NANO REVIEW   **Open Access**

CrossMark

Plant Response to Engineered Metal Oxide Nanoparticles

Khwaja Salahuddin Siddiqi[1] and Azamal Husen[2*] (iD)

Abstract

All metal oxide nanoparticles influence the growth and development of plants. They generally enhance or reduce seed germination, shoot/root growth, biomass production and physiological and biochemical activities. Some plant species have not shown any physiological change, although significant variations in antioxidant enzyme activity and upregulation of heat shock protein have been observed. Plants have evolved antioxidant defence mechanism which involves enzymatic as well as non-enzymatic components to prevent oxidative damage and enhance plant resistance to metal oxide toxicity. The exact mechanism of plant defence against the toxicity of nanomaterials has not been fully explored. The absorption and translocation of metal oxide nanoparticles in different parts of the plant depend on their bioavailability, concentration, solubility and exposure time. Further, these nanoparticles may reach other organisms, animals and humans through food chain which may alter the entire biodiversity. This review attempts to summarize the plant response to a number of metal oxide nanoparticles and their translocation/distribution in root/shoot. The toxicity of metal oxide nanoparticles has also been considered to see if they affect the production of seeds, fruits and the plant biomass as a whole.

Keywords: Metal oxide nanoparticles, Growth response, Antioxidant enzymes, ROS, Phytotoxicity

Review

Introduction

Because of huge production and inadvertent use of nanomaterials, the whole environment is affected. Although, many of them are useful, some are toxic to plants, algae and microorganisms. They may, therefore, pose potential risk to the environment. Nanomaterials are frequently used in plant growth, cosmetics, drug delivery, photonic crystals, analysis, food, coatings, paints, bioremediation, catalysis and material science [1–12]. Keller and Lazareva [13] have reported that about 3000 tons of titanium dioxide (TiO_2) nanoparticles are produced every year and more than 50% of which is used in personal care products [14]. Copper oxide (CuO) nanoparticles cause membrane damage to *Escherichia coli* as demonstrated by K^+ leakage [15]. A study on Zebrafish (*Danio rerio*) has shown that as exposure days of TiO_2 nanoparticles were increased, the number of viable embryos was decreased [16]. Some nanomaterials are toxic to flora and fauna as they are used to inhibit their growth to prevent further multiplication [17, 18]. Biouptake and accumulation of nanomaterials in plants may increase shoot length and decrease root length and their proliferation [19, 21]. The toxicity response depends on the concentration, particle size and shape of the nanomaterials [22]. Some studies have demonstrated that nanoparticle exposure improves free-radical scavenging potential and antioxidant enzymatic activities and alters microRNAs expression that regulates different morphological, physiological and metabolic processes in plants [22]. The toxicity of the free metal ions has been shown to be greater than that of the nanoparticles. For instance, silver nanoparticles are less toxic to plants than the silver ions [23] mainly due to greater solubility of $AgNO_3$ and greater mobility of Ag^+ ions in aqueous medium. Lipid peroxidation is an important parameter which indicates the cell membrane integrity [24–26]. Reactive oxygen species (ROS) generation is known to damage cell membrane through lipid peroxidation leading to ion leakage and disruption of the cellular metabolism leading to cell death. ROS also cause oxidative damage to photosynthetic apparatuses and biomolecules [27, 28].

* Correspondence: adroot92@yahoo.co.in
[2]Department of Biology, College of Natural and Computational Sciences, University of Gondar, PO Box #196, Gondar, Ethiopia
Full list of author information is available at the end of the article

Thus, plants protect cellular and sub-cellular system from the cytotoxic effects of active oxygen radicals with antioxidative enzymes (superoxide dismutase, SOD; catalase, CAT; peroxidase, POD and ascorbate peroxidase; etc.) and low molecular weight antioxidants (ascorbate, glutathione, proline, carotenoids, a-tocopherols and phenolics, etc.) and non-enzymatic components (carotenoids, ascorbate and tocopherol, etc.) [26, 29–31]. These components minimize the oxidative damage during exposure to metal oxide nanoparticles [18, 32, 33]. *Zea mays* exposed to CeO_2 nanoparticles [34] did not show lipid peroxidation and any physiological changes, although activity of catalase, ascorbate and upregulation of heat shock proteins was observed. However, no elevation of lipid peroxidation in rice treated with CeO_2 nanoparticles (0–500 mg/L) was recorded but ion leakage was observed at higher doses [35].

In recent years, the efficiency of photosystem II (PSII), considered as chlorophyll fluorescence (maximum quantum yield *Fv/Fm*), has been used as a diagnostic tool in various studies to check the impact of abiotic stress as well as metal or metal oxide nanoparticle toxicity in various plant species [26, 36–40]. Thus, potential variations in *Fv/Fm* act as an indicator of seedling-stock quality/physiological status of plants, in vivo [30, 41–44]. Shaw et al. [40] have shown that CuO nanoparticles reduced shoot and root growth of *Hordeum vulgare* seedlings with passage of time in a dose-dependent manner. However, exposure of CuO nanoparticles in barley seedlings exhibited insignificant alteration in the *Fv/Fm* ratio. They have also reported that the CuO nanoparticles induced the release of ROS, membrane damage and overall enzymatic activity not enough to cope with stress at 20-day exposure.

Superparamagnetic iron oxides, Fe_3O_4 nanoparticles (SPION) owing to their magnetic properties, are widely used in instruments, medical devices, as drug carrier, and the treatment of many diseases [9]. Like other metal oxide nanoparticles, SPION are cytotoxic to many aquatic organisms and terrestrial plants because they also generate ROS [32]. Bioaccumulation of SPION and other toxic nanoparticles may reach animals through feed and may alter biodiversity. Mushtaq [45] has reported that Fe_3O_4 nanoparticles inhibited the seed germination and root elongation of cucumber over a wide range of concentration (500, 2500, 5000 μg/mL). In cucurbits, aggregation of Fe_3O_4 nanoparticles occurred followed by their translocation in stem and roots [46].

Replacing biofertilizers by bionanomaterials may sometime be beneficial if they increase the fruit count, seed and biomass without producing toxic effects. Hydroponically grown soybean plants bioaccumulate metal ions, metal nanoparticle such as Zn/ZnO and CeO_2 [47], which influence soil and microbes associated with plants and biomass

[48]. The nitrogen-fixing bacteria are most affected because certain nanoparticles (CeO_2) eliminate the nitrogen fixation potential and plant growth in soybean. Thus, the soil contaminated with huge quantity of waste material containing a variety of metal/metal oxide nanoparticles may impact both microbes and plants.

Biotransformation of nanomaterials may either enhance toxicity or detoxify the living system [49]. Such transformations are related to redox reaction, sulfidation, phosphorylation and molecular modification [50]. The sulfidation of silver nanoparticles decreased toxicity of *E. coli* owing to lower solubility of Ag_2S. Similarly, the formation of AgCl from $AgNO_3$ in presence of chloride ions also has the same effect.

$$AgNO_3 + HCl \longrightarrow \begin{array}{c} AgCl + HNO_3 \\ Solid \end{array}$$

The plants grown in presence of nanoparticles may absorb and translocate them in different tissues. It has been shown that CuO nanoparticles were reduced to Cu_2O and Cu_2S in maize plants [51]. Similar transformation and phytotoxicity of La_2O_3 and Yb_2O_3 in cucumber have been reported by Ma et al. [52] and Zhang et al. [53]. They were converted to their phosphates in the cucumber roots. The solubility of La_2O_3 and Yb_2O_3 was enhanced by the organic acids secreted by the cucumber roots. If there are phosphate salts, the biotransformation of oxides to phosphates is enhanced. From a 3-week study of corn plant grown in presence of CeO_2 nanoparticles, Zhao et al. [34] showed that H_2O_2 was accumulated in phloem, xylem and epidermal cells of shoots. Catalase and ascorbate peroxidase activities were also enhanced in the shoot. Since the plants treated with 400 and 800 mg CeO_2/kg triggered the upregulation of heat shock protein 70 (HSP70) in roots, it is believed that it was due to systemic stress response. The increased activities of enzymes and that of HSP70 are due to the induced reaction against CeO_2 nanoparticle. CeO_2 nanoparticle-plant-root interaction and translocation in hydroponically grown wheat and pumpkin plant for 8 days (17–100 nm) at 100 mg/L in the absence and presence of fulvic acid and gum arabic have been reported by Schwabe et al. [54]. The above plants did not exhibit any reduction in root growth. However, the CeO_2 nanoparticles were translocated in pumpkin shoot but not in wheat plants. SEM and TEM images showed the deposition of nanoparticles on the root surfaces of both the plants which suggested that fulvic acid or gum arabic does not interfere with translocation of CeO_2 nanoparticles but helps in sticking them to the roots. It has been ascribed to specific alterations in root structure and its interaction with nanoparticles in presence of root exudates [55, 56].

Recently, Rico et al. [57] have shown that CeO_2 nanoparticles promoted plant development (*H. vulgare*) to the extent of 331% increase in shoot biomass without showing any toxic effect; nevertheless, at higher concentration (500 mg/kg), the plant did not produce grain which is a big loss. Effect of a variety of metal nanoparticles (Ag, Co, Ni) and metal oxide nanoparticles (CeO_2, Fe_3O_4, SnO_2, TiO_2) on the translocation of nutrients in tomato plant has been investigated. Higher concentration of metal nanoparticles was found to be accumulated in roots as well as shoots. However, Fe_3O_4 nanoparticles promoted root growth and SnO_2 reduced it [58]. Plant response against some metal oxide nanoparticles is summarized in Table 1.

The main aim of this review article is to present the impact of a number of metal oxide nanoparticles on plants and their distribution in root/shoot. Their toxic effect has also been considered to see if they produced oxidative stress and inhibited the growth of plant, seed or fruit.

Cerium Oxide Nanoparticles

The CeO_2 metal oxide nanoparticles are present in the soil by default due to biosolids disposal from wastewater treatment plant, which are released from the exhaust pipe of automobiles. Priester et al. [59] have studied the impact of nano-CeO_2 and ZnO nanoparticles on the growth and yield of soybean which is a major crop containing protein. Hydroponically grown soybean plants accumulate metal and metal oxide nanomaterials. It has been found that TiO_2 and ZnO nanomaterials influence the useful microbes and biomass of the plant especially the nitrifying symbiotic bacteria in the root nodules of soybean and many other plants of fabaceae family. Substantial amount of bioaccumulated ZnO nanoparticles was translocated into leaves and beans while CeO_2 accumulated into root nodules of soybean plant reduced nitrogen fixation potential and growth. The soil fertility and plant growth are equally affected, and therefore, the controlled amount of metal and metal oxide nanoparticles must only be released in the environment [55]. ZnO and CeO_2 nanoparticles affect hydroponic plants [18, 47, 60] and microorganisms [7, 48, 61], but their affect on plant growth and crop yield has not been fully explored [62]. There was an increase in the number of pods of soybean treated with cerium oxide (0.1–1.0 g/kg of soil) and nano-ZnO (0.05–0.5 g/kg of soil). It has been noted that CeO_2 generally reduced the pod and biomass while ZnO nanoparticles increased the pod count and had stimulatory effect on soybean.

Zhao et al. [34] have studied the stress response and tolerance of *Zea mays* to CeO_2 nanoparticles. It has been reported that CeO_2 nanoparticles are toxic to bacteria, green algae, fish and soybean plants [47, 63, 64].

The plants and fishes are, therefore, equally affected by the toxicity of these nanoparticles due to contamination of water or soil by CeO_2. Since the pores of corn primary roots have an average diameter of 6.6 nm, the CeO_2 nanoparticles with a diameter [65] smaller than these may penetrate root and could be transferred from root to corn shoots [33]. The nanoparticles attached to the roots of corn plant inhibit the water transpiration to the leaves [65]. The above ground parts of plants showed low toxicity. The maize plants were grown for 20 days in soil with CeO_2 at 400 and 800 mg/kg level, and stress-related responses such as H_2O_2, antioxidant enzyme, heat shock protein 70 (HSP70), lipid peroxidation and cell death were recorded every 5 days. About ten times over production and accumulation of H_2O_2 in shoots was recorded which indicated a concentration-dependent oxidative stress. In the later stages (after 20 days), the H_2O_2 production was reduced, perhaps, the plant growth and adaptation prevented over expression of H_2O_2. The enzyme catalase and ascorbate peroxidase detoxify the plant by converting H_2O_2 to water and oxygen as shown below:

$$2H_2O_2 \xrightarrow[\text{Ascorbate peroxidase}]{\text{Catalase}} 2H_2O + O_2$$
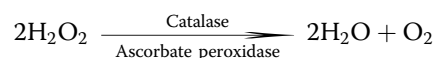
The catalase activity in shoots of plants at lower CeO_2 concentration (400 mg/kg) was 39 times higher but at higher concentration (800 mg/kg), it was reduced to only 30 times. It seems that the enzyme is activated by CeO_2 but at higher concentration, the activity gradually decreased. Similarly, the ascorbate peroxidase activity also declined with 800 mg/kg dose with a concomitant decrease in H_2O_2 level. However, both the enzymes eliminate the excess of H_2O_2 to prevent the lipid damage by CeO_2 nanoparticles.

Biotransformation of CeO_2 in cucumber has been thoroughly investigated by Zhang and co-workers [66]. During this process of biotransformation, either the toxicity of the nanoparticles is enhanced or it is detoxified [49]. The environmental and the biological systems together alter the toxicity of nanoparticles to organism [67]. Several steps, such as redox reaction sulfidation, phosphorylation and molecular modification, are involved in biotransformation [50]. Biotransformation of $Ni(OH)_2$ to Ni^{2+} in plant shoots and leaves was observed by Parsons et al. [68], but no transformation occurred in roots. Some metal nanoparticles or metal oxide nanoparticles are oxidized or reduced depending on the chemical compounds present in certain parts of the plant. For instance, silver nanoparticles were oxidized to Ag(1) by *Lolium multiforum* [69] while CuO nanoparticles were reduced to Cu_2O and Cu_2S in maize plants [51]. The toxicity is therefore dependent on the form of element if they are in reduced or oxidized form. Root elongation of

Table 1 Plant response to some metal oxide nanoparticles

Nanoparticle	Size (nm)	Plant	Concentration	Plant response	Key references
CeO$_2$	7	Soybean	0, 500, 1000, 2000, 4000 mg/L	Genotoxicity recoded at 2000 and 4000 mg/L concentration; a new band in the roots' RAPD profile was observed	[47]
	7	Alfalfa, corn, cucumber, tomato	0, 500, 1000, 2000, 4000 mg/L	In corn, tomato and cucumber seed germination was reduced at 2000 mg/L; promoted root elongation for corn and cucumber; reduced root growth of alfalfa and tomato	[60]
	8.0 ± 1.0	Coriander	125 mg/kg	Increased shoot, root length and biomass; increased ascorbate peroxidase activity in roots and catalase activity in shoots	[175]
	<8.0 ± 1.0	Rice	0, 62.50, 125, 250, 500 mg/L	Reduced H$_2$O$_2$ generation in shoots and roots; increased electrolyte leakage and lipid peroxidation in shoots	[35]
	8 ± 1	Corn	0, 400, 800 mg/kg	No impact on chlorophyll contents and gas exchange	[176]
	8 ± 1	Barley	0, 125, 250, 500 mg/kg	Increased the plant height, chlorophyll contents, biomass, reduced spike production; increased Ca, K, Zn, Mg, Cu, Al, Fe, P and S in grains	[57]
	8 ± 1	Wheat	0, 100, 400 mg/kg	Changes in microstructure of leaf cells, swollen chloroplasts, squeezed nuclei, bent and loosely arranged thylakoids; decreased chlorophyll contents and exhibits variation in protein content	[177]
	10 ± 3.2	*Bacillus thuringiensis* transgenic cotton	0, 100, 500 mg/L	Swollen and destructed chloroplasts, reduced Zn, Mg, Fe and P levels in xylem sap of cotton	[178]
	50–105	Tomato	20 mg/kg	Increased Ca, K, Mg, P in roots; Ca, Mg in stems; decreased Na contents stems; K, Na, P and S in leaves	[58]
	8 ± 1	Wheat	0, 125, 250, 500 mg/L	Changes the amounts S and Mn in grains, amino acid composition and linolenic acid contents	[179]
ZnO	8	Soybean	0, 500, 1000, 2000, 4000 mg/L	No change in germination; genotoxicity recoded at 4000 mg/L concentration; a new band in the roots' RAPD profile was observed	[47]
	10	Soybean	0–500 mg/kg	Reduced Fe at all treatments; Mg and K were decreased at 500 mg Zn/kg treatment	[180]
	<50	Soybean	500 mg/kg	Reduced roots and shoots; had smaller surface area and volume; no seed formation	[181]
	20	Radish, rape, ryegrass, lettuce, corn, cucumber	2000 mg/L	Reduced root growth and elongation	[19]
	<10	Zucchini	1000 mg/L	Reduced biomass (78–90%)	[182]
	10	Cucumber	400–800 mg/kg	No impact on growth, gas exchange or chlorophyll contents	[183]
	90	Corn	800 mg/kg	Reduced growth and inhibition of arbuscular mycorrhizal fungi	[184]
	10	Alfalfa	250, 500, 750 mg/kg	Reduced root biomass (80%)	[185]
	44.4	Arabidopsis	400, 2000, 4000 mg/L	Reduced seed germination, root elongation and number of leaves	[93]
	<100	Arabidopsis	100 mg/L	Reduced biomass (81.4%), seed germination, 660 up-regulated genes and 826 down-regulated genes	[92]
	<50	Garden pea	100–1000 mg/L	No impact on germination; root length, stem length, leaf surface area, transpiration and root nodulation was affected	[186]
	1.2–6.8	Clusterbean	10 mg/L	Increased biomass (27.1%), shoot length, root length, root area, chlorophyll content and total soluble leaf protein	[98]

Table 1 Plant response to some metal oxide nanoparticles *(Continued)*

	25	Tomato	0–1000 mg/L	Plant height was increased (24%) at 250 mg ZnO/Kg; increased root length in foliar sprayed plants with 250 mg ZnO/L; concentrations above 250 mg ZnO/kg affected root length in both methods of application	[99]
	<100	Wheat	50 mg/kg	Reduced biomass	[103]
	<100	Wheat	500 mg/kg	Reduced root growth, increased reactive oxygen species production	[187]
CuO	<50	Arabidopsis	0, 0.5, 1, 2, 5, 10, 20, 50, 100 mg/L	Reduced biomass, root growth retardation, increased reactive oxygen species production	[116]
	<50	Indian mustard	0, 20, 50, 100, 200, 400, 500 mg/L	Reduced shoot and root growth	[128]
	10–50	Mung bean	0, 20, 50, 100, 200, 500 mg/L	Reduced 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	[127]
	<50	Wheat	500 mg/kg	Inhibition in root and shoot growth; produced oxidative stress possibly due to Cu released from nanoparticles, Cu bioaccumulates	[187]
	<50	Squash	0, 100, 500 mg/L	Reduced growth and transpiration (60–70%)	[188]
	<100	Radish, grasses	10, 100, 500, 1000 mg/L	Growth inhibition; DNA damage	[21]
TiO$_2$/inorganic bentonite clay	30/1–60	Maize	300, 1000 mg/L	Inhibited hydraulic conductivity, leaf growth and transpiration	[65]
Activated carbon-based TiO$_2$	30–50	Tomato	0–500 mg/L	Improved germination, reduced germination time	[189]
	30–50	Mung bean	0–500 mg/L	Improved germination, reduced germination time	[189]
TiO$_2$	–	Soybean	0, 0.01, 0.03, 0.05%	Increased height (0.05%) and dry weight	[190]
	<100	Wheat	~91 mg/kg	Reduced biomass, nanoparticles found mostly stick on surface of roots	[103]
	<25	Tobacco	0, 0.1, 1, 2.5, 5%	Reduced biomass, inhibited germination and root length; upregulation of alcohol dehydrogenase and ascorbate peroxidase	[191]
	4–6	Spinach	0.25%	Improved growth; increased glutamate dehydrogenase, glutamine synthetase and glutamic piruvic transaminase activity	[146]
	7–40	Chickpea	2–10 mg/kg	Reduction in electrolyte leakage and malondialdehyde content at 5 mg/kg treatment	[192]
	6.22	*Ulmus elongata*	0.1–0.4%	Increased Cu accumulation in leaves; reduced net photosynthetic rate; increased carbohydrates and lipids	[193]
	27 ± 4	Cucumber	0, 250, 500, 750 mg/kg	Enhanced catalase; activity in leaves; enhanced P and K availability in fruit	[194]
Fe$_3$O$_4$	20	Pumpkin	500 mg/L	No toxic effect; nanoparticles are translocated throughout the plant tissues, detected in stem and leaves, accumulated on the surface of root	[46]
	7	Cucumber, lettuce	62, 100, 116 mg/L	Low to zero toxicity on germination	[195]
	6	Lettuce, radish, cucumber, spinach, tomato, leek, peppers	0.67 mg/mL	Reduced germination	[196]
	25	Ryegrass, pumpkin	30, 100 and 500 mg/L	Increased root elongation; no uptake; block of aquaporins; oxidative stress	[32]
Fe$_2$O$_3$	20–100	Sunflower	50, 100 mg/L	No uptake and translocation; reduced root hydraulic conductivity	[158]

Table 1 Plant response to some metal oxide nanoparticles *(Continued)*

	22–67	Arabidopsis	4 mg/kg	Reduced biomass and chlorophyll contents	[197]
	–	Soybean	0, 0.25, 0.5, 0.75, 1.0 g/L	Increased leaf and pod dry weight; increased grain yield (48%)	[167]
	246	Lettuce, radish, cucumber	1000 mg/L	Found to be adsorb on the surface of seed	[198]
Al_2O_3	13	Maize, cucumber, carrots, cabbage	2000 mg/L	Reduced root growth	[168]
	–	Corn	2000 mg/L	Reduced root length	[19]
	–	Tobacco	0, 0.1, 0.5, 1%	Increased root length, biomass; decreased leaf count; the seedlings significantly decreased; 1% Al_2O_3 exposure has shown extreme increase in microRNA expression	[171]

cucumber seedlings were inhibited by La_2O_3 and Yb_2O_3 nanoparticles as a consequence of their biotransformation to rare earth phosphates in the cucumber roots [52, 53] due to the phosphorous compounds exuded by the root of plant.

The CeO_2 nanoparticles are not toxic to cucumber plants up to 2000 mg/L; however, the major part is accumulated in the root, and about 35% is translocated to leaf and stem, perhaps, because of size constraints. The CeO_2 nanoparticles mixed with needle-like clusters were found on the outer epidermis of the root. The image of the cluster showed the presence of $CePO_4$. It has been reported that the absorbed Ce^{3+} ions on the cell wall of the *Saccharomyces cerevisiae* can react with phosphate released from inside the yeast cells and form Ce(III) phosphate nanocrystallites [70]. Since $CePO_4$ is insoluble, it remains on the surface of the root which has been confirmed from TEM/EDS results. The nanocrystals were found to be deposited on the root epidermis and in the intercellular spaces of the cucumber plant. During the biotransformation of CeO_2 to $CePO_4$ in biological system, CeO_2 undergoes a valence change from Ce^{4+} to Ce^{3+} as a consequence of one electron reduction and formation of $CePO_4$.

$$^{4+}CeO_2 \longrightarrow {}^{3+}CePO_4$$

Both positive and negative results of the CeO_2 nanoparticles on plant system have been reported [71]. Lopez-Moreno et al. [60] have shown that CeO_2 nanoparticles of 7 nm were taken up into seedlings of cucumber, alfalfa, tomato and corn at concentrations of up to 4000 mg/L. Particles of 7 to 25 nm were found to be translocated to the shoots of cucumber. It is perhaps the variation in the interaction of nanoparticles with macromolecules present in the root which causes aggregation around the root tips. Besides, uptake and translocation of nanoparticles also depend on the shape, solubility, agglomeration and surface chemistry [5, 22].

Schwabe et al. [54] exposed wheat and pumpkin (hydroponic plant culture) to uncoated CeO_2 nanoparticle (of 7–100 nm of 100 mg/L) suspension in the presence of fulvic acid and gum arabic. Although the suspension alone was stable, changes in pH, particle agglomeration rate and hydrodynamic diameter in nanoparticles occurred in presence of wheat and pumpkin plants. CeO_2 nanoparticles were found to be translocated into pumpkin shoots but not in wheat plants. However, no toxic effect was observed in both plants. In a recent experiment, Anderson et al. [72] have chosen ten plant species and found that CeO_2 and TiO_2 nanoparticles do not cause widespread acute toxicity during germination and early growth stage.

Fulvic acid and gum arabic stabilize the CeO_2 nanoparticles on one hand and reduce their adsorption by root on the other. However, CeO_2 nanoparticles of 17 to >1 μm are partially available for uptake by pumpkin similar to those found by Zhu et al. [46] and Zhang et al. [73]. Translocation of Ce into shoot of wheat was not detected as the monocots are less likely to take up nanoparticles because water uptake by them (wheat) is only 25% to that of pumpkin.

A recent study on the uptake and accumulation of CeO_2 nanoparticles in different parts of barley (*Hordeum vulgare* L.) has been made by Rico et al. [57]. The effect of CeO_2 nanoparticles on the vegetative growth and production of barley grown in soil treated with different quantities of CeO_2 nanoparticle has been reported (Table 1). It is important to note that at higher dose (500 mg/kg), there occurred rapid shoot development resulting in 331% enhancement of biomass. It is more surprising that at this concentration (500 mg/kg), the barley did not produce grain. It is, however, encouraging that at lower concentration of CeO_2-amended soil (125 and 250 mg/kg) and also in control-produced grains with large quantity of Ce accumulated in leaves and grains (Table 2) along with P, K, Ca, Mg, S, Fe, Zn, Cu and Al.

Barley treated with CeO_2 nanoparticles (250 mg/kg) enhanced methionine, aspartic acid, threonine, arginine and linolenic acid contents in the grain. It is clear that the moderate concentration (125–250 mg/kg) of CeO_2 nanoparticles is highly beneficial while the higher doses (500 mg/kg) are toxic to barley. The accumulation of other metal ions in barley leaves and grains (e.g. P, K, Ca, Mg, S, Fe, Zn) is catalyzed by CeO_2 nanoparticles. It

Table 2 Cerium concentrations (μg/kg dry wt) in different organs of *Hordeum vulgare* cultivated to grain production in cerium oxide nanoparticles-amended soil

Soil treatments (mg/kg)	Leaves	Grains
0-control	571 ± 40	200 ± 5 c
125-nCeO$_2$-L	595 ± 140	449 ± 51 b
250-nCeO$_2$-M	524 ± 73	787 ± 58 a
500-nCeO$_2$-H	701 ± 92	–

Values are means ± SE ($n = 3$). Same letters mean no statistical difference between treatments at Tukey's test ($p \leq 0.05$) [57]

is perhaps due to the biomolecules coordinated with these metals to make them available as trace elements which also act as nutrient for the plant. CeO$_2$ nanoparticles promoted plant growth in soybean and tomato [59, 74] but did not affect the growth of cucumber.

Cerium uptake in root of rice (*Oryza sativa*), wheat (*Triticum aestivum*) and barley (*H. vulgare*) at different doses has been determined. Although CeO$_2$ are not translocated in shoots of wheat, they are taken up by rice and barley [35] in fairly large quantity. Recent study [57] suggests that rice, wheat and barley could accumulate CeO$_2$ in their root tissues without influencing the rate of germination and root elongation of the seedlings. CeO$_2$ nanoparticles may induce modification in plants at molecular levels [35, 75, 76]. Oxidative stress and membrane damage of rice roots have been observed. It has been found from FTIR spectra of the rice, wheat and barley germinated in cerium oxide suspension that changes in amide I and amide II bands (1700–1600 cm^{-1} and 1600–1500 cm^{-1}) are significant due to the presence of phenols and proteins [76, 77]. These results suggest that the cerium oxide nanoparticles produce modification in the root xylem of the cereal crops.

The impact of CeO$_2$, Fe$_3$O$_4$, SnO$_2$, TiO$_2$ and metallic Ag-, Co-, Ni-engineered nanoparticle uptake and translocation in tomato plant has thoroughly been investigated in the recent years [58]. The plant exposed to different quantities of nanoparticles showed different vegetative growth (Table 3). CeO$_2$-treated plants showed a very slight increase in stem growth. Fe$_3$O$_4$ nanoparticles significantly promoted the growth and elongation of tomato plant but reduced its green biomass. SnO$_2$ remarkably decreased root growth and the dry stem and leaf weight. Though Fe$_3$O$_4$ was not significantly translocated into stem and leaf, fairly large amount of iron was found to be deposited in fruit and root of tomato plants. However, titanium, tin and cerium were not translocated even under control or treated plants. It is important to note that in all cases of nanoparticles treated tomato plants, the Ca contents in stem and root increased from 25.6 to 69.8% with respect to control. The bioavailability of nanoparticles depends on the coating, original matter in the soil or even clay because they can alter their behaviour leading to aggregation. Thus, the toxicity of nanoparticles is reduced due to their slow release. It is, therefore, concluded that soil polluted by metals can produce adverse effects if they are present above permissible/tolerance limits.

Priester et al. [59] have already reported that soybean plants grown in organic farm soil containing ZnO or CeO$_2$ nanoparticles absorb and translocate Zn and Ce in all parts of the plant. The results indicated that the low amount of Ce is translocated in soybean pods [78]. The Ce in pods and nodules exists mainly as Ce^{4+} and some amount as Ce^{3+}, which suggests that nearly 20% CeO$_2$ is reduced to Ce^{3+} [34]. Zhao et al. [34] have shown that Ce was coordinated as CeO$_2$ nanoparticles inside the roots of corn plants grown in organic soil amended with alginic acid coated with CeO$_2$ nanoparticles. They also showed, from confocal microscopy images, the presence of CeO$_2$ nanoparticles in the cell wall of the corn root cortex. They termed it passive uptake of the CeO$_2$ nanoparticles. It must be made clear at this juncture that the

Table 3 Effect of metal and metal oxide nanoparticles on dry matter of roots, stems and leaves of *Lycopersicon esculentum* plants grown in pots

Treatment	Root		Stem		Stem		Root elongation		Plant height	
	g	SD	g	SD	g	SD	cm	SD	cm	SD
Control	1.9 b	0.1	20.5 b	0.9	25.2 a	1.1	22 ab	1.3	98 a	3.8
Ag-NPs	1.6 b	3.3	26.2 a	1.2	24.2 a	0.9	19 b	1.5	82 b	5.3
Co-NPs	1.5 b	0.3	10.3 d	1.1	18.3 b	1.5	15 b	2.8	84 b	4.2
Ni-NPs	1.0 bc	0.3	26.1 a	1.2	12.1 d	0.9	15 b	3.2	93 ab	5.1
CeO$_2$-NPs	2.2 ab	0.2	13.1 cd	1.4	15.7 c	0.7	23 ab	2.1	109 a	3.1
Fe$_3$O$_4$-NPs	4.8 a	0.2	18.1 c	0.8	18.9 b	1.3	25 a	2.3	106 a	3.5
SnO$_2$-NPs	0.7 c	0.2	5.4 e	0.7	16.8 c	1.5	11 b	3.7	104 a	3.4
TiO$_2$-NPs	1.4 b	0.1	19.2 b	1.1	18.8 b	0.8	17 b	2.1	110 a	4.1

Means followed by a different letter within a row are significantly different at $p < 0.05$ according to Duncan's multiple range test [58]

CeO_2 nanoparticles are neutral species which cannot co-ordinate with any ligand carrying lone pair of electrons or negative charges because these electrons are to be partially donated to an electron pair acceptor. However, it is quite likely that the CeO_2 nanoparticles are translocated to the root cortex with support of the alginic acid coating.

Zinc Oxide Nanoparticles

Riesen and Feller [79] have shown the accumulation of zinc in the phloem of wheat plant and also in the soybean grain, but not zinc oxide (ZnO) nanoparticles. Zinc is supposed to be bonded to the oxygen of the carboxyl acid as ZnO [80, 81]. Thangavel et al. [82], from a study of red spruce cell culture, suggested that in living cells, it is more likely that Zn ions bind to the sulphur of phytochelatins rather than the oxygen of organic acids. However, Zn(II) in soybean plants has been found to be associated with oxygen of acids which has also been confirmed on the basis of model compounds [78].

Kopittke and co-workers [83] analyzed cowpea exposed to Zn and found that nearly 65–85% of the zinc was coordinated as a zinc-phytate complex. Phytic acid is present in all beans and is a source of phosphorous storage [84]. It is known that the Zn(II) ions activate the enzyme phytase but it may be bonded to phytic acid to give zinc phytate. Phytic acid is highly unstable and therefore it is stabilized in the form of a metal salt. The free zinc ions are therefore bonded to phytic acid through oxygen giving zinc-phytate complex.

Hu and co-workers [85] have recently investigated the adverse effects of ZnO nanoparticles of 25 nm diameter on the aquatic plant, *Salvinia natans* (L.). During 7-day exposure of plant to different concentrations of ZnO nanoparticles, no significant difference was observed in growth. However, the $ZnSO_4$-treated plants showed marked decrease in growth. Generally, 50 mg/L ZnO nanoparticles were found to produce oxidative stress and depressed the photosynthetic pigments. SOD and CAT activities were increased but chlorophyll pigments decreased in the leaves of *S. natans*. It has been already reported that the antioxidant enzymes SOD, CAT and POD can protect plant cells against adverse effects of ROS [26, 28, 29, 32]. While POD acts as scavenger of ROS, SOD and CAT jointly convert O_2^- and H_2O_2 to H_2O and O_2 and also reduce overall free ·OH radical. Zinc has been reported [86, 87] to increase the biosynthesis of antioxidant enzymes in the duckweed, *Spirodela polyrhiza*. The POD activity was remarkably inhibited by large quantity of ZnO nanoparticles (50 mg/L). In a recent study Zafar et al. [88] have reported that ZnO nanoparticles (500 to 1500 mg/L) negatively affects the *Brassica nigra* seed germination and seedling growth; and also increased antioxidative activities and non-enzymatic antioxidants contents. The toxicity of ZnO nanoparticles depends on the quantum of dissolved zinc in the solution [89, 90]. It is true that only a fraction of dissolved zinc is bioavailable which can be absorbed and translocated in different parts of the plants; nevertheless, the solubility of zinc oxide is pH dependent because being amphoteric in nature, it dissolves in both the acidic and alkaline media as shown below:

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$
$$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$$

The ZnO nanoparticles diffuse in the plant cells if size is relatively smaller than the pores in the plant cells. Phytotoxicity of ZnO nanoparticles has been investigated by Watson et al. [91] under both acidic and alkaline soils. In acid soil, inhibition of elongation of roots of wheat (*T. aestivum*) was observed whereas phytotoxicity was mitigated in the alkaline soil, although absorption of ZnO nanoparticle was doubled even when Zn concentration in soil was low. Soluble zinc in the acid soil was 200-fold higher and shoot levels were tenfold higher than those in the alkaline soil. Phytotoxicity was observed in soil spiked with humic acid but it did not influence the plant responses. The ZnO nanoparticle aggregation with humic acid provides bioavailable zinc. But these nanoparticles may be distributed to the plant only if they are taken up through diffusion. The plant roots are stunted in the acid soil as the quantity of soluble zinc was 100 times higher in acid soil than the alkaline soil. However, higher dose of Zn (500 mg/L) causes phytotoxicity to the plants.

ZnO nanoparticles (100 mg/L) treated *Arabidopsis* seedlings showed reduced biomass to 81.4 ± 11.5% after 2 weeks [92]. Lee et al. [93] have also reported that ZnO nanoparticle at 400 mg/L inhibited the germination, root growth and leaf development in *Arabidopsis* similar to other plants [20]. ZnO nanoparticles also caused remarkable transcriptomic changes in terms of number of genes and their expression. It has been suggested that ZnO nanoparticles release Zn^{2+} ions and damage root tissues. Under such stress conditions, the plant initiates new root growth as an alternative to the damage by ZnO nanoparticles/Zn^{2+}. ZnO nanoparticles promote ROS production in exposed roots [94, 95]. The presence of Zn^{2+} ions is either due to the presence of zinc salt in the ZnO nanoparticle or due to the conversion of ZnO nanoparticles to Zn^{2+} ions. It is, therefore, proposed that stress and defence responses of plants are due to a combined effect of ZnO nanoparticles and Zn^{2+} ions.

Higher toxicity of ZnO nanoparticles with respect to the Zn^{2+} ion in hydroponic solution using *Allium cepa* has been attributed to higher release of ROS [96]. Further, a study with *Vigna unguiculata* in soil amended with either ZnO nanoparticles or Zn^{2+} showed no difference in plant growth, accumulation or speciation between the zinc ion and ZnO nanoparticle treatment [97]. However, foliar exposure of ZnO nanoparticles to *Cyamopsis tetragonoloba*

and *Solanum lycopersicum* has revealed a positive response in terms of biomass production, chlorophyll and total soluble leaf protein contents [98, 99].

Effect of citrate-coated Ag and ZnO nanoparticles and uncoated $AgNO_3$ and $ZnSO_4$ on *Zea mays* L. and *Brassica oleracea* var. *capitata* L. has been explored in vitro. The Ag nanoparticles have been shown to be more toxic to plants than free $AgNO_3$. Considerable changes in metaxylem count of maize were observed with Ag nanoparticle, $AgNO_3$ and $ZnSO_4$ treatments. However, ZnO nanoparticles did not show any significant change in maize. In case of cabbage and maize, the germination and root elongation measurements revealed that nanoparticles were more toxic to plants than the free metal ions [100]. ZnO nanoparticles reduce seed germination [19] and damage tissues [20] in hydroponically grown plants. Kim and co-workers [101] have reported that ZnO nanoparticles at 2000 mg/kg did not affect the root length and biomass production of *Cucumis sativus* grown in a loamy sand soil at pH 5.5. Manzo et al. [102] have reported that ZnO nanoparticles at 286 mg/kg affected the root elongation in *Lepidium sativum* sown in an artificial standard soil. However, Du et al. [103] reported that at only 45.45 mg/kg (5 g/110 kg soil), these nanoparticles reduced the biomass production of wheat (*T. aestivum*) cultivated in loamy clay soil at pH 7.36. X-ray absorption spectroscopic studies have shown absence of ZnO nanoparticles in roots [47, 81]. However, confocal microscopic study showed the presence of FITC-stained ZnO nanoparticles in the stele of corn roots, although these particles were not found in the shoots [33]. It indicated that the ZnO nanoparticles were absorbed and incorporated into the plant transport system.

Copper Oxide Nanoparticles

The phytotoxicity of CuO nanoparticles in a 1:1 mixture of CuO and ZnO nanoparticles in plants colonized by *Pseudomonas chlororaphis* in a sand matrix has been investigated by Dimkpa et al. [104]. Bean root growth was inhibited and shoot was elongated by CuO nanoparticles [105, 106]. The CuO nanoparticles were found to release copper to the shoot where maximum copper loading was noted with the minimum dose of 100 mg/kg CuO nanoparticles and lower level of copper with higher doses of 250 and 500 mg/kg. The accumulation of Cu was 10–20-fold higher than the normal level (10 mg/kg). At higher CuO nanoparticle concentration, the major part was accumulated in the root which inhibited its growth. The other essential metal ions in presence of CuO or Cu^{2+} ions are either unavailable to the plant or their absorption was reduced. For instance, accumulation of Fe and Ca in the shoot tissue decreased as a consequence of antagonistic effect of Cu on Fe and Ca [107]. In fact, copper increases the absorption of Fe in animals if

iron is available in ferrous form. The reduction of ferric to ferrous occurs by the enzyme ferric reductase but if Cu is in excess, it may be bonded to the enzymes making it unavailable for the reduction of Fe^{3+} to Fe^{2+}. As a result, the iron and calcium accumulation in shoot of plant declines [108, 109]. Dimkpa et al. [104] have suggested that Cu(II) is partially reduced to Cu(I) by citrate present in roots of beans and cucumber but chemically Cu(I) is highly susceptible to oxidation in presence of water and air which cannot be avoided in plant system. The redox process is very rapid and hence, the presence of Cu(I) is extremely difficult. CuO/ZnO nanoparticle exposure of bean plants affected both root and shoot. Improved plant growth has been attributed to lower solubility of CuO nanoparticles. It has been suggested that due to alkaline soil, the other metals (Cu and Fe) may be precipitated as their hydroxides and may not be available for absorption by plants. The reduction and accumulation of iron may be due to its hydroxide formation. The exposure of CuO nanoparticles to bean plants reduced Mn, Zn and Ca concentration and increased Na levels in the shoot tissues without disturbing Mn and K levels. In the bacterial culture medium, CuO nanoparticle treatment showed root growth perhaps due to bacteria which formed a protective layer around the root which does not allow copper to be absorbed. However, the plant cells act against the toxic effects of copper nanoparticles and in doing so, certain metals are absorbed and certain others are precipitated. Phytotoxicity of commercial CuO (<50 nm) and Zn nanoparticles (<100 nm) against sand-grown wheat (*T. aestivum*) has been investigated. Since these nanoparticles contained some metallic and non-metallic substances, they may also influence the growth rate of the plant. Changes in shape of ZnO nanoparticles were noted when mixed with sand in aqueous medium.

The sand amended with CuO and ZnO (500 mg/kg) significantly reduced root growth. Dissolved Cu from CuO nanoparticles showed toxic behaviour towards wheat plant but zinc did not influence the shoot growth. CuO and Cu(I)-sulphur complexes were found to be accumulated in the shoot while zinc was detected as Zn phosphate. Oxidative stress in the nanoparticle-treated plants was reflected by an increase in lipid peroxidation and oxidized glutathione and higher peroxidase and catalase activities in roots. The solubility of nanoparticles decreased with increasing aggregation causing morphological changes in ZnO nanoparticles [110]. It has been shown that the amount of Cu and Zn ions released from CuO and ZnO are almost negligible to cause phytotoxicity to plants. Plants grown with nanoparticles showed increased accumulation of Cu and Zn (20 fold Cu and 24 fold Zn) which altered root metabolism in wheat plants. Both CuO and ZnO nanoparticles have been detected in shoot of the plants. However, the quantitative

difference between the two metals is mainly due to their solubility/diffusion. The zinc as zinc-phytate accumulates in the plants.

CuO nanoparticles have been shown to induce DNA damage in plants [21]. Growth inhibition in radish (*Raphanus sativus*), perennial ryegrass (*Lolium perenne*) and annual ryegrass (*Lolium rigidum*) under laboratory conditions has been reported. Germination of radish seeds in presence of CuO nanoparticles induces substantial accumulation of mutagenic DNA lesions. Radish and similar other plants produce oxygen-derived species (O_2^-, H_2O_2, ·OH) during germination [111]. H_2O_2 enhances seed germination but in presence of peroxidase or transition metal ions such as iron or copper produce an excess of OH via the Fenton reaction [112]. It is therefore suggested that copper ions produced from CuO nanoparticles may catalyze the formation of OH. CuO nanoparticles inhibited the radish root growth to the extent of 79% which is relatively much larger than that observed for Cu^{2+} ions alone. The stunted growth has been observed mainly in the root/shoot [113].
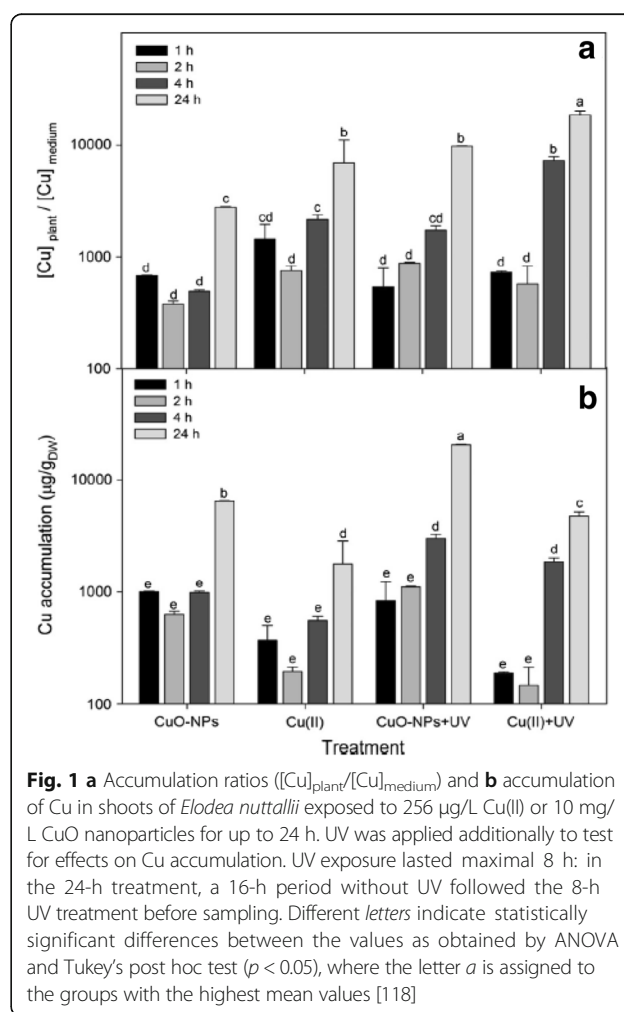
CuO nanoparticles have been shown to be cytotoxic and genotoxic [114, 115] to mammalian cells. It is thought to be due to nanoparticles which produce oxidative stress within living cells and cause DNA damage in plants or animals. Nair and Chung [116] have studied the impact of CuO nanoparticles on the growth of *Arabidopsis thaliana* and changes at molecular level. The seedlings were exposed to different concentrations of CuO nanoparticles (0.5 to 100 mg/L) for 3 weeks under laboratory conditions. Total chlorophyll contents were significantly reduced at all concentrations starting from 2 to 100 mg/L. Root growth was reduced even with 0.5 mg/L CuO nanoparticles. Superoxide and hydrogen peroxide increased in roots and leaves with increasing concentration of nanoparticles in plant. Oxidative stress, sulphur assimilation of glutathione and proline biosynthesis were also influenced by CuO nanoparticle exposure. In another study, *A. thaliana* plants exposed to cerium oxide and indium oxide showed reduction in plant biomass and total chlorophyll contents [117]. The increase in anthocyanin (the flavonoid) concentration in *A. thaliana* plant exposed to CuO nanoparticles may be due to oxidative stress. Anthocyanin acts as antioxidant to protect the plant cells against ROS-induced oxidative stress [29]. It is obvious that when a foreign matter is absorbed by the plant, it acts against this material through defensive mechanism for protection. Thus, it produces antioxidants which act as scavenger of ROS. As a result of stress by CuO nanoparticles, lignin was also deposited in *A. thaliana*.

It has been proposed that CuO nanoparticles would have been translocated via the vascular tissues and subsequently dissolved to produce Cu ions which resulted in deposition of lignin. Translocation of CuO nanoparticles is apparent but the production of Cu ions by dissolution is impossible because generation of Cu ions from copper nanoparticles is a redox process which requires a reducing agent such as hydrogen, phenol, protein or an acid. However, CuO being weakly basic dissolves in HCl to give ions as follows:

$$CuO + 2HCl \longrightarrow CuCl_2 + H_2O$$
$$CuCl_2 \longrightarrow Cu^{2+} + 2Cl^-$$
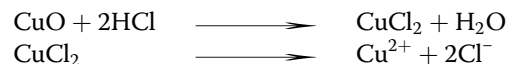
A comprehensive study of uptake and toxic effects of CuO nanoparticles, Cu^{2+} ions and also in combination with UV radiation has been done on the aquatic macrophyte, *Elodea nuttallii* [118]. Growth of the plants was inhibited when treated with $CuSO_4$ or CuO nanoparticles. However, the amount of copper accumulated in *E. nuttallii* was lower in $CuSO_4$-treated plants than those treated with CuO nanoparticles (Fig. 1). The difference has been attributed to the solubility of Cu^{2+} in CuO nanoparticle medium. Surprisingly, the relation between

Fig. 1 a Accumulation ratios ([Cu]$_{plant}$/[Cu]$_{medium}$) and **b** accumulation of Cu in shoots of *Elodea nuttallii* exposed to 256 µg/L Cu(II) or 10 mg/L CuO nanoparticles for up to 24 h. UV was applied additionally to test for effects on Cu accumulation. UV exposure lasted maximal 8 h: in the 24-h treatment, a 16-h period without UV followed the 8-h UV treatment before sampling. Different *letters* indicate statistically significant differences between the values as obtained by ANOVA and Tukey's post hoc test ($p < 0.05$), where the letter *a* is assigned to the groups with the highest mean values [118]

accumulated Cu and dissolved Cu^{2+} was higher in plants exposed to 256 μg/L Cu^{2+} than those exposed to 10 mg/L CuO nanoparticles containing nearly 2.0 mg/L dissolved Cu (Fig. 1). The accumulated Cu is directly proportional to the amount of Cu dissolved in the medium but it is not related to higher concentration of Cu in the solution [119]. Perhaps at higher concentration, agglomeration occurs which is prevented from absorption. When the dissolved copper is in small quantity, it has greater degree of freedom for movement and can be accumulated in different parts of the plant. However, enhanced Cu uptake in plants exposed to CuO nanoparticles with dissolved Cu concentration has also been reported which is contradictory to above results [120]. It has been suggested that plants exude some acid to dissolve additional Cu from CuO nanoparticles which is transported and accumulated in different parts of the plant [121]. Formation of large agglomerates prevents the dissolution of Cu. It is interesting that Cu accumulation is enhanced, under UV radiation, in shoots after 4 h but there is no direct evidence of enhanced solubility of Cu^{2+} in CuO nanoparticle suspension. Accumulation of Cd under UV radiation has been ascribed to membrane damage of the plant [122]. Rai et al. [123] suggested altered membrane permeability due to lipid peroxidation in cell membranes of UV-exposed cells in cynobacteria. In plants, under UV radiation, photosynthetic capacity is strongly reduced. When higher quantity of Cu is accumulated in plants, the response of the oxidative stress-related enzymes peroxidase and superoxide dismutase is also high.

Duckweed exposed to CuO nanoparticles showed inhibition of photosynthetic activity due to the Cu^{2+} ions released from it [120]. Andreotti et al. [124] have found that *Phragmites australis* can relocate Cu from roots to shoots. CuO nanoparticle exposure to cotton and Bt cotton has shown significant alterations of the concentrations of indole-3-acetic acid and abscisic acid [125]. Cu-based nanoparticles have been found to increase P and S in alfalfa shoots but decreased Fe and P in lettuce shoots [126]. Carotenoids remained unchanged and chlorophyll reduction began at 100 mg/L CuO nanoparticles in mung beans [127]. Carotenoid contents diminished at 400 mg/L CuO nanoparticles in soybean plants, but chlorophyll started decreasing at 400 mg/L [116]. In another study, CuO nanoparticles reduced carotenoids and chlorophylls in mustard [128] while Cu-based nanoparticles did not affect chlorophyll production in cilantro [129].

Titanium Oxide Nanoparticles

Although TiO_2 is used in many consumable materials like cosmetics, sunscreen and colouring matter in medicine, paints, surface coating and water contamination process, it causes pulmonary inflammation in man if inhaled [130–132]. The quantity and exposure time of TiO_2 significantly increase toxicity. Clément and co-workers [133] have reported that TiO_2 nanoparticles (25 nm) with anatase crystal structure are more toxic to cladocerans, algae, rotifers and plants. At high concentration, they promoted growth of roots in plants. Since the rutile crystalline structures of TiO_2 nanoparticles form aggregates in aqueous medium and are less available for absorption, they are less toxic than the anatase TiO_2 (1 μm). When the exposure time is increased from 24 to 72 h, toxic effect is enhanced. However, at higher concentration (100 mg/L) of anatase TiO_2 nanoparticles, the germination of seeds and root growth of flax seeds was enhanced. The positive effect has been suggested to be due to antimicrobial properties of anatase TiO_2 which increases plant resistance to stress. Similar results have also been obtained by Zheng et al. [134].

Larue et al. [135] have studied the effect of anatase and rutile TiO_2 on the development and germination of wheat (*Triticum aestivum*) over a period of 7 days. It has been observed that anatase TiO_2 nanoparticle of diameter lower than 140 nm is accumulated in wheat roots. They are translocated to leaves if their diameter is smaller than 36 nm even if it is below the detection limit. TiO_2 nanoparticles neither dissolve nor their crystal phase undergoes any change during translocation. The exposure of wheat plant to 14 and 22 nm TiO_2 nanoparticles causes enhancement in root elongation without influencing seed germination, vegetative growth, photosynthesis or redox reaction. These are short-term effects of TiO_2 nanoparticles but during the whole cycle of the plant, it may have some adverse effects.

Accumulation and translocation of TiO_2 nanoparticles in plants suggest that it is not biodegradable. Long-term deposition may interfere with biological function of plants. Servin and co-workers [136] have studied the effect of TiO_2 nanoparticles in cucumber plants (*Cucumis sativus*) over a large accumulation range (0–4000 mg/L). They found that root was significantly increased up to a concentration of 500 mg/L but above this concentration, it ceases to grow further. Nitrogen in the root was converted to organic nitrogen showing an increase of about 51.1%, compared to control. It is thought that TiO_2 nanoparticles promote plant root growth by stimulating nitrogen accumulation.

Nanomaterials of the same metal with different structural motifs have different effects on plants, although there is no distinction in their chemical behaviour. Of the three crystalline structures of TiO_2 nanoparticles (anatase, rutile and brookite), anatase exhibits the highest catalytic activity [137] and can inhibit the growth of many microbes such as algae, fungi and bacteria. It promotes carotene and chlorophyll synthesis in cucumber. TiO_2

nanoparticles increase the Hill reaction and chloroplast activity by enhancing light absorption in chlorophyll a, electron transfer and oxygen evolution rate in spinach leaves [138–142]. Ba [143] showed that nano-TiO_2 solution can inhibit the germination and growth of cucumber seedlings due to accumulation of nanoparticles. However, rutile TiO_2 nanoparticles can protect chloroplast membrane against reactive oxygen and free radicals and enhance the protective activities of antioxidant enzymes such as SOD, CAT and POD [144, 145].

Nano-anatase TiO_2 promotes the activity of spinach nitrate reductase and accelerates the conversion of nitrogen as nitrates or ammonium salts to organic nitrogen (protein, etc.) [146] but the uptake of other essential metals like Mg and Mn is not affected. TiO_2 nanoparticles, however, stimulated the synthesis of carbohydrates and lipid as a consequence of stress caused by nanomaterials. Tomato seeds treated with TiO_2 nanoparticles and Ag nanoparticles did not influence the germination, perhaps, the thick seed coat did not allow the absorption of nanomaterials. The Ag nanoparticles, at higher concentration (500 to 5000 mg/kg), are toxic to tomato plant during germination and the plant could not grow to full length. Silver nanoparticles in the mature tomato plants showed lower chlorophyll contents, higher SOD activity and less fruit productivity, while nanoTiO_2 exhibited higher SOD activity at the highest concentration (5000 mg/kg). Both nano-Ag and nano-TiO_2 were also taken up into plant stem, leaves and fruits [147]. The soil fortified with TiO_2 nanoparticles enhances the chlorophyll content, POD, CAT and nitrate reductase of many plant species [148, 149].

Iron Oxide Nanoparticles
Hazeem et al. [150] have studied the effect of Fe_3O_4 nanoparticles on the growth of *Picochlorum* sp. in aqueous medium. The small (20 and 40 nm) and large (>100 nm) particles at 200 mg/L were used to examine the growth and chlorophyll content at different stages of growth of algae. The nanoparticles of 20 nm with different concentrations promoted the algal growth besides their aggregation and sedimentation. It prompted the authors to believe that this phenomenon can be used in bioremediation of environment from nanoparticles.

The metal oxide nanoparticles are more toxic to microorganisms than the bulk material of the same metal [151], despite the fact that bulk Fe_3O_4 is used as an algal fertilizer and also a source of iron as nutrient [152]. The smaller nanoparticles penetrate into plant cells or microbial cells but larger ones adhere to cell wall causing agglomeration.

The toxicity of SPION against an aquatic plant *Lemna gibba* has been investigated [153]. It was found that chlorophyll contents decreased, photosynthetic activity

reduced and growth was hampered. The toxicity of nanoparticles is mainly dependent on their size and solubility in aqueous medium. Inhibitory effects of Fe_3O_4 nanoparticles after 6 days on cucumber (*Cucumis sativus*) seed germination and root elongation have also been reported [45]. Germination index of seeds was decreased by exposure of Fe_3O_4 nanoparticles at 500, 2500 and 5000 μg/mL. The effect of manufactured iron oxide nanoparticles on uptake and accumulation in pumpkin (*Cucurbita maxima*) plants grown hydroponically was investigated by Zhu and co-workers [46]. They showed that different amounts of Fe_3O_4 nanoparticles were taken up and translocated throughout the root, stem and leaves and indicated the nanoparticle transport pathways and bioaccumulation into the plant system. Chen et al. [154] have shown that Fe_3O_4 nanoparticles caused a decrease in net photosynthetic rate and chlorophyll a content when alga *Chlorella vulgaris* was exposed for 72 to 100 h and 200×10^3 μg/L of Fe_3O_4 nanoparticles. Iron oxide nanoparticles at 3.2 mg/kg showed reduced mycorrhizal clover biomass by 34% by reducing the glomalin content and root nutrient acquisition of *Arbuscular mycorrhizal* fungi [155]. Wang et al. [32] reported that Fe_3O_4 nanoparticles induced oxidative stress as compared to Fe_3O_4 bulk particles in the ryegrass and pumpkin roots and shoots as indicated by increased SOD and CAT activities and lipid peroxidation. Authors have shown that the tested Fe_3O_4 nanoparticles were unable to translocate in the ryegrass and pumpkin plants. The clogging effects of iron oxide nanoparticles reduce the root hydraulic conductivity by inhibiting the adequate water uptake [117, 156, 157]. Iron oxide nanoparticles have been found to reduce macronutrients such as Ca, K, Mg and S in sunflower's shoots [158]. It has been suggested that it was due to the water blocking effects of nanoparticles, which altered the dissolved nutrients in water. Wang et al. [32, 159] have reported an increase in lipid peroxidation and attributed to Fe_3O_4 blockage of the aquaporins and disturbance of the respiration rate in the root. Many other studies on the use of iron oxide nanoparticles have shown reduced accumulation of chlorophylls in the leaves. However, this response is also associated with the reduction of the root hydraulic conductivity and the transport of dissolved nutrients, particularly of Mg since this nutrient is an essential constituent of the chlorophyll pigment [158, 117, 156, 160].

In a recent study, Shankramma et al. [161] have shown enhanced growth parameters of *S. lycopersicum* exposed to Fe_2O_3 nanoparticles. They found nanoparticles deposited preferentially in root hairs, root tips followed by nodal and middle zone of plant. They have suggested biomineralization of nanoparticles due to rich phytochemicals in plants. However, in another study, Nhan et al. [162] showed that 1000 mg/L Fe_2O_3 exposure to Bt

transgenic and non-transgenic cotton exhibited presence of dark dots (particles) primarily localized in the endodermis and vascular cylinder (Fig. 2). Absorption of Fe_2O_3 nanoparticles and their aggregation in the roots were apparent. Iron contents in the shoots and roots increased with increasing concentration of Fe_2O_3 nanoparticles. It has been suggested that the bioaccumulation of Fe_2O_3 nanoparticles in Bt transgenic and non-transgenic cotton may cause potential risk for environment and human health. Affect of citrate-coated Fe_3O_4 nanoparticles on hydroponically grown wheat plant (*T. aestivum*) has recently been studied by Iannone et al. [163]. TEM images of root section showed the deposition of Fe_3O_4 in epidermal cell wall via apoplastic route. Fairly large quantities of magnetite (2.01–8.07 mg/g) iron were found in wheat roots. Since no paramagnetic signal was detected in stem and leaves, it suggested that nanoparticles were not translocated through vascular tissues. However, Fe_3O_4 nanoparticles affect the germination, chlorophyll content and plant growth and also did not produce lipid peroxidation or H_2O_2 accumulation. Antioxidant enzyme activity of plant reasonably increased in root and shoot which indicates that the Fe_3O_4 nanoparticles are not toxic to wheat plant under the given experimental conditions. The efficacy of Fe_2O_3 nanoparticles as iron fertilizer for peanut (*Arachis hypogaea*) has been studied to check if it can replace the conventional iron fertilizer [164]. The Fe_2O_3 nanoparticles and Fe_2O_3-EDTA were found to increase root length, height and biomass of the plant by regulating phytohormones and antioxidant enzyme activity. Fe_2O_3 nanoparticles are adsorbed onto the soil increasing easy availability of iron to peanut plant. The adsorption of nanoparticles in presence of organic matter is enhanced. It has been demonstrated from hydroponically grown spinach in presence of Fe_2O_3 nanoparticle and $Fe(NO_3)_3 \cdot 9H_2O$ salt that the growth rate of plant is dose and time dependent [165]. The lengths of spinach stem under different concentrations of Fe_2O_3 (100,

150, 200 mg) were 1.45, 1.91 and 2.27-fold greater than those of the control after 45 days. There was, however, no significant change in the plant growth treated with $Fe(NO_3)_3$. The vegetative growth in the non-fruit-producing plants/vegetables such as cabbage, radish and beat root is highly useful because they increase the rate of photosynthesis. Hu et al. [166] found uptake of Fe_2O_3 nanoparticles in plant roots but no translocation from roots to shoots was observed. In the case of soybean, an increase in leaf and pod production due to uptake of Fe_2O_3 has also been shown in previous studies [167]. The mechanism of uptake of Fe_2O_3 nanoparticles has been explained in terms of reduction of Fe_2O_3 to Fe^{2+}. Since Fe^{3+} is insoluble in aqueous medium, it is converted to Fe^{2+} in the soil when it became slightly acidic and absorbed. In hydroponic condition, the acidity is produced due to the addition of the nutrient, $NH_4H_2PO_4$. The presence of iron phosphate has been evidenced from IR spectrum of the nutrient (containing $NH_4H_2PO_4$ and Fe_2O_3) which is absorbed and translocated to different parts of the plant.

Aluminium Oxide Nanoparticles

In the beginning, Yang and Watts [168] reported inhibition of root elongation in maize, cucumber, soybean, cabbage and carrot exposed to 13 nm Al_2O_3 nanoparticles. Thereafter, Lin and Xing [19] observed no phytotoxicity after 60-nm-sized Al_2O_3 nanoparticle application in radish, rape, ryegrass, lettuce and cucumber, although root elongation was reduced by 35% in maize. In contrast, studies with *Phaseolus vulgaris* and *Lolium perenne* have shown that 100-nm-sized Al_2O_3 nanoparticles had no adverse effect on plant growth [169]. Phytotoxicity of 150-nm-sized Al_2O_3 nanoparticles in *A. thaliana* has been investigated by Lee et al. [93] and no toxic effect was observed. Sadiq et al. [170] have reported the negative effect of below 50-nm-sized Al_2O_3 nanoparticles on the development of microalgae (*Scenedesmus* sp. and *Chlorella* sp.). Effect of Al_2O_3 on the growth and development of *Nicotiana tabacum* and role of microRNA has been investigated [171]. It has been
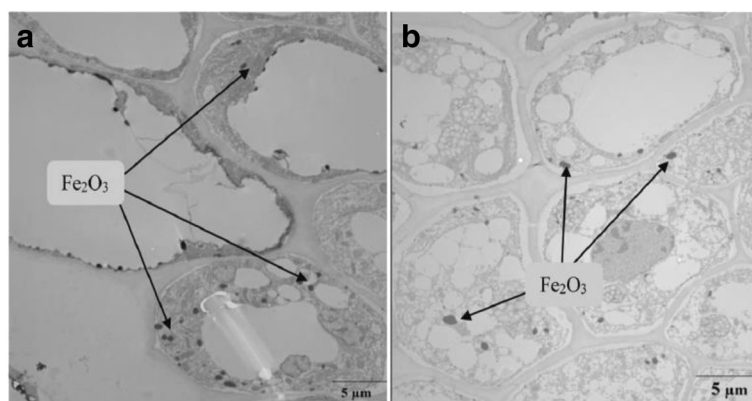
Fig. 2 Transmission electron microscopy images of root sections of non-transgenic cotton (**a**) and Bt transgenic cotton (**b**) plants after 10 days of treatment with Fe_2O_3 nanoparticles [162]

observed that as the concentration of Al_2O_3 nanoparticles increases from 0.1 to 1.0%, the root length, average biomass and the leaf count of each tobacco seedlings decrease. The seedlings form multiple roots with increasing concentration of Al_2O_3, perhaps, as defensive mechanism to avoid contact with excess nanoparticles. They proposed that the micro-RNA genes were upregulated and played a key role in plants' ability to withstand under Al_2O_3 stress. Al_2O_3 nanoparticles (40 nm) had no effect on root elongation of *Triticum aestivum* [172]. However, in a recent study, Yanık and Vardar [173] have reported that Al_2O_3 nanoparticles inhibit root elongation, callose formation, lignin deposition, cellular deformation, enhancement of peroxidase activity, decrease in total protein content and DNA fragmentation in *T. aestivum*. It has been suggested that the negative effects of Al_2O_3 nanoparticles were time and dose dependent. Impact of Al_2O_3 nanoparticles of 30–60 nm on soybean plant under flooding condition has been investigated by Mustafa and Komatsu [174]. The root length was found to increase while proteins related to glycolysis were suppressed. Al_2O_3 nanoparticles mediated the scavenging activity of cells by regulating the ascorbate/glutathione pathway. The results suggested that Al_2O_3 of varying size and shape affects mitochondrial proteins. Since it is a very short-term experiment on soybean seedlings, the plants may recover and tolerate the adverse effects of Al_2O_3 when they are fully grown.

Conclusions

The inadvertent use and release of nanomaterials into the environment affect plant growth and developmental process from seed germination to crop/fruit production. A variety of metal oxide nanoparticles (CeO_2, ZnO, CuO, TiO_2, Fe_3O_4 and Al_2O_3, etc.) has been examined against seed germination, growth of shoot/root, biomass production and physiological and biochemical activities. They have shown beneficial as well as adverse effects on the plant system and production. Plants absorb them on the surface and subsequently translocated and stored in different tissues. Quite often, the innocuous types of nanoparticles at low concentration have not exhibited any significant adverse effect and seem to be beneficial. However, at higher concentration, it produces stress/toxicity and enhances the generation of reactive oxygen species which results in the disruption of the cellular metabolism. In those conditions, plants protect cellular and sub-cellular system from the cytotoxic effects of active oxygen radicals with antioxidative enzymes and non-enzymatic components. Most of the studies have been carried out on the early developmental stages of the plant which requires full-term study to reach final results. It is hoped that some of the nanomaterials will minimize the use of toxic chemicals and fertilizers in near future. Additionally, detailed research investigations are required to examine the impact of these nanoparticles on the environment and human health.

Author details
[1]Department of Chemistry, Aligarh Muslim University, Aligarh 202002, Uttar Pradesh, India. [2]Department of Biology, College of Natural and Computational Sciences, University of Gondar, PO Box #196, Gondar, Ethiopia.

References

1. Falcaro P, Ricco R, Yazdi A, Imaz I, Furukawa S, Maspoch D, Ameloot R, Evans JD, Doonan CJ (2016) Application of metal and metal oxide nanoparticles@MOFs. Coord Chem Rev 307:237–254
2. Zuverza-Mena N, Martínez-Fernández D, Du W, Hernandez-Viezcas JA, Bonilla-Bird N, López-Moreno ML, Komárek M, Peralta-Videa JR, Gardea-Torresdey JL (2016) Exposure of engineered nanomaterials to plants: insights into the physiological and biochemical responses—a review. Plant Physiol Biochem 110:236–264
3. Anker JN, Hall WP, Lyandres O, Shah NC, Zhao J, van Duyne RP (2008) Biosensing with plasmonic nanosensors. Nat Mater 7:442–453
4. Husen A, Siddiqi KS (2014) Carbon and fullerene nanomaterials in plant system. J Nanobiotechnol 12:16
5. Husen A, Siddiqi KS (2014) Phytosynthesis of nanoparticles: concept, controversy and application. Nano Res Lett 9:229
6. Husen A, Siddiqi KS (2014) Plants and microbes assisted selenium nanoparticles: characterization and application. J Nanobiotechnol 12:28
7. Siddiqi KS, Husen A (2016) Fabrication of metal nanoparticles from fungi and metal salts: scope and application. Nano Res Lett 11:98
8. Siddiqi KS, Husen A (2016) Green synthesis, characterization and uses of palladium/platinum nanoparticles. Nano Res Lett 11:482
9. Siddiqi KS, Rahman A, Tajuddin HA (2016) Biogenic fabrication of iron/iron oxide nanoparticles and their application. Nano Res Lett 11:498
10. Siddiqi KS, Husen A (2017) Recent advances in plant-mediated engineered gold nanoparticles and their application in biological system. J Trace Elements Med Biol 40:10–23
11. Du W, Tan W, Peralta-Videa JR, Gardea-Torresdey JL, Ji R, Yin Y, Guo H (2016) Interaction of metal oxide nanoparticles with higher terrestrial plants: physiological and biochemical aspects. Plant Physiol Biochem 110:210–225
12. Baruah S, Dutta J (2009) Nanotechnology applications in pollution sensing and degradation in agriculture: a review. Environ Chem Lett 7:191–204
13. Keller AA, Lazareva A (2013) Predicted releases of engineered nanomaterials: from global to regional to local. Environ Sci Technol Lett 1:65–70
14. Weir A, Westerhoff P, Fabricius L, Hristovski K, von Goetz N (2012) Titanium dioxide nanoparticles in food and personal care products. Environ Sci Technol 46:2242–2250
15. Zhao J, Wang Z, Dai Y, Xing B (2013) Mitigation of CuO nanoparticle-induced bacterial membrane damage by dissolved organic matter. Water Res 47:4169–4178
16. Ramsden C, Henry T, Handy R (2013) Sub-lethal effects of titanium dioxide nanoparticles on the physiology and reproduction of zebrafish. Aquat Toxicol 126:404–413
17. Navarro E, Piccapietra F, Wagner B, Marconi F, Kaegi R, Odzak N, Sigg L, Behra R (2008) Toxicity of silver nanoparticles to *Chlamydomonas reinhardtii*. Environ Sci Technol 42:8959–8964
18. Siddiqi KS, Husen A (2016) Fabrication of metal and metal oxide nanoparticles by algae and their toxic effects. Nano Res Lett 11:363
19. Lin D, Xing B (2007) Phytotoxicity of nanoparticles: inhibition of seed germination and root growth. Environ Pollut 150:243–250
20. Lin DH, Xing BS (2008) Root uptake and phytotoxicity of ZnO nanoparticles. Environ Sci Technol 42:5580–5585

21. Atha DH, Wang H, Petersen EJ, Cleveland D, Holbrook RD, Jaruga P, Dizdaroglu M, Xing B, Nelson BC (2012) Copper oxide nanoparticle mediated DNA damage in terrestrial plant models. Environ Sci Technol 46:1819–1827

22. Siddiqi KS, Husen A (2016) Engineered gold nanoparticles and plant adaptation potential. Nano Res Lett 11:400

23. Gubbins EJ, Batty LC, Lead JR (2011) Phytotoxicity of silver nanoparticles to *Lemna minor* L. Environ Pollut 159:1551–1559

24. Mittler R (2002) Oxidative stress, antioxidants and stress tolerance. Trends Plant Sci 7:405–410

25. Mittler R, Vanderauwera S, Gollery M, Van Breusegem F (2004) Reactive oxygen gene network of plants. Trend Plant Sci 9:490–498

26. Husen A (2010) Growth characteristics, physiological and metabolic responses of teak (*Tectona grandis* Linn.f.) clones differencing in rejuvenation capacity subjected to drought stress. Silvae Gene 59:124–136

27. Miller G, Suzuki N, Ciftci-Yilmaz S, Mittler R (2010) Reactive oxygen species homeostasis and signalling during drought and salinity stresses. Plant Cell Environ 33:453–467

28. Das K, Roychoudhury A (2014) Reactive oxygen species (ROS) and response of antioxidants as ROS-scavengers during environmental stress in plants. Front Environ Sci 2:53

29. Gill SS, Tuteja N (2010) Reactive oxygen species and antioxidant machinery in abiotic stress tolerance in crop plants. Plant Physiol Biochem 48:909–930

30. Getnet Z, Husen A, Fetene M, Yemata G (2015) Growth, water status, physiological, biochemical and yield response of stay green sorghum (*Sorghum bicolor* (L.) Moench) varieties—a field trial under drought-prone area in Amhara Regional State, Ethiopia. J Agron 14:188–202

31. Ozyigit II, Filiz E, Vatansever R, Kurtoglu KY, Koc I, Öztürk MX, Anjum NA (2016) Identification and comparative analysis of H_2O_2-scavenging enzymes (ascorbate peroxidase and glutathione peroxidase) in selected plants employing bioinformatics approaches. Front Plant Sci 7:301

32. Wang H, Kou X, Pei Z, Xiao JQ, Shan X, Xing B (2011) Physiological effects of magnetite (Fe_3O_4) nanoparticles on perennial ryegrass (*Lolium perenne* L.) and pumpkin (*Cucurbita mixta*) plants. Nanotoxicology 5:30–42

33. Zhao L, Peralta-Videa JR, Ren M, Varela-Ramirez A, Li C, Hernandez-Viezcas JA, Aguilera RJ, Gardea-Torresdey JL (2012) Transport of Zn in a sandy loam soil treated with ZnO NPs and uptake by corn plants: electron microprobe and confocal microscopy studies. Chem Eng J 184:1–8

34. Zhao L, Peng B, Hernandez-Viezcas JA, Rico C, Sun Y, Peralta-Videa JR, Tang X, Niu G, Jin L, Varela-Ramirez A, Zhang JY, Gardea-Torresdey JL (2012) Stress response and tolerance of *Zea mays* to CeO_2 nanoparticles: cross talk among H_2O_2, heat shock protein, and lipid peroxidation. ACS Nano 6:9615–9622

35. Rico CM, Hong J, Morales MI, Zhao L, Barrios AC, Zhang JY, Peralta-Videa JR, Gardea-Torresdey JL (2013) Effect of cerium oxide nanoparticles on rice: a study involving the antioxidant defense system and in vivo fluorescence imaging. Environ Sci Technol 47:5635–5642

36. Husen A (2009) Growth, chlorophyll fluorescence and biochemical markers in clonal ramets of shisham (*Dalbergia sissoo* Roxb.) at nursery stage. New For 38:117–129

37. Jiang HS, Li M, Chang FY, Li W, Yin LY (2012) Physiological analysis of silver nanoparticles and $AgNO_3$ toxicity to *Spirodela polyrhiza*. Environ Toxicol Chem 31:1880–1886

38. Husen A, Iqbal M, Aref IM (2014) Growth, water status and leaf characteristics of *Brassica carinata* under drought and rehydration conditions. Braz J Bot 37:217–227

39. Husen A, Iqbal M, Aref IM (2016) IAA-induced alteration in growth and photosynthesis of pea (*Pisum sativum* L.) plants grown under salt stress. J Environ Biol 37:421–429

40. Shaw AK, Ghosh S, Kalaji HM, Bosa K, Brestic M, Zivcak M, Hossain Z (2014) Nano-CuO stress induced modulation of antioxidative defense and photosynthetic performance of Syrian barley (*Hordeum vulgare* L.). Environ Exp Bot 102:37–47

41. Baker NR (2008) Chlorophyll fluorescence: a probe of photosynthesis in vivo. Ann Rev Plant Biol 59:89–113

42. Husen A (2013) Growth characteristics, biomass and chlorophyll fluorescence variation of Garhwal Himalaya's fodder and fuel wood tree species at the nursery stage. Open J For 3:12–16

43. Husen A, Khali R, Nautiyal S (2004) Altitudinal variation in chlorophyll fluorescence/photosynthetic efficiency in seedlings of some indigenous fodder species. Ind For 130:89–94

44. Embiale A, Hussein M, Husen A, Sahile S, Mohammed K (2016) Differential sensitivity of *Pisum sativum* L. cultivars to water-deficit stress: changes in growth, water status, chlorophyll fluorescence and gas exchange attributes. J Agron 15:45–57

45. Mushtaq YK (2011) Effect of nanoscale Fe_3O_4, TiO_2 and carbon particles on cucumber seed germination. J Environ Sci Health 46:1732–1735

46. Zhu H, Han J, Xiao JQ, Jin Y (2008) Uptake, translocation, and accumulation of manufactured iron oxide nanoparticles by pumpkin plants. J Environ Monit 10:713–717

47. López-Moreno ML, de la Rosa G, Hernández-Viezcas JA, Castillo-Michel H, Botez CE, Peralta-Videa JR, Gardea-Torresdey JL (2010) Evidence of the differential biotransformation and genotoxicity of ZnO and CeO_2 nanoparticles on soybean (*Glycine max*) plants. Environ Sci Technol 44:7315–7320

48. Ge Y, Schimel JP, Holden PA (2011) Evidence for negative effects of TiO_2 and ZnO nanoparticles on soil bacterial communities. Environ Sci Technol 45:1659–1664

49. Abramowicz DA (1990) Aerobic and anaerobic biodegradation of PCBs: a review. Crit Rev Biotechnol 10:241–251

50. Lowry GV, Gregory KB, Apte SC, Lead JR (2012) Transformations of nanomaterials in the environment. Environ Sci Technol 46:6893–6899

51. Wang Z, Xie X, Zhao J, Liu X, Feng W, White JC, Xing B (2012) Xylem- and Phloem-based transport of CuO nanoparticles in maize (*Zea mays* L.). Environ Sci Technol 46:4434–4441

52. Ma Y, He X, Zhang P, Zhang Z, Guo Z, Tai R, Xu Z, Zhang L, Ding Y, Zhao Y (2011) Phytotoxicity and biotransformation of La_2O_3 nanoparticles in a terrestrial plant cucumber (*Cucumis sativus*). Nanotoxicology 5:743–753

53. Zhang P, Ma Y, Zhang Z, He X, Guo Z, Tai R, Ding Y, Zhao Y, Chai Z (2012) Comparative toxicity of nanoparticulate/bulk Yb_2O_3 and $YbCl_3$ to cucumber (*Cucumis sativus*). Environ Sci Technol 46:1834–1841

54. Schwabe F, Schulin R, Limbach LK, Stark W, Bürge D, Nowack B (2013) Influence of two types of organic matter on interaction of CeO_2 nanoparticles with plants in hydroponic culture. Chemosphere 91:512–520

55. Rico CM, Majumdar S, Duarte-Gardea M, Peralta-Videa JR, Gardea-Torresdey JL (2011) Interaction of nanoparticles with edible plants and their possible implications in the food chain. J Agric Food Chem 59:3485–3498

56. Judy JD, Unrine JM, Rao W, Wirick S, Bertsch PM (2012) Bioavailability of gold nanomaterials to plants: importance of particle size and surface coating. Environ Sci Technol 46:8467–8474

57. Rico CM, Barrios AC, Tan W, Rubenecia R, Lee SC, Varela-Ramirez A, Peralta-Videa JR, Gardea-Torresdey JL (2015) Physiological and biochemical response of soil-grown barley (*Hordeum vulgare* L.) to cerium oxide nanoparticles. Environ Sci Pollut Res 22:10551–10558

58. Vittori Antisari L, Carbone S, Gatti A, Vianello G, Nannipieri P (2015) Uptake and translocation of metals and nutrients in tomato grown in soil polluted with metal oxide (CeO_2, Fe_3O_4, SnO_2, TiO_2) or metallic (Ag, Co, Ni) engineered nanoparticles. Environ Sci Pollut Res Int 22:1841–1853

59. Priester JH, Gea Y, Mielkea RE, Horsta AM, Moritzb SC, Espinosae K, Gelbf J, Walkerg SL, Nisbetb RM, Ani YJ, Schimelb JP, Palmere RG, Hernandez-Viezcasc JA, Zhaoc L, Gardea-Torresdeyc JL, Holdena PA (2012) Soybean susceptibility to manufactured nanomaterials with evidence for food quality and soil fertility interruption. Proc Natl Acad Sci U S A 109:14734–14735

60. Lopez-Moreno ML, De La Rosa G, Hernandez-Viezcas JA, Peralta-Videa JR, Gardea-Torresdey JL (2010) X-ray absorption spectroscopy (XAS) corroboration of the uptake and storage of CeO_2 nanoparticles and assessment of their differential toxicity in four edible plant species. J Agric Food Chem 58:3689–3693

61. Pelletier DA, Suresh AK, Holton GA, McKeown CK, Wang W, Gu B, Mortensen NP, Allison DP, Joy DC, Allison MR, Brown SD, Phelps TJ, Doktycz MJ (2010) Effects of engineered cerium oxide nanoparticles on bacterial growth and viability. Appl Environ Microbiol 76:7981–7989

62. Gutierrez-Boem FH, Thomas GW (2001) Leaf area development in soybean as affected by phosphorus nutrition and water deficit. J Plant Nutr 24:1711–1729

63. Kosynkin VD, Arzgatkina AA, Ivanov EN, Chtoutsa MG, Grabko AI, Kardapolov AV, Sysina NA (2000) The study of process production of polishing powder based on cerium dioxide. J Alloys Compd 303–304:421–425

64. Johnston BD, Scown TM, Moger J, Cumberland SA, Baalousha M, Linge K, van Aerle R, Jarvis K, Lead JR, Tyler CR (2010) Bioavailability of nanoscale metal oxides TiO_2, CeO_2, and ZnO to fish. Sci Total Environ 44:1144–1151

65. Asli S, Neumann M (2009) Colloidal suspensions of clay or titanium dioxide nanoparticles can inhibit leaf growth and transpiration via physical effects on root water transport. Plant Cell Environ 32:577–584

66. Zhang P, Ma Y, Zhang Z, He X, Zhang J, Guo Z, Tai R, Zhao Y, Chai Z (2012) Biotransformation of ceria nanoparticles in cucumber plants. ACS Nano 6: 9943–9950

67. Van Hoecke K, De Schamphelaere KAC, Van der Meeren P, Smagghe G, Janssen CR (2011) Aggregation and ecotoxicity of CeO$_2$ nanoparticles in synthetic and natural waters with variable pH, organic matter concentration and ionic strength. Environ Pollut 159:970–976

68. Parsons JG, Lopez ML, Gonzalez CM, Peralta-Videa JR, Gardea-Torresdey JL (2010) Toxicity and biotransformation of uncoated and coated nickel hydroxide nanoparticles on mesquite plants. Environ Toxicol Chem 29: 1146–1154

69. Yin L, Cheng Y, Espinasse B, Colman BP, Auffan M, Wiesner M, Rose J, Liu J, Bernhardt ES (2011) More than the ions: the effects of silver nanoparticles on *Lolium multiflorum*. Environ Sci Technol 45:2360–2367

70. Jiang M, Ohnuki T, Kozai N, Tanaka K, Suzuki Y, Sakamoto F, Kamiishi E, Utsunomiya S (2010) Biological nano-mineralization of Ce phosphate by *Saccharomyces cerevisiae*. Chem Geol 277:61–69

71. Birbaum K, Brogioli R, Schellenberg M, Martinoia E, Stark WJ, Gunther D, Limbach LK (2010) No evidence for cerium dioxide nanoparticle translocation in maize plants. Environ Sci Technol 44:8718–8723

72. Andersen CP, King G, Plocher M, Storm M, Pokhrel LR, Johnson MG, Rygiewicz PT (2016) Germination and early plant development of ten plant species exposed to titanium dioxide and cerium oxide nanoparticles. Environ Toxico Chem 35:222–2229

73. Zhang ZY, He X, Zhang HF, Ma YH, Zhang P, Ding YY, Zhao YL (2011) Uptake and distribution of ceria nanoparticles in cucumber plants. Metallomics 3:816–822

74. Wang Q, Ma XM, Zhang W, Pei HC, Chen YS (2012) The impact of cerium oxide nanoparticles on tomato (*Solanum lycopersicum* L.) and its implications for food safety. Metallomics 4:1105–1112

75. Rico CM, Morales MI, McCreary R, Castillo-Michel H, Barrios AC, Hong J, Tafoya A, Lee WY, Varela-Ramirez A, Peralta-Videa JR, Gardea-Torresdey JL (2013) Cerium oxide nanoparticles modify the antioxidative stress enzyme activities and macromolecule composition in rice seedlings. Environ Sci Technol 47:14110–14118

76. Backmann J, Schultz C, Fabian H, Hahn U, Saenger W, Naumann D (1996) Thermally induced hydrogen exchange processes in small proteins as seen by FTIR spectroscopy. Proteins 24:379–387

77. Fischer G, Braun S, Thissen R, Dott W (2006) FT-IR Spectroscopy as a tool for rapid identification and intra-species characterization of airborne filamentous fungi. J Microbiol Meth 64:63–77

78. Hernandez-Viezcas JA, Castillo-Michel H, Andrews JC, Cotte M, Rico C, Peralta-Videa JR, Ge Y, Priester JH, Holden PA, Gardea-Torresdey JL (2013) In Situ synchrotron X-ray fluorescence mapping and speciation of CeO$_2$ and ZnO nanoparticles in soil cultivated soybean (*Glycine max*). ACS Nano 7:1415–1423

79. Riesen O, Feller U (2005) Redistribution of nickel, cobalt, manganese, zinc, and cadmium via the phloem in young and maturing wheat. J Plant Nutr 28:421–430

80. Serret G, Williams G, Isaure MP, Marcus MA, Fakra SC, Frerot H, Pairis S, Geoffroy N, Manceau A, Saumitou-Laprade P (2009) Zinc distribution and speciation in *Arabidopsis halleri* x *Arabidopsis lyrata* progenies presenting various zinc accumulation capacities. New Phytol 184:581–595

81. Hernandez-Viezcas JA, Castillo-Michel H, Servin AD, Peralta-Videa JR, Gardea-Torresdey JL (2011) Spectroscopic verification of zinc absorption and distribution in the desert plant *Prosopis juliflora-velutina* (velvet mesquite) grown with ZnO nanoparticles. Chem Eng J 170:346–352

82. Thangavel P, Long S, Minocha R (2007) Changes in phytochelatins and their biosynthetic intermediates in red spruce (*Picea rubens* Sarg.) cell suspension cultures under cadmium and zinc stress. Plant Cell Tissue Organ Cult 88:201–216

83. Kopittke PM, Menzies NW, de Jonge MD, McKenna BA, Donner E, Webb RI, Paterson DJ, Howard DL, Ryan CG, Glover CJ, Scheckel KG, Lombi E (2011) In situ distribution and speciation of toxic copper, nickel and zinc in hydrated roots of cowpea. J Plant Physiol 156:663–673

84. Hurrell RF, Juillerat MA, Reddy MB, Lynch SR, Dassenko SA, Cook JD (1992) Soy protein, phytate, and iron absorption in humans. Am J Clin Nutr 56: 573–578

85. Hu C, Liu X, Li X, Zhao Y (2014) Evaluation of growth and biochemical indicators of *Salvinia natans* exposed to zinc oxide nanoparticles and zinc accumulation in plants. Environ Sci Pollut Res 21:732–739

86. Cakmak I (2000) Possible roles of zinc in protecting plant cells from damage by reactive oxygen species. New Phytol 146:185–205

87. Upadhyay R, Panda SK (2010) Zinc reduces copper toxicity induced oxidative stress by promoting antioxidant defense in freshly grown aquatic duckweed *Spirodela polyrhiza* L. J Hazard Mater 175:1081–1084

88. Zafar H, Ali A, Ali JS, Haq IU, Zia M (2016) Effect of ZnO nanoparticles on *Brassica nigra* seedlings and stem explants: growth dynamics and antioxidative response. Front Plant Sci 7:535

89. Adams LK, Lyon DY, Alvarez PJJ (2006) Comparative eco-toxicity of nanoscale TiO$_2$, SiO$_2$, and ZnO water suspensions. Water Res 40:3527–3532

90. Franklin NM, Rogers NJ, Apte SC, Batley GE, Gadd GE, Casey PS (2007) Comparative toxicity of nanoparticulate ZnO, bulk ZnO, and ZnCl$_2$ to a freshwater microalga (*Pseudokirchneriella subcapitata*): the importance of particle solubility. Environ Sci Technol 41:8484–8490

91. Watson JL, Fang T, Dimkpa CO, Britt DW, McLean JE, Jacobson A, Anderson AJ (2015) The phytotoxicity of ZnO nanoparticles on wheat varies with soil properties. Biometals 28:101–112

92. Landa P, Vankova R, Andrlova J, Hodek J, Marsik P, Storchova H, White JC, Vanek T (2012) Nanoparticle-specific changes in Arabidopsis thaliana gene expression after exposure to ZnO, TiO$_2$, and fullerene soot. J Hazard Mater 241:55–62

93. Lee CW, Mahendra S, Zodrow K, Li D, Tsai YC, Braam J, Alvarez PJ (2010) Developmental phytotoxicity of metal oxide nanoparticles to *Arabidopsis thaliana*. Environ Toxicol Chem 29:669–675

94. Nel A, Xia T, Madler L, Li N (2006) Toxic potential of materials at the nanolevel. Science 311:622–627

95. Cuypers A, Vangronsveld J, Clijsters H (2001) The redox status of plant cells (AsA and GSH) is sensitive to zinc imposed oxidative stress in roots and primary leaves of *Phaseolus vulgaris*. Plant Physiol Biochem 39:657–664

96. Kumari M, Khan SS, Pakrashi S, Mukherjee A, Chandrasekaran N (2011) Cytogenetic and genotoxic effects of zinc oxide nanoparticles on root cells of *Allium cepa*. J Hazard Mater 190:613–621

97. Wang P, Menzies NW, Lombi E, McKenna BA, Johannessen B, Glover CJ, Kappen P, Kopittke PM (2013) Fate of ZnO nanoparticles in soils and cowpea (*Vigna unguiculata*). Environ Sci Technol 47:13822–13830

98. Raliya R, Tarafdar JC (2013) ZnO nanoparticle biosynthesis and its effect on phosphorous-mobilizing enzyme secretion and gum contents in Clusterbean (*Cyamopsis tetragonoloba* L.). Agric Res 2:48–57

99. Raliya R, Nair R, Chavalmane S, Wang WN, Biswas P (2015) Mechanistic evaluation of translocation and physiological impact of titanium dioxide and zinc oxide nanoparticles on the tomato (*Solanum lycopersicum* L.) plant. Metallomics 7:1584–1594

100. Pokhrel LR, Dubey B (2013) Evaluation of developmental responses of two crop plants exposed to silver and zinc oxide nanoparticles. Sci Total Environ 452–453:321–332

101. Kim S, Lee S, Lee I (2012) Alteration of phytotoxicity and oxidant stress potential by metal oxide nanoparticles in *Cucumis sativus*. Water Air Soil Pollut 223:2799–2806

102. Manzo S, Rocco A, Carotenuto R, Picione Fde L, Miglietta ML, Rametta G, Di Francia G (2011) Investigation of ZnO nanoparticles ecotoxicological effects towards different soil organisms. Environ Sci Pollut Res Int 18:756–763

103. Du WC, Sun YY, Ji R, Zhu JG, Wu JC, Guo HY (2011) TiO$_2$ and ZnO nanoparticles negatively affect wheat growth and soil enzyme activities in agricultural soil. J Environ Monit 13:822–828

104. Dimkpa CO, McLean JE, Britt DW, Anderson AJ (2015) Nano-CuO and interaction with nano-ZnO or soil bacterium provide evidence for the interference of nanoparticles in metal nutrition of plants. Ecotoxicology 24:119–129

105. Adhikari T, Kundu S, Biswas AK, Tarafdar JC, Rao AS (2012) Effect of copper oxide nano particle on seed germination of selected crops. J Agric Sci Technol A2:815–823

106. Lei X, CeHui M, XiHong L, XiaoLian W, YanWen L, XianPei H, XiangLong Q, Yan H (2011) Toxicity of copper oxide nanoparticles to the seed germination of Chinese cabbage. J Agro Environ Sci 30:1830–1835

107. Yruela I (2009) Copper in plants, acquisition, transport and interactions. Funct Plant Biol 36:409–430

108. Barton LL, Johnson GV, O'nan AG, Wagener BM (2000) Inhibition of ferric chelate reductase in alfalfa roots by cobalt, nickel, chromium and copper. J Plant Nutr 23:1833–1845

109. Welch RM, Norvell WA, Schaefer SC, Shaff JE, Kochian LV (1993) Induction of iron(III) and copper(II) reduction in pea (*Pisum sativum* L) roots by Fe and Cu status—does the root-cell plasmalemma Fe(III)-chelate reductase perform a general role in regulating cation uptake? Planta 190:555–561

110. Voegelin A, Pfister S, Scheinost AC, Marcus MA, Kretzschmar R (2005) Changes in zinc speciation in field soil after contamination with zinc oxide. Environ Sci Technol 39:6616–6623

111. Schopfer P, Plachy C, Frahry G (2001) Release of reactive oxygen intermediates (superoxide radicals, hydrogen peroxide, and hydroxyl radicals) and peroxidase in germinating radish seeds controlled by light, gibberellin, and abscisic acid. Plant Physiol 125:1591–1602

112. Halliwell B, Gutteridge JMC (2007) Free radicals in biology and medicine. Oxford University Press, New York

113. Fernandes JC, Henriques FS (1991) Biochemical, physiological and structural effects of excess copper in plants. Bot Rev 57:246–273

114. Karlsson HL, Cronholm P, Gustafsson J, Moller L (2008) Copper oxide nanoparticles are highly toxic: a comparison between metal oxide nanoparticles and carbon nanotubes. Chem Res Toxicol 21:1726–1732

115. Fahmy B, Cormier SA (2009) Copper oxide nanoparticles induce oxidative stress and cytotoxicity in airway epithelial cells. Toxicol In Vitro 23:1365–1371

116. Nair PMG, Chung IM (2014) Impact of copper oxide nanoparticles exposure on *Arabidopsis thaliana* growth, root system development, root lignification, and molecular level changes. Environ Sci Pollut Res 21:12709–12722

117. Ma C, Chhikara S, Xing B, Musante C, White JC, Dhankher OP (2013) Physiological and molecular response of *Arabidopsis thaliana* (L.) to nanoparticle cerium and indium oxide exposure. ACS Sus Chem Eng 1:768–778

118. Regier N, Cosio C, von Moos N, Slaveykova VI (2015) Effects of copper-oxide nanoparticles, dissolved copper and ultraviolet radiation on copper bioaccumulation, photosynthesis and oxidative stress in the aquatic macrophyte *Elodea nuttallii*. Chemosphere 128:56–61

119. Ivask A, Juganson K, Bondarenko O, Mortimer M, Aruoja V, Kasemets K, Blinova I, Heinlaan M, Slaveykova V, Kahru A (2014) Mechanisms of toxic action of Ag, ZnO and CuO nanoparticles to selected ecotoxicological test organisms and mammalian cells in vitro: a comparative review. Nanotoxicology 8:57–71

120. Perreault F, Samadani M, Dewez D (2014) Effect of soluble copper released from copper oxide nanoparticles solubilisation on growth and photosynthetic processes of *Lemna gibba* L. Nanotoxicology 8:374–382

121. Shi JY, Abid AD, Kennedy IM, Hristova KR, Silk WK (2011) To duckweeds (*Landoltia punctata*), nanoparticulate copper oxide is more inhibitory than the soluble copper in the bulk solution. Environ Pollut 159:1277–1282

122. Agrawal SB, Mishra S (2009) Effects of supplemental ultraviolet-B and cadmium on growth, antioxidants and yield of *Pisum sativum* L. Ecotoxicol Environ Saf 72:610–618

123. Rai LC, Tyagi B, Mallick N, Rai PK (1995) Interactive effects of UV-B and copper on photosynthetic activity of the cyanobacterium *Anabaena doliolum*. Environ Exp Bot 35:177–185

124. Andreotti F, Mucha AP, Caetano C, Rodrigues P, Gomes CR, Almeida CMR (2015) Interactions between salt marsh plants and Cu nanoparticles effects on metal uptake and phytoremediation processes. Ecotoxicol Environ Saf 120:303–309

125. Le Van N, Ma C, Shang J, Rui Y, Liu S, Xing B (2016) Effects of CuO nanoparticles on insecticidal activity and phytotoxicity in conventional and transgenic cotton. Chemosphere 144:661–670

126. Hong J, Rico CM, Zhao L, Adeleye AS, Keller AA, Peralta-Videa JR, Gardea-Torresdey JL (2016) Toxic effects of copper-based nanoparticles or compounds to lettuce (*Lactuca sativa*) and alfalfa (*Medicago sativa*). Environ Sci Process Impact 17:177–185

127. Nair PMG, Kim SH, Chung IM (2014) Copper oxide nanoparticle toxicity in mung bean (*Vigna radiata* L.) seedlings: physiological and molecular level responses of in vitro grown plants. Acta Physiol Plant 36:2947–2958

128. Nair PMG, Chung IM (2015) Study on the correlation between copper oxide nanoparticles induced growth suppression and enhanced lignification in Indian mustard (*Brassica juncea* L.). Ecotoxicol Environ Saf 113:302–313

129. Zuverza-Mena N, Medina-Velo IA, Barrios AC, Tan W, Peralta-Videa JR, Gardea-Torresdey JL (2015) Copper nanoparticles/compounds impact agronomic and physiological parameters in cilantro (*Coriandrum sativum*). Environ Sci Process Impact 17:1783–1793

130. Warheit DB, Brock WJ, Lee WJ, Webb KP, Reed KL (2005) Comparative pulmonary toxicity inhalation and instillation studies with different TiO₂ particle formulations: impact of surface treatments on particle toxicity. Toxicol Sci 88:514–524

131. Warheit DB, Webb TR, Sayes CM, Colvin VL, Reed KL (2006) Pulmonary instillation studies with nanoscale TiO₂ rods and dots in rats: toxicity is not dependent upon particle size and surface area. Toxicol Sci 91:227–236

132. Warheit DB, Webb TR, Reed KL, Frerichs S, Sayes CM (2007) Pulmonary toxicity study in rats with three forms of ultrafine—TiO₂ particles: differential responses related to surface properties. Toxicology 230:90–104

133. Clément L, Hurel C, Marmier N (2013) Toxicity of TiO₂ nanoparticles to cladocerans, algae, rotifers and plants—effects of size and crystalline structure. Chemosphere 90:1083–1090

134. Zheng L, Hong F, Lu S, Liu C (2005) Effect of nano-TiO₂ on strength of naturally aged seeds and growth of spinach. Biol Trace Elem Res 104:83–91

135. Larue C, Laurette J, Herlin-Boime N, Khodja H, Fayard B, Flank AM, Brisset F, Carriere M (2012) Accumulation, translocation and impact of TiO₂ nanoparticles in wheat (*Triticum aestivum* spp.): influence of diameter and crystal phase. Sci Total Environ 431:197–208

136. Servin AD, Castillo-Michel H, Hernandez-Viezcas JA, Diaz BC, Peralta-Videa JR, Gardea-Torresdey JL (2012) Synchrotron micro-XRF and micro-XANES confirmation of the uptake and translocation of TiO₂ nanoparticles in cucumber (*Cucumis sativus*) plants. Environ Sci Technol 46:7637–7643

137. Yin HC, Liu QJ, Lin Q, Chen SN, Zhou LJ (2005) Inhibitory effects of nano-TiO₂ loaded on Pd on cyanobacteria growth. Acta Bot Boreali-Occidentalia Sin 25:1884–1887

138. Hong FS, Yang P, Gao FQ, Liu C, Zheng L, Zhou J (2005) Effect of nano-anatase TiO₂ on spectral characterization of photosystem II particles from spinach. Chem Res Chin Univ 21:196–200

139. Su MY, Hong FS, Liu C, Wu X, Liu XQ, Chen L, Gao FQ, Yang F, Li Z (2007) Effects of nano-anatase TiO₂ on absorption, distribution of light, and photoreduction activities of chloroplast membrane of spinach. Biol Trace Elem Res 131:101

140. Zheng L, Su MY, Chao L, Liang C, Hao H, Xiao W, Liu XQ, Yang F, Gao FQ, Hong FS (2007) Effects of nanoanatase TiO₂ on photosynthesis of spinach chloroplasts under different light illumination. Biol Trace Elem Res 119:68–76

141. Zheng L, Su MY, Xiao W, Chao L, Qu CX, Chen L, Hao H, Liu XQ, Hong FS (2007) Effects of nano-anatase on spectral characteristics and distribution of LCHII on the thylakoid membranes of spinach. Biol Trace Elem Res 120:273–283

142. Wang XM, Gao FQ, Ma LL, Liu J, Yin ST, Yang P, Hong FS (2008) Effects of nano-anatase on ribulose-1, 5-bisphosphate carboxylase/oxygenase mRNA expression in spinach. Biol Trace Elem Res 126:280–289

143. Ba CL (2010) Study on the uptake, transport, and accumulation of nano-TiO₂ in plants and its protein mechanism. Master dissertation, Hebei University

144. Hong F, Yang F, Liu C, Gao Q, Wan Z, Gu F, Wu C, Ma Z, Zhou J, Yang P (2005) Influences of nano-TiO₂ on the chloroplast aging of spinach under light. Biol Trace Elem Res 104:249–260

145. Hong F, Zhou J, Liu C, Yang F, Wu C, Zheng L, Yang P (2005) Effect of nano-TiO₂ on photochemical reaction of chloroplasts of spinach. Biol Trace Elem Res 105:269–279

146. Yang F, Hong FS, You WJ, Liu C, Gao FQ, Wu C, Yang P (2006) Influence of nano-anatase TiO₂ on the nitrogen metabolism of growing spinach. Biol Trace Elem Res 110:179–190

147. Song G, Jun H, Waldman B, Roh J, Kim Y, Yi J, Lee EJ (2013) Functional analyses of nanoparticle toxicity: a comparative study of the effects of TiO₂ and Ag on tomatoes (*Lycopersicon esculentum*). Ecotoxicol Environ Saf 93:60–67

148. Hruby M, Cigler P, Kuzel S (2002) Contribution to understanding the mechanism of titanium action in plant. J Plant Nutr 25:577–598

149. Feizi H, Moghaddam PR, Shahtahmassebi N, Fotovat A (2012) Impact of bulk and nanosized titanium dioxide (TiO₂) on wheat seed germination and seedling growth. Biol Trace Elem Res 146:101–106

150. Hazeem LJ, Waheed FA, Rashdan S, Bououdina M, Brunet L, Slomianny C, Boukherroub R, Elmeselmani WA (2015) Effect of magnetic iron oxide (Fe₃O₄) nanoparticles on the growth and photosynthetic pigment content of *Picochlorum* sp. Environ Sci Pollut Res 22:11728–11739

151. Manzo S, Miglietta M, Rametta G, Buono S, Francia G (2013) Toxic effects of ZnO nanoparticles towards marine algae *Dunaliella tortiolecta*. Sci Total Environ 445–446:371–376

152. WHOI (Woods Hole Oceanographic Institution) (2007) Iron fertilization in southern ocean increased growth of algae that absorb greenhouse gases, and could cool climate. Available at: http://www.whoi.edu/main/news-releases/1995-2004?tid=3622&cid=971

153. Barhoumi L, Oukarroum A, Taher LB, Smiri LS, Abdelmelek H, Dewez D (2015) Effects of superparamagnetic iron oxide nanoparticles on photosynthesis and growth of the aquatic plant *Lemna gibba*. Arch Environ Contam Toxicol 68:510–520

154. Chen X, Zhu X, Li R, Yao H, Lu Z, Yang X (2012) Photosynthetic toxicity and oxidative damage induced by nano-Fe₃O₄ on *Chlorella vulgaris* in aquatic environment. Op J Ecol 2:21–28

155. Feng Y, Cui X, He S, Dong G, Chen M, Wang J, Lin X (2013) The role of metal nanoparticles in influencing arbuscular mycorrhizal fungi effects on plant growth. Environ Sci Technol 47:9496–9504

156. Ma X, Gurung A, Deng Y (2013) Phytotoxicity and uptake of nanoscale zerovalent iron (nZVI) by two plant species. Sci Total Environ 443:844–849

157. Martínez-Fernández D, Vítková M, Bernal MP, Komárek M (2015) Effects of nano-maghemite on trace element accumulation and drought response of *Helianthus annuus* L. in a contaminated mine soil. Water Air Soil Pollut 226:1–4

158. Martínez-Fernández D, Barroso D, Komárek M (2016) Root water transport of *Helianthus annuus* L. under iron oxide nanoparticle exposure. Environ Sci Pollut Res 23:1732–1741

159. Wang Z, Li J, Zhao J, Xing B (2011) Toxicity and internalization of CuO nanoparticles to prokaryotic alga *Microcystis aeruginosa* as affected by dissolved organic matter. Environ Sci Technol 45:6032–6040

160. Trujillo-Reyes J, Majumdar S, Botez CE, Peralta-Videa JR, Gardea-Torresdey JL (2014) Exposure studies of core—shell Fe/Fe$_3$O$_4$ and Cu/CuO NPs to lettuce (*Lactuca sativa*) plants: are they a potential physiological and nutritional hazard? J Hazard Mater 267:255–263

161. Shankramma K, Yallappa S, Shivanna MB, Manjanna J (2016) Fe$_2$O$_3$ magnetic nanoparticles to enhance *S. lycopersicum* (tomato) plant growth and their biomineralization. Appl Nanosci 6:983–990

162. Nhan LV, Ma C, Rui Y, Cao W, Deng Y, Liu L, Xing B (2016) The effects of Fe$_2$O$_3$ nanoparticles on physiology and insecticide activity in non-transgenic and Bt-transgenic cotton. Front Plant Sci 6:1263

163. Iannone MF, Groppa MD, de Sousa ML, Fernández van Raap MB, Benavides MP (2016) Impact of magnetite iron oxide nanoparticles on wheat (*Triticum aestivum* L.) development: evaluation of oxidative damage. Environ Exp Bot 131:77–88

164. Rui M, Ma C, Hao Y, Guo J, Rui Y, Tang X, Zhao Q, Fan X, Zhang Z, Hou T, Zhu S (2016) Iron oxide nanoparticles as a potential iron fertilizer for peanut (*Arachis hypogaea*). Fron Plant Sci 7:815

165. Jeyasubramanian K, Thoppey UUG, Hikku GS, Selvakumar N, Subramania A, Krishnamoorthy K (2016) Enhancement in growth rate and productivity of spinach grown in hydroponics with iron oxide nanoparticles. RSC Adv 6: 15451–15459.

166. Hu J, Guo H, Li J, Gan Q, Wang Y, Xing B (2017) Comparative impacts of iron oxide nanoparticles and ferric ions on the growth of *Citrus maxima*. Environ Pollut 221:199–208

167. Sheykhbaglou R, Sedghi M, Tajbakhsh Shishevan M, Seyed Sharifi R (2010) Effects of nano-iron oxide particles on agronomic traits of soybean. Not Sci Biol 2:112–113

168. Yang L, Watts DJ (2005) Particle surface characteristics may play an important role in phytotoxicity of alumina nanoparticles. Toxico Lett 158:122–132

169. Doshi R, Braida W, Christodoulatos C, Wazne M, O'Connor G (2008) Nano-aluminum: transport through sand columns and environmental effects on plant and soil communication. Environ Res 106:296–303

170. Sadiq IM, Pakrashi S, Chandrasekaran N, Mukherjee A (2011) Studies on toxicity of aluminum oxide (Al$_2$O$_3$) nanoparticles to microalgae species: *Scenedesmus* sp. and *Chlorella* sp. J Nanopar Res 13:3287–3299

171. Burklew CE, Ashlock J, Winfrey WB, Zhang B (2012) Effects of aluminum oxide nanoparticles on the growth, development, and microRNA expression of tobacco (*Nicotiana tabacum*). PLoS One 7:e34783

172. Riahi-Madvar A, Rezaee F, Jalali V (2012) Effects of alumina nanoparticles on morphological properties and antioxidant system of *Triticum aestivum*. Iran J of Plant Physiol 3:595–603

173. Yanık F, Vardar F (2015) Toxic effects of aluminum oxide (Al$_2$O$_3$) nanoparticles on root growth and development in *Triticum aestivum*. Water Air Soil Pollut 226:296

174. Mustafa G, Komatsu S (2016) Insights into the response of soybean mitochondrial proteins to various sizes of aluminum oxide nanoparticles under flooding stress. J Proteome Res 15:4464–4475

175. Morales MI, Rico CM, Hernandez-Viezcas JA, Nunez JE, Barrios AC, Tafoya A, Flores-Marges JP, Peralta-Videa JR, Gardea-Torresdey JL (2013) Toxicity assessment of cerium oxide nanoparticles in cilantro (*Coriandrum sativum* L.) plants grown in organic soil. J Agric Food Chem 61:6224–6230

176. Zhao LJ, Sun Y, Hernandez-Viezcas JA, Hong J, Majumdar S, Niu GH, Duarte-Gardea M, Peralta-Videa JR, Gardea-Torresdey JL (2015) Monitoring the environmental effects of CeO$_2$ and ZnO nanoparticles through the life cycle of corn (*Zea mays*) plants and in situ μ-XRF mapping of nutrients in kernels. Environ Sci Technol 49:2921–2928

177. Du WC, Gardea-Torresdey JL, Ji R, Yin Y, Zhu JG, Peralta-Videa JR, Guo HY (2015) Physiological and biochemical changes imposed by CeO$_2$ nanoparticles on wheat: a life cycle field study. Environ Sci Technol 49:11884–11893

178. Nhan LV, Ma CX, Rui YK, Liu ST, Li XG, Xing BS, Liu LM (2015) Phytotoxic mechanism of nanoparticles: destruction of chloroplasts and vascular bundles and alteration of nutrient absorption. Sci Rep 5:11618

179. Rico CM, Lee SC, Rubenecia R, Mukherjee A, Hong J, Peralta-Videa JR, Gardea-Torresdey JL (2014) Cerium oxide nanoparticles impact yield and modify nutritional parameters in wheat (*Triticum aestivum* L.). J Agric Food Chem 62:9669–9675

180. Peralta-Videa JR, Hernandez-Viezcas JA, Zhao L, Diaz BC, Ge Y, Priester JH, Holden PA, Gardea-Torresdey JL (2014) Cerium dioxide and zinc oxide nanoparticles alter the nutritional value of soil cultivated soybean plants. Plant Physiol Biochem 80:128–135

181. Yoon SJ, Kwak JI, Lee WM, Holden PA, An YJ (2014) Zinc oxide nanoparticles delay soybean development: a standard soil microcosm study. Ecotoxicol Environ Saf 100:131–137

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

183. Zhao L, Sun Y, Hernandez-Viezcas JA, Servin AD, Hong J, Niu G, Peralta-Videa JR, Duarte-Gardea M, Gardea-Torresdey JL (2013) Influence of CeO$_2$ and ZnO nanoparticles on cucumber physiological markers and bioaccumulation of Ce and Zn: a life cycle study. J Agric Food Chem 61:11945–11951

184. Wang F, Liu X, Shi Z, Tong R, Adams CA, Shi X (2016) Arbuscular mycorrhizae alleviate negative effects of zinc oxide nanoparticle and zinc accumulation in maize plants—a soil microcosm experiment. Chemosphere 147:88–97

185. Bandyopadhyay S, Plascencia-Villa G, Mukherjee A, Rico CM, José-Yacamán M, Peralta-Videa JR, Gardea-Torresdey JL (2015) Comparative phytotoxicity of ZnO NPs, bulk ZnO, and ionic zinc onto the alfalfa plants symbiotically associated with *Sinorhizobium meliloti* in soil. Sci Total Environ 515:60–69

186. Huang YC, Fan R, Grusak MA, Sherrier JD, Huang CP (2014) Effects of nano-ZnO on the agronomically relevant Rhizobiumelegume symbiosis. Sci Total Environ 497:78–90

187. Dimkpa CO, McLean JE, Latta DE, Manangón E, Britt DW, Johnson WP, Boyanov MI, Anderson AJ (2012) CuO and ZnO nanoparticles: phytotoxicity, metal speciation, and induction of oxidative stress in sand-grown wheat. J Nanopart Res 14:1–15

188. Musante C, White JC (2012) Toxicity of silver and copper to *Cucurbita pepo*: differential effects of nano and bulk-size particles. Environ Toxicol 27:510–517

189. Singh P, Singh R, Borthakur A, Srivastava P, Srivastava N, Tiwary D, Mishra PK (2016) Effect of nanoscale TiO$_2$-activated carbon composite on *Solanum lycopersicum* (L.) and *Vigna radiata* (L.) seeds germination. Energ Ecol Environ 1:131–140

190. Rezaei F, Moaveni P, Mozafari H (2015) Effect of different concentrations and time of nano TiO$_2$ spraying on quantitative and qualitative yield of soybean (*Glycine max* L.) at Shahr-e-Qods, Iran. Biol Forum 7:957–964

191. Frazier TP, Burklew CE, Zhang B (2014) Titanium dioxide nanoparticles affect the growth and microRNA expression of tobacco (*Nicotiana tabacum*). Funct Integr Genomics 14:75–83

192. Mohammadi R, Maali-Amiri R, Abbas A (2013) Effect of TiO$_2$ nanoparticles on chickpea response to cold stress. Biol Trace Elem Res 152:403–410

193. Gao J, Xu G, Qian H, Liu P, Zhao P, Hu Y (2013) Effects of nano-TiO$_2$ on photosynthetic characteristics of *Ulmus elongata* seedlings. Environ Pollut 176:63–70

194. Servin AD, Morales MI, Castillo-Michel H, Hernandez-Viezcas JA, Munoz B, Zhao LJ, Nunez JE, Peralta-Videa JR, Gardea-Torresdey JL (2013) Synchrotron verification of TiO$_2$ accumulation in cucumber fruit: a possible pathway of TiO$_2$ nanoparticle transfer from soil into the food chain. Environ Sci Technol 47:11592–11598

195. Barrena R, Casals E, Colon J, Font X, Sanchez A, Puntes V (2009) Evaluation of the ecotoxicity of model nanoparticles. Chemo 75:850–857

196. García A, Espinosa R, Delgado L, Casals E, González E, Puntes V, Carlos B, Font X, Sánchez A (2011) Acute toxicity of cerium oxide, titanium oxide and iron oxide nanoparticles using standardized tests. Desalination 269:136–141

197. Marusenko Y, Shipp J, Hamilton GA, Morgan JLL, Keebaugh M, Hill H, Dutta A, Zhuo X, Upadhyay N, Hutchings J, Herckes P, Anbar AD, Shock E, Hartnett HE (2013) Bioavailability of nanoparticulate hematite to *Arabidopsis thaliana*. Environ Pollut 174:150–156

198. Wu SG, Huang L, Head J, Chen DR, Kong IC, Tang YJ (2012) Phytotoxicity of metal oxide nanoparticles is related to both dissolved metals ions and adsorption of particles on seed surfaces. J Pet Environ Biotechnol 3:1–6