Plant Response Strategies to Engineered Metal Oxide Nanoparticles: A Review

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17.1 Introduction

Nanotechnology has got wide range of application in medicine, agriculture, targeted drug delivery, energy, electronics, sensor technology, and imaging. Due to wide range of application of nanoparticles (Nel et al. 2006), there is a great concern on the potential releases of nanoparticles into the environment. Plants constitute a major component of the ecosystem, and interaction of nanoparticles with plant system is an important factor to understand the fate of engineered nanoparticles in the environment and its associated risks. There were reports that the concentration of nanoparticles in the environment is much lower than the toxic concentration; however, it is important to evaluate the environmental effects of nanoparticles for its large-scale commercial application (Batley et al. 2013). Soil is an important source for the accumulation of nanoparticles in the environment, and the concentration of nanoparticles in soil was reported to be higher than in air and water (Gottschalk et al. 2015). There were several reports that plants provide a potential pathway for the transport of nanoparticles (Rico et al. 2011; Nair et al. 2010; Morales-Díaz et al. 2017; Raliya et al. 2016). The interaction of nanoparticles with plant system results in the uptake, transport, and accumulation of nanoparticles, and the response of plants to nanomaterials varies with the type of plants and nature of nanomaterials. There are different entry routes for nanoparticles into the plants, and uptake rate depends on the size, shape, concentration, and surface charge of nanoparticles (Tarafdar et al. 2012). The roots of plants are an important entry route as the soil constitutes one of the major medium for the accumulation of nanoparticles. Nanoparticles enter the root system through lateral root junctions and reach xylem through cortex and pericycle (Dietz and Herth 2011). However, entry of nanoparticles into plants is difficult due to the presence of cell wall, and the

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entry rate is closely related to the morphology of nanoparticles and pore size of cell walls. The nanoparticles that could effectively cross the cell wall pores reach the plasma membrane and be translocated to different plant parts (Fleischer et al. 1999; Navarro et al. 2008). Larger nanoparticles can enter into plant system through aerial openings such as leaf stomata, hydathodes, and flower stigma. These aerial openings act as an important route for the entry of airborne nanoparticles which can be dispersed by wind, thus reaching the leaves and promote foliar uptake through aerial plant openings (Nair 2016). Other aerial transport pathways for nanoparticles include cuticle, bark surfaces, and trichomes.

Nanoparticles interact both physically and chemically with the plant system. They can be physically adsorbed to plant surface, resulting in physical damage to plant parts, or chemically interact with the system causing changes in different cell metabolic pathways. Chemical interactions result in the production of reactive oxygen species (ROS), oxidative damage to cells, and changes in ion-membrane transport activity (Auffan et al. 2008; Foley et al. 2002; Kamat et al. 2000). Nanoparticles can impart both positive and negative effects on plants (Yang et al. 2017; Nair et al. 2011, 2012), and the effects of different types of nanoparticles such as metal and metal oxide nanoparticles, carbon-based nanomaterials, magnetic nanoparticles, and polymeric nanoparticles were well studied. This chapter focuses on different response strategies by plants on interaction with metal and metal oxide nanomaterials. For the utilization of metal-based nanoparticles in agriculture for the development of smart fertilizers and nanopesticides, it is important to understand their impact on various morphological, physiological, and metabolic activities of plants.

17.2 Effects of Metal and Metal Oxide Nanoparticles on Morphological and Physiological Attributes in Plants

The major plant physiological parameters to be studied include germination efficiency, elongation of root, biomass, and leaf number. The impact of different nanoparticles on these physiological factors varies with the type of plants and the type of nanoparticles. The effects of green synthesized gold nanoparticles, without any capping and reducing agents, on the germination percentage of rice were studied (Ndeh et al. 2017). A very high germination percentage (95–98.38%), followed by a slight decrease in the root and shoot length compared to control, was reported. Increased hydrogen peroxide formation and lipid peroxidation in roots and shoots was observed, but not statistically significant which recommended the safe use of green synthesized gold nanoparticles as nanocarriers in plants. Studies on the effects of silver nanoparticles (AgNPs) on the germination and growth of 11 species of wetland plants reported both positive and negative effects depending upon the concentration of nanoparticles and coating agents. Root growth was found to be more affected than leaf growth on exposure to AgNPs (Yin et al. 2012). Zuverza-Mena et al. (2016) reported that nano-silver had null effects on the germination of radish even at a higher concentration (Zuverza-Mena et al. 2016). This can be correlated to the presence of hard seed coat for radish that could prevent the entry of contaminants including nanoparticles (Koul et al. 2000). A reduction in water content and root and shoot length was observed at higher concentrations with respect to control plants. On exposing rice seedlings to different concentrations of AgNPs, it was investigated that there was significant reduction in root elongation, fresh weight of shoots and roots, and total carotenoid and chlorophyll contents. A dose-dependent increase in the amount of reactive oxygen species (ROS), lipid peroxidation, and hydrogen peroxide formation in roots and shoots was also reported along with increased proline and decreased sugar content (Nair and Chung 2014). A dose- and size-dependent decrease in the germination rate and further seedling growth of rice with AgNPs was also reported by Thuesombat et al. (2014). It was reported that large-sized nanoparticles caused more negative effects on seedling growth; however, smaller-sized nanoparticles were efficiently transported through the shoots, which highlighted the size effects. In peanut (*Arachis hypogaea* L.) plants, it was investigated that AgNPs caused severe damage to plant growth with respect to several physiological parameters such as plant biomass, height of the plants, grain weight, and yield. AgNPs were detected even in the edible plant parts in a dose-dependent fashion (Rui et al. 2017).

A significant reduction in seed germination was reported in response to nano-CuO stress in rice seedlings (Shaw and Hossain 2013) with stress-induced oxidative damage. Da Costa and Sharma reported that copper nanoparticles of size less than 50 nm showed inhibitory effects on rice seed germination rate, root and shoot length, and total biomass. Increased nanoparticles uptake was observed at higher concentration with more accumulation in chloroplasts which further led to decline in the amount of photosynthetic pigments, photosynthetic rate, and transpiration rate (Da Costa and Sharma 2016). Copper nanoparticles were also used to evaluate its effects on rice root growth, formation of ROS, and the expression of two genes associated with root growth. Reduced root growth with inhibited gene expression associated with root elongation and greater ROS production was reported on nanoparticle treatment (Wang et al. 2015). Moon et al. reported reduction in germination and inhibited root growth for cucumber on treatment with CuO NPs compared to bulk CuO (Moon et al. 2014). Studies on morphological, physiological, and molecular level effects of CuO NPs on Indian mustard reported shoot growth reduction, shortened primary and lateral root architecture, and reduced total chlorophyll and carotenoids contents. A significant increase in the amount of hydrogen peroxide, peroxidase enzyme activity, and lignification of shoots and roots was also observed (Nair and Chung 2015). Studies on soybean and chick pea with CuO NPs of size less than 50 nm reported a concentration-dependent change in growth of the selected plants. Effective growth was observed at certain optimal concentration; thereafter, an inhibited growth beyond this concentration was reported with adsorption and uptake of nanoparticles by roots (Adhikari et al. 2012). The effects of a range of CuO nanoparticles with different size and concentration on the germination and growth of *Phaseolus vulgaris* L. were investigated, and it was reported that seed germination was not affected by nanoparticles and again seedling weight was promoted by lower concentration and inhibited by higher concentration of 25 nm CuO. The high surface area of 25 nm CuO at higher concentration might be the reason for its deleterious effects (Duran et al. 2017). This study highlighted the importance of nanoparticle structure for its physiological impacts. Altered root morphology was reported in wheat on treatment with CuO NPs due to Cu release from dissolution at root surface. An increase in Cu level modified the exogenous Indole Acetic Acid (IAA) distribution with inhibited root elongation and proliferated root hair formation (Adams et al. 2017).

Yang et al. studied the effects of nZnO on maize and rice plants, and null effect on seed germination was reported. However, at higher concentration of 2000 mg/L, root elongation was significantly inhibited (Yang et al. 2015). The effects of cobalt and ZnO nanoparticles on onion bulbs were investigated, and an inhibited root elongation with increase in concentration of nanoparticles was reported (Ghodake et al. 2011). Effects of different concentrations of engineered ZnO nanoparticles on the growth parameters, production of steviol glycosides, and antioxidant activities on *Stevia rebaudiana* were investigated, and a concentration-dependent favorable and adverse effects on physiology and glycoside production was reported (Javed et al. 2017). The effects of nano-CeO_2 and ZnO nanoparticles on the growth and yield of soybean were studied. It was reported that nano-CeO_2 caused a reduction in the growth and yield of plants. A negative impact on nitrogen fixation by soybean was also reported with high nano-CeO_2 concentration. An efficient uptake and distribution of nano-ZnO was also observed in soybean, and nanoparticles were detected in the edible plant tissues (Priester et al. 2012). Stress response and tolerance of *Zea mays* to CeO_2 NPs were studied by Zhao et al. (2012a, b). Nanoparticles triggered the increased production of several stress-related parameters which helped the plants to defend against oxidative injury caused by exposure to CeO_2 NPs. In radish (*Raphanus sativis* L.), it was reported that CeO_2 nanoparticles at a concentration of 10 mg/L had no effects on the growth of plants, whereas bulk CeO_2 enhanced plant biomass and ionic cerium (Ce^{3+}) had a negative effect on plant growth (Zhang et al. 2015). This study outlined that the effects on plant growth and physiological processes varied with the characteristics of the element. Rico et al. studied the impacts of cerium oxide nanoparticles on the physiology, productivity, and macromolecular composition of barley (*Hordeum vulgare* L.). Improved plant growth with increase in shoot biomass was observed with nano-CeO_2 at 125 mg/kg compared to the control plants. No grains were found in plants treated with 500 mg/kg of nano-CeO_2 (Rico et al. 2015). A positive effect on tomato plant growth and fruit production was determined on treatment with studied concentrations of CeO_2 NPs (Wang et al. 2012). A good level of cerium was detected in plant tissues upon treatment which suggested the uptake of nanoparticles by plant roots and further translocation to shoots and edible tissues. The growth cycle of barley plants treated with CeO_2 and TiO_2 nanoparticles was investigated, and it was observed that n-CeO_2-treated plants produced less number of tillers, reduced leaf area, and reduced number of spikes per plant whereas n-TiO_2 stimulated plant growth, which made clear that the plant response varies widely with the type of nanoparticles (Wang et al. 2012).

Engineered iron oxide nanoparticles have been extensively used for environmental remediation, and hence it is important to study the various effects of iron-based nanoparticles on plant system. No negative effects were reported in maize seedlings grown under stress condition with different concentrations of hematite and ferrihydrite NPs. Surprisingly, an increased growth and chlorophyll content was observed with majority of the concentrations used (Marchiol et al. 2016). Similar results were observed in corn plants in which lower concentration of γ-Fe_2O_3 NPs had positive effects on seedling growth of corn (Pariona et al. 2017). The impacts of iron oxide nanoparticles and ferric ions on the growth of *Citrus maxima* were investigated by Hu et al. It was reported that γ-Fe_2O_3 NPs did not affect the biomass and root length. An upward translocation of nanoparticles were not observed which matched with the appearance of more γ-Fe_2O_3 NPs on the roots of corn (Li et al. 2016). The increase in the chlorophyll content due to treatment with γ-Fe_2O_3 NPs was reported to be concentration dependent.

Recent studies on effects of magnetite nanoparticles on oak trees reported improved germination and early growth (Hu et al. 2017). An increase in chlorophyll concentration was also observed due to increased iron supply from Fe_3O_4 NPs. This study potentially suggested the use of magnetite NPs to improve conservation and reforestation of threatened trees. The uptake of iron oxide nanoparticles by spinach plants grown hydroponically was studied. A dose- and time-dependent increase in the plant growth and biomass was reported due to the uptake of magnetic nanoparticles. This study provided new insights to application of nanoparticles in agriculture (Jeyasubramanian et al. 2016). Cobalt ferrite nanoparticles ($CoFe_2O_4$) have found several application in medical sciences for magnetic resonance imaging, drug delivery, and cell labeling (Liu et al. 2013; Park et al. 2015). However, their effects on plant system are least studied. The tolerance of tomato plants to $CoFe_2O_4$ NPs was studied, and it was reported that these nanoparticles did not affect germination and growth of plants. A concentration-dependent increase in the amount of Fe and Co in plant tissues was observed. An increased Mg and Ca uptake was noted on treatment with 125 mg/L $CoFe_2O_4$ whereas it decreased at higher nanoparticle concentration. A decreased catalase activity in tomato roots and leaves was also reported (López-Moreno et al. 2016). Toxicity and biotransformation of $Ni(OH)_2$ nanoparticles by mesquite plants (*Prosopis spp.*) were investigated, and it was reported that there was no reduction in plant size or chlorophyll production (Parsons et al. 2010).

Studies were carried out with TiO_2 NPs and Cd to understand the joint toxicity in rice seedlings (Ji et al. 2017). TiO_2 NPs did not cause any impact on rice seedling growth in terms of fresh and dry biomass whereas Cd toxicity to rice seedlings resulted in significant reduction of root length, plant height, fresh and dry biomass, and other physiological parameters. However, presence of TiO_2 NPs in the media reduced Cd toxicity to rice plants due to the adsorption of Cd by TiO_2 NPs, thus making Cd unavailable to plants. An investigation of early genotoxic and phytotoxic effects of cerium oxide nanoparticles ($n$$CeO_2$) and titanium dioxide nanoparticles ($nTiO_2$) in barley seedlings reported high oxidative stress with increased generation of ROS and ATP content. The nanoparticles did not cause any negative effect on caryopses germination; however, reduced root elongation was observed in seedlings treated with higher concentration of nanoparticles (Mattiello et al. 2015). Feizi et al.

reported that nano-TiO_2 at low concentration did not cause any changes in the germination rate of wheat whereas high concentrations had inhibitory effects (Feizi et al. 2012). Uptake and impact of TiO_2 nanoparticles on wheat and rapeseed reported that the germination, evapotranspiration, and plant biomass were not affected whereas increased root elongation was observed on exposure to nanoparticles (Larue et al. 2012). The developmental phytotoxicity of different metal oxide nanoparticles on *Arabidopsis thaliana* was investigated, and studies reported that direct exposure to nanoparticles caused significant phytotoxicity with reduced seed germination, root elongation, and leaf number (Lee et al. 2010). Rossi et al. reported that CeO_2 nanoparticles caused root anatomical changes in rapeseed (*Brassica napus* L.) that improved the salt stress tolerance in plants. The nanoparticles modified the formation of apoplastic barriers in plants that allowed the transport of more Na^+ ions to shoots and less Na^+ ion accumulation in roots. These changes in Na^+ ion flux resulted in better physiological response in plants which can be utilized for more nanotechnological applications in agriculture (Rossi et al. 2016). Priester et al. reported that soybean grown in soil amended with nano-CeO_2 or nano-ZnO experienced plant damage. Nano-CeO_2 caused oxidative stress in leaves due to reduced root nodule fixation, and nano-ZnO caused decrease in leaf chlorophyll concentration; however, such a decrease in leaf chlorophyll was not related to diminished plant growth, yield, or N_2 fixation potential (Priester et al. 2017).

The phytotoxicity of alumina nanoparticles was investigated, and it was reported that surface characteristics of nanoparticles play an important role in phytotoxicity. Studies were conducted on five different plant species, and inhibition of root elongation with nanoparticles got decreased with their surface modification (Yang and Watts 2005). Riahi-Madvar investigated the effects of alumina nanoparticles on the morphological properties of wheat seedlings and reported that root growth was affected by NPs but not the seed germination, shoot length, and dry biomass (Riahi-Madvar et al. 2012). Studies on the toxic effects of aluminum oxide nanoparticles on the root growth and development in wheat (*Triticum aestivum*) plants reported reduced root elongation with cellular damage in root cortex cells. Histochemical analysis revealed lignin accumulation and callose deposition (Yanık and Vardar 2015). Antisari et al. reported the effects of different engineered metal oxide (CeO_2, Fe_3O_4, SnO_2, TiO_2) nanoparticles and metallic (Ag, Co, and Ni) engineered nanoparticles on the morphological parameters of tomato plants. It was observed that root growth was promoted by Fe_3O_4 NPs and reduced by SnO_2 NPs. Accumulation of nanoparticles was mainly seen in tomato roots whereas engineered metal nanoparticles were observed both in above ground and below ground parts (Antisari et al. 2015).

17.3 Effects of Metal and Metal-Based Nanoparticles on Photosynthesis and Biochemical Characteristics in Plants

The interaction of plants with nanoparticles induces several biotic and abiotic stresses that accelerate the formation of reactive oxygen species (ROS). Several antioxidant enzymes such as catalase (CAT), ascorbate peroxidase (APX), guaiacol peroxidase (GPX), glutathione reductase (GR), and malondialdehyde (MDA) play a significant role to interrupt the cascades of uncontrolled oxidation which results in the alteration of ROS concentration (Santos et al. 2010; Gechev et al. 2006). The photosynthetic activities in plants can be altered by nanoparticles that result in the generation of ROS and activated the defense mechanisms in plants to combat oxidative stress damage (Du et al. 2017). The generation of ROS and antioxidant responses vary with the type of nanoparticles and plant species and exposure conditions.

In Indian mustard (*Brassica juncea*), on treatment with gold nanoparticles (GNPs), a regular increase in the antioxidant enzyme activities, H_2O_2, and proline content was recorded with increase in the concentration of GNPs. Results indicated that the production of ROS is highly dependent on the concentration of nanoparticles which imposed physiological and biochemical stress in mustard seeds (Gunjan et al. 2014). The toxicity of AgNPs and ionic silver, in mustard seedlings, at various concentrations was analyzed by investigating the root and shoot length, fresh mass, protein content, amount of photosynthetic pigments, cell viability, DNA damage, oxidative enzyme activities, etc. (Vishwakarma et al. 2017). Both nanoparticles and ionic silver reduced seedling growth with severe inhibition to photosynthesis and caused oxidative stress with DNA degradation and ultimate cell death. Antioxidant enzyme activities were inhibited by both forms of silver. These studies in toxicological research could help in designing novel strategies to reduce the adverse effects of nanoparticles on plants. In peanut plants, AgNPs did not change the predominant isozymes of each antioxidant enzyme; however, the amount of antioxidant isozymes got significantly increased in comparison to control plants (Rui et al. 2017). In a model aquatic plant *Spirodela polyrhiza*, it was reported that AgNPs affected photosynthesis and inhibited photosystem II maximum quantum yield and effective quantum yield (Jiang et al. 2017). AgNPs induced the formation of ROS, and the activity of Rubisco was found to be very sensitive to nanoparticles, thus slowing down CO_2 assimilation. This had resulted in decrease in solar energy consumption and promoted ROS generation in chloroplasts by excess excitation energy. Studies reported that AgNPs enhanced the growth of soybean plants under flood-stressed conditions (Mustafa et al. 2015, 2016). An increase in proteins related to amino acid synthesis and wax formation was observed in soybean plants on treatment with 15 nm AgNPs, which further improved the growth of plants under flood stress conditions (Mustafa et al. 2016). Tripathi et al. reported that nitric oxide protected the pea (*Pisum sativum*) seedlings from adverse effects of silver nanoparticles on growth and photosynthesis by regulating the accumulation of Ag and ROS and antioxidant defense system (Tripathi et al. 2017a).

Siddiqui et al. reported that nano-SiO_2 improved seed germination and growth characteristics by reducing malondialdehyde, H_2O_2 levels, and electrolyte leakage. Also, the application of nano-SiO_2 reduced chlorophyll degradation and enhanced net photosynthetic rate, stomatal conductance, rate of transpiration, and water use efficiency. An improved expression of several antioxidant enzymes resulted in reduced oxidative damage which resulted in an increased germination and growth characteristics (Siddiqui et al. 2014). Improved seed germination of soybean with nano-SiO_2 and nano-TiO_2 particles by increasing the amount of nitrate reductase was reported by Lu et al. (2002). Nanoparticles also enhanced the ability of plants to absorb and utilize water and fertilizer and also stimulate the antioxidant system with increased activities of SOD, POD, and CAT. This resulted the plants to thrive under adversities. The ability of silicon nanoparticles (SiNPs) in alleviating UV-B stress in wheat seedlings was investigated, and data indicated that SiNPs triggered the NO-mediated antioxidant defense system which neutralized the damage to photosynthesis that had occurred by ROS (Tripathi et al. 2017b).

In *Brassica rapa*, it was reported that treatment with bulk CeO_2 resulted in increased concentration of H_2O_2 in plant tissues at vegetative stage, and CeO_2 NPs increased the level of H_2O_2 at floral stage. A growth stage response was observed for SOD activity in response to different sized NPs and CAT activity was not at all affected with any sized NPs over the entire growth stages of plant (Ma et al. 2016). Hussain et al. reported that biologically synthesized cerium nanoparticles protected tomato seedlings against ferulic acid stress. The exogenous application of nanoceria resulted in reduced MAL and electrolyte leakage with an increase in the pigment content. As an antioxidant, nanoceria could protect the plants from autointoxication which is an important problem in monocropping (Hussain et al. 2017).

In corn plants (*Zea mays*), on treatment with CeO_2 NPs, it was investigated that the level of H_2O_2 increased in phloem, xylem bundle sheath cells, and shoot epidermal cells up to 15 days after germination. The CAT and APX activities also increased in corn shoots. At higher concentrations, nanoparticles triggered the upregulation of the HSP70 in roots which is an indication of stress response. Lipid peroxidation with increase in thiobarbituric acid and ion leakage was reported in this study. Nanoparticles did not affect leaf net photosynthetic rate, transpiration, and stomatal conductance. The antioxidant enzymes provided protection against the oxidative stress that might have occurred due to nanoparticle interaction (Zhao et al. 2012a, b). Rico et al. studied the impact of nano-CeO_2 on the oxidative stress and antioxidant defense system in germinating rice seeds. H_2O_2 generation in roots and shoots was found to be reduced in comparison to control plants at the studied two least concentrations. Concentration-dependent electrolyte leakage and lipid peroxidation were reported in seedling shoots. Enhanced membrane damage and photosynthetic stress due to the altered enzymatic activities with changes in the level of ascorbate and free thiols were observed in shoots. Modifications of antioxidant defense system with no consequential change in oxidative stress were observed in root system (Rico et al. 2013). In Bt-transgenic cotton, it was observed that the chloroplasts were swollen due to aggregation of CeO_2 NPs on the external surface of chloroplasts which had led to its rupture. The vascular bundles were also got destroyed with CeO_2 NPs (Nhan et al. 2015).

The full life cycle of wheat (*Triticum aestivum* L.) plants was assessed on treatment with CeO_2 nanoparticles of low and high concentration. Decreased chlorophyll content and increased antioxidant enzyme activities were observed in plants treated with higher concentration of nano-CeO_2. Both low and high concentration delayed the flowering by one week and reduced the size of starch grain (Du et al. 2015). There were reports that catalase activity was significantly increased in shoots and ascorbate peroxidase in roots on growing cilantro plants in soil amended with CeO_2 NPs (Morales et al. 2013). Venkatachalam et al. reported that phycomolecules-coated ZnO NPs triggered heavy metal (Cd and Pb) tolerance in *L. leucocephala* by activating different biochemical pathways, thus avoiding cellular damage. An increase in the levels of MDA, photosynthetic pigments, and proteins was reported along with overexpression of antioxidant defense enzymes and favored genetic alterations (Venkatachalam et al. 2017). Zhao et al. studied the effects of nano-ZnO and nano-CeO_2 in corn plants, and it was reported that nano-ZnO at 800 mg/kg reduced the net photosynthesis in corn (Zea mays) plants by 12%, stomatal conductance by 15%, and relative chlorophyll content by 10% at day 20 of plant growth whereas these factors were not impacted with all studied concentrations of nano-CeO_2 (Zhao et al. 2015).

The biochemical and molecular response in *Arabidopsis thaliana* (L.) Heynh. plants to tetracycline (TC) and TiO_2 NPs was investigated, and it was reported that 1 mg/L TC reduced the plant biomass and the presence of nanoparticles alleviated TC toxicity. Higher antioxidant enzyme activity was observed in roots and shoots in the presence of TC which indicated the increased activity of ROS scavengers; however, TiO_2 NPs reduced the antioxidant enzyme activity during co-exposure treatments (Liu et al. 2017). The effects of $Cu(OH)_2$ nanopesticides of different concentrations to 3-week-old maize plants were studied to understand the gene expression of nine antioxidant-related enzymes, and this study provided important information on the responses of maize plants to $Cu(OH)_2$ nanopesticides at genetic, metabolic, and physiological levels (Zhao et al. 2017). Song et al. investigated the phytotoxicity of two differently synthesized nanoparticles, aerosol nano-TiO_2 and colloidal Ag NPs, on tomato (Song et al. 2013). No acute toxicity was observed on germination by either of nanoparticles, whereas root elongation was significantly reduced with Ag NPs at all studied concentrations due to its higher uptake. Ag NPs caused increased phytotoxicity which resulted in lower chlorophyll content, higher SOD activity, and less fruit productivity. Higher antioxidant enzyme activity was observed with nano-TiO_2 only at higher concentration.

To understand the effects of environmental conditions on the uptake and toxicity of ENPs, soil grown herbaceous annual plant (*Clarkia unguiculata*) was exposed to different nanoparticles such as TiO_2, CeO_2, and $Cu(OH)_2$ at different concentrations under distinct light and nutrient levels for 8 weeks. It was reported that during the maximum growth stage, the photosynthetic rate and CO_2 assimilation efficiency was decreased by TiO_2 and CeO_2 treatment under high light and nutrient growth conditions. $Cu(OH)_2$ nanoparticles disrupted photosynthesis in plants grown under highly stressed conditions of high light and limited nutrients. The accumulation of nanoparticles was highly dependent on light and nutrient levels, and the results revealed the impact of abiotic conditions in mediating the uptake and further physiological effects in plants (Conway et al. 2015). Effect of alumina nanoparticles on miRNA expression profile in tobacco plants was studied. Plants were exposed to nanoparticle stress, and it was found that the root length, plant biomass, and leaf count were significantly decreased with increase in nanoparticle exposure. Also, an increase in expression of different type of miRNAs was observed with maximum expression for treatment with 1% Al_2O_3 NPs. This study suggested that miRNAs might play an important role in mediating the stress response in plants caused by nanoparticles in the environment (Burklew et al. 2012). Elevated activity of antioxidant enzymes such as superoxide dismutase and catalase was observed in wheat seedlings on treatment with 200 and 500 mg/L alumina NPs. This reduced the level of free radicals which helped to inhibit the phytotoxic effects of these nanoparticles on wheat seedlings (Riahi-Madvar et al. 2012). Yanik and Vardar reported increased peroxidase activity due to the application of nanoparticles to wheat seedlings with decreased total protein content with respect to control plants (Yanık and Vardar 2015). There were reports that foliar application of ZnO nanoparticles at low concentration of 10 ppm increased the chlorophyll, phosphorous, and total soluble leaf protein concentration in cluster bean (Raliya and Tarafdar 2013). Response of soybean mitochondrial proteins to aluminum oxide NPs of various sizes under flooding situation was studied. A large increase in voltage-dependent anion-channel protein on exposure to 135 nm Al_2O_3 NPs and increased isocitrate dehydrogenase upon exposure to 5 nm Al_2O_3 under flood-stressed condition were reported. This study suggested that Al_2O_3 NPs of different sizes had affected mitochondrial proteins under flood stress conditions by regulating membrane permeability and TCA (Tri carboxylic acid) cycle activity (Mustafa and Komatsu 2016). The effects of magnetite iron oxide nanoparticles (Fe_3O_4 NPs) of different size at a concentration of 200 mg/L were investigated on *Picochlorum* sp. (Trebouxiophyceae, Chlorophyta) during different phases of growth. Nanoparticles of size 20 nm at 200 mg/L reduced the viable cell concentration and chlorophyll a content during exponential growth phase compared to other sized nanoparticles (Hazeem et al. 2015).

17.4 Effects of Metal and Metal Oxide Nanoparticles on the Nutritional Quality of Crops

It is important to assess the effects of nanoparticle on the nutritional quality of plants. The effects of coated and uncoated nanoceria on the quality of tomato fruits were studied, and it was reported that citric acid-coated CeO_2 nanoparticles increased the B content and reduced the dry weight, total and reducing sugar content at different used concentrations (Barrios et al. 2017). B, Ca, Mg, and Mn amount were decreased at 500 mg/kg of $nCeO_2$ and bulk CeO_2 reduced the lycopene content at all the studied concentrations. It was observed that citric acid coated nanoceria affected the fruit macromolecules and nutritional elements were affected by CeO_2 nanoparticles. Interaction of boron (B) with CeO_2 NPs and its responses in sunflower plants was studied, and it was reported that nano-CeO_2 reduced the B nutritional status of sunflower in original soil and B phytotoxicity in boron amended soil (Tassi et al. 2017).

Du et al. reported that there was no change in the starch and sugar content of wheat grains; however, an increase in the protein content of grains was observed in wheat plants on treatment with nano-CeO_2 (Du et al. 2015). Studies with nano-CeO_2 of 250 mg/Kg on barley plants reported remarkable increase in P, K, Ca, Mg, S, Fe, Zn, Cu, and Al in grains. An increase in methionine, aspartic acid, threonine, tyrosine, arginine, and linolenic acid contents in the grains was also reported (Rico et al. 2015). Morales et al. reported that CeO_2 nanoparticles could change the nutritional properties of cilantro by changing the chemical environment of carbohydrates in cilantro shoots (Morales et al. 2013). In cotton plants, it was reported that CeO_2 NPs significantly reduced the Zn, Mg, Fe, and P amounts in xylem sap compared to control plants. Also, a decrease in Indole-3-Acetic Acid (IAA) and abscisic acid (ABA) was also reported (Nhan et al. 2015).

The effects of CeO_2 and ZnO NPs on the nutritional value of soil cultivated soybean plants were investigated (Peralta-Videa et al. 2014). At higher concentration, nano-CeO_2 increased the amount of Cu and P and reduced the amount of Ca in pods. Low level of Na was detected in pods at all concentrations of nano-CeO_2, and high level of Zn was detected in pods at all concentrations of nano-ZnO. At medium concentration of nano-ZnO, the level of Mn and Cu in pods got increased. Hong et al. studied the impact of nanoscale and microscale CeO_2 and CuO on the fruit quality of cucumber (Hong et al. 2016). It was reported that fruit firmness was reduced with nano- and microscale CuO and nano-CeO_2 at 50 mg/L and bulk CeO_2 at 200 mg/L. The Zn and Mo levels of fruits were also impacted upon treatment with different concentrations of nano- and bulk CeO_2 and CuO. Change in the nutritional qualities of cucumber (*Cucumis sativus*) on treatment with CeO_2 and ZnO NPs was investigated (Zhao et al. 2014). Results showed that none of the ZnO nanoparticle concentrations affected fruit sugars, carbohydrate and protein, and antioxidant contents in comparison to control plants. An increase in starch and protein content was reported with 400 mg/kg of ZnO NPs which might increase the caloric value of fruit. A decrease in the concentration of micronutrients such as Cu and Mo was reported with ZnO nanoparticles. Several changes in fruit quality have been noted for CeO_2 treatment, such as changes in the amount of nonreducing sugars, phenolic content, and fractionation of proteins which further impacted fruit flavor and antioxidant ability. In corn plants (Zea mays), it was reported that nano-CeO_2 and n-ZnO reduced the yield of corn and altered the quality of corn. On treatment with nano-CeO_2, it was observed that Cu, K, Mn, and Zn were mainly localized at the insertion of kernels into cobs whereas Ca and Fe were distributed in other parts of the kernel (Zhao et al. 2015).

The effects of CuO NPs on conventional and Bt-transgenic cotton were studied, and it was reported that CuO NPs inhibited the plant growth and development, nutrient content, and also IAA and ABA concentrations in conventional and

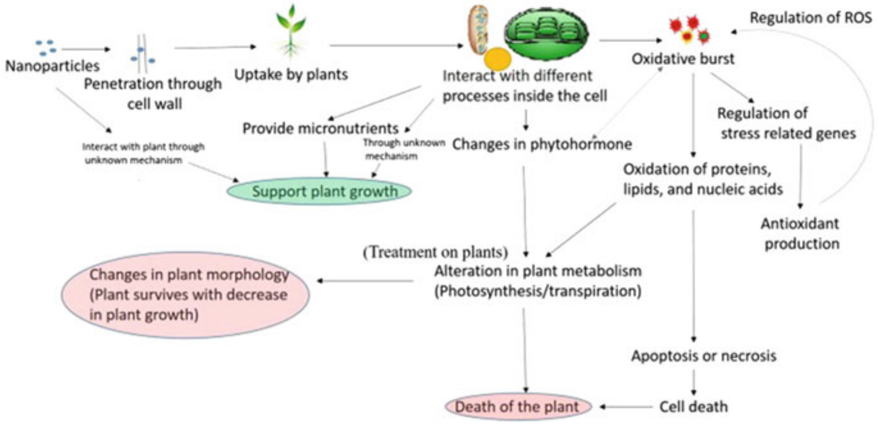

Fig. 17.1 General mechanism of interaction of nanoparticles with plant system resulting in various morphological, physiological, and biochemical effects (adopted with permission from Reference 100)

transgenic cotton plants. At low concentration, nanoparticles enhanced the expression of exogenous gene encoding Bt toxin protein in leaves and roots, thus providing added benefit for Bt cotton insect resistance (Van et al. 2016). Changes in the fatty acid content were observed in peanut grains on exposure to different doses on AgNPs (Rui et al. 2017), which indicated the effects of metal-based nanoparticles on crop yield and quality. Studies by Antisari et al. reported contamination of tomato fruits with Ag when the plants were treated with AgNPs (Antisari et al. 2015). The impact of CeO_2 NPs on the nutritional composition in wheat was investigated, and modifications in the storage of S and Mn in grains were reported. Changes in amino acid composition, increased linolenic acid, and decreased linoleic acid in grains were also reported on treatment with nano-CeO_2 at 125 mg/Kg. The study suggested the potential of nanoceria to modify the crop food quality that might cause unknown consequences for living organisms (Rico et al. 2014). Figure 17.1 shows the general mechanism of interaction of nanoparticles with plant system with various morphological, physiological, and biochemical effects [adopted with permission from Rastogi et al. (2017)].

17.5 Conclusion

Increased application of nanomaterials to the environment affects the growth of plants morphologically, physiologically, and biochemically. Metal-based nanomaterials have shown both beneficial and adverse effects on plant growth and production. Nanoparticles can be adsorbed on the plant surface or can be successfully absorbed and translocated to different plant parts including the edible portion of plants. Hence, it is high time to understand the risks associated with the interaction of nanomaterials with plant system. Reports suggested that nanoparticles at innocuous concentration have not exhibited any adverse effects and seem to be beneficial to plants in many ways. However, toxicity at higher concentrations results in the production of antioxidant enzymes in plants to protect the cellular and subcellular system from cytotoxic effects. Nanomaterials at right concentration can be used for the smart delivery of agrochemicals and fertilizers that promote plant growth and production, thus reducing the use of conventional chemicals to prevent soil damage and to protect the environment.

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