Metal-Based Nanoparticles' Interactions with Plants

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1 Introduction

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

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

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

2 Classification of Nanoparticles

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

3 Metal-Based Nanoparticles

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

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

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

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

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

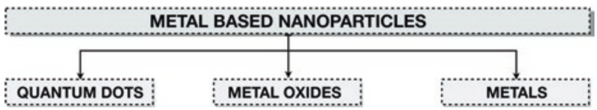


Fig. 1 Classification of metal-based nanoparticles

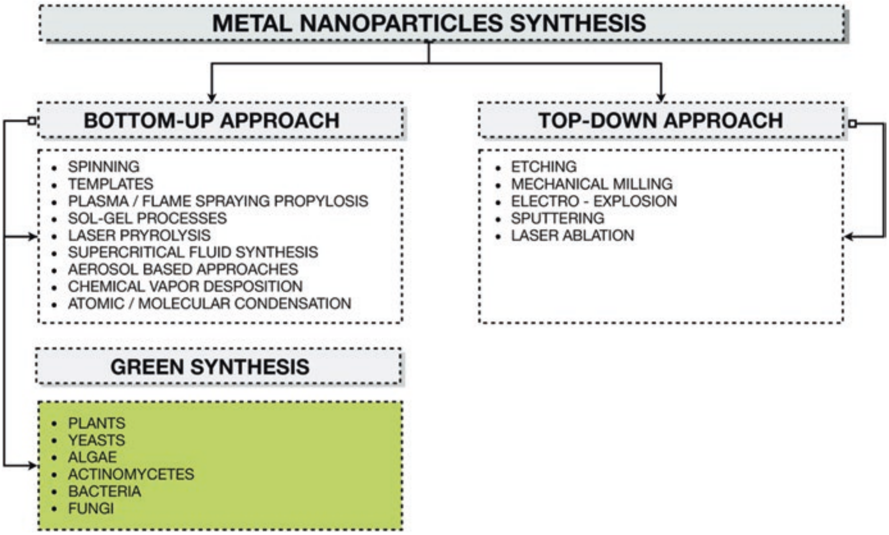


Fig. 2 Classification of methods for the synthesis of metal-based nanoparticles

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

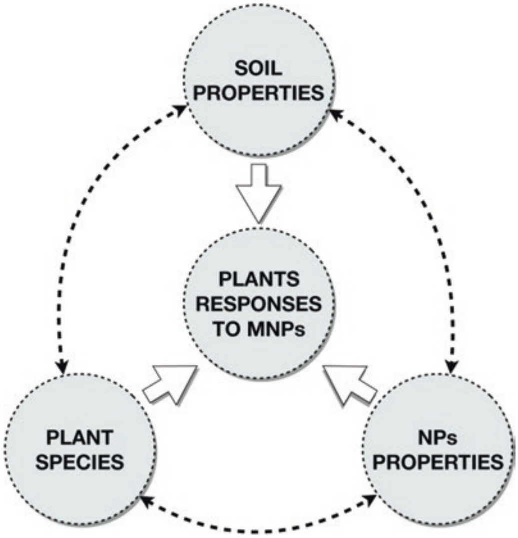
4 Plant Responses to Metal-Based Nanoparticles

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

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

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

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



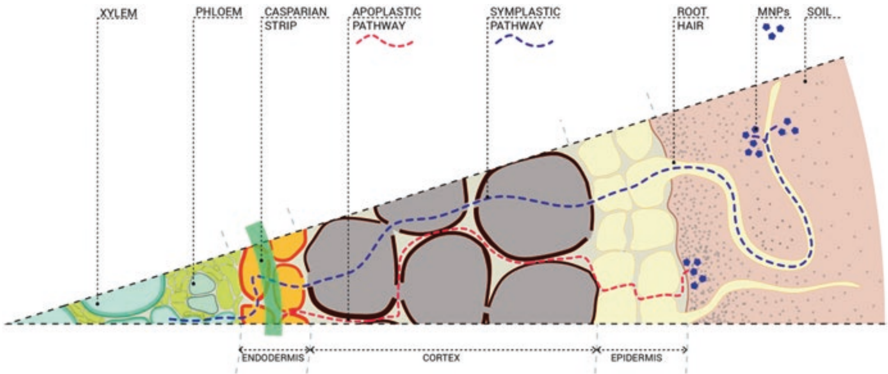


Fig. 4 MNPs uptake by the plant root and their further translocation

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

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

5 Mechanisms of Metals and Metal Nanoparticles Uptake by Plants

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

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

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

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

Table 2. Metal ion transporters in plants

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

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

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

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

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

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

6 The Toxicity of MNPs in Plant

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

6.1 Quantum Dots

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

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

7 Procedure Standardization

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

8 Phytonanotechnology in Agriculture

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

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

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

9 Conclusions and Future Perspective

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

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

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

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