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REVIEW

Nanoparticles in the soil–plant system: a review

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Abstract

Nanoparticles are increasingly used in many industrial sectors due to their unique properties, yet their introduction in ecosystems is of concern for health and food security. In particular, the accumulation of nanoparticles in soils may disturb the soil and plant system, possibly inducing a risk for crop production. Here, we review recent advances on nanoparticles in the soil–plant system. We focus on sources, emission, transformation, bioavailability, interactions, phytotoxicity and plant uptake of nanoparticles. We emphasize the genomic, metabolomic and proteomic alterations in plants caused by nanoparticles. Besides negative impacts, benefits of nanoparticles for plant growth are discussed.

Keywords Nanoparticles · Transformation · Bioaccumulation · Phytotoxicity · Plant safety · Toxicity mechanism

Introduction

The term nanoparticle, which forms the basis of nanotechnology, is a particle having a diameter less than a 100 nm. Nanoparticles have size-dependent physicochemical properties that are usually different from their bulk or sub-micron/micron-sized counterparts (Dasgupta et al. 2017). Among many qualities, relatively higher surface area (S)-to-volume (V) ratio is the foremost peculiar feature of nanoparticles which provides them high reactivity and physicochemical dynamicity (Mauter et al. 2018). Besides this, the distinguish behavior of nanoparticles than their bulk materials in the environment is also determined by the greater surface energy and quantum confinement (Ma et al. 2010). Based on structure and chemical compositions, nanoparticles are categorized in different groups including zero-valent metals, metal oxides, nano-polymers, quantum dots, lipids, semiconductors, dendrimers, and carbonaceous materials, with varying morphological features such as particles, fibers, rods, wires, sheets, and flowers (Gentile et al. 2016; Sudha et al. 2018). Due to multiple properties, they are used in many sectors from agriculture to industries (Srivastava et al. 2018; Yata et al. 2018).

However, the large-scale production of nano-enabled goods and leaching of nanoparticles either from industrial discharge (e.g., tannery effluents) or from nano-based household products (e.g., sewage waste) into different environments threats their sustainability, adding massive amounts of nanoparticles to both terrestrial and aquatic environment (Ma et al. 2014; Eduok et al. 2015; Brown 2017) and other biosphere (Kulizhskiy et al. 2017). The agricultural soils generally encounter nanoparticles, incidentally, via untreated wastewater used for irrigation or via bio-solids applied for fertilization (Rawat et al. 2018). Since nanoparticles are biologically nondestructive, they persist in soil system for longer durations and their alone or combined action alters the fertility of soils, population of soil microflora, and physiology and metabolism of important plants (Fayiga 2017; Pittol et al. 2017; Yanga et al. 2017). However, reports on impact of nanoparticles on plants are conflicting. For example, nanoparticles such as Cu_2O (0–160 ppm) and TiO_2 (0.05–0.2 g L^{-1}) in some studies, enhanced the growth of tomato by increasing germination, root/shoot elongation (Ananda et al. 2019), transpiration, and chlorophyll

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synthesis (Qi et al. 2013). In contrast, nanoparticles when entering plant cells either via endocytosis or by other transport systems and accumulating inside plant tissues (Palocci et al. 2017; Burman and Kumar 2018) have been found to interact with plant molecules leading eventually to the distortion of morpho-anatomical features and many physiological activities of plants (García-Gómez et al. 2018a).

Phytotoxic nanoparticles when interacting with plants can cause mutagenic DNA lesions (Atha et al. 2012), generate reactive oxygen species, destruct cellular membranes, enhance membrane lipid peroxidation, and thus inhibit metabolism and growth of plants (Du et al. 2017b; García-Gómez et al. 2017). Moreover, the trans-generational impact of nanoparticles has been reported (Hawthorne et al. 2014). This impact of nanoparticles on plants is determined by extent of nanoparticles' (i) uptake, (ii) accumulation in plant organs and (iii) subsequent translocation to various sites. These three processes also depend upon physicochemical features of nanoparticles, genotypes, and anatomy of plants (Landa et al. 2016; Rastogi et al. 2017). Despite the growing amount of research, the available scientific literature providing details on nano-phytotoxicity is scattered here and there and, hence, requires meaningful and immediate attention to better explain the inhibitory or promoting consequences of nanoparticles on crop production in a systematic manner. Realizing the gap in this area, an attempt is made in this review to provide a holistic view on how nanoparticles influence the overall performance of crops. Also, the biotransformation, bio-distribution, fate, and translocation of nanoparticles in plants are discussed.

Source, emission and release of nanoparticles

The major source, which adds nanoparticles to the environment, is presented in Fig. 1. Due to the increasing applications of nanotechnology, varying range and types of individual nanoparticles are fabricated each day whose concentration in soil, water, and other ecosystem is likely to upsurge massively in the near future.

The production of nano-enabled goods is likely to increase multiple times in near future (Boyes 2018). An estimate shows that globally, the nanotechnology industry will attain a gross value of 75.8 billion USD by 2020 (Global Nanotechnology Market Outlook 2024, 2020). The North American Free Trade Agreement (NAFTA) region shared the principal fraction from the nanotechnology market size. On the other hand, Europe and Asia especially Japan, India, and China are also stepping ahead very dynamically. Nano-enabled products are being produced worldwide. Among nano-enabled products manufacturing countries, the USA, China, Germany, Switzerland, and South Korea are the top five nations, which produce a maximum of 2777, 719, 707, 457, and 319 nano-enabled products, respectively (Fig. 2a) for use in industrial divisions such as electronics, medicine, cosmetics, construction, textile, automotive, environment, renewable energy, and food (Fig. 2b). An inventory of nano-enabled products suggested that > 1814 nano-enabled products have been manufactured and are projected to increase threefold by the end of 2020 (www.nanoproduct.org/inventories/consu

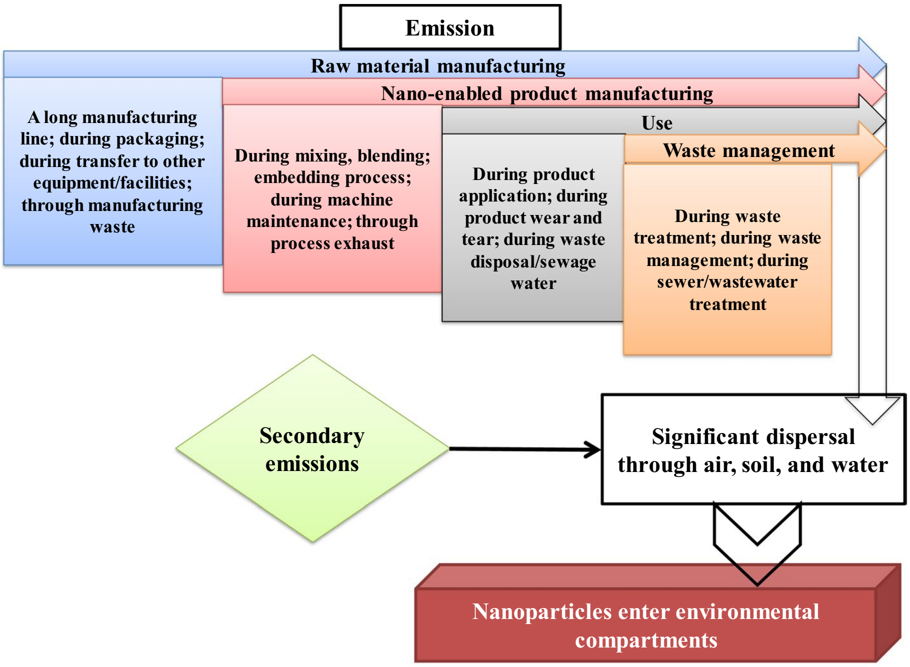


Fig. 1 Sources of emission and release of nanoparticles into the environment during: (i) raw materials manufacturing, (ii) nano-enable product manufacturing, (iii) use of nano-products, and (iv) management of nano-waste leading to nanoparticle dispersion in air, soil, and water. Secondary emissions from humans or non-human species may also contribute to nanoparticles' concentration in the environment

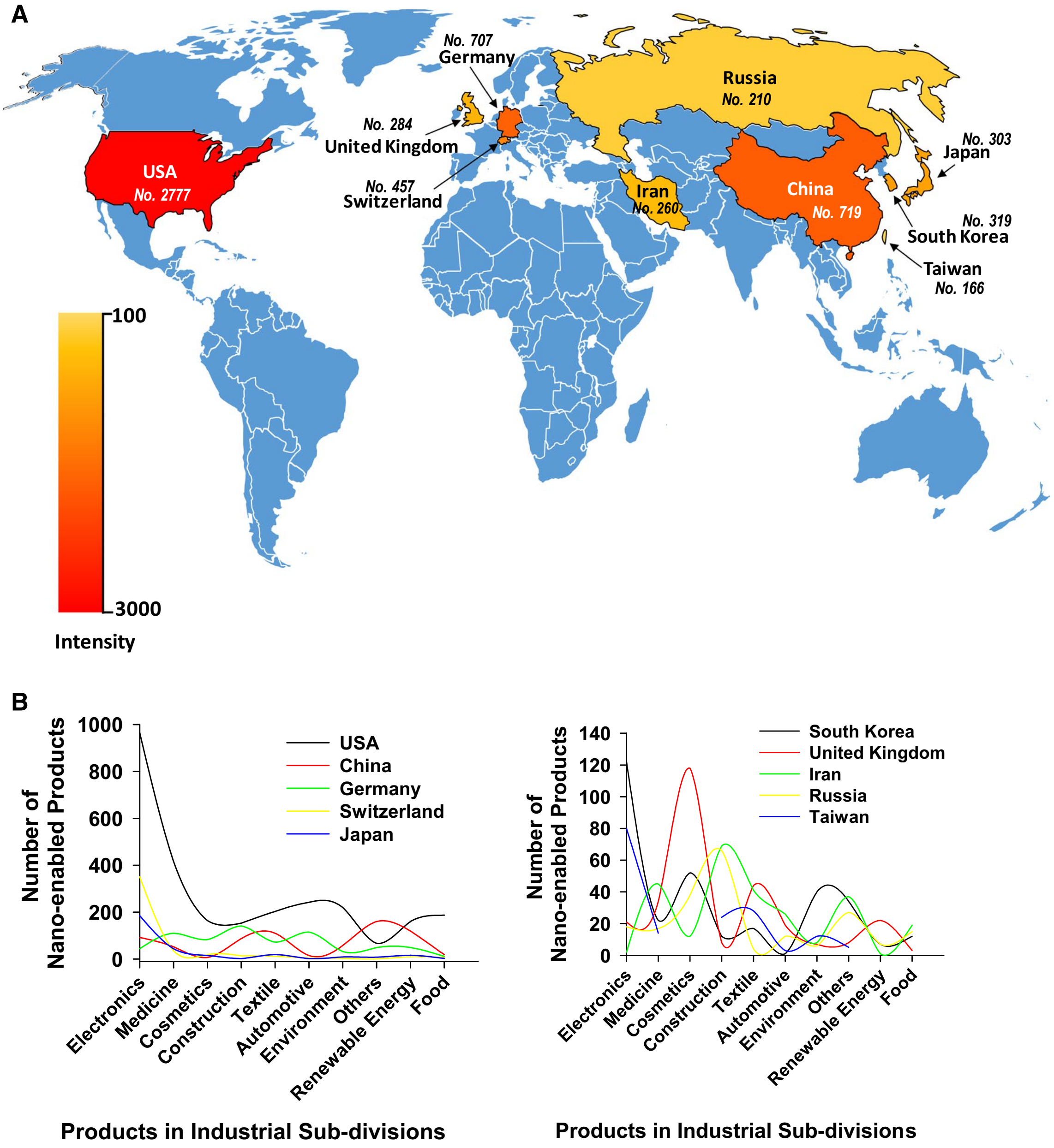


Fig. 2 **a** Number of nano-products in industrial divisions by major world countries. The number (No.) adjacent to a country name indicates the total number of nanotechnology products from that country. The scale bar represents lower (orange) to higher (red) intensity of nanotechnology products at a scale from 100 to 3000. The data have been obtained from the Nanotechnology Product Database (https://product.statnano.com/) and presented graphically. Accessed date April 02, 2020. **b** Number of nanotechnology products in industrial subdivisions. The data have been obtained from the Nanotechnology Product Database (https://product.statnano.com/) and presented graphically. Accessed date April 02, 2020

mer). However, > 8800 nanotechnology-based products are now in commercial market from 60 countries and > 2300 manufacturers.

Among the nano-enabled products, nanoparticles used in paints, pigments, and coatings have the maximum chances of being discharged into water, air, and soil, whereas nanoparticles used in optics and electronics are prospective to be disposed of in landfills. The nanoparticles used in cosmetics and personal care products are released when in use and hence further contaminate both the surface water and soil (Keller et al. 2013). The leaching speed may, however, vary among nanoparticles and depends on the manufacturing process (Rajput et al. 2018b). For instance, dynamic probabilistic modeling of nanoparticles emissions showed that titanium dioxide (TiO_2) nanoparticles had far greater concentrations in the environment than zinc oxide (ZnO) nanoparticles and Ag nanoparticles. In the worst case, sediment analysis revealed that the nanoparticles concentrations might range from 6.7 μg kg^{-1} for carbon nanotubes to approximately 40,000 μg kg^{-1} for TiO_2 nanoparticles. Moreover, this concentration in most cases may increase up to mg kg^{-1} level (Sun et al. 2016).

Nanoparticle accumulated in soils systems may also reach to the ground through the soil (Mahdi et al. 2018) and from there can directly affect human health. Some nanoparticles have been used for ground water remediation to remove organic and inorganic pollutants (Matlochová et al. 2013). Such nanoparticles may also be an additional source of nano-pollution to ground water. Besides soil system and ground water, a significant amount of engineered nanoparticles is released out to the atmosphere by various industrial activities including both point (manufacturing units, waste incineration, power plants wastewater treatment plants, during transportation, and landfilling) (Gottschalk and Nowack 2011) and non-point sources (vehicle emission, during washing or abrasion of nano-enabled products) (Peng et al. 2017b). In addition, accidental release of nanoparticles may increase the magnitude of localized atmospheric concentration. As per an estimate, globally, approximately 8,100 metric tons of engineered nanoparticles are emitted into the atmosphere annually (Keller and Lazareva 2013) relative to nanoparticles' discharge in water and soil; however, the atmospheric fraction of nanoparticles have a shorter dwelling period (John et al. 2017) and ultimately get deposited in soil or water bodies (Giese et al. 2018). Also, the transformational processes occurring in the atmosphere may influence the interactions and fate of atmospheric nanoparticles in soil or aquatic system (Abbas et al. 2020).

The increased applications of nano-enabled/nano-engineered products (Villaseñor and Ríos 2018), however, are likely to add enhanced concentration of nanoparticles in the environment through various routes with unknown impacts on water, soil, and biota (Eduok and Coulon 2017). In many cases, the nanoparticles do not remain bound to the products at the end of its life cycle (Cao and Liu 2016). This can be explained by the presence of nanoparticles in landfill chelates (Bolyard et al. 2013), sewage sludge (Wang et al. 2012b), and wastewater effluents (Brar et al. 2010). Of these, 55% wastewater containing sewage sludge is applied as soil amendment to agricultural soils enriching soil nutrients. Due to these, the use of wastewater containing aged nanoparticles becomes the primary source of nanoparticle to the environment (Eduok and Coulon 2017).

The use of nano-based pesticides/fertilizers in agriculture to effectively control the growth of plant pathogenic microbes and hence to optimize plant growth/yields has also been the major source of nanoparticles in soil ecosystems (Mukherjee et al. 2016; Chhipa 2017). In agrochemicals formulation prepared with nanoparticles are aimed to specifically deliver their active ingredients to the target sites. The nanoparticles which are applied for crop production include nano-based fertilizers (Adisa et al. 2019), nano-fungicides (Capaldi Arruda et al. 2015; Saharan et al. 2015), and insecticides (Wibowo et al. 2014). In agricultural systems, nano-metal-based pesticides are generally applied through foliar spray (Hong et al. 2015). For instance, among nano-agrochemicals, pesticides containing nanoscale $Cu(OH)_2$ as active ingredient are in the marketplace and applied in agricultural fields at an increasing annual input; however, the toxicity of these kind of nano-pesticides may prevent their use in pest control (Zhao et al. 2016b; Zhang et al. 2019b). Once released as aerosolized sprays, waste effluents, and dry powders containing aged and pristine nanoparticles, pollutes soil ecosystem (Keller et al. 2013; Cornelis et al. 2014a; Ju-Nam and Lead 2016). Nanoparticles may also reach to soils accidentally; for example, diesel fuel combustion emits CeO_2 nanoparticles in the atmosphere. Due to the deposition of nanoparticles in soils, it becomes imperative to assess its overall impact on biotic component of soils.

Nanoparticles and plants

The nanoparticles prevalent in atmosphere, water and soil interact with plants (Fig. 3). When accumulated in plants, nanoparticles enter the food chain via uptake by plants and decide their fate in the environment (Rai et al. 2018). Atmospheric nanoparticles can easily deposit on various plant surfaces and hence can infiltrate into the plant system via wounds and stomatal apertures (Pérez-de-Luque 2017). Within soil ecosystems, the purposely applied water-borne nanoparticles may also have interaction with plant tissues (Mauter et al. 2018). The plant roots first come in contact with soil released nanoparticles or soil containing wastewater effluents applied for crop nutrition (Gottschalk et al. 2009; Cox et al. 2017). Considering these, the overall impact of nanoparticles on edible crops and plants grown for longer duration in soils contaminated with nanoparticles must be evaluated. For testing nanoparticles against various crop plants, in vitro approaches such as nanoparticles amendment in nutrient agar media and different strengths hydroponic solutions have been tested which are simpler providing control over nanoparticles' distribution in media and therefore maximize the contact and uptake of nanoparticles with plant system (Sharma et al. 2020; Ullah et al. 2020). As an example of semi-solid plant growth media, Murashige and Skoog (MS) is amended with varying concentrations of nanoparticles (Nechitailo et al. 2018; Plaksenkova et al. 2019). Moreover, hydroponic nutrient media providing nutrients and aeration to the growing seedlings have been tested for more than seven days in many studies with variably shaped

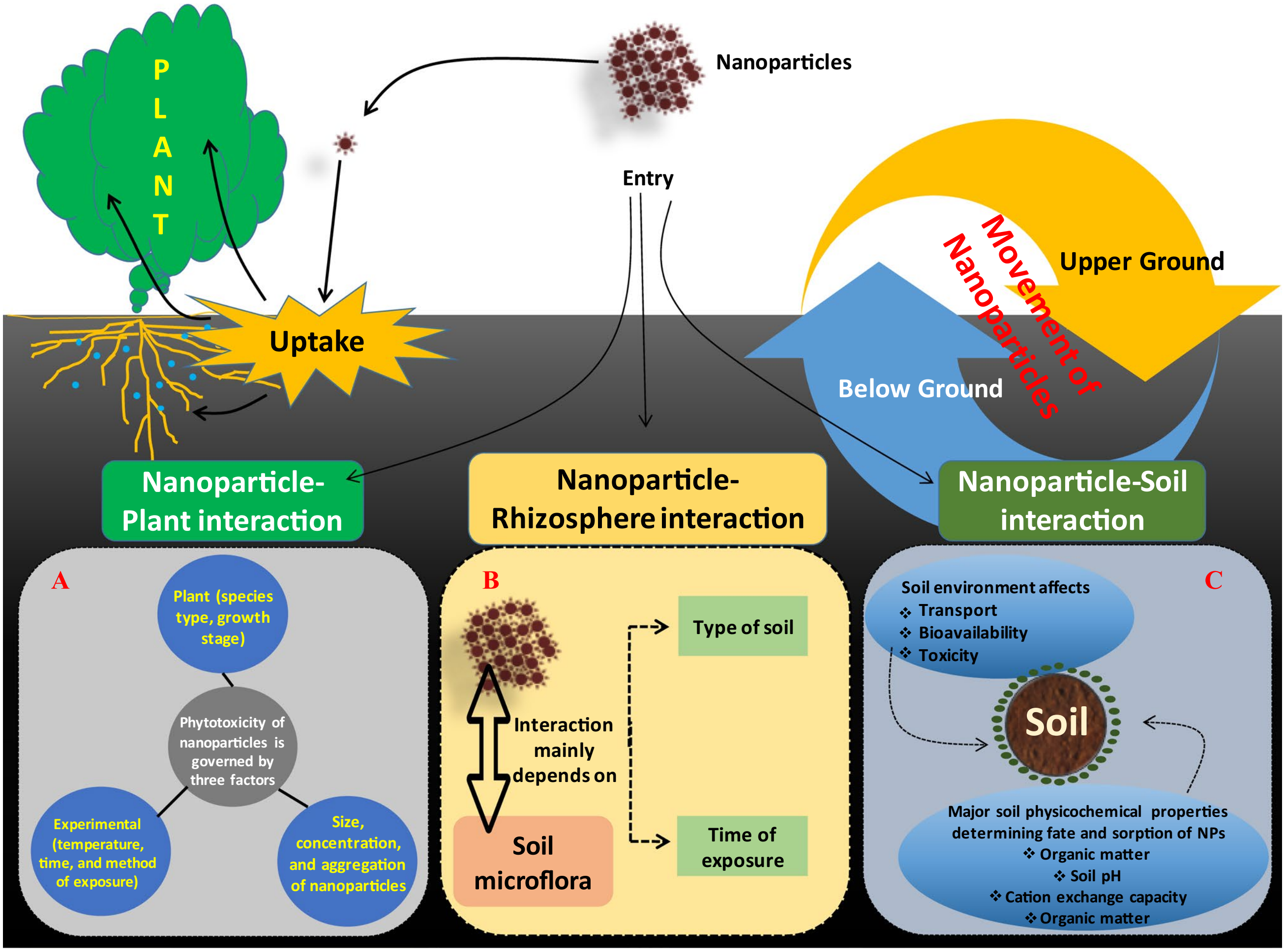


Fig. 3 Interactions of nanoparticles with three components of soils (i) plants, (ii) soil microflora, and (iii) soil itself. Plant and nanoparticle dependent: panel A) phytotoxicity of nanoparticles is governed by three factors which are: (i) plant dependent: growth stage and type of plant species, (ii) experimental: test method, time of exposure, temperature and pH of growth media, and (iii) dependent on physicochemical features of test nanoparticles, i.e., chemical composition, aggregation, size, and concentration; environment dependent: panel B) interaction between nanoparticles and rhizosphere also determine their impact on plants. Such interactions include biological activity of indigenous soil microflora, exposure time, and soil type, and panel C) physicochemical properties of soil also influence the transport of nanoparticles in soil, their bioavailability, and subsequent impact on plants

and sized nanoparticles (Wang et al. 2012c; Sun et al. 2019a; Li et al. 2020).

Soil mixed media or soil itself is considered more practical due largely to its buffering capacity that can modify the reactivity of test nano-species. Besides this, porous materials such as sand along with soil may also alter the available fraction of nanoparticles to plants or affect their stability (Khodakovskaya et al. 2013; Gómez-Sagasti et al. 2019). Therefore, to reveal the phyto-toxicological profile of a nanoparticle, detailed and systemic phyto-toxicity studies should be conducted keeping in view the various abiotic factors of soils, type of soil, simultaneous interactions with soil microflora, time, and concentration of nanoparticle exposure (Fig. 3). This is needed because the uncontrolled disposal and persistence of nanoparticles in the environment are likely to enhance the exposure time of important crops which in turn affects their accumulation kinetics and toxic impact (Dev et al. 2018). For this, life cycle studies have been carried out assessing the impact of CeO_2 nanoparticles on tomato crop for 210 days potting soil (Barrios et al. 2016), CeO_2 and ZnO nanoparticles on soybean (Hernandez-Viezcas et al. 2013), and TiO_2, CeO_2, and $Cu(OH)_2$ on elegant clarkia (Conway et al. 2015).

Plant exudates and nanoparticles

Indeed, the plant secretions strongly influence soil structure and binding of nanoparticles on plant surfaces (Fig. 4) (Siddiqi and Husen 2017a). Plant roots are known to secrete

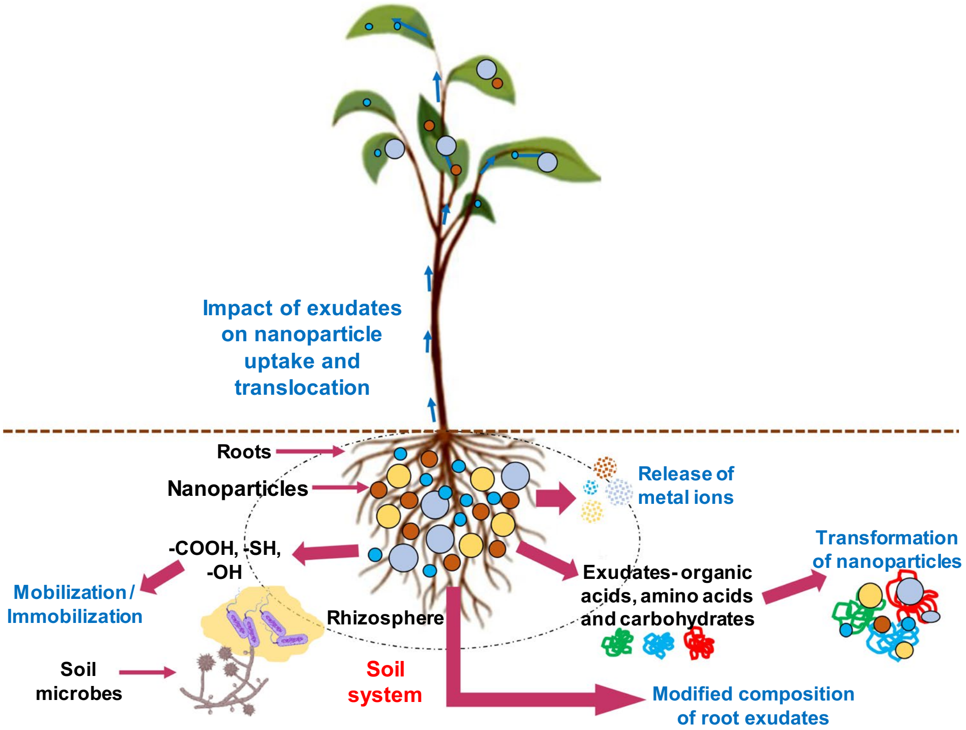


Fig. 4 Interactions between plant root exudates and nanoparticles: (i) Root exudates (organic acids, amino acids, and carbohydrates) induce transformation of nanoparticles, and (ii) nanoparticles can also alter the root exudate pattern of plant facilitating nanoparticle's transformation

exudates containing large quantities of varying molecular weight biomolecules and inorganic ions, which differ in composition and concentration. The root exudation pattern may vary with plant species and may include variable amounts of high molecular weight organics like fatty acids and polysaccharides, and low molecular weight substances including amino and organic acids forming a nutritional environment to a certain distance around root surface known as "rhizosphere" (Bais et al. 2006). Nanoparticles applied to soils, when comes in direct contact of exudates, can easily be deposited on or adhered to root surface (Ma et al. 2013c; Zhao et al. 2016a; Gao et al. 2018). Consequently, the adsorbed nanoparticles undergo extensive physicochemical modification following specific or random interactions with root exudates, and sometimes simultaneously with humic acids (Rico et al. 2011). The oxidizing and reducing agents secreted by plants into the soil can transform metal containing nanoparticles of variable valance shell by performing various redox reactions (Wang et al. 2012a; Zhang et al. 2017).

The physicochemical modification by plant exudates can therefore alter the magnitude of bioaccumulation and ultimate fate of nanoparticles in soil or plant system. Similarly, nanoparticles can also change the exudation pattern of plants (Dimkpa et al. 2012; Wang et al. 2013a; Lv et al. 2015) (Fig. 4). For instance, it has been suggested that Ag nanoparticles could induce a change in root exudation pattern of wheat, cowpea, and mustard that resulted in modified rhizosphere microbial composition which is highly specific to plant root exudate profile of plants (Pallavi et al. 2016). On the other hand, zinc applied as ZnO nanoparticles to soybean plants was found to exist as a transformed species (Zn^{2+}), zinc citrate due to the influence of root exudates (Hesrnandez-Viezcas et al. 2013). Root tips and root hairs secrete a considerable amount of a hydrated polysaccharide, the mucilage on root surface (Driouich et al. 2013; Holz et al. 2018). Mucilage creates an acidic environment in the rhizosphere and passively protects both rhizosphere and plant from biotic and abiotic stresses. Thus, mucilage can also assist in adsorption of nanoparticles on the surface of root. The acidic environment dissolves nanoparticles and liberates free metal ions which are then metabolized by plants to other chemical forms or just deposited somewhere in plant tissues. For instance, Au and ZnO nanoparticles are oxidized due to acidic environment (Taylor et al. 2014; García-Gómez et al. 2018a). Furthermore, CuO nanoparticles are dissolved to Cu ions under the influence of root exudate organic acids lowering the soil pH (Shi et al. 2011).

It can be inferred from nano-phyto interactions that nanoparticles are aggregated around roots under the influence of single or a mixture of root exudates. Plant exudates may also precipitate the metal species as described for Fe and Cu which were precipitated as copper or iron hydroxides and therefore were not available for uptake by plants (Dimkpa et al. 2015). Recently, a metabolomic study of cucumber root exudates based on ^{1}H-NMR and GC–MS analyses has revealed that Cu nanoparticles at 10 and 20 mg L^{-1} dose rate-induced defense response against Cu nanoparticles stress (Zhao et al. 2016a). The production of amino acids, ascorbic acid, and phenolic compounds increased the sequestration of Cu nanoparticles/ions, combats against reactive oxygen species, and enhanced the antioxidant enzyme activity. In contrast, citric acids were down-regulated reducing the mobilization of copper ions (Zhao et al. 2016a).

Soil microflora especially the fungal and bacterial population on the other hand also affects the nanoparticle's conversion with the help of extracellular enzymes including phosphatases and phytases having Zn as a co-factor (Singh and Satyanarayana 2011). Rhizosphere microbes secrete considerable amounts of phosphatases and phytases which mobilize the native phosphorus and help in phosphorus acquisition by plant roots (Richardson 2001). In a study, mung bean plant exposure to ZnO nanoparticles increased activity of phytase and phosphatase (both alkaline and acid) in soil due to enhanced fungal, bacterial, and actinomycetes population. The application of ZnO nanoparticles (23 nm) increased phytase activity by 108%, alkaline phosphatase by 93.02%, acid phosphatase by 98.07%, and dehydrogenase by 84.21% over their bulk counterparts (Raliya et al. 2016b). Also, the activity of dehydrogenase was increased indicating higher microbial density (Raliya et al. 2016b). Moreover, the role of compounds like organic acids, carbohydrates, proteins, and extracellular byproducts from indigenous soil microbial population in nanoparticle's transformation is yet to be explored.

Transformation of nanoparticles

The ultimate environmental fate, extent of transport, behavior in the environment and toxicity of nanoparticles are influenced by various transformational processes such as (A) physical (i) agglomeration/aggregation, (ii) adsorption, and (iii) deposition, (B) chemical (i) sulfidation, (ii) dissolution, and (iii) redox reactions, and (C) interaction of nanoparticles with macromolecules. Many of these transformations may occur both in environmental and biological systems. Hence, the behavior and magnitude of these transformations must be understood so that the strategy to contain/reduce the environmental risks posed by nanoparticles, if any, can be devised.

Physical transformations

Agglomeration/aggregation

Aggregation is the process by which nanoparticles form a cluster of varying sizes (Wang et al. 2016b). Aggregation of nanoparticles results majorly due to van der Waals force and formation of electric double layer of counter ions (Adamczyk and Weroński 1999). Some other interactions significantly affecting the aggregation of nanoparticles include magnetic and hydrophobic interactions, and hydration force (Dwivedi et al. 2015; Sendra et al. 2017). The agglomeration or aggregation could be of two types: (a) homo-aggregation—it occurs when the aggregates of similar nanoparticles are produced, and (b) hetero-aggregation—in this process, a cocktail of other components interacts with nanoparticles and promotes aggregation (Fig. 5) (Xu et al. 2018). Of these, hetero-aggregation is the more common phenomenon that occurs in the environment (Schultz et al. 2015). The aggregation of nanoparticles generally decreases the chemical reactivity and bioavailable concentration of nanoparticles and increases the aggregate size with increasing time periods (Quik et al. 2014). Additionally, when present in higher concentrations, the nanoparticles form aggregates rapidly due to enhanced collision frequency. In this event, the surface energy of nanoparticles is drastically reduced in a thermodynamically determined progression. This has been confirmed by a faster aggregation rate of nanoparticles of ZnO (Yung et al. 2015), TiO_2 (Botta et al. 2011), and CeO_2 (Marie et al. 2014). Furthermore, nanoparticle's coating may also increase or decrease the rate of aggregation in the environment (Xu et al. 2018).

Adsorption

Nanoparticles have the tendency to adsorb to various environmental substances such as natural organic matter. This adsorption is governed by two factors: physicochemical

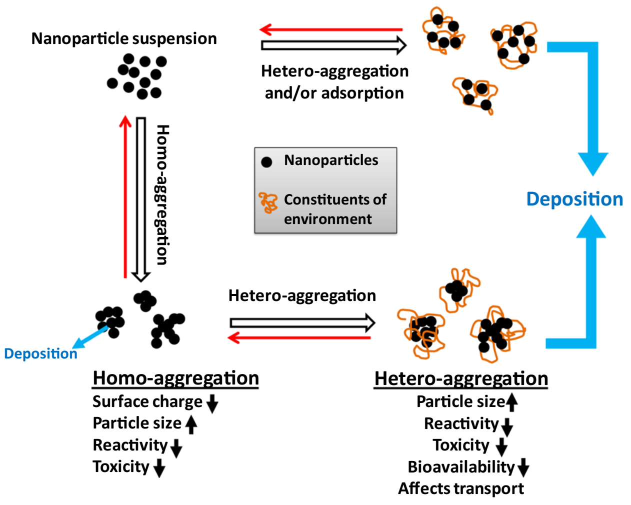


Fig. 5 Homo-aggregation, hetero-aggregation and deposition of nanoparticles in the environment. Red arrows show disaggregation of nanoparticles due to lower pH and the presence of natural organic matter. Like homo-aggregation, which increases particle size and thereby reduces surface charge, reactivity, and toxicity of nanoparticles, hetero-aggregation also reduces these important physicochemical parameters of nanoparticles but with the involvement of other constituents of the local environment

properties of natural organic matter and surface chemistry of nanoparticles. If the surface functionalization of nanoparticles is not strong, then the natural organic matter will stabilize the nanoparticle; on the opposite site, higher N and S content of natural organic matter will increase the adsorption of nanoparticle (Gunsolus et al. 2015; Jorge de Souza et al. 2019). In an earlier study, the surface adsorption of natural organic matter either neutralizes the surface charge or reverses it (Baalousha et al. 2008). Also, the natural organic matter after adsorbing on nanoparticle surface may hinder the release of ions due to natural organic matter mediated blocking of oxidation sites or reduce the already released metal ions to their zero-valent form by fulvic and humic acids. The adsorption of nanoparticles to different surfaces is also influenced by other factors too. These include environmental fluids or biomolecules. The protein fraction of these environmental fluids may form a corona around nanoparticles known as "protein corona." Generally, it is termed as eco-corona or corona when formed by the collective adsorption of environmental constituents ranging in size from 10 Da to 2×10^6 Da (Nasser et al. 2020). This adsorption is capable of altering the size, charge, and aggregation of nanoparticles (Pinďáková et al. 2017). The process of nanoparticles adsorption under different environmental scenarios needs to be investigated further due to its importance in affecting the nanoparticle–cell interactions.

Deposition

Deposition is the process by which nanoparticles dispersed in aqueous environment tend to settle down on bottom, which mainly occurs in the aquatic environment. The deposition, however, may differ with types, the extent of aggregation, and availability of natural organic materials. Overall, agglomeration, aggregation, and deposition are interrelated. When aggregation increases, the deposition also increases which may be controlled by nanoparticles features and the physicochemical properties of the media (Amde et al. 2017).

Chemical transformations

Dissolution

The process of dissolution of nanoparticles (release of soluble metal ions from nanoparticles) is dependent on both the physicochemical features of nanoparticles and chemistry of the environmental system (Cross et al. 2015).

Physicochemical features of nanoparticles Among various physicochemical features, size, morphology, and surface chemistry are major in controlling the dissolution of nanoparticles. The change in surface area-to-volume (S/V) ratio of nanoparticles affects the dissolution process (Soenen et al. 2015). Due to the inherent property of greater surface area, such nanoparticles release high amount of free metal ions over their larger counterparts (Zhang et al. 2018b). For example, dissolution of ZnO nanoparticles (4–130 nm) at pH 7.5 revealed that the higher S/V ratio of smaller sized ZnO nanoparticles was more favorable for dissolution as compared to larger ones (Mudunkotuwa et al. 2012). Similarly, the rate of dissolution was also found higher for smaller (7 nm) CuO nanoparticles (Chakraborty et al. 2018). Similar impact of nanoparticle size on dissolution was observed for Fe_2O_3 nanoparticles where the rate of dissolution of 8 nm sized particles was increased up to tenfold compared to 40 nm sized particles (Lanzl et al. 2012). Surface chemistry of nanoparticles may also significantly increase or decrease the rate of dissolution which is otherwise useful for some applications. For instance, in a comparative dissolution study, organic coating of ZnO nanoparticles delayed the rate of dissolution which reached to its maxima in seven days. On the other hand, uncoated ZnO nanoparticles showed maximum dissolution in just one hour (Gelabert et al. 2014). For various purposes, the shape and size of nanoparticles are tuned using surface capping/functionalizing agents; however, the use of surface modifying agents alters the dissolution of nanoparticles in one or the other way. As a classical example among metal-based nanoparticles, Ag nanoparticles (50 nm) have shown variable dissolution when capped by citrate or polyvinylpyrrolidone (PVP) (Kittler et al. 2010). The dissolution was 14% and 50% for citrate and PVP capped Ag nanoparticles, respectively, at 25 °C.

Chemistry within the environmental system The dissolution of nanoparticles also depends on environmental factors such as pH (Son et al. 2015), natural organic matter content (Jiang et al. 2015; Wang et al. 2016b), ionic strength (Yung et al. 2015; Liu et al. 2018), and temperature (Majedi et al. 2013). Taking the example of pH mediated dissolution, dissolution of ZnO and CuO nanoparticles were found higher at acidic pH and lower at alkaline pH (Miao et al. 2010; Mohd Omar et al. 2014; Son et al. 2015; Odzak et al. 2017). In a recent study, the dissolution behavior of CuO nanoparticles measuring the size of 7 nm and 31 nm in artificial lysosomal fluid, simulated body fluid, artificial seawater, and sodium nitrate (1 mM) was assessed (Chakraborty et al. 2018). The results revealed significant differences in the dissolution of CuO nanoparticles which was attributed to variation in composition and concentration of media. The dissolution was > 80% in biological media within 12–24 h, whereas < 15% in environmental media even after 7 days (Chakraborty et al. 2018). In addition, the presence of natural organic matter inhibits the release of metal ions by reducing them to nanoparticles through fulvic acids such as the formation of Ag^+-fulvic acid complex leading to the formation of Ag nanoparticles and thus reducing the rate of dissolution (Tiwari et al. 2013). Similarly, significant dissolution was observed for CuO and ZnO nanoparticles and among them, ZnO nanoparticles reflected greater influence (Liu et al. 2018). The sedimentation rates of ZnO nanoparticles and CuO nanoparticles in five types of water followed the order: tap water > wastewater > lake water > pool water > rainwater (Liu et al. 2018).

Sulfidation

The presence of sulfide in the surrounding medium also influences fate of nanoparticles. In the process of sulfidation, sulfide is oxidized to sulfate and metal ions released from nanoparticles reduced. For example, reduction of Cu^{2+} released from CuO nanoparticles to Cu^{+} forming copper sulfate hydroxides (Ma et al. 2013b). Moreover, after dissolution of nanoparticles such as CuO and Cu nanoparticles, the sulfidation process could compete with the high dissolution (Kent and Vikesland 2016). The process of nanoparticle sulfidation is dependent of the total concentration of sulfides in the media. Sometimes, excess presence of sulfide results in the 100% sulfidation of nanoparticles in a solution (Ma et al. 2013b). For example, low concentration of sulfide (< 1 mg L^{-1}) could initiate release of Ag^{+} ions from Ag nanoparticles which then form silver sulfide (Ag_2S) nano-linkages with adjacent nanoparticles by reacting with sulfide. On the other hand, when the sulfide concentration is between 1 and 100 mg L^{-1}, the formation of Ag_2S is direct following the oxy-sulfidation pathway (Liu et al. 2011). Similarly, zinc sulfide (ZnS) was detected as a result of ZnO nanoparticle transformation in the presence of sulfide with the total ZnS yield of up to 90% (Brunetti et al. 2015).

Reduction–oxidation reactions

These reactions include oxidation and reduction transferring the electrons from one species to another. This is of importance because nanoparticles also have various surface constituents which may be influenced by redox reactions. Moreover, these reactions transforming nanoparticles may vary depending upon the type of environment. For example, oxidation is predominant in aerated soils and waters, while reduction occurs mainly in groundwaters and carbon-rich sediments (Cendrowski et al. 2017). In the aquatic environment, natural organic matter may hinder the oxidation reduction process due to its ability to inhibit the electron transfer. Biological constituents of the environment by redox reactions may alter the oxidation of metal component of nanoparticles. For example, interaction of CeO_2 nanoparticles with environmental media disturbs ratio of Ce III/IV in CeO_2 nanoparticles (Baalousha et al. 2010). Similarly, NiO nanoparticles were also found reduced to zero valent Ni by soluble proteins under aqueous condition (Gong et al. 2011). Redox reactions bring two changes which significantly affect the environmental fate of nanoparticles. If redox reactions make the nanoparticle's surface active, then the reaction of environmental constituents and nanoparticles will be facilitated. On the contrary, if insoluble surface is resulted due to redox reactions, it will increase nanoparticle's stability, thus increasing the persistence of nanoparticles. Moreover, the dissolution of nanoparticles can also be enhanced by the oxidation process. Nanoparticle's capping may also affect the oxidation–reduction processes. As an example, silica coating of iron oxide (Fe_2O_4) nanoparticles was found more resistant than uncoated particles toward oxidation process (Cendrowski et al. 2017).

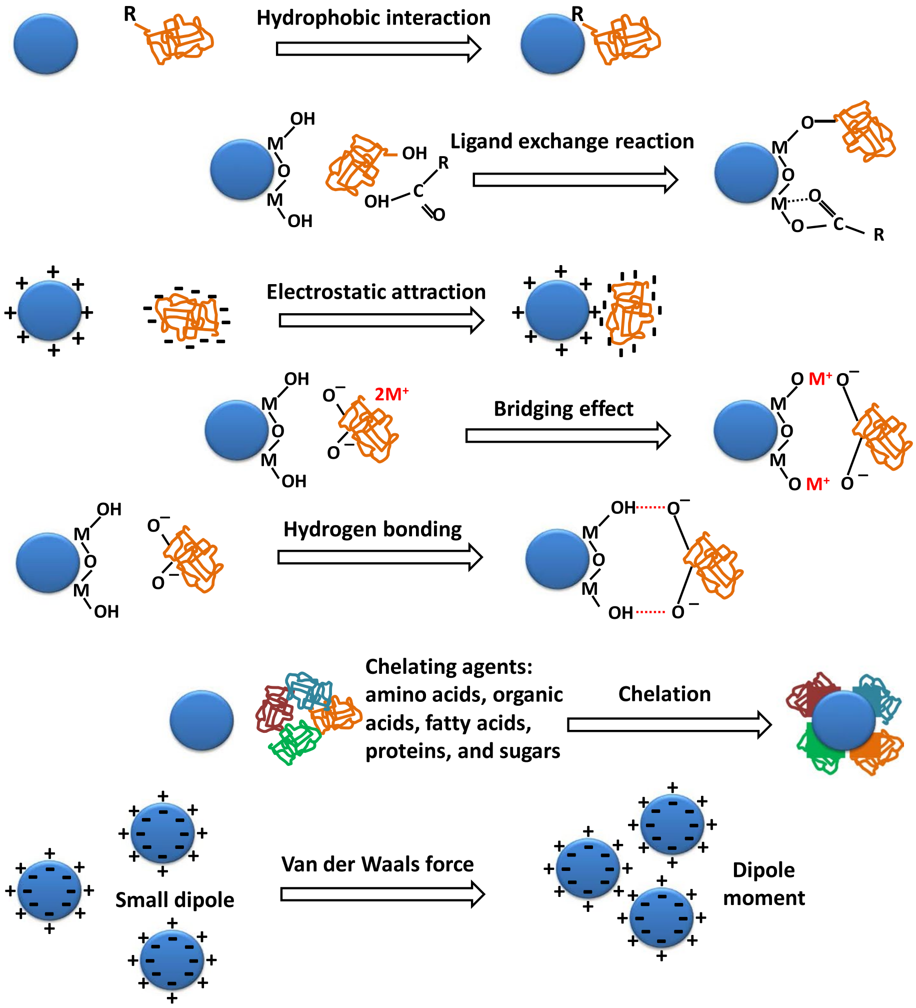
Interaction of nanoparticles with macromolecules

The nanoparticles have been reported to interact with macromolecules such as proteins, polysaccharides, surfactants, and varying types of natural organic matter modifying their surface and physicochemical features (Ansari et al. 2014; Wang et al. 2016b; Schwaminger et al. 2017). This interaction between the nanoparticle and macromolecules depends on the concentration, type of molecules/nanoparticles, pH, and binding affinity (Philippe and Schaumann 2014; Yu et al. 2018). These interactions include electrostatic, H-bonding, hydrophobic, bridging between macromolecules and nanoparticles, van der Waals force, ligand exchange reaction, and chelation (Fig. 6). Furthermore, the macromolecules by one or multiple interactions with nanoparticles can cause co-aggregation or provide electrostatic/steric stability reducing the aggregation and thus deposition of nanoparticles (Huangfu et al. 2014; Sheng et al. 2016; Chen et al. 2018). Besides these, other chemical processes including surface oxidation, reactive oxygen species generation, and degradation of coat material can influence the nanoparticle–plant interactions either in a positive or negative way (Amde et al. 2017).

Transformation of nanoparticles in the atmosphere

Annually, a small amount of engineered nanoparticles is emitted into the atmosphere as compared to other environmental compartments (Keller and Lazareva 2013). Despite having a shorter span in the atmosphere (John et al. 2017), the nanoparticles undergo atmospheric physical and chemical transformations impacted by physicochemical features of nanoparticles, atmospheric gases, and weather-related conditions (Kumar and Al-Dabbous 2016). Interaction of nanoparticles with atmospheric gases such as CO_2 can potentially change nanoparticle's features as well as their rate of

Fig. 6 Forces controlling nanoparticle–macromolecule interactions, including (i) hydrophobic interaction, (ii) ligand exchange reaction, (iii) electrostatic attraction, (iv) bridging between nanoparticles and other molecules, (v) hydrogen bonding, (vi) nanoparticle chelation by chelating agents such as amino/organic/fatty acids, proteins, and sugars, and (vii) van der Waals force



dissolution after deposition in aqueous media. In a study, reaction of CuO and ZnO nanoparticles with CO_2 at varying levels of relative humidity (H_2O) was performed (Gankanda et al. 2016). Results revealed that surface adsorbed hydroxyl groups of both the nanoparticle reacted with CO_2 which led the formation of surface adsorbed bicarbonates. On the other hand, reaction of CO_2 with nanoparticles surface defects and lattice oxygen resulted in surface adsorbed carboxylate and mono- and bi-dentate carbonates. Progressing to high humidity conditions (0–70%) showed water solvated surface adsorbed carbonate. Overall, the change in surface chemistry was limited to near surface region enhancing the dissolution of nanoparticles in liquid media.

Both types of aggregation (homo and hetero) of nanoparticles also occur in the atmosphere subject to Brownian motion and surface area of nanoparticles reducing the number of particles in the air while increasing its size. In the atmosphere, hetero-aggregation is more common due to the occurrence of natural air-borne nanoparticles and this new formation (binding of nanoparticles with airborne particles such as particulate matter) may travel long distances in the atmosphere (Tiwari and Marr 2010; Han et al. 2015). The size of nanoparticles can also be increased by their condensation with atmospheric inorganic (NH_3, NO_3^-, and SO_4^{2-}) or organic moieties or both (Baalousha et al. 2016). Other factors altering the size and morphology of nanoparticles include turbulence, temperature, UV radiation, and free radicals (Zhang et al. 2016b).

Transformation of nanoparticles in soil

Generally, nanoparticles persist for longer duration in sediments and terrestrial locations where nanoparticles and their metal ions respond differently in soils and depend upon the aging process and soil properties (Peijnenburg et al. 2016; Romero-Freire et al. 2017). Nanoparticle's transformation in soil systems has been studied in greater detail recently. In a study, it is reported that the extractable amount of Cu from soils exposed to CuO nanoparticles or Cu $(NO_3)_2$ in different sets of experiments changed over time which was influenced by source and concentration of Cu used (Gao et al. 2017). Similarly, CuO nanoparticles may be transformed in soil upon weathering which in turn affect the availability of Cu both in soil, uptake by lettuce plant, and Cu transport to higher trophic level (Servin et al. 2017). However, the aging of CuO nanoparticles did not significantly affect the chlorophyll and carotenoid synthesis by lettuce plants. This could be due to the above discussed hetero-aggregation of nanoparticles which is more common in soil (Cornelis et al. 2014b). Nanoparticle's aggregation in soil system also prevents their uptake by plants (Dimkpa et al. 2013). For example, hetero-aggregation of ZnO nanoparticles with soil granules hindered their diffusion (Zhao et al. 2012b; Milani et al. 2015). The organic substances of soil also influence the adsorption of nanoparticles on to soil surface and hence enhance the stability of nanoparticles (Ju-Nam and Lead 2016).

The nanoparticles are also dissolved in soils by soil pore water. The released ions are more bioavailable than corresponding nanoparticles, where dissolution largely depends on the type and physicochemical properties of soil, besides the application mode of nanoparticles in the soil such as powder or solution forms. For instance, the ZnO nanoparticles have been reported to undergo dissolution in soils to an extent that the nanoparticles were not detected in nanoparticles spiked soil (Wang et al. 2013a). Likewise, the dissolution of citrate coated CeO_2 nanoparticles (8 nm) was found considerably high in acidic media at pH 4.0 (Cornelis et al. 2011). A similar mechanism for enhanced dissolution of metal oxide nanoparticles by plants has been suggested which could be assigned to organic acids and siderophores present in rhizosphere soils (Dimkpa et al. 2013; Schwabe et al. 2015). The dissolution of CuO and ZnO nanoparticles was enhanced by wheat roots from less than 0.3 to 1 and 0.6 to 1–2.2 mg kg^{-1}, respectively. In contrast to higher dissolution, some metal–oxide nanoparticles such as TiO_2 nanoparticles exhibit little dissolution in soils (Du et al. 2011).

Plant-mediated transformation of nanoparticles

The nanoparticles present in a different environment can also be influenced or modified by biotic factors. For example, nanoparticles prepared from CuO and ZnO were found accumulated as copper–sulfur complexes and zinc phosphate in wheat shoots, respectively, that was likely be due to the dissolution of CuO and ZnO nanoparticles followed by their uptake and transformation inside the plant (Dimkpa et al. 2013). Nanoparticles also undergo various other transformations in the plant physiological environment. In this context, a study revealed that CeO_2 nanoparticles were influenced by structural and chemical changes occurring within the plants (Zhang et al. 2012a). In a similar study, the use of X-ray-based fluorescence and absorption techniques confirmed various transformations in the chemical status of ZnO and CeO_2 nanoparticles in plant system (Hernandez-Viezcas et al. 2013; Cui et al. 2014). The transformation of nanoparticles in plant system may also occur in a way that nanoparticle's size is increased in plant organs. For example, Ag nanoparticles taken up by tomato roots were found in large clusters ranging from 100 to 200 nm as compared to the size in water suspension (1–10 nm). Also, some spherical clusters of SnO_2 nanoparticles were detected (Vittori Antisari et al. 2015a). These and other studies are suggestive of extensive processing of nanoparticles in plant cell environment following their uptake, modifying its original form. Some evidences are shown in Fig. 7.

The plant-mediated transformation in turn may reduce or enhance the phytotoxicity of nanoparticles. For instance, nano-CuO (copper II oxide) was found reduced to Cu_2O and Cu_2S (copper I oxide) in maize plants with symptoms of growth reduction (Wang et al. 2012c; Servin et al. 2017). Similar transformation of nano-CuO from Cu (II) → Cu (I) Cl is evident from the enhancement of degree of saturation in fatty acids (Yuan et al. 2016a). Copper may be partially biotransformed from Cu (II) to Cu (I) by interacting with root secreted citrate from bean (Dimkpa et al. 2015). In a micro-X-ray fluorescence analysis of plant roots, the deposition of Cu nanoparticles was restricted to the outer region of root tissues, most likely due to intracellular transformation of nano-Cu which limits its movement to other part of root tissue (Servin et al. 2017). Similarly, cucumber-mediated transformation of nano-ytterbium oxide (Yb_2O_3) and nano-lanthanum oxide (La_2O_3) has been documented (Ma et al. 2011; Zhang et al. 2012b). Phosphate salts and organic acid from cucumber roots played a role in the solubilization of Yb_2O_3 and La_2O_3 and biotransformed them into their respective phosphates. Similarly, following the adsorption of Fe_2O_3 nanoparticles on various regions of root such as hairs, tips, and meristematic zone and uptake inside the root cells, Fe_2O_3 nanoparticles were bio-mineralized under the root phytochemical influence (Shankramma et al. 2016). A scheme for biotransformation of nanoparticles by plant secretion and the internal environment of plants and their impact is shown in Fig. 7I.

Bioavailability of nanoparticles to plants

The bioavailability of nanoparticles to plants is a stability-dependent factor (Von Moos et al. 2014). The more stable the nanoparticles are in the environment, the lesser will be their bioavailability, and hence, the nanoparticles exhibit low toxicity (Auffan et al. 2009). For instance, the reduction of Ce from Ce(IV) to relatively more stable Ce (III) within the soil resulted in decreased bioavailability of CeO_2 nanoparticles to plants (Cui et al. 2014). In contrast, enzymes and other chelating agents released by soil organisms cause the transformation of nanoparticles and make it more available

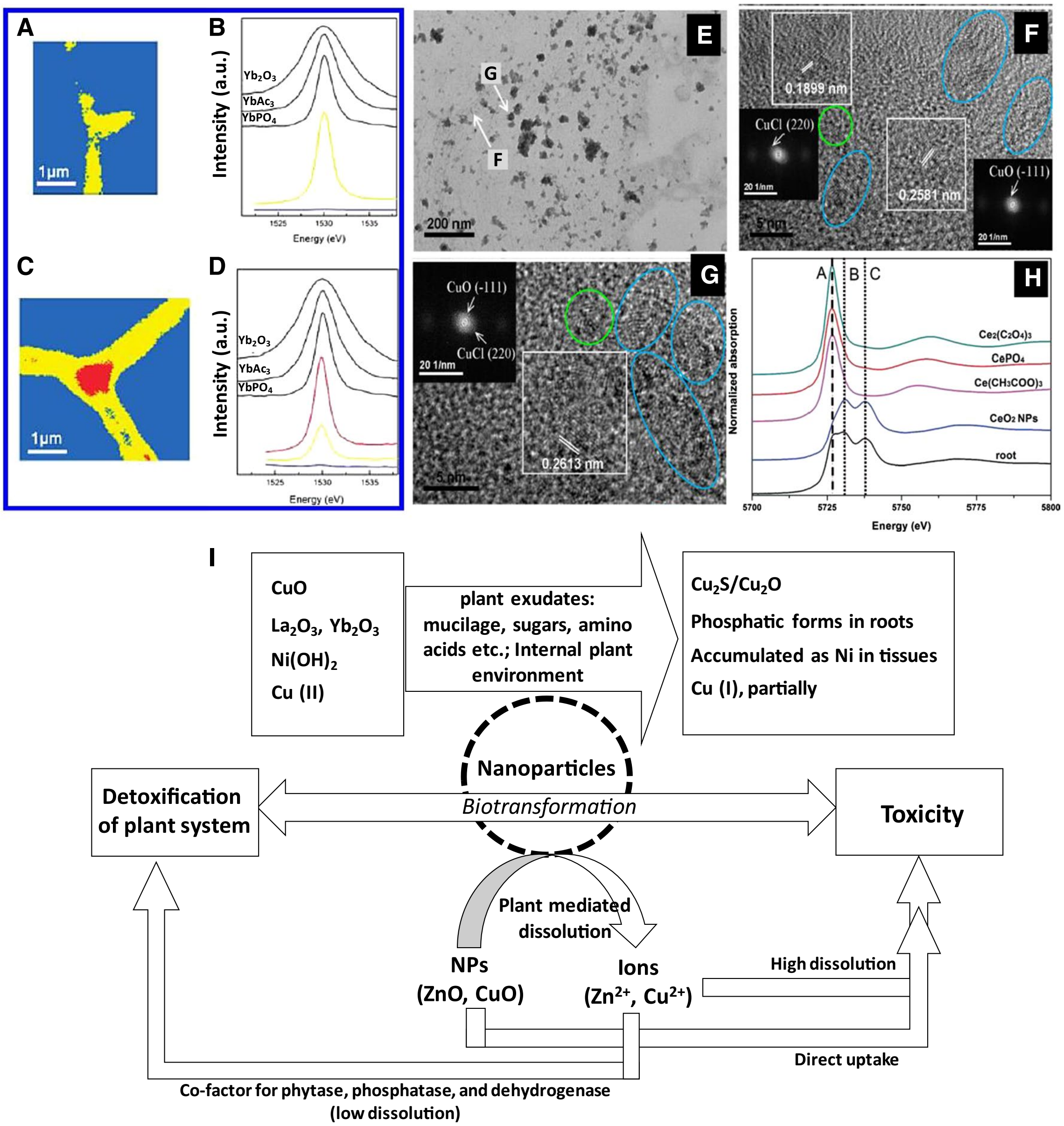


Fig. 7 Plant-mediated transformation of nanoparticles: Ytterbium component color maps of cucumber roots treated with 2000 mg L^{-1} Yb_2O_3–nanoparticles (panel A) and and 200 mg L^{-1} $YbCl_3$ (panel C) derived from scanning transmission X-ray microscopy. Red, yellow, and blue regions show high, low, and zero Yb containing zones, respectively. Panels B and D represent 3D spectra of Yb component from panels A and C, respectively. In panels B and D, the 3D Yb spectra of root samples are comparatively analyzed with reference Yb compounds such as $YbPO_4$, Yb_2O_3, and Yb $(Ac)_3$. Analysis showed that the compound present in roots treated with Yb_2O_3–nanoparticles can be inferred to be $YbPO_4$. Adapted with permission from (Zhang et al. 2012b). Transmission electron microscopy (TEM) (panel E) and high-resolution (HR) TEM (panels F and G) images of CuO nanoparticles exposed *A. thaliana* roots after 10 days of exposure. Panels G and F are magnified pictures of deposit G (high electron dense deposits) and F (loosely dispersed flocci). Fast Fourier transform (FFT) analysis (inset) was done of the regions indicated in white rectangles. Interplanar crystal spacing data from FFT confirm the signal (-111) for CuO and signals (111) and (220) for CuCl. Regions encircled in green and blue also indicate signals for CuCl and CuO, respectively. Adapted with permission from (Yuan et al. 2016b). Panel H shows XANES Ce LIII-edge spectra lettuce roots grown with CeO_2 nanoparticles (2000 mg L^{-1}) and spectra of reference compounds. The dotted and dashed lines are for Ce (IV) and Ce (III) containing compounds, respectively. There are three peaks A, B, and C in panel H. Peak A is the characteristic of Ce (II), which comes from three Ce compounds such as and $Ce_2(C_2O_4)_3$, $Ce(CH_3COO)_3$, and $CePO_4$. Peaks B and C represent Ce(IV) of CeO_2 nanoparticles (NPs) accumulated in lettuce roots. Comparative analysis of sample with reference Ce compounds revealed that there were two oxidation states of Ce present in roots, Ce(III) and Ce(IV). Quantitative analysis showed 78.3% root Ce was present as CeO_2, while 21.7% was from carboxylates of Ce as a fraction of applied CeO_2 nanoparticles underwent plant-mediated transformation. Adapted with permission from (Cui et al. 2014). Panel I depicts plant mediated transformation of nanoparticles under the influence of plant secretion and the internal environment of plants

to plants (Schwabe et al. 2015). Moreover, the other factors like the use of coating materials, size of nanoparticles, and homo/hetero-aggregation are also crucial in determining the bioavailability of nanoparticles and hence should be monitored cautiously (Zhang et al. 2015; Máté et al. 2016).

Furthermore, proteins, humic acids, fulvic acids, and polysaccharides are also responsible for the surface adsorption of nanoparticles and their intracellular uptake (Khan et al. 2015; Amde et al. 2017). In a study, Lv et al. reported the presence of ZnO nanoparticles within the roots of maize plants; however, ZnO nanoparticles were not detected in maize shoots possibly due to dissolution of ZnO nanoparticles in plant tissues and hence showed their differential availability to various plant parts (Lv et al. 2015). It has been established that nanoparticles are easily bioavailable to plants after dissolution. For instance, ZnO nanoparticles are reported to become frequently bioavailable primarily in its ionic or dissolved form which is indicative of rapid dissolution of ZnO nanoparticles (Du et al. 2011). Further, it has been reported that ZnO nanoparticles–wheat interactions result in Zn–phosphate accumulation in shoots which could be due to dissolution of ZnO nanoparticles and internalization of Zn^{2+} ions (Dimkpa et al. 2013). Similarly, equal bioavailability of Zn^{2+} dissolved from ZnO nanoparticles and zinc chloride ($ZnCl_2$) to cowpea plants further supported the role of dissolution in the uptake of nanoparticles (Wang et al. 2013a). Identical results were also obtained with *Solanum lycopersicon*, *Zea mays* (Lv et al. 2015), *Phaseolus vulgaris* (García-Gómez et al. 2017), *Glycine max* (Hernandez-Viezcas et al. 2013), and *Prosopis juliflora-velutina* (Hernandez-Viezcas et al. 2011) plants. In a study, not the ZnO nanoparticles, but modified Zn forms resembling Zn–citrate and Zn–phosphate were observed indicating the transformation of ZnO nanoparticles (Hernandez-Viezcas et al. 2013; Lv et al. 2015).

Accumulation and deposition of nanoparticles at subcellular sites

Once internalized in the plant system, nanoparticles either accumulate at various sub-cellular locations like cellular membranes, walls, tonoplast, vacuoles, endodermis, pericycle, cortex, cytoplasm, mitochondria, chloroplast, and nucleus or travel to various plants organs, for example, stem nodes, foliage, flowers, and fruits (Yanga et al. 2017; Rajput et al. 2018b). In general, though the accumulation of nanoparticles occurs at various sites (Fig. 8) (Lv et al. 2019), vascular bundle among plant tissues serves an important role in nanoparticle transportation through plant organs (Fig. 9) (Pradas Del Real et al. 2017). Once nanoparticles reach the vascular system or tissues like xylem, their movement toward aerial parts of the plant becomes rapid. The nanoparticles also accumulate in fruits with help of phloem. As an example, tomato plants-accumulated cerium dioxide (CeO_2) nanoparticles in not only shoots, but also a fraction of it was stored in tomato fruits (Wang et al. 2012c). This suggests that nanoparticles with specific size are able to cross and travel in phloem tissues, the only channel entering fruit tissues. In yet other experiments, soybean raised with metal and metal–oxide nanoparticles in hydroponic solution had nanoparticles accumulated in roots, nodules, stems, and pods (Priester et al. 2012, 2017). However, different nanoparticles behave differently in plant system and most of them are largely accumulated in plant root tissues. For instance, CeO_2 nanoparticles were found deposited in root system of three cereal plants, rice, barley, and wheat without showing any visible change in germination and elongation of roots (Zhao et al. 2012b; Rico et al. 2015b); however, some molecular changes were observed in rice plants (Rico et al. 2013b). Similar kind of impact of corn roots was exerted on fluorescently labeled ZnO nanoparticles, where ZnO nanoparticles were just deposited in root's stele with nil transportation to upper ground organs (Zhao et al. 2012b). However, Cu nanoparticles when internalized in root tissues of cucumber plant as higher as 10–20-fold over untreated control inhibited the root expansion (Arif et al. 2018).

Mechanisms of nanoparticle uptake by plants

When taken up from external environment into plant tissues, nanoparticles can penetrate plant cells through various mechanisms including (i) ion channel transport, (ii) passive transport, (iii) transport along with water molecules by aquaporins, (iv) with the help of carrier proteins, (v) endocytosis, (vi) by creating new pores, and (vii) by associating with organic matter (Hillaireau 2016; Jha and Pudake 2016; Yanga et al. 2017). Among crops where maximum uptake, accumulation and toxicity of nanoparticles have been reported include onion (Rajeshwari et al. 2015), wheat (Gao et al. 2018), cucumber (García-Gómez et al. 2018b), tomato (Raliya et al. 2015), zucchini/pumpkin (De La Torre Roche et al. 2018), soybean (Rezaei et al. 2015), lettuce (Margenot et al. 2018), and rice (Da Costa and Sharma 2016). Of these, cucumber and zucchini/pumpkin are considered preferred crops for evaluating the uptake and translocation of nanoparticles due largely to higher water uptake by these plants and comparatively larger sized vascular bundles (Baas 2006). Here, the routes/modes through which nanoparticles can enter plant systems are briefly discussed.

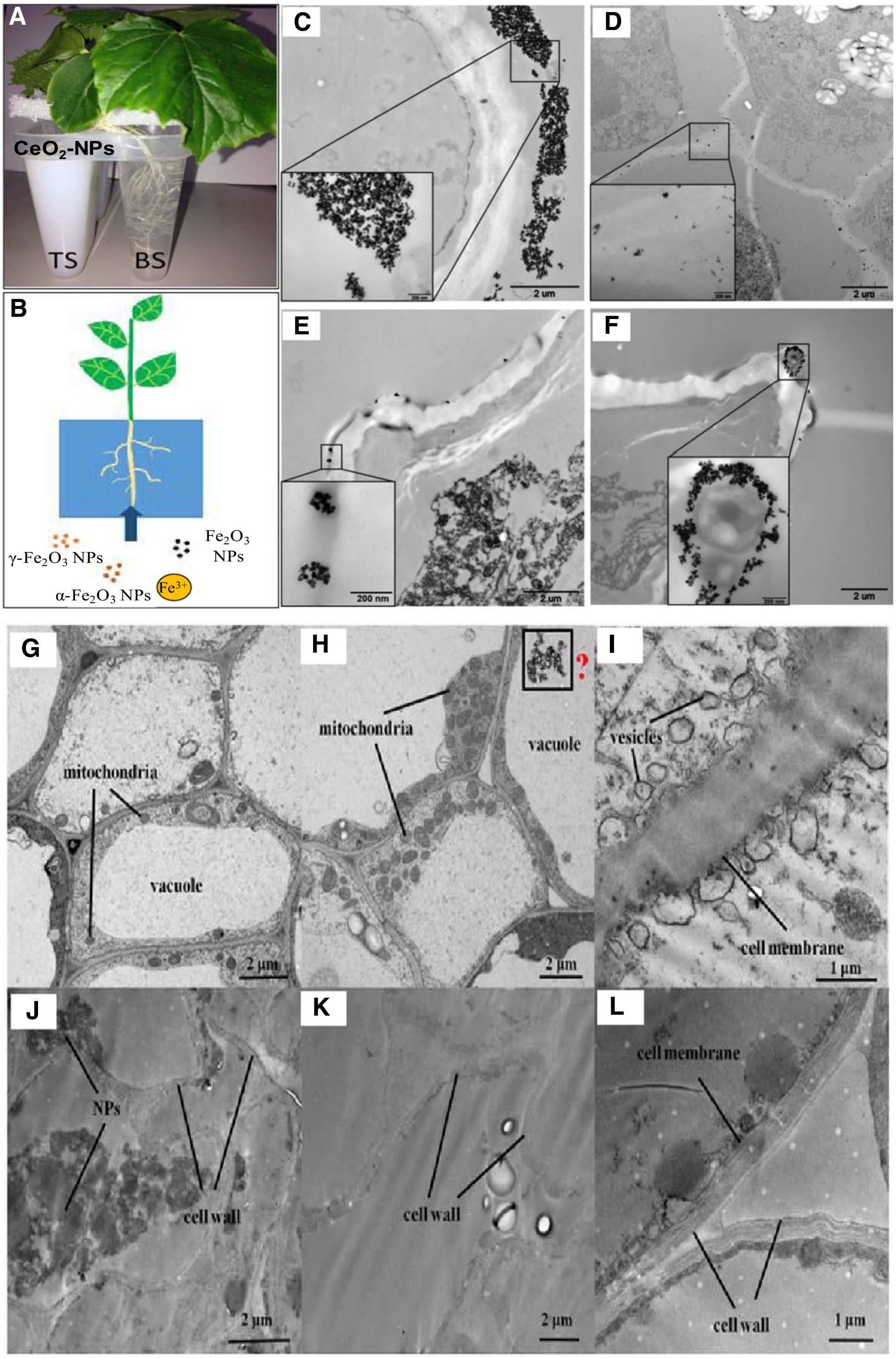


Fig. 8 Bioaccumulation and subcellular deposition of nanoparticles (NPs): microphotograph of split-root exposure hydroponic system (**a**). Treated side (TS) and blank side (BS) indicate the treated (with CeO$_2$ nanoparticles) and blank side of cucumber roots, respectively. Adapted with permission from reference (Ma et al. 2017). Treatment of *Cucurbita maxima* seedlings with iron oxide nanoparticles in the hydroponic system (**b**). Adapted with permission from reference (Li et al. 2018a). Panels C–F show the presence of CeO$_2$ nanoparticles (2000 mg L^{-1}) at various sites of cucumber roots as analyzed by TEM: root surface of treated side (**c**), internal structure of treated side root (D), and root surface of blank sized (**e**, **f**). Inset pictures in panels C–F represent greater magnification of selected regions (scale bar = 200 nm for each inset). Panels G-K represent TEM micrographs of *C. maxima* ultrathin root sections as control (**g**), roots treated with 50 mg L^{-1} each of γ-Fe$_2$O$_3$ nanoparticles (**h**, **i**), α-Fe$_2$O$_3$ nanoparticles (**j**, **k**), and bare Fe$_3$O$_4$ nanoparticles (**l**) for 10 days

Root-mediated uptake of nanoparticles

Roots are in direct contact with nanoparticles and hence can absorb nanoparticles from soils and transport them to various plant tissues. This uptake is facilitated by permeable and more thinner cuticle of roots and cell wall of root hairs (Galway 2006). Uptake and accumulation of various nanoparticles by plant root cells have been reported (Li et al. 2016; Raliya et al. 2016a; Vithanage et al. 2017; Ahmed et al. 2018b). The transpiration may facilitate the uptake of nanoparticles (Zhai et al. 2014) with positive correlation between rate of water absorbed and nanoparticle's uptake (Rico et al. 2013a). For instance, along with water uptake through the xylem, the CuO nanoparticles also travel from

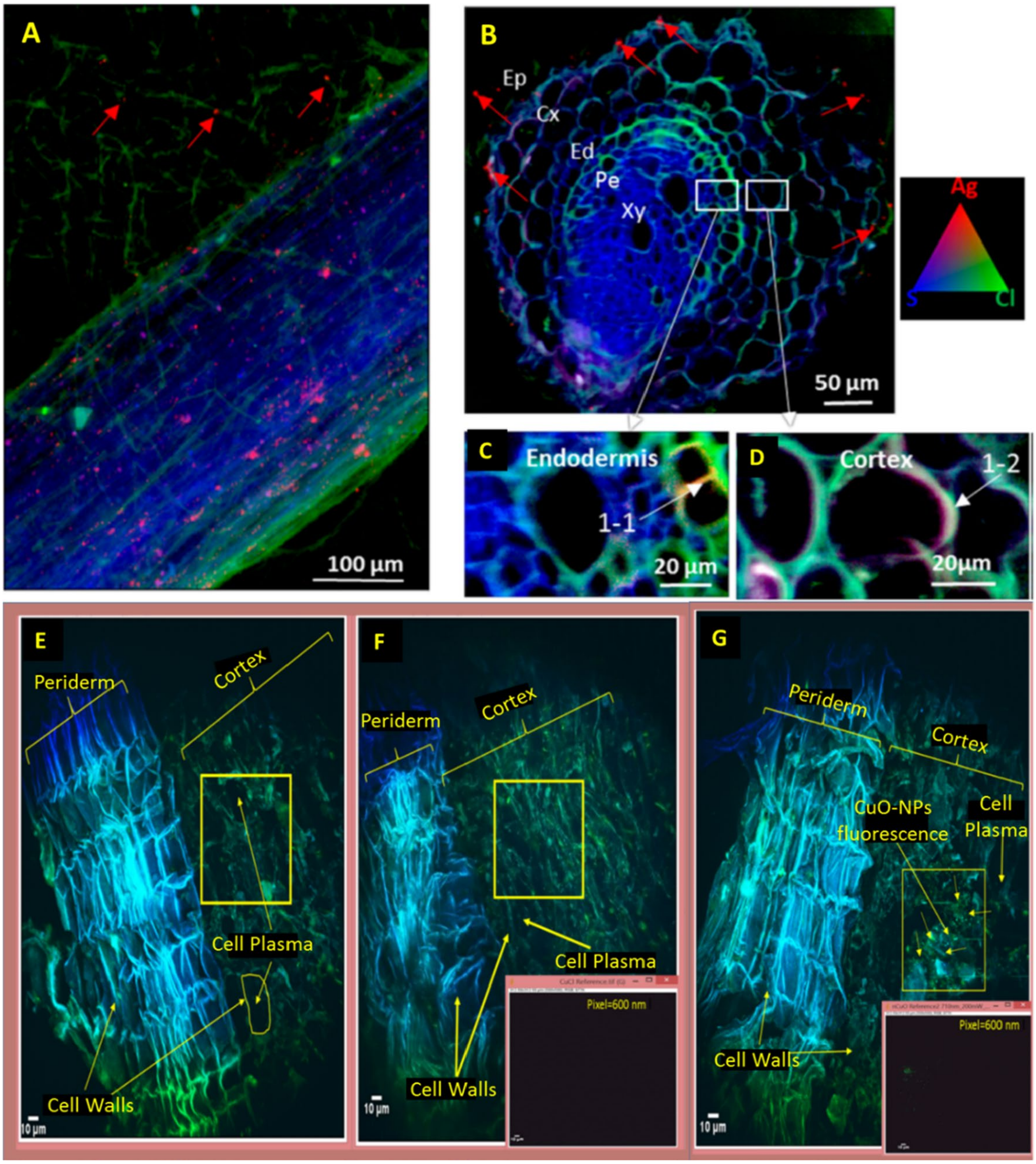


Fig. 9 Examples of distribution of nanoparticles in plants. Panels A-D show Ag nanoparticle's distribution in wheat roots. Tricolor maps of wheat root captured through micro-X-ray fluorescence (μ-XRF) technique (**a**), cross section of root (**b**), a magnified picture of endodermis (**c**), and cortex (**d**). Arrows in red indicate preferential deposition locations of Ag nanoparticles, while white arrows indicate the points of root tissues where μ-XANES analysis was performed. Abbreviations Ep, Cx, Ed, Pe, and Xy stand for epidermis, cortex, endodermis, pericycle, and xylem, respectively. Adapted with permission from reference (Pradas Del Real et al. 2017). Panels E–G represent the two-photon microscopic analysis of sweet potato roots: untreated (**e**), treated with 75 mg L^{-1} each of $CuCl_2$ (**f**) and CuO nanoparticles (NPs) (**g**). Fluorescence of lignin present in periderm is shown (**e**) where arrows point the cellular structure of cortex and periderm, while opaque region represents cortex only. The inset picture in panel F corresponds to aqueous solution of $CuCl_2$ showing no fluorescence. However, panel G indicates lignin fluorescence in periderm. Yellow rectangle in panel G confirms the fluorescence of CuO nanoparticles present in the cortex which is also visible in aqueous suspension of CuO nanoparticles in inset of panel G. Adapted with permission from reference (Bonilla-Bird et al. 2018)

roots to shoot of maize (a cereal crop) as viewed under TEM and energy-dispersive X-ray (EDX) of xylem sap (Fig. 10) (Wang et al. 2012c). Furthermore, root pore size also influences nanoparticle's internalization. As an example, the pore diameter (6.6 nm) of maize primary roots selectively allows the uptake of smaller sized CeO_2 nanoparticles in root

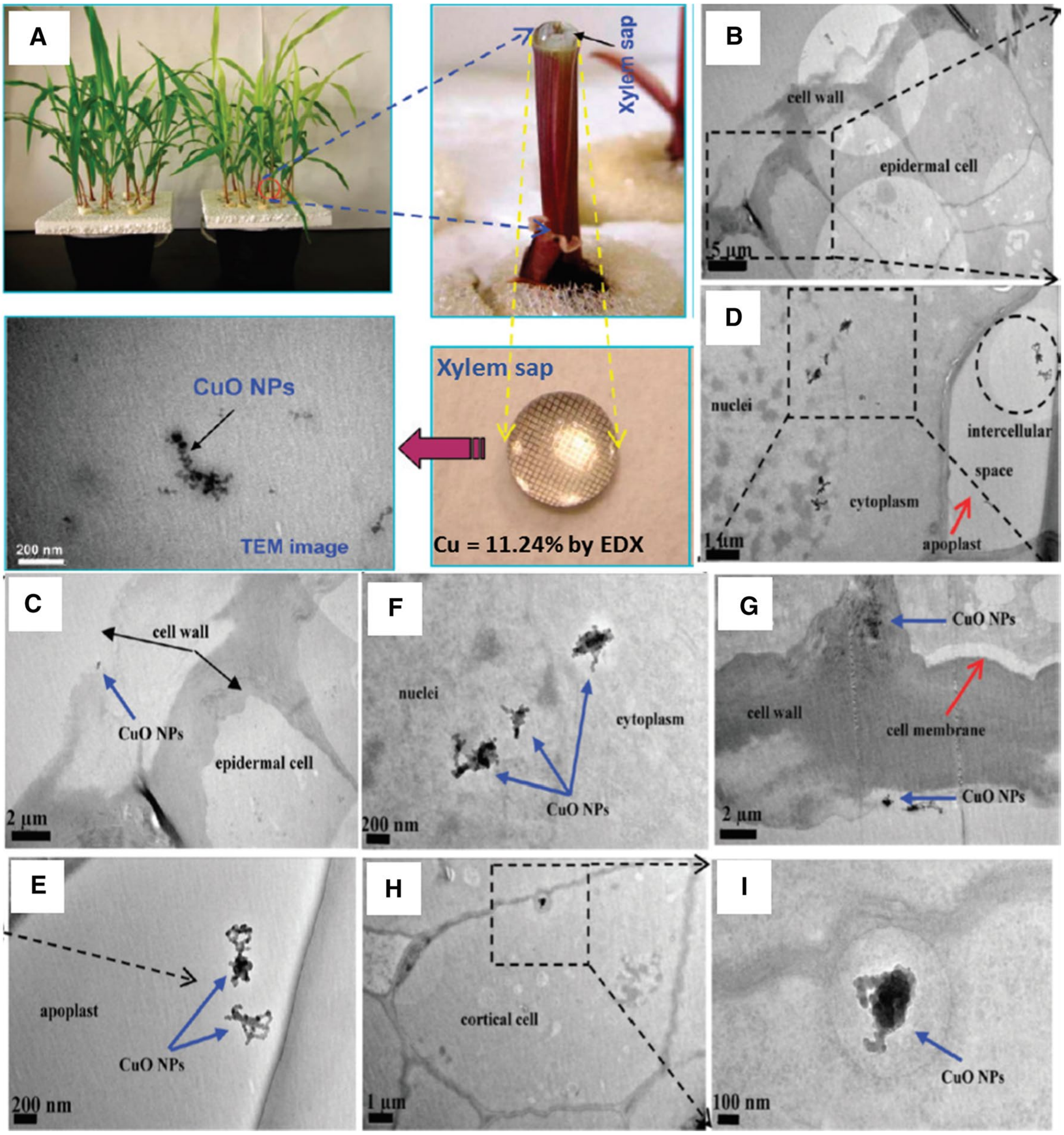


Fig. 10 Uptake of CuO nanoparticles (NPs) by maize plants and its visualization by TEM after 15 days of growth in hydroponic nutrient solution. Magnified view of panel A shows transverse cut in maize stem with xylem sap coming of it. TEM analysis of xylem sap revealed the presence of CuO nanoparticles aggregates being transported through xylem vessels. Panels B and C represent CuO nanoparticles entrapped in epidermal cell walls, while panel C is the magnified view of square drawn in panel B. Panels D, E, and F show internalized CuO nanoparticles in intracellular spaces and within the cortical cells of maize root. Panels E and F are enlarged views of encircled and squared area shown in panel C. Panel G reveals translocation of CuO nanoparticles across cell wall of epidermis, and the presence of CuO nanoparticles like aggregates at the interface of cell membrane and cell wall. In addition, the endocytosis-like structure was observed in the cells (H, I). Adapted with permission from (Wang et al. 2012c)

cells with subsequent transmission to aerial parts (Zhao et al. 2012a). On the other hand, CeO_2 nanoparticles of > 7 nm in diameter can be taken up by other crops including alfalfa, tomato, cucumber, and corn (López-Moreno et al. 2010). The CeO_2 nanoparticles having a diameter of more than seven nm up to 25 nm are taken up by cucumber roots and travel to its shoots. These studies suggest that the mode of nanoparticle's uptake varies between cereal and vegetable crops and even among vegetable crops based on nanoparticle's and root pore diameter. Also, nanoparticles with size greater than those mentioned above have been found to flow in the epidermal cells, across the cortex, and vascular system (Aubert et al. 2012).

Foliar uptake

Foliar application has been found useful in understanding the mode of uptake and distribution of nanoparticles from leaves to shoot and then to belowground regions, and hence, the toxicity of nanoparticles on plants is resulted (Fig. 11). Engineered nanoparticles, similar to those of naturally occurring atmospheric particles, are in direct surface contact with exposed organs like (i) stomatal apertures, (ii) leaf hydathodes, and (iii) trichomes (Fig. 11). Nanoparticles, when applied foliarly as suspension or aerosol-based spray, are deposited on foliar surfaces and able to directly penetrate inside the plant system largely due to nanoscale size and along with gaseous uptake by plants (Wang et al. 2013b). During foliar applications, nanoparticles with an average size of approximately < 100 nm can easily be taken up through stomatal openings typically ~ 100 nm in size (Schwabe et al. 2015).

If the nanoparticles have a coating of polar material, then their uptake is highly likely due to enhanced permeability of stomata for polar substances (Schreiber 2005). In an experiment, leaf pore size in three dicot plants has been reported to be more than 100 nm based on the uptake efficiency of C^{13} and N^{15} (Eichert and Goldbach 2008). Sometimes, the stomata are clogged during the uptake of individual nanoparticles or nano-sized aggregates (Hussain et al. 2013) resulting in reduced rate of water transpiration and elevation in foliage temperature ultimately retarding the production of photosynthetic pigments (Hirano et al. 1990). To validate this, an experiment was conducted, where an aerosol-based spray of TiO_2 and ZnO nanoparticles at the concentration range of 0–1000 mg kg^{-1} on 14 days grown tomato plants. The plant height was increased by both nanoparticles up to 250 mg kg^{-1}. Of the two nanoparticles, the TiO_2 significantly toxified tomato roots at all test concentrations except 1000 mg kg^{-1} (Raliya et al. 2015). Besides stomata, nanoparticles can also be taken up or excreted with the help of leaf tip hydathodes (Hong et al. 2014) more effectively after guttation when small droplets of water are hooked on leaf (Huang 1986). In a study, the inside entry of insoluble radioactive $^{141}CeO_2$ nanoparticles through

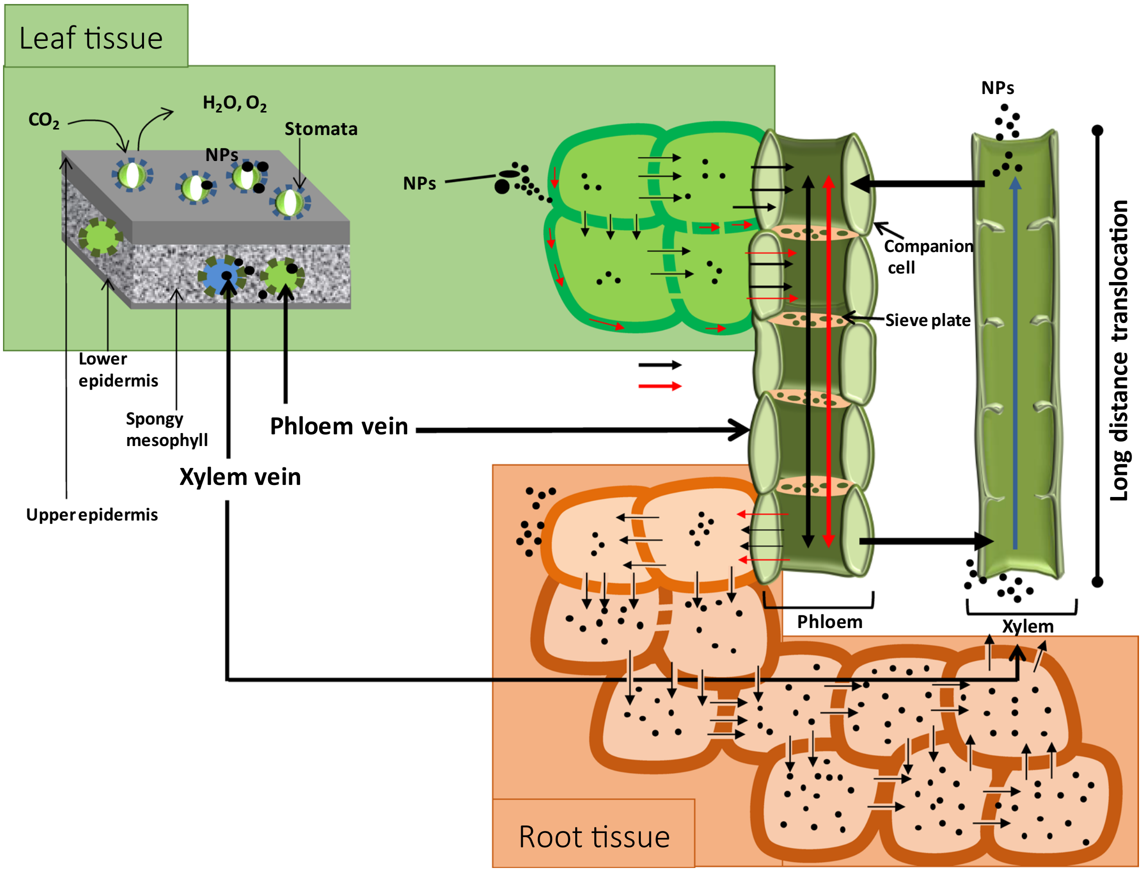


Fig. 11 Major sites (root and leaf) of nanoparticles (NPs) access to intracellular environment of plants and subsequent translocation to various sites. Two types of nanoparticle's movement are depicted: (i) apoplastic movement (red arrows) and (ii) symplastic movement (black arrows). Blue arrow in xylem vessel indicates long distance transport of nanoparticles to aerial parts. Small black arrows in root cell walls are showing the movement of nanoparticles from one cell to another via plasmodesmata

hydathodes of cucumber plants was observed as ^{141}Ce (Zhang et al. 2011).

Role of plant cell wall and membrane in root or foliar uptake

The cell wall-mediated uptake of nanoparticles generally depends both on (i) nanoparticle's diameter and (ii) cell wall structure—thickness of cell wall (which varies from 100 nm to several µm), pore size, and biochemical composition (cellulose, hemicellulose, and pectin) (Glenn et al. 2012; Bidhendi and Geitmann 2016; Kumar et al. 2018). The pore size of the cell walls mostly remains constant acting as a selective barrier for nanoparticles. Research has revealed the dynamicity in porosity of pectin (a component of cell wall) due to structural heterogeneity of cell wall (Willats et al. 2001; Fry 2011). A study revealed the spaces in hemicellulose structure of an average size of ~ 100 nm (McCann et al. 1990). Due to this, nanoparticles of approximately 50 nm traversed across and along the cell wall with consequent internalization in cell matrix (Lee et al. 2008). Similarly, nanoparticles ranging between 5 and 20 nm were also able to cross the plant cell wall (Navarro et al. 2008; Ma et al. 2010). For instance, the uptake and movement of Au nanoparticles with ≤ 20 nm have been confirmed in watermelon plants (Raliya et al. 2016a). Moreover, the smaller sized nanoparticles encourage creation of new pores in cell envelope due to higher surface reactivity which perhaps enhances influx of hydro-minerals and nutrients carrying more nanoparticles inside the plant (Castiglione et al. 2011).

In some cases, even the larger sized nanoparticles, for example, ZnO nanoparticles > 40 nm, have, however, also been found to increase root cell permeability by forming variable sized holes (Lin and Xing 2008). This mode of nanoparticle's uptake is unlike the assumption of restricted size (only ≤ 20 nm) entry of nanoparticles through cell walls (Ma et al. 2010). In yet other experiment assessing the cell wall dependency of nanoparticle's uptake, it was revealed that zero-valent iron nanoparticles can enhance the loosening of cell wall in radical-induced manner (Kim et al. 2014). This occurred in two steps: (i) enhanced hydrogen peroxide level due to strong oxidizing potential of zero-valent iron nanoparticles followed by (ii) hydroxyl radical formation, which induced loosening of *A. thaliana* root cell wall by creating asymmetrical distribution of tensional strength due to hydroxyl radicals. It also stimulated endocytosis-mediated uptake of nanoparticles. In contrast to ionic counterpart (Zn^{2+}), ZnO nanoparticles also induced endocytosis in roots of *A. thaliana* grown on agar-based medium containing ½ strength MS medium (Wan et al. 2019). To confirm this, actin-binding domain 2 (ABD2)/GFP transgenic line was used. ZnO nanoparticles caused actin microfilament rearrangement in epidermal cells of root elongation zone repressing the growth of primary roots (Fig. 12).

Following penetration, nanoparticles can move across the cellular membrane through various mechanisms as depicted in Fig. 13. The cell membrane due to its polar nature acts as

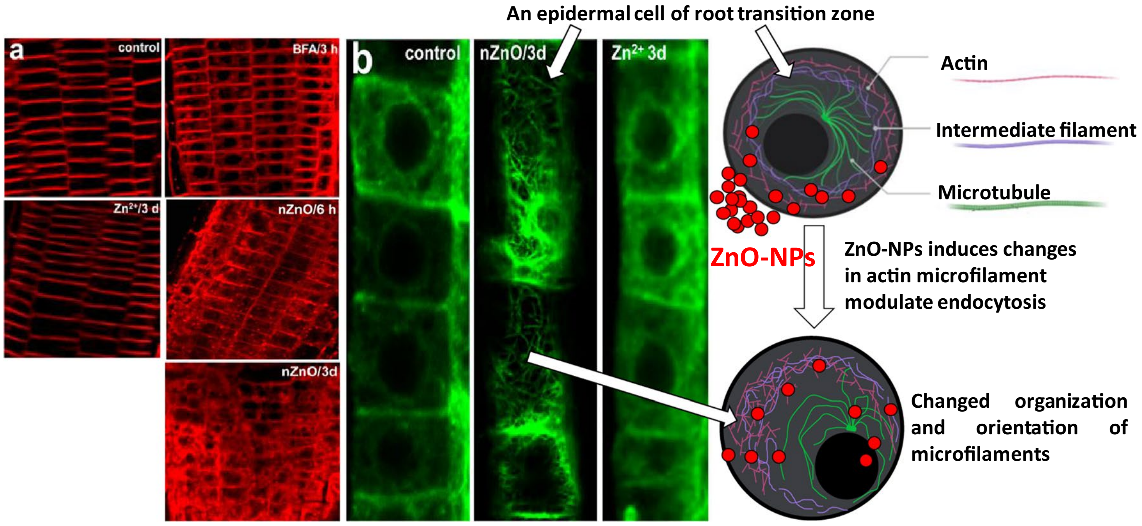


Fig. 12 **a** Endocytosis of ZnO nanoparticles (NPs) in root cells of *A. thaliana*. Five-day-old seedlings were exposed to (i) ZnO nanoparticles for 6 h or 3 days at 100 mg L^{-1}, (ii) Zn^{2+} for 3 days at 200 mg L^{-1}, and (iii) brefeldin A for 3 h at 25 µM and then stained with red fluorescence emitting FM4-64 fluorescent dye. **b** ZnO nanoparticles rearranged microfilaments such as actin, microtubules, and other filaments of epidermal cells. Emission of green fluorescent protein (GFP) from the roots of ABD2::ABD2-GFP seedlings of *A. thaliana* exposed for three days to 200 and 100 mg L^{-1} of Zn^{2+} and ZnO nanoparticles, respectively. Animation shows rearrangement of microfilaments under ZnO nanoparticle stress. Adapted and recreated with permission from (Wan et al. 2019)

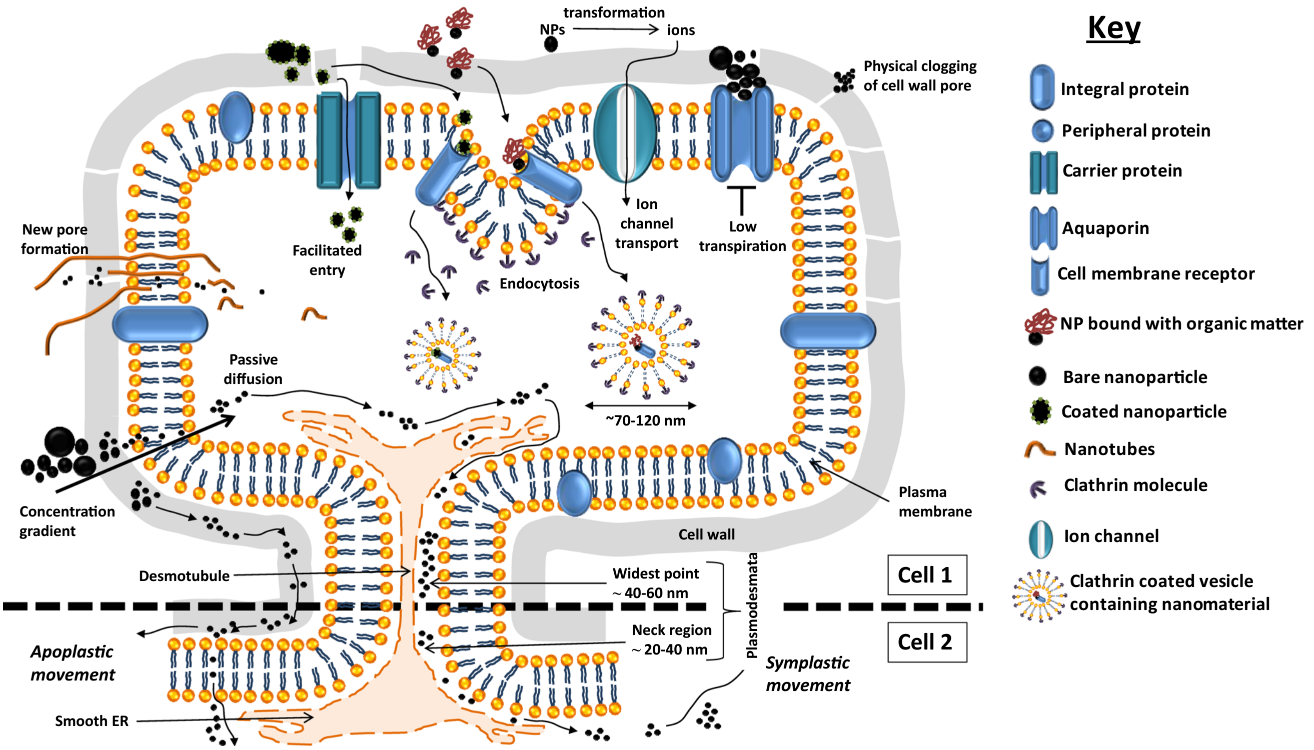


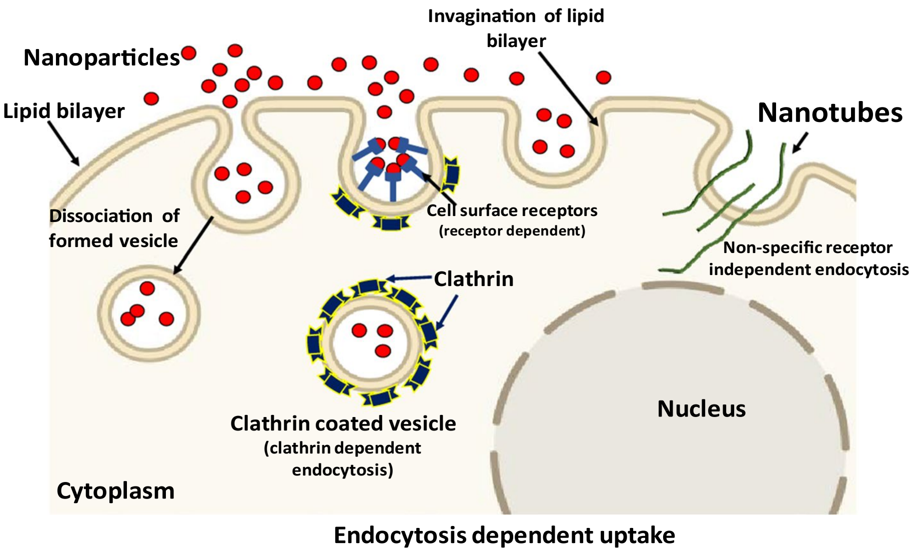
Fig. 13 A model of nanoparticles (NPs) entry into plant cell, across the plant cell wall and membrane followed by their apoplastic and symplastic movement. Nanoparticles are taken up by facilitated transport of coated nanoparticles, ion channel transport (after dissolution of nanoparticles), through endocytosis of nanoparticles bound to organic matter, passive diffusion, and through new pore formation by carbon nanotubes or surface reactivity of smaller size nanoparticles. During the process of cellular uptake, nanoparticles may clog the cell wall's pores and aquaporins present in membrane

a selective channel for the across movement of solutes and substances. As per the surface and morphological features of nanoparticles, the cell membrane can regulate the inside passage of nanoparticles by facilitated uptake or passive diffusion. The entry passage of nanoparticles in cells critically depends on many physicochemical and physiological factors including: (i) nanoparticle-dependent factors such as chemical composition, size, morphology, surface charge, hydrophobicity, or hydrophilicity and (ii) membrane-dependent factors like composition of lipids, fluidity of cell membrane, and the presence of molecular species and membrane-embedded ligands (Karami Mehrian and De Lima 2016). Selectively permeable channel proteins limit the influx of polar and large molecules such as ions dissolved from nanoparticles or polar, negative, or positive nanoparticles (Schwabe et al. 2015).

The nanoparticles are also taken up while entrapped in endocytic vesicles, which can be of two types either dependent of endocytosis or independent of endocytosis (Fig. 14). Endocytosis is a natural process that allows communication among cells, helps in cellular signaling and nutrient transfer, and induces defense response against xenobiotics. The very first event in the endocytosis in the invagination of lipid bilayer entrapping the surface adsorbed nanoparticle followed by its dissociation but inside the cell by tightly controlled cell signals (Karami Mehrian and De Lima 2016). The endocytosis may occur as receptor independent or dependent (Schwabe et al. 2015). In the latter one, nanoparticles first adsorbed to a membrane bound macromolecule, which could be a carbohydrate, protein, or lipid followed by cellular internalization of the formed vesicle (Karami Mehrian and De Lima 2016). Charge nanoparticles are taken up via a clathrin-dependent and receptor-mediated endocytosis (Onelli et al. 2008). Clathrin molecules are cellular coat proteins producing endocytic vesicles of size ranging between 70 and 120 nm (Robinson 2015; Faisal et al. 2018). This size of vesicles may therefore limit the entry of bigger sized nanoparticles into the vesicle such as carbon nanotubes (Fig. 14).

For the uptake of carbon nanotubes through cell membranes, a non-specific mode of uptake has been proposed (Liu et al. 2009b). Endocytosis can differentiate nanoparticles based on their charge; for example, positively charged Au nanoparticles are internalized in plant cells through nonspecific fluid phase endocytosis more effectively than negatively charged Au nanoparticles (Onelli et al. 2008).

Fig. 14 Uptake of nanoparticles in plant cells through endocytosis of clathrin-coated vesicles, uncoated vesicles, and receptor independent vesicles.



Enhanced uptake of nanoparticles may also alter the gene expression for aquaporin channels (Rico et al. 2011) of cell membrane in an inversely proportional manner, i.e., higher uptake of nanoparticles clogs the aquaporins, and in response, cell starts to down-regulated the expression of aquaporin genes (Lü et al. 2010; Taylor et al. 2014). Aquaporins also serve as non-selective passage for the uptake of non-ionic solutes or substances less than one nanometer in size (Zangi and Filella 2012) and assist to switch over the symplastic or apoplastic movement (Schwabe et al. 2015).

In Planta translocation of nanoparticles

Translocation of nanoparticles from one organ to other parts of plant occurs via xylem and phloem tissues. However, translocation differs from nanoparticle to nanoparticle. For example, TiO_2 nanoparticles in cucumber roots are translocated to leaves and fruits without their bioconversion (Servin et al. 2012). In contrast, nano-ceria is first dissolved and then liberate cerium ions which then interacts with plant organics inside the plant system (Gui et al. 2015). The translocation of nanoparticles is generally dependent of four factors: (i) size of nanoparticle, (ii) surface chemistry and charge, (iii) growth phase of plant, and (iv) inside environment of plant cell. Broadly, the nanoparticles translocation occurs through symplastic or apoplastic pathways as depicted in Fig. 13. In the apoplastic pathway, the nanoparticles move either by one of the following ways or simultaneously via longitudinal channels in cell wall, intercellular spaces, and xylem vessels (Sattelmacher et al. 1998; Geisler-Lee et al. 2013); however, when travelling symplastically, nanoparticles cross cell membrane reaching to next adjacent cell through plasmodesmata (Figs. 10 and 13) or move via sieve tissues present in phloem vessels (Zangi and Filella 2012). In symplastic movement, microscopic channels called plasmodesmata are key because it is the only connection adjoining two plant cells regulating the transfer of different molecules and nanoparticles from one cell to another across the plant (Corredor et al. 2009). The apoplastic route is more preferred due to the fact that it is a non-selective passage of least resistance, thereby translocating many non-essential metal complexes and nutrients (Sattelmacher and Horst 2007). If there is any blockage of apoplastic way due to the presence of casparian strip, nanoparticles choose to traverse the protoplast of endodermal cells and gain access to vascular tissues (Lin and Xing 2008) as nanoparticles have been detected in xylem vessels (Zhang and Zhang 2020).

In a recent study, when *A. thaliana* was treated with differentially charged (positive and negative) Au nanoparticles, two different modes of nanoparticles uptake and translocation were detected based on the charge on nanoparticle surface (Avellan et al. 2017). The data recorded through two highly sophisticated microscopy techniques: (i) X-ray computed nanotomography (nano-CT) and (ii) dark-field microscopy combined with hyperspectral imaging (DF-HSI), revealed that the detachment of border-like cells from root cap and secreted mucilage could adsorb and entrap the Au nanoparticles regardless of their surface charge. In contrast, the behavior of root cap border cells toward Au nanoparticles depends on particle charge. Positively charged Au nanoparticles enhanced the secretion of mucilage and subsequently are trapped in it, which in turn prevents their accumulation and transposition in root tissue. On the other hand, negatively charged Au nanoparticles bypassing the mucilage adsorption could get entered the root tissue and were translocated in apoplast (Fig. 15a). In a different study, CeO_2 nanoparticles when applied on leaves of *Cucumis sativus*, approximately 3% of the total amount of nanoparticles was found in roots suggesting that the nanoparticles were translocated from leaf to root via phloem (Hong et al. 2014) with subsequent adsorption of up to 81% of CeO_2 nanoparticles on outer surface of leaf. Numerous studies have shown that nanoparticles can travel through plant cell walls and are localized within cell organelles or cytosol. For instance, the presence of TiO_2 nanoparticles was observed using EDX on the rice chloroplast membrane when treated with 1000 mgTiO_2 nanoparticles L^{-1} (Ji et al. 2017). In a study, TiO_2 nanoparticles were translocated to leaf trichomes and fruits of cucumber as reveled by micro-X-ray near edge spectroscopy (μ-XANES) analysis of cucumber tissues (Servin et al. 2012, 2013). In a similar study, CeO_2 nanoparticles have also been detected in vacuole, chloroplast, and plasma membrane of cotton plants grown under hydroponic environment (Nhan et al. 2015).

Among various factors, the solubility of nanoparticles profoundly affects their translocation; for example, up to 26.14% of total applied concentration of highly soluble MgO nanoparticles was translocated from leaf to root compared to only 5.45% fraction of low soluble TiO_2 nanoparticles (Wang et al. 2013b). However, TiO_2 nanoparticles with low solubility were able to penetrate leaves and translocated to vascular supply and roots (Larue et al. 2014). In a hydroponic nutrient solution, soybean plants accumulated and distributed nanoparticles of Zn/ZnO and CeO_2, and their corresponding metal ions in various tissues (López-Moreno et al. 2010). However, a distinctive mode of translocation of ZnO and CeO_2 nanoparticles has been suggested, where CeO_2 nanoparticles remained bio-accumulated in root nodules causing a substantial reduction in N_2 fixation, while ZnO nanoparticles were able to pierce into leaves and beans (Priester et al. 2012). In a recent study, ZnO nanoparticles and $ZnSO_4$ were foliarly applied on the winter wheat under field conditions and after the growth, analysis of grain by μ-XRF microscopy and XANES showed that ZnO translocation somewhat increased the zinc content of grain endosperm (Zhang et al. 2018a). Zinc was also distributed in the crease of grain and aleurone layer (Fig. 15b, c). Besides these, the translocation of nanoparticles also varies with growth conditions. To prove this, studies on copper-based nanoparticle

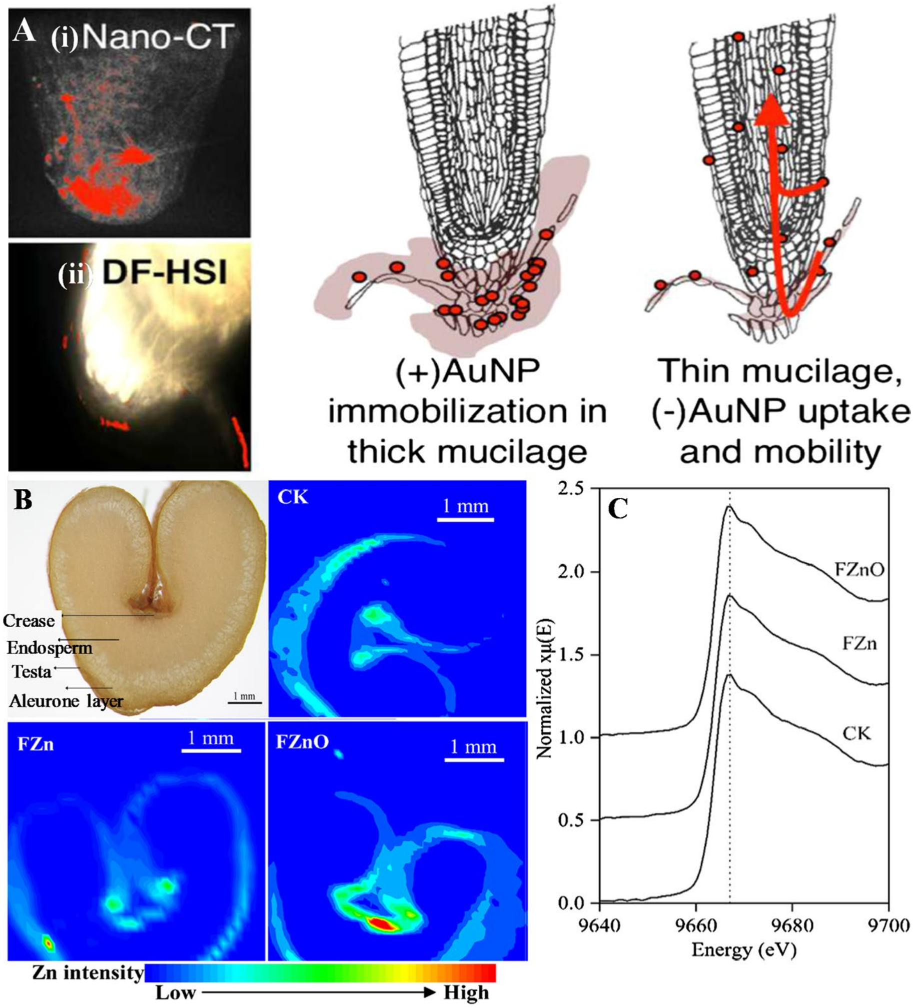


Fig. 15 Panel A shows translocation of Au nanoparticles (NPs) in A. thaliana roots detected through: (i) Nano-CT and (ii) DF-HSI. Negatively (−) or positively (+) charged Au nanoparticles were stabilized by polyethylenimine or citrate coating. Adapted with permission from (Avellan et al. 2017). Panel B shows a section of wheat grain under light microscopy which were picked from foliarly applied ZnO nanoparticles exposed wheat plants. Examination of zinc distribution in grain section by synchrotron X-ray fluorescence microscopy: panel CK, FZnO, and FZn represent control, treatment of ZnO nanoparticles, and zinc sulfate, respectively, while panel C shows XANES spectra of control and each test Zn species. The vertical dotted line in panel C corresponds to 9.671 keV for ZnO (9.671 keV) which confirms the translocation of ZnO nanoparticles to wheat grain. Adapted with permission from (Zhang et al. 2018a)

and plant interactions are discussed as an example. When nano-forms of three copper materials, namely Cu, CuO, and Cu(OH)$_2$, were tested on cilantro, lettuce, and alfalfa, copper was mostly found accumulated in roots approximately more than 87% with some translocation to stem but not to leaves (Hong et al. 2015; Zuverza-Mena et al. 2015). However, copper from Cu nanoparticles translocated to only to stems leaves but also accumulated in fruits of tomato and cucumber raised in soil (Zhang et al. 2016a; Rajput et al. 2018c). In one of our previous studies on comparative analysis of CuO nanoparticle translocation in hydroponically and soil grown tomato plants, the CuO nanoparticles translocated to every plant organ but uptake were low in soil raised plants as compared to hydroponic culture (Ahmed et al. 2018a). The limited internalization and hence translocation of CuO nanoparticles could be due to the above discussed hetero-aggregation of nanoparticles which is more common in soil system.

Phytotoxic impact of nanoparticles

Prolong persistence, low biodegradability, and massive increase in environmental deposition of nanoparticles built additional survival pressure on edible crops. The prevalence of nanoparticles in the environment and their interactions with plants induce toxicity (Fig. 16). Irrespective of the routes, bioaccumulation, transport, and effects of nanoparticles on plant's performance depend upon three factors: (A) [Plants]—(i) genotypes, (ii) growth stage, and (iii) physiological and metabolic activities; (B) [Nanoparticles] (i) size and shape, (ii) surface functionalization and chemical composition, (iii) stability of nanoparticles, and (iv) duration of exposure; and (C) [Soils] (i) physicochemical properties and (ii) microbiological composition (Rico et al. 2011; Raliya et al. 2015; Carrière and Larue 2016; Zhao et al. 2016a; Gao et al. 2018). The lethality of nanoparticles (Table 1) on different growth stages/physiological processes of numerous plant species is reviewed and discussed briefly in the following sections.

Seed germination and growth of seedlings under nanoparticle stress

Nano-phytotoxic impacts on plants starting from seed germination and on both seedling (Kasana et al. 2017) and adult stage have been studied (Chichiriccò and Poma 2015). Of these, seed germination, considered an important process of plant (Bewley 1997), is tightly regulated and a well-protected

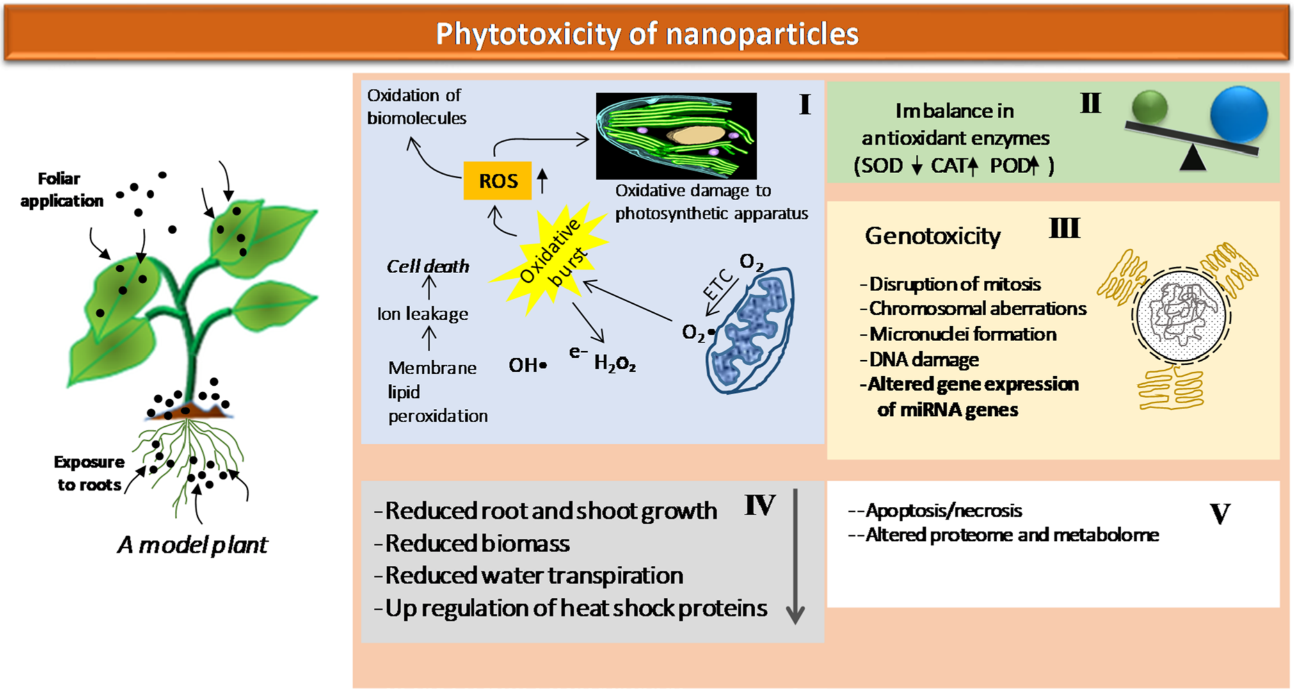


Fig. 16 Toxic impacts of nanoparticles on the plant through reactive oxygen species production, membrane lipid peroxidation, destruction of chloroplasts, and mitochondria (Box-I). Intracellular oxidative stress causes imbalance in antioxidant enzymes such as superoxide dismutase (SOD), catalase (CAT), and peroxidase (POD) (Box-II); interaction of nanoparticles with genetic material of plant cells causes genotoxicity via disruption of normal cell cycle, micronuclei generation, chromosomal anomalies, and altering miRNA gene expression (Box-III). Disruptive impacts of nanoparticles on plants include reduced biomass and water transpiration with up-regulation of heat shock proteins (Box-IV). Nanoparticle interaction with plant cells results in apoptosis, necrosis, and overall change in proteome and metabolome (Box-V), and oxidative stress, which ultimately lead to plant cell death

Table 1 Toxic responses of nanoparticles to agriculturally important plants

Nanoparticle	Size (nm)	Test crop(s)	Dose rate	Activity/toxicity	References
Ag	10	*Lycopersicon esculentum*	10–50 mg kg^{-1}	Ag nanoparticles' uptake induced reactive oxidative stress that reduced photosynthesis, CO_2 assimilation and fruit yield	Das et al. (2018)
	10	*Allium cepa, Raphanus sativus*	0.001–10,000 mg L^{-1}	Root growth was inhibited	Pittol et al. (2017)
	17	*Triticum aestivum*	20–60 ppm	Generation of oxidative stress was evident, antioxidants' level was enhanced, and Ag nanoparticles induced cell deformation	Barbasz et al. (2016)
	20	*Vigna radiata*	5–50 mg L^{-1}	Ag nanoparticles induced formation of reactive oxygen species and reduced overall yield	Nair and Chung (2015)
	20, 51, 73	*Vicia faba*	100 mg L^{-1}	Ag nanoparticles induced excessive production of oxidative stress, reduced CO_2 assimilation and stomatal conductance, inhibitory impact Ag nanoparticles increased with increasing diameter	Falco et al. (2020)
CuO	20–100	*Lactuca sativa*, *Brassica oleracea* var. sabellica and *B. oleracea* var. viridis	34.4 g/m^2 on leaf surface	Foliar application: highest amounts of CuO nanoparticles were accumulated on lettuce leaf surface followed by collard green and kale	Keller et al. (2018)
	16	*L. sativa, Daucus carota*	0.8–798.9 mg L^{-1}	Water transport and growth assessment was done following 10 days of growth. Dose related increase in root diameter of lettuce by 52% and carrot by 26% seedlings relative to control	Margenot et al. (2018)
	40–80	*Zea mays, Oryza sativa*	500, 1000, 2000 mg L^{-1}	At 2000 mg L^{-1}, 95% and 97% inhibition in root length of maize and rice	Yang et al. (2015)
	10–100	*Coriandrum sativum*	0–80 mg kg^{-1} soil	Nanoparticle solutions were mixed with commercial potting mix. Cu accumulation caused approximately 50% inhibition of germination, depression in micro and macro nutrient element accumulation	Zuverza-Mena et al. (2015)
	38	*T. aestivum*	500 mg kg^{-1}	Fresh and aged mixture of CuO nanoparticles and loamy sand soil were tested. Compromised root growth and aged CuO nanoparticles further aggravate the toxicity	Gao et al. (2018)
	25–55	*B. rapa*	50–500 mg L^{-1}	Seedlings exposed to CuO nanoparticles for 15 days in a growth room. Synthesis of photosynthetic pigments and sugar was decreased with simultaneous enhancement in proline level, generation of reactive oxygen species, malondialdehyde, and H_2O_2; decreased amount of glucosinolate and phenols	Chung et al. (2019b)

Table 1 (continued)

Nanoparticle	Size (nm)	Test crop(s)	Dose rate	Activity/toxicity	References
	< 50	*Hordeum vulgare*	50–1000 mg kg^{-1}	Soil–nanoparticle mixture of pH 4.8 and 5.8 before and after aging. Soil aging increased CuO nanoparticles toxicity; root elongation was suppressed	Qiu and Smolders (2017)
	43	*O. sativa*	50–1000 mg kg^{-1}	Low water uptake by root and aerial parts; grain production was considerably reduced	Peng et al. (2017a)
	< 50	*T. aestivum*	3–300 mg kg^{-1}	Reduction in root elongation and zone of cell division was shortened	Adams et al. (2017)
	< 50	*Cucumis sativus*	50–200 mg L^{-1}	Foliar application on soil grown plants. Inhibition of leaf transpiration, net photosynthesis, reduction in fruit firmness and molybdenum of fruits	Hong et al. 2016)
	25–55	*D. carota*	1–1000 mg L^{-1}	Plants were treated in coarse sand mixed with CuO nanoparticles for 13 weeks. The CuO nanoparticles dose dependently decreased plant biomass, Cu accumulation in taproot was limited to the periderm, radial penetration of Cu into the taproot, and subsequent translocation to shoots was observed	Ebbs et al. (2016)
	< 50	*O. sativa*	2.5–1000 mg L^{-1}	Accumulation of CuO nanoparticles in chloroplast, reduced transpiration, stomatal conductance, photosynthesis, enhanced activity of ascorbate peroxidase and superoxide dismutase	Da Costa and Sharma (2016)
	40	*T. aestivum*	Freshly added and 28 days aged CuO nanoparticles at 500 mg kg^{-1} soil	Aging of CuO nanoparticles further reduced root growth, wheat root system had somewhat compensatory effects on nanoparticles dissolution, plant activity enhanced the pH by 0.4 and 0.6 units by fresh and aged CuO nanoparticles, root exudates enhanced Cu content in pore water	Gao et al. (2018)
ZnO	< 100	*Pisum sativum, T. aestivum, Z. mays, R. sativus, L. sativa, Solanum lycopersicum, Beta vulgaris,* and *C. sativus*	20–900 mg kg^{-1} soil	Accumulation and toxicity of ZnO nanoparticles varied with plant species; interaction of ZnO nanoparticles with calcareous soil reduced Zn availability and thus toxicity to biomass accumulation by cucumber, beet, and wheat; in acidic soil, pea, wheat, and maize showed resistance	García-Gómez et al. (2018c)
	< 50	*Glycine max*	500 ppm	Effect on seedlings was studied. Inhibition of root elongation, cell viability, and biomass, generation of superoxides, reduced biomass of foliage, alteration of gene expression	Hossain et al. (2016)

Table 1 (continued)

Nanoparticle	Size (nm)	Test crop(s)	Dose rate	Activity/toxicity	References
	90	*Z. mays*	400–32,000 mg kg^{-1}	Plants were grown in soil for 56 days. Increased production of superoxide anions and superoxide dismutase activity decreased mineral nutrient acquisition, decreased photosynthesis and root activity, dose-dependent enhancement in Zn bio-uptake	Wang et al. (2016a)
	15	*S. lycopersicon, T. aestivum*	50–1600 mg L^{-1}	Seed germination in Petri dishes; plants were exposed in vermiculite receiving hydroponic nutrient medium. Lower doses of ZnO nanoparticles increased seed germination and growth attributes, while higher doses showed toxicity to germination, growth attributes, photosynthetic pigments, enhanced bio-uptake of Zn, 200 mg L^{-1} concentration increased hydrogen peroxide and malondialdehyde production; overall, *S. lycopersicon* experienced more toxicity than *T. aestivum*	Amooaghaie et al. (2017)
	10	*G. max*	0.05, 0.1, 0.5 g kg^{-1} soil	Seed protein, chlorophyll, reactive oxygen species, lipid peroxidation, genotoxicity were taken as toxicity end points. Leaf damage, genotoxicity appeared at 0.5 g kg^{-1}	Priester et al. (2017)
	15	*T. aestivum*	100, 200 µM	Hydroponic exposure to plants. Reduced photosynthesis, production of H_2O_2, lipid peroxidation, nitric oxide ameliorated the toxicity	Tripathi et al. (2017)
	< 100	*P. vulgaris, S Lycopersicon*	3, 20, 225 mg kg^{-1}	Plants were raised with ZnO nanoparticles at pH 5.4 and 8.3 in acidic and calcareous. Reduced photosynthesis, enhanced oxidative stress, reactive oxygen species generation, higher toxicity were observed in acidic soil for *P. vulgaris* and opposite for *S. lycopersicon*	García-Gómez et al. (2017)
	30–40	*Z. mays*	0.02–2 g L^{-1}	Petri dish assay to assess germination and seedling growth. Negative effect on seed germination at 0.02 g L^{-1} after 24 h; root length increased after 68 h at 0.02 and 0.2 g L^{-1}	Fellmann and Eichert (2017)
	< 100	*S. lycopersicum*	300, 600, 1000 mg kg^{-1}	Plants were grown in soil for 90 days. Root uptake of ZnO nanoparticles, generation of H_2O_2, and oxidative stress in leaves; enhanced superoxide dismutase activity, total flavonoids, phenols, lycopene, and β-carotene were significantly reduced	Akanbi-Gada et al. (2019)
	90	*Z. mays*	800 mg kg^{-1}	Reduced growth and inhibition of arbuscular mycorrhiza fungi	Wang et al. (2016a)
	10	*Medicago sativa*	250, 500, 750 mg kg^{-1}	Reduced root biomass up to 80%	Bandyopadhyay et al. (2015)

Table 1 (continued)

Nanoparticle	Size (nm)	Test crop(s)	Dose rate	Activity/toxicity	References
	64 and 80	*Vigna angularis*	20–200 µg mL^{-1}	ZnO nanoparticles readily accumulated in roots, disrupted plant physiology of plant, enhanced oxidative stress, and reduced photosynthetic pigment	Jahan et al. (2018)
TiO_2	20 ± 5	*O. sativa*	50 and 200 mg L^{-1}	Reduced grain yield and biomass, enhanced Mg, Ca, Zn, P, and Ti in grains	Du et al. (2017a)
	25	*C. sativus, B. oleracea* var. capitata, *Avena sativa,* *D. carota, Z. mays,* *L. sativa, A. cepa,* *Lolium perenne*, *S. lycopersicum*	250–1000 mg L^{-1}	Inhibition of root growth of oat, corn, cabbage, oat, lettuce, and reduction of soybean and cucumber germination	Andersen et al. (2016)
	< 25	*S. lycopersicum*	100–1000 mg kg^{-1}	Plants were raised in nanoparticles amended soil. Root elongation, plant height, and biomass increased at 250 mgTiO_2 nanoparticles kg^{-1}, 100 mgTiO_2 nanoparticles kg^{-1} enhanced the lycopene and fruit yield, photosynthetic pigment increased up to 750 mg kg^{-1}	Raliya et al. (2015)
	5–15	*Z. mays*	0.02–2 g L^{-1}	Inhibition of germination, root and shoot growth	Fellmann and Eichert (2017)
	8	*Spirodela polyrrhiza*	0.05–10 mg L^{-1}	Exposure was given in specific nutrient solution. Significant decrease in biological attributes, peroxidase activity, increased superoxide dismutase activity	Movafeghi et al. (2018)
	< 20	*T. aestivum*	20–100 mg kg^{-1} soil	60 days exposure in soil (sandy loam, pH 7.6). Root, shoot elongation and P uptake were lower at 80 and 100 mg kg^{-1}, 11.1% less chlorophyll at 100 mg kg^{-1}	Rafique et al. (2018)
	20	*O. sativa*	100–500 mg L^{-1}	Plants were exposed in hydroponics. Decreased production of glucose-6-PO_4^{2-}, glucose-1-PO_4^{2-}, Reduced biomass and altered antioxidant defense, dose-dependent accumulation of Ti in root and shoot	Wu et al. (2017a)

Table 1 (continued)

Nanoparticle	Size (nm)	Test crop(s)	Dose rate	Activity/toxicity	References
Al_2O_3	13	*Z. mays, O. sativa*	2000 mg L^{-1}	Roots were exposed in deionized water for 5 days (*Z. mays*) and 7 days (*O. sativa*). No effect on seed germination; low phytotoxicity of Al_2O_3 nanoparticles was observed in maize only	Yang et al. (2015)
	< 50	*Sinapis alba*	10–1000 mg L^{-1}	Effects on germinating seeds were observed. At all concentrations, seed germination was affected negatively	Landa et al. (2016)
	< 50	*A. cepa*, *Z. mays*	0.1, 1 and 10 g L^{-1}	Plants were cultivated in liquid nutrient media. Highest Al accumulation in roots; highest translocation factors were recorded for *Zea mays* grown in liquid medium; results suggested that Al_2O_3 nanoparticles sediment certainly but are available for bio-uptake	Asztemborska et al. (2015)
	13	*T. aestivum*	5, 25, 50 mg mL^{-1}	Time (24–96 h) and dose dependent effects were observed. Reduction in root elongation by 40.2%, 50.6%, and 54.5% at 5, 25, 50 mg mL^{-1} after 96 h; callose deposition, lignin accumulation and cellular damage in roots cortex, enhanced peroxidase, Al_2O_3 nanoparticles induced DNA fragmentation	Yanlk and Vardar (2015b)
	13	*T. aestivum*	5, 25, 50 mg mL^{-1}	Effects on seedlings were observed for 96 h. Increased H_2O_2 content, superoxide dismutase activity, lipid peroxidation; reduced production of photosynthetic pigment and anthocyanin	Yanık and Vardar (2018)
α-Fe_2O_3, γ-Fe_2O_3 and Fe_3O_4	30, 20 and 20	*Citrus maxima*	50 mg L^{-1}	Nanoparticles were accumulated in plant roots; at 50 mg L^{-1}, nanoparticles were still in Fe deficiency state; chloroplast was very sensitive to nanoparticles, enhanced ferric reductase activity	Li et al. (2018a)
Fe_3O_4	6	*R. sativus,* *C. sativus, Spinacia oleracea,* *S. lycopersicon*	0.67 mg mL^{-1}	Inhibition of seed germination	García et al. (2011)
Cr_2O_3	50 nm	*G. max*	0.01, 0.05, 0.1 and 0.5 g L^{-1}	Reduction of 46.3% and 9.9% in biomass of root and shoot, respectively, inhibition of photosynthesis, RUBISCO activity	Li et al. (2018b)

Table 1 (continued)

Nanoparticle	Size (nm)	Test crop(s)	Dose rate	Activity/toxicity	References
CeO_2	10–30 nm	*Phaseolus vulgaris*	250–2000 mg L^{-1}	Stomatal morphology, photosynthesis, osmotic, and redox balance were impaired; electrolyte leakage increased with increasing concentrations of nanoparticles and altered electron transport chain biochemical machinery and photosynthesis	Salehi et al. (2018)

stage against different stresses. However, soon after absorption (imbibition) of water and concurrent onset of vegetative developmental processes, they become sensitive to all forms (physical, biotic and molecular) of stresses (Srivastava 2002). On the contrary, seeds have certain sensing mechanisms, which enable them to germinate even under nanoparticle stressed environment (Singh 2016). When exposed to nanoparticles, germination and development of many edible crops have been found to be adversely affected (Yan and Chen 2019). As compared to germination, root growth is, however, more sensitive to contamination (Rees et al. 2016) and inhibition of root elongation is linked with alteration in root architecture and morphology. As an example, Fe_3O_4 nanoparticles at 0.5–5 mg mL^{-1} reduce germination and development of *Cucumis sativus* roots (Mushtaq 2011). Similarly, Ag nanoparticles and ZnO nanoparticles significantly inhibited seed germination and root development of *B. oleracea* and *Z. mays* relative to corresponding free metal species (Pokhrel and Dubey 2013). Other nanoparticles like CuO, ZnO, Al_2O_3, and TiO_2 considerably inhibited germination and seedling growth of radish, tomato, wheat, and maize at the concentration range of 10–1000 mg L^{-1} (Atha et al. 2012), 50–1600 mg L^{-1} (Amooaghaie et al. 2017), 5–50 mg mL^{-1} (Yanlk and Vardar 2015a) and 0.02–2 g L^{-1} (Fellmann and Eichert 2017), respectively.

Toxicity to cell envelope and intracellular oxidative stress

Plant cell wall is the first site that is exposed to nanoparticles. The nanoparticles or their metal ions dissolved from nanoparticles enter into the cell wall of root tissues forming a complex with the –COOH groups of pectin (Jian et al. 2008). This binding may alter the symplastic or apoplastic mode of solute transport across the cell wall and membrane which leads to inhibition of root elongation (Horst et al. 2010). Moreover, the duration of exposure and metal concentration may also influence the cell wall rigidity (Kopittke et al. 2008). In a study, Fe nanoparticles appeared to be harmful to the plants and the majority of Fe nanoparticles were found to be aggregated into cell walls of *Capsicum annum* roots and then transported via apoplastic pathway potentially blocking the transfer of iron nutrients (Yuan et al. 2018). The plasma membrane is yet another target to which nanoparticles can bind and disrupt its physiological functions (Contini et al. 2018).

Depending on chemical composition, size, and charge of nanoparticles, the changes in membrane occur due to absorption and permeation by nanoparticles leading eventually to complete disruption of membrane permeability (Contini et al. 2018). Variation in physiological functions of biological membranes due to stressor molecules often causes structural alterations in the composition of membrane lipids and their peroxidation (Nasim and Dhir 2010; Meisrimler et al. 2011). The uptake of nanoparticles begins with initial adhesion onto cells and subsequent interactions with cell membrane stuff as described above. The internalization and translocation are then followed in an energy driven mode (Lesniak et al. 2013) ending sometimes in lysosomal accumulation (Salvati et al. 2011). Variation in the local stability of membranes (Wang et al. 2011b), membrane fluidity (Liu et al. 2009b), disruption of electron transport chain (Jhanzab et al. 2019), and dissipation of proton motive force (Mirzajani et al. 2014) are some of the toxic consequences of nanoparticles in plants. Among different nanoparticles, Fe_3O_4 nanoparticles, for example, when absorbed by pumpkin roots, caused local instability of the cell wall and/or membrane and thus produced oxidative stress (Wang et al. 2011a). Whole rice plant metabolomic analysis by 2-DE and NanoLC/FT-ICR MS analysis after exposure with Ag nanoparticles revealed protein precursor accumulation which was indicative of membrane proton motive force dissipation (Mirzajani et al. 2014). Further, gel-free/label-free proteomic analysis of whole wheat plants under chemo-blended Ag nanoparticles showed that proteins related to cell signaling, cell wall, and electron transport chain were decreased (Jhanzab et al. 2019). Among others, CuO nanoparticles also modify the lipid composition of wheat cell membranes in an adverse manner (Sharma and Uttam 2017).

Among stressors, metals have also been found to induce the intracellular production of reactive oxygen species including hydrogen peroxide, hydroxyl, and superoxide radicals (Reddy et al. 2005; Hayyan et al. 2016). The overproduction of reactive oxygen species due to add on pressure of nanoparticle is, however, common among edible crop plants, which further interact with many important plant biomolecules such as lipids, proteins, and cellular organelles. This reaction in turn induces membrane lipid peroxidation leading eventually to ion leakage, damage to photosynthetic apparatus, and consequently plant cell death (Sharma and Dietz 2009; Das and Roychoudhury 2014) (Fig. 5). The enhanced peroxidation of membrane lipids can serve as a biomarker for oxidative stress and also make changes in physiological properties of membranes. Three major among them are permeability, fluidity, and activity of membrane-bound ATPase (ATP synthase) (Shewfelt and Erickson 1991). Due to extremely short half-life, direct measurement of reactive oxygen species is not feasible; however, other by-products produced as a result of reactive oxygen species damage such as thiobarbituric acid reactive species are evaluated (Pryor 1991). The ultimate product of membrane lipid peroxidation is malondialdehyde, whose amount is directly related to oxidation of polyunsaturated fatty acids (PUFAs) (Song et al. 2016). When plant system becomes inefficient to scavenge the reactive oxygen species due to nanoparticle-mediated oxidative stress, malondialdehyde level increases sharply. For example, higher production of malondialdehyde by onion roots under ZnO nanoparticles and Zn^{2+} ions amended hydroponic nutrient solution could be attributed to enhanced intracellular reactive oxygen species generation leading to membrane lipid peroxidation and mitochondrial swelling (Kumari et al. 2011; Ahmed et al. 2017). In a study, even though the malondialdehyde was not detected in tissues of rice plants exposed to CeO_2 nanoparticles at 0–500 mg L^{-1}, ions were leaked due to instability of cell membrane (Rico et al. 2013a). Fe_3O_4 nanoparticles induced considerably high amount of membrane lipid peroxidation in seedlings of ryegrass and pumpkin as 248% and 210%, respectively, over control plants. Also, Fe_3O_4 nanoparticles blocked aquaporin channels inhibiting cellular respiration of roots linked to lipid peroxidation (Wang et al. 2011a). The reactive oxygen species as a prime cause of lipid peroxidation induced by Al_2O_3, CuO, and Co_3O_4 nanoparticles has also been recorded in various tissues of tomato and rape (Faisal et al. 2016; Ahmed et al. 2018a) (Fig. 17).

Impact on photosynthesis

Among other metabolic activities, photosynthesis is one of the significant physiological process of plants which is negatively affected by nanoparticles (Fig. 16) (Jampílek and Kráľová 2019). The toxic nanoparticles attack different photosynthetic apparatus (Sardoiwala et al. 2018), which leads to the following: (i) undesired deposition and distribution of nanoparticles leaf tissue such as mesophyll (Xiong et al. 2017), (ii) altered membrane physiology of photosynthetic apparatus (Rajput et al. 2018a), (iii) reduction in the formation of photosynthetic pigments (Rajput et al. 2019), (iv) variation in cytosolic enzymes and organics (Tighe-Neira et al. 2018), (v) changes in the functioning of photosystem (Fig. 18). Among nanoparticles, CuO nanoparticles have been reported to reduce chlorophyll content in green gram (Gopalakrishnan Nair et al. 2014), field mustard (Chung et al. 2019a), and decreased net photosynthesis rate in cucumber (Hong et al. 2016) and rice (Da Costa and Sharma 2016).

Similarly, photosynthetic pigment content in cowpea (Jahan et al. 2018), maize (Wang et al. 2016a), tomato (Amooaghaie et al. 2017), and wheat (Tripathi et al. 2017) was reduced by ZnO nanoparticles. Besides, nanoparticles of ZnO, CuO, Al_2O_3 (Yanık and Vardar 2018) and TiO_2 (Rafique et al. 2018) also caused a significant reduction in chlorophyll production by wheat foliage. Also, exposure of *Lemna gibba* plants to CuO nanoparticles for 45 h resulted in the inactivation of photosystem-II reaction center and increased dissipation of thermal energy (Perreault et al. 2014). Similarly, the photosynthesis of soybean exposed to 0.01, 0.05, 0.1, and 0.5 g L^{-1} of Cr_2O_3 nanoparticles suspensions was inhibited. The maximum quantum yield of photosystem-II (Fv/Fm) decreased up to 22% which indicates the destruction of photosynthetic apparatus by Cr_2O_3 nanoparticles (Li et al. 2018b). In a study, Cu nanoparticles maximally decreased chlorophyll-a content by 33%, whereas Ni nanoparticles decreased chlorophyll-b content by 68% in wheat seedlings after 2 days of exposure (Korotkova et al. 2017). Similarly, Ag nanoparticles also reduced photosynthesis in *S. polyrhiza* by inhibiting the photoprotective capacity of photosystem-II and RUBISCO activity which resulted in reduced CO_2 assimilation associated with a decrease in solar energy consumption (Jiang et al. 2017). Likewise, CeO_2 nanoparticles notably reduced total chlorophyll in tomato plants grown for 210 days in pot soils mixed with 250 mg kg^{-1} of citric acid coated CeO_2 nanoparticles (Barrios et al. 2016).

Nanoparticle-mediated enhancement in antioxidant enzyme activity

Nanoparticle-induced intracellular oxidative stress in plants leads to enhanced antioxidant activity, and their measurement serves as a toxicity bio-indicator (Sardoiwala et al. 2018). This system comprises the single or combined role of antioxidant enzymes such as peroxidases (glutathione peroxidase, ascorbate peroxidase, and guaiacol peroxidase), superoxide dismutase, and catalase. Moreover, low molecular weight compounds including phenolic compounds, various carotenoids, ascorbate, glutathione, α-tocopherols, and proline are also produced in higher amounts by plant system in response to the damaging impact of reactive oxygen species under nanoparticles stress (Das and Roychoudhury 2014; Getnet et al. 2015; Ozyigit et al. 2016). These are the candidates which either independently or simultaneously act to decrease the elevated level of oxidative destruction. As an example, catalase and superoxide dismutase synergistically convert first superoxide ions $[O{-}O]^{2-}$ to hydrogen peroxide (H_2O_2) and then to H_2O and O_2 with additional role of reduction of hydroxyl radicals ($^{\cdot}OH$), whereas peroxidases act as scavenger of reactive oxygen species.

Plant–nanoparticles interactions have also shown increased production of these enzymes in a concentration dependent manner. As an example, ZnO nanoparticles enhanced the secretion of non-enzymatic antioxidant molecules and thus anti-oxidative response at a concentration range of 500–1500 µg L^{-1} in black mustard (Zafar et al. 2016). Similarly, CeO_2 nanoparticles at 400 mg kg^{-1} caused a 39-fold increase in catalase activity of shoot as compared to control; however, catalase activity was declined by 30-fold at 800 mg kg^{-1}. In a likewise study, Fe_3O_4 nanoparticles induced the higher production of two major antioxidant enzymes (catalase and superoxide dismutase) over bulk material of Fe_3O_4 without travelling from roots to aerial parts (Wang et al. 2011a). The enhanced enzyme activity could be due to the physical blockage of root pores, thus considerably reducing water and nutrient uptake (Ma et al. 2013d; Martínez-Fernández et al. 2015). Similarly, reduced activity of ascorbate peroxidase was recorded under CeO_2 nanoparticle (800 mg kg^{-1}) treatment with a concurrent decline in H_2O_2. These studies suggest that anti-oxidant enzymes activities are decreased (Mukherjee et al. 2014) or increased (Kim et al. 2011) in plant cells based upon the exposure, plant organ, and concentration of test nanoparticles. Taking another example, Amooaghaie et al. assessed the impact of varying concentrations of Zn and ZnO nanoparticles on tomato and wheat plants (Amooaghaie et al. 2017). At 100 mg L^{-1}, both nanoparticles slightly enhanced the activity of three enzymes peroxidase, ascorbate peroxidase, and catalase in both test crops, whereas, at 200 mg L^{-1}, both nanoparticles significantly enhanced the superoxide dismutase level, only in wheat foliage.

Mutations, chromosomal anomalies, and destruction of genetic material

In addition to the physiological impacts, nanoparticles can also induce genotoxic effects either directly or indirectly in plants (Table 2). Of these, physical interactions between DNA and nanoparticles cause direct genotoxic impact altering or modifying (i) phosphorylation, (ii) DNA stacks among DNA bases, (iii) gene regulation/expression, and (iv) trigger adduct formation. The later one can result from altered gene expression due to inhibition of DNA repair mechanisms (Karami Mehrian and De Lima 2016; Ghosh et al. 2019). Plant cell with low number of chromosomes can help to visualize the genotoxic impact of nanoparticles and hence is incorporated in genotoxic studies as a testing model. While assessing the genotoxic impact of nanoparticles, the following toxicological endpoints are considered: appearance of aberrant chromosomes during mitosis or meiosis, change in ploidy levels, exchange between sister chromatids, DNA lesions, and genetic mutations (Pakrashi et al. 2014; Ghosh et al. 2015).

Some examples of chromosomal aberrations, genotoxicity and DNA damage are shown in Fig. 19. In this context, *A. cepa* chromosomal aberration bioassay has been used for genotoxicity assessment in several studies. By using *A. cepa* model, chromosomal aberrations like broken chromosomes, bridges, stickiness, laggings, disorientation during anaphase, disturbed metaphase, and one or many micronucleus by nanoparticles of Al_2O_3 (Rajeshwari et al. 2015), Ag (Cvjetko et al. 2017), Zn (Taranath et al. 2015), ZnO (Sun et al. 2019b), bismuth (III) oxide (Liman 2013), TiO_2 (Pakrashi et al. 2014), and Cu (Nagaonkar et al. 2015) have been documented in *A. cepa* root cells. Moreover, metaphasic and anaphasic disorientation in root meristem cells of *Vicia faba* seedlings after 72 and 120 h exposure of Ag nanoparticles

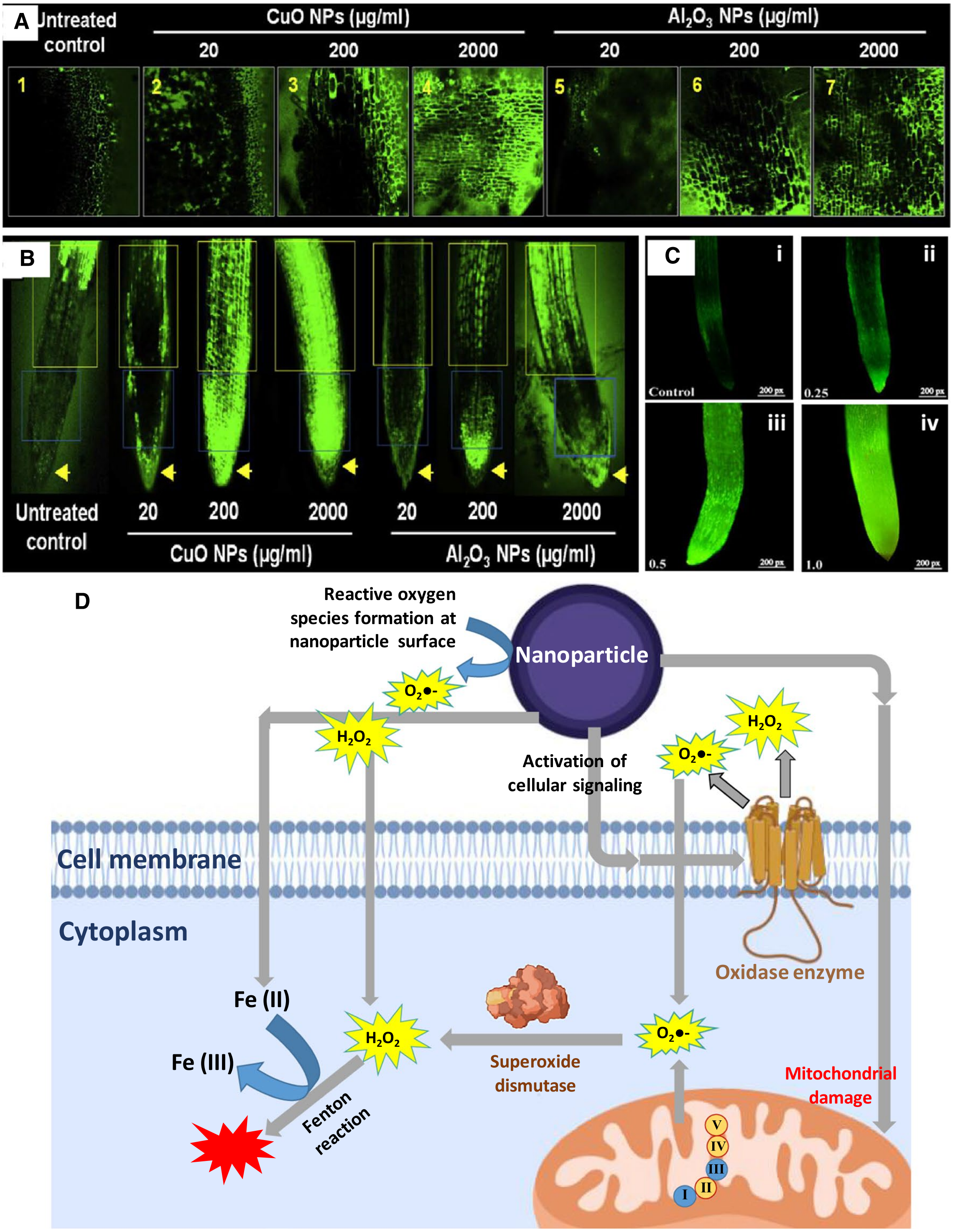


Fig. 17 Nanoparticles induced reactive oxygen generation in plants: confocal laser scanning microscopic analysis of tomato roots and leaf reveals tissue wide localization of enhanced intracellular reactive oxygen species following the exposure to Al_2O_3 and CuO nanoparticles (NPs) compared to controls. Generation of intracellular oxidative stress is shown in panels A2−A4 for CuO nanoparticles treatment and panel A5−A7 for Al2O3 nanoparticles treatment over untreated control of leaf (panel A1). Panel B depicts reactive oxygen species localization in tomato roots. Two physiologically distinct root zones as elongation and meristematic zone are denoted by yellow and blue rectangles, while arrowheads point toward root tip. Adapted with permission from (Ahmed et al. 2018a). Panel C shows the reactive oxygen species generation in roots of eggplant after exposure with Co3O4-nanoparticles. As in tomato roots, green fluorescence specifies reactive oxygen species production at varying concentrations of Co_3O_4-nanoparticles. Adapted with permission from (Faisal et al. 2016). Panel D shows the pathways for the induction of intracellular reactive oxygen species mediated primarily by hydrogen peroxide, superoxide, and hydroxyl radicals

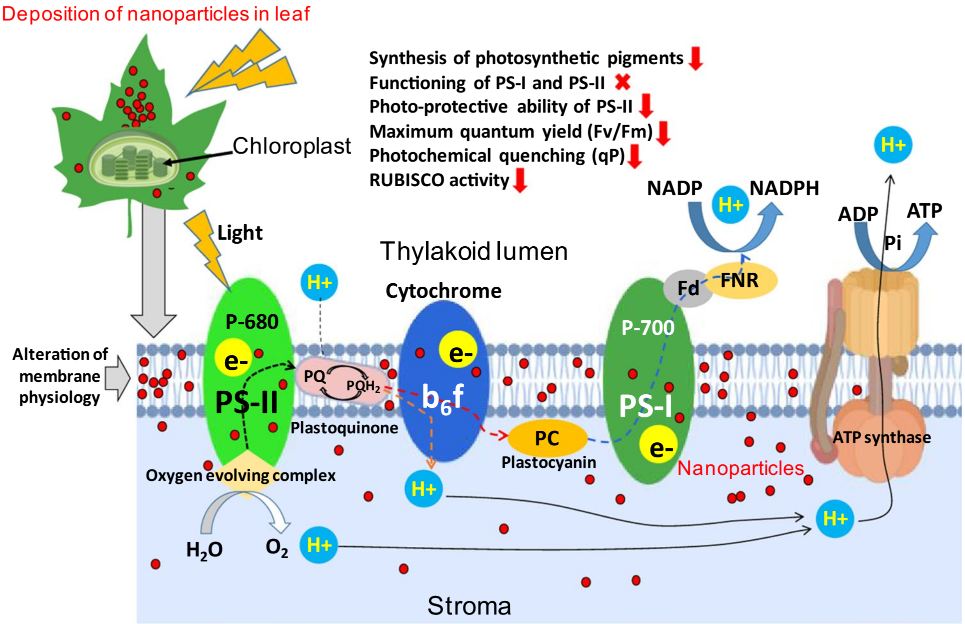


Fig. 18 Nanoparticles induced reactive oxygen generation in plants: Confocal laser scanning microscopic analysis of tomato roots and leaf reveals tissue wide localization of enhanced intracellular reactive oxygen species following the exposure to Al_2O_3 and CuO nanoparticles (NPs) compared to controls. Generation of intracellular oxidative stress is shown in panels A2–A4 for CuO nanoparticles treatment and panel A5–A7 for Al_2O_3 nanoparticles treatment over untreated control of leaf (panel A1). Panel B depicts reactive oxygen species localization in tomato roots. Two physiologically distinct root zones as elongation and meristematic zone are denoted by yellow and blue rectangles, while arrowheads point toward root tip. Adapted with permission from (Ahmed et al. 2018a). Panel C shows the reactive oxygen species generation in roots of eggplant after exposure with Co3O4-nanoparticles. As in tomato roots, green fluorescence specifies reactive oxygen species production at varying concentrations of Co_3O_4-nanoparticles. Adapted with permission from (Faisal et al. 2016). Panel D shows the pathways for the induction of intracellular reactive oxygen species mediated primarily by hydrogen peroxide, superoxide, and hydroxyl radicals

is evident (Abou-Zeid and Moustafa 2014). Genotoxicity of TiO_2 nanoparticles has been confirmed by evaluating DNA comets and ladders. The formation of micronucleus and other chromosomal anomalies validated the genetic manipulation by nanoparticles in preceding cell cycle (Rico et al. 2011). In a study, Xi et al. reported that TiO_2 nanoparticles caused purine oxidation which may cause abrupt DNA replication (Xi et al. 2004). Atha et al. reported DNA lesions caused by CuO nanoparticles in grasses and radish plants (Atha et al. 2012). Considerable accumulation of oxidatively modified three mutagenic DNA base lesions was recorded using GC–MS along with isotope dilution method.

Impact on gene expression, miRNA, proteome and metabolome

The nanoparticles have been reported to alter the gene expression (Table 3), proteome (Table 4), miRNA expression, and metabolome (Table 5) of various crops. Most of the gene expression and miRNA profiling studies have, however, been focused on assessing the impact of nanoparticles on *A. thaliana* gene expression and *N. tabacum* miRNA, both of which are not essentially food crops. Still, several attempts have been made to evaluate the impact of nanoparticles on proteome and metabolome of various cereal, legume, and vegetable crops including wheat, rice, beans, and cucumber. The impact of nanoparticles on gene expressions employing DNA microarrays for *A. thaliana* (Landa et al. 2012; García-Sánchez et al. 2015) while exposing roots to nanoparticles prepared from Ag and TiO_2 for 7 days has shown that nanoparticles suppressed the transcriptional response which is generally needed for resisting and combating the colonization of microbial pathogens. Gene transcription required in phosphorus starvation and for development of roots was inhibited. Likewise, the microarray analysis of *A. thaliana* roots grown with fullerene, ZnO, and TiO_2 nanoparticles revealed that genes for both abiotic and biotic stress response factors such as oxidative stress and wounding were up-regulated, while gene expression essential for maintaining cellular organization and biogenesis was significantly inhibited due to ZnO nanoparticles stress (Landa et al. 2012). In another study, the expression of genes associated with glutathione biosynthesis and sulfur assimilation was altered causing eventually the genotoxicity to *A. thaliana* raised with 50–500 mgCeO_2 nanoparticles L^{-1} of CeO_2 (Ma et al. 2013a). In an identical experiment, it was reported that

Table 2 Genotoxicity of nanoparticles to crop plants

Type of nanoparticle	Characteristics of nanoparticles	Crop	Concentrations tested	Exposure conditions	Toxicity markers	Toxic effect	References
TiO_2	**Size:** spherical < 20 nm by SEM, **Dispersion:** in deionized water, sonication for 30 min	*T. aestivum*	20–100 mg kg^{-1} soil	60 days exposure in soil (sandy loam, pH 7.6)	MN	53.65% at 80 mg kg^{-1} and 62.5% at 100 mg kg^{-1}	Rafique et al. (2018)
Zero valent Fe^0 (nZVI)	**Size:** nZVI-1 (49 nm), nZVI-2 (57 nm), **Dispersion:** in ultrapure water (at 40 W for 15 min), **Size by DLS:** 211 and 254 nm **ZP:**—18.76 to—35.7 mV	*A. cepa*	125, 250, 500 mg L^{-1}	Exposure in hydroponic environment for 24 h at 25 ± 2 °C	MI, MN, CA, NA, DNA comets	Significant reduction in MI from 14.62 ± 1.79% in control to 9.63 ± 0.05% by nZVI-1 and 10.2 ± 1.16% by nZVI-2, Increase in MN by 1.3% under nZVI-1 and 0.4% under nZVI-2 exposure, Significant increase in CAs from 0.19 ± 0.1% in control to 12.67 ± 0.32% by nZVI-1 and 4.24 ± 0.37% by nZVI-2, Significant increase in NA from 0.09% in control to 6.02% by nZVI-1 and 3.23% by nZVI-2, Comet assay revealed increased DNA damage by 35% by nZVI-1 and 20.35% by nZVI-2 compared to control (3–4%)	Ghosh et al. (2017)
Fe_2O_3	**Size:** 22.3 ± 3.1 nm by TEM, and 271 ± 2.4 nm by DLS with ZP of 4.1 ± 0.9 mV **Dispersion:** in ultrapure water (at 40 W for 15 min)	*R. sativus*	0.25–2 mg mL^{-1}	Seeds were exposed for 2 h in rotatory shaker followed by transfer on Petri dish and incubation for 4 days at 25 ± 2 °C	DNA comets	Concentration dependent increase in DNA strand breaks	Saquib et al. (2016)

Table 2 (continued)

Type of nanoparticle	Characteristics of nanoparticles	Crop	Concentrations tested	Exposure conditions	Toxicity markers	Toxic effect	References
NiO	**Size:** 1100–1250 nm by DLS as compared to 33.65 nm recorded by TEM with ZP of 8.42 ± 3.77 mV dispersed in ultrapure water and sonicated at 60 W, 40 kHz for 45 min	Seeds of *A. cepa, A porrum, A. sativum, A. fistulosum* *seeds, A. schoenoprasum*	0–500 mg L^{-1}	Seeds were exposed for 6 h in rotatory shaker followed by washing and transfer on Petri dish and incubated for 7 days at 23 ± 1 °C	MI, CA, MN	Significant reduction in MI from 70% in control to 20% in treatment, Chromosomal breaks as 0.4% in control and 1.6% in treatment, MN as 3% in control and 7% in treatment	Manna and Bandyopadhyay (2017)
Al_2O_3	**Size:** 121–479 nm as recorded by DLS with ZP of -16.5 ± 6.12 mV, dispersed in Milli-Q water, sonicated at 130 W for 30 min	*A. cepa*	0–5 µM	Onion bulbs were exposed in hydroponic solutions for 24 h at 28 ± 0.5 °C	MI, MN, CA, Comet analysis	Significant reduction in MI from 15.22% in control to 4.06% by Al_2O_3 nanoparticles Increase in MN by 2.24, Significant increase in CAs Comet assay revealed increased DNA damage by Al_2O_3 nanoparticles as 10% compared to control (2%)	De et al. (2016)
ZnO	**Size:** 100 nm and 285–317 nm as recorded by TEM and DLS, dispersed in Milli-Q water, sonicated at 100 W, 30 kHz for 30 min	*V. faba* seeds, *A. cepa* roots, and *N. tabacum* seedlings	0.2–0.8 g L^{-1}	Exposure was given in hydroponic for 24–48 h at 25 ± 1 °C	MI, MN, CA, Comet analysis	**MI:** *A. cepa* control 6.78%, treated 0.62% *V. faba* control 4.91%, treated 0.38% **MN:** 4.9% and 19.3% increase in *A. cepa* and *V. faba*, respectively **CA:** 0.18% and 0.19% increase in *A. cepa* and *V. faba*, respectively **Comet:** *A. cepa* control 4%, treated 24% *N. tabacum* control 4%, treated 9.5%	Ghosh et al. (2016)

Table 2 (continued)

Type of nanoparticle	Characteristics of nanoparticles	Crop	Concentrations tested	Exposure conditions	Toxicity markers	Toxic effect	References
Ag (surface functionalized with PVP, citrate and CTAB)	Size ranged between 5 and 50 nm, **Dispersion:** in distilled water	*A. cepa*	0–100 µM	Exposure was given in hydroponic for 72 h at 25 °C	Comet	Number of comets increased significantly compared to control in the following order Ag-ions > CTAB-Ag nanoparticles > PVP-Ag nanoparticles > citrate-Ag nanoparticles	Cvjetko et al. (2017)

TEM: transmission electron microscopy; DLS: dynamic light scattering; ZP: zeta potential; MI: mitotic index; MN: micronucleus index; CA: chromosomal aberration; and NA: nuclear aberration.

the two genes *ORF31* (152u) and *BIP3* (005u) were consistently modulated by CeO_2 nanoparticles, CuO nanoparticles, and La_2O_3 nanoparticles (Pagano et al. 2016) suggesting that these genes can be considered as potential biomarker for identifying the toxicity of nanoparticles to *Cucurbita pepo* and *Solanum lycopersicum*.

The micro-RNA gene expression analysis of *A. thaliana* (Nair and Chung 2014) and *N. tabacum* (Burklew et al. 2012) after nanoparticle exposure is reported. The miRNA can be defined as the small non-coding RNA typically ranging between 22 and 25 nucleotides (Ahmad et al. 2013), acting as an endogenous post-transcriptional regulator of gene expression either by (i) inhibiting or (ii) degrading messenger RNAs (mRNAs) preventing their translation. The miRNAs also control plant response to abiotic stress by mediating expression of related genes. Since nanoparticles alter the gene expression in non-edible plants like tobacco and *A. thaliana*, it is expected that they can also influence the genetic expression in edible crop plants. As an example, carbon nanoparticles stimulated production of aquaporin proteins and enhanced water uptake in tobacco cells (Khodakovskaya et al. 2012). In a study, Al_2O_3 nanoparticles up-regulated the expression of miRNA genes, which helped in the survival of tobacco plants. To substantiate this, *N. tabacum* plant was exposed to 0–1% concentration of Al_2O_3 nanoparticles. As the concentration of Al_2O_3 nanoparticles increased, the biological attributes such as biomass accumulation, root volume, and number of leaves were significantly decreased. Studies on gene expression of at least nine miRNAs with known functions of reducing abiotic stress in plants showed that increasing concentrations of Al_2O_3 nanoparticles considerably up-regulated the miRNAs gene expression (Burklew et al. 2012). In a similar study, two miRNA genes (miR399 and miR395) of tobacco plant under 0.1% and 1% TiO_2 nanoparticle's exposure caused a drastic change in gene expression as 143- and 285-fold, respectively, suggesting the adverse impact of TiO_2 nanoparticles on plant growth and development (Frazier et al. 2014).

Programmed cell death induced by nanoparticles

Apoptosis or programmed cell death is another cytotoxic outcome of nanoparticle's interaction with plant cells. However, there are very few reports on nanoparticles induced apoptosis. In this regard, four pioneer studies have reported apoptosis by nanoparticles of NiO and Co_3O_4, single- and multi-walled carbon nanotubes. In a comet assay and flow cytometry-based analysis of apoptosis in tomato roots, a significant increase in dead cells due to emergence of apoptotic (21.8%) and necrotic (24%) cell population was observed when roots were exposed to 2 mgNiO nanoparticles mL^{-1} (Faisal et al. 2013) compared to negative control (Fig. 20A–D). Data recorded through flow cytometric

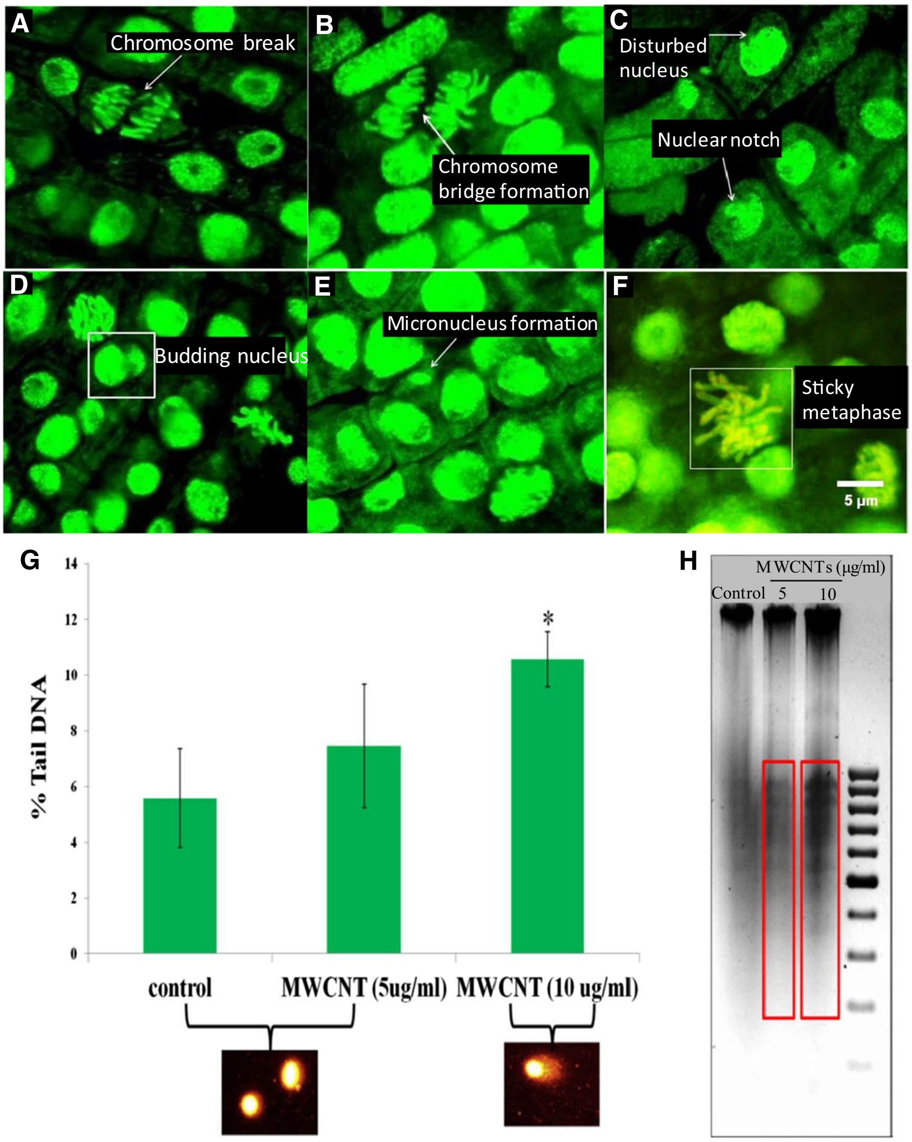


Fig. 19 Genotoxicity and DNA damage induced by nanoparticles. Chromosomal anomalies after exposure to TiO2 nanoparticles in *A. cepa* root meristem cells: panels A and B show two types of anomalies in chromosome fragments, while panels B–D represent nuclear damage and formation of micronuclei. Panel F indicates metaphasic stickiness during the arrangement of chromosomes at metaphasic plate. Adapted with permission from (Pakrashi et al. 2014). Panels G shows formation multi-walled carbon nanotubes (MWCNTs) induced formation of DNA tail in root nuclei of *A. cepa*. Comet data at 10 µg multi-walled carbon nanotubes mL^{-1} were significant at $P < 0.05$ over untreated control. Micrographs at the bottom of bar diagram show representative comets with varying degree of DNA tail formation. Panel H is for DNA laddering of DNA incubated with or without multi walled carbon nanotubes. Bands highlighted in in agarose gel in red correspond to internucleosomal fragments. Adapted with permission from (Ghosh et al. 2015)

experiments revealed a 65.7% increase in dead cells and more than twofold higher activity of caspase-3-like proteases activity at 2 mgNiO nanoparticles mL^{-1}. The apoptosis and necrosis are two different events, which follow some major steps of cytotoxicity illustrated in Fig. 20. Two pathways for apoptosis are widely known intrinsic and extrinsic.

In the study of NiO nanoparticles and tomato root interaction, mitochondrial-dependent intrinsic pathway has been suggested which could be assigned to release of Ni^{2+} ions in the solution from NiO nanoparticles (Faisal et al. 2013). It has also been reported that apoptosis-mediated toxicity in some vegetables, for example, eggplant occurred, when it was exposed to Co_3O_4 nanoparticles (Faisal et al. 2016). Exposure of eggplants to cogrowth enhancing impact as depicted O_4 nanoparticles (1 mg mL^{-1}) revealed approximately 2.4-fold greater DNA damage using comet assay, while cell cycle measurement through flow cytometry exhibited 73.2% more apoptotic cells as compared to negative control (Faisal et al. 2016). In a different study, single-walled carbon nanotubes caused condensation of chromatin fibers with simultaneous production of enhanced intracellular oxidative stress in rice cell suspensions (Shen et al. 2010). Besides, single-walled carbon nanotubes-induced apoptosis was also noticed at 25 µg single-walled carbon nanotubes mL^{-1}. It has also been reported that multi-walled carbon nanotubes in an identical manner can damage rice cells in suspension (Tan et al. 2009) which could probably be mediated by apoptosis at low concentration. On the other hand, higher dose of nanoparticles can inhibit plant growth by induction of necrosis as revealed by alteration of cell membrane permeability leading to the leakage of cytoplasmic fluid. As an alternative way of protecting the large population of cells, rice cells when treated in suspension can precipitate a

Table 3 Transcriptomic studies of nanoparticle–plant interaction

Nanoparticle	Size (nm)	Plant	Plant organ	Dose rate	Total age of plant at treatment	Exposure time	Observation	Overall impact	References
TiO_2	10, 20 and 40	*A. thaliana*	Both roots and aerial part	20 mg L^{-1}	21 days	2 days	No effect	TiO_2 nanoparticles exposure showed almost similar gene expression pattern among the treatments, the impact was very low as compared to salinity, drought, and wounding stress	García-Sánchez et al. (2015)

Table 3 (continued)

Nanoparticle	Size (nm)	Plant	Plant organ	Dose rate	Total age of plant at treatment	Exposure time	Observation	Overall impact	References
TiO_2	33	*A. thaliana*	Both roots and aerial part	500 mg L^{-1}	Seeds	12 days	Positive effect	RT-qPCR analysis showed altered expression of 204 genes, which include the genes associated with oxidative stress, salt stress, transport of water, and respiratory burst. Additionally, a range of metabolic processes was affected	Tumburu et al. (2015)

Table 3 (continued)

Nanoparticle	Size (nm)	Plant	Plant organ	Dose rate	Total age of plant at treatment	Exposure time	Observation	Overall impact	References
TiO_2	33	*A. thaliana*	Both roots and aerial part	500 mg L^{-1}	Seeds	29 days	Nil impact	Microarray analyses showed alteration in transcriptomes of rosette leaves with large number of differentially expressed genes (DEGs), TiO_2 nanoparticles affected photosynthesis associated genes, more DEGs were altered in rosette leaves than those in roots	Tumburu et al. (2017)

Table 3 (continued)

Nanoparticle	Size (nm)	Plant	Plant organ	Dose rate	Total age of plant at treatment	Exposure time	Observation	Overall impact	References
CuO	25–55	*Brassica rapa*	Whole seedlings	50–500 mg L^{-1}	Seeds	15 days	Negative effect	RT-PCR analysis revealed transcriptional alteration of genes associated with biosynthesis of phenolics and oxidative stress, significant up regulation of antioxidant genes was noticed	Chung et al. (2019b)
ZnO	20	*A. thaliana Col-0*	Roots	4 mg L^{-1}	28 days	7 days	Negative effect	Microarray analyses exhibited up-regulation of 416 genes including stress response genes and down-regulation of 961 genes including nucleic acid metabolism, biogenesis, and cell organization	Landa et al. (2015)

Table 3 (continued)

Nanoparticle	Size (nm)	Plant	Plant organ	Dose rate	Total age of plant at treatment	Exposure time	Observation	Overall impact	References
CuO	30–50	*A. thaliana Bay-0*	Roots	10 mg L^{-1}	15 days	2 h	Negative effect	Microarray showed variable gene expression, of those genes, 47 were up-regulated genes were found associated with oxidative stress	Tang et al. (2016)

fraction of cell population with test nanoparticles thus safe guarding others. This is an indirect mode of self-defense minimizing the nanoparticle's risk (Rico et al. 2011).

Plausible mechanism of nanoparticles' toxicity to crops

From the literature reviewed and the experimental results obtained so far on the toxic behavior of nanoparticles beginning with absorption by leaves and roots to translocation and accumulation in various organs of actively growing plants, the phytotoxic events leading to the death of plants (Fig. 21) can be categorized into the following steps: (i) Adsorption: nanoparticles are adsorbed onto the surface of leaf and root due to repulsive and attractive forces; (ii) uptake: the uptake of nanoparticles inside the cells depends largely on the pore size of cell wall and size of nanoparticles. However, the nanoparticles have been observed to increase the porosity of plant cell membrane. (iii) Internalization: after successful adsorption, the infiltration (internalization) of nanoparticles inside the cell occurs which are then deposited onto various cellular organelles such as the tonoplast of vacuoles; (iv) Translocation: translocation of nanoparticles proceeds via vascular tissues (e.g., xylem) to different plant organs. Cell-to-cell movement of nanoparticles occurs through intracellular junctions. Nanoparticles start disrupting cellular homeostasis with their sequestration on the nuclear membrane, degenerate nuclear constituents, and dissipate mitochondrial membrane potential (ΔΨm) and sometimes the appearance of swollen mitochondria; (v) disruption of homeostasis; (vi) genotoxicity: nanoparticles also exhibit genotoxic effect and cause DNA damage as revealed by disruption of mitosis (mitotic index) and induction of chromosomal aberrations. Also, nanoparticles induce caspase-dependent degradation of nuclear DNA (sub-G1 phase) which indicates apoptosis; (vii) lipid peroxidation and antioxidant generation: nanoparticles increase lipid peroxidation (malondialdehyde content) and generation of intracellular reactive oxygen species ($O_2^{\cdot-}$, $OH^{\cdot}$, and H_2O_2) which are responsible for alteration in ΔΨm; (viii) destruction of physiological and metabolic functions leading to reduction in biological attributes and yield of plants; and (ix) death of plants due to one or simultaneous activity of nanoparticles. Conclusively, when composition, concentration, size, morphology, and surface adsorbing ability of nanoparticles differ, the toxic impact of nanoparticles is very likely to change dramatically. Hence, the phytotoxicity mechanism of nanoparticles requires further elaborative research. In this regard, a few cutting-edge molecular strategies such as proteomics and genomics are likely to enhance the understanding on phytotoxicity of nanoparticles.

Table 4 Proteomic studies of nanoparticle–plant interaction

Nanoparticle	Size (nm)	Plant	Plant organ	Dose rate	Total age of plant at treatment	Exposure time	Observation	Overall impact	References
Ag	18.3	*O. sativa*	Whole plant	30 and 60 mg L^{-1}	10 days	20 days	Negative effect	The Ag nanoparticles resulted in protein precursor accumulation indicative of proton motive force dissipation, proteins measured were involved in Ca^{2+} regulation, cell signaling, transcription, oxidative stress mitigation, cell division, protein degradation, cell wall and apoptosis	Mirzajani et al. (2014)

Table 4 (continued)

Nanoparticle	Size (nm)	Plant	Plant organ	Dose rate	Total age of plant at treatment	Exposure time	Observation	Overall impact	References
PVP-Ag	10	*T. aestivum*	Roots and shoots	10 mg L^{-1}	Seeds	5 days	Negative effect	2-DE based proteomic analysis revealed relatively low amount of differentially expressed proteins (DEPs), exposure induced changes in redox regulation, sulfur metabolism, change in protein synthesis associated with endoplasmic reticulum and vacuoles	Vannini et al. (2013)
CeO_2	8	*P. vulgaris*	Seeds	62.5–500 mg kg^{-1}	Seeds	102 days	No effect	Proteomic analysis showed up regulation of stress related proteins at 62.5 and 125 mg kg^{-1}, major proteins associated with nutrient storage (phaseolin) and carbohydrate metabolism (lectins) were down-regulated	Majumdar et al. (2015)

Table 4 (continued)

Nanoparticle	Size (nm)	Plant	Plant organ	Dose rate	Total age of plant at treatment	Exposure time	Observation	Overall impact	References
Al_2O_3	30–60	*G. max*	Root including hypocotyl	5–500 ppm	2 days	1–3 days	Positive effect	Using gel-free (nano-LC MS/MS), proteins that were significantly altered by Al_2O_3 nanoparticles were mainly associated with energy metabolism, hierarchical clustering analysis, proteins associated with glycolysis exhibited major changes in abundance, among all responsive proteins, major population was found related to protein synthesis or degradation, lipid metabolism and glycolysis	Hossain et al. (2016)
Al_2O_3	30–60	*G. max*	Root	5–500 ppm	2 days	2–4 days	Positive effect	211 proteins of cell wall, protein synthesis, stress and signaling were up regulated	Yasmeen et al. (2016)

Table 4 (continued)

Nanoparticle	Size (nm)	Plant	Plant organ	Dose rate	Total age of plant at treatment	Exposure time	Observation	Overall impact	References
Chemo blended-Ag	15–20	*T. aestivum*	Whole plant		6 days	11 days	Positive effect	Gel-free/label-free proteomic analysis showed that proteins related to photo- and protein synthesis were increased, whereas cell signaling, glycolysis, cell wall, redox, mitochondrial electron transport chain related proteins were decreased	Jhanzab et al. (2019)

Table 5 Metabolomic and micro-RNA profiling studies of nanoparticle–plant interaction

Nanoparticle	Size (nm)	Plant	Plant organ	Dose rate	Targeted organ	Exposure time	Observation	Overall impact	References
micro-RNA (miRNA) profiling studies									
Al_2O_3	Not specified	*N. tabacum*	Whole plant	0.1%, 0.5% and 1%	Seeds	21 days	Negative effect	Four micro-RNAs related to plant stress management showed remarkable enhanced expression when plants were exposed to 1% w/v Al_2O_3 nanoparticles	Burklew et al. (2012)
TiO_2	<25	*N. tabacum*	Whole plant	0.1% and 1%	Seeds	21 days	Negative effect	TiO_2 nanoparticles greatly enhanced the expression of miR399 and miR395 by 143 and 285, respectively	Frazier et al. (2014)
Metabolomic studies									
CeO_2	10–30	*P. vulgaris*	Whole plants	250–2000 mg L^{-1}	Leaves sprayed for 14 days on leaves or added in soil after every 48 h	15 days	Negative effect	Foliar application of CeO_2 nanoparticles enhanced the bio-uptake of Ce, which caused production of proline up to 0.65 mg g^{-1}, production of phyto-siderophores like mugineate and muconate was found increased by more than 16-fold, translation of folding related proteins was also increased	Salehi et al. (2018)
Cu	40	*C. sativus*	Mixture of exudates	10–20 mg L^{-1}	Exudates from root and leaves	21 days		^{1}H-NMR, GC–MS and ICP-MS revealed interference of Cu nanoparticles with the accumulation of micro- and macro-elements including P, Mo, Na, Fe, Zn, and S, some metabolic alterations were also noticed in exudation pattern of roots and leaves, Cu nanoparticles caused up-regulation of ascorbic acid, amino acids, and phenolic compounds related gene, however, genes associated with citric acid were down-regulated	Zhao et al. (2016a)

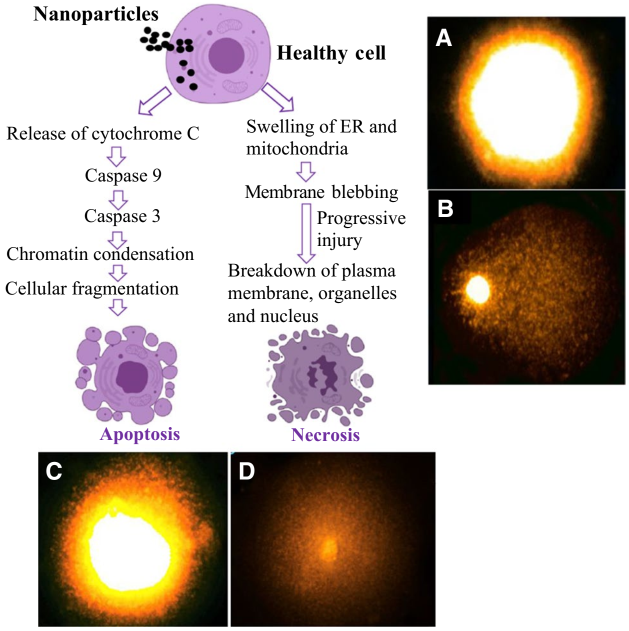


Fig. 20 Apoptosis and cell death induced by nanoparticles: sequence of events starting from the interaction of nanoparticles with plant cells ending in cell death by either apoptosis or necrosis. Panels A and B show untreated cell (negative control) and ethylmethane sulfonate (2 mM) treated cell (positive control) of tomato roots. Nickel oxide nanoparticles at 2 mg mL^{-1} caused apoptosis (panel C) and necrosis (panel D) in nuclei of tomato roots. Figures in panels A–D are adapted with permission from (Faisal et al. 2013)

Beneficial impacts of nanoparticles on plants

Nanoparticles exhibit negative effects on physiology, morphology, overall plant development, and yield of many agriculturally important crops, yet they have also been found exhibiting plant growth enhancing impact as depicted in Fig. 22. The beneficial impacts also vary with growth stage of plants, test species of nanoparticle and plants, exposure concentration and condition, and duration of treatment. Some examples are summarized in Table 6. The positive impact of nanoparticles on major growth parameters leading to enhancement in yield of some useful crops is explained in the following sections.

Enhancement of nutrient absorption and water uptake

Some nanoparticles may positively affect the nutrient uptake and water absorption from soils as reported in few studies. For instance, ZnO nanoparticles significantly affect three major growth factors in mung bean rhizosphere including the availability of soluble form of phosphorus, root colonization by growth promoting microbes, and increased root surface area (Raliya et al. 2016b). The overall increased growth of mung bean plants has been attributed to enhanced activity of dehydrogenase enzyme indicating microbial metabolic activity, which produces organic acids and thus increases the available forms of phosphorus in soil for subsequent plant uptake. The rhizospheric microbial population regulates soil fertility by performing essential biogeochemical cycling of nutrients (Raliya et al. 2016b). In another study, dissolution of Zn^{2+} ions from ZnO nanoparticles and their internalization in plant cells was found beneficial for the activity of carbonic anhydrase mediating more carbon dioxide fixation into carbohydrates. The combination of nanoparticles such as SiO_2 with TiO_2 has also been found to increase the nitrate reductase activity which catalyzes nitrate (NO_3^-) to nitrite (NO_2^-) and intensifies the absorption capacity of plants, which in effect enhances the uptake of soil nutrients and water (Rico et al. 2011). Some metallic and metal–oxide nanoparticles tested against tomato plants increased Ca content of root and shoot of tomato plants up to 69.8% (Vittori Antisari et al. 2015b). Similarly, nanoparticles those prepared from ceria and carbon also facilitate growth and improve the yield of edible crops such as bitter melon, wheat, and tomato (Raliya et al. 2015). One possibility is that if nanoparticles at some concentrations dependent on various factors increase the biomass accumulation of plant tissues and fruits with nil toxicity, then they can also be used in synergy with bio-fertilizers, thus optimizing benefits and producing organic crops.

Improvement in whole plant biomass, length, and volume

When present exposure media, nanoparticles have also shown growth stimulatory influence on edible crop plants while growing under both soil-less media and in natural soil environment (Table 6; Fig. 22). For example, 1–10 mgCeO_2 nanoparticles mL^{-1} though marginally increased shoot length; however, it substantially enhanced the total weight of tomato fruits at highest test concentration (10 mg L^{-1}) (Wang et al. 2012a). In a different study, 500 mgCeO_2 nanoparticles kg^{-1} of soil caused rapid elongation of stem length and also increased the dry matter accumulation in barley by 331% over control but declined the grain production considerably. On the contrary, CeO_2 nanoparticles at 125 and 250 mg kg^{-1} added to soil stimulated grain yield with concurrent accumulation of high amounts of cerium in leaves and grains (Rico et al. 2015a). Likewise, the impact of varying concentrations of CeO_2 nanoparticles on root growth of cucumber, alfalfa, maize, and tomato was inconsistent, but on shoot elongation, it was consistent for all four-plant species (Chichiriccò and Poma 2015).

Certain concentrations of nanoparticles may also detoxify plant system by reducing overall intracellular oxidative stress increasing biomass; for example, Zn acting as a cofactor of two antioxidant enzymes, namely catalase and

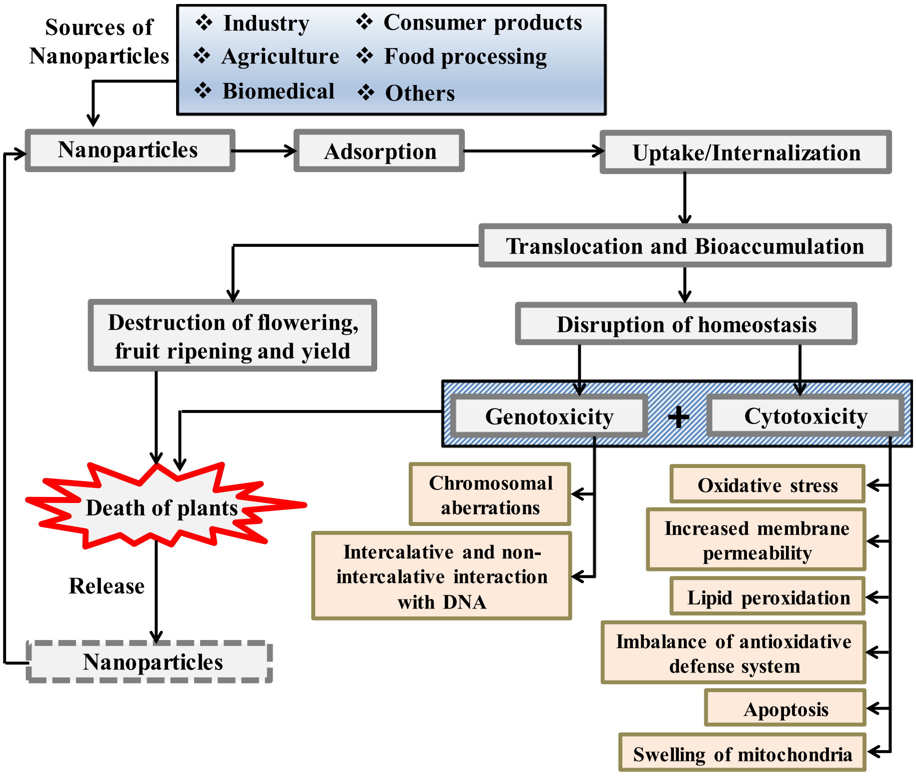


Fig. 21 Genotoxicity and DNA damage induced by nanoparticles. Chromosomal anomalies after exposure to TiO_2 nanoparticles in *A. cepa* root meristem cells: panels A and B show two types of anomalies in chromosome fragments, while panels B-D represent nuclear damage and formation of micronuclei. Panel F indicates metaphasic stickiness during the arrangement of chromosomes at metaphasic plate. Adapted with permission from (Pakrashi et al. 2014). Panel G shows formation multi-walled carbon nanotubes (MWCNTs)-induced formation of DNA tail in root nuclei of *A. cepa*. Comet data at 10 μg multi-walled carbon nanotubes mL^{-1} were significant at $P < 0.05$ over untreated control. Micrographs at the bottom of bar diagram show representative comets with varying degree of DNA tail formation. Panel H is for DNA laddering of DNA incubated with or without multi-walled carbon nanotubes. Bands highlighted in in agarose gel in red correspond to internucleosomal fragments. Adapted with permission from (Ghosh et al. 2015)

superoxide dismutase, may help to mitigate oxidative damage to plants. Moreover, the foliar application of ZnO nanoparticles has been reported to augment the growth and biomass of tomato (Mikkelsen 2018) and rice (Bala et al. 2019) suggesting that ZnO nanoparticles could be used as a future nano-fertilizer. The exposure of iron oxide nanoparticles has been reported to increase the dry biomass of leaf and pods of soybean. Also, iron oxide nanoparticles acted as iron facilitators assisting in transfer of photosynthates to peanut leaves. This could be due to the dissolution of iron from nanoparticles followed by its uptake by plant roots, which also enhanced root growth (Rico et al. 2011). In a similar experiment, iron oxide nanoparticles have been found to promote substantially the growth and biomass of tomato plants (Siddiqi and Husen 2017b). Among carbon nanoparticles, fullerene at 4.72 and 47.2 nM increased the production of bitter melon by 128 to 112%, respectively, when seeds were grown in a supplemented medium. Also, the synthesis of some important molecules such as cucurbitacin-B, lycopene, insulin, and charantin was also promoted by 74%, 82%, 91%, and 20%, respectively, compared to negative control (Kole et al. 2013). Some better performance of mustard has been obtained with 2.3 μg mL^{-1} of oxidized multi-walled carbon nanotubes (Mondal et al. 2011).

Enhanced photosynthetic rate

Nanoparticles, in general, have been observed to have a positive impact on many physiological activities including photosynthesis of plants (Fig. 22). In this category, nanoparticles of TiO_2, CeO_2, and ZnO are significant. As an example, the TiO_2 nanoparticles substantially improved spinach growth (i) by improving light absorbance, (ii) by enhancing the production of RUBISCO enzyme, and (iii) by reducing the UV radiation mediated oxidative stress in chloroplast (Yang et al. 2007; Umeyama et al. 2015). A TiO_2 nanoparticle has one of the three crystalline phases: (a) brookite, (b) rutile, and (c) anatase. Mechanistically, TiO_2 nanoparticles in anatase phase show highest catalytic activity than two other forms (Yan and Chen 2012),

Table 6 Nanoparticles-mediated growth enhancement of food crops

Nanoparticle	Size (nm)	Test crop	Dose rate	Activity/impact	References
ZnO	1.2–6.8	*Cyamopsis tetragonoloba*	10 mg L^{-1}	Significant improvement in plant length, biomass accumulation, surface area of roots, photosynthesis, and soluble protein	Raliya and Tarafdar (2013)
	20	*T. aestivum*	2 g L^{-1} (foliar application) at a rate of 1.2 kg ha^{-1}	Synchrotron X-ray absorption spectroscopy and X-ray fluorescence microscopy revealed enhancement in Zn concentration in grain	Zhang et al. (2018a)
	Not specified	*V. radiate*	20 ppm (foliar spray)	Increased biomass	Dhoke et al. (2013)
	18	*T. aestivum*	6 mg kg^{-1} soil	15% decrease in grain yield with simultaneous internalization of Zn in grain by 229% and 186% under fresh and weathered ZnO nanoparticle exposure	Dimkpa et al. (2018)
	18	*Sorghum bicolor*	6 mg kg^{-1}	Enhanced accumulation of nitrogen and potassium by sorghum plants	Dimkpa et al. (2017)
TiO_2 conjugated with activated carbon	30–50	*S. lycopersicon*	0–0.5 g L^{-1}	Enhanced percent seed germination with less germination time	Singh et al. (2016)
TiO_2	Not specified	*G. max*	0, 0.01, 0.03, 0.05%	Enhancement in dry matter accumulation and plant height	Rezaei et al. (2015)
	20	*O. sativa*	25–750 mg L^{-1}	Enhanced accumulation of palmitic acid, amino acids and glycerol in rice grain, improved shoot growth, and phosphorus concentration in whole plant and grains	Zahra et al. (2017)
	32–171	*T. aestivum*	10, 100, 1000 mg L^{-1}	Enhanced growth of lateral roots and biomass with concurrent uptake of titanium	Zhang et al. (2019a)
	27	*C. sativus*	250, 500, 750 mg kg^{-1}	Increased potassium and phosphorus in cucumber fruits, TiO_2 nanoparticles induced oxidative defense response as shown by catalase activity in other organs	Servin et al. (2013)
	16.04	*S. lycopersicon*	0.05–0.2 g L^{-1}	Transpiration, photosynthesis, and conductance to H_2O in tomato leaves was improved	Qi et al. (2013)
Fe_3O_4	13.9	*P. vulgaris*	1–1000 mg L^{-1}	Fe_3O_4-PEG at 1000 mg L^{-1} increased radicle growth	Duran et al. (2018)
	Not specified	*G. max*	500–750 mg L^{-1}	Quality and yield	Sheykhbaglou et al. (2010)

Table 6 (continued)

Nanoparticle	Size (nm)	Test crop	Dose rate	Activity/impact	References
SiO_2	4–10	*O. sativa*	5 mM	SiO_2 nanoparticles increased grain yield and weight	Liu et al. (2009a)
CuO	Not specified	*T. aestivum*	0.5 g kg^{-1} (sand culture)	Enhanced biomass accumulation	Dimkpa et al. (2012)
Cu	50	*S. lycopersicon*	50–500 mg L^{-1}	Cu nanoparticles enhanced lycopene, vitamin-C in tomato fruits, number of fruits, and fruit firmness	López-Vargas et al. (2018)
Cu_2O	Not specified	*S. lycopersicon*	0–160 ppm	Highest percent germination, increased leaf pigment and increased root/shoot elongation at 20 ppm	Ananda et al. (2019)

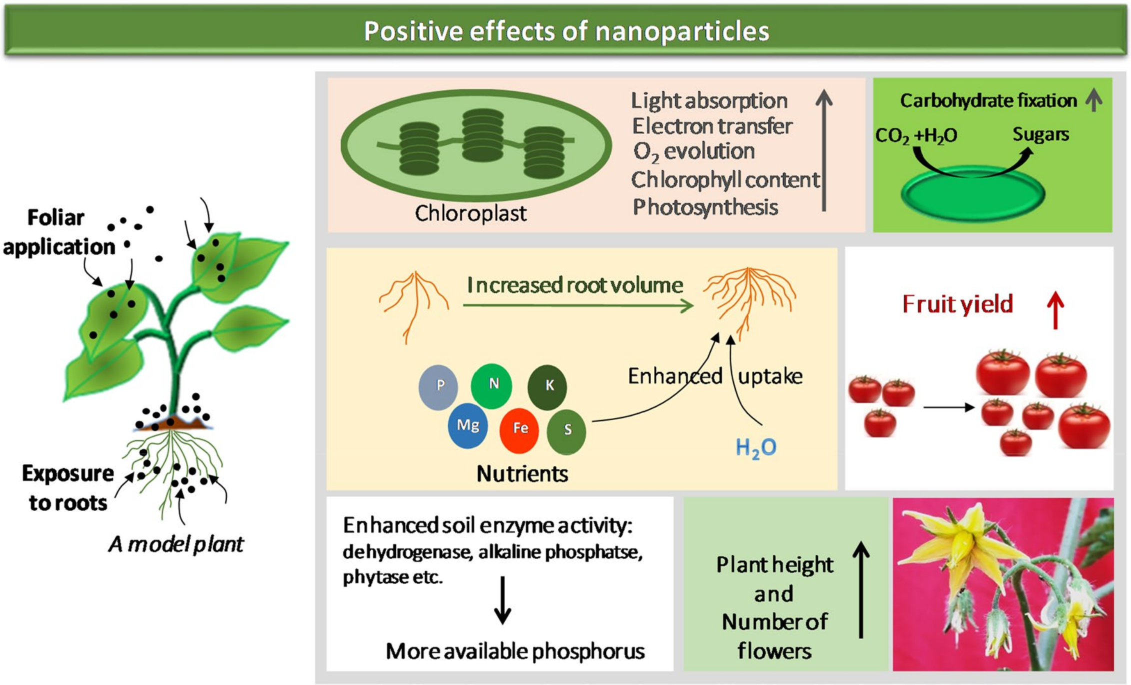


Fig. 22 A model illustrating the beneficial impacts of nanoparticles on plants including enhanced photosynthesis, increased root volume, nutrient uptake, enhanced soil enzyme activities, increased plant biomass, number of flowers and fruits, and fruit mass

which promotes chlorophyll and carotene formation, as reported in *C. sativus*. The TiO_2 nanoparticles facilitate photosynthetic activity in spinach leaf by enhancing light absorption rate by chlorophyll-a molecules, evolution of molecular oxygen, and rate of electron transfer (Xuming et al. 2008; Lyu et al. 2017). Similar to anatase, nano-TiO_2 having rutile crystal structure can prevent the generation of intracellular reactive oxygen species and thus protect chloroplast membrane from the action of free radicals (Hong et al. 2005; Iswarya et al. 2015). Also, an aerosol-based foliar spray of 500 mgTiO_2 nanoparticles kg^{-1} soil brought an increase by 227.42% in chlorophyll synthesis by tomato foliage, while the soil application of 750 mgTiO_2 nanoparticles kg^{-1} increased the chlorophyll content maximally by 216.29% (Raliya et al. 2015).

When applied in soil, TiO_2 nanoparticles enhance photosynthetic pigment content with simultaneous increase in antioxidant activities in *T. aestivum* (Feizi et al. 2012). Some other nanoparticles like ZnO nanoparticles have shown a considerable increase in total soluble protein by 25% and photosynthetic pigment production by 34.5% of green gram plants grown in nanoparticles amended soils (Raliya et al. 2016b). Foliarly applied ZnO nanoparticles increased biomass accumulation, leaf protein, and chlorophyll synthesis (Raliya and Tarafdar 2013; Raliya et al. 2015). In *A. thaliana* chloroplasts, exposure of negatively charged poly (acrylic acid) CeO_2 nanoparticles (PNC) augmented reactive oxygen species scavenging and enhanced photosynthesis (Wu et al. 2017b). CeO_2 nanoparticles via a non-endocytic pathway and through the electrochemical gradient of membrane potential enter into chloroplasts. PNC with a low Ce^{3+}/Ce^{4+} ratio of about 35% reduced leaf reactive oxygen species ($O_2^{-} + H_2O_2 + OH^{\cdot}$) levels by 52% and increased up to 19% of quantum yield in photosystem-II, up to 67% of carbon assimilation and 61% of RUBISCO carboxylation rate over untreated control. The possible mechanism of enhanced photosynthetic rate in *A. thaliana* chloroplast is depicted in Fig. 23.

Transmission of nanoparticles to progeny and higher trophic level

The accumulation of nanoparticles in grains/fruits or consumable parts of plants paves a way for their transfer to progeny and to higher trophic level consumers via food web (Zhu et al. 2008). Some studies report the genetic transmission of nanoparticles to progeny (Lin et al. 2009; Rico et al. 2011). For example, in a trans-generational study, the bean and rice in their second generation revealed the presence of ZnO nanoparticles and fullerene which, however, varied greatly with age and organs of plants (Lin et al. 2009; Medina-Velo et al. 2018). In a study with ZnO nanoparticles, *P. vulgaris* plants were raised in soil artificially contaminated with two types of ZnO nanoparticles (i) coated with triethoxycaprylylsilane and (ii) bare surface ZnO nanoparticles at a concentration range of 125–500 mg kg^{-1} soil. Seeds of first generation (S1) accumulated ZnO nanoparticles, which were sown, and seedlings were grown in soil without the amendment of ZnO nanoparticles followed by evaluation of trans-generational Zn accumulation in second generation seeds (S2) and its impact. Results revealed that ZnO nanoparticles had low residual trans-generational impact on seed composition, which could be beneficial in agricultural production (Fig. 24) (Medina-Velo et al. 2018). The uptake followed by subsequent transport to higher organism can be driven by the solubility of nanoparticles (Uddin et al. 2020). The capillary movement through which nanoparticles can travel to broader channel locations can also influence the transport.

Scientists have also tried to explain CeO_2 nanoparticle's transmission via food chain in detail (Hawthorne et al. 2014; Majumdar et al. 2016). In one of such studies, Hawthorne et al. grew zucchini plants in soil amended with 1228 µg g^{-1} CeO_2 nanoparticles and, after 28 days, observed that leaf tissues which were used to feed crickets had significant amount of Ce (Hawthorne et al. 2014). The crickets were analyzed after 14 days for Ce uptake and also fed to wolf spiders. Crickets fed on zucchini leaves contained a significant amount of Ce (33.6 ng g^{-1}) which was higher than control. Feces of crickets contained 1010 ng g^{-1} of Ce. Spiders that consumed crickets from the nanoparticle-exposed group accumulated 5.49 ng g^{-1} of Ce (Fig. 24). Similarly, *Phaseolus vulgaris* grown in CeO_2 nanoparticles mixed soil at a concentration range of 1000–2000 mg kg^{-1} were fed to Mexican bean beetles which were then eaten by spined soldier bugs (Majumdar et al. 2016). Following 36 days of growth with 1000 mgCeO_2 nanoparticles kg^{-1}, 1.02 µg g^{-1} Ce was translocated to the upper ground parts. The beetle larvae when fed on CeO_2 nanoparticles treated leaves contained low Ce concentration; meanwhile, 98% of Ce was excreted. However, accumulation of Ce in adults was higher than excreted Ce. Moreover, the bio-magnification of Ce

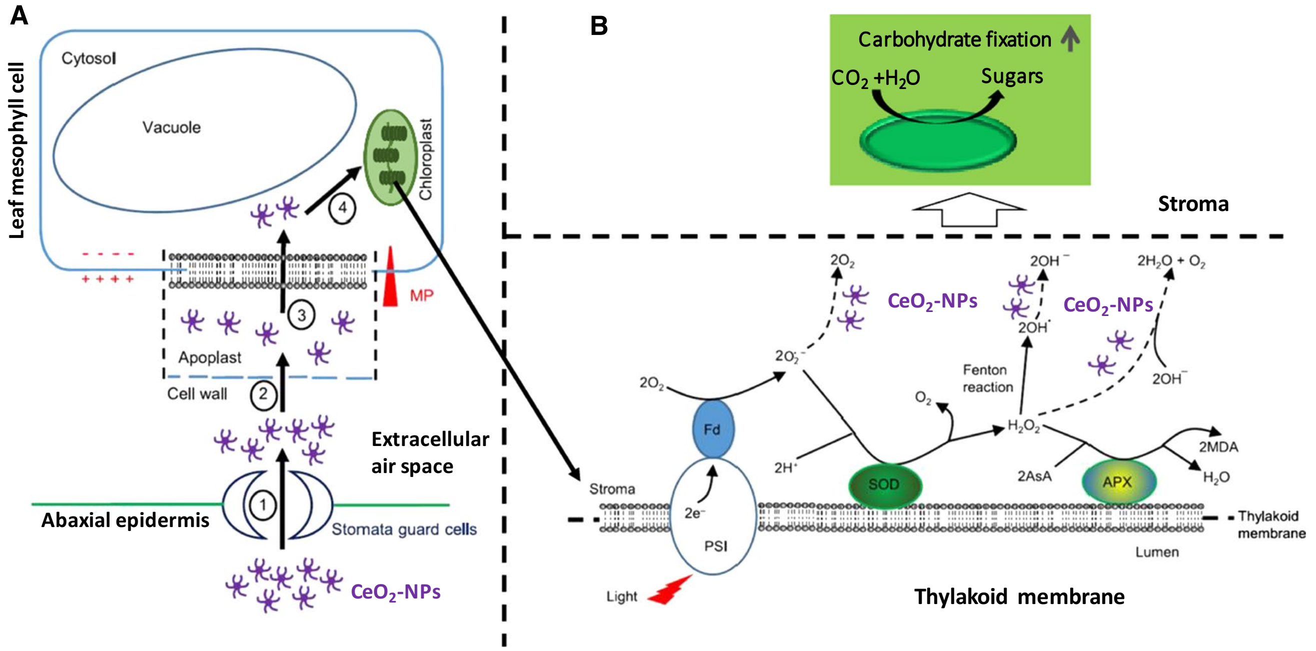


Fig. 23 Transport of CeO_2 nanoparticles (NPs) into chloroplast (panel A) and reactive oxygen species scavenging by CeO_2 nanoparticles (panel B) in the following steps: (i) incident light leads to electron transfer via fd (ferredoxin) to molecular oxygen which forms superoxide radicals (O_2^-); (ii) superoxide dismutase (SOD) enzyme catalyzes the transformation of O_2^- to H_2O_2. H_2O_2 by reacting with ascorbate (AsA) which is either converted to H_2O and O_2 by catalase or forms malondialdehyde (MDA) and H_2O through the reaction with AsA catalyzed by enzyme ascorbate peroxidase (APX). Alternatively, it is transformed to hydroxyl radical ($OH^{\cdot}$) via Fenton reaction. In the presence of CeO_2 nanoparticles, O_2^-, H_2O_2, and $OH^{\cdot}$ are catalyzed to O_2, H_2O, and OH^-, respectively. Adapted and modified with permission from (Wu et al. 2017b)

content was observed by a factor of 5.3 from plants to Mexican bean beetles and then to spined soldier bugs (Fig. 24) (Majumdar et al. 2016). In another study, lettuce was treated in soil with weathered/un-weathered CuO nanoparticles for 70 days and crickets fed on its leaves for 15 days followed by consumption of crickets by lizards (Servin et al. 2017). The XANES and μ-XRF analysis showed that weathered CuO nanoparticles were transformed into Cu_2O and Cu_2S which were mainly localized in main and secondary roots; however, un-weathered CuO nanoparticles were present as CuO in roots. CuO nanoparticles taken up in shoots were transferred to crickets and then to lizards through trophic levels where they were found in crickets' abdomen and head, intestine and body of lizards.

Conclusion

The massive production and unrestricted use of nanoparticles in nano-enabled products and their unregulated disposal in ecosystems have raised serious concerns over crop yields. Due to nano-size, greater surface area, reactivity, and surface charge, the nanoparticles when present in soils can enter easily and rapidly into the intracellular environment of plant system. Following entry, the nano-specific properties that make nanoparticles so special and so powerful could damage agricultural crops and human health through trophic transfer. Nanoparticles taken up by plants (through stomata and roots) bio-accumulate or are translocated to subcellular compartments and various plant organs including fruits/grains. Inside the plant cells, due to multiple action sites, nanoparticles can destruct cellular organelles and morphology, alter physiological and metabolic reactions of plants, and modify gene expression, proteome and metabolome. Besides harmful effect, some nanoparticles can modulate growth, development, and yield of crops, which makes them prospective candidates to be included in agricultural practices. However, the biologically nondestructive properties and ability of nanoparticles to persist indefinitely in the environment are still questionable and require urgent attention. Also, nanoparticles can find their way to animals and humans through the consumption of nanoparticles enriched foods and feeder via levels of the food chain. Considering these, the safe-by-design approaches need to be adopted to produce nanoparticles/nano-products, which should be attractive and target specific but has little or nil inhibitory impacts on plant cells. Furthermore, scientists, industries, and environmental agencies need to work hand in hand to regulate its safe disposal into the environment to avoid the nanoparticle toxicity to plants and humans/animal.

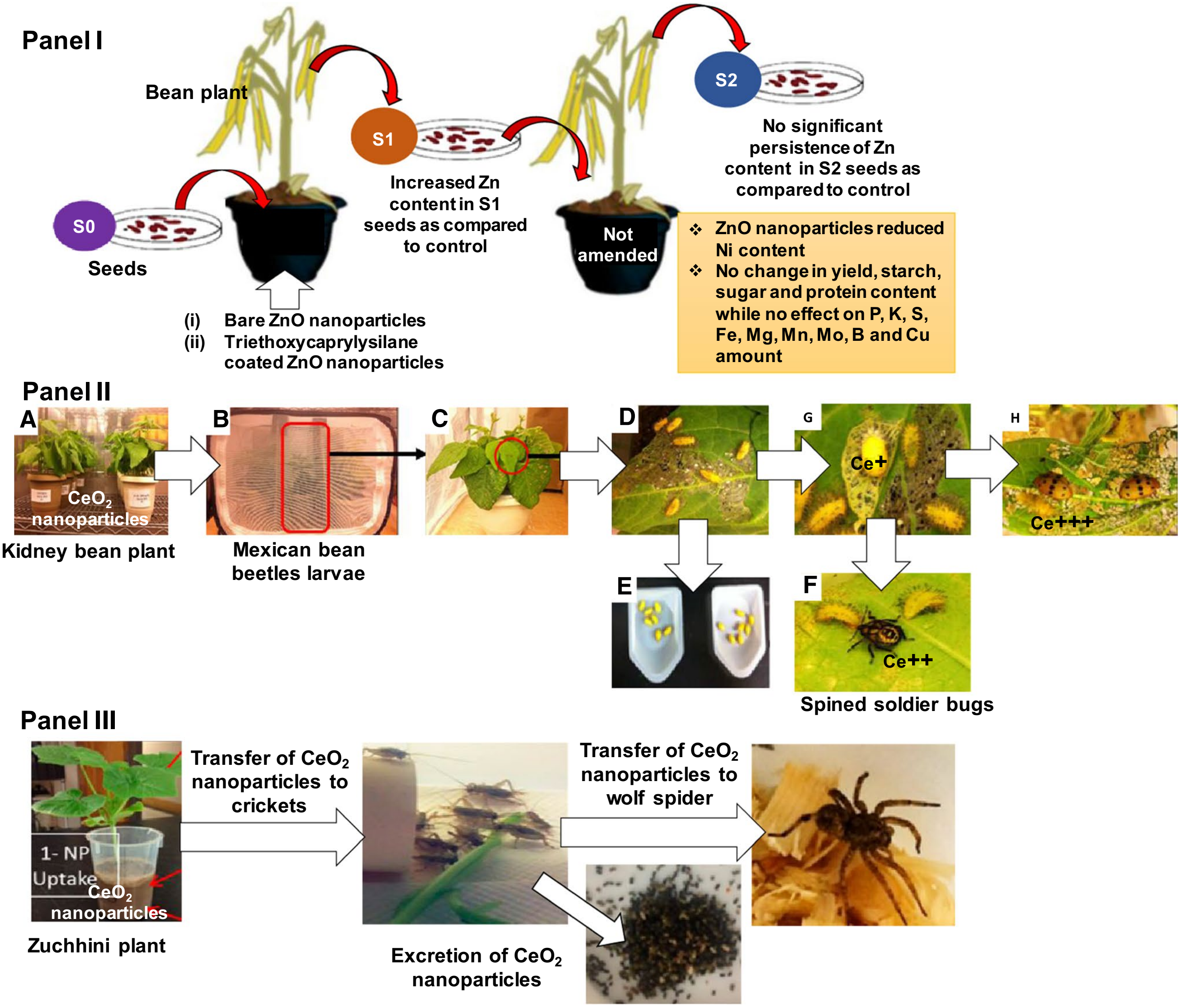


Fig. 24 Transmission of nanoparticles to the next trophic level. Panel I shows the trans-generational flow of ZnO nanoparticles in bean plants raised in soil contaminated with coated and bare ZnO nanoparticles. ZnO nanoparticles were taken up and transmitted to progeny without showing trans-generational effects in nutrient composition of seeds. Adapted and modified with permission from (Medina-Velo et al. 2018). Panel II shows a scheme assessing the trophic movement of CeO_2 nanoparticles: **a** Treatment of kidney bean plants with CeO_2 nanoparticles; **b** infestation of plants with larvae of Mexican bean beetle; **c** and **d** leaf eating by Mexican bean beetles larvae (picture was taken after 22 days of treatment); **e** Mexican bean beetles were collected to feed next consumer; **f** consumption of Mexican bean beetles by spined soldier bugs; **g** Mexican bean beetle larvae metamorphose into pupae (dormant phase); picture was taken after 25 days of treatment; and H⁻ Mexican bean beetle adults feeding on plant leaf. (Picture was taken after 36 days of treatment.) Adapted and modified with permission from (Majumdar et al. 2016). Scheme (Panel III) showing the trophic transfer of CeO_2 nanoparticles (NPs) taken up by zucchini plants followed by their accumulation in crickets and then to wolf spider or excretion of some fraction of CeO_2 nanoparticles from crickets. Adapted and modified with permission from (Hawthorne et al. 2014)

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