100 nm	–	0.075, 0.84, 1.68 or 3.36 g ZnO NP/kg (soil) which was equivalent to 20, 225, 450 and 900 mg Zn/kg (soil)	7–10 + 35 days	Calcareous or acidic soil (pot experiment)	Whole plant	Photosynthetic pigments ↑ ns (acidic soil); oxidative enzyme activities ↓ (calcareous soil)	García-Gómez et al. (2018b)

(continued)

Table 1c (continued)

	Plant name	Size of ZnO NP	Duration of pre-cultivation	Concentration of the ZnO exposure	Time of exposure	Growth conditions	Plant organ investigated	Main effects (physiological/ biochemical/ morphological)[a]	Reference
	Zea mays L. Golden variety	24 ± 3 nm	–	0, 50, 100, 200, 400, 800 and 1600 mg/L	15 days	Petri dishes with wet filter paper (germination test)	Whole plant	Temperature may alter the plant-ZnO NP interaction, e.g. at 20 °C germination ↓ at 400 and 1600 mg/L, while at 25 °C germination ↓ only at 400 mg/L	López-Moreno et al. (2017)
	Zea mays L. cv. Zhengdan 958	30 ± 5 nm	1 week	2, 5, 10, 15, 20, 40, 60, 80 and 100 mg/L	7 days	Hydroponics	Whole plant	Zn accumulation; ZnO NPS mainly occurred in the rhizodermis	Lv et al. (2015)
	Zea mays L. cv. NK-199	17.4 ± 4.9 nm	–	0.001, 0.1, 1, 10, 100, 500 and 1000 µg/ml	7 days	Wet filter paper (germination test)	Root	Germination and root elongation is less sensitive to NPs than to free ions; ZnO caused tunnelling-like effect in the root tips	Pokhrel and Dubey (2013)
	Zea mays L.	386–1116 nm	30 days	100, 200, 400, and 800 mg/kg (soil)	30 days	Pot experiment	Whole plant	High Zn accumulation and translocation to shoot	Zhao et al. (2012)

[a]↑ indicates significant and ↑ ns indicates non-significant increase, while ↓ refers to significant decrease and ↓ ns to non-significant reduction

Table 1d Negative effects of ZnO NPs in higher plants

	Plant name	Size of ZnO NP	Duration of pre-cultivation	Concentration of the ZnO exposure	Time of exposure	Growth conditions	Plant organ investigated	Main effects (physiological/biochemical/morphological)[a]	Reference
Negative effect	*Allium cepa* L.	~50 nm	3 days	5, 10 and 20 μg/ml	3 days	Hydroponics	Root	Concentration-dependent root growth inhibition	Ghodake et al. (2011)
	Allium cepa L.	<100 nm	Grown until 2–3 cm root lenght	25, 50, 75 and 100 mg/L	4 h	Hydroponics	Root	Lipid peroxidation ↑, chromosomal aberrations ↑ and mitotic index ↓	Kumari et al. (2011)
	Allium sativum L.	4 nm	Until radicals reached 2 cm length	10, 20, 30, 40, 50 mg/L	24 hours	Beakers with water	Root	Concentration-dependent root growth and mitosis inhibition, mitotic aberrations	Shaymurat et al. (2012)
	Arabidopsis thaliana 'Col-0'	~44 nm	5 days at 4 °C (in dark)	400, 2000 and 4000 mg/L	18 days	1/2 MS medium	Whole plant	Seed germination % ↓, number of leaves ↓, root elongation ↓	Lee et al. (2010)
	Beta vulgaris L. cv. Detroit	<100 nm	–	3, 20 and 225 mg Zn/kg (soil)	60 and 90 days	Calcareous or acidic soil (pot experiment)	Leaves	6–12-fold higher Zn content and ROS ↑ in leaves (acidic soil), MDA content ↑, altered photosynthetic pigment ratios	García-Gómez et al. (2018a)
	Brassica juncea L.	<100 nm	Germination	0, 200, 500, 1000 and 1500 mg/L	96 h	Hydroponics	Whole plant	Plant biomass and chlorophyll ↓, lipid peroxidation and proline content ↑	Rao and Shekhawat (2014)

(continued)

Table 1d (continued)

	Plant name	Size of ZnO NP	Duration of pre-cultivation	Concentration of the ZnO exposure	Time of exposure	Growth conditions	Plant organ investigated	Main effects (physiological/ biochemical/ morphological)[a]	Reference
	Brassica napus L. cv. Hayola 401	<50 nm	–	5, 10, 25, 50, 75, 100, 125, 250 and 500 mg/L	6 days	Petri dishes (germination test)	Whole plant	Germination % ↓ns, root length ↓, shoot length ↓ ns and ↓	Kouhi et al. (2014)
	Carthamus tinctorius L. cv. Isfahan	nd	Until the two leaf stage	0, 10, 100, 500 and 1000 mg/L	Three spraying with 14 day intervals	Soil (pot experiment)	Leaves (?)	Malondialdehyde (MDA) content ↑	Hafizi and Nasr (2018)
	Cucumis sativus L.	50 nm	–	2000 mg/kg (soil)	8 weeks	Soil (pot experiment)	Whole plant	Soil dehydrogenase activity ↓; no change in biomass and shoot length; root length ↓ ns	Kim et al. (2011)
	Cucumis sativus L.	≤50 nm	2 h	10, 20, 50, 100, 200 and 500 mg/L	5–12 days	Petri dishes (filter paper or soil)	Whole plant	Germination % ↓ns, root length and shoot length ↓	Kumar et al. (2015)
	Glycine max L.	<50 nm	7 days	500 ppm	3 days	Hydroponics	Whole plant	Severe oxidative burst, changes in protein expression	Hossain et al. (2016)
	Helianthus annuus L. hybr. Kongo	nd	2 weeks	0.6 and 6 mg/l	1, 2 and 3 weeks	Hydroponics	Whole plant	Plant growth and protein production ↓	Sturikova et al. (2018)

	Ipomoea batatas var. Georgia jet	30–40 nm	7 days	100, 500 and 1000 mg/kg DW (soil)	130 days	In potting mix, under natural conditions	Tubers	Biomass and number of tubers ↓ at 1000 mg/kg ZnO; >70% of the accumulated Zn was in the flesh (compared to the peel)	Bradfield et al. (2017)
	Lemna minor L.	20 nm	nd	0, 0.03, 0.3, 1, 10, 30 mg/L for 1 or 7 days; 0, 1, 10 mg/L for 6 weeks	1 day, 1 week or 6 weeks	Hydroponics, 1/2 Hutner's medium	Whole plant	Photosynthetic efficiency of PSII ↓ after 1 day; biomass and root length↓ after 1 week; Zn content ↑ and growth ↓ until 6 weeks	Chen et al. (2018b)
	Lolium perenne L.	20 ± 5 nm	2 weeks germination+1 week	10, 20, 50, 100, 200 and 1000 mg/L	12 days	Hydroponics	Root	Plant biomass ↓, root tissue degradation	Lin and Xing (2008)
	Medicago sativa L. 'WL 535'	8 nm	–	50, 100, 200, 400, 800 and 1600 mg/L	Until 65% of the seeds were germinated	Petri dishes (germination test)	Whole plant	Germination % ↓ at 800-1600 mg/L conc., root length ↓ at 400-1600 mg/L ZnO NP	de la Rosa et al. (2013)
	Oryza sativa L.	nd	1–3 days	10, 100, 500 and 1000 mg/L	7 days	Moistened filter paper	Root	No change in germination %; root length ↓ and number of roots ↓at 100–1000 mg/L	Boonyanitipong et al. (2011)

(continued)

Table 1d (continued)

	Plant name	Size of ZnO NP	Duration of pre-cultivation	Concentration of the ZnO exposure	Time of exposure	Growth conditions	Plant organ investigated	Main effects (physiological/ biochemical/ morphological)[a]	Reference
	Oryza sativa L. ssp. japonica	<50 nm	14 days	25, 50 and 100 mg/L	7 days	Hydroponics	Whole plant	Biomass ↓, photosynthetic pigment content ↓, root length ↓, shoot length ↓; oxidative damage; root-to-shoot transport of ZnO NPs	Chen et al. (2018a)
	Oryza sativa L.	≤50 nm	2 h	10, 20, 50, 100, 200 and 500 mg/L	5–12 days	Petri dishes (filter paper or soil)	Whole plant	No change of germination %, root length and shoot length	Kumar et al. (2015)
	Oryza sativa L. Jijing No.6.	<50 nm	–	0, 25, 50, 100, 500, 1000 and 2000 mg/L	2 h priming then germination for 5 days	Wet filter paper (germination test)	Whole plant	Germination % was not affected at 2000 mg/L concentration, root length ↓ at 100–2000 mg/L, shoot length was not affected	Yang et al. (2015)
	Pisum sativum L. cv. Negret	<100 nm	–	3, 20, and 225 mg Zn/kg (soil)	30 and 60 days	Calcareous or acidic soil (pot experiment)	Leaves	6–12-fold higher Zn content and ROS ↑ in leaves (acidic soil), MDA content ↑, altered photosynthetic pigment ratios	García-Gómez et al. (2018a)

	Schoenoplectus tabernaemontani	19–47 nm	4 weeks	10, 100 and 1000 mg/L	3, 7, 14 and 21 days	Hydroponics	Whole plant	Growth inhibition and zinc accumulation	Zhang et al. (2015)
	Solanum lycopersicum L. ‘Bombyx’	30 nm	nd	10, 25, 50 and 75 nmol/L	48 h	Soft agar (in Petri dishes)	Whole plant	Vigour index ↓, Azotobacter-treatment ameliorated ZnO tolerance	Boddupalli et al. (2017)
	Solanum lycopersicum L. ‘Roma FV’	8 nm	–	50, 100, 200, 400, 800 and 1600 mg/L	Until 65% of the seeds were germinated	Petri dishes (germination test)	Whole plant	Germination % ↓ at 800–1600 mg/L concentration, root length ↓	de la Rosa et al. (2013)
	Solanum lycopersicum L.	<50 nm	–	0, 100, 250, 500, 750 and 1000 mg/L	7 days	Petri dishes (germination test)	Whole plant	Germination % ↓ at 750–1000 mg/L; root length ↓ at 500–1000 mg/L. concentration; shoot length ↓ at 750–1000 mg/L ZnO NP	Jain et al. (2017)
	Solanum melongena L.	18 nm	nd	100, 250, 500 and 1000 mg/L	15 days	Petri dishes (germination test)	Whole plant	Shoot length ↓ and root length ↓	Baskar et al. (2018)
	Triticum aestivum ‘HD 2967’	30 nm	nd	10, 25, 50 and 75 nmol/L	48 h	Soft agar (in Petri dishes)	Whole plant	Vigour index ↓, Azotobacter-treatment alleviated ZnO toxicity	Boddupalli et al. (2017)

(continued)

Table 1d (continued)

	Plant name	Size of ZnO NP	Duration of pre-cultivation	Concentration of the ZnO exposure	Time of exposure	Growth conditions	Plant organ investigated	Main effects (physiological/biochemical/morphological)[a]	Reference
	Triticum aestivum L.	<100 nm	–	500 mg/kg	14 days	Grown in sand	Whole plant	Root growth ↓; bioaccumulation of Zn as Zn-phosphate in shoot; lipid peroxidation ↑, GSSG ↑, peroxidase and catalase activity ↑ in root, chlorophyll content ↓ in shoot	Dimkpa et al. (2012)
	Triticum aestivum L.	<50 nm	–	0, 100, 250, 500, 750 and 1000 mg/L	7 days	Petri dishes (germination test)	Whole plant	Germination % ↓ and root length ↓ from 250 mg/L ZnO NP; no change in shoot length	Jain et al. (2017)
	Triticum aestivum L.	≤50 nm	2 h	10, 20, 50, 100, 200 and 500 mg/L	5–12 days	Petri dishes (filter paper or soil)	Whole plant	Germination % ↓ ns, root length and shoot length ↓	Kumar et al. (2015)
	Triticum aestivum L.	15.37 nm	15 days	0, 100 and 200 mM	7 days	Hydroponics	Whole plant	Seedling fresh weight ↓, chlorophyll content ↓, H_2O_2 content and lipid peroxidation ↑, antioxidant enzyme activities ↓	Tripathi et al. (2017)

	Vigna angularis L.	Nanorods with ~64 nm length	1 week	0–200 µg/ml then 200 µg/ml	1 + 2 or 3 weeks	Hydroponics	Whole plant	Germination % ↑; root length ↓ and ↓ ns, while shoot length ↑ ns and ↑; ROS ↑, induction of oxidative stress, chlorophyll and carotenoid content ↓	Jahan et al. (2018)
	Vigna radiata L.	≤50 nm	2 h	10, 20, 50, 100, 200 and 500 mg/L	5–12 days	Petri dishes (filter paper or soil)	Whole plant	Germination % ↓ ns, root length and shoot length ↓	Kumar et al. (2015)
	Zea mays L. Zhengdan No. 958.	<50 nm	–	0, 25, 50, 100, 500, 1000 and 2000 mg/L	2 h priming then germination for 7 days	Wet filter paper (germination test)	Whole plant	Germination % was not affected at 2000 mg/L conc., root length ↓ at 500–2000 mg/L, shoot length root length ↓ at 2000 mg/L	Yang et al. (2015)
	Zea mays L. Golden variety	24 ± 3 nm	–	0, 400 and 800 mg/kg (soil)	84 days	Pot experiment (soil)	Whole plant	Stomatal conductance, photosynthesis and yield of corn plants ↓ at 800 mg/kg ZnO NP; no change in shoot length	Zhao et al. (2015)

[a] ↑ indicates significant and ↑ ns indicates non-significant increase, while ↓ refers to significant decrease and ↓ ns to non-significant reduction

along with an antioxidant enzyme (SOD and POX) activity increase (Venkatachalam et al. 2017b; Table 1a).

Nonetheless, numerous studies focused on toxic effects, like oxidative stress and malondialdehyde (MDA) formation expressing lipid peroxidation as a response to larger doses of ZnO NPs. Mukherjee et al. (2014) described oxidative stress in green peas treated with 500 mg/kg (soil) ZnO NPs. An oxidative burst was observed in soybean (Hossain et al. 2016), in beet and pea (García-Gómez et al. 2018a) and in safflower (Hafizi and Nasr 2018) (Table 1d). In onion, a concentration-dependent increase of LP was detected, followed by a decreased mitotic index and an increased number of chromosomal aberrations suggesting a genotoxic effect of ZnO NPs (Kumari et al. 2011), which was further supported by Shaymurat et al. (2012) in garlic and Ghosh et al. (2016) in onion, tobacco and broad bean. Dose-dependent activation of SOD, CAT and ascorbate peroxidase (APX) was observed in tomato, while the plants showed growth retardation at higher (400–800 mg/L) ZnO NP concentration (Wang et al. 2018a; Table 1c). In *Salicornia* a significant increase in ROS and reactive nitrogen species (RNS) levels were displayed, coupled with a significant MDA increment. Peroxidase and APX activity declined, while Mn SOD, Fe SOD and cAPX were induced in response to the treatment (Balážová et al. 2018; Table 1c). Furthermore, in rice ZnO NP treatment triggered positive response of antioxidant enzymes was examined at molecular level, where levels of CSD1, CSD2, CATa, CATb, CATc, MSD1, FSD1, APXa and APXb were measured and mostly upregulated (Chen et al. 2018a). Summarily, we can say data published up to now suggest that ZnO NPs may act controversially in respect of oxidative processes depending on several factors like concentration, duration of exposure, age of the plant, the application of priming, etc.

4 ZnO NPs Influence Nutrient Homeostasis and Photosynthetic Efficiency

The last unexplained biochemical mechanism of ZnO NP effect is the impact on nutrient homeostasis and photosynthesis. As seen previously, different concentrations of ZnO have different effects on photosynthesis ranging from beneficial to toxic effects. In cilantro (Pullagurala et al. 2018a) chlorophyll content increased in response to the treatment, the same as in case of peanut (Prasad et al. 2012), cotton (Venkatachalam et al. 2017b) or bean (Ewais et al. 2017) (Table 1a). Foliar application of 10 ppm ZnO caused an increment of phosphorus and chlorophyll content in cluster bean (Raliya and Tarafdar 2013). On the contrary, in green peas (Mukherjee et al. 2014), Indian mustard (Rao and Shekhawat 2014), corn (Zhao et al. 2015), *Arabidopsis* (Wang et al. 2015) and wheat (Tripathi et al. 2017) chlorophyll content attenuated in ZnO-treated plants (Table 1d). In rice, a significant decline of chlorophyll content was observed and upon the examination of chlorophyll synthesis genes CHLD and CHLM expression levels reduced as response to the treatment

(Chen et al. 2018a). The toxic effects are similar to the effects of bulk metal ions, where a total chlorophyll decrease was described, resulting in disorganised chloroplast with a reduced number of thylakoid and grana (Souza et al. 2005; Jiang et al. 2007; Ebbs and Uchil 2008). A similar effect was described by Dewez and Oukarroum (2012) in case of silver nanoparticles, where the NP treatment caused PS II complex degradation. Changes in the zinc homeostasis of plants can also affect metabolism of other micro- and macronutrients (Jain et al. 2013). For instance, ZnO NPs altered the nutritional values of soybean (Peralta-Videa et al. 2014) or decreased the amount of potassium, sulphur, phosphorus, copper and iron in *Arabidopsis* seedlings (Nair and Chung 2017).

5 ZnO NPs and Plant Development

5.1 ZnO NPs Affect Seed Germination and Vegetative Growth

The effect of ZnO NPs on plant development and physiological processes is an intensely researched area, providing numerous results and raising many other questions on the topic. It has been shown in numerous plant species that optimal amount of ZnO NP supplementation might also exert a positive effect on plants, including increased seed germination rate, plant growth (i.e. root length and shoot length), yield, photosynthetic efficiency or antioxidant capacity (Table 1c). In some cases, in experiments executed in Petri dishes, seed germination rate showed to be induced by ZnO NP application in case of cucumber (de la Rosa et al. 2013), mung bean (Jayarambabu et al. 2014) or pepper (Afrayeem and Chaurasia 2017). The form of ZnO NP exposure seems to be determinative in the early development of the plants. When peanut seeds were primed for 3 h with ZnO NPs before sowing, enhanced seedling vigour, root and shoot length were detectable (Prasad et al. 2012). Similarly, lower doses of ZnO NPs generated the increment of root and shoot length of sesame grown in soil (Narendhran et al. 2016). Nevertheless, ZnO NP exposure also may have no influence on germination as it was assessed in barley (Doğaroğlu and Köleli 2017) and bean (Medina-Velo et al. 2017) cultivated in pots (Table 1a).

On the other hand, ZnO NPs can act as a stressor, resulting in reduction in seed germination, growth inhibition of plant biomass, photosynthetic activity or abnormalities of chromosomes (Table 1d). Negative effects on germination or on seedling vigour were observed at higher ZnO NP concentrations in alfalfa (de la Rosa et al. 2013), tomato (Boddupalli et al. 2017; Jain et al. 2017) and wheat (Jain et al. 2017). In most cases published, the typical and visible symptom of ZnO NP toxicity is retarded development of the root and/or the shoot (Kumar et al. 2015; Baskar et al. 2018), occasionally with necrotic lesions and degradation of the tissues, as it was documented in ryegrass (Lin and Xing 2008), maize (Pokhrel and Dubey 2013) and *Salicornia* (Balážová et al. 2018). It may be hypothesised that there is a correlation between the inhibition of root elongation and mitotic aberrations in the root tip cells, followed by the increment of root diameter (Balážová et al. 2018) or lateral root number (Nair and Chung 2017), which suggests the potential reorientation of root cells like in stress-induced morphogenic responses (SIMR, Potters et al. 2007) (Table 1c and 1d).

In the background of these negative processes, probably Zn content of the different plant organs was increased, causing changes in the physiological homeostasis, like lipid peroxidation, oxidative stress, nutrient imbalance or decreased protein production, as here we previously discussed.

5.2 ZnO NP Affects Reproductive Processes

Although there are many data about the impact of ZnO NPs on vegetative growth, it is noteworthy to mention that these agents may influence the reproductive traits of the plants, as well. There are both positive and negative impacts published. Laware and Raskar (2014) discovered that foliar spraying with ZnO NP may cause earlier flowering and elevated seed production of onion. Similarly, induced productivity of cowpea (Srinivasan et al. 2017; Table 1a) and bean (Ewais et al. 2017) was recorded after ZnO NP foliar application. At the same time, in pot experiments filled with treated soil bean exhibited a decrease of fruit number and seed number per pod (Medina-Pérez et al. 2018).

6 Stress Alleviation by ZnO NPs

In some cases, stress-alleviating effect of ZnO NPs was also exhibited, for example in case of drought-stressed wheat (Taran et al. 2017), Cd- and Pb-stressed *Leucaena leucocephala* (Venkatachalam et al. 2017b) or As-treated rice (Wang et al. 2018b) (Table 1b).

7 Conclusions and Future Perspectives

Nowadays, ZnO nanoparticles (NPs) seem to be an indispensable part of our life due to the wide range of its usage (e.g. medicines with anticancer and antimicrobial activities or nanofertilisers in agriculture), therefore their emission to the environment and food chain remarkably has grown. Here, we tried to overview that plants being immovable how evolve strategies to protect themselves from these abiotic stress factors, but it was also proved that ZnO NPs may mitigate the negative effects of other toxic agents like heavy metals. Though there are an increasing number of reports dealing with the impact of ZnO NPs on plants, there is still little evidence of the potential translocation from root to shoot and there is only a few information about the anatomical changes in the root and/or shoot-like cell wall modifications triggered by ZnO NPs.

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Effect of TiO_2 as Plant Growth-Stimulating Nanomaterial on Crop Production

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1 Introduction

Nanoparticles (NPs) are microscopic particles defined to have at least one dimension within three vectors smaller than 100 nm (CODATA-VAMAS Working Group and Rumble 2016), although several authors also include particles greater than 100 nm that have analogical "nanoparticle" effects in biological systems (Cox et al. 2016). The materials consisting of NPs demonstrate unique physical, physico-optical, chemical and biological properties (Franklin et al. 2007; Rotello 2004) and are usually classified into various categories according to their origin (natural and anthropogenic), composition (organic and inorganic), technological preparation (top-down and bottom-up) or general purpose (quantum dots, drug delivery, etc.) (Ma et al. 2010; Nagarajan 2008; Rotello 2004).

Nowadays, the ever-growing field of nanotechnology is linked to all areas of human life including nanomaterials' application in electronics (Chen and Mao 2007), optical devices (Višňovský et al. 2015), magnetic materials (Baibich et al. 1988), human implants (Vandana et al. 2019), chemical analysis (Hagarová 2018;

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Hagarová et al. 2012a, b; Matúš et al. 2009; Šebesta and Matúš 2018) and bionanotechnology (Holišová et al. 2019; Kolenčík et al. 2014, 2019). The progress in nanomaterial research is also reflected in agriculture, where the simple premise of size reduction of already existing bulk fertilizers allowed agricultural industry to decrease the costs of active substances while preserving their beneficial effects on plants, as well as to increase the delivery efficiency by more effective control of agrochemicals' release and uptake (Liu and Lal 2015; Prasad et al. 2014, 2017; Tripathi et al. 2015, 2017a, b, c). However, there is still much unknown when it comes to behaviour of NPs in natural matrices, particularly about their translocations, effects on the uptake of other nutrients, transport in plants, accumulation and bioavailability (Liu and Lal 2015; Kořenková et al. 2017; Wang et al. 2016; Shweta et al. 2018; Vishwakarma et al. 2018). From the consumer perspective, the plant food quality (e.g. taste, nutritional value and visual attractivity) and the final product price are the most relevant subjects which are also addressed in research. There is also continual search for the new cultivation approaches, which include the development of new chemically active growing media (hydroponics) that utilize NPs, such as TiO_2, ZnO, MnO, Al_2O_3, Fe_2O_3 for plant production more efficiently.

2 TiO_2 Nanoparticles' Characterization and Biological Properties

One of the most commercially and industrially applied NPs, whose effects on plants have been extensively researched recently, are TiO_2 NPs. These are generally synthesized by physical or chemical processing of their precursors or bulk parent materials (Chen and Mao 2007; Truong et al. 2017); however, there are also new green experimental methods for their synthesis via mediated transformation in the presence of organisms, e.g. microscopic filamentous fungi such as *Aspergillus flavus* (Raliya et al. 2015), bacterial strains of *Bacillus subtilis* (Kirthi et al. 2011) and *B. licheniformis* (Suriyaraj and Selvakumar 2014), yeasts (Patidar and Jain 2017), and plants such as *Justicia gendarussa* (Senthilkumar and Rajendran 2018).

Figure 1 highlights the structural model of three different stable polymorphic modifications of TiO_2, rutile, brookite and anatase (Chen and Mao 2007), which possess relatively high mechanical and chemical resistance (Morton and Hallsworth 1999) and extraordinary photochemical properties (Gao et al. 2006). While brookite has an orthorhombic crystal symmetry (space group *Pcab*), rutile and anatase have tetragonal crystal symmetries of space group *P42/mnm* and *I41/amd*, respectively, and contain TiO_6 octahedron where each Ti^{4+} ion is surrounded by six O^{2-} ions, associated with distorted octahedrons. The most variable characteristics of TiO_2 polymorphs are the size of unit cell dimension, the distorted octahedron configuration, and the pattern of octahedral chains. These variabilities are primarily responsible for the differences of polymorphs in mass densities and the electronic band structures (Chen and Mao 2007).

The TiO_2 NPs, especially those with dimensions below 50 nm, belong to a group of photo-semiconductors with photocatalytic activity (Cox et al. 2016; Wang et al. 2016) which is based on absorbance of specific light wavelengths by electron that is

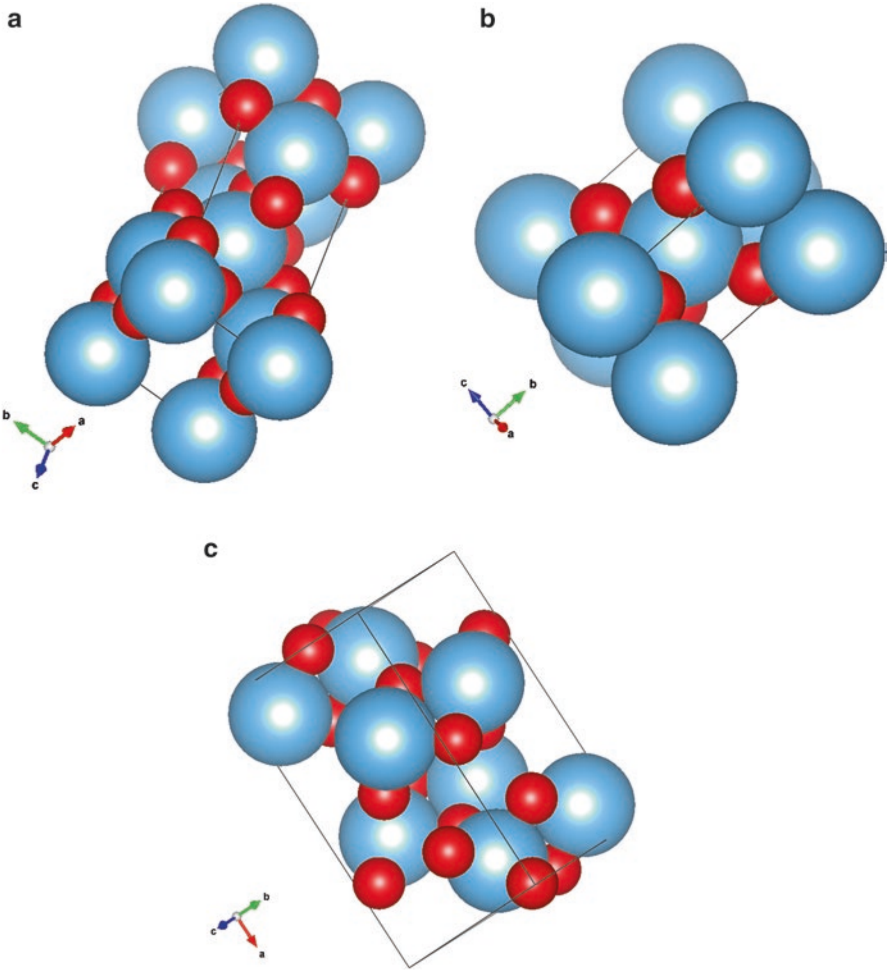

Fig. 1 Geometrical arrangement of atoms in the unit cell of TiO_2polymorphic modifications, (**a**) anatase, (**b**) rutile and (**c**) brookite, which were designed and visualized using VESTA software in space-filling regime (Momma and Izumi 2011)

exited from the valence layer into the conduction band forming electron-hole pairs (Fig. 2). These charged carriers are transferred to the catalytic particles' surface, where they are ultimately trapped and act as redox-active components allowing the formation of ·OH and ·O radicals. However, due to their large band-gap energy of approximately 3.2 eV, TiO_2 NPs are mostly excited by the UV light which usually makes up less than 10% of daylight radiation (Chen and Mao 2007; Wang et al. 2016). However, because of the different conditions in synthesis, engineered TiO_2 NPs vary in surface properties (Chen and Mao 2007; Weng et al. 2005) and the morphology and modification of crystal structures with substituting elements also affect the photochemical characteristics of TiO_2 reaction to UV irradiation (Chen and Mao 2007; Weng et al. 2005).

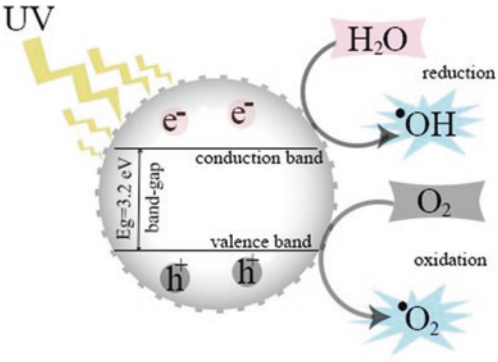

Fig. 2 Photogeneration of charged carriers in TiO_2 nanoparticle and consequent formation of reactive oxygen species (Yadav et al. 2016)

Due to their photocatalytic properties and formation of reactive oxygen species upon irradiation, TiO_2 NPs were applied to protect plants against pathogenic microorganisms (Prasad et al. 2014, 2017; Yadav et al. 2016). Although their exact role in biological systems is unknown, it has been shown that TiO_2 enhances chlorophyll synthesis (Cox et al. 2016; Wang et al. 2016). Thus, titanium is regarded beneficial for plant production, particularly at lower concentrations, where it stimulates the activity of certain enzymes, increases the uptake of other essential nutrients (e.g. Fe), increases photosynthesis and production of chlorophylls, improves crop yields and stress tolerance (Lyu et al. 2017).

Nevertheless, the TiO_2 is still potentially toxic to cells due to its negative effects on cell respiration and the cell membrane permeability (Yadav et al. 2016). Although TiO_2 NPs have been progressively utilized in medical devices and are considered to be fully biocompatible (Chiang et al. 2009), their potential carcinogenic risk to human health after exposure by inhalation was acknowledged by the International Agency for Research on Cancer (IARC 2010).

3 Behaviour of Nanoparticles in Culture Media and Soils

3.1 Behaviour of Nanoparticles in Growth Media

For experimental evaluation of interactions between NPs and plant roots, it is desirable to choose less complex matrices for plant growth than soil, such as liquid culture media. Compared to soils, culture media provide faster growth, enhance biomass production, reduce the occurrence of diseases, utilize smaller area, and are easier for control of conditions such as temperature, humidity and light intensity (Hong et al. 2005b; Savvas 2003; Wang et al. 2013). For plants cultivation, the most commonly used culture media are Hoagland culture medium with various modifications (Dhoke et al. 2013; Kořenková et al. 2017) and Steinberg medium (Song et al.

2012). However, the growth medium composition is usually adjusted to the plant's specific growth requirements (Dhoke et al. 2013; Savvas 2003).

Growth media are divided into two main categories – the inorganic and organic media. The inorganic media contain materials relatively inert towards NPs, e.g. sand, gravel, perlite, vermiculite, clay pebbles and rock wool. However, especially in case of silicates (e.g. zeolites and vermiculites), the potential NPs sorption onto mineral surfaces should be taken into consideration during experiments. The organic culture media contain organic materials, such as coco coir, coffee husk, wood dust or rice husk, which can strongly influence behaviour of NPs not only by providing an active surface for sorption, but also by increasing dissolved organic compounds due to their decomposition (Savvas 2003).

The thermodynamic stability of NPs in growth media depends on the chemical composition and pH of the growth medium, as well as on the nature and chemical properties of NPs (Amde et al. 2017; Reed et al. 2012). As all of the polymorphic modifications of TiO_2 NPs are insoluble, they are also considered not being bioavailable as ions (Amde et al. 2017). Therefore, their phytotoxic effect usually depends on the properties of their active surface area (Ma et al. 2010). On the other hand, some NPs dissolve easily, thus their phytotoxic effect is more complex and involves the effects of released ions. Furthermore, released ions can precipitate with other culture media components or plant exudates and form new stable phases with different characteristics compared to parent material (Amde et al. 2017; Cox et al. 2016; Reed et al. 2012).

Nanoparticles behaviour also depends on the stability of their electric double layers. The destruction of electric double layer's integrity, resulting from changes in the medium during plant growth, enhances aggregation and sedimentation. This process significantly affects root exposition to nanoparticles as the nanoparticles' concentration in media, as well as their reactive surface, decreases (Amde et al. 2017; Cox et al. 2016). Growth media solidified with agar have almost similar chemical composition to their liquid counterparts, but significantly higher viscosity. This affects interactions of NPs with both culture medium and the roots (Amde et al. 2017; Cox et al. 2016; Ma et al. 2010). Achieving uniform distribution of NPs is relatively difficult as they are introduced into agar at higher temperatures and when the temperature gradually decreases, the NPs become position-fixed. Furthermore, this can cause alteration in both growth media and NPs (Reed et al. 2012). This process can partially or completely destruct NPs, dissolve them, or create more stable surfaces (Amde et al. 2017; Reed et al. 2012). Furthermore, when NPs are fixed in solid growth medium, their motion is limited to very short distances.

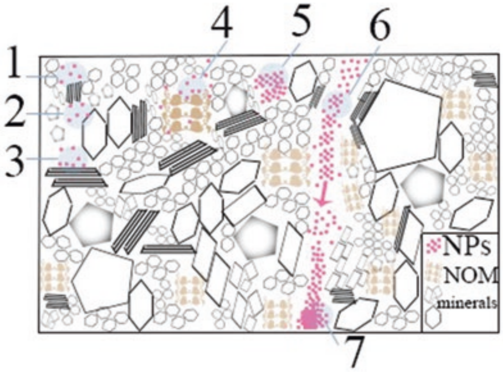

Fig. 3 The illustrative behaviour of nanoparticles (NPs) in soil system: 1. freely suspended NPs in soil solution, 2. sorption and desorption of NPs onto mineral surfaces, 3. heteroaggregation of NPs with inorganic colloids and chelators, 4. heteroaggregation of NPs with natural organic matter (NOM) or organic chelators, 5. homoaggregation of NPs, 6. transport of NPs, 7. dissolution of NPs and subsequent micro-particle formation

3.2 Behaviour of Nanoparticles in Soils and Specific Aspects of Field Experiments

There are significant differences between soil systems and solid or liquid culture growth media. While growth media are usually homogenous in nature (Savvas 2003), soils are complex matrices that include solid phase which is comprised of 95 to 99% inorganic rocks and minerals of different size and composition, and 1 to 5% soil organic matter. Additionally, it contains living organisms and atmospheric gases and aqueous soil solutions entrapped in heterogeneously distributed pores of differing sizes. Thus, an examination of the interactions between NPs and soil environments must take all of these phases into account, as well as the mutual interactions between them (Amde et al. 2017; Šebesta et al. 2017). Therefore, the results from experiments with plants grown in liquid or solid culture media spiked with NPs are less comparable to the real environmental conditions but still represent less complex systems where the behaviour of NPs can be more easily predicted. They also provide us with answers to specific mechanism-related questions, whereas experiments with soils simulate the natural conditions and show us the complex nanoparticle-plant interactions that should be involved in evaluation of the viability of NPs application in agriculture.

Based on the nature of NPs in soils and the soil physico-chemical properties, NPs could predominantly be (i) bound onto the surfaces of oxides and hydroxides of Fe, Mn and Al, or retained by clay minerals via hetero-aggregation, (ii) attached to natural organic matter, e.g. to humic substances, (iii) amended with inorganic ions such as PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, or some inorganic chelators, (iv) precipitated or crystallized to modify their reactivity, mobility and toxicity (Amde et al. 2017; Šebesta et al. 2017). As highlighted in Fig. 3, many complex interactions take place when

NPs are applied to soil systems, which influence mobility, reactivity, distribution, bioavailability, and potential toxicity of NPs. Thus, in the field experiments, various interactions and factors must be considered when evaluating the effects of NPs. This includes site-specific environmental conditions (e.g. geographic location, altitude, terrain, soil types, soil quality, climatic and weather conditions), intrinsic factors of the plant (e.g. photosynthetic activity, respiration, the root system, resistance against adverse effects, plant growth and development, seed biological value) and field management (e.g. soil cultivation, forecrop, pre-seed germination, pre-sowing seed treatments, intensity of fertilization) (Hussain et al. 2018; Ion et al. 2015). Also, during the life cycle of a plant, many morphological and physiological changes occur which partially influence the input of NPs and their effects.

Plants' leaves and stomata have a tendency to absorb a certain range of NPs' concentrations via the same mechanisms as gas uptake (Wang et al. 2013), thus, to omit complex influence of soil matrices on NPs uptake, foliar application is often considered as a viable method. The spray liquids for foliar application usually contain pesticides, some growing regulators (this includes NPs) and adjuvants, which are surface-active substances with various roles (Brausch and Smith 2007; Räsch et al. 2018). Adjuvants can affect the ability to alter the plants' surface tension and viscosity which promotes penetration of active substances (including NPs) through wax substructures (Burghardt et al. 1998; Räsch et al. 2018) and accelerates the active substance translocation flow into plant vascular system (Hunsche 2006; Hunsche et al. 2006). Foliar solutions' components can influence NPs stability in a spray liquid, and subsequently crop production and biomass development (Capaldi Arruda et al. 2015; Khot et al. 2012; Wang et al. 2016). Their stability is also affected by their exposure to sunlight which can lead to photodegradation of less stable NPs (Amde et al. 2017).

4 The Impacts of Nanoparticle Amendments on Crop Development and Yield

4.1 The Plant Uptake of Nanoparticles Applied to the Roots (Hydroponically) or Leaves (Foliarly)

Generally, the uptake efficiency of NPs by plant as well as their effects on the plant growth and metabolic functions depend on combination of several factors such as particle size and concentration, working environment (light, water and gas), plant species, NPs application method, etc. (Nair et al. 2010; Wang et al. 2013). NPs dispersed in culture media (either solid or liquid) and in soil can penetrate plant cell walls and translocate in plants (Nair et al. 2010; Rico et al. 2011). This process is accompanied by a variety of positive and negative effects (Govorov and Carmeli 2007; Hong et al. 2005a; Jiang et al. 2012). When applied in appropriate concentrations and under favourable conditions, NPs can enhance the ability of plants to

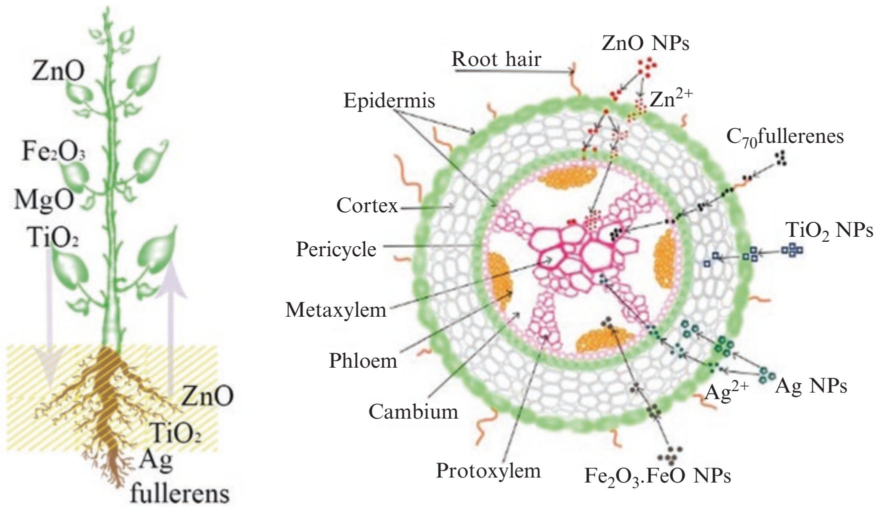

Fig. 4 (**a**, **b**) Transport pathways of nanoparticles via the root system and their translocations in the plant. (Reprinted (adapted) with permission from RICO et al. (2011). Copyright (2019) American Chemical Society)

absorb and utilize nutrients (Li et al. 2016), promote nitrogen metabolism (Yang et al. 2006) and photosynthesis (Hong et al. 2005b), thereby improving plant growth. On the other hand, the symptoms of phytotoxicity include stunted or delayed plant growth, root cap deformities (Ranjan et al. 2017), and reduced biomass production. Nonetheless, the rising interest in nanotechnology has triggered the emergence of various studies related to NPs toxicity mechanisms, which have not yet been satisfactorily explained. When NPs in liquid growth medium come in contact with the root surface, they either (i) adhere to the surface where they can be resuspended, (ii) dissolve or (iii) penetrate roots and translocate further into the plant (Fig. 4a, b). Root cell walls represent a porous network for molecule movement that allows substances as large as 3.5–8.6 nm to enter at atmospheric pressure (Read and Bacic 1996).

The entry of larger chemical structures may be restricted; however, some NPs can induce the formation of new larger pores in the epidermal cell wall, thus facilitating their access to the cells (Du et al. 2011; Lin and Xing 2008). Particles are then conducted through vascular tissues upwards from the root to the leaves. Kořenkova et al. (2017) investigated the effect of TiO_2-NPs on early stages of barley (*Hordeum vulgare* L.) growth and development. Plants were cultivated hydroponically and in agar-based media contaminated with different concentrations of TiO_2 anatase nanopowder for one week. The diameter of synthesized NPs ranged in size from several nanometres up to 50 µm. The results showed that the contents of chlorophyll *a* and *b* and the biomass weight were not significantly affected by the application of NPs. Furthermore, hydroponics treatment with TiO_2-NPs in the presence of up to 1000 mg L^{-1} did not considerably influence the shoot growth. Regarding the plants cultured on agar medium, only high doses of TiO_2-NPs (10% and 20% w/w) resulted in significant inhibition of the shoot growth. On the other hand, the root length parameters recorded demonstrated an apparent TiO_2-NPs toxicity with increasing NPs concentration in both experiments. Although ICP-MS eventually detected the presence of titanium in the aerial plant parts, the roots seem to act as an effective barrier that limits the transport of NPs into shoots.

Leaves are the main organs of photosynthesis and transpiration in most flowering plant species, they also function in gas exchange (Starr et al. 2018). There are two possible pathways for foliar uptake of NPs by plant – cuticular and stomatal (Eichert et al. 2008). Cuticular pathway is highly size selective and differs only slightly between plant species (Buchholz et al. 1998); the upper limit for penetrating particles is ~ 5 nm. The stomatal pathway is considered as highly capacitive because of its large size exclusion limit 10 nm-1 μm and high transport velocity (Eichert et al. 2008).

Nonetheless, once inside the plant, NPs interact with the cells causing an array of morphological and physiological changes, depending on the NPs' properties and concentration. The last years have produced a great number of studies exploring the role of NPs in a key process for plants – a photosynthesis. The process of photosynthesis involves a series of reactions that utilize solar energy to convert water and CO_2 into O_2 and carbohydrates. Light-dependent part of photosynthesis is associated with the absorption of light by chlorophyll and its conversion into chemical energy in the form of electron carrier molecules; light-independent (dark) reactions involve reduction of CO_2 into carbohydrate molecules.

Several papers have reported that the presence of NPs in photosynthetic organisms influences photosynthetic performance. Queiroz et al. (2016) confirm an existence of effective interactions between chlorophyll (extracted from *Vicia faba* L. leaves) and Ag-NPs. Their findings suggest that Ag-NPs may represent a potential risk for plants, since chlorophyll molecules may be adsorbed at Ag-NPs surfaces, transferring their excited electrons to these metallic surfaces which results in chlorophyll fluorescence quenching and lifetime decrease (Queiroz et al. 2016). In addition, Jiang et al. (2012) demonstrated a significant decrease in the chlorophyll content, plant biomass and photosynthetic efficiency of photosystem II (Fv/Fm) in *Spirodela polyrhiza*, induced by Ag-NPs. In turn, quite different observations have been reported on TiO_2-NPs, probably the most extensively studied NPs from the point of photocatalytic properties. TiO_2 is a photocatalyst, acting as an electron conducting material after absorbing the light. Therefore, TiO_2-NPs are believed to promote photosynthesis (Lei et al. 2007; Ping et al. 2008), thus enhancing the plant growth.

Examining the photosynthetic efficiency in TiO_2-NPs-treated spinach, Hong et al. (2005b) suggest that TiO_2-NPs can enhance light absorbance, accelerate transport and transformation of light energy and protect chloroplasts from ageing due to the delay of effective photosynthetic tenure of chloroplasts. Similar results were obtained by Lei et al. (2007) who demonstrated that TiO_2-NPs could considerably improve whole chain electron transport, photoreduction activity of photosystem II, O_2 evolution and photophosphorylation activity of chlorophyll under both visible and ultraviolet light. However, the authors could not satisfactorily clarify the mechanism of TiO_2-NPs on promoting the conversion of light energy into electron energy, and subsequently into active chemical energy. Even though working with gold and silver NPs, the positive effect of metal NPs on the efficiency of chemical energy production was well documented by Govorov and Carmeli (2007). By modelling a hybrid photosystem composed of photosynthetic molecules and gold and silver NPs and nanoshells, the two illustrated a significant enhancement in the chemical production rate due to the plasmon resonances.

Foliar application of anatase TiO_2-NPs in an appropriate concentration results in an increase in chlorophyll content which enables plants to synthesize more light-harvesting pigment-protein complexes (LHCII) to capture a greater amount of light energy. Nanoanatase under light can cause an oxidation-reduction reaction that leads to the transfer of charge between NPs and LHCII (Kuang 2003) and contributes to photosynthesis enhancement. Using different engineered NPs (TiO_2, Fe_2O_3, MgO, ZnO) and watermelon as a sample plant, a simplifying process of the uptake, translocation and accumulation of NPs in the plant after foliar application was described by Wang et al. (2013) as follows: (i) application of NPs on the leaves of 12-day-old plants by dropping and spraying; (ii) NPs penetrate the plant tissues through the stomatal pathway, still, many of these NPs are prevented from entering by the waxy cuticle on the leaf; aerosolized NPs are found easier to enter the stomata via gas uptake compared to those in drops; (iii) NPs are being translocated by the phloem system along with the photosynthetic products, such as sucrose, proteins and some mineral ions necessary for plant growth; (iv) delivery of NPs to shoots and roots as a result of pressure differentials between source (leaves) and sink (e.g. growing shoot apex) based on mass flow or pressure flow hypothesis.

Besides beneficial aspects related to the increased content of bioactive compounds (TiO_2 and ZnO-NPs, Raliya et al. 2015; Cu-NPs, López-Vargas et al. 2018), fruit quality (Cu-NPs, López-Vargas et al. 2018), increased root and shoot length and biomass production (Dhoke et al. 2013), the foliar NPs treatment may be associated with some harmful effects, such as necrotic speckling on the leaves at the spot of application (Fe_2O_3-NPs, Wang et al. 2013) and the decrease in activity of APX and GPX enzymes in fruits (Cu-NPs, López-Vargas et al. 2018). Also, an accumulation of NPs on photosynthetic surface can cause foliar heating that leads to gas exchange alterations due to stomatal obstruction resulting in changes of various physiological and cellular functions of plants (Silva et al. 2006).

4.2 The Effect of Nanoparticles on Plants with Regard to Morphological, Physiological and Biochemical Characteristics

NPs can interact with the plant on different hierarchical levels. Figure 4a, b shows various interactions, e.g. uptake, translocation, accumulation and transformation that occur within the plant. As implied from the above, these interactions can have positive, negative or neutral impacts on the species involved. The researchers who work with NPs and plants cultivated in growth media of diverse composition and in soil often focus on some particular effects, such as the change in length of roots and shoots, biomass production, the amounts of accumulated NPs, etc. Although after the evaluation of the obtained results some specific conclusions are always drawn, possibly with some suggestions for future research, many mechanisms of transport, accumulation and fate of NPs still remain a topic of discussion and speculation. Regarding the root system, the most observed parameters include germination and root growth, main and lateral root length, diameter and branching, root architecture changes, size, structure, and deformities of epidermal pores, the ability to produce exudates, enzymatic activity, interactions of NPs with the cells in a root zone and their accumulation, etc.

The soybean (*Glycine max*) treated with mixed TiO_2-NPs and SiO_2-NPs showed an increased nitrate reductase activity, accelerated germination and promoted growth by enhancing the absorption and utilization of water and fertilizer by the plant (Lu et al. 2002). The lettuce (*Lactuca sativa*) cultivated on sandy-loam soil amended with metal oxides NPs over a 3-month period exhibited enhanced growth, biomass and moisture content at all tested concentrations (50, 100, 150, 200 and 250 $mg.kg^{-1}$). Also, affinity of NPs to adsorb phosphate ions, modifications in phosphorus speciation, and NP-induced stress in the rhizosphere had possibly contributed to enhanced root exudation and acidification, which led to improved availability of naturally soil-bound inorganic phosphorus and its uptake by the plants.

Another study that used soil as a growing medium was aimed at the effect of TiO_2-NPs and ZnO-NPs on wheat (*Triticum aestivum*) growth and soil enzyme activities. Probably due to low solubility of TiO_2, most of the TiO_2-NPs applied could not enter the root cells of wheat, they agglomerated in soil medium and adhered and/or agglomerated on the surface of periderm cells. Only a few individual NPs penetrated through and were later observed in the wheat root cells. Nevertheless, this may cause changes in the microenvironment of the contact area, increase the solubilization of metals, or generate extracellular reactive oxygen species (ROS) that can damage cell membranes (Heinlaan et al. 2008). Unlike TiO_2, the solubility of bulk ZnO as well as ZnO-NPs is much higher. Thus, ZnO-NPs most likely do not remain nanosized in soil, they dissolve, allowing Zn^{2+} to enter the cells and tissues. As indicated by inhibited soil enzyme (protease, catalase and peroxidase) activity and by the biomass decrease, the wheat plants were harmed by both types of NPs (Du et al. 2011).

In contrast to TiO_2-NPs, the toxicity of ZnO-NPs may be induced by the dissolved Zn (Franklin et al. 2007), or, as indicated by a later study on the ryegrass (*Lolium perenne*), it cannot be explained by the dissolution of ZnO-NPs alone. There is an assumption that root exudates are able to change NPs' properties and behaviour. Particularly when concentrated in the rhizosphere, ZnO-NPs can severely damage the root epidermal and cortical cells, and impair the endodermal and vascular cells, which may be a major reason for root tip shrinkage, significant biomass reduction and plant growth retardation. The phytotoxicity of ZnO-NPs most likely does not directly result from their dissolution in the rhizosphere or on the root surface, it may arise from their physical and chemical interference with root cells' normal physiological processes (Lin and Xing 2008).

5 Conclusions and Future Perspective

It seems that the impact of TiO_2 nanoparticles on plant physiology is still not understood in full detail, even though it appears that their photocatalytic activity may be beneficial for plant health and fitness, they are supportive in terms of photosynthesis performance, higher chlorophyll content and amount of biomass. However, the major research challenges in this field that still remain include nanoparticles' metabolic fate, bioavailability and their potential toxicity in biological systems. These are affected not only by nanoparticles' intrinsic chemical and physical properties, but also by the character of their interactions with various environmental components where the specific alterations of the parent structures take place, resulting in changes in nanoparticles' behaviour. Also, particularly with regard to their use as a new generation of fertilizers in agriculture, only a little is known either about their effect on rhizosphere chemistry, other plant nutrients and physiologically active substances, or about field application-associated factors (e.g. dose-response effect) and optimal conditions for their use.

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Metal-Based Nanoparticles' Interactions with Plants

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1 Introduction

Nanoscience and nanotechnology are among the fastest-growing areas in either research or business. Nanoproducts are regarded as high-tech commodities with wide applicability in technology, medicine and agriculture. In particular, they are key components of electronic devices, advanced fuels, textiles, paintings and coatings, personal care products, pharmaceuticals, cosmetics, dietary supplements and agrochemicals (Khalil et al. 2017; Hwang et al. 2018; Vance et al. 2015; Gautam et al. 2019; Francisco and García-Estepa 2018; Socas-Rodríguez et al. 2017; Hua et al. 2012; Sharifi et al. 2018; Sharma et al. 2018; Tsazuki 2009; Dasgupta et al. 2015; Almeida et al. 2014; Consumer Product Inventory 2018). These steadily growing number of applications make nanoparticles (NPs) highly abundant in the environment and available for plant uptake. The latter problem is strictly related to the toxicity and fate of nanomaterials (Sruthi et al. 2018; Jia et al. 2017; Chen et al. 2018a; Jośko et al. 2017; Tarrahi et al. 2018; Dwivedi et al. 2015; Vishwakarma et al. 2017; Xiao et al. 2018; Amde et al. 2017; Arif et al. 2018; Tiwari et al. 2019; Shweta et al. 2018). Unfortunately, that issue has not been thoroughly recognized and documented yet (Williams et al. 2019; Kuhlbusch et al. 2018; Naasz et al. 2018; Gao and Lowry 2018). Moreover, nanomaterials are species of divergent toxicities and constitutions. They may exist as simply isolated particles or complex entities where nanoparticles are embedded into diverse matrix components.

Natural NPs are being introduced into the environment by a number of processes. Volcanic eruptions, forest fires, sand storms and hydrological cycle components are among the most significant (Lead and Smith 2009). However, the continuously growing amount and increasing diversity of anthropogenic nanoparticles are substantial threats to the global environment. The trustworthy assessment of

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the NPs' impact on the plant environment cannot be made without proper worldwide production estimates. Regrettable, available data are mostly based on estimates and forecasts only (Hendren et al. 2011; Aitken et al. 2006; Keller and Lazareva 2014; Piccinno et al. 2012; European Commission, Commission Staff Working Paper: Types and Uses of Nanomaterials, Including Safety Aspects 2012).

2 Classification of Nanoparticles

Divergent structures and topological properties of nanoparticles can hardly be fitted into simply classification schemes. Attempts as reported in the scientific literature (Table 1) are far from unambiguity (Kabir et al. 2018; Sudha et al. 2018; Ealias and Saravanakumar 2017; Tiwari et al. 2012).

3 Metal-Based Nanoparticles

One of the major groups of nanoparticles is metal-based nanoparticles (MNPs). Their importance for contemporary medicine and technology cannot be overestimated with the world production approaching one-third of the global nanomarket (Niska et al. 2018; Ma et al. 2015; Maynard 2006). Within that group, three major types of species are usually distinguished, namely quantum dots (QDs), metal nanoparticles and metal oxide nanoparticles (Fig. 1).

Nanoparticles of semiconductors (i.e. QDs) were predicted in theory in the 1970s and initially synthesized in the early 1980s. As the reduction of semiconductor particles advances, quantum effects are coming into the play restraining the energies at which electrons and holes can exist in the particles. As energy is related to wavelength (i.e. colour), this means that the optical properties of the particle can be finely tuned depending on its size. Thus, MNPs can be carefully tailored to emit or absorb light of specific wavelengths (colours), merely by controlling their size. Recently, QDs have found applications in composites, solar cells (Grätzel cells) and fluorescent biological labels (e.g. to trace a biological molecule) which use both the small particle size and tunable energy levels. Advances in chemistry have resulted in the preparation of monolayer-protected, high-quality, monodispersed, crystalline QDs as small as 2 nm in diameter. They can be conveniently treated and processed as a typical chemical reagent.

Remarkable progress in fabrication methods had allowed the production of the custom-made MNPs and nanomaterials with special attention paid to their shape, size or structure and further led to numerous new applications. Available technologies are usually categorized over two major groups, i.e. the "top-down" and "bottom-up" approaches (Charitidis et al. 2014; Dhand et al. 2015; Sweet et al. 2012). The former relies on the continuous decrease of the starting macro-material until the nanosize is reached while the latter is a topologically driven process which arranges

Table 1 Classifications of nanoparticles with regard to their origin, number of dimensions which are not confined to the nanoscale, chemistry of core material and state

Diverging feature	Categories	Examples
Origin	Natural	NPs which occurred in environment as a result of natural processes like dust storms, forests fires, volcanic eruption, product of sea water evaporation
	Manufactured	Engineered (produced for a specific purpose), pigments, catalysts, coatings, magnetic nanoparticles
	Adventitious	Unintentionally produced (they occurred as a result of industrial processes, such a diesel exhaust particles, airborne combustion by-products or building demolition)
Dimensions which are not confined to the nanoscale	Zero dimensional – their length, height and breadth are fixed at a single point	Quantum dots, core-shell NPs, nanoparticles arrays, hollow spheres and onions
	One-dimensional – their one dimension is not inside the nanoscale	Nanotubes, nanowires, nanorods, nanobelts, nanoribbons, hierarchical nanostructures
	Two-dimensional – two of their dimensions are outside the nanoscale range	Nanoplates, junctions, branches structures, nanoprisms, nanosheets, nanowalls, nanodiscs
	Three-dimensional – can have three arbitrary dimensions and possess multilayer nano-crystalline structure	Nanoballs, nanocoils, nanocones, nanopillars and nanoflowers
Chemistry of core material	Carbon-based nanomaterials	Different forms are possible like hollow spheres, ellipsoids or tubes, fullerenes
	Metal-based nanoparticles	Quantum dots, metals, metal oxides
	Dendrimers	Three-dimensional nano-sized polymers with controlled structure
	Composites	Nanoclays
State	Free	Single, individual NPs
	Fixed	NPs incorporated in products
	Aggregated	Associations of NPs in a network-like structure

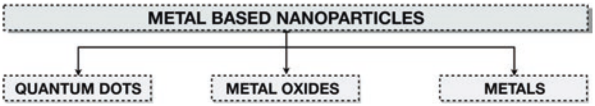

Fig. 1 Classification of metal-based nanoparticles

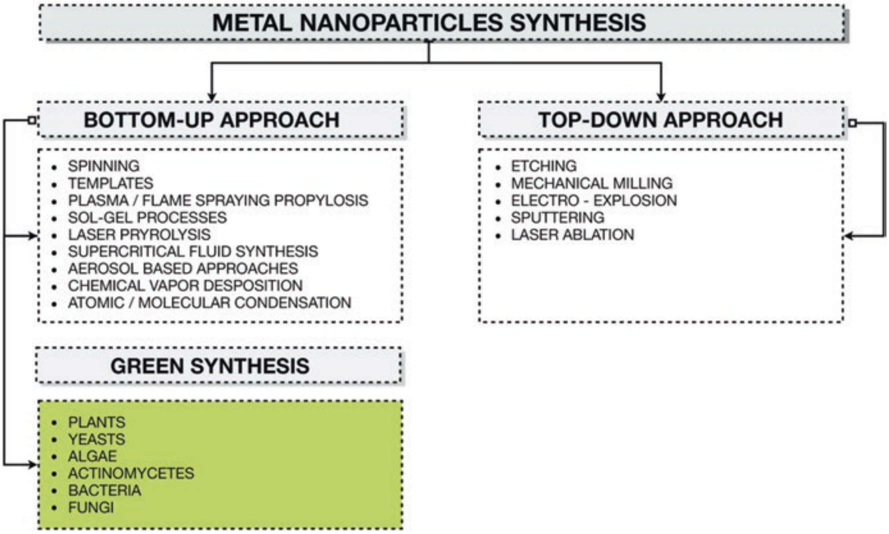

Fig. 2 Classification of methods for the synthesis of metal-based nanoparticles

starting precursors in the final nanostructure. The "top-down" processes involve grinding (Xu et al. 2015), attrition (Verma et al. 2017), etching (Long et al. 2014), repeated quenching (Xing et al. 2018) and molecular nanolithography (Mignot et al. 2013). The more versatile "bottom-up" approach uses several techniques, namely plasma/flame spraying (Karthikeyan et al. 1997; Zhang et al. 2019a), pyrolysis, sol-gel processes (Sui and Charpentier 2012), laser pyrolysis (D'Amato et al. 2013), supercritical fluid synthesis (Byrappa et al. 2008; Philippot et al. 2014), aerosol-based approaches (Buesser and Pratsinis 2012), chemical vapour deposition (Ciprian et al. 2018), atomic/molecular condensation (Kusior et al. 2016), spinning and templates synthesis (Wang et al. 2019; Ianoș et al. 2018). The final nanoproduct of particular synthesis depends on several factors like applied precursors, additives (reducing reagents, capping agents), solvents and the driving force (temperature, pressure and catalysts used) (Patil and Bhange 2016; Ali et al. 2016; Miranda et al. 2010). The alternative classification of production methods is based on the process origin and emphasizes its chemical, physical or biological background (Fig. 2). The latter is sometimes called the green synthesis, often engages plants, fungi or algae and for the nanometalic entities relies on mechanisms involved in the metal ion uptake and translocation inside the plant body and the cell (Shah et al. 2015; Luque and Varma 2013; Koul et al. 2018).

4 Plant Responses to Metal-Based Nanoparticles

Metal nanosized materials are transported through the emissions to air, water and soil. A special attention should be directed towards those nanosized species intentionally introduced into environment with agrochemicals and substances used in remediation technologies (Liu and Lal 2015; Achari and Kowshik 2018; Chen et al. 2019; Hlongwane et al. 2019; Manna and Bandyopadhyay 2019). Remarkable abundance of either natural or anthropogenic MNPs in all compartments of our environment makes their interactions with plants quite likely indeed. They approach plants through a variety of mechanisms which are strongly dependent on the size, morphology, charge, settings and agglomeration (Pérez-de-Luque 2017; Yang et al., 2017; Zhang et al., 2019b). All those factors affect the plant response to MNPs. Nanoparticles enter the plant body through the uptake by either roots or leaves. When MNPs are approaching the phyllosphere[1] they initially have to cross the waxy layer (cuticle). This surface, usually have thickness extending from 0.05 to 225 μm and its composition strongly depends on the apparent plant (Goodwin and Jenks 2005). Cuticle prevents plants from the excessive transpirational water loss and unrestrained gas exchanging. It is a physical barrier, which also protects plant against toxic substances. Many contaminants can be absorbed via cuticular pores and stomata (Shahid et al. 2017; De Nicola et al. 2008; Edelstein and Ben-Hur 2018). There are firm indications that the ability of stomata to transport MNPs depends on their size. For dimensions within the range 10–50 nm the symplastic path (engaging adjacent cytoplasm fragments of the cell) is more likely, while the translocation of larger MNPs (50–200 nm) proceeds rather through the apoplastic route (in spaces outside the plasma membrane) (Raliya et al. 2016). In soil, MNPs interact with rhizosphere components and affects processes involved in nutrients uptake (Rizwan et al. 2017; Rico et al. 2014; Duhan et al. 2017). The final effect is a function of several factors (Fig. 3) like soil texture, temperature, pH, osmotic pressure, content and composition of organic matter, redox status of the soil environment, ionic strength, cation exchange capacity, mineral composition, interaction with other elements as present in the soil matrix and in root exudates (Zhang et al. 2017a, 2019b; Cao et al. 2018; Dimkpa 2018; García-Gómez et al. 2018; Xu 2018; Ma and Yan 2018; Rawat et al. 2018; Amde et al. 2017; Layet et al. 2017; Majumdar et al. 2016; Reddy et al. 2016; Dwivedi et al. 2015; Watson et al. 2015). The specific plant response depends on the MNPs dose and a time of exposure while microorganisms and invertebrates affect this process substantially (Kibbey and Strevett 2019; Mousavi et al. 2018; Sillen et al. 2015; Ma et al. 2013; Tourinho et al. 2012).

Over the years, plants did not develop mature mechanisms exclusively responsible for MNPs uptake and assimilation and use the already existing pathways. A thorough summary of this issue has been recently published by Tripathi et al.

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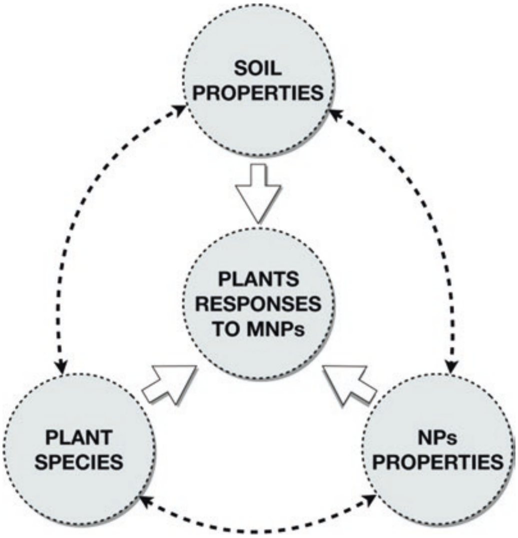
[1] According to Lindow and Brandl (2003) phyllosphere is defined as the system containing the shoots, leaves and other above-grounds organs of plants together with coexisting bacteria, yeasts and fungi colonies.

Fig. 3 Factors and relations which affect plant responses to metal-based nanoparticles



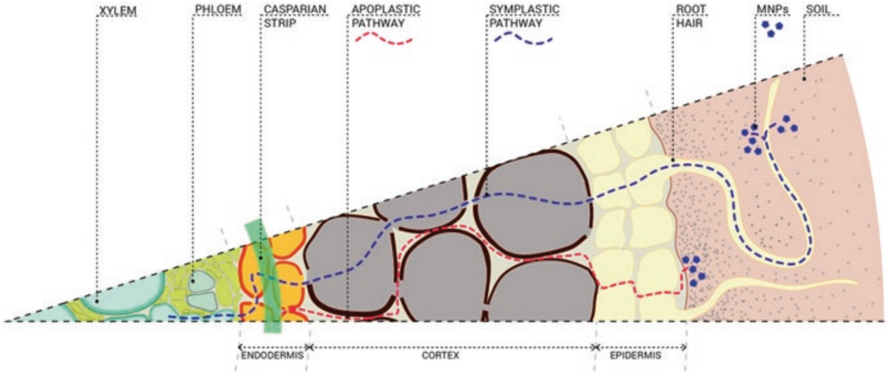


Fig. 4 MNPs uptake by the plant root and their further translocation

(2017a). In general, there are two major pathways for the MNPs root uptake and transport in higher plants (Fig. 4). In the apoplastic pathway, MNPs initially penetrate the pores of the cell walls and subsequently diffuse into the space between the cell wall and the cell membrane or travel through the intercellular space without crossing the membrane (Perez-de-Luque 2017). Their further transport to the xylem is blocked by the impermeable Casparian strips placed in the endodermal layer. Then MNPs are actively transported through the plasma membrane into the symplastic space (Kim et al. 2002). The alternative is direct symplastic pathway in which MNPs either penetrate cell membrane or are transferred to adjacent cell through plasmodesmata (Zhai et al. 2014; Ma et al. 2010a; Kim et al. 2002). The transmembrane transport of MNPs attracted some attention over the years (Zhang et al. 2011; Ma et al. 2015). Those investigations were critically evaluated by Lv et al. (2019) who pointed out that aquaporins, ion channels, pore formation, carrier proteins and to the largest extent the endocytosis are the major players.

Additionally, MNPs approaching the rhizosphere are prone to interactions with root exudates (Bundschuh et al. 2018; Ma and Yan 2018; Zhang et al., 2017b). Those chemically divergent compounds may trigger the MNPs decomposition to metal ionic species and affect their interactions with plants. Therefore, metals initially transported in nanometric forms are taken through pathways already developed for metal ions. This obviously alters MNPs fate and deserves brief discussion presented below.

5 Mechanisms of Metals and Metal Nanoparticles Uptake by Plants

Transport of metal ions into the symplast of the epidermis is facilitated by protein carriers (Table 2). They are classified within diverse transporter families (Palmer and Guerinot 2009; Kwapuliński et al. 2010). The best characterized are: ZIP (ZTR/IRT-related proteins) (Guerinot 2000; DalCorso et al. 2013), NRAMP (Natural Resistance-Associated Macrophage Protein) (Thiomine et al. 2000), CTR/COPT (Copper Transporter) (Yuan et al. 2011), ATPases (Morsomme and Boutry 2000), ATP-binding cassette transporters (ABC) (Verrier et al. 2008), CDF – the cation diffusion facilitators (Williams et al. 2000, Lin et al. 2013). The widely reported in literature, the ZIP protein family contains metal transporters initially identified in plants. They are capable of transporting several cations, namely cadmium, iron, manganese and zinc. Over 15 family proteins have been identified in plants. They are predicted to have eight transmembrane domains and adopt a similar membrane topology in which the amino- and carboxy-terminal ends of the protein chain are located on the outer surface of the plasma membrane (Guerinot 2000). The CTR/COPT (Copper Transporter) mediate copper uptake in plants. Those plasma membrane proteins facilitate Cu transport from extracellular spaces or vacuoles into the cytosol (Yuan et al. 2011).

P-type ATPases form a large family of membrane proteins which use the energy of the ATP hydrolysis to promote the active transport of cations or other species across cell membranes (Morsomme and Boutry 2000).

The uptake and transport of ballast metal ions (Cd, Pb, As and Hg) takes place on a competitive basis with micro- and macroelements for trans-membrane carriers characterized by a broad specificity. Upon ion deficit in the cell, those transporters are synthesized and further activated in biological membranes. As a non-specific carriers, they also transport excess of ballast elements (Briat and Lebrun 1999; Sanita di Toppi and Gabrielli 1999; Clemens 2001).

Metal ions in root cells are loaded into the xylem and further transported to the shoot as complexes with chelators, such as simple organic or amino acids. Bivalent

Table 2. Metal ion transporters in plants

Metal ion	Protein transporter	References
Mn^{2+}	ZIP (zinc-iron permease) IRT1 (iron-regulated transporter1) NRAMP (natural resistance-associated macrophage protein) CDF (cation diffusion facilitator)	DalCorso et al. (2013), Guerinot (2000), Thiomine et al. (2000), Ricachenevsky et al. (2013)
Fe^{2+}	ZIP (IRT1) NRAMP YSL (yellow stripe-like) CDF	Palmer and Guerinot (2009), Guerinot (2000), Thiomine et al. (2000)
Cu^{2+}	CTR/COPT (copper transporter) NRAMP ATPases	Palmer and Guerinot (2009), Yuan et al. (2011)
Zn^{2+}	ZIP (IRT1) ZIP (ZRT – zinc-regulated transporter) NRAMP ATPases CDF	Palmer and Guerinot (2009), DalCorso et al. (2013), Küpper and Andersen (2016), Williams et al. (2000), Lin et al. (2013)
Pb^{2+}	NtCBP4 (calmodulin binding protein) ATPases ABC	Kwapuliński et al. (2010)
Cd^{2+}	ZIP (IRT1) ZNT1 LCT1 NRAMP ABC (AtMRP3, AtATM3, AtPDR8, AtPDR12, AtMRP3) ATPases CDF	Palmer and Guerinot (2009), DalCorso et al. (2013), Lux et al. (2011), Thiomine et al. (2000), Kang et al. (2011), Ricachenevsky et al. (2013)
Co^{2+}	NRAMP ZIP ATPases CDF	DalCorso et al. (2013), Ricachenevsky et al. (2013)
Ni^{2+}	NRAMP CDF	Ricachenevsky et al. (2013)

cations may also be transported by the methionine derivative of nicotinamine (NA) (Krämer et al. 1996; Pich and Scholz 1996; DalCorso et al. 2013).

The root-to-shoot transport also involves several types of transport proteins like the P-type ATPases, MATEs and OPTs. In particular, P-type heavy metal ATPases have been implicated in the transport across cell membranes of either essential or potentially toxic metal ions, e.g. Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} (Williams et al. 2000). MATE (Multidrug And Toxic compound Extrusion) proteins are membrane-bound transporters that extrude drugs and toxic compounds from the cell. The OPT (Oligo Peptide Transporter) superfamily includes the YSL (Yellow-Stripe 1-Like) subfamily, whose members, some located in the lateral plasma membranes of xylem-associated cells in both shoots and roots, may be involved in long-distance transports into the plant body and loading into the vascular system of the Fe, Zn, Cu, Ni, Mn and Cd complexes with phytosiderophores or NA.

Metal ions are also translocated through the phloem following the source-to-sink route. Long-distance transport of Fe, Cu, Zn and Mn is mediated by the formation of NA complexes, despite the presence of the high-molecular-weight compounds that chelate Ni, Co and Fe in the phloem (DalCorso et al. 2013).

Energy derived from ATP is used by the P-type ATPases for the export of zinc into the xylem and its further translocation to the shoot (Hussain et al. 2004; Verret et al. 2004; Song et al. 2014).

Cadmium ion may traverse from the root to the shoot either through the extracellular spaces between cells or through the cytoplasmic continuum of root cells linked by plasmodesmata (White et al. 2002). However, as has been shown by Yin et al. (2015), exposure to excess of cadmium accelerates root maturation and results in the formation of Casparian strips and suberin lamellae closer to the root apex. The latter forms the physical barriers to the apoplastic movement of Cd from the root to the shoot. Manganese can exist in the soil in a number of oxidation states (Adamczyk-Szabela et al. 2015). However, it is mostly taken by the plant roots in the form of free hydrated Mn^{2+} ions. Several transporting proteins like NRAMP and IRT1 may be involved.

6 The Toxicity of MNPs in Plant

The growing interest in MNPs is raising the question of their toxicity. This issue is of particular importance in medical applications where cytotoxicity (Kong et al. 2011) is of primary concern and led to the development of several relevant mechanisms. On the contrary, investigations solely concentrated on nanomaterials toxicity to plants are quite scarce (Ruttkay-Nedecky et al. 2017; Tripathi et al. 2017a, b, c).

Nanoparticles can have either positive or negative impacts on plants. It may be conveniently assessed by several physiological indices like the germination percentage, root elongation, biomass and leaf number (Lee et al. 2010; Tripathi et al. 2015).

Yang and Watts (2005) observed that the alumina nanoparticles at concentrations 20, 200 and 20000 mg L^{-1} showed a phytotoxic effect on the carrot, cabbage, corn, cucumber and soybean. Similarly, Lin and Xing (2007) found that the exposure to concentrations of 2000 mg L^{-1} of aluminium, alumina, zinc and zinc oxide nanoparticles on root development and seed germination has also a phytotoxic effect on the tested radish, rape, ryegrass, lettuce, corn and cucumber plants. The CuO NPs inhibited growth and changed the structure of wheat roots (Dimkpa et al. 2012;

Tang et al. 2016) when plants were grown in a sand matrix. Shaw and Hossain (2013) showed that CuO NPs significantly reduced the fresh weights and root length of *Arabidopsis* seedlings, and the germination rate and biomass of rice seeds (Yang et al. 2017).

Song et al. (2013) demonstrated that treatment of tomato with Ag NPs resulted in a reduction in biomass and root length. TiO_2 NPs significantly improved the germination rate of seeds. However, bulk TiO_2 inhibited germination of seeds (Feizi et al. 2013; Hawthorne et al. 2012). The shape and size of particular MNPs usually affects their reactivity and toxicity (Oberdürster 2000). Moreover, the toxic effect is strictly related to the MNPs concentrations (Rico et al. 2011).

Unfortunately, the emerging picture is not clear as proved by Yasur and Rani (2013) and Lee et al. (2010) who showed that Ag NP treatment had no effect on the growth of castor bean (*Ricinus communis* L.) while its vegetation was limited by Ag ionic treatment.

Ma et al. (2010b) and López-Moreno et al. (2010) found that the rare earth oxide NPs (CeO_2, La_2O_3, Gd_2O_3 and Yb_2O_3) had harmful effect on the growth of radish, tomato, rape, lettuce, wheat, cabbage, cucumber and corn plants when administered to roots at high concentrations. TiO_2 NPs increased the content of total chlorophyll and catalase (CAT) while decreasing ascorbate peroxidase (APX) content in leaves (Servin et al. 2013; Yang et al. 2017).

Zheng et al. (2005) and Yang et al. (2007) highlighted the positive impacts of NPs on the growth, development and physiological parameters of the plants. In particular, the foliar or seed treatments of TiO_2 NPs enhanced the growth of spinach (Gao et al. 2008).

Mixed nano-TiO_2 and nano-SiO_2 introduced into the soybean (*Glycine max*) increased the nitrate reductase activity; this treatment accelerated plant germination and increased further growth by enhancing the water absorption and utilization of the fertilizer (Lu et al. 2001).

Both Stampoulis et al. (2009) and Wang et al. (2012) found that CuO NPs did not affect the germination of zucchini and maize, but suppressed root elongation. However, Zhao et al. (2016) showed that Cu NPs have an impact on the Na, P, S, Mo, Zn and Fe uptake. The Cu NPs at 10 and 20 mg L^{-1} levels triggered significant metabolic changes in cucumber leaves and root exudates. Following the authors, the defence mechanism of Cu NPs stress reduction relies on the up-regulation of amino acids sequestration, down-regulation of citric acid to reduce the mobilization of Cu ions, up-regulation of ascorbic acid to combat reactive oxygen species, and up-regulation of phenolic compounds to improve the antioxidant system.

A decrease in root length, reduction of root biomass and bioaccumulation of Cu mainly in roots of lettuce were observed by Trujillo-Reyes et al. (2014). According to Nair et al. (2014) CuO NPs at low concentrations significantly reduce root and shoot development in mung bean by the production of excess reactive oxygen species and lipid peroxidation.

On the contrary, Zhang et al. (2015) reported that corn exposed to ZnO NPs showed no significant negative physiological effects. ZnO NPs induced oxidative stress in soybean seedlings at a concentration of 500 mg L^{-1}. Soybean growth, rigidity of roots and root cell viability were markedly affected by ZnO NPs generated stress (Hossain et al. 2016; Ruttkay-Nedecky et al. 2017). Yang et al. (2015) observed that ZnO NPs at concentrations of 2000 mg L^{-1} have inhibited the root elongation of maize and rice. Similarly, Xiang et al. (2015) concluded that ZnO NPs did not affect germination rates at concentrations of 1–80 mg L^{-1} but significantly inhibited the root and shoot elongation of Chinese cabbage seedlings. The combined production of free hydroxyl groups and the Zn bioaccumulation in roots or shoots resulted in substantial toxicity of ZnO NPs to Chinese cabbage seedlings.

Metal and metal-based NPs induce oxidative stress symptoms to a number of plants exposed. The resulting production of reactive oxygen species is related to genotoxicity and may lead to cell apoptosis (Kumari et al. 2009; Shaw and Hossain 2013; Cui et al. 2014).

The detailed knowledge on the molecular basis of NPs mediated phytotoxicity in vascular plants is quite limited indeed as stated in the recent review as published by Singh et al. (2017). Moreover, the proteomic studies on Ag NPs induced phytotoxicity revealed that the size of the nanoparticle is the key factor in determining the type and magnitude of the plant cellular kinetics. The plant response towards a specific NPs stress is mediated by a number of proteins involved in oxidation-reduction, reactive oxygen species (ROS) detoxification, stress signalling, and hormonal pathways (Hossain et al. 2016).

The transcriptomic analyses indicate that NPs-induced toxicity in higher plants is closely linked to the up- and down-regulation of genes (Landa et al. 2012; Tripathi et al. 2017a; Singh et al. 2017). Plant hormones are active organic materials that are produced by plant metabolism. They can regulate physiological responses during plant growth and mediate responses to external challenges. Therefore, the content and activity of plant hormones is an important index of toxicity in plants (Yang et al. 2017). Those mechanisms affect the carrier concentration which is strictly related to the rate of particular proteins synthesis. According to Ma et al. (2016) CeO_2 NPs tend to alter the regulation of genes which are responsible either for encoding metal ion transporters or activity of a distinct enzyme. In particular, low accumulation of Fe can be related to the down-regulation of IRT1 and IRT2 iron regulating genes induced by the Ce NPs toxicity. Similar mechanisms developed by plants to avoid the harmful effects of nanoparticles and involving genes of the IRT family for Cd, Cu, Zn, Co and Mn were also reported (Taylor et al. 2014).

6.1 Quantum Dots

Quantum dots are nanocrystals which exhibit a semiconductor nature. Generally, they consist of group II-VI elements in compounds like CdSe, CdS, CdTe, group IV-VI elements in PbS, PbSe, PbTe and SeTe or group III-V elements in InAs and InP. QDs are finding a steadily growing number of applications with high future development potential. Therefore, they deserve to be separately treated as a special, coherent group of MNPs with very unique properties.

So far, they have been applied in composites (Xue et al. 2019), electronic displays (Yoon et al. 2016), solar cells (Khodama et al. 2019) and as fluorescent labels for tracing biological molecules in living species (Chen et al., 2018b). Their technological applications benefit from the small particle sizes of high uniformity combined with the tunable energy levels. QDs interactions with plants are becoming increasingly abundant. They were initially studied by Pagano et al. (2018). The authors addressed the importance of molecular pathways and genetic mechanisms as prompted by QDs in terrestrial plants. The negative effects of cadmium-based QDs exposure were also appreciated. Following, the impact on physiological and biochemical parameters (biomass, root/shoot length, photosynthetic activity) and triggering the oxidative stress response are being the most important. Uptake of the water-dispersible CdSe/ZnS QDs by *Arabidopsis thaliana* plants in hydroponic culture was studied by Navarro et al. (2012). Authors clearly showed that polymer-coated MNPs were not absorbed and translocated in the body of a model plant. The essential factor influencing the amount of MNPs adsorbed was related to their stability in hydroponic media. The risk assessment methodologies combined with the transcriptomics and proteomics are useful in this area and should be kept developing in the future.

7 Procedure Standardization

As the number of papers on the NPs' interactions with plants is steadily growing there is an obvious need for standardization of methodologies and cultivation conditions. They should fully ensure high comparability and transferability of results. This issue presents a real challenge as numerous experimental conditions are combined with diverse plant species and types of engineered MNPs. Moreover, solutions of the latter are stabilized by divergent additives. Therefore, the general conclusion as drawn from investigations emphasizes that non-uniform methodologies can be substantially biased. This issue has been clearly illustrated by the comprehensive review of Montes et al. (2017) on the phytotoxicity of diverse MNPs as administered to *Arabidopsis thaliana*. During the data screening, the authors approached several difficulties related to incomparability of results published by different investigators. In conclusion, they have suggested that model plants with the well-known genome should be combined with standardized MNPs test concentrations of particular sizes. The uniform selection of coating materials and stabilizers is also required. A good example of such approach was recently published by Layet et al. (2017), who proposed the ISO-standardized RHIZOtest to study the transfer of nanoparticles from soil to the plant system. A set of model plant species (*Arabidopsis thaliana*, *Boswellia ovaliofoliolata*, *Phaseolus vulgaris* L, *Zea mays* L., *Vicia faba*, *Vigna radiate*, *Foenicutum vulgare*, *Lemna minor*, *Triticum aestivum*, *Spinacia oleracea*, *Lycopersicon esculentum* Mill, *Glycine max* and *Raphanus sativus* L.) frequently used to study the toxic effects of MNPs was recently published by Núñez and De la Rosa-Alvarez (2018). This approach is of particular importance when risk assessment is to be concerned. Usually, two major methodologies are being applied for evaluation of the MNPs impact on plants. The more popular one relies on the long-term growth in soils administrated with representative concentrations of MNPs. However, the advantages of soilless-hydroponic cultivation have been also recognized as yet (Deng et al. 2014). The latter is well suited for studying the MNPs outcome on plants with distinct advantages over the traditional soil systems. In particular, it facilitates prompt separation of root tissues with a special emphasis put on fine root hairs and precise administration of nanomaterials and nutrients. Furthermore, plants grown in controlled homogeneous liquid solution are more uniform and give statistically significant, reproducible results (Nguyen et al. 2016; Skiba and Wolf 2019).

8 Phytonanotechnology in Agriculture

The rapid development of nanotechnology as applied to plant science and agriculture was reflected by the introduction of a new discipline which name phytonanotechnology was coined out by Wang et al. (2016). Nanocarriers which are used to deliver active ingredients applied for the crop protection were reviewed in a comprehensive way by Kumar et al. (2019). The authors systematically characterized relevant functions and properties of NPs which can be applied for a smart delivery of pesticides. A special emphasis was given to metal-organic frameworks (MOFs). They are synthesized from metal clusters or ions working as coordination centres linked by organic ligands and used for agrochemicals encapsulation. These smart nanoproducts offer enhanced release kinetics of active ingredients within the plant environment. MNPs are also active components for the crop protection formulations. The antifungal and antibacterial properties of copper, zinc, alumina, silver, ZnO and Ag-doped TiO_2 are well recognized. This important issue deserves further studies. A comprehensive study of the emerging trends and future prospects on MNPs being used in agriculture is given by Baker et al. (2017). They firmly point out that "nanoagroparticles" can act as efficient seed and crop protection agents, plant growth promoters, biosensors, nanoherbicides and nanopesticides. The dose dependent-concentration inhibition of spore germination at several silver nanoparticles concentrations is also reported while silver and copper nanoparticles displayed antifungal activity against *A. alternata* and *B. cinerea*. The major constrain of MNPs applicability follows from their toxicity. Moreover, the importance of eco-friendly, non-toxic substrates for the nanoparticles synthesis is highlighted. This strategy may also use biologically driven processes. An important part of the paper is a broad characterization of different types of MNPs and their applications in agriculture with a special attention paid to an emerging field of bionano-hybrid agroparticles as a promising agent against phytopathogens. The relevance of MNPs encapsulation for toxicity mitigation is also stressed out. The impact of nanoparticles on plant growth and development was recently reported by Verma et al. (2018). This comprehensive review addresses the issue of toxicity, plant responses, uptake, translocation and bioaccumulation of almost twenty carefully selected NPs. A special attention was devoted to MNPs. A substantial fragment of the paper is dedicated to molecular foundations of plant response mechanisms highlighting the role of non-coding microRNA (miRNA). Those species are involved in the RNA silencing and post-transcriptional regulation of gene expression in plants. They regulate morphological, physiological and metabolic processes and are likely to play a crucial role in the MNPs stress tolerance. In particular, changes in the miRNA expression levels induced by the exposure to Al_2O_3, TiO_2 and Au NPs are discussed. The final effect of MNPs' interactions with plants is not easy to assess. It depends on several factors like chemical composition, size and shape of particular NP, the type of plant species, its stage of the growth as well as exposure conditions.

At high concentrations, MNPs are toxic by damaging the physiological processes or altering genetic constituent of plants. New efficient forms of agriculture benefit from the nanotechnology developments (Prasad et al. 2018; Sangeetha et al. 2017; Vishwakarma et al. 2018). In particular, the green, ecofriendly synthesized MNPs find application to the "precision agriculture", i.e. the farming concept of measuring and responding to inter and intra-field variations of crops. The final target is the implementation of a decision support system for farm management. It is to be aimed at boosting output from all available resources (Özer et al. 2014). This approach makes intensive use of biosensors and nanoparticle-mediated material delivery to plants. A thorough discussion on MNPs applications in "precision agriculture" is published by Duhan et al. (2017). It is reported there that antimicrobial properties of Ag NPs can reduce the burden of pesticides during the crop cultivation while Zn deficiency in alkaline soils with high level of carbonates can be overcome by Zn nano-fertilizers. Moreover, the promising results of ZnO NPs application as dedicated antifungal agent against *Aspergillus flavus* and *Aspergillus niger* were noticed. A highest efficiency was observed for ZnO NPs in a size range 27 ± 5 nm as produced in a plant-mediated synthesis based on *Parthenium* extracts. The important review on nanoparticles applied as fertilizers is written by Liu and Lal 2015. It presents a detailed description of nanosized materials which enhance the plant growth. Authors divided them into four categories: macronutrient, micronutrient, nanomaterial enhanced fertilizers and new nanoparticulate plant growth enhancers with unclear mechanisms of uptake. Those groups are characterized in detail with the strong emphasis given to applicability, sustainability and future research directions.

The activity of two common, commercial nanofertilizers: Nano-Gro and Avatar 1 were studied by Makarenko et al. (2016). Authors demonstrated that toxic effects of those agrochemicals strongly depend on the size and structure of nanoparticles used in particular formulation. The strongest effect was observed for smaller particles with well-ordered crystal structure while the toxicity of nanoparticles with disordered, amorphous structure was significantly smaller. Authors suggested that ecotoxicological risk assessment should include not only the dose-effect studies but also the detailed investigations of toxic processes which exist in the cell at the organelle and cellular levels. Importance of MNPs for the contemporary horticulture developments is recently reviewed by Feregrino-Perez et al. (2018). The authors critically evaluate "pros and cons" of nanomaterials entering this important branch of agriculture. The negative effects are induced by metal oxide NPs which hamper photosynthesis and induce genetic modifications. The positives result from the better pest control, early disease detection and substantial growing enhancement as triggered by nanometric metal oxides or metals. The relevance of MNPs in strategies developed for diseases control in plants was thoroughly evaluated by Elmer et al. (2018). Authors categorize MNPs into two classes: nanoparticles which possess direct microbial activity and those which activate the defence mechanisms in plant. They conclude that in the forthcoming future, nanomaterials will be one of the major species used to mitigate diseases in either greenhouse or field plant cultivation.

9 Conclusions and Future Perspective

Environmental abundance of either natural or anthropogenic NPs prompted by the steadily increasing production of the latter makes interactions with plants quite likely indeed. MNPs approach plant through a variety of mechanisms which are strongly dependent on their size, morphology, charge, settings and agglomeration. The plant response towards a specific NPs stress is mediated by a number of proteins involved in oxidation-reduction, ROS detoxification, stress signalling and hormonal pathways. Complete characterization of those species at the cellular level should involve tools developed by contemporary transcriptomics. The mechanisms of particular protein synthesis upon signal detection related to the stress in plants induced by MNPs should also be considered. The signal processing upon binding of nanoparticles to specific plant receptors is also an issue.

MNPs rarely interact with plants alone. In the solution they are accompanied by various ingredients which help to stabilize their structure. Those additives may act like reducing and capping agents or solvents. Obviously, they may also affect biochemical processes responsible for nanoparticles uptake and translocation. We therefore postulate that the usual activity and toxicity tests would involve formulations used in either agriculture or industry and not to be limited to MNPs alone. Moreover, the EU legislation and national regulations should bind the manufacturers and suppliers to publish the complete composition of all formulations which are being introduced in the market.

Modern, efficient agriculture should act against decline of the planet biodiversity as prompted by a wide application of pesticides. The latter is strongly coupled with the uncontrolled usage of genetically modified plants. Nanomaterials designed for specific purposes and acting as plant molecular carriers should help to mitigate pesticide consumption and reduce their negative side effects. On the other hand, understanding the mechanisms responsible for the MNPs toxicity to plants is also of crucial importance.

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Impacts of Carbon Nanotubes on Physiology and Biochemistry of Plants

Vishnu Sankar Sivasankarapillai and M. S. Latha

1 Introduction

Nano-biotechnology is an emerging platform with endless opportunities and impact on applied agricultural research including crop production. This area is developing through the amalgamation of biotechnology and nanosciences. Implementation of nanotechnology in agriculture is at the budding stage and requires more pace to cater to the needs of present global demand. Nano-biotechnology is gaining significant research interest as a tool for the design and development of new agricultural production strategies. This chapter summarizes the results of various studies investigating the impact of carbon nanotubes on plant physiology and biochemistry.

2 Uniqueness of Carbon and Its Allotropes

Carbon is a wonderful element with unique properties. It has the magical ability to exist in various allotropes and form a wide range of compounds. The four valence electrons of carbon can take part in compound formation with other elements or with itself. Diamond, graphite, and fullerenes are the three allotropes of carbon with different physical properties due to the difference in the molecular environment. Graphite is a lubricant material whereas diamond is the hardest substance known. Each layer of graphite is called "graphene" which can be transformed into carbon nanotubes (CNT) upon rolling. All these variations in properties can be attributed to the unique chemical environment of the allotropes under consideration.

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3 Types of Carbon Nanostructures

The properties of bulk materials get drastically transformed into nano dimensions due to the dominance of quantum effects. These effects can significantly give rise to extraordinary electronic properties (due to quantum confinement of electrons) and optical properties (due to surface plasmon resonance). Three major nanostructures of carbon are carbon nanotubes (CNT), carbon nanofiber, and fullerenes. The former two belong to linear structures and the latter is having spherical dimensions. These nanomaterials attained significant research interest for potential applications in drug delivery, catalysis, fillers in nanocomposites, and many other areas of material science. The mechanical and electronic properties of CNT and carbon fibers make them suitable for reinforcement and conductivity applications. Fullerenes have exclusive optical behavior making them suitable for targeted drug delivery processes and diagnostic applications either in native nano form or in combination with other nanostructures like quantum dots.

CNT is a class of macromolecular cylindrical nanostructure formed by the rolling of graphene layers. Their building units are sp^2 hybridized carbon framework which is responsible for their unique properties. Carbon nanotubes (CNTs) were introduced by Iijimain 1991 (Iijima 1991). Since then, there has been intense activity related to the synthesis, structure, properties, and applications of CNTs. The strength of the sp^2 carbon-carbon bonds gives them amazing mechanical properties such as high Young's modulus of 1 TPa and a large tensile strength of 150 GPa (Chen et al. 2015a). Common synthetic methods for preparing CNTs include chemical vapor deposition, laser ablation, and arc discharge method. The formation of CNT by rolling up the graphene layer can be schematically represented in Fig. 1.

It is evident that the properties of CNTs are strongly related to the nature of their internal microstructures. Thus properties of CNTs depend on the arrangement of the graphene sheets (how the sheets are "rolled"), the diameter and length of the tubes, and the nanostructure. When the CNT contains only a single graphene layer it is called single-walled carbon nanotubes (SWCNT) and if it is composed of more than one layer of graphene rolled by one over the other they are called multi-walled carbon nanotubes (MWCNT). All CNTs have high aspect ratio and have fiber-like structures. SWNTs have the smallest diameter (0.8–5 nm) of all the CNTs and a variable length from tens

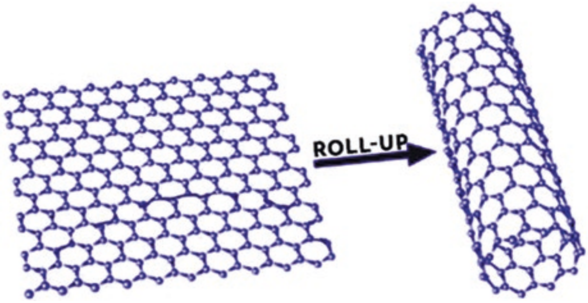

Fig. 1 Formation of CNT from graphene layer

of nanometers to millimeters, whereas MWNTs have a larger diameter (~3 to >100 nm) and lengths similar to those of SWNTs (Li and Pandey 2015).

3.1 Single-Walled Carbon Nanotubes (SWCNTs)

Single-walled carbon nanotubes (SWCNTs) are considered as the simplest member of the CNT family consisting of a graphene monolayer rolled up into a cylindrical shape. SWCNT is more flexible and can be twisted easily. They are not well dispersed and usually form bundle-like structures.

3.2 Multi-Walled Carbon Nanotubes (MWCNTs)

The concentric arrangement of several SWNTs of slightly varying diameter is termed as multi-walled nanotubes (MWNTs). They consist of multiple layers of graphene rolled to form a tube shape. A three-dimensional model of MWCNT is shown in Fig. 1.4 (https://worldofnanoscience.weebly.com/nanotube--carbon-fiber-overview.html). Thus MWNTs are considered as a coaxial assembly of several SWNTs and homogenously dispersed without bundle formation.

3.3 Functionalized Carbon Nanotubes

The specific surface area of fully dispersed CNT is approximately 1600 m^2/g. Since the CNTs are composed of graphite basal plane, both the SWCNT and MWCNT have chemically inert and hydrophobic sidewalls. These walls can be modified by tethering by other molecules depending on the application. Such CNTs in which their walls are modified using other functional moieties are called functionalized carbon nanotubes. These functionalizations are based on weak interactions like π–π stacking or surfactant encapsulation. Chemical functionalization of CNTs also results in oxidation of sidewalls which thus creates sites for covalent functionalization. On the other hand, these modifications may result in the reduction of other properties of CNTs.

4 Role of CNT in Living Systems

Extensive research is taking place for using CNTs in various sections of material science. However, their use in biological systems is still in the infant stage and hence the potential risk associated with their use is not clearly known. Even though they have some profound effects like growth regulation and enhancement of metabolic activities in edible crops, the toxicity of CNTs remains an obstacle for their real implementation. It is reported that pristine CNT induces toxicity in plants and SWCNT is observed for inducing toxicity in *Arabidopsis* and rice (Shen et al. 2010). On the contrary, the toxicity of functionalized CNTs is not significant in both in vitro and in vivo studies. Functionalized CNTs are suitable candidates for targeted drug delivery. The molecule of interest can be encapsulated in the voids and can be used as a vehicle to the target site. Thus recent studies are focusing more on the toxicity aspects of CNTs at the cellular level and ways of reducing them.

5 Effect of CNT in Plants

The uptake and accumulation process of CNT in the plant system can be analogous to other carbon nanomaterials like fullerenes (C_{60} and C_{70}). The absorption mechanism of any carbon nanomaterial depends primarily on factors like interaction with suspended organic materials, colloidal nature, and the nature of the homo-heterogenous media which acts as a medium for the smooth flow of CNT into the plant system. All nanomaterials suspended in water may be selectivelyabsorbed or rejected by plants but essential plant nutrients are generally absorbed. CNTs are absorbed through plant roots while they may get penetrated into the seeds by hole formation in seed coating and further get transported to the shoot system (Husen and Siddiqi 2014). The natural organic matter coupled with MWCNTs is reported for enhancing the hydrophilicity of MWCNT. The penetration of CNTs into the plant system inversely depends on its size and is the key factor toenhance the rate of plant growth and fruit development.

The interaction of CNTs with the chemicals present on the root surface is not observed to have any driving force for their uptake and accumulation process. They are transported by capillary action to the sites where the passage is wider than their size. When CNTs reach a point where the passage is narrow, they get accumulated and blocks the passage for nutrients to flow further. It is observed that the limiting factors for SWCNT penetration in plant cell are diameter and size (Serag et al. 2013). HRTEM studies revealed that long MWCNT (greater than 200 nm) gets accumulated in subcellular organelles while shorter MWCNTs were found in vacuoles, nucleus, and plastids (Serag et al. 2010).

The effects of CNT in plants are contradictory, and often paradoxical results are observed in experiments. This is due to the differences in the nature of CNTs and also on the plants used for the study. Each type of plant is unique with respect to their internal environment, metabolic pathway, and physiology. The influence of CNTs in plants can be explained by classifying the reported plants into their corresponding families (Fig. 2).

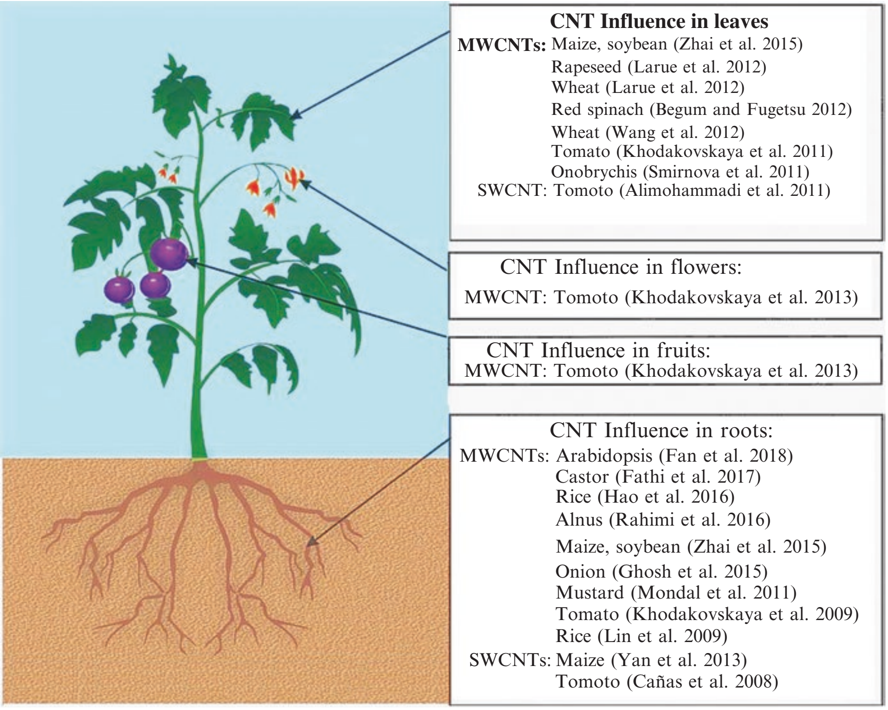

Fig. 2 Studies on CNT influence in various plants

5.1 *Brassicaceae*

Arabidopsis thaliana is the most important member of this family and is an extremely useful model for studying plant biology. Even though it is not edible, the experimental observations in *Arabidopsis* are vital tools for modeling further studies in edible plants. Fan and coworkers reported a detailed study for evaluating the combined effects of methyl viologen (MV) and MWCNT on *A. thaliana.* MV is a broad-spectrum herbicide and the study aims to analyze the extent of interactions between MWCNT and MV. This study reveals that 50 mg/L MWCNT can have beneficial (photosynthesis, lateral root number) as well as toxic (root growth) effects on A. thaliana (Fan et al. 2018).

Brassica juncea (Mustard) is another member of this family on which CNT influence is studied. It is one of the most consumed vegetables in China and widely used as a model for ecotoxicology studies (Luo et al. 2015; Wang et al. 2015). Chen and coworkers reported the effects of MWCNT on the accumulation/depuration behaviors of contaminants along with the permeability and transportability using *B. juncea* as the model plant. They observed an increase in bioaccumulations of most contaminants in the leaves by 10–30% (1 μg/mL) and 20–160% (10 μg/mL) after the mustard plants were irrigated with MWCNTs dispersed in water (Chen et al. 2015b). This result implies the role of MWCNT on contaminant accumulation and also the dependence of contaminants on the concentration of MWCNT in the mustard plant. They further investigated the uptake and transport process of MWCNT using Raman spectroscopy. The spectral data show MWCNT could penetrate cell walls and can be transported to the upper organs. The study leads to an important conclusion that the contaminant accumulation in crops gets enhanced by low doses of MWCNTs.

Thalaspiarvense, also known as Pennycress, is another member of this family on which CNT influence on the whole plant and genomic DNA is investigated. It is an important plant of research interest owing to its oil-rich seeds that can be used as a biodiesel feedstock. Khalifa recently studied germinated Pennycress seedlings on MS Agar media with 25,100 and 200 μg/μL MWCNT for a period of 6 days. Enhancement of plant growth by MWCNT is observed at a concentration of 25 μg/μL but both the pigment content and plant growth are reduced at higher concentrations. The study further revealed the ability of MWCNT to bind genomic DNA at higher concentrations while no binding at a concentration of 25 μg/μL (Khalifa 2018).

Another interesting study used C-14 labeled MWCNT in hydroponics for studying the effect in *Brassica napus* (rapeseed). It is found that the accumulation is low and there is no influence in any of the physiological processes like seed germination, root elongation, dry biomass, and evapotranspiration. Less than 0.005% of the MWCNT dose were taken up by the plant. Also, it does not cause any oxidative stress in this study (Larue et al. 2012).

5.2 *Poaceae*

This family includes plants like rice, wheat, corn, Zea mays, and barley in which the effects of CNT are explored.

Zhang and coworkers studied the influence of both SWCNTs and MWCNTs on rice. They found an enhancement of leaf growth and development of rice seedlings at a low concentration (20 mg/L). Increase in chlorophyll content and net photosynthetic rate is also observed accompanied by an increase in gene expression associated with chloroplast development and cell size (Zhang et al. 2017). This study is important since it shows a link between the accumulation of reactive oxygen species (ROS) and CNTs in the rice seedlings but the molecular mechanism of the process needs further investigation.

Another interesting study investigated the effects of CNTs filled with different ferromagnetic alloys in rice seedlings. This is the only study reported which evaluates the relationship between carbon nanotubes along with carbon nitrogen ratio (C:N) and plant hormones (Hao et al. 2016). They analyzed the phytotoxicity of rice seedlings using three different types of MWCNTs, Fe-filled carbon nanotubes (Fe-CNTs), and Fe-Co-filled carbon nanotubes (Fe-Co-CNTs). This study confirmed the penetration of CNTs through cell wall and cell membrane and subsequent transportation to roots using TEM and EDS studies. CNTs significantly inhibited the rice growth by decreasing the concentrations of endogenous plant hormones. Carbon to nitrogen ratio (C:N ratio) significantly increased in rice roots after treatments with CNTs, and all three types of CNTs had the same effects on the C:N ratio. The increase in the C:N ratio in roots was largely because of decreased N content, which obviously indicates the decrease in N assimilation by the CNTs.

Mukherjee suggests the possibility of CNTs as growth-stimulating additive for wheat in low doses (Mukherjee et al. 2018). They studied the effects of –OH functionalized MWCNTs on wheat seeds and observed an increase in growth parameters (root length, shoot length, fresh weight, and dry weight). It was also accompanied by an improvement in seed germination. Another study investigates the effects of MWCNTs in hydroponics on the physiology and other biochemical processes in wheat (Larue et al. 2012). This is supported by the activity of C-14 labeled MWCNTs used in the study where less than 0.005% of the MWCNT dose were taken up by the plant. Results are paradoxical to the previous observations in wheat and no effect is observed in any of the physiological processes like seed germination, root elongation, dry biomass, and evapotranspiration. Oxidative stress is also not observed in wheat which indicates exposure to very high concentrations of MWCNTs in a dispersed liquid environment cannot affect the plant physiology or metabolism.

The effects of MWCNT on Zea mays were also reported (Tiwari et al. 2014). MWCNTs enhances the growth and affect the mineral nutrient supply to the seedling through the action of the mutually opposing forces of inflow with water and retention in the medium by the ion-CNT transient-dipole interaction. This effect is found to be dependent on the MWCNT concentration and the nature of the ion. This experiment reveals the positive effect of MWCNT in low concentration on enhancement in water absorption ability, increase in essential nutrients of Fe, Ca along with increase in plant biomass.

Barley, corn, and soybean were treated with MWCNT and the effects are compared in another study (Lahiani et al. 2013). They applied MWCNTs in two different methods such as through agar growth medium and by seed coating. The results showed an enhancement in seed germination and other negative effects are not evident on the developed plants.

5.3 Fabaceae

The penetration of MWCNT on the cells of *Onobrychisarenaria* and subsequent influence on plant growth is reported (Smirnova et al. 2011). They used “Taunit” which is an industrial material containing MWCNT. Peroxidase activity inversely depends on the concentration of Taunit and it increased with decreasing Taunit concentration from 1000 to 100 mg/L. Peroxidases are involved in a number of biological processes, such as photosynthesis, respiration, and protein metabolism. It is an antioxidant enzyme with high sensitivity toward external factors, and this allows using peroxidase activity assay as a tool for analyzing testing of the physiological condition of plants. TEM analysis showed the presence of MWCNTs in the seedling roots and leaves. It establishes the penetrating ability of MWNTs to into roots as well as their ability to get transported into seedling leaves.

Glycine max (soybean) is another important candidate of this family in which the effects of MWCNT are investigated (Wang et al. 2017). Plant growth, nodulation, and dinitrogen (N2) fixation potential of the plant were analyzed for a period of 39 days in soil by varying the concentration of MWCNTs. The plant growth parameters followed an inverse dose-response relationship. Lower concentrations of CNMs were relatively more impactful to soybean growth, root nodulation, and N_2 fixation potential. Also the bioavailability is reduced at higher concentration indicating agglomeration in the plant vascular system.

5.4 Solonaceae

Lycopersiconesculentum (tomoto) belongs to this family and is the most explored plant for its effects after exposure with both SWCNT and MWCNT. An interesting study is available for studying the interaction of tomato plant with a multicomponent nanosystem composed of single-walled carbon nanotube quantum dot conjugates (SWCNT–QD) (Alimohammadi et al. 2011). The results showed the addition of QDs to SWCNTs dramatically changed the biological viability of the tomato plants by accelerating leaf senescence and inhibiting root formation. Although the exposure of SWCNTs only to the plants induced positive effects, reduction in chlorophyll content by 1.5-fold in leaves, and the total weight of the root system is reduced by four times for the tomato plants exposed to SWCNT–QDs (50 μg mL^{-1}) compared to control. The results clearly indicate that the exposure of plants to multicomponent nanomaterials is highly influenced independently by the presence and bioactivity of each component.

Another interesting study analyzed growth regulatory activity in tomato by MWCNT (Khodakovskaya et al. 2013). They reported that CNTs can affect the phenotype of tomato plants. Tomato plants grown on soil supplemented with MWCNTs produced two times more flowers and fruits than plants grown in regular soil with the same amount of leaves. This observation opens new perspectives for implementing CNTs as growth regulators in agricultural applications. A controversial result is reported for tomato in which root elongation is significantly inhibited on exposure with nonfunctionalized SWCNTs (Cañas et al. 2008).

Solanum melongena (brinjal) is another member of this family which is studied for response to CNTs due to its slow growing rate. The effects of –OH functionalized MWCNTs on brinjal seeds are reported (Mukherjee et al. 2018). MWCNTs induced enhancement in seed germination and improvement in growth parameters. But toxicity is observed on concentration beyond 50 μg/mL.

5.5 Miscellaneous

There are a number of other plant species of research interest in which the effects of CNTs are investigated. *Pseudokirchneriella subcapitata* is a freshwater alga which is recently reported for the influence of CNT on phenanthrene adsorption and bioavailability (Glomstad et al. 2016). They used five types of CNTs exhibiting different physicochemical properties, including a single-walled CNT (SWCNTs), multi-walled CNTs (MWCNT-15 and MWCNT-30), and functionalized MWCNTs (hydroxyl, −OH, and carboxyl, −COOH). The adsorption capacity is found to be in direct relationship with surface area and inversely on surface functionalization. The presence of SWCNTs reduced phenanthrene toxicity to algae compared to phenanthrene alone and the presence of MWCNTs had no significant effect on phenanthrene toxicity. However, phenanthrene adsorbed to CNTs dispersed with natural organic matter proved to be bioavailable and contribute to exert toxicity to the plant. Cell permeation of MWCNT and subsequent growth enhancement and water uptake for *Brassica oleracea* (broccoli) plant in saline medium is reported (Martínez-Ballesta et al. 2016). MWCNTs can enter the cells in matured plants with higher accumulation under salt stress. Also, enhanced aquaporin transduction occurred, which improved water uptake and transport, alleviating the negative effects of salt stress. *Hibiscus sabdarifa* is explored for the influence of MWCNT and biostimulators (Delfan plus), and their interactions on growth and production of bioactive constituents (Sareea Al-Rekaby 2018). The results showed an increase in the content of all bioactive constituents under consideration.

Ricinus communis is another plant analyzed for the influence on seed germination and growth by a wide range of concentration of MWCNT (Fathi et al. 2017). The results are paradoxical which showed a stimulatory effect of MWCNTs on the biomass and root growth of castor seedlings, at a concentration of 100 μg/mL^{-1} while an inhibitory effect is observed at concentrations 10 and 50 μg/mL^{-1}. The possible mechanism of concentration-dependent action of MWCNT needs to be investigated.

Amaranthustricolor (red spinach) is a very important edible plant and is studied for the adverse effects caused by MWCNT. Results revealed that primary mechanism of CNT toxicity is oxidative stress. Plants exposed to CNTs in hydroponic culture exhibited growth inhibition and undergone cell death after 15 days along with adverse effects on root and leaf morphology (Begum and Fugetsu 2012).

Alnus subcordatais (Caucasian alder) also studied for nano priming effect on seed germination using MWCNT (Rahimi et al. 2016). Results showed that nano priming at the concentration of 100 mg/L^{-1} leads to the highest germination rate and percentage at all levels of drought stress. Also, the highest values of seed vigor index and root and stem lengths and dry weights were observed at treatment with 30 mg/L^{-1}. This study implies that nano priming could result in boosted resistance of Caucasian alder seeds against drought stress and it can be applied in order to increase the seed and seedling tolerance of other members of the genus.

6 Conclusion and Future Perspectives

Implementation of nanotechnology in the agricultural sector is a field of recent research interest. The research outcome and principles of nanotechnology could pave way for the rapid development and resource enhancement of agriculture and its allied fields. Bio-nanotechnology is a tool and remedy which can enhance the pace for agricultural growth and thereby influence the economic development of the country. In this chapter, we have analyzed the studies which explore the influence of CNT on plants and edible crops. These studies are very relevant due to the revival that needed for agriculture and food production industry from nanotechnology. In general, most studies indicate CNTs as a growth stimulator due to its alleviating effects on physiology and growth process of plants. These observations imply CNTs as a potential tool for plant growth and regulation and thereby improving the productivity. On the other hand, the toxicity concerns of CNTs are a major obstacle and are still not explored effectively. The toxicity effects of CNTs in plants are not clear despite various investigations. Further, the studies related to the alteration of genetic components in plants by nanomaterial and its effects on human body are still a matter of debate which are not resolved by scientific community. If CNT can penetrate plant cell, they can definitely enter the food chain and affects human health. Since CNTs are found to have positive effects on plant growth and productivity, it would be very essential to investigate the toxicity aspects before implementing them.

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Silver Nanoparticles and Their Morpho-Physiological Responses on Plants

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1 Introduction

Nanoparticles (NPs) are defined as the materials with particle dimension between 1 and 100 nm, which results in their unique chemical and physical characteristics. These exclusive characteristics of NPs make them highly attractive for implementation in various products for wider application (Benn et al. 2010). The expansion and development of nanotechnology in combination with biotechnology has drastically extended the application of NPs in various fields. The escalating manufacture and utilization of NPs raises significant concerns regarding their release into soil, water, and air (Peralta-Videa et al. 2011), and, as an outcome, may cause detrimental consequences on the environment and human health (Beer et al. 2012; Colman et al. 2013). Natural sources of NPs include meteoric dust, volcanic eruptions, weathering, and microbial action on organic matter of the soil (Morales-Diaz et al. 2017). Various anthropogenic sources comprise engineered NP production for a number of applications following physical, chemical, and biological methods. However, in the field of agriculture, the use of NPs is quite novel research and needs further exploration. Various reports have revealed both positive and negative consequences of NPs on plants.

Nanoparticles interact with the plants, which results in the uptake and then accumulation that affects their fate and transport in the ecosystem. Moreover, NPs could

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remain attached to the plants surface and impart physical and chemical damage to their organs. Usually, NPs enter into the plant roots through their lateral junctions and reach the xylem through the cortex and the pericycle (Dietz and Herth 2011; Tripathi et al. 2017a). Notably, entry of NPs into the plant can be ceased by the cell wall. The specific properties of cell wall that allow the transport of NPs across the cell could be attributed to the pore size of wall. The NPs that are in the size range within the pore size of cell wall could efficiently cross it and outreach the plasma membrane (Navarro et al. 2008a; Tripathi et al. 2017a). The rate of entry of NPs depends on their size and surface properties. Indeed, the smaller NPs can enter into the plant cells easily. In contrast, larger sized NPs, being unable to enter the cells, cannot affect the metabolic pathways (Verano-Braga et al. 2014). However, larger NPs can enter through the hydathodes, flower stigmas, and stomata. The mechanism of interaction between NPs and plants could be chemical or physical. Chemical interactions involve the production of reactive oxygen species (ROS) (Nel et al. 2006; Tripathi et al. 2017b; Rastogi et al. 2019; Vishwakarma et al. 2017), disturbance in membrane transport activity (Auffan et al. 2008), oxidative damage (Foley et al. 2002; Rastogi et al. 2019; Vishwakarma et al. 2017; Tripathi et al. 2017d; Arif et al. 2018; Tiwari et al. 2019), and lipid peroxidation (Kamat et al. 2000). Following entry into the plant cells, NPs after mixing behave as metal ions and react with sulfhydryl and carboxyl groups, and ultimately modify the protein structure and activity.

Among various NPs, silver nanoparticles (AgNPs) are the most widely used nanomaterials due to their well-recognized antibacterial and antifungal effects as well as their plasmonic and opto-electrical properties (Pokhrel et al. 2012). Various researchers have studied the effects of AgNP on seed germination and plant growth with the objective to promote its use for agricultural applications, and their articles summarize the developments and applications of novel NPs in agriculture (Kumari et al. 2009; Lee et al. 2012; Vannini et al. 2013; Yadu et al. 2018; Shweta et al. 2018; Vishwakarma et al. 2018). The antimicrobial properties of AgNPs are being increasingly exploited in consumer products such as toothpaste, fabric, electronic goods, detergents, deodorants, bandages and, cleaning solutions and sprays (Wijnhoven et al. 2009). Toxicological studies of AgNPs have been done on bacteria, algae, and animal cells (Navarro et al. 2008a; Fabrega et al. 2009). Studies that investigated the impact of AgNPs on plants suggested their uptake, accumulation, and translocation in different organs and their consequences on growth and developmental processes (Yin et al. 2012; Dimkpa et al. 2013; Cvjetko et al. 2017; Tripathi et al. 2017b; Yadu et al. 2018). The ramifications due to the AgNPs on plants appear to depend on various factors like species and age of plants, the size and concentration of the particles, the experimental conditions such as temperature, and the time and method of exposure. For instance, 10 mg L^{-1} AgNPs diminished the seed germination in *Hordeum vulgare* and shoot length in *Linum usitatissimum* and *Hordeum vulgare* (El-Temsah and Joner 2010). Though 100 mg L^{-1} AgNPs showed no significant effect on seed germination of *Cucumis sativus* and *Lactuca sativa* (Barrena et al. 2009), reports of other scientists indicated positive role of AgNPs in the growth of *Brassica juncea* (Sharma et al. 2012), *Zea mays* (Berahmand et al. 2012), and *Cajanus cajan* (Yadu et al. 2018). As plants are primary producers and a fundamental part of ecosystem, the phytotoxic consequences of AgNPs should be given particular attention in future studies. Moreover, AgNPs-induced oxidative damage to lipids, proteins, and DNA molecules, as well as alterations in the abundance of hormones and antioxidant enzymes of plants (Yasur and Rani 2013; Cvjetko et al. 2017; Yadu et al. 2018), which suggested that oxidative stress could have a vital role in the AgNP coupled phytotoxicity. A study conducted by Yasur and Rani (2013) on *Ricinus communis* seeds revealed an increased ROS generation and associated stimulation of antioxidants with exposure to AgNPs. Qi et al. (2013) demonstrated that toxicity of AgNPs in *Arabidopsis thaliana* was associated with imbalance between oxidant and antioxidant systems, and also disturbances in water homeostasis and photosynthesis via altered thylakoid membrane and chlorophylls, thus affecting plant growth. Therefore, it is important to increase our knowledge about mechanisms of AgNP toxicity to ensure a controlled and safer implementation of AgNPs in a variety of agricultural products and practices too.

2 Sources of Silver Nanoparticles

2.1 Natural Sources

The escalating utilization of nanosilver has generated substantial interest in the researchers to develop various methods to fabricate different forms of AgNPs, which eventually raised the amount of nanosilver in the surrounding environment. However, evidence has thus proved that all the AgNPs are not produced by anthropogenic activities. Natural leaching from bedrock and mining activities also contributed to Ag contamination in surface waters (Lanzano et al. 2006). In natural and contaminated waters, the measured concentrations of Ag are in the range of ng L^{-1} (Purcell and Peters 1998). Gomez-Caballero et al. (2010) reported that Ag as NP was found in an old Ag mining area of Mexico. Wen et al. (1997) reported the presence of colloidal and particulate Ag in the river and estuarine waters of Texas, USA. In fact, there are various natural reducing agents, such as humic acid (HA), in the environment that occur ubiquitously and contain many functional groups which facilitate it to reduce metal ions.

Yin et al. (2012) revealed that ionic Ag could be photo-chemically reduced to AgNPs by dissolved organic matter of natural water under sunlight within several hours. Naturally formed AgNPs were found to be unstable and easily coalesced due to the presence of inorganic cations such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) in the environmental waters. Further studies have confirmed that the photo-reduction process was pH-dependent and was mediated by superoxide generated from photo-irradiation of the phenolic groups of HA, and dissolved oxygen considerably increased the reduction of Ag^+. As all these processes occurred under environmentally relevant conditions, they demonstrated that all the AgNPs are not of anthropogenic origin but can form spontaneously in nature also.

Another study by Glover et al. (2011) demonstrated that AgNPs could be generated from Ag objects through oxidative dissolution and subsequent reduction reaction. These authors have discovered that when capping-agent stabilized AgNPs were immobilized on positively charged silicon dioxide (SiO_2) grids and were exposed to ambient laboratory conditions, several novel smaller particles appeared around the original NPs. Characterization of these by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) confirmed that the newly formed particles were AgNPs. Upon further investigation, it was found that new NPs could also be generated from large objects like, Ag wire, jewelry, and eating utensils, implying that macroscale elemental Ag objects are a potential source of AgNPs in the environment.

It has also been reported that plants have the capability to take up metal ions and form NPs (Gardea-Torresdey et al. 2003). Gardea-Torresdey et al. (2003) revealed that *Medicago sativa* roots could absorb Ag atoms and transfer them through specific channels to their different parts. Characterization proved that the Ag atoms combined together and nucleated to form AgNPs inside plants. The green syntheses of AgNPs involving environmentally benign reducing agents and non-toxic stabilizing agents have attracted much attention and have been thoroughly reviewed by Nadagouda and Varma (2008), Raveendran et al. (2003), Xie et al. (2007), Sharma et al. (2009), and Yang et al. (2010), indicating that many natural substances or organisms could produce AgNPs.

2.2 Anthropogenic Sources

Various anthropogenic activities play vital role in potential Ag pollution. The widespread use of AgNPs has encouraged the development of the Ag based industries. Worldwide production of AgNPs is estimated to be about 500 tons per annum, and this amount is still increasing steadily (Mueller and Nowack 2008). AgNP has its applications in electronic devices, incorporated into textiles, dressing and medical devices, or directly added to the disinfectants. However, during the production and manufacturing of nanosilver products, AgNPs could be directly released into the environment (Gottschalk and Nowack 2011). The syntheses of nanosilver products often involve various processes including mixing, centrifugation, and filtration steps to remove impurities, and the wastewater may be directly discharged into the environment. In addition, the powder NP occurs as aerosols in workshops and escapes through open windows into the air. Historically the photographic industry contributed significantly to large emission loads of Ag into the aerial environment (Purcell and Peters 1998; Fabrega et al. 2009), but the advent of digital photography resulted in a rapid decrease in the percentage of usage for this application. Moreover, various other activities like sampling for quality control, leaking from broken packaging, and other accidents could lead to unintentional release of AgNPs in the environment. The uncontrollable release of Ag in the environment during the use, recycling, and disposal process poses serious threat.

The exposure of AgNPs may occur over several phases of their lifespan—from synthesis and manufacturing, distribution, end-product use, and end-of-life disposal of consumer products which are nano-functionalized including textiles and fabrics, food-contact materials such as containers and kitchen appliances, cosmetics, deodorants, water filters, toys, and alternative health supplements (Blaser et al. 2008; Mueller and Nowack 2008; Hong et al. 2014).

2.3 Metal Dust

Studies evidenced that metal based nanomaterials may be an anthropogenic source of metal dusts or soluble metals in the atmosphere by heterogenous and multiple reactions (Grassian 2009; Adachi and Buseck 2010). Metal-containing anthropogenic dusts are becoming an increasing source of metals in the environment. Inventories have shown that the metal and metal-oxide-based nanomaterials are a large component of materials being used in consumer products. Therefore, it is logical to assume that metal-containing engineered nanomaterials have the utmost probability to make their way into the atmospheric environment, thus causing a threat to flora and fauna both. Furthermore, engineered NPs have the potential for very different and size-dependent physical, chemical, and biological properties compared to larger-sized particles (Grassian 2009).

3 Syntheses of Silver Nanoparticles

3.1 Physical Methods

Generally, the syntheses of NPs have been carried out using three different approaches: physical, chemical, and biological. In physical methods, NPs are prepared by evaporation-condensation, using a tube furnace at atmospheric pressure (Kruis et al. 2000). The advantages of physical methods are speed, use of radiations as reducing agents, and absence of hazardous chemicals, but the disadvantages are low yield and high energy consumption, solvent contamination, and lack of uniform distribution (Tsuji et al. 2005; Shameli et al. 2010). Silver NPs could be synthesized by laser ablation of metallic bulk materials in solution (Mafune et al. 2000; Kim et al. 2005). The ablation efficiency and the characteristics of produced AgNPs depend upon many parameters, such as the wavelength of the laser impinging the metallic target, the duration of the laser pulses (in the femto-, pico-, and nano-second regime), the laser fluence, duration of ablation, and the effective liquid medium, with or without the presence of surfactants (Kim et al. 2005).

3.2 Chemical Methods

Chemical method of AgNP synthesis uses water or organic solvents (Tao et al. 2006; Abou et al. 2010). This process usually employs three main components: metal precursors, reducing agents, and stabilizing/capping agents. Basically, the reduction of Ag salts involves two stages: (1) nucleation and, (2) subsequent growth. Generally, Ag nanomaterials can be obtained by two methods, classified as “top-down” and “bottom-up” (Deepak et al. 2011). The “top-down” method is the mechanical grinding of bulk metals with subsequent stabilization using colloidal protecting agents (Amulyavichus et al. 1998; Mallick et al. 2004). The “bottom-up” method includes chemical reduction, electrochemical methods, and, sono-decomposition. The major advantage of chemical methods is high yield, contrary to physical methods, which have comparatively low yield. Chemical methods make use of techniques such as cryochemical synthesis (Sergeev et al. 1999), lithography (Hulteen et al. 1999), electrochemical reduction (Zhu et al. 2001), laser irradiation (Abid et al. 2002), sono-decomposition (Talebi et al. 2010), and chemical reduction (Zhang et al. 2011). The advantages of the chemical syntheses of NPs are the ease of production, low cost, and high yield; however, the use of chemical reducing agents is harmful to life forms.

3.3 Biological Methods

To overcome the shortcomings of physical and chemical methods, biological methods have emerged as a viable option for syntheses of various NPs including AgNPs. Recently, biological syntheses of different NPs have been shown to be simple, cost-effective, dependable, and environment-friendly approaches, and much attention has been given to the high yield production of AgNPs of defined size using various biological systems including bacteria, fungi, plant extracts, and small biomolecules like vitamins and amino acids as alternatives to chemical reducing agents (Kalimuthu et al. 2008; Kalishwaralal et al. 2008). In this green chemistry approach, bacteria are known to produce inorganic materials either intra- or extracellularly. This property of bacteria makes them potential biofactories for the syntheses of NPs including AgNPs. The first bacteria-mediated AgNP synthesis was done using Ag resistant bacteria *Pseudomonas stutzeri* AG259 (Klaus et al. 1999). Several other bacteria as biofactories of AgNPs include *Lactobacillus sp.* (Nair and Pradeep 2002), *Bacillus licheniformis* (Kalimuthu et al. 2008), *Escherichia coli* (Gurunathan et al. 2009), *Brevibacterium casei* (Kalishwaralal et al. 2010), etc.

Similar to bacteria, fungi have been of interest in biological production of the metallic NPs due to their tolerance and metal bioaccumulation ability, high binding capacity, and intracellular uptake (Murali et al. 2003). Fungi secrete large amounts of enzymes, which are used to reduce Ag ions that induce the formation of the metal NPs (Mandal et al. 2006). The first AgNP synthesis involving fungus-mediated approaches was performed with *Verticillium* (Mukherjee et al. 2001). Other fungi used for syntheses of AgNPs were *Fusarium oxysporum* (Shankar et al. 2003), *Ganoderma neo-japonicum* Imazeki (Gurunathan et al. 2013), etc.

Similarly, yeasts were also widely investigated for AgNP synthesis (Mandal et al. 2006; Apte et al. 2013). Silver-tolerant yeast strain MKY3 was first used for extracellular synthesis of AgNP (Kowshik et al. 2003).

Synthesis of NPs using plants is very cost-effective and safer, and thus can be used as an economic and valuable alternative for the large-scale production of NPs. Plant parts like leaves, roots, latex, bark, stem, and seeds are being used for NP synthesis (Kharissova et al. 2013). Plant extracts contain biomolecules such as phenolics, terpenoids, polysaccharides, flavones, alkaloids, proteins, enzymes, amino acids, and alcoholic compounds, which act as both reducing and capping agents that form stable and shape-controlled NPs (Huang et al. 2007; Sharma et al. 2009). Plant extracts such as *Allophylus cobbe* (Gurunathan et al. 2014), *Artemisia princeps* (Gurunathan et al. 2015), and *Typha angustifolia* (Gurunathan 2015) have already been utilized by scientists for syntheses of AgNPs.

The biological syntheses of NPs depend on three factors: (1) the solvent, (2) the reducing agent, and (3) the non-toxic biological material. The chief advantages of biological methods are the availability of amino acids, proteins, and/or secondary metabolites present in the synthesis process; the elimination of the extra step required for the prevention of particle aggregation; and the use of biological molecules for the syntheses of AgNPs which are eco-friendly. Biological methods seem to provide controlled particle size and shape, which are important factors for various biomedical applications (Gurunathan et al. 2014). Shape, size, and monodispersity of the NPs can be controlled by using bacterial protein or plant extracts as reducing agents (Gurunathan et al. 2009). The biological activity of AgNPs depends on the morphology and structure of AgNPs and is controlled by size and shape of the particles (Morones et al. 2005; Pal et al. 2007). The other advantages of biological methods are the availability of a vast array of bioresources, a decreased time requirement, high density, stability, and the solubility of prepared NPs in water (Thakkar et al. 2010). Compared to chemical methods, biological methods allow more ease in the control of shape, size, and distribution of the produced NPs by optimization of the synthesis methods, including the amount of precursors, temperature, pH, and the amount of reducing and stabilizing factors (Singh et al. 2013).

4 Characterization of Silver Nanoparticles

The physicochemical properties of NPs are important for their behavior, bio-distribution, safety, and efficacy. Therefore, the characterization of AgNPs is important in order to evaluate the functional aspects of the synthesized nanomaterials. Characterization is performed using a variety of analytical techniques, including UV-visible spectroscopy, X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), XPS, dynamic light scattering (DLS), scanning electron microscopy (SEM), TEM, and atomic force microscopy (AFM). The basics of the important techniques used for the characterization of AgNPs are detailed below for ease of understanding.

4.1 UV-Visible Spectroscopy

This technique is very useful and reliable for primary characterization of synthesized NPs and is also used to monitor the syntheses and stabilities of nanomaterials (Sastry et al. 1998). Silver NPs have exceptional optical properties, which strongly facilitate them to interact with specific wavelengths of light. Additionally, this technique is fast, easy, simple, sensitive, and selective for different types of NPs, needs only a fraction of time for measurement, and finally calibration is not required for particle characterization of colloidal suspensions (Huang et al. 2007). The absorption of light over AgNPs depends on the particle size, dielectric medium, and chemical surroundings (Nath and Gope 2007).

4.2 X-Ray Diffraction

The ray diffraction is a popular analytical technique used for the analyses of AgNPs. When X-rays fall on any crystal, it leads to the formation of many diffraction patterns, and the patterns reflect the physicochemical characteristics of the crystal structure. In a powder specimen, diffracted beams typically come from the sample and reflect its structural physicochemical features. Thus, XRD can analyze the structural features of a wide range of materials, such as inorganic catalysts, superconductors, biomolecules, glasses, polymers, and so on (Robin 2009). Analyses of materials largely depend on the formation of diffraction patterns. Each material has a unique diffraction beam which can defined and identified it by comparing the diffracted beams with the reference database in the Joint Committee on Powder Diffraction Standards library. Recently, the applications have extended to the characterization of various nanomaterials and their properties.

4.3 Dynamic Light Scattering

Among the various techniques of NP characterization, the most commonly used is DLS. This method depends on the interaction of light with particles and can be used for the measurement of narrow particle size distributions, especially in the range of 2–500 nm (Tomaszewska et al. 2013). It measures the light scattered from a laser that passes through a colloid, and mostly relies on Rayleigh scattering from the suspended NPs (Fissan et al. 2014). Subsequently, the modulation of the scattered light intensity as a function of time is analyzed, and the hydrodynamic size of particles can be determined (Dieckmann et al. 2009). To evaluate the toxic potential of any nanomaterial, its characterization in solution is essential. Therefore, DLS is mainly used to determine particle size and size distributions in aqueous or physiological solutions (Murdock et al. 2008). It has the special advantage of probing a large quantity of particles simultaneously; however, it has a number of sample-specific limitations (Dolatmoradi et al. 2013; Das et al. 2014).

4.4 Fourier Transform Infrared Spectroscopy

This technique is accurate, reproducible, and provides precise signal-to-noise ratio. It is frequently used to find out whether biomolecules are involved in the syntheses of NPs, which is more pronounced in academic and industrial research (Shang et al. 2007). Furthermore, FTIR has also been extended to the study of nano-scale materials, such as confirmation of functional molecules covalently grafted onto Ag, carbon nanotubes, graphene and gold (Au) NPs, or interactions occurring between enzyme and substrate during the catalytic process (Baudot et al. 2010). Further advancement has been made in FTIR method called attenuated total reflection (ATR)-FTIR spectroscopy (Hind et al. 2001). Using ATR-FTIR, chemical properties of the surfaces of polymers can be identified (Kazarian and Chan 2006). Therefore, FTIR is a suitable, valuable, non-invasive, cost-effective, and simple technique to identify the role of biological molecules in the reduction of silver nitrate ($AgNO_3$) to Ag.

4.5 X-Ray Photoelectron Spectroscopy

It is a quantitative spectroscopic surface chemical analysis technique used to estimate empirical formulae (Manna et al. 2001; Acosta et al. 2005; Joshi and Bhattacharyya 2008). It plays a unique role in giving access to qualitative, quantitative/semi-quantitative, and speciation information concerning the sensor surface (Desimoni and Brunetti 2015). Irradiation of X-rays on the nanomaterial leads to the emission of electrons, and the measurement of the kinetic energy and the number of electrons escaping from the surface of the nanomaterials provides XPS spectra of that particular sample (Acosta et al. 2005; Joshi and Bhattacharyya 2008). The binding energy can be calculated from the kinetic energy. Specific groups of starburst macromolecules such as P=S, aromatic rings, C–O, and C=O can be identified and characterized by XPS (Gautam et al. 2012).

4.6 Scanning Electron Microscopy

Among various electron microscopy (EM) techniques, SEM is a surface imaging method, fully capable of resolving different particle sizes, size distributions, nanomaterial shapes, and the surface morphology of the synthesized particles at the micro- and nano-scales (Ranter et al. 2004; Johal 2011). The combination of SEM with energy-dispersive X-ray spectroscopy (EDX) can be used to scrutinize morphology of Ag powder and conduct chemical composition analysis. The limitation of SEM is that it is not able to resolve the internal structure but provides valuable information regarding purity and the degree of particle aggregation. The modern high resolution SEM is able to identify the morphology of NPs below the level of 10 nm.

4.7 Transmission Electron Microscopy

This is a valuable, frequently used, and important technique for the characterization of nanomaterials, used to obtain quantitative measures of particle and/or grain size, size distribution, and morphology (Joshi and Bhattacharyya 2008; Williams and Carter 2009). The magnification of TEM is mainly determined by the ratio of the distance between the objective lens and the specimen, and the distance between objective lens and its image plane (Williams and Carter 2009). It has two advantages over SEM; it can provide better spatial resolution and the capability for additional analytical measurements (Williams and Carter 2009).

4.8 Atomic Force Microscopy

Atomic force microscopy is used to examine the dispersion and aggregation of nanomaterials, in addition to their size, shape, sorption, and structure (Koh et al. 2008; Picas et al. 2012). Additionally, AFM can also be used to characterize the interaction of nanomaterials with supported lipid bilayers in real time, which is not achievable with currently used EM techniques (Stephan et al. 2006). It has three operating modes (contact mode, non-contact mode, and intermittent sample mode), which is a crucial factor in sample analysis (Bhushan and Marti 2004).

5 Factors Affecting Production of Silver Nanoparticles

Several factors affect the syntheses, characterization, and application of NPs (Zhang et al. 2011). Some of the important factors are summarized below.

5.1 pH of the Solution

The pH plays a vital role in syntheses of NPs. Several reports indicated that pH of the solution influences the size, shape, and rate of the synthesized NPs (Armendariz et al. 2004). This fact is due to the formation of nucleation centers, which increases with augmentation in the solution pH. As the nucleation center increases, the reduction of metallic ions to NPs also increases. Also, the pH of solution influences the activity of the functional groups in the plant extract/biomass and also influences the rate of reduction of a metal salt (Bali and Harris 2010).

5.2 Temperature

Temperature is another chief factor that influences the size, shape, and rate of NP synthesis. Similar to pH, formation of nucleation centers increases with increase in temperature, which in turn enhances the rate of NP synthesis. Sheny et al. (2011) compared the reduction processes of Au and Ag ions by leaf extract of *Anacardium occidentale* at different temperatures to evaluate the optimum condition for bimetallic Au-Ag synthesis. The authors revealed that a high quantity of leaf extract was required to synthesize stable NPs at low reaction temperature than at high temperature. However, the impact of temperature on size of the AgNPs produced by cyanobacteria (*Plectonema boryanum* UTEX 485) was also investigated, which exhibited increase in size with increase in temperature. Moreover, the results displayed distinctive morphologies of NPs along with varied temperature regimes (Maggy et al. 2007).

5.3 Reaction Time

The size, shape, and extent of NP synthesis are also influenced by the length of reaction time. Gericke and Pinches (2006) revealed that smaller size particles and good monodispersity were observed when cells were exposed to ion solution for shorter time (1 h) than obtained after exposing the cells to ion solution for longer duration (24 h). It indicated that the particle size and monodispersity can be controlled by manipulating the reaction time of NP synthesis.

5.4 Plant Extract/Biomass Dosage

During plant mediated synthesis, the concentration of plant biomass/extract often decides the efficiency of NP synthesis. Researchers identified that increase in biomass dosage not only enhances the production of NPs but also alters their shape (Balamurugan et al. 2014). Hence, it is often important to determine optimum biomass quantity for the process.

6 Properties of Silver Nanoparticles

Various physical and chemical properties of AgNPs such as surface chemistry, size, size distribution, shape, particle morphology, particle composition, coating/capping, agglomeration, dissolution rate, particle reactivity in solution, efficiency of ion release, cell type, and type of reducing agents used for synthesis are fundamental factors for determination of cytotoxicity (Carlson et al. 2008; Zhang et al. 2011; Han et al. 2014). Shape is equally important for the toxicity determination of AgNP (Stoehr et al. 2011). For instance, using biological reducing agents, such as culture supernatants of various *Bacillus sp.*, AgNPs can be synthesized of different shapes, like spherical, rod, octagonal, hexagonal, triangle, flower-like, etc. Previous studies supported the assertion that smaller size particles could cause more toxicity than the larger ones, because they have wider surface area (Sriram et al. 2012). Also, the toxicity of AgNPs chiefly depends on the availability of chemical and/or biological coatings on their surfaces (Suresh et al. 2012).

7 Transportation of Silver Nanoparticles in Plants

The transportation of AgNPs in the cells depends on their structure, permeability, size of the particles, and several other properties of cells (Carlson et al. 2008; Li et al. 2015). Transportation of AgNPs in plants takes place in the following steps: uptake, translocation, and accumulation (Fig. 1).

7.1 Uptake

Plant cells uptake AgNPs by two different modes based on their site of exposure: foliar exposure and root exposure.

Foliar exposure: The leaves of higher plants are protected by waxy cuticle layer, which is a natural barrier against water loss and uncontrolled exchange of other solutes including the entry of NPs. Based on the polarity of solute, there are two routes of uptake across the cuticle (cuticular pathway): (1) lipophilic pathway and, (2) hydrophilic or stomatal pathway. Non-polar solutes enter into the cell through lipophilic pathway via diffusion and permeation; however, polar solutes go through hydrophilic pathway by polar aqueous pores. For instance, when the cotyledons of *Arabidopsis thaliana* were indulged in the medium containing AgNP, subsequent accumulation of this was observed in stomatal guard cells, which was further taken by the leaf apoplast (Geisler-Lee et al. 2013).

Root exposure: Following root exposure, progressive accumulation of AgNP was observed in the root cap, epidermis, root tips, columella, and root meristems. At an early stage after exposure of AgNPs in *Arabidopsis thaliana*, first it accumu-

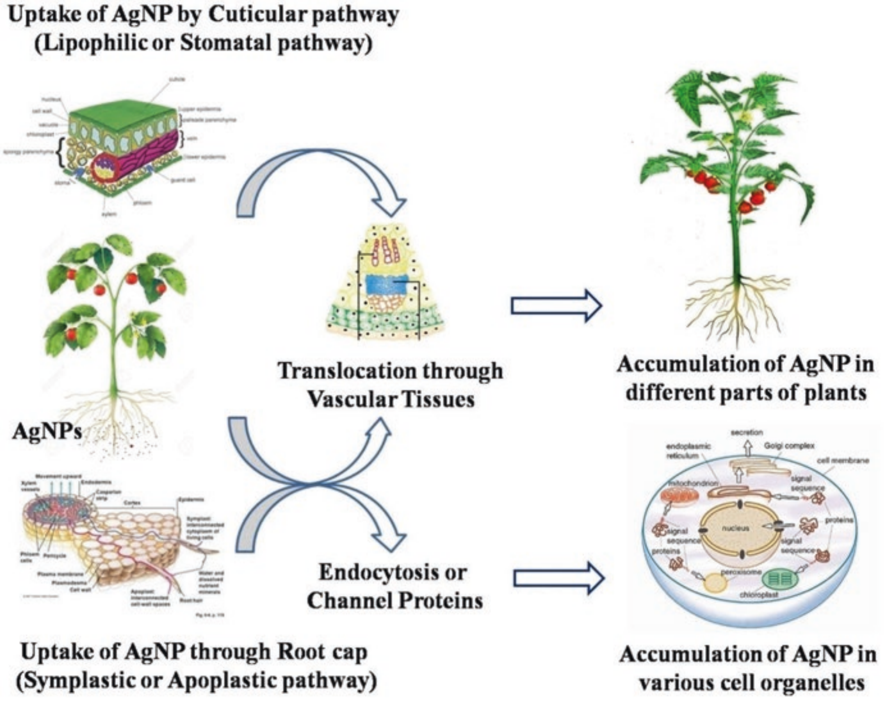

Fig. 1 Schematic representation of uptake, transportation, and accumulation of silver nanoparticles in plants

lated in the surface of primary roots and then entered into the tips (Geisler-Lee et al. 2014). After 14 days of exposure, AgNPs gradually moved into roots and entered into lateral root primordia and root hairs. The cell wall of the root cells functions as a natural barrier for the entry of AgNPs. It is the prime site through which AgNPs enter in plant cells. Plant cell wall is a porous network of polysaccharide fiber matrices, which act as natural sieves, precisely permitting the entry of smaller particles and inhibiting the larger ones (Tripathi et al. 2017b). The AgNPs that eventually reach to the cell wall may further be translocated through apoplastic (intercellular spaces) or symplastic (protoplast connected by plasmodesmata) movement (Ma et al. 2010).

After penetrating the cell wall, another mode of entry by plasma membrane has also been discussed by some researchers (Navarro et al. 2008b; Leonardo et al. 2015), wherein cavities-like structures of membrane lipid encompass the AgNP, which further enter into the cell through the process of endocytosis (Siddhanta et al. 2015). Apart from this, channels and carrier proteins present in cell membrane could also be used by AgNP as a mode of entry into the cell (Mueller and Nowack 2008). Subsequently, these NPs get attached with the various cell organelles like golgi body, endoplasmic reticulum, chloroplast, mitochondria, and lysosomes and alter the metabolic processes by over-accumulation of ROS (Miao et al. 2010). Moreover, entries of AgNPs in seeds are regulated by aquaporins present on seed coats (Mahakham et al. 2017).

7.2 Translocation

After penetrating the cell or inflowing inside the apoplast, AgNPs enter into the vascular tissues for further translocation. Once the AgNPs enter into the vascular tissues of crop plants, long-distance transportation takes place, which leads the AgNPs into various plant organs including fruits and seeds (Tripathi et al. 2017b; Yan and Chen 2019).

7.3 Accumulation

As the AgNPs are up-taken by the leaves and/or roots, their transportation takes place via vascular tissues; therefore, it is possible that the various parts of plants like root, shoot, fruits, seeds, and/or other edible parts may be subjected to contamination/accumulation of AgNPs through translocation. Tripathi et al. (2017b) observed the accumulation of AgNPs in the roots and shoots of *Pisum sativum*. Moreover, Li et al. (2017) compared the uptake, translocation, and accumulation of AgNPs in *Glycine max* and *Oryza sativa* following the root versus foliar exposure. They found that the foliar exposure is more prominent (17–200 times) for Ag accumulation in comparison to root exposure. Resultant accumulation of AgNP in different parts of the plants could trigger phytotoxicity by overproduction of ROS, which can damage the structures of cellular macromolecules (Atha et al. 2016; Qian et al. 2013).

8 Anatomical and Morpho-Physiological Impacts of Silver Nanoparticles on Plants

After getting accumulated in the plant cells, AgNPs pose a number of side effects including anatomical, physiological, biochemical, and molecular (Fig. 2) (Tripathi et al. 2017b). The effects of AgNPs on anatomy and, overall growth and developmental processes of plants are positive, negative, or neutral depending on the size, shape, applied dose, and duration of treatment along with species, organ, and status of treated plants (Tripathi et al. 2017b). Primary modification observed in root was enhanced width of root hairs, which might be an adaptive approach of roots to dilute the concentration of AgNP (Lee et al. 2012). Moreover, microscopic observations of transverse sections of roots exposed to AgNP showed disappearance of the characteristic air chambers and partitioning filaments. In case of shoot, remarkable variations in size and shape of the xylem ring and central extensions of xylem elements

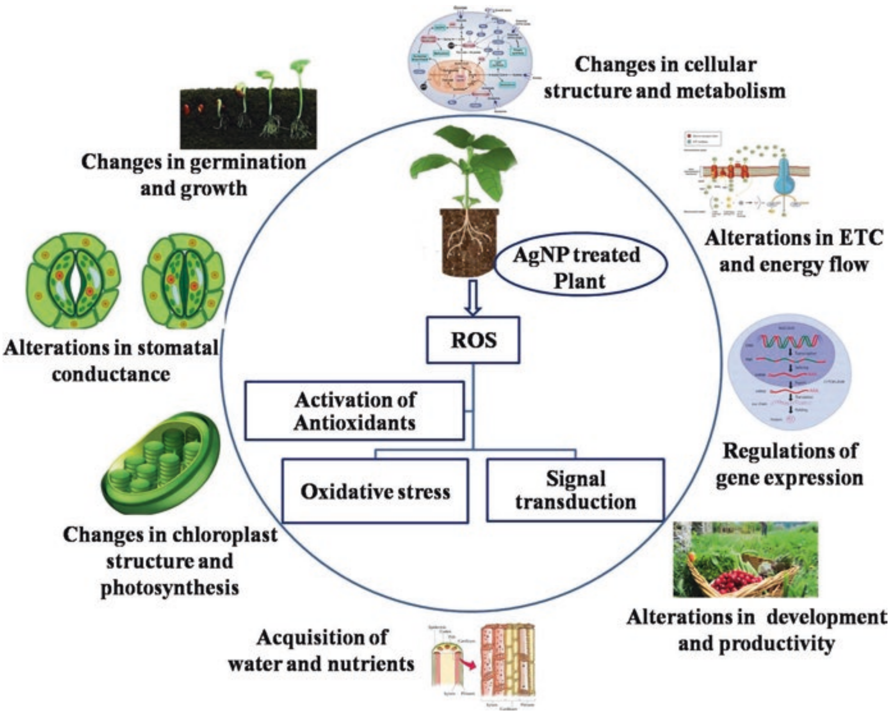

Fig. 2 Diagrammatic representation of silver nanoparticle-induced alterations in various metabolic processes of plants

were determined after treatment with AgNPs. However, crystalline structure appeared in their cortical cells. Further, cross-sections of AgNP exposed root epidermis cells revealed the presence of dark brown colored patches in them, which may be due to the cellular uptake of AgNP (Geisler-Lee et al. 2013).

Researchers have also documented significant alterations in the morpho-physiological properties like growth, productivity, membrane integrity, photosynthetic system, energy flow, and uptake of water and nutrients, etc. of plants after their exposure to AgNPs. Correspondingly, alterations in the lengths of root and shoot, fresh and dry mass, photosynthetic efficiency, and protein turnover were documented under AgNP compared with control *Brassica sp.* (Vishwakarma et al. 2017).

8.1 Growth and Productivity

8.1.1 Seed Germination

Germination is an important determinant, discerning the seed quality, viability, and final plant density. Studies have reflected both positive and negative or neutral effects of AgNP on seed germination. A study conducted by Geisler-Lee et al.

(2013) showed that seed germination of *Arabidopsis thaliana* was not affected by green synthesized AgNP treatment in hydroponic conditions. However, seeds of *Bacopa monnieri* and *Boswellia ovailifoliolata* showed enhanced germination and seedling growth after treatment with AgNP (Krishnaraj et al. 2012). Similar effects were also registered after exposure of *Asparagus officinalis* seeds to AgNP (An et al. 2008). Based on studies on the effects of NPs on seed germination mechanism, researchers concluded that the NPs might have helped the seed germination in some plant species by increasing the water absorption capacity, fertilizer utilizing ability, activity of nitrate reductase enzyme, and reducing the ROS accumulation by promoting the antioxidant system (Almutairi and Alharbi 2015). In contrast, exogenous addition of AgNP caused decline in the germination efficiency in many plant species, like *Vicia faba* and *Arabidopsis thaliana* (Abdel-Azeem and Elsayed 2013; Geisler-Lee et al. 2013). Moreover, neutral effect of AgNP treatment was observed on the rate of germination of hydroponic cultures of *Solanum lycopersicum* and *Raphanus sativus*, whereas significant reduction was recorded in the photosynthetic activity and, elongation of roots and shoots.

8.1.2 Root Elongation

Seed germination was found to be increased, in some of the varieties, with decline in the concentration of AgNP. Similar trend was observed in case of root and shoot lengths; hence, a negative correlation was calculated between the rate of elongation and AgNP concentration. The mechanism responsible for enhanced root elongation is unclear. Lin and Xing (2007) showed an inhibition in root growth of a few higher plants after application of certain NPs, while some other NPs, such as AgNPs, have been used as growth stimulator, especially in coniferous seedlings, like *Citrullus lanatus* and *Cucurbita pepo* (Almutairi and Alharbi 2015). On the other hand, an insignificant effect of AgNP on the plant height and formation of root hair was observed in *Bacopa monnieri* (Krishnaraj et al. 2012). Browning and necrosis in the root tips were detected in the AgNP exposed roots of *Phaseolus radiatus* and *Sorghum bicolor* (Lee et al. 2012).

8.1.3 Plant Height

Recent applications of NPs have concerns over the phytotoxic effect(s) on plants. Growth inhibition versus dose of AgNP and time of exposure were observed in many plant species. Particle size is also important for toxicity; specifically, smaller sized AgNPs (6 nm) were proven to be more toxic to *Spirodela polyrhiza* than the larger ones (20–1000 nm) (Jiang et al. 2012). Use of various NPs had a significant role in the physiology of crop plants. Qian et al. (2013) reported that under AgNP treatment, its accumulation increases with concomitant decrease in the levels of some of the beneficial elements, like potassium (K), iron (Fe), and zinc (Zn). It could also be an impotent factor to affect seedling growth. In *Phaseolus radiatus* and *Sorghum bicolor*, growth inhibition due to the AgNP addition was stronger when the plants were grown in a nutrient medium but not in soil system (Lee et al. 2012).

8.1.4 Biomass

Silver NP causes toxicity in plants to a greater extent, which can be assessed by analyzing physiological, biochemical, and structural traits (Tripathi et al. 2017b). Toxicity of AgNP can be seen right from seed germination to seedling growth and fully developed plant stage (Yin et al. 2011). It has been seen to invariably induce adverse impacts on growth and biomass accumulation of plants by reducing root elongation and proliferation. Several studies indicated that AgNP can only be toxic to plants when come in direct contact with their tissues. Tripathi et al. (2017b) recorded that AgNPs cause morphological modifications not only on the contact parts of the roots but also in the stem and leaves. Colloidal Ag showed higher inhibitory effect over biomass accumulation in *Cucurbita pepo* than done by bulk Ag (Hawthorne et al. 2012).

8.1.5 Cell Division, Elongation, and Expansion

Along with morphological amendments, AgNP-induced phyto-toxicity was also observed at the cellular and molecular levels. Studies have shown inhibition in plant growth after their exposure to AgNP, which may have caused due to the altered cell division and structure. Yin et al. (2011) observed that the seedlings of *Lolium multiflorum* failed to develop root hairs after exposure to AgNP. Moreover, the epidermis and root cap cells were damaged, and cortical cells were seen to be highly vacuolated and collapsed. However, reduction in size of the vacuole, cell turgidity, and cell size were observed in a number of AgNP treated species, like *Zea mays* and *Brassica oleracea* (Pokhrel and Dubey 2013; Tripathi et al. 2017b). Furthermore, Kumari et al. (2009) reported that exposure of *Allium cepa* to AgNP caused significant decrease in the mitotic index by impairing the cell division, possibly through formation of improper chromatin bridge at metaphase stage, multiple chromosomal breaks, stickiness, and cell disintegration. Similarly, increase in chromosomal aberrations, micronuclei formation, and decline in the mitotic index were observed in root tips of AgNP treated *Vicia faba*, which suggested that the cell cycle was greatly affected by applied nanomaterials (Patlolla et al. 2012). The study by Abdel-Salam et al. (2018) confirmed the root tip cell internalization of AgNPs in *Triticum aestivum.* Further, the root tip cells exhibited various types of chromosomal aberrations, such as chromosomal breakage, incorrect orientation at metaphase, fragmentation, spindle dysfunction, unequal separation, and distributed chromosomes, which seriously influenced the cell function. However, based on the proteomic study, it was hypothesized that AgNPs can inhibit cell division by condensing the DNA/protein due to the ill impacts of NPs on the metabolic processes like protein synthesis/degradation, etc. (Mirzajani et al. 2014).

8.2 Membrane Integrity

The integrity of plasma membrane can be defined as the eminence or state of absolute membrane in perfect condition. Studies revealed signs of oxidative stress and change in membrane structure after exposure to high concentration of AgNP. A study on AgNP exposed *Ricinus communis* seeds demonstrated an increase in ROS generation (Yasur and Rani 2013). In various algal species, mechanisms of AgNP toxicity depend on various processes occurring in the cells such as alterations in their permeability or ion transport properties which disturbs cellular phosphate management, ROS-antioxidant homeostasis, proton pump,DNA synthesis and leads to DNA damage, denaturation of ribosome, and inactivation of proteins and enzymes (Moreno-Garrido et al. 2015; Kwok et al. 2016; Taylor et al. 2016). Generation and accumulation of ROS may not be viewed as entirely negative, as it plays important signaling role and promotes root elongation up to a certain concentration. Antioxidant defense system of plant maintains the homeostasis between ROS generation and their scavenging during normal cellular metabolism (Ribeiro et al. 2014). However, during the stress condition the equilibrium between ROS and antioxidants gets perturbed; thus, this excessively accumulated ROS primarily affects the membrane integrity by reacting with lipid moieties and imposes irreversible damage that can lead to cell death (Li et al. 2015).

8.2.1 Cellular Membrane Damage

Silver NP-induced over-accumulated ROS and inefficient functioning or failure of ROS scavenging system cause oxidation of cellular macromolecules, namely, lipids, proteins, and nucleic acids, thereby altering the structures and functions of these (Taylor et al. 2016). Among these, lipids, particularly poly unsaturated fatty acids (PUFAs) of cell membranes, are quite sensitive to ROS, and peroxidation of membrane lipids is the major reason of phyto-toxicity (Oukarroum et al. 2012). Due to the dynamic nature of cell membranes, and the sensitivity of their lipid fractions toward biotic and abiotic stresses, changes in the membrane lipids serve as a stress marker (Kim et al. 2013). Membrane damage is sometimes taken as a single parameter to determine the level of cellular destruction under various stresses (Yin et al. 2012).

8.2.2 Release of Electrolytes

The ROS accumulation due to the AgNP treatment has shown to be related intimately with loss of membrane integrity, because of alterations in redox signaling and damage to macromolecules (Moreno-Garrido et al. 2015). Electrolyte leakage is a trademark of stress response in intact plant cells. It is ubiquitous among different species, tissue, and cell types. Accumulating evidence shows that electrolyte leakage is mainly related to K^+ efflux from cells, which is mediated by plasma membrane cation conductance. In moderate condition, K^+ efflux could play an essential role in metabolic switching for repair requirements, while in severe condition the dramatic loss of K^+ stimulates proteases and endonucleases and, promotes cell death (Demidchik et al. 2014).

8.3 Photosynthetic System

Toxicity of AgNP at the physiological level is predicted by reduction in chlorophyll content, decline in nutrient uptake, reduction in the rate of transpiration, and alterations in hormonal activities (Yan and Chen 2019). ROS and lipid peroxidation reaction were seen to be increased in AgNP treated plants, which were shown to inhibit photosynthetic pathways under elevated concentrations (Dewez and Oukarroum 2012). Accumulation of Ag and severe inhibition in photosynthesis was observed in seedlings of *Brassica sp.* after exposure to AgNP (Vishwakarma et al. 2017). Olchowik et al. (2017) also observed that plants treated with AgNP exhibited a disturbed ultrastructure of leaves, especially in the photosynthetic apparatus. Contradictorily to this, Farghaly and Nafady (2015) and Latif et al. (2017) observed that AgNP significantly promoted photosynthesis, which was closely related with change in the rate of nitrogen metabolism.

8.3.1 Chlorophyll Synthesis

Silver NPs can affect the photosynthesis adversely by disturbing the synthesis of chlorophyll. Exposure of *Skeletonema costatum* to AgNP decreased the cell viability and chlorophyll content due to an excess of ROS (Huang et al. 2016). Similarly, Nair and Chung (2014) and Al-Huqail et al. (2018) demonstrated decreased chlorophyll and carotenoids, shoot-root elongation, fresh weight and protein in *Oryza sativa* and *Lupinus termis* seedlings, respectively, after exposure to AgNP. Contradictorily, Racuciu and Creange (2007) reported that chlorophyll of *Zea mays* increased with low concentration of AgNP treatment while declined in response to higher concentration of it. Higher content of photosynthetic pigments, that is, chlorophylls and carotenoids, would increase the rate of photosynthesis, due to which there was more synthesis of photosynthetic products, which in turn increased the weight and growth of plant. Similarly, Govorov and Carmeli (2007) observed an induction in chemical energy production in photosynthetic systems due to the metal NPs.

8.3.2 Chloroplast Membrane

Chloroplasts are responsible for photosynthetic conversion of CO_2 to carbohydrates. In addition, it synthesizes amino acids, fatty acids, and the lipid components of their own membranes. Moreover, these are only one of the several types of related organelles (plastids) that play a variety of roles in plant cells. Plant chloroplasts are large organelles, bounded by a double membrane called the chloroplast envelope. In addition, chloroplasts have a third internal membrane system, called the thylakoid membrane. The thylakoids are formed by membrane network of flattened discs, which are subsequently arranged in stacks called grana. In leaves of *Arabidopsis thaliana*, AgNP caused disruption in membranous structure of thylakoid and decreased the chlorophyll content, and ultimately terminated the plant growth (Qian et al. 2013). Similar alterations in thylakoids, decline in chlorophyll, and disruption in essential elements of *Physcomitrella patens* were documented by Liang et al. (2013) in response to AgNP. Moreover, Olchowik et al. (2017) observed small plastoglobules on chloroplasts of non-treated *Quercus robur*, whereas larger starch granules in AgNP treated leaves.

8.3.3 Stomatal Conductance

Stomata are microscopic pores in plant epidermis surrounded by a pair of guard cells. Opening and closure of stomatal pore is regulated by change in guard cell turgor pressure. Reactive oxygen species are important signals involved in the regulation of stomatal movement (Song et al. 2014; Murata et al. 2015). Regulation of stomatal aperture requires coordinated functioning of ROS-generating enzymes, signaling proteins, and downstream executors such as ion pumps, transporters, and plasma membrane channels that control guard cell turgor pressure (Sierla et al. 2016). Stomatal opening can be promoted by activation of plasma membrane H^+-ATPase. Researches on well-known components including blue light receptors and plasma membrane H^+-ATPase regulating light-induced stomatal opening showed *AHA2* to be the major gene related to the stomatal opening process. However, accumulation of ROS in the apoplast and chloroplasts is among the earliest hallmarks of stomatal closure (Kim et al. 2015). During AgNP treatment, ROS accumulation directs the changes in gene expression and stomatal closure, with subsequent decline in the rate of transpiration, gaseous exchange, and water loss (Mattila et al. 2015). Due to the AgNP-induced stomatal closure, remarkable decline in the rate of transpiration was observed in *Cucurbita pepo* (Hawthorne et al. 2012).

8.4 ATP Synthesis and Energy Flow

Mitochondria provide majority of the energy required for proper cellular functioning; hence, any damage to it results in decreased or inefficient energy production and consequently hindrance in ATP-dependent cellular mechanisms (Maurer and Meyed 2016). Generation of intracellular ROS is postulated to be an important mitochondrial mechanism of AgNP toxicity and has been documented in cell too. Multiple mechanisms exist for AgNP-mediated ROS generation, including NP surface chemistry, depletion of antioxidant molecules via binding of dissolved ions with their thiol groups, altered production of ROS, and inhibition in the electron transport chain (AshaRani et al. 2009). Tripathi et al. (2017b) documented that in most cell types and under most circumstances, mitochondria are the major source of ROS production and also major target for oxidative damage, resulting in the mitochondrial specific dysfunction such as ATP production.

8.5 Nutrient and Water Uptake

In plants, uptake of nutrients is the principal process involving absorption of essential elements from the environment. Regulation of nutrient uptake has mostly been considered in relation to the factors that directly affect the rate of membrane transport. Nutrient uptake and transport through the cell membrane is an important task of all the living organisms. However, AgNPs significantly affect the membrane fluidity and permeability and consequently influence the uptake of water and nutrients. Decline in water content was observed, in dose-dependent manner, in seedlings of *Raphanus sativus* after AgNP treatment (Zuverza-Mena et al. 2016). They also observed the reductions in many plant nutrients like Ca, Mg, boron (B), copper (Cu), manganese (Mn), and Zn by exposure of AgNP, which ultimately affect the plants growth and development. Tips of primary roots are major sites of AgNP accumulation. However, plants mitigate this toxic effect of AgNP by forming lateral roots which compensate for the loss of primary root growth, continuing to absorb the water and nutrients that sustain a overall growth of plants (Pokhrel and Dubey 2013).

9 Genotoxic Effects of Silver Nanoparticles

Various studies have indicated that AgNPs possess the ability to affect gene expression and cause genotoxicity, which may be a serious concern for the ecosystem. A gene expression study following microarray suggested that exposure of AgNP to *Arabidopsis thaliana* led to the up-regulation of genes associated with various stresses (metal, salt, and oxidative stress), including the genes encoding antioxidants, whereas pathogens and hormonal stimulus related genes were down-regulated. Accordingly, a total of 286 genes were up-regulated whereas 81 genes were down-regulated in *Arabidopsis thaliana* after AgNP treatment (Kaveh et al. 2013). Among up-regulated genes in plants treated with AgNPs, the most remarkable ones are those involved in the thalianol biosynthetic pathway. Particularly, the operon-like gene clusters related to the thalianol pathway are of keen interest, because they are thought to be associated with plant defense mechanisms (Field et al. 2011). Interestingly, AgNPs posed down-regulated expression included genes related to ethylene signaling, other hormonal stimuli, and systemic acquired resistance against pathogens (fungi and bacteria). Another study on *Arabidopsis* *thaliana* has shown up-regulation in the expression of genes of sulfur assimilation and important antioxidants like glutathione-S-transferase (GST) and glutathione reductase (GR) upon exposure to AgNP (Nair and Chung 2014).

10 Tolerance Mechanisms of Plants Against Toxicity of Silver Nanoparticles

Phytotoxicity of AgNPs is coupled with oxidative stress, which is caused by excessive production and accumulation of ROS. Plants have several enzymatic and non-enzymatic defense mechanisms to avoid the detrimental effects of ROS. Enzymatic antioxidants/defense mechanism involves the activities of several enzymes like superoxide dismutase (SOD), catalase (CAT), ascorbate peroxidase (APX), guaiacol peroxidase (POD), dehydroascorbate reductase (DHAR), GR, GST, etc. (Tripathi et al. 2017b). As different types of ROS have varied modes of action and exhibit different effects on cellular organelles of plant cells, thus the homeostasis between ROS production and antioxidant protection is of great concern (Apel and Hirt 2004; Ma et al. 2015). Superoxide radicals are the first ROS, produced during cellular metabolism, which can rapidly convert into hydrogen peroxide by the action of an enzyme, SOD. There are three types of SOD in plant cells, which includes Fe-SOD, Mn-SOD, and Cu-Zn-SOD. Thus, produced hydrogen peroxide serves as a substrate for CAT, which converts it to water and oxygen. Another enzyme, APX, is also able to convert hydrogen peroxide to water via ascorbate oxidation into monodehydroascorbate (MDHA) and dehydroascorbate (DHA), both of which can be recycled to produce more ascorbate by the catalysis of MDHA reductase (MDHAR) and DHAR (Apel and Hirt 2004). Elevated activities of these enzymes were observed upon exposure of AgNP to protect the cells from oxidative stress. For example, increased activity of SOD was recorded to overcome the oxidative damage in seedlings of *Wolffia globosa* when exposed to AgNP, suggesting that the ROS-scavenging mechanism was activated (Zou et al. 2016). Similarly, elevated SOD activity was also observed after AgNP exposure in *Lycopersicon esculentum* (Song et al. 2013). Furthermore, enhanced activities of POD and CAT were also observed in *Bacopa monnieri* and *Spirodela polyrhiza* after exposure of AgNP (Jiang et al. 2012). Similarly, Bagherzadeh Homaee and Ehsanpour (2016) examined the effects of AgNPs on *Solanum tuberosum* and observed the enhanced activities of SOD, CAT, APX, and GR in AgNP-treated plantlets. Moreover, the SOD and POD activities and glutathione content were increased in a dose-dependent manner after exposure to 6 nm AgNP.

Non-enzymatic antioxidants include ascorbate, glutathione, anthocyanin, and thiols, which also contribute to the antioxidant defense mechanisms (Tripathi et al. 2017b; Rico et al. 2015). Anthocyanin is a type of pigment, associated with tolerance of various biotic and abiotic stresses, like drought, pathogens, ultraviolet radiation, cold, and heavy metals. It has the property of ROS scavenging and can chelate metal ions under metal stress conditions (Carocho and Ferreira 2013). Dose-dependent accumulation of anthocyanin was reported in *Arabidopsis thaliana* and *Brassica rapa* after AgNP exposure (Syu et al. 2014; Thiruvengadam et al. 2015). However, other antioxidants such as carotenoids, ascorbic acid, and proline are also implicated in antioxidant defense responses of plants to AgNPs (He et al. 2011). After AgNP exposure, an increase in shoot carotenoid content was observed in *Oryza sativa*, suggesting that plants employ it to reduce the effects of ROS (Mirzajani et al. 2013). Likewise, an increase in ascorbic acid content was observed in *Asparagus officinalis* in response to AgNP treatment (An et al. 2008).

At the molecular level, the expression patterns of genes associated with response to AgNPs may induce the antioxidant defense mechanisms of plants upon treatment of AgNP. Transcription of a gene encoding metallothionein, a cysteine-rich protein, involved in detoxification and sequestration of metal ions was found to be highly induced after AgNP treatment in *Triticum aestivum* (Dimkpa et al. 2013). Similarly, differential transcription of genes associated with oxidative stress tolerance, such as SOD, CAT, and APX, was observed in shoots and roots of *Oryza sativa* after AgNP exposure (An et al. 2008).

11 Silver Nanoparticle as Ameliorative Molecule Against Other Toxicity

The combined effects of AgNPs with other treatments (heavy metal, salt stress, pathogens) were observed in various studies, which showed diverse impacts on different plant species (Berahmand et al. 2012). Treatment of AgNP in combination with magnetic field improved growth and yield of *Zea mays* (Berahmand et al. 2012). Moreover, Belava et al. (2017) observed the oxidative stress condition and enhancements in lipid peroxidation after alone treatments of AgNP and infectious agents (pathogens) in *Triticum aestivum*. However, the combined treatment of AgNP and plant-pathogenic fungi showed the reverse impact and eliminated this organism, due to the fungicidal activity of AgNP (Jo et al. 2009). Traces of essential heavy metals such as Cu, molybdenum (Mo), and Zn can be necessary for plant metabolism, but their excess can harm plant growth and development. However, non-essential heavy metals are toxic for plant metabolism and have damaging effects, even if available in trace amounts, on enzyme activity, photosynthetic properties, cell membrane permeability, and plant growth (Emamverdian and Ding 2017). Yadu et al. (2018) reported ameliorative impacts of AgNP on the growing radicles of *Cajanus cajan* against fluoride (F^-) toxicity. Exogenous application of AgNP under fluoride stress not only down-regulated the expression of NADPH oxidase gene and lipoxygenase activity but also promoted the membrane stability, percent germination, and growth by reducing the levels of ROS. Moreover, AgNP unveiled enhancement in F^- stress tolerance through up-regulation of stress responsive gene like pyrroline-5-carboxylate synthatase and increased the synthesis of proline in *Cajanus cajan* radicles. Additionally, enhanced levels of defensive components such as glutathione, glyoxalase I, glyoxalase II, and lower malondialdehyde also approved the ameliorative abilities of AgNP to F^- stress. Likewise, toxic impacts of arsenic (As), cadmium (Cd), and Cu were compared with their combinations made with citrate-coated AgNPs (c-AgNPs). The surface of c-AgNP has negative charge, which interacts with the surface of heavy metals and affects metal toxicity in aquatic environment. The acute toxicities of As and Cu were not affected by the addition of c-AgNPs, while significant decline in bioaccumulation was observed. In contrast to this, the presence of c-AgNPs increased both the acute toxicity and bioaccumulation of Cd. The diverse toxicity and bioaccumulation pattern can be attributed due to the altered interactions between the AgNP surface and the heavy metals. The As and c-AgNPs compete due to the negative charge on their surfaces, while Cu adheres to the surface of c-AgNP, consequently decreasing the toxicity and bioavailability of As and Cu, respectively (Kim et al. 2016).

12 Conclusions and Future Prospects

Nanoparticles have recently been exploited in immense applications including agricultural system, but due to their size, toxicity, and reactivity with the several environmental factors, the dispersion and permeation of NPs into the ecosystem pose a challenge for the researchers. A great concern is arising related to the potential risk of human health, destruction in the ecosystem, decline in the food quality and yield due to AgNPs. Thus, the development of understanding about transfer of AgNPs through the ecosystem and their impacts on plants is of crucial importance. During the last decades, the researchers undertook the responsibility to increase the knowledge about the possible impacts of AgNPs on plants following various studies. Most of these studies revealed the detrimental effects of AgNPs on plants in various aspects including, anatomical, cellular, morphological, physiological, and molecular levels. However, positive impacts of AgNPs were also reported by few on the plants' growth and development. These contrasting results indicated the complexity of the responses of plants to AgNPs, which are not only dependent on the properties of AgNPs (size, shape, concentration, source of Ag, and reducing agents, etc.) but are also determined by the plant system used (species, developmental stage, organ, tissue, etc.) and the methodology of experiments (exposure method, medium, exposure time, etc.). From various studies it is clear that the NPs play divergent role and can positively or negatively influence the morphological or physiological traits of the plants.

Different detoxification strategies were employed by different plant species to eliminate the toxic effects of AgNPs. Therefore, it is difficult to make a general conclusion about the tolerance mechanism of different plants species in response to AgNPs. To address this issue, it is necessary to use representative species, such as the commonly used model plant *Arabidopsis thaliana*, to evaluate the phyto-toxicity of AgNPs and tolerance mechanisms. Meanwhile, the establishment of a standardized protocol is required to conduct the experiments, thereby allowing comparisons between different plant species.

Most of the experimental outcomes were based on controlled conditions (laboratory experiments), which are very different from field conditions with respect to growing media (hydroponic vs. soil), treatment time (acute vs. chronic), and exposure dosage. Therefore, it is hard to predict the response of same plant species under two distinct growing conditions (laboratory and field conditions) against exposure of AgNP. Consequently, the establishment of well-designed, plant life-cycle based experimental system is required to accurately mimic the impacts of AgNPs on plants and to generate environmentally relevant implications.

Most of the studies performed during the last decade focused on the morphological and physiological impacts of AgNPs on plant systems. However, profound impacts of AgNPs at the molecular level did not draw enough attention. Thus, more extensive and detailed studies are needed to explain the mechanisms and factors behind this unexplored research area. Therefore, systems biology and multiple omics methodologies (transcriptomics, proteomics, and metabolomics) can be employed in future studies to assess the phyto-toxicity and tolerance mechanisms of AgNPs and plants, respectively.

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Nanoparticles: Sources and Toxicity

Dhriti Kapoor and Mahendra P. Singh

1 Introduction

Nanoparticles (NPs) in various application domains signify vigorous research areas and techno-economic fields with wide extension. NPs have earned eminence for the improvement in technology because of certain physicochemical properties like their wettability, melting point, electrical and thermal conductivity, light absorption, etc., which trigger their increased performance (Jeevanandam et al. 2018). They are 1–1000 nm in one dimension; on the other hand, they possess the diameter of 1–100 nm.

Various organizations have defined nanoparticles differently. According to the Environmental Protection Agency (EPA), these particles possess inimitable characteristics different from the corresponding chemical compound in a wide aspect". The U.S. Food and Drug Administration (USFDA) considers nanoparticles as "particles having at least one aspect about 1 to 100 nm range" (FDA 2011). In the same way, the International Organization for Standardization (ISO) demonstrated them as a "material having exterior nanoscale dimension" (ISO/TS 2010). Nanofibers, nanowires, nanoplates, quantum dots, and interrelated terminology have been used by the ISO based on the above-mentioned statement (Bleeker et al. 2012). Similarly, according to the EU Commission, "nanoparticles are synthesized or natural particles having unregimented, aggregated particles where exterior dimensions range between 1–100 nm" (Potocnik 2011).

Richard Feynman, Norio Taniguchi, and Eric Drexler introduced the fundamental concepts of nanotechnology in the mid-twentieth century, where extensive literatures on nanoparticles were collected and intricate. Considerable advancement in materials like fullerene and carbon nanotubes (CNTs) triggers the progress of

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methodology and apparatus for the characterization of nanoparticle (Maskos and Stauber 2011). After getting inspiration from these strategies, various scientists currently support nanoparticles with some new advanced features over redundant massive particles. In the starting of 2000s, these particles initiated to intensify their influence on day-to-day life's common requirements like furniture, food, clothing, cosmetics, etc. For example, nanoparticles, namely titanium dioxide (TiO_2), act as a chief constituent of sunscreen lotion, which contributes in protecting the skin against harmful ultraviolet (UV) radiations. Besides, silica dioxide (SiO_2) is commonly utilized as a food additive to reduce viscosity and control acidity. Due to anti-microbial and light-weight properties, silver (Ag) nanoparticles and carbon nanotubes (CNTs) are widely used in cleansers and as sporting tools (Lewinski et al. 2008).

Cytotoxicity due to nanoparticles is caused by various factors. In some cases, cytotoxicity of nanoparticles is due to the substance itself, but sometimes they do not show clear mechanism (Favi et al. 2015). Nanoparticles of some specific materials considered to cause higher risks than bulky particles made up of same material (Napierska et al. 2009). Ingestion, absorption, and inhalation of these particles through the skin lead to the production of reactive oxygen species (ROS), which include free radicals (Brown et al. 2002). The formation of ROS leads to oxidative stress, inflammation, and consequently deterioration of protein and nucleic acids like RNA, DNA, etc. The factors apart from free radicals, including size, shape, chemical composition, solubility, etc., affect their toxicity (Holsapple et al. 2005). Structural damage of mitochondria or DNA mutations by invasion is commonly caused due to their smaller size as small-sized particles can enter into the tissue junctions (Salnikov et al. 2007) and consequently lead to death of the cell (Wilson 2006). The above-mentioned factors can be classified on the basis of five main features of nanoparticles including morphology, size, surface area, agglomeration status, and electrostatic nature of surface (Shin et al. 2015).

2 Categories of Nanoparticles

Nanoparticles are classified on the basis of their origin apart from dimension and material; they are broadly classified as natural or synthetic based on their origin. Natural nanoparticles (NPs) are produced in nature either by biological species or through man-made activities. The production of artificial surfaces with micro- and nano-scale settings and merits for technological applications are generally available from natural sources. Naturally occurring NPs are present in the Earth's spheres like in the hydrosphere, atmosphere, lithosphere, and also in the biosphere. The Earth is comprised of several NPs that are naturally formed and are present in the atmosphere (Earth's spheres), including comprised of rocks, soils, magma, or lava during evolution and the biosphere, covers micro-organisms and even higher organisms, including humans (Hochella Jr et al. 2015; Sharma et al. 2015). In case of synthetic (engineered) NPs, these are produced by mechanical grinding, automobile exhaust, and smoke or are synthesized through biological, physical, chemical, or hybrid methods. The major challenge among engineered NPs is whether existing knowledge is enough to forecast their behavior, or if they exhibit a distinct environment-related behavior, different from natural NPs. Currently, different sources related to potential applications are being used for the production of engineered NPs (Wagner et al. 2014).

2.1 Developmental History of Nanoparticles

For over 4500 years, humans have been exploiting the strength of ceramic matrices along with natural asbestos nanofibers (Heiligtag and Niederberger 2013). Even the ancient Egyptians were also utilizing nanoparticles excessively for more than 4000 years, which was based on a synthetic chemical process to form about 5 nm diameter PbS nanoparticles for the purpose of hair dye (Walter et al. 2006). Likewise around third century BC, the first synthetic pigment was “Egyptian blue,” which was utilized by Egyptians with the help of sintered mixture nanometer-sized glass and quartz (Johnson-McDaniel et al. 2013). During archeological explorations it was observed that Egyptian blue was excessively used in ancient geographical regions of the Roman Empire, which also included the countries like Egypt, Mesopotamia, and Greece. The thirteenth and fourteenth centuries BC were considered as the beginning of the metallic nanoparticle epoch, when Egyptians and Mesopotamians initiated the work of making glass by the use of metals and hence synthesized the metallic nanoparticles through chemical methods. Such materials were the earliest examples of synthetic nanoparticles in context with the practical applications. From the Late Bronze Age (1200–1000 BC) in Frattesina di Rovigo (Italy) red glass was observed which was dyed by surface plasmon excitation of Cu NPs (Artioli et al. 2008).

Reports suggested that the Lycurgus Cups possess Ag–Au alloy nanoparticles, with a ratio of 7:3 along with approximately 10% Cu. Afterwards in medieval period churches, red and yellow stained glasses were formed by adding colloidal gold and silver nanoparticles, correspondingly. For decoration with metallic luster in the ninth century, Mesopotamians had initiated the use of glazed ceramics (Heiligtag and Niederberger 2013). These decorations led to astonishing optical features due to the presence of divergent Ag and Cu NPs extracted from the furthest glaze layers. Such decorations included metal nanoparticles that showed gleaming bright green and blue colors under specific reflection. Twofold layer of silver nanoparticles with 5–10 nm in the outer layer and larger ones with 5–20 nm in the inner layer were examined by transmission electron microscope. Michael Faraday in 1857 investigated the production of colloidal Au NP solution, which is considered as the first scientific demonstration to show the formation of nanoparticles, and started their development in the scientific field. According to Faraday, optical properties of Au colloids are different in comparison to their corresponding volume counterpart (Leonhardt 2007).

Properties of heavy particles like their strength, buoyancy, conductivity, and durability can be greatly improved by synthesized nanoparticles, and hence they can possess some beneficial characteristics such as antibacterial, anti-freezing, auto-healing, and auto-cleaning. Therefore, these can work as a strengthening matter for the manufacturing intelectin constituents for the purpose of safety (Déry et al. 2008). The industrial utilization of nanoparticles is generally restricted to the bulky particles which remain implanted in an inactive matrix, lead to the formation of nanocomposite. Reports mainly emphasized the synthesis of increased Earth-based astronomical telescopes in addition to adaptive optics and magnetic mirrors along with the ability of translocating the shape which is manufactured by ferrofluids. TiO_2 nanoparticles are mainly utilized in solar cells and having dye-sensitization capability which showed first crucial utilization of dye-sensitized solar cells. In the pharmaceutical industry, Abraxane™ was synthesized, commercialized, and released in 2005 that acted as a human serum albumin nanoparticle having paclitaxel (Kreuter 2007). Approximately 1814 nanotechnology-based consumer products were commercially accessible in 2014 over 20 countries (Vance et al. 2015).

2.2 Synthesis of Nanoparticles

Nanoparticles can be majorly synthesized by two prominent methods:

1. Chemical synthesis
2. Green synthesis

Nowadays green synthesis of nanoparticles is the main focus because it is an eco-friendly technique for the production of well-characterized nanoparticles. It does not require stabilizing agents as biomolecules present within the organisms that stabilize it during the synthesis process.

Green synthesis is cost-effective. Silver nanoparticles are nontoxic to human beings but effective to bacteria, viruses, and microorganisms. Green synthesis using plants is a protective method and beneficial over chemical and physical method but, however, can be used for small-scale synthesis of nanoparticles only. To produce large quantity of nanoparticles is not easy. Chemical methods are not suitable for biological activity due to its toxicity.

Different categories come under the biological approach. In this approach nanoparticles are synthesized from the bacteria, fungi, algae, and plant materials (Mukherjee et al. 2001; Koul et al. 2018). In green approach, completion of synthesis of nanoparticles requires two main agents: (1) reducing agent and (2) capping or stabilizing agent. Both agents are compulsory for the biosynthesis of nanoparticles (Singh et al. 2011). Three steps are required in green synthesis of NPs: (1) selection of the solvent medium, (2) selection of eco-friendly material, (3) selection of reducing and chemical agents for the completion of synthesis (Mohanpuria et al. 2008).

In biological approach, synthesis of different types of nanoparticles from plants requires very simple protocol as compared to synthesis of nanoparticles by bacteria and fungi, because maintenance of bacteria and fungi culture requires highly complex protocol, whereas in case of plants, sample can be collected directly for study. No doubt fungi and bacteria are also used for the biosynthesis of NPs, but plant sources are the best for biosynthesis of NPs because phyto-synthesized NPs have several advantages. Plant material can be easily collected, and also it can be handled easily. Plants can also be used in the biosynthesis of NPs on a large scale (Sastry et al. 2005).

2.3 Sources of Nanoparticles

Nanoparticles are abundant in nature, as they are produced in many natural processes, including photochemical reactions, volcanic eruptions, forest fires, erosion, and also through animals and plants, like shedding of skin and hair. They are also produced through anthropogenic activities that are associated with air pollution, namely, cars, burning of charcoal and industry pollutants. Major natural sources of NPs like dust storms, volcanic eruptions, and forest fires can produce vast quantities of NPs matter, and it profoundly affects air quality across the globe. Ninety percent aerosols of NPs are having natural origin whereas 10% is generated through human activities (Taylor 2002).

A. Natural sources of nanoparticle exposure to the environment:

   1. Dust storms
   2. Forest fires
   3. Volcanic eruptions

B. Anthropogenic sources of nanoparticle exposure to the environment:

   1. Diesel and engine exhaust
   2. Indoor pollution
   3. Cigarette smoke
   4. Building demolition
   5. Cosmetics and other consumer products
   6. Engineered nanoparticles

The combustion during cooking and fuel oil in vehicles, burning of coal for power generation (Linak et al. 2000), chemical manufacturing, airplane engines, welding, ore refining, and smelting are some of the major anthropogenic activities that lead to excessive production of NPs. Nanomaterials such as carbon NPs, TiO_2 NPs (Weir et al. 2012), and hydroxyapatites (Sadat-Shojai et al. 2010) are present in commercial cosmetics, sunscreen, sporting goods, and toothpaste. Therefore, these artificially synthesized NPs are new-generation NPs that may significantly impose adverse effects on the environment and human health (Fig. 1).

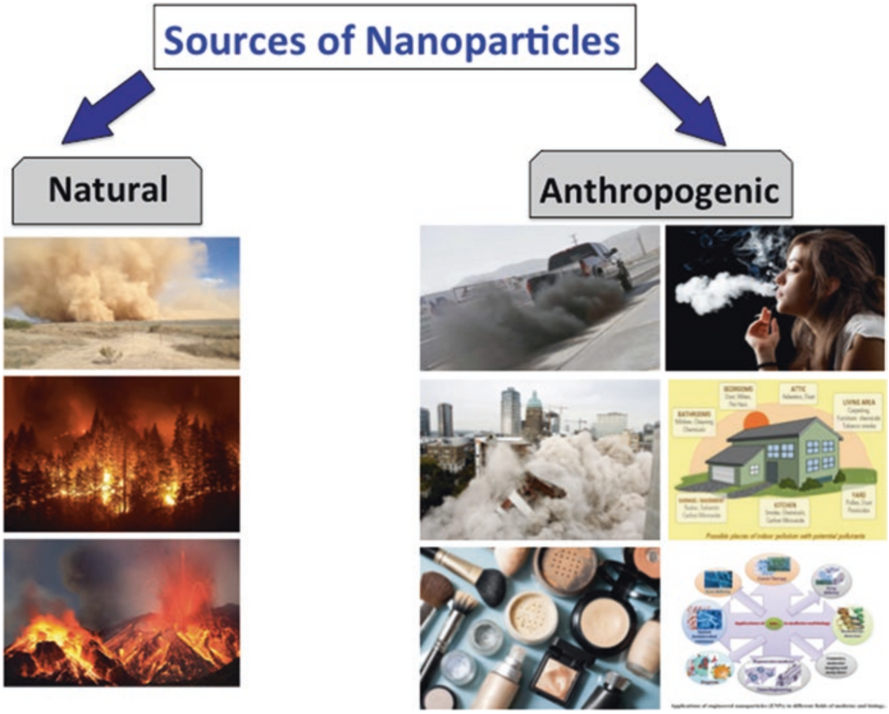

Fig. 1 Different sources of nanoparticle presence in the environment through natural and man-made activities (adopted and modified after Xue et al. 2016)

3 Occurrence of Nanoparticles in Different Organisms

3.1 Nanoparticles in Plants

Nanoparticles are present on the plant surfaces, specifically on the leaves, which has a large number of applications like sliding of insects, enhancing visible radiation and hazardous reflection of UV light, and mechanical stability (Pfündel et al. 2008). Superhydrophobicity is a unique property of nanoparticles in plants, specifically in the leaves of lotus, which contributes in self-cleaning and super-wettability (Bargel et al. 2006). Reports indicated that nanoparticles contribute for the circular layer in plants and insects that leads them to float on water without sinking (Nguyen et al. 2014; Xue et al. 2016). According to literature, various synthesized superhydrophobic particles having self-cleaning capacity have been constructed (Zhang et al. 2012) via different strategies like colloidal systems electrodeposition and photolithography (Chow 2007) including critical appearance and coarseness (Koch and Bathlott 2009). Such superhydrophobic particles were helpful in applications like water treatment (Cong et al. 2012), smart actuators (Zang et al. 2013), transparent coatings, and electrodes (Wang et al. 2015) etc.

3.2 Nanoparticles in Animals and Birds

Living organisms with different body weight like flies, spiders, and geckos can fix with the ceilings and move along with vertical walls. Their surface structures possess some pattern, which is having correlation with the profile of substrate, consequently leading to capability and strategy to attach with the walls. Strong contrary scaling effect through the widespread microscopic observation is explored in the attachment devices (Autumn et al. 2000). Research was initiated on the mechanism of fixation and movement of insects on the vertical walls by the use of their hairy appendages 300 years back. Certain specific features like microsuckers, electrostatic forces, and sticking fluids are the main factors that explain the attachment mechanism. Certain data generated from experiments and combination of capillary attractive forces induced due to secretion and molecular or van der Waals interaction which cause adhesion lead to rejection of the theories (Autumn et al. 2002). Secretary fluids are thus synthesized by certain animals, specifically at the junction that causes the fundamental force which creates adhesion physically. Evidences indicate that van der Waals interaction mechanism replaces the capillary adhesion in case of gecko setae (Arzt et al. 2002).

Nacre is a hierarchical nanocomposite, possessed by mollusk shells, which is invented by interchanging micro and sub-micrometer sized calcium carbonate aragonite platelets that lead to separation by glue, a thin layer of bio-macromoles. Properties like strength and stiffness make the specific pattern of nacre advantageous. Correspondingly, crystalline structure of calcium carbonate composite and proteins, which are arranged in a column and layers of calcite, leads to the formation of thin and strong eggshell. At the time of production of eggshell, calcium carbonate nanoparticles take a lead as an amorphous material, further amended by c-type lectin proteins into well-arranged crystals. Makeover of the crystal is started by connecting the proteins with ACC NPs and with the growth of crystals it separates (Freeman et al. 2010).

3.3 Nanoparticles in Insects

Wings of insects are made up of 0.5 μm to 1 mm thick building materials. Moreover, the wings of insects are made up of complicated vein system that gives great stability to the wing structure (Moussian 2010). The fundamental framework of the insect wings is made up of long chains of crystalline chitin polymer. Wings' elasticity is improved by resilin, an exclusive constituent acting as an intermediate of vein and the wing (Ditsche-Kuru et al. 2012). Vein system with light-weighted wing matter supports regular and longer migration flights (Watson et al. 2010). Surfaces of the insect wings are described as coarse and well-managed structure, which is composed of micro- and nanoscale characteristics to reduce their mass and provide protection against pollutants and moisture. Setae, fractal, and denticles explain the features of wax crystals generally present on the wing surfaces. Setae possess hairy appendages, whereas denticle ranges from minor hemispherical to longer fractal, whereas nanoscale fine protrusions are considered as pillars (Byun et al. 2009).

Reports suggested that the wings of wood termite and cicada are covered by denticle layer, whereas wings of hornet are enclosed by large number of setae. These are not superhydrophobic as the water contact angles are examined to be less than 150° in both the structures (Sun et al. 2012). The literature revealed that species having refined fractal and layered cuticle structure comprised of superhydrophobic characteristics. Such structures are comprised of the hierarchical structure, which further contributes in enhancing the surface hydrophobicity. Furthermore, colors in the butterflies are complemented with their nice structure of wings. In reality, they consist of nanoparticles in multiple layers that play significant role in stimulating interference, diffraction gratings, and subsequently iridescence (Boulenguez et al. 2012).

3.4 Nanoparticles in Human Body

The human body possesses certain nanoparticles for its proper functioning. Certain nanostructures like proteins, DNA, enzymes, and bones lead to the formation of human body. Bone has been classified as a nanoparticle which possesses organic collagen and inorganic nanohydroxyapatite (Gong et al. 2015). Moreover, bacteria, viruses, etc. like microorganisms are such nanostructures that lead to outbreak of disease in human beings. The architectural pattern of bone ranges from nano- to macro-scale size and possesses unique mechanical features. Through passive mechanical force involving significant stem cell behavior lead to the interaction between the extracellular matrices with the nano- to macro-scale constituents. The main structure of extracellular matrix is made up of structural protein spectrum and polysaccharides of varied length including nanometer-sized collagen fibril strands of approximately 35–60 nm diameter and a micrometer range length (Li et al. 2013).

Storage strategies for different sequence data is about 2.86 bits per linear nanometer density (Becerril-Garcia 2007). On the basis of base pairing between the strands, DNA can be classified into three categories: A-DNA, B-DNA, and Z-DNA. In organisms, these are considered as nanostructures, and these play a crucial role in the synthesis of drugs when interacted with other nanoparticles. Therefore, in bionanotechnology field, research on the synthesized nanoparticles has been stimulated from last few years. For the production of self-assembled structure of nanoparticles, nucleobases, hydrophobic core, and phosphate backbones having metal chelates, aromatic rings, and negative charges, respectively, play major role via interaction with inorganic nanoparticles (Becerril-Garcia 2007). Nanostructures include certain organelles, antibodies, proteins, and enzymes, which are having lesser size when measured on micrometer scale. Currently the presence of lipids, certain auto-assembled peptides, and polysaccharides in humans also has been involved in nanostructures (Wang et al. 2016).

4 Nanotoxicity: Toxicology of Nanoparticles

Recordati et al. (2016) conducted an experiment to investigate the toxicity and tissue distribution of silver nanoparticles (Ag NPs) when administered intravenously in mice. For this experiment, they took the size and coating of the silver nanoparticles into consideration. They used three different sizes, that is, 10, 40, and 100 nm, and two different coatings, that is, citrate and polyvinyl pyrrolidone (PVP). They also used silver acetate as a control to compare and establish if the toxicity of nanoparticles is due to dissociation of silver nanoparticles into silver ions. After intravenous administration, they observed acute toxicity within 24 hours in case of 10 nm sized particles, and toxicity decreased with increase in the size of nanoparticles. Silver nanoparticles of all sizes and coatings caused splenic hyperemia, while silver acetate caused renal lesions. Localization of silver nanoparticles was observed mostly in spleen and then in lungs, liver, and finally in kidneys and brain. Localization was regardless of the size or coating. However, maximum redistribution from organ to blood was shown by 10 nm sized nanoparticles. Toxicity and tissue distribution were regardless of coating. In case of silver acetate, the maximum localization was found in liver. It is evident in literature that the dissolution of silver nanoparticles is low in mouse serum due to the formation of protein corona (Shannahan et al. 2015). All these results employ that the toxicity and localization of nanoparticles is not due to their dissolution into silver ions but due to their nanoparticulate form in the blood (Fig. 2).

Pratsinis et al. (2013) investigated the in vitro cytotoxicity of Ag NPs on murine macrophage cell lines as these cells form first line of defense. They used particles with size varying from 5.7 to 20.4 nm. Uncoated NPs supported by a nanostructured SiO_2 were used so that coating will not interfere with the release of silver ions. The experiment was conducted with the vision of comparing the toxicity caused by both dissolved silver ions and nanoparticles in suspension with respect to the size of nanoparticle. They prepared three concentrations for this experiment: 5, 10, and 20 mg/L.

At the concentration 5 mg/L, the suspension containing nanoparticles with size ranging from 5.7 to 7.8 nm showed more toxicity as compared to suspension containing nanoparticles with size 11.5 nm or more. At 10 mg/L concentration, cytotoxicity increased as compared to 5 mg/L for all the suspensions containing both particles and ions, but for suspensions with no particles, only with suspension with small nanoparticles (<10 nm) showed significant cytotoxicity. At 20 mg/L, cell viability was reduced by all the samples, except for the suspension with nanoparticles of size 12.6–20.4 nm containing no particles. Observing these results, they concluded that the toxicity of small-sized nanoparticles is owed to the dissolved silver

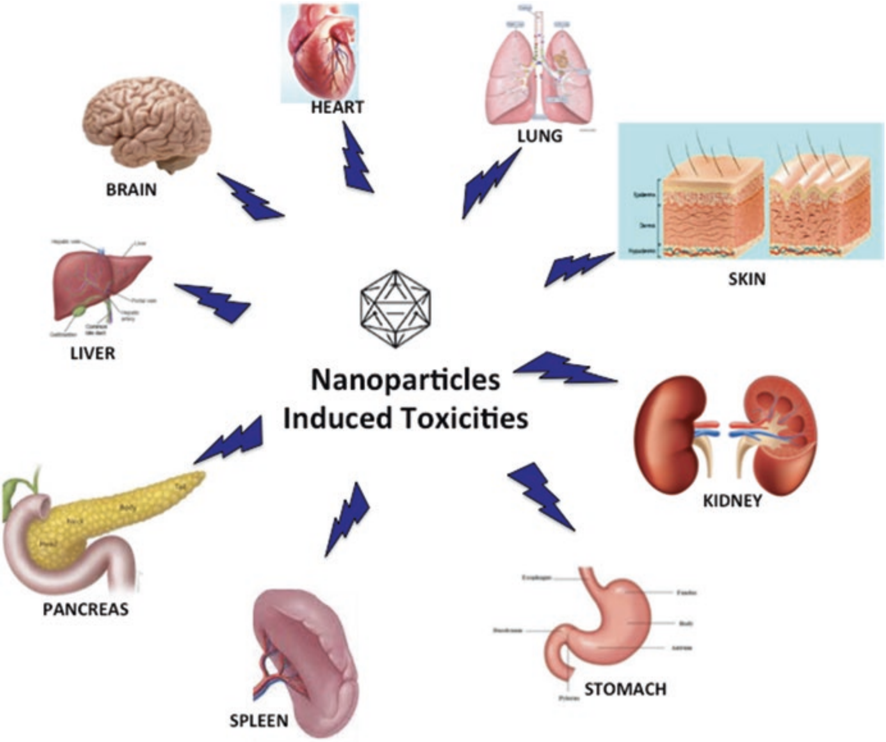

Fig. 2 Nanoparticle induced toxicities: different important target organs in the human body against various nanoparticles (NPs) (adopted and modified after Asharani et al. 2008)

ions, whereas with increasing size, the toxicity of these nanoparticles gets attributed to their direct interaction with cells, rather than initial release of ions.

Navarro et al. (2008) carried out a study to examine the toxic effects of silver nanoparticles on the photosynthesis in Chlamydomonas reinhardtii. The purpose of this study was to determine what fraction of this toxicity was caused by silver ions. For this purpose, they used cysteine as a ligand that would bind to silver ions and inhibit their effect. They also used $AgNO_3$ as a positive control. The use of cysteine did not cause any effect on the toxicity suggesting the complexation of Ag^+ ions. In case of silver nanoparticles, to determine the toxicity due to silver ions, a range of cysteine concentrations was used. They used concentrations from 10 to 100 nm on 40 nm particles. They observed that the toxicity was completely abolished at a concentration of 100 nm, suggesting that Ag^+ ions have a determinant role in toxicity of silver nanoparticles, and that this toxicity was not solely dependent on the physical and chemical characteristics but also on their biological interaction with the algal media.

Asharani et al. (2008) conducted an experiment to demonstrate the toxic effects of silver nanoparticles in zebra fish (*Danio rerio*) larvae. They synthesized and capped nanoparticles with either starch or bovine serum albumin to make them water soluble. Size was characterized by TEM and was found to be 5–20 nm, on an average. The exposed zebra fish larvae were observed, and it was found that toxicity was concentration dependent. Also, the toxicity resulted in various phenotypic abnormalities, such as twisted notochord, cardiac arrhythmia, abnormal body axis, etc.

van der Zande et al. (2012) demonstrated the toxic effects of silver nanoparticles in rats on oral exposure. Two different kinds of nanoparticles were used; one of them being <20 nm in size and uncoated, and the other being <15 nm in size and PVP coated. Rats were also exposed to $AgNO_3$ to check the toxicity due to silver ions. The rats were exposed for 28 days. Accumulation of silver nanoparticles was highest in liver, and spleen was observed which is similar to previous studies (Loeschner et al. 2011). The rats were dissected on the 29th day and cleaned for 2 months to observe the accumulation, and it was observed that the accumulation disappeared from all organs after 2 months of cleaning, except from brain and testis. This accumulation of silver nanoparticles was not only found in nanoparticle-treated rats but also in $AgNO_3$-treated rats, suggesting that there was an in vivo synthesis of nanoparticles inside the rats.

Kawata et al. (2009) studied the effect of silver nanoparticles in human hepatoma cell lines, Hep G2. They used silver nanoparticles sized 7–10 nm and polystyrene nanoparticles (15 nm) and silver carbonate for comparison of toxicity. They observed that up to the concentration of 0.5 mg/L, no cytotoxicity was observed in any of the treated cell lines; instead there was an increase in cell viability as compared to non-treated cells. However, when the cell lines were treated with a concentration of 1 mg/L, no cytotoxicity but abnormality in cell morphology was observed. The cells apparently shrunk and became irregular in shape. In the presence of cysteine, no cytotoxicity was observed, even at high concentrations of nanoparticles, but cell morphology still changed.

Recently, Fröhlich (2016) has reviewed an in vitro study to show the comparative toxicity of silver nanoparticles in the enterocytes (intestinal cells) and gut microbiota (*E. coli*) of rats. For this study, they used nanoparticles present in consumer products so that they have the antimicrobial activity. Both cells and bacteria were exposed to nanoparticles for 24 hours. To determine the comparative toxicity, the EC50 concentration was used as a common indicator. They observed that the bacteria are more susceptible to the nanoparticle toxicity as compared to enterocytes, even at low concentrations, because enterocytes have a thick mucus coating on their surface. It was also established that smaller nanoparticles were more toxic as compared to larger ones. However, they concluded that these results could vary in humans due to difference in species, gastrointestinal pH, composition of gut microbiota, etc.

5 Regulation of Nanoparticles

Nanoparticles possess certain unique characteristics like higher bioavailability, penetration up to cells, tissues, and organs, and higher chemical reactivity. Due to such exclusive features, nanoparticles are considered advanced in various biomedical applications. Nevertheless, these advances of nanoparticles are also possibilities for their impending toxicity. Therefore, through the implementation of certain rules, laws, or legislation by the government agencies, toxicity risks of these nanoparticles can be avoided up to a certain level. To introduce the nanoparticles in the biomedical field, certain medical standards regarding ethics, safety of environment, and medical governance have been customized. Nowadays, the United States and the European Union (EU) are well-known regulatory bodies and possess guidelines legislation to regulate the probable risks of nanoparticles. The legislation has been implemented in the EU countries so as to certify compliance across legislative areas and to guarantee that in those countries nanoparticles in one zone will also be treated like the another sector where it is used (Marchant et al. 2009).

In case of cosmetics, regulations are implemented by Cosmetic Act (FFDCA), Personal Care Products Council (PCPC), USFDA's Federal Food, EU cosmetics product notification portal (CPNP), REACH, Scientific Committee on Consumer Safety (SCCS), etc. Countries like Japan and Canada along with the United States and EU reported that nanoparticles produced from these cosmetic products create major risks, and this is a critical issue for both scientific policymakers and various industries who manufacture them (Johnson 2016). These policies also included the way to avoid the hazardous impacts of nanoparticles produced from various sources like cosmetics, food, etc. These recommendations suggest the industries to approve elaborated policies related to the use and publish the safety measures (Nanomaterial Fact Sheet, U.S.A. 2015).

At the same time, educating researchers and manufacturers regarding the regulatory laws and legislations before the synthesis of nanoparticles should be mandatory so as to avoid the different types of bans against them. Recent studies indicate that all the nanoparticles are not inherently detrimental, while several among them are not toxic, and even few of them also possess some favorable impacts on health. But still, risk assessment should be able to find out whether a particular nanoparticle and its product may be harmful in future or any needful actions are required.

6 Conclusion

Nowadays, nanoparticle toxicity profiling has been considered as a highly demanded area of research. Naturally existing nanoparticles have been in the environment for many years, which cause very mild effects on the living organisms. Reports suggest that such nanoparticles may cause acute toxicity in living beings. In the present review article, it is emphasized that these nanoparticles have originated from various anthropogenic conducts, which further trigger the deleterious influences on the ecosystem. Various physicochemical features of nanoparticles should be observed to examine their interactions at cellular and subcellular levels. Such type of research will lead to the development of advanced technologies for synthesizing harmless nanoparticles and hence spawn the criteria for the smart designing of nanoparticle that can be utilized in vivo. Apart from this, various rules and regulations have been implemented in various countries to reduce the detrimental effects of engineered nanoparticles. Thus, to recognize the nanoparticles and reduce their toxicity, extensive research in this field is required along with following the strict rules and regulations implemented by the government.

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Impact of Silver Nanoparticles (AgNPs) on Plant Systems

Dhriti Kapoor and Mamta Pujari

1 Introduction

Nanoparticles (NPs) possess certain unique characteristics, such as their size, shape, and appearance, by which they are able to interact with plants, animals, and microbes (Husen and Siddiqi 2014). Out of different nanoparticles, silver NPs (AgNPs) are the majorly utilized nanomaterial. Reports suggest that 25% of the products used in the field of nanotechnology include AgNPs (Siddiqi and Husen 2016a). As these nanoparticles possess antifungal characteristics, they can be utilized in day-to-day products such as clothing, household products, packing of food, medicines, antiseptics, and other healthcare products (Siddiqi and Husen 2017). They also play a significant role in the management of wastewater and electronic instruments as they are considered a good conductor of electricity and also possess photochemical features (Wei et al. 2015). They also have outstanding bactericidal characteristics to give protection from harmful microorganisms (Siddiqi and Husen 2016b). To study the various external and physical characteristics, they can be synthesized by various strategies. Various applications of AgNPs in different fields like electronics, medicines, and in regulating the growth of microorganisms made them environmental friendly (Lokina et al. 2014).

The importance of these nanoparticles had been recognized long ago, specifically for the purpose of medicines. Approximately 320 tons of AgNPs have been synthesized annually and further used in nanomedical imaging, biosensing, and food (Ahamed et al. 2010). AgNPs were also developed for the purpose of stimulation of plant growth, fungicides to kill the fungus, and to increase the ripening rate of the fruits (Wei et al. 2015). Increased utilization of these particles enhanced their liberation in the environment during the process of their synthesis

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and product formation along with their handling, reusing, and finally disposing into the environment (Shahverdi et al. 2007).

Among all the nanoparticles that have been developed and characterized so far, AgNPs are considered to be having a significant place as incessant enhancement in their amount leads to the formation of multidrug, which is resistant to bacterial and viral strains because of mutation, pollution, and extreme environmental conditions (Jones et al. 2004). Avoiding such conditions, drugs have been invented by the scientists for treating the microbial infections. Evidence suggests that various metal salts and metal nanoparticles have been recognized which have significant influence in reducing the growth and development of infectious bacteria. According to Das et al. (2011), small-sized AgNPs are admirable growth inhibitors of some bacteria.

AgNPs are discovered broadly from water and soil where they are deposited in great amount (Gottschalk and Nowack 2011). In a study, the presence of 1900 ng/L concentration of AgNPs has been estimated along with 9.3 nm size in a sewage treatment plant (Hoque et al. 2012). Besides, their level is drastically enhancing in surface and sewage water (Gottschalk and Nowack 2011). These particles may get leached out into the agricultural fields through the agency of irrigation and fertilization, and ultimately enter the plant rhizosphere (Lazareva and Keller 2014). As a result, these particles are certainly up-taken by the crops and then enter into the food chain (Ma et al. 2010), consequently spoiling the quality of food and also leading to health hazards to the living organisms (Cvjetko et al. 2018). After mercury, silver is the second most hazardous metal to the aquatic life. In fact, AgNPs may cause leaching of Ag^+, which are relentless, bio-accumulative, and produce much toxicity (Moreno-Garrido et al. 2015). Hence, the release of these AgNPs into the environment enhances major concerns regarding environmental toxicity and safety. Plants represent the first trophic level and also the primary component of food chain, thus acting as a significant part of the food chain (Ma et al. 2015).

2 Biosynthesis of Silver Nanoparticles

There are various physical, chemical, and biological methods for the formation of AgNPs (Roldán et al. 2013). Chemical method for the synthesis of nanoparticles is further divided into various other methodologies like chemical reduction, electrochemical, irradiation-assisted chemical, and pyrolysis (Zhang et al. 2007). Metal precursors and stabilizing and reducing agents are required for the synthesis of AgNPs. Ascorbic acid, borohydride, sodium citrate, hydrazine, etc. are frequently used reducing compounds. AgNPs sustained on nanostructured silica dioxide were achieved by the flame aerosol technology that permits regulation of silver content and size (Sotiriou and Pratsinis 2010). Flame spray pyrolysis leads to small-sized allocation of nanoparticles like silica or silver (Sotiriou et al. 2011).

Fatal or extremely reactive chemicals are not required in the physical methods, and usually they need quick processing time. Such methodologies involve physical vapor condensation, arc-discharge, energy ball milling method, direct current magnetron sputtering, etc. Due to the narrow-sized distribution of AgNPs, physical

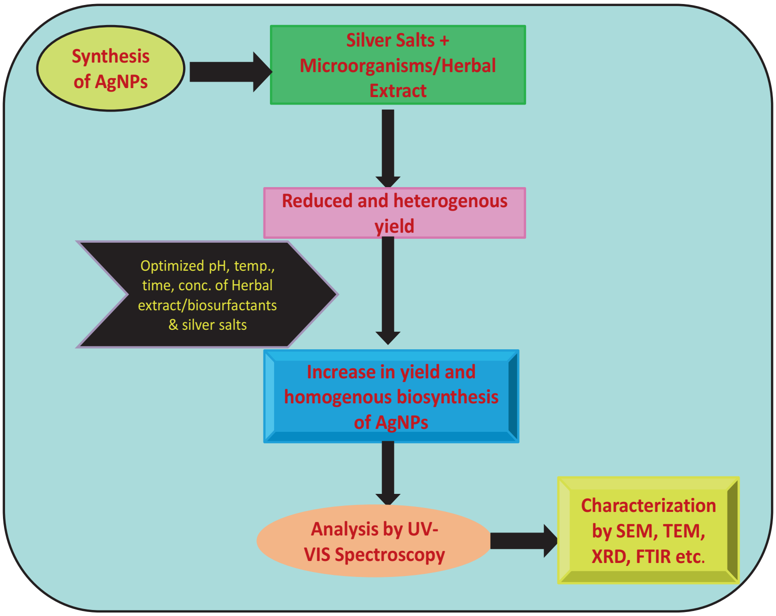

Fig. 1 Synthesis of silver nanoparticles. (Modified after Siddiqi et al. 2018)

methods have advantage over the chemical methods, but these methods use very high energy (Asanithi et al. 2012). Therefore, biological methods for their synthesis act as better substitute for physical and chemical methods, as this method includes the herbal extract and microorganisms. Such biological methods (Fig. 1) are well known for their simplicity, cost-effectiveness, and for promoting high productivity, as well as they are also environment friendly (Husen and Siddiqi 2014). In the field of nanotechnology, certain biotic agents like plants, algae, bacteria, fungi, yeast, etc. have become famous for the purpose of synthesis of metal and metal oxide nanoparticles (Siddiqi et al. 2016).

Various plant parts containing secondary metabolites such as nucleic acids, carbohydrates, proteins, fats, and pigments function as reducing agents for the formation of nanoparticles from metal salts without production of any toxic substance. Besides, certain biomolecules like enzymes, proteins, and bio-surfactants which exist in microorganisms also act as reducing as well as stabilizing agents. On the outer surfaces of cells, metal ions are trapped for the formation of AgNPs, and enzymes or biomolecules contribute in reducing them. At the same time, the formation of AgNPs may take place. Evidences suggested that extracellular formation of nanoparticles is more beneficial as it leads to cost-effective high yield and also demands simpler downstream processing; hence, this method is preferred for nanoparticle synthesis (Durán et al. 2005) compared to the intracellular method. Certain additional steps such as ultrasound treatment or reactions with suitable detergents so as to liberate the newly formed silver nanoparticles are also needed for the intracellular formation of silver nanoparticles (Ganesh Babu and Gunasekaran 2009; Kalimuthu et al. 2008).

3 Uptake, Accumulation, and Translocation of Silver Nanoparticles in Plants

AgNPs in plants are transported via the intercellular spaces (short-distance transport) and through vascular tissues (long-distance transport) (Ma et al. 2010; Geisler-Lee et al. 2013). When AgNPs are exposed to plants, penetration of cell walls and plasma membranes of epidermal layers in roots takes place by them (AgNPs). In the distribution and translocation of NPs, xylem is the important part that plays a key role as a vehicle (Aslani et al. 2014; Tripathi et al. 2017a, b). AgNPs can be taken up and translocated to the leaves through xylem. In some plants like *Arabidopsis thaliana*, the roots can take up AgNPs and transport them to the shoots (Ma et al. 2010). Geisler-Lee et al. (2013) reported that AgNPs were found to be up-taken, deposited, and translocated from root tips to various other parts like root cap initials of the root meristem. Studies have shown that in *Arabidopsis*, AgNPs were found attached to the surface of primary roots. These particles then entered the root tips at an early stage. After a period of 14 days, AgNPs were found to move into roots which then migrated to root hairs and lateral root primordia.

Site through which AgNPs enter the plant cell is the cell wall of the root cell (Tripathi et al. 2017a, b). The first requirement for AgNPs to enter into the plant is the penetration of the cell wall, plasma membrane, and root epidermal layer. As the cell wall is just like a perforation, it acts as a permeable center for polysaccharide fiber matrices (Navarro et al. 2008). Sometimes the AgNPs are so small that they can pass through the pores, but sometimes they are so large that they cannot enter into the plant cell and are eventually sieved out (Tripathi et al. 2017a, b). The large-sized pores in the cells allow the entry of AgNPs through the cell wall. AgNPs have the ability to induce the formation of large-sized pores (Navarro et al. 2008).

Plasmodesmata are 50–60 mm diameter cytoplasmic bridges through the cell wall connecting the cytoplasm of neighboring plant cells (Ma et al. 2010). In *Arabidopsis*, there are cases of obstruction between cells due to accumulation of AgNPs at the plasmodesmata (Geisler-Lee et al. 2013). Due to heavy accumulation of these particles at these sites, the intercellular nutrient transport gets affected (Geisler-Lee et al. 2014).

Roots are the main parts that transport AgNPs throughout the plant. Another plant part associated with transportation of these particles is plant leaf. Geisler-Lee et al. (2014) observed the effect of AgNPS on *Arabidopsis* cotyledons. He found that if the seedlings of *Arabidopsis* containing cotyledons are dipped in AgNP-containing medium, the guard cells of the stomata uptakes it and as a result the particles aggregate over there (guard cells). According to Larue et al. (2014), AgNPs also have the capacity to penetrate the leaf tissue through stomata. When lettuce leaf tissues underwent foliar exposure, AgNPs were found to be trapped by the cuticle. A comparative study of root exposure and foliar exposure of AgNPs uptake in rice and soybean was done by Li et al. (2017). Results revealed more accumulation (17–200 times) of Ag particles in the foliar parts than the root parts of the plant. After the entry of AgNPs into the vascular system of the crops, the xylem tissues take up these particles and transport them to the rest of the parts, also known as "long distance transport" (Ma et al. 2010; Geisler-Lee et al. 2014). Therefore, AgNPs can also cause contamination of edible parts of the plant like fruits or seeds through the translocation of these particles in the various parts of the plant.

4 AgNPs Phytotoxicity in Plants

4.1 Morphological Effects

Morphology of the plants is greatly affected when exposed to AgNPs. Toxic effects of AgNPs can be studied by analyzing certain growth parameters of the plants like biomass, leaf surface area, seed germination, etc. (Singh et al. 2016; Tripathi et al. 2017a, b, c; Vishwakarma et al. 2017; Rastogi et al. 2019). Reports suggest that these nanoparticles cause retardation of root growth and also decrease the leaf surface area and biomass of the plants. In *Spirodela polyrhiza,* drastic reduction in shoot length and plant biomass was found, when kept in AgNPs exposure, which further led to root abscission (Jiang et al. 2012). According to Kaveh et al. (2013), increased doses of these nanoparticles from 5 to 20 mg/L cause decrease in the biomass of *Arabidopsis.*

In wheat plants, results of experimentation revealed that AgNPs are responsible for inhibition in the root and shoot length with enhancing their concentrations (Dimkpa et al. 2013). On the other hand, Nair and Chung found that these nanoparticles extensively decreased the elongation of root and shoot and also resulted in reduced root fresh weights in rice (Nair et al. 2014). Similarly, studies conducted on *Cucurbita pepo* by Stampoulis et al. showed that greater concentrations of AgNPs (>100 mg/L) reduced the percentage germination of seed and hence the biomass (Stampoulis et al. 2009). Similar results showing the adverse effects of AgNPs were found in various other plants like *Brassica nigra*, Lemna, *Lolium multiflorum*, rice, *Arabidopsis*, Phaseolus radiates, Sorghum bicolor, wheat, *Lupinus termis* L., which showed the toxicity symptoms in terms of the reduction in seed germination, accumulation of biomass, and root and shoot length (Ejaz et al. 2018; Yang et al. 2018; Al-Huqail et al. 2018).

4.2 Physiological Effects

Adverse effects of AgNPs in plants can be estimated by studying their physiological aspects like disturbance in the transpiration rate, reduction in photosynthetic pigments such as chlorophylls and carotenoids, and changes in mineral and nutrients uptake and in the level of plant growth regulators. These nanoparticles inhibit the formation of chlorophylls and consequently disrupt the photosynthetic system of plants (Tripathi et al. 2017a, b). In the leaves of *Arabidopsis*, accumulation of

AgNPs caused inhibition of chlorophylls, disruption of thylakoid membrane, and hence the growth of the plants (Qian et al. 2013). Nair and Chung reported that after 7 days' exposure to these nanoparticles in rice seedlings, pigments like chlorophylls and carotenoids were found to reduce drastically (Nair and Chung 2014). According to Vishwakarma et al. (2017), these AgNPs also got accumulated in the seedlings of mustard and led to brutal decrease in photosynthetic rate. A study revealed that *Physcomitrella patens* upon exposure to AgNP altered the thylakoid and also caused inhibition in the chlorophyll b content, and hence disturbed the balance of certain indispensable elements in the leafy gametophytes (Liang et al. 2018). A recent study showed that in *Lupinus termis* L. seedlings, after 10 days' exposure to these nanoparticles, drastic inhibition in root and shoot length, level of pigments, and protein was observed (Al-Huqail et al. 2018). On the other hand, significant inhibition in transpiration rate was found in *Cucurbita pepo*, when exposed to AgNP (Hawthorne et al. 2012).

Apart from this, AgNPs also influence the fluidity and permeability of the membrane and, as a result, affect the uptake of minerals and water. In radish seedlings, exposure to AgNPs caused reduction in water and mineral/nutrient content such as calcium, magnesium, zinc, boron, etc. was observed with increase in nanoparticles concentrations, significantly retarded the growth (Zuverza-Mena et al. 2016). Evidences also suggested that these nanoparticles also adversely affect the level of plant hormones. It was observed by Sun et al. that in *Arabidopsis* seedlings, root gravitropism was also reduced when exposed to AgNPs with increasing their concentrations. Reports also revealed that these nanoparticles also led to inhibition in auxin level, whereas auxin receptor-related genes were also found to be downregulated when gene expression was studied after AgNP exposure (Sun et al. 2017). Vinkovi'c et al. performed the hormonal analysis in pepper tissue with the help of ultra-high-performance liquid chromatography electrospray and analyzed that the accumulation of AgNP in pepper led to considerable enhancement in the level of cytokinin, which indicated the significance of cytokinin under AgNPs (Vinkovi'c et al. 2017). Similarly, growth in wheat and cucumber was also found to be retarded due to Ag2S-NPs (Wang et al.) where upregulation of genes were observed which were involved in the ethylene signaling and consequently influenced the growth of the plants (Wang et al. 2017).

4.3 Effects at Cellular and Genetic Level

Size, shape, pathogen type (against which their toxicity is investigated), and the coating agents are certain factors which estimate the cytotoxicity of nanomaterials. Reactive oxygen species (ROS) is the chief factor that decreases the level of glutathione in the cells by drastically increasing their number, and hence cytotoxicity is caused due to AgNPs. Animal tissue or cultured cell when exposed to such nanoparticles in in vitro conditions oxidative stress, genotoxicity, and apoptosis is enhanced (Kim and Ryu 2013). Similar studies had been conducted with different types of

AgNPs. According to Hackenberg and co-workers (2011) report, certain people do not find any toxicity while decreasing the viability at AgNPs dose of 10 μg/mL over 50 nm size in human mesenchymal cells. At the same time similar results were analyzed even at a higher dose (100 μg/mL) (Samberg et al. 2012). Whereas aged AgNPs released silver ions when kept in water approximately for half year, enhancement in toxicity was observed; therefore, aging and stability of nanoparticles proved as significant factors (Kittler et al. 2010). According to the above-mentioned experiment, it seemed that AgNP toxicity is the combined action of AgNPs and Ag ions. Though few scientists revealed that toxicity of AgNPs is due to the liberation of silver ions, others proved that it may be due to AgNPs (Cronholm et al. 2013).

Similarly, chromosomal aberrations, micronuclei, and decrease in the mitotic index in the root tip cells of broad bean were drastically found to increase, which further disrupted the cell cycle and mitosis when exposed to AgNPs (Patlolla et al. 2012). The study by Abdelsalam et al. suggested that the root tip cells of wheat have the tendency to internalize the AgNPs where root tips further possess various types of chromosomal aberrations, like dysfunctioning of spindles, disorientation at metaphase, disintegration, unequal separation, rupturing of chromosomes, and which critically cause interference in cellular functioning (Abdelsalam et al. 2018) (Table 1).

5 Oxidative Stress by AgNPs

Production of excess of AgNPs induced reactive oxygen species (ROS), which results in oxidative stress in plant cells, further triggers the phytotoxicity of AgNPs (Tripathi et al. 2017b). Studies revealed that plants intoxicated with AgNPs show significant increase in ROS production in plants. Singlet oxygen ($^1O_2$), superoxide (O_2^-), hydrogen peroxide (H_2O_2), and hydroxyl radical (HO^-) are the four types of ROS reported to be produced in plant cells (Ma et al. 2015). ROS may be generated as by-products of normal metabolic pathways like mitochondrion, peroxisomes, and chloroplasts under normal environmental conditions (Møller et al. 2007; Tripathi et al. 2017a, b; Vishwakarma et al. 2017). Excessive amounts of ROS have been observed to be generated, causing severe oxidative damage to biomolecules with the help of electron transfer (Carocho and Ferreira 2013). AgNPs' exposure of plants can cause excess production of ROS, which leads to oxidative stress. It causes lipid peroxidation (peroxidation of polyunsaturated fatty acids) and also damages the permeability of cell membrane, which leads to the alteration in cell structure as a result of which growth of plant is inhibited and potential cell death occurs (Ma et al. 2017; Tripathi et al. 2017a, b; Capaldi Arruda et al. 2015). *Allium cepa* is a good example of this process reported by Panda et al. (2011). He found that the generation of superoxide ion and H_2O_2 is increased in *Allium cepa* when treated with (phyto-synthesized from silver nitrate $AgNO_3$) or commercial AgNP they are also seen to cause cell death in a dose-dependent manner in the give order

Table 1 Synthesis of AgNPs by different plant parts

S. no.	Name of plant	Plant parts used	Constituents responsible for $AgNO_3$ reduction	References
1.	Horseweed	Leaf	Flavonoids, steroids, sugars, triterpenes, glycosides, etc.	Kumar et al. (2015)
2.	Nutmeg	Bark and seeds	Secondary metabolites	Jelin et al. (2015)
3.	Star fruit	Fruit	Ascorbic acid, polysaccharides, polyols	Chowdhury et al. (2015)
4.	Arak	Stem	Phenolic compounds	Tahir et al. (2015)
5.	Swallowwort	Aerial parts	Alkaloids, flavonoids	Barbinta-Patrascu et al. (2016)
6.	Tropical chestnut	Fruit	Gallic acid, pyrogallol, polyphenols	Bogireddy et al. (2016)
7.	Japanese thistle	Complete plant	Protein, flavonoid, saponin	Khan et al. (2016)
8.	Indian pennywort	Leaf	Glycosides, flavonoids	Devi et al. (2016)
9.	Jasmine	Seeds	Phenols and carbohydrates	Basu et al. (2016)
10.	Ashoka	Leaf	Steroids, flavonoids	Perugu et al. (2016)
11.	Large caltrops	Leaf	Protein, rosins, saponins, alkaloids, etc.	Anandalakshmi et al. (2016)
12.	Chinese Salacia	Powdered plant	Protein, carbohydrates, saponins, alkaloids, etc.	Jadhav et al. (2015)
13.	Alpinia	Root	Polyphenols, proteins, flavonoids	Pugazhendhi et al. (2015)
14.	Indian screw tree	Root	Alkaloids, tannins, sugars, proteins, etc.	Bhakya et al. (2016)
15.	Senegal	Leaf	Phenols	Harshiny et al. (2015)
16.	Pod mahogany	Bark	Proteins	Moyo et al. (2015)
17.	Golden trumpet	Flower	n-pentacosane, n-tricosane, 1,8-cineole	Karunakaran et al. (2016)
18.	Rohan	Leaf	Amino acids, phenols, aliphatic and aromatic amines	Sowmyyan and Lakshmi (2015)
19.	Balloon vine	Leaf	Phenols and polyphenols	Sundararajan et al. (2015)
20.	Blistering ammannia	Leaf	Proteins, flavonoids, polyphenols	Jadhav et al. (2016)
21.	Paradise tree	Leaf	Amino acids and hydroxyl groups	Kanchana and Zantype (2016)
22.	Silk cotton tree	Gum	Hydroxyl and carbonyl groups	Krishna et al. (2016)
23.	False waterwillow	Leaf	Tannins, quinines, steroids, anthraquinones, alkaloids, triterpenoids, saponins, etc.	Elangovan et al. (2015)
24.	Geranium	Flower	Tannins, glycosides, terpenes, carbohydrates, flavonoids, saponins, etc.	Nalvolthula et al. (2015)

(continued)

Table 1 (continued)

S. no.	Name of plant	Plant parts used	Constituents responsible for $AgNO_3$ reduction	References
25.	China rose	Petals	Proteins	Nayak et al. (2015)
26.	Ziziphus	Fruit	Alcohols, phenols	Sreekanth et al. (2016)
27.	Pongam oil tree	Seed	Pongaflavanol, pongamol, galactoside, tunicatachalcone, etc.	Beg et al. (2017)
28.	Betel nut	Nut	Polyphenolic compounds	Rajan et al. (2015)
29.	Sink bean	Pod	Phenols	Fatimah (2016)
30.	Indian beech	Flower	Multifunctional aromatic groups	Rajakumar et al. (2017)
31.	Mango	Seed	Tannins, gallotannins, phenolic compounds	Sreekanth et al. (2015)
32.	Bitter melon	Leaf	Momorcharins, momordenol, momordin, charantin, charine, momordolo, etc.	Ajitha et al. (2015)
33.	Black pepper	Seeds	Amino acids, alkaloids, proteins, vitamins, polysaccharides, etc.	Mohapatra et al. (2015)
34.	Tamarind	Seed coat	Tannins, saponins, flavonoids	Ramamurthi et al. (2015)
35.	Banyan	Bark	Terpenoids, phenols, flavonoids	Nayak et al. (2015)

and at doses 20 mg/L of AgNPs-S > AgNP-P. AgNP-P was very effective in significantly decreasing the mitotic index. According to comet assay, AgNP-P and AgNP-S treatment significantly increased the DNA damage in a dose-dependent manner. It was found that AgNP-S is more genotoxic than AgNP-P; the threshold dose is 20 mg/L (Panda et al. 2011).

It was suggested by Qian et al. (2013) that the balance between oxidant and antioxidant systems can be altered by AgNPs as they can accumulate in *Arabidopsis* leaves, changing the transcription of antioxidant and aquaporin genes. In the same way, in vitro toxicity of AgNP experiments were done on kiwifruit pollen by Speranza et al. (2013), where he found that the process of germination of kiwifruit pollen and ROS generation took place at the same time. It was seen that H_2O_2 production was delayed by AgNP treatment, while ROS overproduction was induced during pollen germination, which resulted in decreased pollen viability and performance. Torre-Roche et al. (2013) reported a great increase of about 54–75% in malondialdehyde formation when exposed to AgNP at the rate of 500 and 2000 mg/L in *Glycine max*. Under stress conditions malondialdehyde has been found as a major peroxidation product that indicates the level of lipid production (Lin et al. 1996).

Similar results were reported by Nair and Chung (2014) in *Arabidopsis* when it was exposed to 0.2, 0.5, and 1 mg/L AgNPs; the level of lipid peroxide increased significantly. He also found a significant increase in H_2O_2 formation and lipid peroxidation in shoots and roots of rice plants where studies revealed that AgNPs promoted ROS production in a dose-dependent manner. The effect of AgNPs on the seedling of turnip showed that AgNPs in higher concentration result in the generation of superoxide radicals and lipid peroxidation in high amounts; on the other hand, excessive increase in the formation of H_2O_2 was found when exposed to 5 and 10 mg/L AgNPs. Similarly, oxidative stress was seen in the turnip seedling roots when exposed to AgNPs, and it was concluded that dichlorofluorescein (DCF) fluorescence has increased the production of free radicals in the plant. Studies revealed that AgNPs have the ability to induce cell death through the process of apoptosis. The above result was confirmed from the comet assay and terminal deoxynucleotidyl transferase–mediated dUTP nick-end labeling (TUNEL) assay analysis, and it was observed that there was a significant damage of DNA (Thiruvengadam et al. 2014).

6 Tolerance Mechanisms

The overproduction of ROS in plants when exposed to AgNPs can cause the phytotoxicity of AgNPs, which is associated with oxidative stress. There are a series of antioxidant defense mechanisms that can be activated in plant cells to avoid the deadly effect of ROS. A number of enzymatic antioxidant activities like superoxide dismutase (SOD), catalase (CAT), ascorbate peroxidase (APX), guaiacol peroxidase (GPX), dehydroascorbate reductase (DHAR), and glutathione reductase (GR) are there to combat with the detrimental effects of ROS (Rico et al. 2015). The ROS are of different types and have different effects on various cell organelles in plants. To remove or to combat with the various effects of ROS, specific antioxidant enzymes can be used (Ma et al. 2015; Apel and Hirt 2004).

There are certain compounds to reduce the toxic effects of ROS and to convert them into less toxic compounds (H_2O_2). For this purpose, three types of SOD are present in plant cells. CAT has the ability to convert H_2O_2 into O_2 and H_2O. APX is another compound that can convert H_2O_2 into H_2O with the help of ascorbate oxidation into monodehydroascorbate (MDA) and dehydroascorbate (DHA) (Ma et al. 2015). When a plant is exposed to AgNPs, the enzymatic antioxidant activities are increased in the plant cells, and these increased activities help the plant cell to protect it from oxidative stress. *Wolffia globosa* exhibits a good example of such activities. On exposure to 10 mg/L AgNPs, there was a significant oxidative damage to this plant (Zou et al. 2016). During this period, the increased activity of SOD by 2.52 times indicates activated ROS-scavenging mechanism. Similar observations of increased activity of SOD were also noted in *Lycopersicon esculentum* (Song et al. 2013) when they were exposed to AgNPs. In *Bacopa monnieri* (Linn.), the treatment of AgNP resulted in the enhancement of peroxidase and also in catalase (Bagherzadeh Homaee and Ehsanpour 2016; Jiang et al. 2014). Another observation was made by Jiang et al. (2014) who noticed significant increase in catalase activity in cells of *Spirodela polyrhiza*. When exposed to 6 nm AgNPs, the SOD and peroxidase activity and glutathione content were found to be increased in a dose-dependent manner. The effect of AgNPs on potato was examined by

Bagherzadeh Homaee and Ehsanpour in 2016. They observed that the activities of CAT, GR, SOD, and APX were found to be increased significantly in plantlets treated with AgNPs.

There are some non-enzymatic antioxidants, like anthocyanin, glutathione, thiols, and ascorbates, which contribute to the antioxidant defense mechanisms (Rico et al. 2015). The pigment anthocyanin is associated with tolerance to various biotic or abiotic stresses, for example, drought, cold, ultraviolet radiation, herbivores, pathogens, and heavy metals (Gould 2004). A non-enzymatic antioxidant, anthocyanin is helpful in scavenging free radicals and chelate metals in adverse or stressed conditions (Ma et al. 2014; Carocho and Ferreira 2013; Gould 2004). Reports revealed that a significant induction in anthocyanin accumulation was seen in AgNP-treated *Arabidopsis* seedlings in a dose-dependent manner (Syu et al. 2014). Similar results were found in turnip, where a significant increase in anthocyanin accumulation was seen when exposed to higher concentrations of AgNPs (Thiruvengadam et al. 2015).

Some other antioxidants like carotenoids, proline, and ascorbic acid are also associated with antioxidant defense responses to AgNPs. The toxic effects of ROS are potentially reduced, and the antioxidant activity is induced by carotenoids (He et al. 2011). Carotenoids are used by plants to lower the effects of ROS induced by AgNPs that is the indication of that AgNPs exposure increases shoot carotenoid content (Mirzajani et al. 2013). Ascorbic acid content was reported to be increased in *Asparagus officinalis* (An et al. 2008). The expression changes of genes that are associated with AgNPs responses may trigger the antioxidant defense mechanism of plants at the molecular level when plant is exposed to AgNPs. Dimkpa et al. (2013) found that expression of a cysteine-rich protein metallothionein (MT) was highly induced when treated with AgNP. Metallothionein (MT) is a cysteine-rich protein which is associated with detoxification by metal ion sequestration. On exposure to AgNPs in *Arabidopsis*, there was a significant upregulation of the expressions of sulfur assimilation, glutathione S-transferase, glutathione reductase genes, and glutathione biosynthesis (Nair and Chung 2014). Sulfur metabolism is of great importance to deal with stress tolerance in plants and plays a major role in the maintenance of cellular redox homeostasis (Montes et al. 2017).

7 Conclusion

Reports showed the deleterious effects of AgNPs on the morphology, physiology, cellular, and molecular levels of the plants. But some studies also revealed their positive influence on the growth and development of the plants, which shows their complex nature dependent on their size, dose, shape, chemical form, etc., type of experimental methods, and model plant used. These also act as biosensors, antimicrobial agent, and electrochemical sensors in various fields such as agriculture, medicine, and biotechnology. Against the toxicity of AgNPs, various detoxification strategies are boosted up by plants to ameliorate their toxic effects.

To assess the effects of AgNPs on plants, organization of nicely designed life cycle of plants in the experimental setup under the natural conditions is required so as to produce the applicable environmental insinuations. Even though the collaborative joint attempts by various scientists can also impart the knowledge of influence of these nanoparticles on the ecosystem, results of such experiments are dependent on laboratory practices under regulated conditions. In such cases, it is difficult to expect the similar toxic influences and tolerance strategies of these nanoparticles in in vitro and in vivo conditions. Most of the studies related to nanoparticle toxicity are mainly focused on the morphological and physiological aspects, whereas molecular aspect has not yet been covered much. For the better understanding of toxicity and benefits as well as their tolerance strategies, certain advanced methods including proteomics, transcriptomics, etc. should be developed.

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Impact of Cobalt Oxide Nanoparticles on the Morpho-physiological and Biochemical Response in Plants

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1 Introduction

Metallic nanoparticles are manufactured worldwide in order to fulfill the requirements of different fields of application. It is revealed that, by the year 2020, the expected production should increase from 1000 to 58,000 tons globally. Metal-based and metal oxide nanoparticles are gaining much importance in areas like agriculture, medicines, fillers, paints, cosmetics, electronics, textiles and energy. Multifold production and application of these NPs will lead to relevant release into the environment. Accordingly, these particles can enter the environment through possible mechanisms and led serious concerns to human health, plants and other environmental compartments like water, air and soil (Tripathi et al., 2017; Singh et al., 2017). Research community generally classify the NPs on the basis of their chemical structure or composition (inorganic, organic and from the living organisms) like carbon based, dendrimers, composites and metal based (Chirayil et al., 2017). Another classification system based on origin (synthetic or anthropogenic), form (amorphous or crystalline) and size (from 1 to 100 nm) of nanoparticles is also gaining much importance (Arruda et al., 2015). With unique physiochemical properties cobalt oxide (CoO) and zinc oxide (ZnO) are gaining importance as commercially important metal oxide nanoparticles. These NPs are playing a pivotal role in

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industrial goods as magnetism, sensor development, electrochemistry, pigments and catalytic processes (Papis et al. 2009). Plants being the most important factor of all ecosystems, mediates the uptake and transport of NPs from soil up to the plant tissues. Accumulation of these particles into plant biomass and their transport decides the final fate and potential effects of these NPs to plants and environment (Karl-Josef and Simone 2011). Most of the plant surfaces provide easy passage to these NPs by getting adsorbed on the surface through micrometer and nanometer scaled plant openings. The rate of transport depends on the size, shape, concentration and surface charge of NPs (Tarafdar et al. 2012). Airborne NPs interact with the plants through aerial shoot surfaces and leaves also they get dispersed through wind and causes the contamination on plants surfaces (Nair 2016). From the leaf surfaces they enter into the stomatas and hydathodes to promote foliar uptake of NPs. As stomatas have large size apertures, provides the high transport velocity to these NPs of size ranging from 1-10 nm (Eichert et al. 2008). However plants show different behaviours with diffrent nano particles and are of greater concern for the future scientific studies.

2 Synthesis of Cobalt Oxide (CoO) Nanoparticles

There are three basic methods for the synthesis of nanoparticles, viz., physical, chemical, and biological, which are further classified into the following categories (Luechinger et al. 2010):

Physical Methods	**Chemical Methods**	**Biological Methods**
I. Arc discharge method	I. Co-precipitation method	I. By plant extract
II. Electron beam lithography	II. Sono-chemical method	II. By microorganisms
III. Ion implantation	III. Electrolysis	III. By algae
IV. Inert gas condensation	IV. Microemulsion method	IV. By biomolecules or enzymes
V. Mechanical grinding	V. Chemical reduction method	V. By agricultural and industrial waste
VI. Milling	VI. Phytochemical method	
VII. Spray pyrolysis	VII. Sol-gel method	
VIII. Vapor phase synthesis	VIII. Solvothermal method	

Metal-oxide-based nanomaterials such as ZnO and CoO are used in various industrial processes and products, such as catalysts, cosmetics, pigments, sunscreens, and food additives because of which their production and utilization have increased remarkably (Aitken et al. 2006; Shi et al. 2013). The minimum global production of CoO was estimated to be approximately 5 tons in 2014 and are considered as a low-volume product (Nanomaterial: Future markets 2015). In spite of very less global production, the potential application of CoO nanoparticles in various industrial purposes, such as pigments, catalytic processes, energy storage, sensor development, electrochemistry, magnetism (Liu et al. 2005; Papis et al. 2009; Li et al. 2011), development of nonenzymatic glucose sensors (Madhu et al. 2015), magnetic resonance imaging (Bouchard et al. 2009), etc. is attracting huge research interest in recent times.

Cobalt oxide could be an important magnetic material having several applications in different processes, such as in chemical processes, sensing of gas, in electrochromic films, heterogeneous chemical change materials, as cathodes in batteries, lepton transfer supporter and also the small-sized nanoparticle exhibit novel properties which are totally different from their bulk counterparts. The following method has been used to synthesize cobalt oxide nanoparticles.

2.1 Precipitation Method

Katalin et al. (2011) used nitrates and chlorides with different surfactants at different temperatures and reported that the structural and magnetic properties depended on the surfactants and applied temperature in both methods. In case of cobalt oxide-precipitation method, the size of the particle decreased till 700 °C and increased above this temperature. The average particle size of prepared cobalt oxide nanoparticle was 100–150 and 70–100 nm in co-precipitation and sol-gel method, respectively, characterized by XRD and SEM (Sinkó et al. 2011).

S. L. Sharifi et al. (2013) had synthesized cobalt nitrate with different solvents and surfactants at different calcination temperatures ranging 300–700 °C. They reported that the prepared samples of particles were characterized by XRD, SEM and showed that the particles morphology was depended on the calcination temperature. The particle size of cobalt oxide nanoparticles ranged between 2 and 80 nm. They compared the three synthetic methods, viz. co-precipitation, thermal decomposition and micro-emulsion, and believed that co-precipitation was the best method for the synthesis of cobalt oxide nanoparticles. Also co-precipitation is believed to be a very eco-friendly method for the synthesis of cobalt oxide nanoparticles. The size of cobalt oxide nanoparticles increased with the increase in the temperature of the reaction. Structural and magnetic properties were totally dependent on the amount of surfactants added to the solution (Sharifi et al. 2013).

2.2 Sol-Gel Method

B. I. Nandapure et al. (2012) synthesized cobalt oxide nanoparticles using cobalt chloride with starch solution and sodium hydroxide by sol-gel method at varying temperatures, 100–750 °C. They reported that the magnetic properties of the cobalt oxide nanoparticles depended on particle morphology and that they showed ferromagnetic and paramagnetic behavior, studied by VSM and PANI, respectively. The color changed from green to black when temperature was increased from 100 to 750 °C. The average particle size of the cobalt oxide nanoparticles was 14 nm characterized by XRD and 10–50 nm with irregular structure by TEM. They were reported as the cobalt oxide nanoparticles are used as soft magnetic materials (Nandapure et al. 2012).

Harish et al. used cobalt nitrate as precursor with oxalic acid by sol-gel method at 600 °C to synthesize cobalt oxide nanoparticles and the prepared sample were characterized by XRD, UV, TEM and FTIR. The results about the morphology of the particles by XRD and TEM were nearly the same with an average particle size of 45 nm. The optical and magnetic properties of the synthesized particles were studied by using UV and FTIR method, respectively. They mentioned that cobalt oxide nanoparticles can be used as magnetic materials, battery cathodes, electrochromic films and heterogeneous catalytic materials.

2.3 *Solvothermal Method*

M. Alagiri et al. (2013) synthesized cobalt nanoparticles from hydrated cobalt chloride in ethanol as solvent with hydrazine and TEA at 50–120 °C in stainless steel autoclave by using the solvothermal method. The time required for the synthesis of cobalt particles by this method was 12 h. They reported that the synthesized cobalt nanoparticles showed super magnetic behavior which in turn depended on the applied temperature. The magnetic anisotropy constant value of cobalt nanoparticles increased with a decrease in the morphology of the particles, showing that the magnetic anisotropy constant value of cobalt nanoparticles is greater than the bulk material. The size of the prepared sample was 2 nm average having FCC (Face Centered Cubic) and spherical structure characterized by XRD and TEM characterization, respectively.

2.4 *Thermal Decomposition Method*

In this method, cobalt oxide nanoparticles are synthesized by using cobalt chloride with ammonium hydroxide and glycerol at a calcination temperature of 450 °C. The synthesized nanoparticles were reported to be non-electroactive with higher activity for the detection of nitrobenzene. The optical properties of cobalt oxide particles was studied by UV and the prepared sample was characterized by XRD, which showed that the average particle size of cobalt oxide was 49 nm with a cubic morphology whereas the SEM characterization showed irregular rodlike structures (Manigandan et al. 2013).

2.5 Chemical Reduction Method

It is one the simple methods for synthesizing cobalt oxide nanoparticles. Markova et al. (2007) synthesized cobalt nanoparticles from iron sulphate with $NaBH_4$ at room temperature and pressure using two hydrodynamic conditions: one was an ideal mixing condition known as T-Method and other an ideal displacement regime known as A-Method. The mixing conditions of these two determine the morphology and color of the prepared cobalt nanoparticles. The prepared sample was characterized by using SEM, which showed that the particles have a black color with an amorphous structure prepared by T-method and a color with crystalline anisotropic structure prepared by A-method. They further reported that the conductivity, density, and the morphology of the cobalt nanoparticles were also dependent on the heating temperature of the reaction (Deneva et al. 2000).

2.6 Green Synthesis Method

Different plant extracts were used to synthesize cobalt oxide nanoparticles with the green synthesis method. M. Ullah et al. (2014) synthesized cobalt oxide nanoparticles by using cobalt nitrate and pomegranate peel and a microorganism (fungus) with sodium hydroxide, which was used as the precipitating agent. This was done at a temperature of 500 °C and reported that the synthesized cobalt oxide nanoparticles were characterized by SEM and XRD. The average size of the cobalt oxide particles was 49 nm with crystalline morphology and spherical structure by XRD and SEM characterization, respectively. The morphology of the prepared cobalt oxide particles was dependent on the temperature applied in the reaction (Ullah et al. 2014).

2.7 Hydrothermal Method

This method is totally a temperature dependent. A. Fernández et al. (2009) used this method to synthesize cobalt oxide nanoparticles from cobalt chloride with ammonium hydroxide. They prepared the samples at different temperatures ranging 2–33 K and characterized the prepared samples of cobalt oxide particles by XRD, UV, TEM, and SEM. They reported the particles of cobalt oxide showed antiferromagnetic behavior at 33k which was Neel temperature, and just after this temperature particles showed supermagnetic behavior, and above this Neel temperature particles showed paramagnetic behavior. The average size of the prepared cobalt oxide nanoparticles was about 16.4 ± 3.1 nm with an octahedral structure. Cobalt oxide can be used as gas sensor, pigment, or as a catalyst (Osorio et al. 2009).

3 Uptake, Translocation, and Toxicity Mechanism of Cobalt Oxide (CoO) Nanoparticles in Plants

The production and implications of various metal oxide nanoparticles such as copper oxide (CuO) nanoparticles and cobalt oxide (CoO) nanoparticles, may affect the terrestrial ecosystems and environment through changes in soil-plant profiles (Belal and El-Ramady 2016; Bouguerra et al. 2019). Nanoparticles are generally >100 nm in size and nonpersistent polymers (Gogos et al. 2012). Most commonly nanomaterials are used as either additives or active constituents of various agrochemicals, viz., fertilizers, pesticides, herbicides, etc. These nanoparticles may be released into the ecosystem during their manufacturing and/or applications in/as plant protection, soil remediation, plant growth regulators, and other agrochemicals (Belal and El-Ramady, 2016; Dubas and Pimpan, 2008; Gogos et al. 2012; Khot et al. 2012; Naderi and Danesh-Shahraki, 2013). The uptake of metal oxide nanoparticles by plant roots and then translocation into the plant system may result in phytotoxicity (Du et al. 2017). Nanoparticles-induced phytotoxicity symptoms may vary, depending upon the type/size/chemical composition/surface activity or concentration of metal oxide used, plant species, and their uptake by the plants (Rastogi et al. 2017). Thus, increased use of nanoparticles may potentially pollute the soil system and affect crop productivity and the quality of food produced.

Nanoparticles can enter the plant system by passing through the complicated extracellular matrix, i.e., plant cell wall in which cellulose, hemicellulose and pectin form multilayered structures (Serag et al. 2013). The plant cell walls have pores with an average width of about 5 nm and these pores act as limiting the point for the passage of macromolecules across the cell wall. The distinct characteristics of metal oxide nanoparticles help them to penetrate the cells and intercellular spaces, resulting in nano-phytotoxicities in the plants (Ma et al. 2015a). The CoO nanoparticles are either supplied through the amended nutrient medium (hydroponics) or soil media (soil cultures) into plants (Du et al. 2017). Besides, metal oxide nanoparticles can be applied in foliar applications. During soil or foliar application, these nanoparticles may be released into the environment (mainly in soil). The plants can uptake the nanoparticles through cell walls via on of the following two pathways: It can be an upward movement (root-to-leaf or fruit), i.e., from soil to root and then translocation to aboveground plant parts (leaves or fruits); or downward movement (leaf-to-root), i.e., through foliar spray to leaf surface/stomata to leaf cells towards roots (Ma et al. 2015a, b). The tentative pathway of uptake and translocation of CoO nanoparticles into plants is represented in Fig. 1.

Recently it has been reported that ZnO nanoparticles enter plant roots (root epidermis and cortex cells) through apoplast. Further through the symplastic pathway, these nanoparticles are absorbed by the cells of the root endodermis and xylem vessels, thereby penetrating the vascular bundle (Zhao et al. 2012a). Thus, metal oxide nanoparticles can follow either apoplastic or symplastic route for the translocation into various plants parts (stem, fruit, leaf, grain, seed), which can be either through xylem vessels or phloem cells (Du et al. 2017). In the leaf-to-root pathway, the

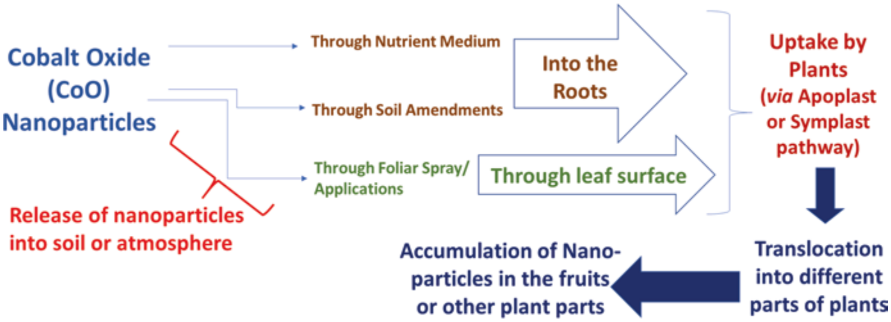

Fig. 1 Possible mechanism of CoO nanoparticles uptake and translocation into plants

metal oxide nanoparticles enter the plant system through the stomata followed by redistribution in the stem and their translocation through phloem cells to plant roots. These nanoparticles may get accumulated into the plant parts and may cause biochemical/morphological or physiological damage to the plants depending upon the size, type, or concentration of the nanoparticles (Rastogi et al. 2017).

Recently, in a study in canola, it was found that CoO-nanoparticles-induced toxicities were concentration dependent. Low concentrations had either no or a positive impact on various biochemical or morpho-physiological parameters studied. However, higher concentrations led to severe and irreversible physiological damage and also caused instability in cell membranes (Jahani et al. 2019). Therefore, the higher doses of CoO nanoparticles cause the damage in first line of defense, i.e., plant cell membrane and after penetration into cell membrane they may change the cellular homeostasis thereby leading to phytotoxicity. Bouguerra and co-workers (2019) reported that nano-CoO aggregates can potentially alter not only the rate of seedling emergence and plant growth but also the metabolic activities of important soil invertebrates. The impact of CoO on plants and soil invertebrates depends upon the duration (short term or long term) of exposure. Long-term exposure of CoO nanoparticles may have a negative impact on soil microflora, soil invertebrates, and also in diverse plant functions.

CoO nanoparticles are partially soluble. Nano-CoO-aggregates-induced phytotoxicity is primarily due to the particle-induced production of reactive oxygen species (ROS), resulting in morpho-physiological damage to plant cell membranes (Sharan and Nara 2019). Burgeoning research revealed that the implications of nano-metal oxide aggregates have posed a threat of nano-waste or nano-pollution (Yanik and Vardar 2018). These nanoparticles can get accumulated in the form of colloids or/and aggregates inside plant parts, soil, or water bodies. The precise mechanism of uptake, translocation, and accumulation of CoO nanoparticles into plants/soil/water is not yet known. But ROS generation has been reported to be associated with the release of metal ions into plant parts or accumulation of these nanoparticles inside plants. The ROS production further leads to apoptosis or programmed cell death (PCD) in plants. Further investigations into CoO nanoparticle induced regulation of ROS homeostasis and execution of PCD might be crucial to understand the phytotoxicity mechanisms.

3.1 Effects of CoO Nanoparticles on Plants

Cobalt (Co) belongs to the transition elements and has been listed as an essential element due to its requirement for the functioning of several enzymes and co-enzymes (Palit et al. 1994). It has an imperative role in many biological processes, such as biological fixation of nitrogen through symbiotic association and synthesis and activation of enzymes and co-enzymes for several biological processes (Sonia and Thukral 2014; Jahani et al. 2019). The toxicity of Co at excessive doses leads to many ailments in plants, such as reduced dry weight, chlorosis, leaf closure at premature stage, leaf abscission, and reduction in active transport (Sonia and Thukral 2014; Jahani et al. 2019). The nanoparticles of Co usually in the form of Co_3O_4 have been reported to have application in electrochemistry, sensors, storage of energy, magnetism, etc. (Faisal et al. 2016). Certain reports have also suggested its probable role in plant morphology, physiology and biochemistry, which has opened a complete new area of research.

3.2 Morphological Effects

The changes in morphology of plants in response to any changes in external stimuli are first to be noticed, which then further open a path of research for exploring the physiological and biochemical reasons behind such alterations. Several studies have reported phytotoxic effects of Co nanoparticles in which plant morphology had been found to be affected significantly. The roots of *Allium cepa* were checked for morphology and elongation to study the effect of cobalt (II and III) oxide nanoparticles at concentrations of 5, 10, and 20 μg/mL. It was reported that root elongation was drastically inhibited in a dose-dependent manner. It was suggested that high adsorption of cobalt (II and III) oxide nanoparticles in the roots led to phytotoxic effects in the roots (Ghodake et al. 2011). Plants of *Solanum melongena* when treated with various concentrations (0.025, 0.05, 0.1, 0.25, 0.5, and 1 mg/mL) of Co_3O_4 nanoparticles, the highest concentration of 1 mg/mL caused a retardation in root length by 81.5% along with enhanced appearance of peroxisomes and vacuoles, increased production of reactive oxygen species (ROS), and degeneration of mitochondrial cristae. Even at concentrations of 0.25 and 0.5 mg/mL along with the highest concentration, reduction in root length, thickening of roots, and disappearance of root hairs was observed in a dose-dependent manner (Faisal et al. 2016). A study carried out by Jahani et al. (2019) on *Brassica napus* subjected to various concentrations of Co_3O_4 nanoparticles demonstrated that low concentrations of 50 and 100 mg/L stimulated shoot length, fresh and dry weights of shoot during the exposure time of 5 weeks. However, these parameters showed decline at concentrations of 250, 500, 1000, 2000, and 4000 mg/L, thereby indicating its toxic effects at higher levels. The authors suggested that the low doses of Co_3O_4 nanoparticles might have a role in the activation of some enzymes related to growth and synthesis of some plant growth regulators. The higher doses, however, were thought to cause enhanced production of reactive oxygen species (ROS) and lipid peroxidation, which led to lower growth in plants. Another study was carried out on *Zea mays*, *Avena sativa*, *Lycopersicon lycopersicum*, and *Brassica oleracea* to test seed germination and seedling growth in response to Co_3O_4 nanoparticles with concentrations of 269.3, 350.1, 455.2, 591.7, 769.2, and 1000 mg/kg of soil (Bouguerra et al. 2019). Out of the four plants tested, significant adverse effects were observed on fresh and dry weights of *Z. mays* and seed germination of *L. lycopersicum*.

On the contrary, nanocrystalline powder of Co was observed to have positive effects on the soybean seeds of Vietnamese species DT-51. The experimentation was carried out both in laboratory and in fields and the seeds were treated at concentrations of 0.080, 0.200, and 0.320 g/ha for laboratory experiments and for field experiments, the concentration used was 0.080 g/ha. The best beneficial effects were found on seed germination, root length, shoot length, and seed vigor index for the lowest dose of nanocrystalline powder (Ngo et al. 2014). Similarly, results were also reported by Talankova-Sereda et al. (2016) in *Mentha longifolia* explants exposed to Co nanoparticles at the concentrations 0.4, 0.8, and 1.2 mg/L. The plants, after 28 days of exposure, showed better shoot height, growth index, shoot quantity, and internode quantity in comparison to control plants. The authors concluded the study with positive influence of Co nanoparticles but also claimed that effects are dependent on the concentrations used. Table 1 summarizes the effects of Co nanoparticles on various plant species.

3.3 Physiological Effects (Elaborate with Examples).

The various physiological effects are leaf abscission, inhibition of greening, chlorosis, premature leaf closure, and decrement of dry weight due to cobalt toxicity (Sonia and Thukral 2014). Cobalt oxide nanoparticles and their constituents like Co_3O_4 NPs also show physiological effects in various plant species (Faisal et al. 2016). Some of physiological effects are shown in Table 2.

3.4 Various Physiological Processes Depend Upon the Concentration of CO_3O_4NPs

Malihe et al. (2019) reported that CO_3O_4 NPs at different concentrations show various effects on *Brassica napus* plant.

Table 1 Effects of Co nanoparticles on the morphology of various plant species

S.No	Plant	Concentration used	Effects	References
1.	*Allium cepa*	5, 10, 20 μg/mL	Elongation of roots was inhibited	Ghodake et al. (2011)
2.	*Avena sativa*	269.3, 350.1, 455.2, 591.7, 769.2, and 1000 mg/g	No significant effects noticed	Bouguerra et al. (2019)
3.	*Brassica napus*	50, 100 mg/L	Length, fresh weight, dry weight of shoot enhanced	Jahani et al. (2019)
4.	*Brassica napus*	250, 500, 1000, 2000, 4000 mg/L	Decline in length, fresh weight, dry weight of shoots	Jahani et al. (2019)
5.	*Brassica oleracea*	269.3, 350.1, 455.2, 591.7, 769.2, and 1000 mg/g	No significant effects noticed	Bouguerra et al. (2019)
6.	*Lycopersicon lycopersicum*	269.3, 350.1, 455.2, 591.7, 769.2, and 1000 mg/g	Fresh and dry weights showed decline	Bouguerra et al. (2019)
7.	Soybean DT 51	0.80, 0.200, 0.320, g/ha	Seed germination, root length, shoot length, seed vigor index enhanced at lowest dose	Ngo et al. (2014)
8.	*Zea mays*	269.3, 350.1, 455.2, 591.7, 769.2, and 1000 mg/g	Decline in fresh and dry weights	Bouguerra et al. (2019)
9.	*Mentha longifolia*	0.4, 0.8, and 1.2 mg/L	Improvement in shoot height, growth index, shoot quantity	Talankova-Sereda et al. (2016)

At low concentrations (<100 mg L^{-1}) the various effects are:

(a) Enhanced shoot length
(b) Increased fresh weight of shoot
(c) Increased dry weight of shoot
(d) Enhanced chlorophyll *a* and chlorophyll *b* pigments
(e) Enhanced carotenoid content

At high concentrations (>500 mg L^{-1}) the various effects are:

(a) Reduction in shoot length
(b) Decreased fresh weight of shoot
(c) Decreased dry weight of shoot
(d) Decreased chlorophyll *a* and chlorophyll *b* pigments
(e) Reduced carotenoid content

CO_3O_4 NPs stimulate the biosynthesis of chlorophyll at low concentrations, which enhances the content of pigments in plants (Jiaoand Frei 2009; Gopal 2014). Sonia and Thukral (2014) reported reduced chlorophyll pigment in *Hordeum vulgare* when CO_3O_4 NPs content was increased, this results in ROS overproduction and damage to the photosynthetic apparatus and biomolecules (Tighe-Neira et al. 2018).

Table 2 Physiological effects of CoO nanoparticles in different plants

S. No	Plant name (algae, food and agricultural crops, fruits, other plants)	Physiological/morphological/biochemical effect	Nanoparticle CoO or its constituents	Effects	References
1.	*Allium cepa*	Physiological	Co_3O_4	Reduced root length	Ghodake et al. (2011)
2.	*Sesbania cannabina*	–	CoO	Chromosomal aberrations	Srivastava (2015)
3.	*Lycopersicon lycopersicum*	Physiological	Nano-Co_3O_4	Inhibition germiNation	Bouguerra et al. (2019)
4.	*Solanum melongena*	Physiological	Co_3O_4	Reduced root growth Phytotoxicity	Ghodake et al. (2010)
5.	*Solanum lycopersicum*	Physiological	$CoFe_2O_4$	Increased root length	López-Moreno et al. (2016)
6.	*Raphanus sativus*	Physiological	Co_3O_4	Reduced germination	Wu et al. (2012)
7.	*Cucumis sativus*	Physiological	Co_3O_4	Reduced germination	
8.	*Hordeum vulgare*	Physiological	Co_3O_4	Reduced root length	Sonia and Thukral (2014)
9.	*Triticum aestivum*	Physiological	$CoFe_2O_4$	Reduced photosynthetic pigments	López-Luna et al. (2018)

3.5 Protective Mechanism After Damage by CO_3O_4NPs

Plants have developed various defense mechanisms to cope with various stresses (Ma et al. 2015a, b). Simultaneously, CO_3O_4 NPs help in increasing the content of flavonoid and flavanol, which involve in preserving the cellular components from damages of oxidative stress in *Brassica nigra* (Zafar et al. 2016). Flavonoids is an antioxidant component involve in nullifying the free radicals (Skórska et al. 2019). Flavonoid production is increased at a certain level of CO_3O_4NPs, but at very high concentrations the flavonoid content is decreased and also proline and GB concentration is increased, which help in scavenging the ROS (Malihe et al. 2019).

3.6 Biochemical Effects

CoO nanoparticles have a huge impact on many physiochemical and biochemical processes in many plants and algae such as *Chlamydomonas reinhardtii* and *Pseudokirchneriella subcapitata* due to their significant catalytic properties (Sørensen et al. 2016; Książyk et al. 2015; Tighe-Neira et al. 2018). They mainly regulate plant growth and metabolism, under different abiotic and biotic stress conditions, and control the quality and yield of different agricultural crops (Apodaca et al. 2018; Panpatte et al. 2016; Hossain et al. 2015).

The tremendous use of CoO nanoparticles can affect plants and aquatic life in different ways by generating ROS. It has been reported by Griffitt et al. (2008), in *P. subcapitata* that Co nanoparticles inhibited many physiological and biochemical processes of plants. Furthermore, it was investigated in *Navicula* sp. that 0.2 mg/mL concentration of CoO nanoparticles for 5 days led to cell shrinkage, agglutination, and nuclear damage (Rebello et al. 2010). It has also been revealed by Ghodake et al. (2011) in *Allium cepa* that CoO nanoparticles (60 nm) caused cell aggregation in root system of plants that also blocked the water channels and penetration abilities. Nanoparticles can also induce the formation of large-sized pores or channels in order to assist their entry (Navarro et al. 2008). A study by Faisal et al. (2016) reported that *Solanum melongena* showed a higher adsorption ability of nanoparticles on seeds via electrostatic/hydrophobic bonds leading to inhibition of the first line of defense followed by the release of different ions from nanoparticles to induce phytotoxic effects in plant roots. Moreover, the translocation of nanoparticles to aboveground parts of the plants has also been revealed through electron microscopy. Along with this, many biochemical studies showed degeneration of cristae of mitochondria, ROS generation, and DNA damage, implicating the phytotoxic properties of CoO nanoparticles (Faisal et al. 2016; Lin et al. 2011).

NPs causing oxidative damage via ROS species further interact with many functional groups and proteins to denature them (Gorczyca et al. 2015). The increase in oxidative stress occurs in a dose-dependent manner in different plant species (Cui et al. 2014). For instance, higher electrolyte leakage was observed in wheat and rice roots in the presence of NPs (125 mg L^{-1} concentration) that led to lipid peroxidation, H_2O_2 accumulation in roots (Rico et al. 2013). Furthermore, 400–800 mg kg^{-1} NPs stimulated H_2O_2 production in maize leaves (xylem, phloem, epidermal, and bundle sheath cells) (Zhao et al. 2012a, b). Increase in H_2O_2 and MDA (Malondialdehyde) levels has also been reported in barley (Shaw et al. 2014), rice (Shaw et al. 2013), and chickpea plants along with enhanced levels of oxidized glutathione (Nair and Chung 2015). The production of oxidative stress markers occurs as by-products of various biochemical and metabolic processes occurring in mitochondria and chloroplasts (Ma et al. 2015a, b). The activation of a well-developed antioxidative defense system in plants is the first line of defense that comprises of enzymatic and non-enzymatic antioxidants to combat the oxidative damage caused by the presence of NPs (Rui et al. 2014; Regier et al. 2015). Consequently, various enzymatic activities of SOD (Superoxide dismutase), POD (Peroxidase), CAT (Catalase), and APOX (Ascorbate peroxidase) in wheat were reported to be decreased under the influence of 200 mg L^{-1} NPs in contrast to controls (Riahi-Madvar et al. 2013). Additionally, NPs-induced modulation in the activities of CAT (Catalase), SOD (Superoxide dismutase), DHAR (Dehydroascorbate reductase), MDHAR (Monodehydroascorbate reductase), GR (Glutathione reductase), and APOX (Ascorbate peroxidase) have also been revealed in wheat (Gorczyca et al. 2015), barley (Shaw et al. 2014), lettuce (Cui et al. 2014), and cilantro (Morales et al. 2013).

Studies have revealed that NPs triggered significant changes in soil properties and their enzymes such as proteases, dehydrogenases, β-glucosidases, peroxidases, catalases, and acid phosphatases (Kim et al. 2011). Therefore, various studies showed that NPs trigger oxidative stress through free radical production followed by its scavenging by antioxidative enzymes depending upon the plant type, NPs type, duration, and other experimental factors. Subsequently, plants have the ability to tolerate only mild quantities of NPs through the activation of defense systems, establishing equilibrium between production and detoxification of ROS. However, many positive and negative properties of CoO nanoparticles have been studied; much more research needs to be oriented towards studying their role in plants. Various biochemical changes in plants under the influence of CoO NPs are presented in Table 3.

4 Conclusion

Nanoparticles have both positive and negative effects on growth, yield, and quality of agricultural crops as well as they show morphological, physiological and biochemical changes in the plant system. Higher doses of Cobalt oxide nanoparticles shows detrimental effects in case of plants, with respect to the growth stage, time of exposure and method of translocation. With the advancement in nanotechnology we have to look forward for the sustainable use of these NPs and also there is a need to

Table 3 CoO nanoparticles and associated biochemical changes in different plant species

S. No	Plants/algal species	CoO	Biochemical changes	References
1.	*Brassica napus* L.	Co_3O_4 50 and 100 mg/L	Enhanced lipoxygenase (LOX) activity, MDA, H_2O_2, DHA content along with reduction in membrane stability index (MSI), ascorbate and glutathione levels	Saadatmand (2019)
2.	*L. lycopersicum*	Co_3O_4 269.3 mg/kg	Oxidative stress and enhanced lipid peroxidation	Bouguerra et al. (2019)
3.	*Zea mays*	Co_3O_4 269.3 mg/kg	Enhanced activity of antioxidative enzymes (CAT, GST), lipid peroxidation and acetylcholinesterase	Bouguerra et al. (2019)
4.	*Platymonas subcordiforus*	CoO 0.5, 1, 2, 5, 10, 20, 30, 50, 80, and 100 mg/L	Increased antioxidative enzyme activities along with increased oxidative damage	Chen et al. (2018)
5.	*Skeletonema costatum*	CoO 100 mg/L	Disruption of electron transport chain reactions with agglomeration of Co NPs	Chen et al. (2018)
6.	*Chaetoceros curvisetus*	CoO 100 mg/L	Nuclear damage and cell apoptosis mediated through the inhibition of biochemical processes associated with photosynthesis	Chen et al. (2018)
7.	*Lycopersicon lycopersicum*	$CoFe_2O_4$ 250–1000 mg/L	Decreased Ca and Mg translocation along with reduced catalase activity	López-Moreno et al. (2016)
8.	*Raphanus sativus*	Co_3O_4 1.0 mg/mL	Accumulation of ROS, mitochondrial membrane potential, Ca^{2+} influx, lipid peroxidation, and antioxidative enzyme activities (SOD, CAT, GSH)	Saquib et al. (2016)
9.	*Lycopersicon esculentum*	Co_3SO_4 100 ppm, 200 ppm, and 300 ppm	Enhanced metabolic and biochemical activities that promoted overall growth and development of the plants	Salem et al. (2016)
10.	*Artemia salina*	CoO 100 nm	Accumulation of CoO NPs led to higher oxidative stress as revealed through MDA assay	Ates et al. (2016)
11.	*Chlorella vulgaris*	$CoFe_2O_4$ 6.3, 12.5, 25, 50, and 100 μ mol/L	Induced oxidative and mechanical stress, mutagenic glutathione-s-transferase activity, acid phosphatase, and antioxidative enzymes in algal species. Reduced catalase activity with higher genetic alterations, metabolic and cellular signal transduction dysfunction	Ahmad et al. (2015)
12.	*Sesbania cannabina*	Co_3O_4 5–80 nm	Chromosomal alterations, disruption in metaphasic plate, spindle apparatus and anaphase stage	Srivastava (2015)

(continued)

Table 3 (continued)

S. No	Plants/algal species	CoO	Biochemical changes	References
13.	*Allium cepa*	Co_3O_4 5–20 μg/mL	Phytotoxic effects on cellular systems through the inhibition of cellular homeostasis and root architecture	Ghodake et al. (2011)
14.	*Navicula* sp.	CoO 0.2 mg/mL	Cell damage and aggregation along with reduced cell density and higher nuclear damage was observed	Rebello et al. (2010)
15.	*Chetoceros* sp.	CoO 2 mg/mL	Shrinkage of cells and cell fragmentation was seen through LDH and acid phosphatase assay	Rebello et al. (2010)

identify the long-term effects of these nanomaterials on the ecosystem. Further studies may also include the interaction of NPs with the signal transduction processes in plants.

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Nanoparticle-Induced Oxidative Stress in Plant

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1 Introduction

In recent years, nanotechnology emerged as a revolutionary science, with a tremendous evolution for various industries. These uprising nanoparticle (NP) industries are expected to contribute diverse products and services in a society. Nanoparticle has very unique chemical, physical, as well as biological properties that have a serious impact on the living system. Nanoparticles also play an important role in the electronic device, antimicrobial gene expression, and catalytic and electromagnetic properties. Rapid advancement in every aspect of these modern field forces the production and usage of nanoparticles at the large sclaes (Weir et al. 2012). Mainly through industrialization waste and various other means, nanoparticles enter into the environment. These nanoparticles get accumulated into the ecosystems and pose a serious threat to living organisms. Inside the plant system, toxicity of nanoparticles creates negative as well as undesirable consequences such as membrane damage, induction of oxidative stress or of cellular dysfunctions, etc. which finally cause the morphological, physiological, and molecular level damage. However, the most important mechanism adapted by the plant against toxicity created by nanoparticles is the production of the reactive oxygen species (ROS) which could cause

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oxidative stress, cell organelle damage, and finally cell death. Inside plants in physiological environment, NPs reacted with H_2O or O_2 result in direct production of ROS which imbalances the functionality of mitochondria and NADPH oxidase that successively results in the indirect production of ROS. Thus, different kinds of nanoparticles have potential ability to induce ROS generation through either direct or indirect mechanisms. From plant system, animal bodies, and microbes, NPs have a potential to get transferred into the human system mainly through the food chain (Judy et al. 2011; Werlin et al. 2011). Thus, more study regarding this serious issue should be necessary in order to spread the awareness among peoples.

2 Origin of Nanoparticles

Nanoparticles originated around the nineteenth century when the Mesopotamia artisans used them to decorate the pots for glittering effect on them. In 1857, Faraday in his study mentioned the properties of nanoparticles. The USA in the year 1940 manufactured silica nanoparticles for carbon black (ultrafine) for strengthening of rubber. Later in the 1960s and 1970s for magnetic recording tapes, metallic nanopowders were used. Nanotechnology concept was highlighted by Richard Feynman in 1959, and the term nanotechnology was identified in 1974 by Norio Taniguchi.

Nanoparticles are referred to as particulate matter having a size less than 100 nm in at least one dimension. It is considered as subfraction of colloidal particles (SCENIHR 2005, IUPAC 1997) due to its size-based classification. Particles within the range of 1–100 nm are present everywhere in the environment. Nanoparticles possess the extremely high surface area to volume ratio representing the surface area as an important component. These particles are considered as complex mixtures surrounded mainly by interfacial layers – surface, shell, and core layer. These layers mainly composed of ions and organic and inorganic molecule coating which play crucial role in providing nanoparticle characteristic properties. For example, silica, the simplest nanoparticle, contains SiO_2 in its core and has surface chemistry of $Si(O)_{2-x}.OH_{2x}$ (Paparazzo et al. 1992). It is considered that one layer of an atom is around 0.4 nm in thickness. This shows that the 6-nm-sized silica particle contains around 7% of the Si atoms on the surface representing a significant role of surface chemistry of the Si atom. Nanoparticles are designed by keeping in mind the role of surface chemistry, small surface area, and enhanced reactivity (Wang et al. 2016). Except in some cases, these particles lose their unique application once aggregated and precipitated in suspension. So in order to avoid that, some coating has been applied which facilitates dispersion. For example coating with metal ions, polymers, and small molecules (amines, thiols, carboxylates) by a covalent-like bond to carry charge on the surface. Qiu et al. (1999) demonstrated the use of surfactant like sodium dodecyl sulfate (SDS) to reduce aggregation and precipitation of the particles. Polyethylene glycol (PEG) is also used to modify the surface

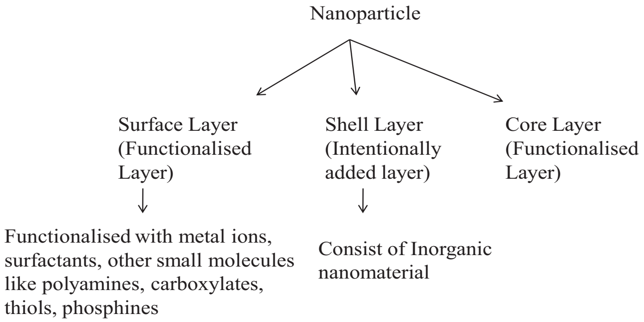

Fig. 1 Structure of nanoparticle

chemistry of the particles. The shell layer is the second layer that has a different chemical composition than the core layer. Any inorganic nanomaterial that is different from the core layer has been considered as the shell layer. Malik et al. (2002) in their study showed core/shell quantum dots in which core consists of cadmium selenide and shell of zinc sulfide. The core is the center of the nanoparticle and sometimes referred to as nanoparticle itself (Fig. 1). Wuister et al. (2004) reported that the exact role of nanoparticle depends upon its whole composition. But in some cases, the core of the nanoparticle plays a key role in the toxicology of nanoparticle. Cox et al. (2016) documented some nanoparticles with size more than 100 nm. They also showed that these particles may also show agglomeration. The primary particle may be less than 100 nm in size agglomerate and increases its size from 100 nm. Clement et al. (2013) reported that agglomeration is the process of loose attachments of primary particles and it also depends upon surface chemistry, composition of the medium, and concentration of particles.

In recent years nanoparticles have been widely used in manufacturing and medical and diagnostic field like cancer therapy, drug delivery, waste water treatment, biosensors, and cosmetic industries (Hu et al. 2015; Peralta-Videa et al. 2011). An emerging field of nanotechnology results in countless demand from consumer and industries, providing a mild alarm to the scientific community regarding the consequences associated with these particles. In 2005, Roco estimated the annual turnover of nanoparticle production to be more than $1 trillion by 2015. Bioavailability of a large amount of these particles in fresh water, soil, air, etc. results in the altered ecological balance as well as affects human health (Prasad et al. 2016; Tripathi et al. 2017c). From the past few years, nanotoxicology is dealing with the risk associated with the nanoparticles of <100 nm in size. Plants easily uptake these particles from root system and transport it to different parts of the plant through symplastic and apoplastic pathways and cause severe injuries to plants (Siddiqui et al. 2015).

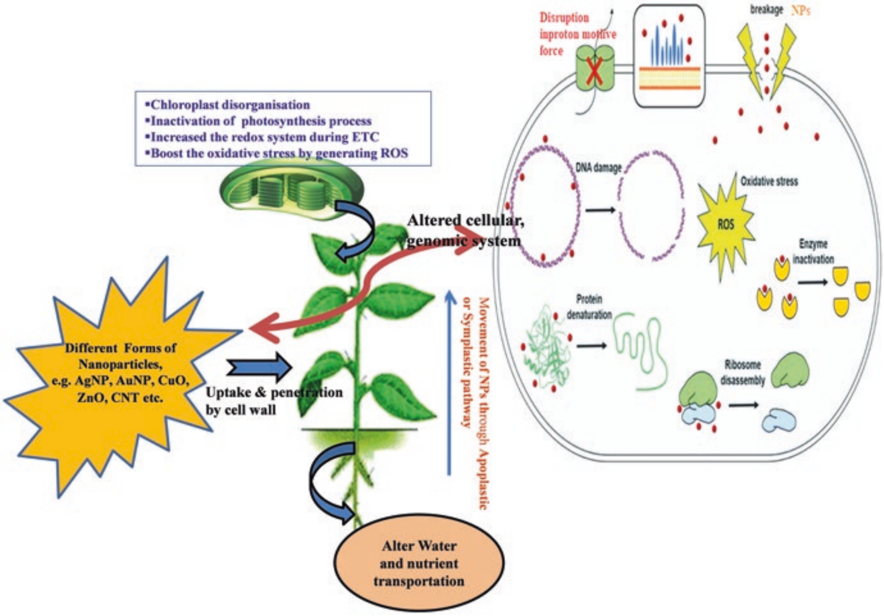

Fig. 2 An overview on nanoparticle interaction in plant system and their phytotoxic effects at all stages of plant development

3 Nanoparticle-Induced Oxidative Stress and Plant Phytotoxicity

Nanomaterials have gained exceptional arrays in the field of agriculture, environment, and health (Hossain et al. 2015; Mapara et al. 2015; Patil et al. 2016; Kumar et al. 2018) and have significant applications in biomedicines, electronic devices, and biosensors (Ma et al. 2015). The highly reactive property of NPs (Ghosh et al. 2016) results in increased toxicity through different mechanisms. Therefore, highly reactive nature allows them to easily penetrate into cells, thus causing possible nanotoxicity to living organisms like animals, microorganisms, and plants. Thus ever-increasing synthesis of nanoparticles in different fields has raised the risks of environmental exposure (Ghosh et al. 2016).

The agricultural area is facing a higher risk of their exposure, particularly to engineered nanoparticles (Keller and Lazareva 2014). Nanoparticles released in the environment by various processes may interact with plants causing many morphological, anatomical, physiological, and genetic changes (Fig. 2). Many earlier findings suggested both positive and negative effects of NPs on plant growth and development that based on the composition, concentration, size, and physical and chemical properties of NPs as well as plant species (Table 4.1) (Ma et al. 2010; Rico et al. 2015; Shweta et al. 2016; Arif et al. 2018; Shweta et al. 2018; Vishwakarma et al. 2018; Rastogi et al. 2019; Tiwari et al. 2019). Thus, depth understanding of the toxicity level of NPs and their interactions with plants is a present need for the safe usage of NPs. Nanoparticles may interact with plant system through various agricultural chemicals, leakage of nanoparticles from landfills and atmospheric release, etc. Earlier studies have revealed that nanotoxicity of nanoparticles on plants mainly occurs via generating a reactive oxygen species (ROS), which could lead to oxidative stress and ultimately cell death. NPs with highly reactive property could interact with H_2O or O_2 in the physiological environment, resulting in the direct production of ROS. The level of ROS generation depends on the physicochemical nature of NPs, including their composition, size, shape, and surface chemistry. Different NPs can induce ROS generation through direct and indirect mechanisms (Thwala et al. 2013; Hossain et al. 2015; Xia et al. 2015; Sun et al. 2017). These ROS, such as singlet oxygen, superoxide radical, hydrogen peroxide, and hydroxyl radical, cause serious damage to lipid membranes and other essential macromolecules including proteins and nucleic acids, which cause cell death in plants (Fig. 2) (Khare et al. 2014; Wani et al. 2016; Kumar et al. 2017; Marslin et al. 2017). Thus, consequence of stress conditions faced by plants is the excess generation of ROS (Khare et al. 2014; Kumar and Khare 2014), and therefore overproduction of ROS in plant cells after their exposure to nanoparticles indicates their negative impacts on plants.

Due to small sizes of NPs, shape, and larger surface area to mass ratio, they enhance plant growth and productivity and provide protection against various abiotic stresses. Depending on the type, different engineered nanoparticles (ENPs), like TiO_2, ZnO, Mg, Al, Pd, Cu, Si, and carbon nanotubes, may cause either a reduction or increase of growth in higher plants. ENMs have a tremendous beneficial contribution, but they also results into the harmful/toxic effects as they are known to generate oxidative, cytotoxic, and genotoxic stress in plants (Table 1; Fig. 2) (Ghosh et al. 2016; Yadav et al. 2014) and leading to devastating effects on growth and physiological and biochemical activities and thereby reduced nutritional quality of crops (Gunjan et al. 2014; Tripathi et al. 2016, 2017a, b, c, d; Singh et al. 2016; Shweta et al. 2016). Earlier reports demonstrated that engineered NPs such as ZnO, CeO_2, AgNPs, and carbon nanotubes have the ability to penetrate tissues of roots and vascular bundle (xylem) and travel symplastically to leaves and seeds of various plants such as *Solanum lycopersicum*, bean, *Zea mays*, and *Triticum aestivum* (Tripathi et al. 2017d). It was reported that upregulation of genes which are involved in transport, reduction, and oxidation of isoelectronic NPs (Ag, Fe, and Cu) may lead to oxidative stress to plants (Nagy et al. 2011; Dimkpa et al. 2013; Kaveh et al. 2013; Wang et al. 2014).

Recently there has been a debate over oxidative damage in plants as a consequence of nanoparticle exposure and the responsive antioxidant machinery deployed by plants to mitigate this damage, though greater insights at the molecular level are needed and should be a matter for future research. We present here in this chapter a

Table 1 ROS-dependent plant phytotoxicity in response to some metal oxide nanoparticles

S. No.	Nanoparticle	Nanoparticle size (nm) and concentration	Plant species	ROS-dependent phytotoxic effect	References
1.	AgNPs	>100 nm 500 mg/L^{-1}	*Cucurbita pepo* (*leaves*)	Transcription rate and biomass declined up to 66–84%	Musante and White (2012)
		25 nm 500,1000 mg/L 18.34 nm 0.3–0.6 mg/L 20 nm 0.2, 0.5, 1 mg/L	*Oryza sativa* Cell wall, membrane *Roots and shoots*	The cell wall broke under in the influence of nanomaterial and inhibited root growth by damaging vacuoles of root cell Reduction in Chl b concentration and thereby altered antioxidative activity of carotenoids and production of the ROS Significant increase in H_2O_2 content, lipid peroxidation level, foliar proline accumulation, and decreased sugar contents A dose-dependent increase in ROS generation; changes in mitochondrial membrane potential in the roots of seedlings	Mazumda and Ahmed (2011), Mirzajani et al. (2013), Nair and Chung (2014a)

(continued)

Table 1 (continued)

S. No.	Nanoparticle	Nanoparticle size (nm) and concentration	Plant species	ROS-dependent phytotoxic effect	References
		10 nm 0.2–3 mg/L 41 nm 100–5000 mg/L	*Arabidopsis thaliana* Root, leaves, and plasma membrane	Root growth inhibition Decrease in chlorophyll molecules, downregulation of transcription expression for antioxidative and aquaporin genes Induced ROS accumulation, induced Ca2+ in cytoplasm, inhibited plasma membrane K+ efflux and Ca2+ influx currents	Qian et al. (2013), Sosan et al. (2016)
		60 nm 50, 100 mg/L	*Vicia faba* root tip cells	AgNPs induced chromosomal aberration and caused genotoxicity by reducing mitotic index (MI) and micronucleus induction (MN) Also caused imbalance in mitochondria by increasing ROS	Patlolla et al. (2012)
		10 nm 0–5 mg/kg^{-1}	*Triticum aestivum* (root and shoot)	Reduction plant growth In dose-dependent manner accumulation of oxidized GSSG occurred	Dimkpa et al. (2013), Pallavi et al. (2016), Wang et al. (2013)
		6 and 20 nm 0.5–10 mg/L	*Spirodela polyrhiza*	Increase in ROS levels based on concentration	Jiang et al. (2014a)

(continued)

Table 1 (continued)

S. No.	Nanoparticle	Nanoparticle size (nm) and concentration	Plant species	ROS-dependent phytotoxic effect	References
		20 nm 2, 10, 20 mg/L	Potato (*Solanum tuberosum* L.)	Higher production of reactive oxygen species (ROS) and superoxide anions, significant increases in the activities of antioxidative enzymes; higher ion leakage and cell death	Bagherzadeh and Ehsanpour (2016)
		10 nm 1, 2, 5, 8, 10 mg/L	*Wolffia globosa*	Toxicity caused oxidative damage, higher malondialdehyde content, and an upregulation of SOD activity; reduction in contents of chlorophyll a, carotenoids, and soluble protein	Zou et al. (2016)
		20 nm 1000, 3000 μM	*Pisum sativum*	Lower the growth, photosynthetic pigments, and chlorophyll fluorescence; inhibited activities of glutathione reductase (GR) and dehydroascorbate reductase (DHAR)	Tripathi et al. (2017c)
		17.2 ± 0.3 nm and 1, 10, and 30 mg/L 0.1, 0.5, 1 mg/L	Soybean Rice Plant, leaves	Reduced plant biomass increased the malondialdehyde and H_2O_2 contents of leaves	Li et al. (2017)
		47 nm 1, 3 nm	Mustard (*Brassica* sp.) seedlings	Growth of *Brassica* seedlings inhibited induced oxidative stress	Pallavi et al. (2016), Vishwakarma et al. (2017)
		79.0 ± 8.0 nm 0.05–2 mg/L	*Lemna minor*	Responsible for decays growth rate and fronds per colony caused oxidative stress	Oukarroum et al. (2013), Pereira et al. (2018)

(continued)

Table 1 (continued)

S. No.	Nanoparticle	Nanoparticle size (nm) and concentration	Plant species	ROS-dependent phytotoxic effect	References
		25–70 nm 7.5–25.0 10, 20, 40, 50 ppm	Wheat (*Triticum aestivum* L.)	Generate genotoxicity by inducing various types of chromosomal aberrations	Abdelsalam et al. (2018)
2.	ZnO NP	8 nm 500, 1000, 2000, 4000 mg/L	Soybean seedlings	No change in germination at 4000 mg/L concentration genotoxicity was recorded; a new band in the roots' RAPD profile was noticed	Lopez-Moreno et al. (2010)
		10 nm 100, 200, 400, and 800 mg/kg	Corn Root Leaves	No change on APX activity but reduced CAT activity in leaves at 400 mg/kg in the presence of alginate	Zhao et al. (2013)
		–	*Fagopyrum esculentum*	Reduction in plant biomass, shortened roots, and declined growth with the generation of ROS	Lee et al. (2013)
		10 nm 125, 250, and 500 mg/L	Green pea Root Leaves	ZnO NP caused downregulation in APX in roots and leaves and CAT in leaves	Mukherjee et al. (2014)
		10–22 nm 125, 250, 500 mg/kg	Garden pea	Generate less toxicity as based on ROS, H_2O_2, and chlorophyll content	Mukherjee et al. (2014)
		10 nm 250, 500, and 750 mg/L	Alfalfa root	Lower level of protein, diminish plant biomass	Bandyopadhyay et al. (2015)

(continued)

Table 1 (continued)

S. No.	Nanoparticle	Nanoparticle size (nm) and concentration	Plant species	ROS-dependent phytotoxic effect	References
		< 50 nm; 200 and 300 mg/L	*Arabidopsis*	Plant growth reduced by 20–80%, chlorophylls a and b content reduced up to 50%, inhibited expression of chlorophyll synthesis and photosystem structure genes	Wang et al. (2016)
		90 ± 10 nm 400, 800, 1600, and 3200 mg/kg	Maize root	Increased O2 at 400e3200 mg/kg and increased SOD activities at 3200 mg/kg in leaves	Wang et al. (2016)
		35 ± 5 nm 10, 100, and 1000 mg/L	*Schoenoplectus tabernaemontani*	Reduction in biomass content at 1000 mg/L	Zhang et al. (2015)
		85 nm 200, 400, 800 mg/L	*Allium cepa*	An increase in cytotoxicity in root cells, DNA fragmentation; observation indicated an increase in ROS and glutathione peroxidase production, whereas a decrease in catalase activity	Ghosh et al. (2016)
		500 to 1500 mg/L ZnO NPs	*Brassica nigra*	Adversely affects the seed germination and seedling growth, leads to an increase in the antioxidative activities and nonenzymatic antioxidants	Zafar et al. (2016)

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Table 1 (continued)

S. No.	Nanoparticle	Nanoparticle size (nm) and concentration	Plant species	ROS-dependent phytotoxic effect	References
		15.37 nm 100, 200 µM	*Triticum aestivum*	Caused reduction in photosynthetic efficiency and higher level in hydrogen peroxide and lipid peroxidation, antioxidant activity	Tripathi et al. (2017d)
		200, 400, or 800 mg/L	Tomato (*Solanum lycopersicum* L.)	The content of chlorophylls molecules got reduced to affect photosynthetic efficiency, enhanced the transcription of genes which are responsible to antioxidant capacity	Wang et al. (2018)
		20, 50, 100, and 200 mg/L	*Arabidopsis thaliana* seedlings	Triggered primary root growth	Prakash et al. (2017)
		250, 500, or 1000 mg/L	*Citrus maxima* seedlings	Caused leaf vein chlorosis and strong oxidative stress to plant shoots	Lian et al. (2019)
3.	CuO	<50 nm 0.5, 1, 2, 5, 10, 20, 50, 100 mg/L	*Arabidopsis*	Retardation in root growth, dose-dependent increase in anthocyanin content, superoxide, and hydrogen peroxide. Reactive oxygen species production Significant induction of genes related to oxidative stress responses, sulfur assimilation, glutathione, and proline biosynthesis	Nair and Chung (2014b)

(continued)

Table 1 (continued)

S. No.	Nanoparticle	Nanoparticle size (nm) and concentration	Plant species	ROS-dependent phytotoxic effect	References
		10–50 nm 0, 20, 50, 100, 200, 500 mg/L	Mung bean	Decreased biomass and root length at all concentrations; reduced chlorophyll content above 100 mg/L; no changes in carotenoid content; increased H_2O_2 and lipid peroxidation; increased reactive oxygen species production with increase in concentration; modulations in gene expression	Nair et al. (2014)
		<50 nm 0.5, 1, 1.5 mM	Barley	Dose-dependent reduction in shoot and root growth Significant decrease in GSH/GSSG ratio Increase in hydrogen peroxide and lipid peroxidation with increased concentration of NP	Shaw et al. (2014)
		<50 nm 2.5, 10, 50, 100, 1000 mg/L	*Oryza sativa*	Dose-dependent decrease in photosynthetic rate, transpiration rate, stomatal conductance, and photosynthetic pigment contents Dose-dependent increase in ascorbate peroxidase and superoxide dismutase	Costa and Sharma (2016)

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Table 1 (continued)

S. No.	Nanoparticle	Nanoparticle size (nm) and concentration	Plant species	ROS-dependent phytotoxic effect	References
		40 nm 10, 50, 100, 150, 200 mg/L	*Lemna minor*	Increase in peroxidase, catalase, superoxide dismutase activity Increase in lipid peroxidation Inhibition of plant growth	Song et al. (2016)
		10–30 nm 100 and 200 mg/L	Cucumber (*Cucumis sativus*)	Increase in H_2O_2 and MDA contents caused adverse phenotypical changes along with decreased biomass in a concentration-dependent manner	Mosa et al. (2018)
		<50 nm 25, 50, 100, 150 and 200 mg/L	*Zea mays*	Retardation in germination and enzymatic antioxidants (SOD, CAT, POD, and APX) and nonenzymatic antioxidants (phenolics and flavonoids) under elevating concentrations of Cu NP	El-Shazoly and Amro (2019)
4.	CeO_2	7 nm 500, 1000, 2000, 4000 mg/L	Soybean	At higher concentrations induced genotoxicity, a new band in the roots' RAPD profile was observed	Lopez-Moreno et al. (2010), Hernandez-Viezcas et al. (2013)
		<8.0–1 nm 0, 62.50, 125, 250, 500 mg/L	Coriander	Improved growth of plant with enhanced biomass; increased ascorbate peroxidase activity in roots and catalase activity in shoots	Morales et al. (2013)

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Table 1 (continued)

S. No.	Nanoparticle	Nanoparticle size (nm) and concentration	Plant species	ROS-dependent phytotoxic effect	References
		8 ± 1 nm 400, 800 mg/kg	*Oryza sativa*	Reduced H_2O_2 generation in shoots and roots but increased electrolyte leakage and lipid peroxidation in shoots	Rico et al. (2013)
		8 ± 1 nm 0, 125, 250, 500 mg/kg	Corn	No impact on chlorophyll contents and gas exchange	Zhao et al. (2015)
		8 ± 1 nm 100, 400 mg/kg	Wheat (roots and leaf)	Changes structure of leaf cells, chloroplasts, nuclei, bent, and loosely arranged thylakoids, decreases chlorophyll contents, and exhibits variation in protein content	Du et al. (2015)
		500, 1000, and 2000 mg/L	Barley (roots, shoots, genetic material)	An increase in oxidative stress and chromatin modifications nCeO2 were able to induce an increase of a ROS formation at all the concentrations assayed	Mattiello et al. (2015)
		1000 mg kg/L	Lettuce (*Lactuca sativa*)	Maximum concentration significantly deteriorates plant growth and biomass production. The stress-responsive antioxidant enzyme activity such as superoxide dismutase (SOD), peroxidase (POD), and malondialdehyde (MDA) activity was disrupted	Gui et al. (2015)

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Table 1 (continued)

S. No.	Nanoparticle	Nanoparticle size (nm) and concentration	Plant species	ROS-dependent phytotoxic effect	References
		Higher concentration	*Arabidopsis thaliana*	Higher concentrations, CeO_2-NPs reduced growth and had adverse effects on the antioxidant systems and photosystem	Yang et al. (2017)
		<25 nm 10, 50, and 100 mg/kg	*Radish* Raphanus sativus Root, leaves, cellular part	Mainly absorbed by the root and improved the activity of antioxidant enzyme system to scavenge the damage of free radicals in radish root and leaf	Gui et al. (2017)
		8 ± 1 nm 200, 400, and 800 mg/kg	Sunflower (*Helianthus annuus* L.) soil root, leaves	Recorded necrosis and chlorosis in old leaves, as well as an increase of superoxide dismutase (SOD) at high nano-CeO2 level, SOD activity decreased	Tassi et al. (2017)
5.	AuNPs	24 nm 10 µg/mL, 10 and 80 µg mg/L 10 to 18 nm 0, 1, 10, and 100 mg/L	*Arabidopsis thaliana* primary and lateral roots	It enhances total seed yield, seed germination rate, vegetative growth, and free radical scavenging activity Length of primary roots damaged at highest concentration	Kumar et al. (2018), Siegel et al. (2018), Milewska-Hendel et al. (2019)
		– 1 mM	*Vigna unguiculata*	No significant change on growth, proline, and malondialdehyde	Shabnam et al. (2014)
		2–19 nm 10 µg mL^{-1}	*Hordeum vulgare*	Lower the plant biomass, yellowing of leaves due to ROS production and lipid peroxidation	Shukla et al. (2014), Feichtmeier et al. (2015)

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Table 1 (continued)

S. No.	Nanoparticle	Nanoparticle size (nm) and concentration	Plant species	ROS-dependent phytotoxic effect	References
		50 nm 100, 200, 300, and 400 ppm	*Brassica juncea*	A decrease in overall growth was attributed to increase in free radical stress and increase in biomarkers such as antioxidative enzymes, proline, and hydrogen peroxide due to the formation of reactive oxygen species	Gunjan et al. (2014)
6.	TiO_2 NP	25.9 ± 12.6 nm 22.3 ± 7.5 nm 250, 500, and 1000 mg/mL	Oat, cucumber Tomato Cabbage Soybean *Root*	Altered germination of cabbage, cucumber, oat, and soybean and affected root length of cabbage, corn, cucumber, lettuce, oat, and onion	Andersen et al. (2016)
		27 ± 4 nm 250, 500, and 750 mg/kg	Cucumber, soil root	CAT activity activated at low concentration, while at 500 mg/kg decreased APX activity Caused change in contents of lipids, amide, lignin, and carbohydrates	Servin et al. (2013)
		15 nm 100 mg/L	*Linum usitatissimum* seeds	Reduction in root biomass and root length. Seed germination also got affected after 24 h	Clement et al. (2013)

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Table 1 (continued)

S. No.	Nanoparticle	Nanoparticle size (nm) and concentration	Plant species	ROS-dependent phytotoxic effect	References
		–	*Ulmus elongata*	Leads to reduced photosynthetic rate via non-stomatal regulation, increased chlorosis of leaf, defoliation, and caused disrupted growth due to ROS generation	Gao et al. (2013)
		20 nm 1200, 1500, 1700, and 2000 mg/L	*Brassica napus*	TiO_2 improve the germination and root growth	Mahmoodzadeh et al. (2013)
		90–98 nm 12.5 to 100 mg/L	*Allium cepa* Bulb	Increase in ROS content based on concentration-dependent increase Concentration-dependent increase in genotoxicity	Pakrashi et al. (2014)
		< 25 nm 0.01, 0.1, 1, 10 mg/L	*Hydrilla verticillata* plant	Increase in catalase and glutathione reductase activity at 10 mg/L concentration increase in hydrogen peroxide level happened, decreased ratios of GSH/GSSG indicated an activation of GSH-dependent pathways counteracting ROS formation	Okupnik and Pflugmacher (2016), Spengler et al. (2017)
		–	*Spinacia oleracea*	Increases light absorption and quantum yield in photosystem II	Yang et al. (2006), Lei et al. (2008), Qi et al. (2013)

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Table 1 (continued)

S. No.	Nanoparticle	Nanoparticle size (nm) and concentration	Plant species	ROS-dependent phytotoxic effect	References
		<25 nm 0.1, 1, 2.5, 5%	*Tobacco*	Reduced biomass, inhibited germination and root length; upregulation of alcohol dehydrogenase and ascorbate peroxidase	Frazier et al. (2014)
		7–40 nm 2–10 mg/kg	*Chickpea*	Reduction in electrolyte leakage and malondialdehyde content at 5 mg/kg treatment	Mohammadi et al. (2014)

review about various engineered nanoparticle interactions with plants and their roles in inducing oxidative stress.

3.1 Nanoparticle in Plants

Different types of nanoparticles (NPs) and nanomaterials, each with specific physicochemical characteristics, are increasingly used in agriculture in the form of fertilizer, herbicides, and insecticides to increase crop productivity. Although their use has improved our agri-enterprise but NPs get accumulate and contaminate the environment due to their harmful effects on living systems, including plants. As per Siddiqui et al. (2015), engineered nanoparticles are able to enter into plant cells and can transport chemicals into a different compartment of plant cells. Nanoparticles interact with plants causing many morphological and physiological changes, depending on the properties of NPs. Scientists from their findings suggested both positive and negative effects on plant growth and development, and the impact of engineered nanoparticles (ENPs) on plants depends on the composition, concentration, size, and physical and chemical properties of ENPs as well as plant species (Ma et al. 2010; Siddiqui et al. 2015) (Table 1). The literature in concern to the response of plants to nanoparticle exposure reveals chemical interactions that involve disturbance of ion cell membrane transport activity (Auffan et al. 2008; Nel et al. 2006), oxidative damage (Foyer et al. 2002), and lipid peroxidation (Kamat et al. 2000); toxic effects on photosynthesis and level of antioxidants could be partially alleviated by treating nanoparticle (Tripathi et al. 2017b, c). Hence, in the following section, we are discussing in details about the toxic impact of widely used nanomaterials on plants.

3.1.1 Silver Nanoparticle in Plants

The silver nanoparticles are intensively used daily and have broader applications in many commercial and industrial sectors (Piccinno et al. 2012). Various studies show marked positive and negative impacts of AgNPs which depend on factors regulating the uptake, accumulation, and translocation in plants (Siddiqui et al. 2015; Tripathi et al. 2017b). AgNP uptake depends upon the cellular permeability of plant species and on the size and shape of AgNPs (Tripathi et al. 2017b). After their entry into the cells, they regulate the accumulation of protein and various physiological enzymes; in turn, their toxicity affects plants by producing ROS together with DNA destruction (Siddiqui et al. 2015).

Silver nanoparticle causes phytotoxicity from seedling growth to a fully developed stage of the plant (Tripathi et al. 2017b, c) (Fig. 2; Table 1). The dreadful toxicity of AgNPs is more visible in roots as compared to shoots because roots are the main site of interaction (Yin et al. 2012; Tripathi et al. 2017c).

The main reason for the toxicity of AgNPs in the plants is its impact on the biochemical properties of plants and inducing free radical generation resulting in oxidative stress in plant cells. In earlier reports it was reviewed that toxicity has been recognized to different mechanisms: (a) to the release of silver ions (Ag^+) (Kaveh et al. 2013), (b) to oxidative damage (Yin et al. 2013), and (c) to the coating as well as to the size and the shape of AgNPs (Gorka et al. 2015; Kim et al. 2012; Osborne et al. 2015). In green plants, photosynthesis occurs within the chloroplasts that are the main source of reactive oxygen species (ROS) (Asada 2006; Jaspers and Kangasj€arvi 2010), and in the aquatic plant, *Spirodela polyrhiza*, the chloroplasts seem to be one of the targets of AgNPs (Jiang et al. 2014a, b). Similarly, in the duckweed, *Wolffia globosa*, the effect of AgNPs was related to the blocking of electron transfer that induces oxidative stress under the light. The previous finding showed that (1) AgNPs affect photosynthesis that promotes ROS generation by inducing the imbalance of energy transfer and (2) AgNPs can be internalized by the plant cell and their ion release (Ag^+) affects photosynthesis (Zhu et al. 2016; Jiang et al. 2017). Therefore the impact of AgNPs on morphology and physiology of plants depends on the size and shape of NPs. Syu et al. (2014) studied the effect of three different morphologies of AgNPs on physiological and molecular response of *Arabidopsis* and suggested that decahedral AgNPs showed the highest degree of root growth promotion; however, the spherical AgNPs had no effect and triggered the highest level of anthocyanin accumulation in *Arabidopsis* seedlings.

Several studies on the phytotoxicity of AgNPs proved that the phytotoxicity of AgNPs is positively correlated with the concentration of AgNPs during exposure. AgNPs can only cause negative effects on plants when applied with a concentration above a certain threshold. Mirzajani et al. (2013) showed that AgNPs were not effective to change cell morphology or structure of rice root at low concentrations

(30 μg/mL); however, with an increased concentration of 60 μg/mL, AgNPs not only penetrated the cell wall but also destroyed structure, morphology, and the structural features of the cells. Oukarroum et al. (2013) found that AgNP treatment induced oxidative stress by enhancing intracellular ROS production in the aquatic plant *Lemna gibba* with the increasing concentration of AgNPs. Therefore AgNPs induced oxidative stress and exhibited phytotoxicity only when applied in higher concentrations in different plant parts (Yan and Zhong Chen 2019).

3.1.2 Zinc Oxide Nanoparticles

Zinc oxide nanoparticles (ZnO NPs) are most commonly used NPs in a variety of applications (Wang et al. 2018), and they increased the potential of their direct release into the environment. The earlier evidence suggests that ZnO NPs increase plant growth and development at a lower concentration in peanut, soybean, wheat, and onion (Prasad et al. 2012; Sedghi et al. 2013; Ramesh et al. 2014). However, a higher dose of ZnO NPs impaired plant growth. Zinc oxide nanoparticles had extensive effects on many morphological, physiological, and molecular traits of a plant (Raliya and Tarafdar 2013). Prakash et al. (2017) treated seedlings of *Arabidopsis thaliana* with five concentrations of zinc oxide nanoparticles (0, 20, 50, 100, and 200 mg/L) and analyzed morphological changes. The obtained data confirmed that the fresh weight as well as the length of primary root was decreased after exposure to higher concentrations (except for 20 mg/L) of zinc oxide nanoparticles (Table 1).

The toxicity effects of ZnO NPs have been observed in several different plant species including *Arabidopsis* (Lee et al. 2010), buckweed (Lee et al. 2013), wheat (Du et al. 2011), dotted duck meat (Thwala et al. 2013), cucumber (Zhao et al. 2013), rapeseed (Kouhi et al. 2014), alfalfa (Bandyopadhyay et al. 2015), and cowpea (Wang et al. 2013) (Table 1). The majority of the studies proved that the inhibitory effect of ZnO NPs on plant growth and development is mainly due to the induction of oxidative stress (Hernandez-Viezcas et al. 2011; Thwala et al. 2013; Bandyopadhyay et al. 2015). To further investigate the mechanisms of the toxicity effects of ZnO NPs on plant growth and development, Wang et al. (2016) examined the effects of ZnO NPs on biomass accumulation and photosynthesis in *Arabidopsis* and observed that ZnO NPs led to decrease in biomass accumulation in shoots and roots, but not in carotenoid contents. Phytotoxicity of NMs is not only dose-dependent, but it is also related with the size and shape of NPs. Mukherjee et al. (2016) found that alumina-doped ZnO NPs (15 nm) exerted higher negative effects than bare (10 nm) and aminopropyl triethoxysilane-coated ZnO NPs (20 nm) in green pea. Burman et al. (2013) results have also demonstrated that the effect of nano-ZnO could be either beneficial or toxic and this depends on plant species, plant part, and concentration used (Table 1).

3.1.3 Copper Oxide Nanoparticles (CuO NPs)

Copper is seen as the third most important metal due to its involvement in various physiological and enzymatic activities in plants (Liu et al. 2018). Cu is an important micronutrient required by plants at administered concentrations. Quantity above threshold limit in agriculture has contributed to major environmental pollution (Pandya-Lorch 2012).

In farming, copper oxide nanoparticles have used in different ways as fertilizers, plant growth regulators, pesticides, herbicides, and additives for soil remediation (Xiong et al. 2017). A study on the accumulation of CuO NPs on lettuce and cabbage at concentration of up to 250 mg/L shows reduced water content and growth of the vegetables (Xiong et al. 2017). The absorbed quantities also depend on the type of plant, soil, and environmental factors, as it has been reported that 0.3 mg/L Cu^{2+} released from 1000 mg/L of copper nanoparticles increases plant growth and is not toxic to the plant. However, some reactions may lead to release of copper ions inside the plant cells that could be toxic. Toxicity of copper nanomaterials results from their solubility in the medium of application and redox processes arising from their interactions with other substances (Xiong et al. 2017; Elemike et al. 2019). CuO NPs tend to be more toxic than copper nanoparticles due to their oxidative nature, even at low concentrations, but positively impact on the photosynthetic process of the plant. Based on previous studies, the phytotoxic dose of CuO nanoparticles varies according to the plant species (Table 1). For example, Wu et al. (2012b) reported that the phytotoxic dose of CuO NPs was 397.6 mg/L^{-1} for radish, 175.4 mg/L^{-1} for cucumber, and 12.9 mg/L^{-1} for lettuce.

Other than morphological changes, Cu NPs can also affect the biochemical content of plants as demonstrated by reduced chlorophyll content and increased hydrogen peroxide and lipid peroxidation that increased reactive oxygen species (ROS) production in cucumbers (Mosa et al. 2018). It has been already highlighted earlier that metal toxicity in plants leads to enhanced production of ROS which is causing oxidative stress by increased electrolyte leakage, protein oxidation, lipid peroxidation, DNA damage, and finally cell death due to Cu catalysis activity (Fidalgo et al. 2013; Sharma et al. 2012; Wani et al. 2018). Cu NP showed a significant diminish in chlorophyll contents, augment in H_2O_2, and MDA contents, as well as an increase in electrolyte leakage which induced damage to cucumber root plasma membrane. Collectively, this demonstrated that Cu NP induced oxidative stress in *C. sativus*. Also Prakash et al. (2014) recorded drastic root growth retardation and triggering their lignification in soybean under 400–500 mg/L^{-1} CuO NPs. Hence, chlorophyll is the critical photosynthetic pigment, and its levels can be a significant indicator of toxicity to plants (Ma et al. 2015). The effect of the copper nanoparticle also extends to the DNA level by inducing DNA damage in radish and grasses (Atha et al. 2012), as well as cucumbers (Mosa et al. 2018). AlQuraidi et al. (2019) focused on estimating the phytotoxic effect of Cu NP in *C. sativum*, and they confirmed by XRF analysis that Cu NP (20 nm) had a toxic effect on *C. sativum* root length and biomass along with a significant reduction in total chlorophyll content. Nano-sized particles of CuO proved more phytotoxicity than bulk particles and showed more drastic effect. Enzymatic antioxidants (SOD, CAT, POD, and APX) and nonenzymatic antioxidants (phenolics and flavonoids) could not maintain the survival of maize seedlings under elevating concentrations of Cu NP. Oxidative stress, sulfur assimilation of glutathione, and proline biosynthesis were also influenced by CuO nanoparticle exposure. The capacity of defense systems against ROS could be overwhelmed at sustained free radical action, leading to growth retardation and death incidence (El-Shazoly and Amro 2019).

3.1.4 Cerium Oxide NPs

Cerium oxide nanoparticles (CeO_2 NPs) are a rare earth metal oxide NPs and used in automotive industries and semiconductor industry. They can interfere with the cell metabolism due to its oxidative properties. Earlier reports showed that CeO_2 NPs be present in nanoparticle form and affect physiological and molecular response to plants (Zhang et al. 2012). CeO2 NP was observed to behave differently in tomato plant when coated with citric acid, in comparison to bare CeO2 NP (Barrios et al. 2015). The change in behavior of NP can be attributed to different chemical properties and size of the nanoparticle (Majumdar et al. 2014). Field and soil experiments with wheat, rice, and cotton have shown that application of CeO2 NP diminishes the quality of grain and reduced the physiological activity by destroying the vascular system (Rico et al. 2013; Du et al. 2015; Nhan et al. 2015).

The impact of CeO_2 NPs on antioxidant enzymes and oxidative stress in rice seedlings was examined by Rico et al. (2013). CeO_2 NPs could modify glutathione and sulfated metabolic pathways' expression in *Arabidopsis thaliana* (Ma et al. 2013). Further studies proved that at low concentrations of CeO2 NPs, H_2O_2 content decreases in root and shoot, while at high concentrations it leads to a variation in enzymatic activity, membrane damage, and photosynthetic stress in the shoots (Mura et al. 2013). The toxicity was probably attributed to the biotransformation of CeO2 NPs and the high sensitivity of plants to the released Ce^{3+} ions (Gui et al. 2015). CeO_2 NPs increase lipid peroxidation and H_2O_2 production in rice and maize (Zhao et al. 2012a, b; Rico et al. 2013a, b). Nanoparticle concentrations and plant species are main factors which can modulate the physiological responses of plants to nCeO2 exposure. Majumdar et al. (2014) establish an increased yield of kidney bean seeds exposed to nCeO2 at different concentrations. However, these researchers also observed a downregulation in phaseolin and lectins, proteins related to nutrient reserves, and carbohydrate metabolism, respectively (Zuverza-Mena et al. 2017). As reviewed in Table 1, CeO_2 NP toxicity has been linked to ROS generation followed by a response of the antioxidative defense mechanisms in plants.

3.1.5 Gold Nanoparticles

Large scale Usages of gold nanoparticles (AuNPs) in industries and research causes the unavoidable release into the environment. Gold is not an element required by plants for development, but the accidental absorption may often show change in plant growth (Siddiqi and Husen 2016). There are very few reports on negative impact of gold nanoparticles with different plant taxa. The effect of AuNPs of different sizes (10, 14, and 18 nm in diameter) and concentrations (1, 10, and 100 mg/L) on root growth of *A. thaliana* was investigated by Siegel et al. (2018). Similarly, Taylor and team (2014) and Kumar et al. (2013) have observed the consequence of gold nanoparticles on levels of microRNAs expression that regulates various morphological, physiological, and metabolic processes in *Arabidopsis thaliana*. They found that its root length was reduced by 75% at 100 mg/L^{-1} concentration.

Several studies have investigated the binding of various states of gold and gold-silver-copper alloy nanoparticles in *Medicago sativa*, *Brassica juncea*, and other living plant systems (Bali et al. 2010). The uptake of gold nanoparticles and their effect on different plant systems have been studied and summarized in Table 1. Barrena and coworkers have found that there is less toxicity of gold at doses of 62, 100, and 116 μg mL^{-1} for cucumber and lettuce plants, respectively. Similarly Jain et al. (2014) have accounted a dose-dependent effect of $KAuCl_4$ on primary root length of *Arabidopsis* seedling and observed that the treatment of the root with 10 ppm $KAuCl_4$ triggered a significant increase in length but at higher concentrations a significant decrease noted. It has been due to the production of ROS or stress-induced antioxidants (Poschenrieder et al. 2013). Feichtmeier et al. (2015) have studied the effect of spherical gold nanoparticles of 2–19 nm on barley seed germination. There was no significant effect on germination, but yellowing of leaves, darkening of roots, and decreased biomass were observed which further deteriorated with increasing concentration of gold nanoparticles due to ROS production and lipid peroxidation alleviation. Another study showed that AuNPs of different sizes were accumulated by tobacco but were not found to be taken up by wheat (Milewska-Hendel et al. 2019).

Shah and Belozerova (2009) believed that gold nanoparticles induced phytotoxicity in plants by inhibiting the function of aquaporins. Similarly, downregulation of gene-encoding proteins involved in the transport of aquaporins bonded to gold. Gold disrupts protein structure and may also displace some essential metal nutrients from proteins (Milewska-Hendel et al. 2019). Exposure of gold nanoparticles from 100 to 400 ppm decreases plant growth and was attributed to increase in free radical stress. In addition, proline (osmolyte) and hydrogen peroxide were also increased due to the formation of ROS. These findings have indicated that production of ROS depends on the concentration of gold nanoparticles, which impose physiological and biochemical stress over the seedlings of *B. juncea* (Gunjan et al. 2014).

3.1.6 Titanium Dioxide Nanoparticles

TiO2 is the oxide form of titanium and is naturally occurring; TiO_2NPs are used in a wide variety of applications, including cosmetics, sunscreens, food preparation, and drug delivery systems (Grand and Tucci 2016; Shi et al. 2013b). Compared to the number of investigations carried on AgNP phytotoxicity, TiO_2NP research is far from being sufficient. As with other substances such as carbon nanomaterials, TiO_2NPs exhibit a dual nature of both beneficial and toxic effects depending upon many experimental factors (Mukherjee et al. 2016). There have been several studies that have investigated the genotoxic potential of TiO_2NPs on different species of plants. A study on *Allium cepa* (onion) has shown that TiO_2NPs have high potential to interact with DNA and cause damage in root meristem cells after 18 h of exposure (Demir et al. 2014). A soil study by Servin et al. (2013) has demonstrated oxidative stress in *Cucumis sativus* L. fruit after growing plants in TiO_2NP-treated soil. At all concentrations higher levels of hydrogen peroxide (H_2O_2) were observed. Therefore an increase in catalase activities was recorded, while ascorbate peroxidase assay showed decreases in activity at 500 and 750 mg/kg. This indicates stress on the plant under the effect of TiO2NPs dosages in soil. A study by Song et al. (2013) has shown significant increase in superoxide dismutase enzyme activity in *L. esculentum* (tomato) when exposed to 200 mL of 5000 mg/L TiO_2NPs (27 nm) under greenhouse growing conditions. Gui et al. (2015) found significant increase of nitrate content and disruption in the activity of antioxidative enzymes and malondialdehyde (MDA) in *Lactuca sativa* under the influence of higher concentrations 100 and 1000 mg/kg nano-CeO_2 in soil, respectively. Similarly, Rico et al. (2013a, b, c, 2015) also reported a significant modification in the antioxidant system of rice (*Oryza sativa*) and a negative impact on rice grain quality. TiO_2NPs regulate various enzyme activities which involved in nitrogen metabolism and help the plants to absorb nitrate and also favor the conversion of inorganic nitrogen to organic nitrogen in the form of protein and chlorophyll that could increase the fresh weight and dry weight of plant (Yang et al. 2006; Mishra et al. 2014). TiO_2NPs act as a photocatalyst and induces an oxidation-reduction reaction (Crabtree 1998). TiO_2NPs noticeably promote aged seeds' vigor and chlorophyll formation and stimulates ribulose 1, 5-bisphosphate carboxylase (Rubisco) activity and increase photosynthesis, thereby increasing plant growth and development (Yang et al. 2006). TiO2NPs increase light absorbance, hasten the transport and conversion of the light energy, protect chloroplasts from aging, and prolong the photosynthetic time of the chloroplasts (Yang et al. 2006). It may be due to TiO_2NPs which protect the chloroplast from excessive light by augmenting the activity of antioxidant enzymes, such as catalase, peroxidase, and superoxide dismutase (Hong et al. 2005).

3.1.7 Oxidative Burst and Its Consequence in Plants

Commonly used metal and metal oxide nanoparticles in industries are silver, zinc oxide, titanium dioxide, cerium dioxide, aluminum, copper, copper oxide, nickel, iron, etc. In addition to these nonmetal nanoparticles carbon nanotubes and fullerene are also used. Some of the studies depicted negative impacts of nanoparticles on plants, whereas others depicted positive impacts of nanoparticles on plant growth and development. Toxic impact of nanoparticle on plants depends on various physical and chemical properties of nanoparticle. Investigatory report shows existence of a clear correlation between size and toxic effects of NPs on the plants. Smaller-sized NPs were always observed to be more toxic to plants than larger-sized NPs (Rastogi et al. 2017). Other important aspects which determine the toxicity of nanoparticles are also included: plant tissue/organ, length of exposure, plant genotype, and developmental stage of the plant. Usually, the higher concentration of nanoparticles reduced plant growth, induced chlorosis in young leaves, reduced pigment content, altered enzymatic function, and damaged protein, DNA, and lipids (Arruda et al. 2015).

One of the common consequences of nanoparticle exposure in a concentration higher than the threshold value to plants at some stage is the induction of oxidative stress by enhancing the production of ROS such as superoxide radical (O_2^-), hydrogen peroxide (H_2O_2), hydroxyl radical ($OH^·$), and alkoxyl radical ($RO^·$). Although under normal growth conditions, the production of ROS in cells is low but, on an acquaintance of nanoparticles, may disrupt the cellular homeostasis of cells which in turn enhance the production of ROS. These ROS cause oxidative stress by initiating lipid peroxidation and degrading proteins, lipids, and nucleic acids (Melegari et al. 2013). Oxidative stress occurs when there is a serious imbalance in any cell compartment between the production of ROS and antioxidative defense, thereby leading to cell damage. The resistance of plants to oxidative stress depends on the overall balance between the production of ROS and antioxidant capability of cell (Fig. 3).

In plant systems these ROS are removed by antioxidative defense system comprising important enzymes like superoxide dismutase (SOD), guaiacol peroxidase (POD), ascorbate peroxidase (APOX), catalase (CAT) and glutathione reductase (GR), monodehydroascorbate reductase (MADHAR), dehydroascorbate reductase (DHAR), and antioxidants (α-tocopherol, ascorbic acid, glutathione, etc.) (Asada and Takahashi 1987). The superoxide radical (O_2^-) is dismutated by SOD into H_2O_2 and is further scavenged by CAT and various peroxidases. APOX and GR reduced H_2O_2 to water through the ascorbate-glutathione cycle. Consequently, the role of antioxidative enzymes becomes very important to combat the oxidative stress generated by nanoparticles to boost the resistance capacity of plants. These all enzymes act in a coordinated manner and constitute a pathway called as "Asada-Halliwell pathway" (Arora et al. 2002).

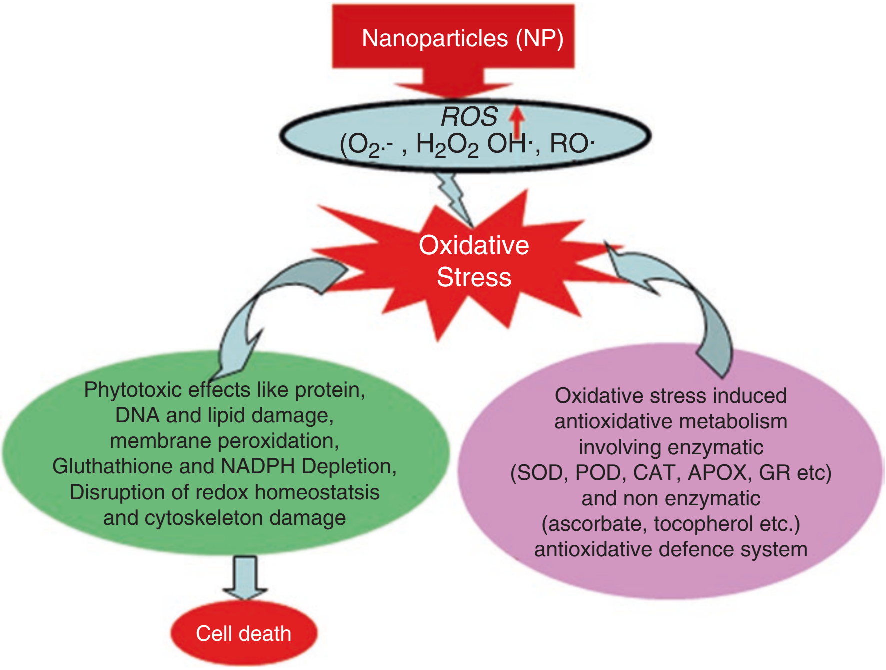

Fig. 3 Nanoparticles induced oxidative stress and related cellular damage in plants

3.1.8 Nanoparticle-Induced Phytotoxicity (Morphological, Physiological, Cellular, and Molecular Damage Caused by Nanoparticle)

Nanoparticle (NP)-induced oxidative stress causes various morphological, physiological, cellular, and molecular damages in plants (Fig. 4). Nanoparticles mainly caused toxic effects either because of physical restraints or release of toxic ions or by the induction of ROS. Accumulation of nanoparticles on cell surface might reduce the rate of photosynthesis as later decreased the exposed area. Further deposition of NPs might block the cell wall and obstruct nutrient molecules from entering the cells (Chen et al. 2012; Schwab et al. 2011). NPs could also adhere to plant roots and thereby inhibit the uptake of micronutrients (Arruda et al. 2015). The toxicity of NPs may also be attributed to excessive production of ROS. NPs produce ROS upon interaction with organisms or agents present in the environment (Navarro et al. 2008). The antifungal effects of ZnO NPs were due to excessive generation of ROS (Patra et al. 2012).

Li et al. (2015) have evaluated the phytotoxicity of titanium (TiO_2) nanoparticles (TiNP) in algae. Two different algae, *Karenia brevis* and *Skeletonema costatum*, were exposed to nano-TiO_2 (size 5–10 nm). Electron microscopy revealed the aggregation of nanoparticles in the algal suspension which inhibits the growth of algae. Further electron microscopy revealed that TiNP induced cellular damage by deforming cell membrane and cell organelles. TiNPs-induced oxidative stress

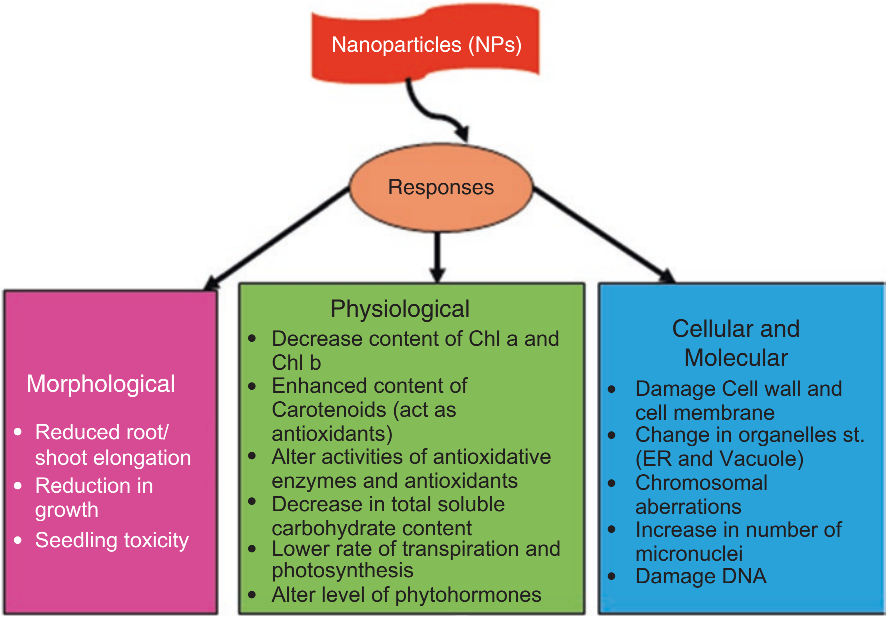

Fig. 4 Nanoparticle-induced phytotoxic effects in plants

enhanced the level of malondialdehyde (MDA) contents of algae and also alters the activities of antioxidative enzymes (SOD, CAT). The inhibitors of the electron transfer chain predicted that the site of ROS production and accumulation in algal cells was the chloroplast.

In another study on AgNPs, it was observed that AgNPs (size 20–80 nm) stunted the growth of seedlings of *Arabidopsis thaliana* in concentration- and size-dependent manner (Ma et al. 2010). FeNPs (size 22–67 nm) also retarded the growth of *Arabidopsis thaliana* by reducing the content of chlorophyll pigments (Morusenko et al. 2013).

Faisal et al. (2013) have reported the phytotoxic effects of NiO-NPs in roots of tomato (*Lycopersicum esculentum L.*). NiO-NPs translocated to root cells where they influence ultrastructural changes in organelles. NiO-NPs release Ni ions which enhanced the production of intracellular ROS, altered the activities of antioxidative enzymes (CAT and SOD), and enhanced level of lipid peroxidation. NiO-NPs also trigger the apoptotic pathway in tomato plant. Further Song et al. (2013) observed the phytotoxic effects of Ti and AgNPs on growth of *Lycopersicum* roots. Phytotoxicity of hydroxyapatite (HAP) which is widely used in bone reconstruction was verified by Jiang et al. (2014b) in mung bean plants.

Gubbin et al. (2011) while working on AgNPs proposed that NP-induced phytotoxicity is size, shape, concentration, and exposure time dependent. AgNPs at higher concentration (60 μg/ml) show growth inhibitory effects in *Oryza sativa* (Mirzajani et al. 2013). AgNPs at concentration of 60 μg/ml were able to penetrate the cell by destroying the cell structure. AgNPs decreased the level of chlorophyll b and total soluble carbohydrate content whereas increased the level of carotenoid which may be related to antioxidant activities of later.

Exposure of NPs is reported to be detrimental for plant growth. AgNPs (size <30 nm) were found to inhibit the growth of different plants, e.g., *Capsicum annum* L., *Pisum sativum* L., and *Arabidopsis thaliana* L. (Vinković et al. 2017; Tripathi et al. 2017c; Qian et al. 2013). The adverse effects of AgNPs are attributed to excessive production of ROS which enhanced the activities of antioxidative enzymes and also influenced the DNA damage and expression of different stress-related genes (Cvjetko et al. 2017; Saha and Dutta Gupta 2017; Jiang et al. 2014a, b). Physiologically AgNPs were observed to decrease the rate of transpiration and chlorophyll content (Tripathi et al. 2017c). Zuverza-Mena et al. (2016) reported significant alteration in proteins, lipids, lignin, cellulose, pectin, and different macromolecules in AgNP (size 2 nm, concentration 500 mg/L)-treated *Raphanus sativus* seedlings. Even the level of different phytohormones such as auxin and cytokinin was observed to be affected by the AgNPs (Yin et al. 2012; Vinković et al. 2017). CuO NPs have higher toxic effects than Cu NPs because of their oxidative properties. At higher dose of Cu and CuO NPs, the root morphology was reported to be poorly affected (Adamas et al. 2017). CuO NPs show adverse effect on plant growth by enhancing the production of ROS which in turn significantly enhanced the activities of antioxidative enzymes and antioxidant content (Shaw et al. 2014; Song et al. 2016). At physiological level CuO NPs were observed to reduce the rate of photosynthesis, transpiration rate, and stomatal conductance (Costa and Sharma 2016). Similar to silver nanoparticles, CuO NPs (Van et al. 2016) and CeO_2 NPs (Nhan et al. 2015) alter the level of phytohormones (indole-3-acetic acid and ABA) in cotton plants. Higher concentration of TiO_2NPs was observed to be toxic to plants (Rastogi et al. 2017; Rafique et al. 2014). The phytotoxic effects of TiO_2NPs were found to be almost similar to AgNPs and CuO NPs in terms of induction of oxidative stress, growth inhibition, and genotoxicity. Du et al. (2015) reported the toxic effects of CeO2 NPs in wheat and rice where the application of NPs reduced the quality of grain.

3.1.9 Molecular Damage

Kumari et al. (2011) have studied the phytotoxic effects of ZnO NPs at cytogenetic level by analyzing the genotoxic effects in root tips of *Allium cepa* L. At higher concentration of ZnO NPs (100 μg/ml, size <100 μm), chromosomal aberrations (sticky chromosomes) and a large number of micronuclei were reported. These chromosomal aberrations might be due to depolymerization of chromosomal DNA. These genotoxic effects might be induced by excessive production of ROS and TBARS (thiobarbituric acid reactive species). Stress of nanoparticles also alters the expression of different genes and proteins (Hossain et al. 2015). Genes primarily associated with metal and oxidative stresses were upregulated under the influence of AgNPs in *Arabidopsis thaliana* seedlings (Kaveh et al. 2013). Similarly ZnO NPs and FS (fullerene soot)-exposed *Arabidopsis thaliana* seedlings show upregulated expression of both biotic and abiotic stress-responsive genes (Landa et al. 2012). Higher concentration of CuO NPs regulated the level of expression of genes related to sulfur assimilation, glutathione and proline biosynthesis, and oxidative stress responses in *Arabidopsis thaliana* (Nair and Chung 2014b). The expression of photosynthetic genes was significantly decreased on exposure to TiO_2NPs (5 nm, 1 ppm) in case of *Chlamydomonas reinhardtii* (Simon et al. 2013). Increase in expression of proteins related to oxidative stress pathway, cell apoptosis, and protein degradation was observed in AgNP (size 30 nm, concentration 60 ppm)-treated roots of *Oryza sativa* L. (Mirzajani et al. 2014). Further Vannini et al. (2013) reported alteration of some proteins related to the ER and vacuole indicating these two organelles are targets of AgNPs (100 ppm) in roots of *Eruca sativa* seedlings.

Thus, the abovementioned evidence-based study indicates that nanoparticles exhibit an impact on plants at morphological level, biochemical level, and genetic level. So, the presence of different kinds of NPs in environment exemplifies a possible threat to the environment.

4 Possible Mechanism Involved in Induction of Oxidative Stress in Plants by Nanoparticle

Previous scientific studies on nanoparticles suggest most of the nanoparticles are highly toxic to plants when exposed to high concentrations. For exhibiting toxic effects on plants, the nanoparticle uptake and its translocation to different tissues are the prerequisite. Moreover, based on their biological activities and transportation properties, nanoparticles might interrupt with a wide array of metabolic processes to produce harmful effects in plants (Rastogi et al. 2017). The uptake and toxicity of nanoparticles in plants, animals, and humans are directly related to their shape, size, aggregation, constituents, porosity, surface area, concentration, hydrophobicity, and electrical and magnetic properties (Pacheco-Torgal et al. 2018). Nanoparticles undergo a chemical transformation in the soil as well as within the plant system such as alteration of oxidative state or acquiring protein corona which is dependent upon the environmental conditions. Stable nanoparticles are also able to modify chemically and become detrimental for plants (Rui et al. 2016). Similar alterations were observed in cucumber plants exposed to hydroponic conditions; cerium (IV) oxide nanoparticles were reduced to Ce (II) (Rui et al. 2016).

4.1 Uptake of Nanoparticles

Two diverse exposure modes of plants to nanoparticle are foliar exposure and root exposure. The first barrier for the entry of nanoparticles into the plant cells is the cuticle in the higher plants, as the plants cells are protected by a waxy cuticle which protects plants against excessive water loss and unmonitored exchange of various solutes (Pollard et al. 2008). There are two routes for cuticular transfer of nanoparticles, viz., diffusion and permeation, i.e., the lipophilic pathway and the polar solutes are translocated via polar aqueous pores, i.e., hydrophilic pathways (Eichert et al. 2008; Eichert and Goldbach 2008).

The plant cell walls and plasma membranes are injured in response to elevated concentrations of nanoparticles and consequently result in their penetration in the plant cells and interfere with a wide array of physiological processes (Mazumdar and Ahmed 2011; Mirzajani et al. 2013). The nanoparticles enter the plant cells via roots or root junctions and wounds/injuries. Nanoparticles have to pass through a plethora of physiological and chemical obstruction to translocate to the upper parts of the plant. Cell walls are considered a porous matrix composed of polysaccharide fibers through which nanoparticles penetrate in the cells and bind to the protein transporters such as aquaporins and ion channels (Tripathi et al. 2017a; Rico et al. 2011). Cell walls have a property to permit the entry of particles of smaller size and restrict the entry of larger ones, and therefore these nanoparticles can freely enter through this layer comparatively easier than other membranes. The exclusion size range for cell walls is 5–20 nm (Dietz and Herth 2011). A few nanoparticles have been reported to stimulate the development of larger pores in the cell walls, furthermore resulting in entry of nanoparticles through it (Navarro et al. 2008; Kurepa et al. 2010). The nanoparticles that enter via cell walls are subjected to different gradients of osmotic potential and capillary forces and further diffuse through the apoplastic regions into the endodermis (Lin et al. 2009; Deng et al. 2014). The nanoparticles enter the cell wall via endocytosis (Etxeberria et al. 2006) and are translocated to the other plant tissue through symplastic movement (Ma et al. 2010). More recently, Wong et al. (2016) recommended a mathematical model which affirmed lipid exchange machinery for nanoparticle transportation within the plant cells. It was further revealed that the size, zeta potential, and magnitude are the vital determinants modulating the transportation of nanoparticles in the plant cells.

The nanoparticles translocate within the plants cells via the formation of complexes with root exudates and membrane transporter proteins (Yadav et al. 2014). Another pathway for uptake of nanoparticles in the cells is through symplastic movement via the inner side of the plasma membrane. The nanoparticles migrate to neighboring cells through plasmodesmata (20–50 nm diameter channels) (Deng et al. 2014). An additional path of entry of nanoparticles into the plant cells is through the stomatal openings and is further translocated to different parts of plants (Larue et al. 2012a, b; Hong et al. 2014). For example, wheat, corn, beans, rapeseed, cucumber, and lettuce are a few plants in which nanoparticles are internalized through leaves (Chichiricco and Poma 2015). Various nanoparticles including cerai, iron oxide, zinc oxide, titania, and silver are translocated via leaves depending directly upon the size and composition of nanoparticles (Chichiricco and Poma 2015). Morphologically the size of the stomatal opening is about 25 μm in length and 3–10 μm in width (Eichert et al. 2008). Furthermore, Eichert and Goldbach (2008) affirmed using an indirect calculation method the equivalent pore radius of stomata for entry of nanoparticles is larger than 20 nm. Various studies confirmed the occurrence of this pathway for nanoparticle uptake in plants including *Cucurbita*

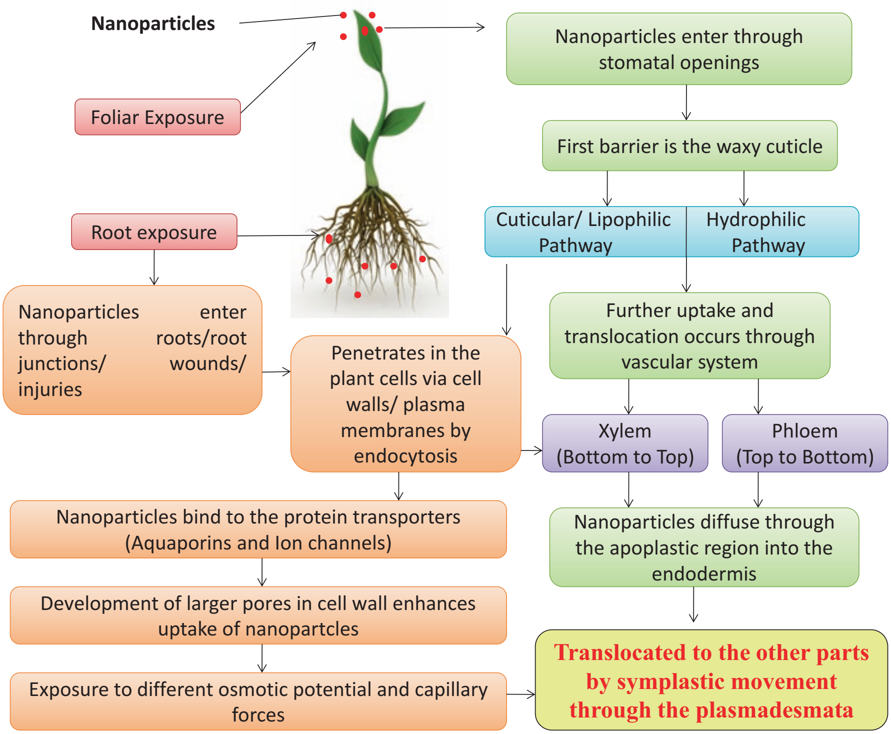

Fig. 5 Schematic representation of nanoparticle uptake in plants

pepo, *Arabidopsis thaliana*, *Allium porrum*, *Citrullus lanatus*, and *Lactuca sativa* by employing TEM, CLSM, and μ-XRF instrumentation (Uzu et al. 2010; Larue et al. 2014).

Vascular system also acts as a pivotal route for long distance translocation of nanoparticles, after their entry from the leaves through the stomatal pathway. Traditionally it was reported that photosynthate and macromolecules specifically sugars in the leaves are translocated to the downward shoots and roots of plants via the phloem pathway (Lough and Lucas 2006). Generally, the long distance translocation of liquids in plants occurs via the xylem and phloem vasculature. The direction of flow of liquids in xylem is from the bottom (roots) to above parts of plants, whereas in phloem it is from the top (leaves/shoots) to bottom (Lough and Lucas 2006). In an investigation by Wang et al. (2013), it was reported that the foliar uptake of four metal oxide nanoparticles by the leaves of watermelon involved stomatal pathway and was affirmed by employing TEM. It was further suggested that the deposits of the metal element were found in the roots and shoots and were concluded that the nanoparticles might have passed through the shoots and reached the roots via phloem sieve tubes. Figure 5 depicts the schematic representation of nanoparticle uptake in plants.

4.2 Nanoparticles and Plant Interaction Pathways

Through translocation of mineral nutrients, the plants regulate the stability athwart the ecosystem involving the food chain and web (Monica and Cremonini 2009). Surfeit literature suggests equally advantageous and lethal effects of nanoparticles on plants. Canas et al. 2008, reported that nanoparticles enhanced the root growth in onion and cucumber plants, although a lowered the same in tomato plants. On the contrary, zinc oxide resulted in an enhancement in root lengths in soybean plants (Lopez-Moreno et al. 2010), whereas in rye grass, broken root tips and shrunken roots were observed (Lin and Xing 2007).

Nanoparticles may hinder various metabolic processes in plants in plethora of ways, including by (i) modulating gene expression (Nair and Chung 2014b), (ii) making available specific micronutrients (Liu and Lal 2015), and (iii) snooping with various oxidative processes in plants and consequently result in oxidative stress (Hossain et al. 2015). The entry of nanoparticles into the plant cells results in disruption of electron transport chain of chloroplast and mitochondria, which eventually leads to enhancement in oxidative burst and rise in ROS generation (Faisal et al. 2013; Pakrashi et al. 2014; Cvjetko et al. 2017). Earlier it has been demonstrated that the rate of carbon fixation is limited, which results in an elevation in the photoinhibition impending to navigation of the photosystems to enhance the production of superoxide anion and hydrogen peroxide radicals (Foyer and Noctor 2005). Excessive ROS produced interacts with the cellular constituent, resulting in protein modification, DNA damage, and lipid peroxidation (Van Breusegem and Dat 2006). A wide array of reports affirm enhanced DNA damage and lipid peroxidation as a consequence of plant-nanoparticle interaction (Belava et al. 2017; Saha and Dutta Gupta 2017). Augmentation in ROS production is capable of inducing apoptosis and necrosis (Rastogi and Pospíšil 2010), eventually resulting in programmed cell death. Nevertheless, ROS despite having a destructive role when the levels are elevated, they also act as an imperative signaling molecule in a range of cellular phenomena's including acclimation to varied environmental cues (Sharma et al. 2012; Kohli et al. 2018, 2019).

Owing to the multifaceted functioning of ROS molecules, the plants cells have employed a sturdy antioxidative defense mechanism to specifically manage the enhanced levels of ROS. The antioxidative defense machinery is comprised of enzymatic component (SOD, CAT, and GPOX) and nonenzymatic components, viz., glutathione, tocopherol, phenols, ascorbate, and carotenoid molecules (Sharma et al. 2012; Kohli et al. 2018). In order to acclimatize to this oxidative burst, the plants increase the activity of antioxidative enzymes and production of antioxidants (Rastogi and Pospíšil 2010; Sharma et al. 2012). Under the sway of nanoparticles, also the levels and activity of antioxidative component are elevated (Faisal et al. 2013; Costa and Sharma 2016), which affirm the modulation of the antioxidative defense system in response to plant and nanoparticle interaction. Recent studies reveal participation of plant hormones in plant stress signaling responses (O'Brien and Benková 2013). An intricate cascade of synergistic and antagonistic interaction

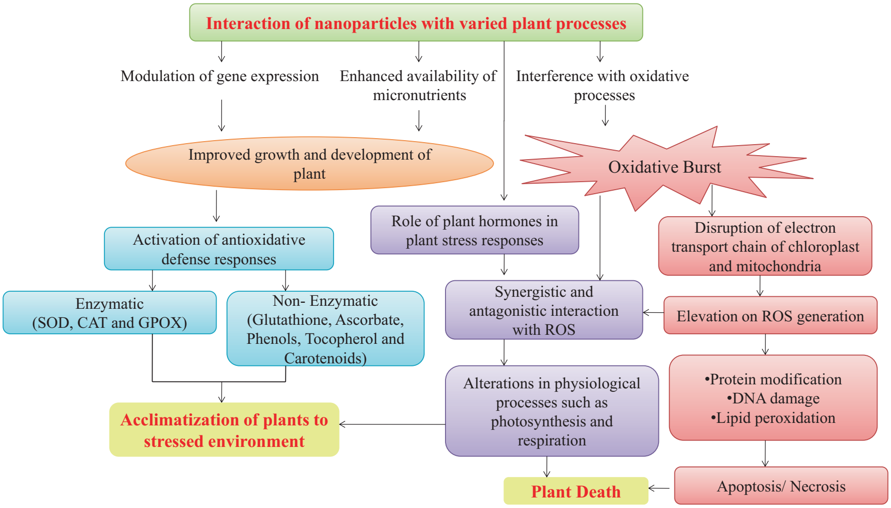

Fig. 6 General machinery of nanoparticles interaction with plants

between various phytohormones modulates plant development and stress acclimatization. A complex cross talk between hormone and ROS signaling consequently influences the activities of each other (Kwak et al. 2006). Various plant hormones are upregulated/downregulated in retaliation to different types of stresses (O'Brien and Benkova 2013).

Figure 6 elaborates the general machinery of nanoparticle interaction with plants.

Photosynthesis is one of the most important phenomena for overall recital of plants (Kalaji et al. 2014). As photosynthesis is the primary energy input process, alterations in photosynthesis result in deleterious impact on plant metabolism and physiology. Assessment of photosynthetic attributes, viz., photosynthetic pigment content and activities, is a significant indicator to access the influence of stressed environment. A wide array of reports have indicated hazardous impact of nanoparticles on the photosynthetic activity and pigment content in plants (Qian et al. 2013; Tripathi et al. 2017a, b, c). Higher levels of nanoparticles lead to brutal influence on plant growth and development and have been tabulated earlier in the chapter.

5 Conclusion

With increasing modernization, there is greater increase in the of nanoparticle utilization. Due to its intensive use, it becomes an undeniable part of human life. But, we also cannot ignore the fact that its excessive use increases its concentration and accumulation in the environment which causes the serious impact on the plant as well as on animal kingdom. Thus, the study of NPs with plant sciences at morphological, physiological, and at molecular level is mandatory to gain further insight into the impact of NPs. NP interaction with plant causes nanotoxicity that triggers production of ROS which is finally induces oxidative stress inside the plants. To cope up with oxidative stress, plant increases the production of the antioxidative activity. Therefore, if the antioxidant molecule is not able to control the ROS production, then ROS oxidized the macromolecule completely and causes the cell death. Nanomaterial, nanoparticle, and nanowaste-related study is essential as it may have the potential to cause a serious impact on the agriculture in the future.

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Variability, Behaviour and Impact of Nanoparticles in the Environment

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1 Introduction

Nanotechnology has been growing in the last few decades in several fields of science, including materials sciences, electronics, optics, medicine, plastics, energy, agriculture and aerospace and thus involved in the continuous production of NMs. NMs enter in the environment through various natural activities like volcanic activities, forest fires, soil erosion, weathering, clay minerals and dust storms or from intentional/unintentional human activities like burning of fossil fuels, mining, automobile traffic, (Smita et al. 2012). These are defined as particles with size ranging from 1 to 100 nm. The destiny of NPs in the environment is controlled by the combined effects of their physicochemical properties and their interactions with other pollutants (Maiti et al. 2016). As they have unique properties, such as extremely small size and high surface-volume ratio, the nanoparticles behave in the environment and as a result are gaining more research attention.

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Nanoparticles after being released into the different spheres of atmosphere behave in different manners. When released into the atmospheric environment NPs are exposed to sunlight and UV wavelengths at higher degrees than those released into other sections of the environment (Mitrano et al. 2015). This exposure increases the possible outcomes of photochemical changes to NPs. Similarly when they enter the soil, their mobility relies upon a number of variables such as physical-chemical properties, characteristics of the soil and environment and interactions of NPs with natural colloidal material (Jafar and Hamzeh 2013). The fate of NPs, after entering the aquatic system from industrial release, dumping of wastewater treatment effluents and/or through surface runoff from soils, is affected by various processes like accumulation, disaggregation, diffusion, interaction with other components, biological degradation and abiotic degradation, including photolysis and hydrolysis. Though these NPs have various technical advantages, when they enter the environment they pose various negative effects on living organisms, which is discussed in the chapter in detail. How the fate of these NPs in the environment changes due to their behaviour and interactions with other particles in the environment is also reviewed.

2 Sources, Classification and Properties of Nanoparticles

2.1 Sources of Nanoparticles

Based on origin, NPs can be classified as follows:

(i) **Natural nanoparticles** are produced in many natural processes, such as volcanic eruptions, forest fires and photochemical reactions.

   (a) **Volcanic eruptions:** Outbursts of volcanoes can lead to propulsion of large amounts of fine particles and aerosols into the atmosphere. Particulate debris from such outbursts affect plants, humans and animals. Furthermore, plant activities get severely affected by scattered and blocked sunlight. These volcanically erupted particles may contain heavy metals, which exert toxic effects on humans (Rogers et al. 2005).

   (b) **Forest fires:** Human activities and lightning are the ultimate source of forest fires across the whole world. These forest fires can spread long distances releasing ash and smoke into the atmosphere. This affects the ambient quality of air by releasing small particles into the atmosphere. Many forest fires have been found to transport micro- and nanosized particles in the form of smoke and ash, causing respiratory problems in humans and animals.

(ii) Figure 1.

Engineered Nanoparticles Numerous anthropogenic activities have created various NMs, such as combustion of coal, fuel oil for power generation of vehicles and aeroplane engines, welding, refining, smelting and combustion during cooking. Many commercial cosmetics, toothpaste and sunscreens contain TiO_2 and carbon

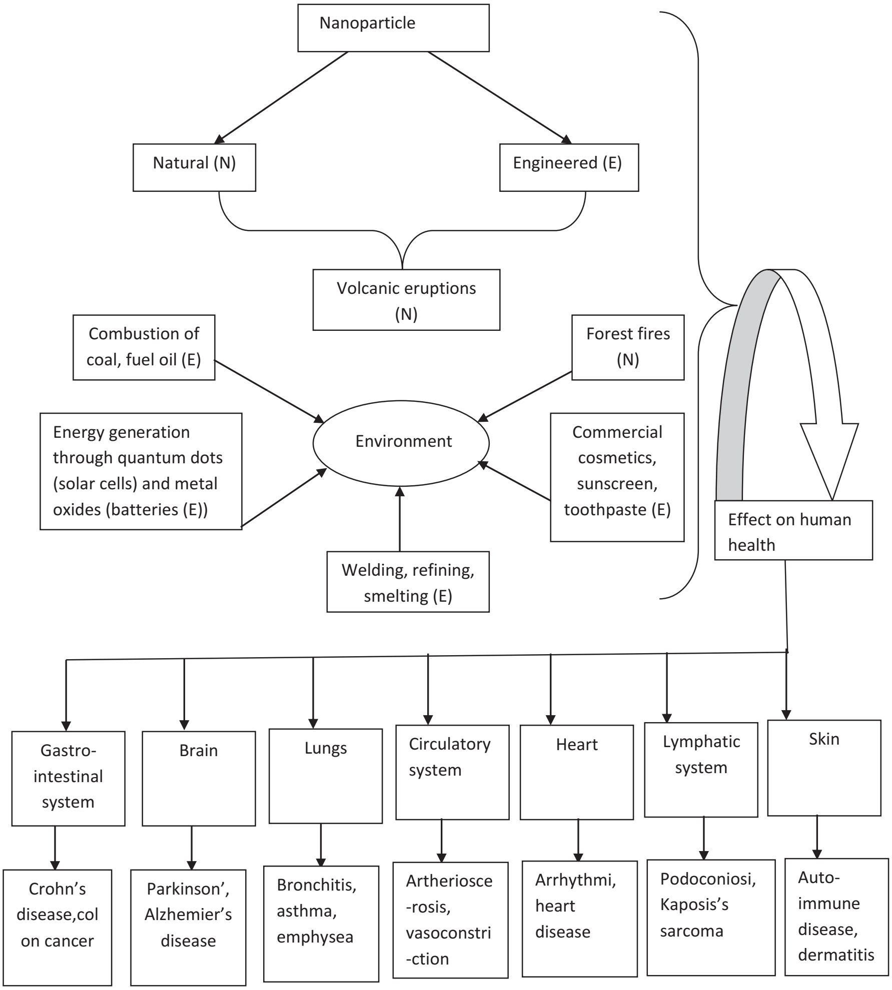

Fig. 1 Sources of nanoparticles in the environment and their effect on human health

nanoparticles and hydroxyapatites. These synthetic nanoparticles are a new category of nanoparticles that induce negative impact on human health and environment (Jeevanandam et al. 2018).

2.2 *Classification of Nanoparticles*

NPs can be classified on the basis of morphology, dimensionality, composition, agglomeration, uniformity or whether they are metallic and non-metallic:

- For morphological characteristics of NPs, the parameters to be considered are flatness, aspect ratio and sphericity.
- On the basis of dimensionality, NPs can be classified into one, two or three dimension. One-dimensional NPs include thin films, two-dimensional ones consist of asbestos fibres and three-dimensional NPs include thin films with atomic scale porosity.
- Due to different chemical and electromagnetic properties, NPs can exist in various forms like colloids, aerosol suspension or agglomerate form.
- NPs can also be classified into metallic and non-metallic. Metallic NPs include gold, zinc oxide, silver, aluminium oxide and titanium oxide. Application of gold NPs includes their usage as drug carriers for thermal cancer therapy due to their surface modification and binding affinity towards thiol and amine group (Jain et al. 2012). Metallic aluminium NPs are being used in paints, coatings, textiles, fuel cells and biomaterials. Metallic silver NPs have wide application in prostheses, wound dressings, coating of surgical instruments along with their antibacterial activity (Huang et al. 2010). Metallic iron oxide NPs are reported to be used in drug delivery and in the biomedical and diagnostic fields. Non-metallic biodegradable NPs are profoundly used in targeted drug delivery in cancer chemotherapy due to their great encapsulation properties. Non-metallic silicon dioxide NPs can be used for drug delivery system due to easy functionalization (Wilczewska et al. 2012). Most widely used NPs include non-metallic carbon-based materials such as fullerenes and single and multi-walled carbon nanotubes.

2.3 Properties of Nanoparticles

Various properties of NPs affect their behaviour within the biological system. Predominantly, morphological properties such as size and shape can have an effect on targeting and circulation within the in vivo system. These properties also influence the variation in degradation rate, specific cell signalling and drug release kinetics of NPs.

(a) **Size:** Preferably, NPs should remain in circulation in the in vivo system until they reach their target site. But these NPs can be eliminated by the immune system as they can be recognized by the endothelial reticulum (ER). Alternatively, NPs can also be cleared by the liver, kidneys, lungs and spleen. Size also affects the diffusion, rolling velocity and adhesion of particles. As far as NPs adhesion is concerned, as their size increases, their attachment rate decreases. This can affect cellular internalization of NPs because this process can be influenced by particle adhesion of cells. Diameter and surface area of NPs also have a pertinent role in drug delivery application. For example, PLGA {poly lactic-co-glycolic acid} NPs were used to evaluate the kinetics of degradation and release of proteins. It was observed that smaller particles degraded and protein release rates were higher in comparison to larger particles (Jiang et al. 2008).

(b) **Shape:** Particle shape (ring, spherical, disc) plays a significant role in the circulation of NPs, their distribution within the body and cellular uptake. Spherical particles are able to move freely within the in vivo system but irregularly shaped particles reveal a much higher probability to align or tumble in filtering organs or vessel bifurcations (Truong et al. 2014). Furthermore, it was shown in an in vitro study that nanocylinders and nanospheres are internalized more rapidly than longer filaments. The interaction of albumin with gold NPs in the blood is also dependant on shape. Cubic gold NPs were able to induce a stronger unfolding than spherical ones (Champion et al. 2008).

(c) **Optical properties:** These properties of NPs are of considerable importance because of their pertinent applications in novel optical sensor technology and lasing devices (Trindade et al. 2001). The factors consist of efficient energy and charge transfer over nanoscale distances, quantum confinement of electrical carriers within NPs and a highly augmented role of interfaces. Non-linear and linear optical properties of NPs can be finely tailored by controlling the crystal dimensions and chemistry of their surfaces. In nanocrystal arrays, it was observed that interactions between nanocrystals can result in long-range resonance transfer (Kagan et al. 1996).

(d) **Mechanical properties:** Many of the mechanical properties of NPs are observed to be different from the bulk materials, such as elastic modulus, fracture toughness, hardness and scratch resistance. Through structural modifications of the NPs, the mechanical properties of the NPs can be enhanced (Guo et al. 2014).

3 Behaviour and Variability of Nanoparticles in Air, Water and Soil

NPs have been engineered nowadays, to be used for an array of consumer products, followed by their release into the environment during different phases of synthesis, production or fate (Williams et al. 2019). The higher surface area/volume is a measure of higher reactivity of NPs and they further affect humans as well as the environment (Goodwin Jr et al. 2018). Although, it has been very difficult to quantify and study the behaviours of NPs in the environment, graphene-based technologies have yet been explored to study different inorganic engineered NPs (Praetorius et al. 2017; Reed et al. 2017). Moreover, the modelling data could be an appropriate means for the estimation of NP concentration in the environment from the different products that have been in use since or those newly produced (Williams et al. 2019). This could enable the assessment and accumulation of NPs present in air, water (sediments, rivers and lakes) and soil along with their uptake by plants and animals (Johnson et al. 2014). It is quite challenging for the simulation of engineered NPs fate in aquatic and other environments and the potential risk of their behaviour in the ecosystem. The best possible approach to study NPs is to generalise the principles of their behaviour and well developed engineered NPs-specific fate models that can provide up to date information and anticipate new NPs in more generic manner (Kroeze et al. 2016).

Numerous studies illustrate the ecotoxicology and chemistry of engineering NPs and revealed that NPs are either introduced by humans or naturally end up in air, water or soil (Handy et al. 2008). The associated pathways or cycles of NP aggregation include the change in their particle size and charge, resulting in the change in surface properties of the particles (Nowack 2009; Kiser et al. 2010). The variability and behaviour of NPs in the environment give insights into NP association with the different components of the ecosystem (Quik et al. 2010).

The key behavioural variability of engineered NPs in different environments is studied by specific models comprising understanding related to chemical fate and mass flow of NPs into different compartments of the environment (Dale et al. 2015). In water systems, the advection with the running water, suspended particulate matter and sediments are cause of concern. NPs may get attached to one another to form aggregates or to suspended particulate matter in water bodies. These are irreversible processes based upon partition coefficients to maintain the equilibrium between the distribution of chemical components among particles associated and dissolved forms (Praetorius et al. 2014). The aggregates formed are accumulated in the water bodies to form beds/sediments and further can be removed by burial to depth. They may also get re-suspended into the water column by change in flow conditions (Nowack et al. 2012). There might be a possibility of loss of NPs to bed sediments through direct deposition in rivers that lose water flow to ground levels or may have an active hyporheic zone (Peijnenburg et al. 2015). Moreover, they can also undergo dissolution into different ionic forms, such as nano-ZnO (Nowack and Bucheli 2007). Further, the rate in their solubility may be altered due to the presence of metal complexing ligands such as natural organic matter (NOM) and aggregated particles that can influence stability due to agglomeration (Jiang et al. 2015; Chinnapongse et al. 2011). Other reactions comprises sulphidation and oxidation, such as photooxidation of Ag NPs onto Ag_2O and oxidation of Cu to CuO in the presence of different organic ligands (Thalmann et al. 2014; Grillet et al. 2013). NPs exist in the environment in multiple states, therefore it is necessary to study the physical and chemical structure and composition of NPs individually (Lofts et al. 2016). Such studies encompass different considerations such as whether the NP retains the outer coating, environmental corona of the material adsorbed, like the outer shell and physicochemical characteristics of the inner shell (core), or are they lost due to chemical transformation during the different phases of the particle (Gottschalk et al. 2013). The term “state” is used to identify the physical status of the NP existing in the environment, the degree to which they exist in free form, homo- or hetero-aggregate and complexed to solid matrix in the soil (Williams et al. 2019). All these factors starting from the state of existence to their fate are regulated through the aggregation behaviours, solubility and density of the particles in the living systems (Nowack 2017).

NPs' abundance in the environment has also shown adverse effects towards humans and the environment. The most critical aspect is to understand the associations of NPs in the soil ecosystem (Zhang et al. 2011). Plants being the most significant part of the ecosystem show the migration of NPs from the soil into their different parts, executing the essential role in transport and fate of NPs via uptake and bioaccumulation (Monica and Cremonini 2009). Subsequently, morphological and biochemical toxicity is observed in different plants, and the increase in the levels of NPs in soil and sediments increases the level of NPs at a rapid pace (Lin and Xing 2008). From different parts of the environment such as air, water, soil and plants, the transfer of NPs to various other living organisms of the ecosystem and humans can occur very effectively (Du et al. 2011; Sabo-Attwood et al. 2012). Many researchers found that NPs impose a serious threat to plants by crossing the cellular barriers because of small particle size (Phogat et al. 2016). They can further penetrate plants through roots, stomatal pores and leaves. The capability of NPs to infiltrate plant cells is based upon the pore size in cell walls ranging between 5 and 20 nm (Shrivastava et al. 2019). It was further investigated that NPs when reacting with cell wall components channelize to form new large-sized pores to increase the permeability of cell wall (Navarro et al. 2008). Furthermore, NPs show higher reactivity in the biological system due to higher surface area to volume ratio. Regardless, of many advancements in the characterization of NPs, research related to translocation, accumulation and toxicity of NPs in plant species needs to expand. However, various techniques, such as NP tracking analysis, light scattering, UV/Vis measurements, are concrete evidences about NP behaviour in the environment. These methods are mainly associated with the determination of size, adsorption, charge, density, agglomeration, composition, concentration and surface area to charge ratios of NPs in different environmental systems.

4 Impact of Nanoparticles in the Environment

4.1 Impact of Nanoparticles in Aquatic Environments

Escalating applications of metal-based nanoparticles in diverse commercial and industrial goods have caused environmental concern due to the inevitable discharge of nanoparticles (Peng et al. 2017). These nanoparticles accumulate in the aquatic surroundings and ultimately pose toxic risk for aquatic life. Ferreira et al. 2016, studied the effect of gold nanoparticles (Au-NP) on *Pomatoschistus* microps. It was observed that fish take up gold nanoparticles through water. Fish exposed to gold nanoparticles for 96 h accumulated gold in their body. Niemuth et al. (2019), investigated the impact of engineered nanomaterials getting into the environment on freshwater midge *Chironomus riparius*. The larvae of *C. riparius* were exposed to different concentrations of next-generation complex metal oxides, viz., lithium cobalt oxide and lithium nickel manganese cobalt oxide. It was observed that these metal oxides have a negative impact on the size of larvae, delay in emergence to adults and the level of haemoglobin. CuO nanoparticles have toxic effects on the development of embryos of zebrafish. Embryos (4 h after post fertilization) were exposed to different concentration of CuO nanoparticles till 96 h post fertilization. It was observed that the mortality rate increased, hatching delayed and heartbeat rate decreased. Furthermore, exposure to CuO nanoparticles also caused numerous abnormalities like malformations of head and tail, vertebral deformities, pericardial oedema and yolk sac oedema (Aksakal and Ciltas 2019). The absorption of Cadmium selenide nanoparticles by aquatic plant *Lemna minor* caused toxic effect on plants and resulted in the activation of the defence system of the plant to alleviate the oxidative stress generated due to ROS generation (Tarrahi et al. 2019). Zinc selenide nanoparticles were found to alter the morphological and physiological parameters in the aquatic plant *Lemna minor*. The concentration of non-enzymatic antioxidants and enzymatic activities of enzymes was enhanced (Tarrahi et al. 2018). Exposure of titanium dioxide nanoparticles to *Hydrilla verticillata* resulted in the generation of ROS. A decreased GSH/GSSG ratio was observed, which revealed high GSH-dependent metabolic activity to avoid the negative effects of reactive oxygen species (ROS) produced due to exposure to titanium dioxide nanoparticles. Enhanced activities of catalase (CAT) and glutathione reductase (GR) were observed, indicating the activation of the enzymatic defence system (Okupnik and Pflugmacher 2016). A reduction in cell viability was observed in marine diatom *Skeletonema costatum* exposed to silver nanoparticles. Reduced chlorophyll content was also reported (Huang et al. 2016). Zinc oxide nanoparticles adversely affected the neurotransmission in *Hydra magnipapillata.* It altered the expression of some genes involved in Wnt signalling pathway, which resulted in irregular regeneration of polyps. It also disrupted the endocrine system, which affected the maturation of oocytes (Yamindago et al. 2018). Zinc oxide nanoparticles are also responsible for enhanced mortality rate, reduced hatching of embryos and increased abnormality of newly hatched larvae (Cong et al. 2017).

4.2 Impact of Nanoparticle on Soil

Nowadays, most consumer products, such as electronics, pharmaceuticals, cosmetics, textiles and water treatment reagents, involve engineered nanoparticles (ENPs). These ENPs possess unique chemical and physical properties, which are mainly responsible for their toxic effects on both the environmental and humans (Klaine et al. 2008; Tourinho et al. 2012; Handy et al. 2008). NPs enter the environment either through the application of various biosolids, pesticides, herbicides, weedicides, fertilizers, soil remediation, waste from the above-mentioned consumer products, various kinds of biomedicine applications or by mean of many other pathways. Thus, NPs are responsible for causing a toxic effect on living systems.

Due to a wide range of commercial applications, these NMs, NPs and nanowaste products find their way into the soil ecosystem (Fig. 2), where they cause

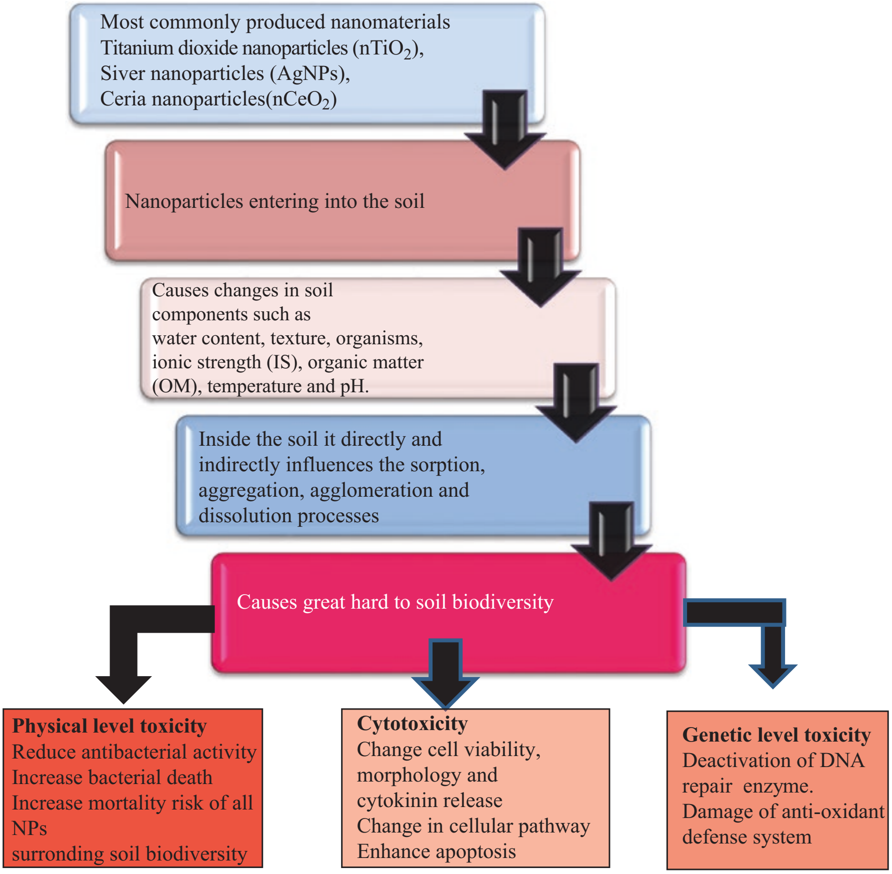

Fig. 2 Nanoparticles-induced toxicity in soil biodiversity flora

alterations in the normal healthy soil physical, biological and chemical properties (Fig. 2). Investigation shows that the addition of NPs causes soil flocculation, which reduces the soil's physical properties, i.e. bulk density, whereas increases its porosity (Taha and Taha 2012). One more similar report had shown that multi-walled carbon nanotubes are responsible for reducing microbial biomass, especially C and N, in the soil and enzymatic activity (Chung et al. 2011). Similar studies on titanium oxide (TiO_2) and zinc oxide nanoparticles (ZnO) showed reduced microbial biomass and bacterial community. Reduction in microbial biomass due to TiO2 and ZnO was detected by the decline in the substrate induced respiration (SIR) and total extractable soil DNA whereas reduction in bacterial community was analysed by the terminal restriction fragment length polymorphism (T-RFLP) (Ge et al. 2011). Inside soil, the toxicity level of NPs depends upon the type of NPs present, that is, either metal, metal oxide NPs or organic NPs, also called carbon-based NPs. Generally, metal NPs are considered to be more toxic than organic NPs (Simonin and Richaume 2015). Metal and metal oxide NPs cause toxicity even when present at concentrations below 1 milligram per kilogram of soil (mg per kg) mainly depending on activity, abundance and diversity of soil microorganisms (Simonin and Richaume 2015). Moreover, nanoscale zero valent iron (nZVI) was detected abundantly on microbial functional groups and shown to potentially reduced the functioning of the ecosystem (Fajardo et al. 2012). Investigations have shown that 34 and 10 g nZVI kg^{-1} soil is responsible for decreasing the denitrifying bacteria (Fajardo et al. 2012) and chloroaromatic mineralizing microorganisms (Tilston et al. 2013) inside the soil. The nZVI tremendously affect the nitrogen cycle and the bio-degradative potential of microbes present in the soil, which is an important aspect of microorganism function in the field of soil bioremediation.

4.3 Impacts of Nanoparticles in Air

NPs are released into the air through various sources, including road traffic exhaust, combustion, explosion and oxidation of atmospheric gases (John et al. 2017). In the life cycle of NMs at every step from transportation to end product, these NPs are released into the atmosphere (Caballero-Guzman and Nowack 2016). When NMs enter the atmosphere they undergo various changes, such as reduction in the size of the particle through adsorbed water or other volatiles or through the condensation of the compounds having low volatility (Soni et al. 2015). NPs are also released into the air accidently through explosion, fire and carrier leakage (John et al. 2017). When these NPs are released into the air, they play a very crucial role in degrading the quality of air. They are also responsible for the formation of dust clouds in the air after being released (Turkevich et al. 2015). When they enter the human body, they have various harmful effects. Their size allows them to enter the human body through skin, digestive system and lungs. It was observed by Pedata et al. (2013), that nanoparticles which are produced through smoke increased inhibition and apoptosis of endothelial cells. Symptoms like flu, cold, fatigue, weakness and migraine are also some of the effects produced by nanoparticles as observed by Savabieasfahani et al. (2015).

5 Conclusion: Future Prospective

There is no doubt that due to the unique properties of nanoparticles, they have been applied in many fields like air pollution control, wastewater treatment and as energy conservation fuel, but due to lack in knowledge for proper disposal of these nanoparticles after use, they constantly enter the environment. On entering the ecosystem, they pose serious threats to the living organisms present in these ecosystems, as discussed in the chapter. Literature is quite limited related to the effects of nanoparticles on the environment. All the focus is on their short-term effects and the data for long-term effect is scant and still these nanoparticles are being used at rapid rate. So, there is a lot of scope for studies to be conducted on the life cycle assessment of these particles, their proper disposal and removal from the environment and how these they will affect the environment and humans in the long term.

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Correction to: Effect of TiO_2 as Plant Growth-Stimulating Nanomaterial on Crop Production

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The author names in the chapter earlier were mentioned incorrectly which have been updated properly hereby:

Correct names	Correct surnames
Marek	Kolenčík
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