Chapter 4
Plant Nano-nutrition: Perspectives and Challenges

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Abstract The global agriculture is facing many challenges including sustainable use and conservation of natural resources, climate change, urbanization, and pollution resulting from agrochemicals (e.g., fertilizers and pesticides). So, the sustainable agriculture is an urgent issue and hence the suitable agro-technological interventions are essential (e.g., nano- and bio-technology) for ensuring the safety and sustainability of relevant production system. Biotechnology and nanotechnology also can be considered emerging solutions to resolve the global food crisis.

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Nanoparticles or nanomaterials can be used in delivering different nutrients for plant growth. These nanoparticles as nanofertilizers have positive and negative effects on soils, soil-biota and plants. These effects mainly depend on multiple factors including nanofertilizer properties, plant species, soil fate and dynamics as well as soil microbial communities. Nanofertilizers could improve the nutrient use efficiencies through releasing of nutrients slowly and steadily for more than 30 days as well as reducing the loss of nutrients in agroecosystems and sustaining farm productivity. Here we review the plant nano-nutrition including the response of plants and soils to nanonutrients and their fate, dynamic, bioavailability, phytotoxicity, etc. Concerning the effects of nanonutrients on terrestrial environments are still an ongoing processes and it demands further researches as well as a knowledge gap towards different changes in shape, texture, color, taste and nutritional aspects on nanonutrients exposed plants as a major component in the food chain. Moreover, the interaction between nanonutrients and plants, soils, soil biota and the entire agroecosystem will be also highlighted.

Keywords Agri-nanotechnology • Plant nano-nutrition • Nanonutrients • Nanoparticles

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4.1 Introduction

A great challenge faces all countries all over the world concerning the feeding population from 6 to 9 billion by 2050 (Ditta et al. 2015). Due to about 40% of the population depends on agriculture in the developing countries; hence the agriculture can be considered a backbone in these countries. The global agriculture is facing several challenges including climate changes (Chalise and Naranpanawa 2016; Chen et al. 2016a, b; Ma et al. 2016; Villoria et al. 2016; Brown 2017), conservation of natural resources and their sustainable use (Ditta et al. 2015; Ma et al. 2016; Duran-Encalada et al. 2017), and urbanization (Maheshwari and Bristow 2016; Henderson et al. 2017) as well as environmental issues (e.g., pollution resulting from runoff and accumulation of fertilizers and pesticides) (Jacobsen and Hansen 2016; Qureshi et al. 2016; Ma et al. 2016; Kuppusamy et al. 2016a, b). So, the sustainable agriculture is an urgent issue and hence the suitable agro-technological interventions are essential like nano- and bio-technology for ensuring the safety and sustainability of relevant production system (Dasgupta et al. 2015a, b; Abhilash et al. 2016; Magalhães et al. 2017; Dasgupta et al. 2017; Ranjan et al. 2014; Shukla et al. 2017).

A great progress has been achieved in the nanotechnology sector in the last two decades (Belal and El-Ramady 2016; Liu et al. 2016; Reddy et al. 2016; Shalaby et al. 2016; Magalhães et al. 2017). The agricultural sector was one of the most important fields, which nanotechnology science involves leading a revolution in many applications such as the agri-food industries (Dasgupta et al. 2015a, b; Handford et al. 2015; He and Hwang 2016; Sarkar et al. 2016; Vélez et al. 2017), remediation of soils and waters from pollutants or nanoremediation (Belal and El-Ramady 2016; Jain et al. 2016a, b; Gillies et al. 2016; Gil-Díaz et al. 2016a; Kuppusamy et al. 2016a, b; Shao et al. 2016; Pulimi and Subramanian 2016), fertilizers and pesticides production (Mastronardi et al. 2015; Solanki et al. 2015; Subramanian et al. 2015; Chhipa and Joshi 2016; Dubey and Mailapalli 2016; Dwivedi et al. 2016; Panpatte et al. 2016), the precision farming (Gemtos et al. 2013; Ditta et al. 2015; Chhipa and Joshi 2016; Li et al. 2016a, b, c; Dubey and Mailapalli 2016; Shaw et al. 2016; Shalaby et al. 2016), post harvest and storage of crops (Flores-López et al. 2016; Luo et al. 2016; Mohammadi et al. 2016; Sogvar et al. 2016; Song et al. 2016; Li et al. 2017; Ray et al. 2017), etc.

Nanotechnology may have a hidden face in soils. The apparent face not only include the direct effects on soil microbial communities, and remediate of polluted soils, but also using natural nanoparticles like zeolites and nano-clays as soil amendments. Therefore, several applications of nanoparticles or nanomaterials in soils including (1) use of nanoparticles like zeolites and nano-clays in soil improvement (Xiong et al. 2015; Lateef et al. 2016; Danish et al. 2016), (2) soil application of nanofertilizers (Mastronardi et al. 2015; Subramanian et al. 2015; Dwivedi et al. 2016), (3) remediation of polluted soils (Araújo et al. 2015; Jain et al. 2015; Fajardo et al. 2015; Ibrahim et al. 2016; Jain et al. 2016a, b; Gillies et al. 2016; Gil-Díaz et al. 2016a), (4) using nano zero valent iron technique in the degradation of pollutants (Raman and Kanmani 2016; Yang et al. 2016; Vítková et al. 2016;

Yirsaw et al. 2016; Zhao et al. 2016; Xie et al. 2017) etc. Concerning the hidden face of nanotechnology in soils, it may be include the interaction between different nanoparticles and different environments. These different environmental compartments include plants, microbes, air and soil, which have been extensively studied (e.g., Abhilash et al. 2016; Du et al. 2016; Gil-Díaz et al. 2016b; Gillies et al. 2016; Song and Lee 2016; Yausheva et al. 2016; Wang et al. 2016a, b). So, the fate and behavior of nanomaterials in soils including transport, bioavailability and bio-toxicity of these nanoparticles should be addressed (Watson et al. 2015; Gogos et al. 2016; Li et al. 2016a, b, c; Wang et al. 2016a; Yirsaw et al. 2016, Shukla et al. 2017; Walia et al. 2017; Siripireddy et al. 2017; Maddinedi et al. 2015, 2017; Tammina et al. 2017; Sannapaneni et al. 2016; Ranjan et al. 2014, 2015, 2016; Nandita et al. 2016; Jain et al. 2016a, b). On the other hand, this behavior of nanoparticles in soils is mainly controlled by soil characterization particularly soil pH (Conway and Keller 2016), soil clay content (Zhang et al. 2016a; Chen et al. 2016a, b), soil organic matter (Majumdar et al. 2016), and soil cation exchange capacity (Watson et al. 2015; Gogos et al. 2016).

Plant nano-nutrition as a science is dealing with nanonutrients from different aspects including the uptake, translocation, metabolism, bioavailability of nanonutrients in rhizosphere for plant growth and development or it is nanotechnology application for the provision of nano-nutrients for the production of crops (Ditta et al. 2015). This branch of plant nutrition also includes nanoparticles phytotoxicity, the interaction between nanonutrients and plants (de la Rosa et al. 2016; Reddy et al. 2016; Zuverza-Mena et al. 2016; Wang et al. 2016b), soils (He et al. 2016; Dwivedi et al. 2016; Pachapur et al. 2016; Lateef et al. 2016), soil biota (Ibrahim et al. 2016; Maliszewska 2016) and the entire agroecosystem (Costa and Fadeel 2016; Fraceto et al. 2016; Servin and White 2016). Therefore, this review will focus on the plant nano-nutrition including the response of plants and soils to nanonutrients and their fate, dynamic, bioavailability, phytotoxicity, etc.

4.2 Nanotechnology in Agriculture and Its Challenges

More than 30,000 articles have been published since 2013 concerning nanotechnology with about 8,000 of those studies occurring in this year (June 21, 2016 through Science Direct or Springer Link). This reflects the significance of this science in our life including all fields or sectors. The agricultural field is an important one, which nanotechnology strongly invasives it. More than 100 books till now (June 21, 2016) have been published by Springer including some handbooks or encyclopedia (e.g. Bhushan 2016; Aliofkhazraei 2016; Aliofkhazraei and Makhlouf 2016; Egorova et al. 2016). Concerning nanotechnology definition, it is defined as "*the science, engineering and technology of controlling, building, and restricting materials and devices at the nanoscale*" according to Wang et al. (2016a, b). Nanotechnology penetrates all fields including medicine (Olivo and Dinish 2016; Khanna 2016; Ahmed and Jackson 2016; Steinhoff 2016; Zhang et al. 2016), pharmacology (Garvie-Cook 2016), industry (Bindal and Hamedi-Hagh

2016; Meguid 2016; Andrievski and Khatchoyan 2016), engineering (Jorio 2016; Singh and Gaharwar 2016), energy (Zhang 2016) and agriculture (Parisi et al. 2015; Dwivedi et al. 2016; Egorova et al. 2016; Ibrahim et al. 2016; Mehlhorn 2016; Piperigkou et al. 2016; Peters et al. 2016; Servin and White 2016; Wang et al. 2016a, b).

It is well known that, nanotechnology deals with the manufacturing, manipulation and characterization of different materials having a size range at the nanometer scale. Furthermore, reduction of the material size into the nano scale changing the physico-chemical properties comparing with the same material at larger-size scales (Peters et al. 2016). Therefore, it could be classified the agri-nanotechnology into three categories including plant- (phytonanotechnology), microbes (microbial or bio-nanotechnology) and animal-nanotechnology (zoo-nanotechnology). Phytonanotechnology refers to different applications of nanotechnology in both plant sciences and plant production systems (Wang et al. 2016a, b). Regarding the benefits and potential uses of nanotechnology in agriculture, there are significant applications including producing greater quantities of food with lower cost as well as energy sector and waste remediation (Fraceto et al. 2016; Servin and White 2016). However, many questions regarding different previous approaches and their risk in agricultural production remain unanswered. Numerous applications in agri-nanotechnology have developed engineering nanoparticles as smart delivery systems (e.g., Piperigkou et al. 2016; Peters et al. 2016; Servin and White 2016; Wang et al. 2016a).

Regarding the potential applications of nanotechnology in agricultural field, it is reported about these impacts including (1) increasing the crop productivity through using nano-agrochemicals (e.g. nanopesticides and nanofertilizers), (2) improving food security and its productivity, (3) improving soil quality *via* enhancing the water-holding capacity of soil (e.g. using nanoclays, nano-zeolites and hydrogels), (4) stimulating plant growth using nanomaterials by enhancing elemental uptake and use of nutrients (e.g. nano-SiO_2, TiO_2, ZnO and carbon nanotubes), (5) providing smart monitoring using nanosensors by wireless communication devices help farmers in maintaining farm with precise control and report timely needs of plants (Fraceto et al. 2016). These applications of nanotechnology in agricultural researches have been intensively used in both academic and industrial levels (Dasgupta et al. 2015a, b; Parisi et al. 2015; Fraceto et al. 2016) due to the unique properties of nanomaterials as well as its suitability candidates in designing and developing such novel nano-tools supporting the sustainability of agriculture (Ditta et al. 2015; Dwivedi et al. 2016).

It should be considered some important information regarding nanotechnology and its effects on plants including size, composition, concentration, surface charge and physical chemical properties of used nanoparticles/nanomaterials as well as their susceptibility of the plant species (Fraceto et al. 2016). Concerning the challenges of using nanotechnology in agriculture, some urgent issues should be kept in mind remain to be resolved in the near future including (1) the ecotoxicology of nanomaterials in agroecosystem (Bhatt and Tripathi 2011; Ma et al. 2013; Judy and Bertsch 2014; Anjum et al. 2015; Bour et al. 2015; Costa and Fadeel 2016;

Hu et al. 2016), (2) the pollution resulted from nanomaterials and its advanced regulations (Amenta et al. 2015; Du et al. 2016), (3) the sustainability and its biosafety of nanomaterials, (4) the development of carrier of nanomaterials (De Oliveira et al. 2014), and (5) the investigation of nanomaterial on the applied scale like the industrial level (Fraceto et al. 2016). Therefore, more developed techniques should be saved to monitor the fate of nanoparticles in different environments under different concentrations (Sadik et al. 2014). Moreover, more advanced carriers should be used for nanoparticles achieving high delivering the active agents (e.g. pesticides, nutrients, and fertilizers) enhancing the maximization of their efficiency seeking the sustainability (De Oliveira et al. 2014; Van Koetsem et al. 2016). Concerning the applied side, it should be investigated and then evaluated the nanomaterials on the commercial scale by comparing these nanoparticles with the commercial products as well as the interaction between different kinds of nanoparticles (Dimkpa et al. 2015). Regarding the ecotoxicology of nanoparticles, it should be studied the phytotoxic effects of nanoparticles on agroecosystems including plants, soil microbial communities, soil biota, water, air as well as human health (Bouguerra et al. 2016; Costa and Fadeel 2016; Fraceto et al. 2016; Servin and White 2016). Therefore, it could be concluded that, nanotechnology has a very strong link with the agriculture and penetrates several agricultural fields including fertilization, irrigation and water saving, nanoremediation of soils and water from pollutants as well as the agri-food sector. Many challenges are still needed for more researches and investigations for safe and sustainable using of nanomaterials in agriculture.

4.3 Nanotechnology in Soils: The Hidden Face

More than 110,000 articles have been published since 2013 concerning nanoparticles with about 25,000 of those studies occurring in this year (June 22, 2016 through Science Direct), whereas more than 37,000 articles belong nanomaterials from the same and previous period (about 10,000 only for 2016 through Science Direct). Several issues have been published concerning the nanotechnology in soils including nanoremediation of polluted soils (Araújo et al. 2015; Jain et al. 2015; Fajardo et al. 2015; Ibrahim et al. 2016; Jain et al. 2016a, b; Gillies et al. 2016; Gil-Díaz et al. 2016a), using nanoparticles/nanomaterial (e.g. zeolites and nano-clays) in soil improvements (e.g. Xiong et al. 2015; Lateef et al. 2016; Danish et al. 2016), soil application of nanofertilizers (Mastronardi et al. 2015; Subramanian et al. 2015; Dwivedi et al. 2016), using nano zero valent iron (nZVI) technique in the degradation of pollutants (e.g. Raman and Kanmani 2016; Yang et al. 2016; Vítková et al. 2016; Yirsaw et al. 2016; Zhao et al. 2016) etc.

The interaction between nanoparticles/nanomaterials and different environmental compartments including plants, microbes, air and soil was and still one of the most important issues in environmental nanotechnology. This previous interaction has been extensively studied by several researchers (e.g., Adams and Kanaroglou

2016; Abhilash et al. 2016; Du et al. 2016; Gil-Díaz et al. 2016a, b; Gillies et al. 2016; Song and Lee 2016; Yausheva et al. 2016; Wang et al. 2016a, b). Regarding the fate and behavior of nanoparticles in soils, once the nanoparticles enter the soil, different soil physico-chemical properties are largely controlled the transport, bioavailability and bio-toxicity of these nanoparticles (Watson et al. 2015; Gogos et al. 2016; Li et al. 2016a, b, c; Wang et al. 2016a, b; Yirsaw et al. 2016). Like other metals, the transportation, bioavailability, and sorption of metal nanoparticles in soils is totally governed by soil properties including soil pH (Waalewijn-Kool et al. 2014; Conway and Keller 2016), clay content (Zhang et al. 2016b), soil organic matter (Majumdar et al. 2016) and cation exchange capacity (Benoit et al. 2013; Dimkpa et al. 2015; Watson et al. 2015; Gogos et al. 2016).

On the other hand, the interaction between different types of nanoparticles in soils is an emerging issue and needs further studies to evaluate the behavior of nanoparticles in long-term field condition as well as their interactions in soils and the role of these interactions on plant nutrition (Dimkpa et al. 2015). Definitely, the interaction between these nanoparticles themselves in soils is governed by different soil properties as mentioned before and the properties of nanoparticles themselves (e.g. the size, shape and surface charge of nanoparticles). These previous properties of both soil and nanoparticles are the main factors control the dissolution, solubilization, agglomeration and aggregation of nanoparticles in soils (Dwivedi et al. 2016; Pachapur et al. 2016). It is reported that, the high organic content in soil enhances a strong binding between nanoparticles and soil decreasing the mobility, bioavailability and uptake of these nanoparticles and then the bio-toxicity by plants (Shoults-Wilson et al. 2011). Concerning silver nanoparticles in soils, it is also stated that, (1) the aggregation and its retention in soils of these particles is enhanced by both ionic strength and divalent cations (Thio et al. 2012), (2) the bioavailability of Ag ions is decreased by increasing soil pH due to a greater CEC raising the adsorption of Ag ions onto the soil surface and (3) as well as the hetero-aggregation of Ag-nanoparticles with natural colloids in soils reduces their mobility (Cornelis et al. 2013; Dwivedi et al. 2016; Pachapur et al. 2016; Troester et al. 2016).

What about the hidden face concerning the nanoparticles in soils? It could be drawn the complete portrait for nanoparticles in soils through the following questions: what is the interaction between nanoparticles and the different agroecosystem compartments including soil matrix (Dwivedi et al. 2016; Floris et al. 2016; Pachapur et al. 2016; Yang et al. 2016), plants (Zhang et al. 2016a; Yang et al. 2016), soil water (Zhao et al. 2016), soil air (Polis et al. 2013), soil biota (Shen et al. 2015; Xu et al. 2015; Durenkamp et al. 2016; He et al. 2016), aquatic environments like drinking water (Troester et al. 2016; Zhao et al. 2016) as well as the interaction between nanoparticles and pollutants (Xie et al. 2016) or themselves (Dimkpa et al. 2015; Li et al. 2016a, c; Pachapur et al. 2016). Therefore, the hidden face of nanoparticles in soils can be considered still not well understood and further studies should be suggested in monitoring nanoparticles in soils. It is reported that, the production of metal nanoparticles is expected to reach 58,000 tons by year 2020 according to United Nations Environment Programme (UNEP 2007). Concerning the environmental dynamics of metal oxide nanoparticles in homogeneous or heterogeneous systems, there are some factors controlling the fate, transport, transformation and toxicity of these metal nanoparticles. One of the most important factors controlling the dynamic of metal oxide nanoparticles is presence of pollutants in different environmental conditions. Hence, the interaction between these pollutants and metal nanoparticles will govern the transformation of metal oxides and their transport kinetics as well as the effects of pollutants on the toxicity of metal nanoparticles in both homogeneous and heterogeneous systems (Joo and Zhao 2016). In more details, it is resulted from the presence of contaminants decreasing in the bioavailability of these nanoparticles through sorption, hetero-aggregation, and/or complexation. Furthermore, the pollutants also control the fate and transport of these nanoparticles exhibiting their synergistic toxic effects (Joo and Zhao 2016).

One of the most important issues concerning nanoparticles in soils is the pollution resulted from these nanomaterials, which have great impacts on human health and soil ecosystems (Yang et al. 2016). It is found that, nano zero-valent iron (nZVI) represents about 70% from the metal-based nanoparticles widely used in environmental nanotechnologies, which have been extensively applied for *in situ*remediation across the world (Yang et al. 2016; Xie et al. 2016). The large amounts of these nanomaterials (nZVI) have been caused many ecotoxicity impacts on soil ecosystems including toxicity (Lefevre et al. 2016), cytotoxicity (Dong et al. 2016) and phytotoxicity (Xie et al. 2016) as well as increasing in oxidative stress (Chaithawiwat et al. 2016) and disruption of microbial community (Pawlett et al. 2013; Saccà et al. 2014) in both aquatic and terrestrial ecosystems (Yang et al. 2016).

Therefore, it could be concluded that, the nanotechnology has many applications in soil system including nanoremediation polluted lands, nanofertilizers, nanopesticides, precision farming using nanosensors (nano-farm), using nanomaterials in soil improvement, etc. There are further studies should be performed concerning the fate and behavior of nanomaterials in soils and their effects on agroecosystem. So, it could be called this interaction between nanomaterials and soil system by "the hidden face" because a lot of information in this area is still unknown.

4.4 Nanotechnology in Plant Nutrition

More than 110,000 articles have been published several years ago regarding plant nutrition, whereas in general these publications were nearly more than 6,000 annually as recorded by the Science Direct (accessed by June 22, 2016). Like other plant sciences, plant nutrition is a branch dealing with the physiology, metabolism, uptake and translocation of different nutrients by plants as well as the molecular plant nutrition. This science can be also involved the following topics: (1) agronomic or physiological efficiency of nutrients (Chaudhary et al.

2015; Loeppmann et al. 2016), (2) rhizosphere and its architecture (Szoboszlay et al. 2015; Oburger and Schmidt 2016), (3) the mineral nutrition and stress physiology (Matraszek et al. 2016; Kolenc et al. 2016), (4) molecular nutrient uptake and plant sensing (Mitra 2015; Rizwan et al. 2016a), and (5) nutrient cycles (Hobbie 2015; Ford et al. 2016). Many publications have been published several years ago concerning plant nutrition started 5000 BC when the ancient Egyptians recorded their paintings about plant nutrition (El-Ramady et al. 2014a), till Justus von Liebig (1803–1873; El-Ramady et al. 2014b) and the handbook of plant nutrition for Barker and Pilbeam (2015).

Nanoscience and nanotechnology have a great applications in agricultural sciences, although the applications in plant sciences as well as plant production systems have been received comparatively little interest (Wang et al. 2016a, b). Several nanomaterials have been synthesized through the physical, chemical and biological methods *via* bacteria, fungi, plants etc. These nanoparticles or nanomaterials have been investigated including many studies such as studying different effects of nanoparticles on the cellular morphology, functions, behavior and the effectiveness of nanoparticles on plants from the agricultural and the horticultural significance (Patra et al. 2013; Ditta et al. 2015; Rizwan et al. 2016b; Panpatte et al. 2016; Wang et al. 2016a, b). It is reported that, nanoparticles have been used in enhancing the crop productivity through the high efficiency of nutrients in the form of nanofertilizers, nanopesticides, or nanoherbicides by the plants (e.g. Tarafdar et al. 2013; Ditta et al. 2015; Panpatte et al. 2016; Rizwan et al. 2016b). These nanoparticles have several advantages in promoting the agricultural productivity including (1) enhancement plant seed germination and growth against stress (Table 4.1; Khan et al. 2016), (2) increasing the efficiency of water and fertilizer dosage, (3) sustainable management using nanosensors in pest detection, (4) using of nanocapsules for pesticides and herbicides in control pests (Ditta et al. 2015) and these nanoparticles can be considered as a next generation technology for sustainable agriculture (Panpatte et al. 2016; Tolaymat et al. 2016) (Fig. 4.1).

Concerning the nanotechnology and plant nutrition, it is reported that plant nano-nutrition includes nanofertilizers as a source for nutrients (Ditta et al. 2015; Liu et al. 2016; Panpatte et al. 2016), nano-capsules as a nanoscale carriers (Meredith et al. 2016), nano-smart delivery systems (Ditta et al. 2015), nano-oligo cellulosic materials (Mohamed et al. 2016), clay nanotubes or halloysite (Peixoto et al. 2016; Donaldson 2016), micro-fabricated xylem vessels (Ditta et al. 2015), and nanopesticides (Ditta et al. 2015; Subramanian et al. 2016). It could notice that, many agricultural practices can be achieved seeking for the improvement of crop production through using many applications of nanoagrochemicals such as nanopesticides (e.g. nanofungicides, nanoherbicides, etc), nanofertilizers, nanosensors (Subramanian et al. 2016).

Therefore, it could be concluded that, there is a strong link between plant nutrition and nanotechnology through many applications including different nano-agrochemicals such as nanofertilizers, nanopesticides, nanosensors, nano-capsules as a nanoscale carriers etc. Definitely, the using of nanotechnology applications in plant nutrition can help in improving crop production, saving the time and costs as well as

Table 4.1 A comparison between nano copper oxide and nano selenium role in impacting on plants including oxidative stress and antioxidative defense system

Plant species	Stressor level (Exp. medium)	Form & dosage (exposure period)	Different effects of Se on stressed plants and associated potential mechanisms (Reference)
Nano-CuO stress			
Oryza sativa L.	Nano-CuO: 2.5, 10, 50, 100, and 1000 mg L^{-1} (hydroponic)	30 days and size <50 nm nano-CuO	nano-CuO increased MDA and proline contents and APX and SOD activities (Da Costa and Sharma 2016)
Zea mays L.	Nano-CuO: 0.01, 0.02 ppm for root expo.; 8 mg kg^{-1} foliar spray (hydrop.)	Exposure root and leaf 3 weeks and size <50 nm nano-CuO	0.02 ppm root exposure and 8 ppm foliar spray decreased GPX, CAT and succinate dehydrogenase activities but increased SOD and glucose-6-phosphate dehydrogenase activities in leaves (Adhikari et al. 2016)
Transgenic cotton and conventional cotton	10, 200 and 1,000 mg L^{-1} nano-CuO (hydroponics)	10 days and nano CuO diameter were 30 ± 10 nm	Plant hormones IAA and ABA were significantly at high level inhibited and also reduced the uptake of B, Mo, Mn, Mg, Zn and Fe; plants biomass and height not affected at 10 mg kg^{-1} nano-CuO exposure (Le Van et al. 2016)
Halimione portulacoides	Nano-CuO: 10 mg kg^{-1} (hydroponic)	8 days and size of nano CuO <50 nm	No metal translocation Cu in roots of *Halimione*, less Cu accumulation in roots when Cu available in the form of nanoparticles, Cu can form aggregates, reducing SA and thus decreasing Cu availability (Andreotti et al. 2015)
Brassica juncea L.	Nano-CuO: 20, 50, 100, 200, 400, 500 mg L^{-1} (*in vitro* exp.)	14 days and size <50 nm nano-CuO	Nano-CuO increased H_2O_2 and MDA formation; induced POD and SOD but inhibited APX activity in roots and shoots (Nair and Chung 2015)
Medicago sativa L. and *Lactuca sativa* L.	5, 10 and 20 mg L^{-1} nano-CuO (hydroponic)	15 days and nanoparticles 10–100 nm	Nano-CuO reduced CAT activity in alfalfa and increased APX activity in roots of both lettuce and alfalfa. (Hong et al. 2015)

(continued)

Table 4.1 (continued)

Plant species	Stressor level (Exp. medium)	Form & dosage (exposure period)	Different effects of Se on stressed plants and associated potential mechanisms (Reference)
Glycine max L.	Nano-CuO: 50, 100, 200, 400 and 500 mg L^{-1} (*in vitro* ex.)	14 days and size <50 nm nano-CuO	Nano-CuO at 100–500 mg L^{-1} significantly increased the H_2O_2 level, POD activity in roots (Nair and Chung 2014a)
Arabidopsis thaliana L.	Nano-CuO: 0.5, 1, 2, 5, 10, 20, 50, and 100 mg L^{-1} (*in vitro* ex.)	21 days and size 30 nm nano-CuO	Nano-CuO concentration-dependently increased $O_2^{\bullet}$ and H_2O_2 formation in leaves and roots; induced antioxidant, sulfur assimilation, GSH biosynthesis genes (Nair and Chung 2014b)
Nano-Se stress			
Lycopersicum esculentum Mill. cv. Halil	Temperature stress: 10, 25, 40 °C for 24 h (hydroponic)	2.5, 5, 8 μM Se as Na_2SeO_4 & nano-Se 1, 4, 8, 12 μM (3 d)	Se and nano-Se can improve fresh and dry weight of shoot, diameter, root fresh and dry weight and root of tomato plants under high and/or low temperature stress; Se and nano-Se increases relative water content and root volume significantly after a short-term of high and/or low temperature stress (Haghighi et al. 2014)
Arundo donax L. 2 ecotypes Blossom and 20SZ	Nano-Se: 100 mg L^{-1} Se as *Lactobacillus casei* (*in virto* experiment)	0.1, 1, 10, 50, 100 mg L^{-1} Se as Na_2SeO_4 (8–16 d)	Both *Arundo* ecotypes could uptake and accumulate nano-Se however in lower concentration comparing to the selenate; the toxic level of selenate was 20 and 50 mg L^{-1} for Blossom and 20SZ accumulating 920 and 896 mg kg^{-1} Se in clusters resp. (Domokos-Szabolcsy et al. 2014)

(continued)

Table 4.1 (continued)

Plant species	Stressor level (Exp. medium)	Form & dosage (exposure period)	Different effects of Se on stressed plants and associated potential mechanisms (Reference)
Nicotinia tabacum L. cv. Ottawa, Petit, Havana	Nano-Se: 1, 10, 20, 50, 100 mg L^{-1} Se as *Lactobacillus acidophilus* (*in virto* exper.)	1, 10, 20, 50, 100 mg L^{-1} Se as Na_2SeO_4 (8 and 16 d)	Nano-Se (50–100 mg kg^{-1}) stimulated callus initiation, micro-shoot formation on callus surface and root regeneration; SeO_4^{-2} (50–-100 mg kg^{-1}) inhibited both callus and root formation; SeO_4^{-2} can get into plant tissue and in excess as a pro-oxidant can damage directly and/or indirectly root generation growth and regeneration of explants; nano-Se generated roots 80% of plantlets on 8th day and >90% on 16th day (Domokos-Szabolcsy et al. 2012)

Abbreviations: *AsA* Reduced ascorbate, *GST* glutathione-*S*-transferase, *MTs* metallothioneins, *Pn* net photosynthesis, *Gs* stomatal conductance, *Tr* transpiration rate, *APX* ascorbate peroxidase activity, *CAT* catalase activity, *MDA* malondialdehyde, *SOD* superoxide dismutase, *CAT* catalase, *POD* peroxidase, *GPX* guaiacol peroxidase, *IAA* indole-3-aceticacid, *ABA* abscisic acid

alleviating the abiotic stress-induced damage through the activation of plant defense system. This reflects the role of nanomaterials in (1) giving the plant protection against reactive oxygen species, (2) protecting plants against the oxidative stress through enhancing the plant antioxidative enzymes including superoxide dismutase, catalase, peroxidase and (3) the acting of nanomaterials itself as inducers of oxidative stress. The small size of these nanomaterials can help plants easily in penetrating and regulating water channels and then assisting the germination of seeds and plant growth as well as the big surface area of nanomaterials improves the adsorption and delivery substances (Khan et al. 2016).

4.5 Nanofertilizers and Nanonutrients

As mentioned before, a real revolution in nanoparticles or nanomaterials has been achieved to penetrate all fields including industrial, pharmaceutical, medicinal, and agricultural sectors. These nanoparticles represent a magic solution in many sectors such as nanoremediation of polluted water and lands (Gil-Díaz et al. 2016a, b; Gillies et al. 2016; Peters et al. 2016; Zhao et al. 2016). Several studies regarding nanoparticles have been published focusing on many fields including energy sector (Le Croy et al. 2016), food industries (Khan and Oh 2016; Rizwan et al. 2016b; Souza and Fernando 2016), synthesis of nanoparticles (Ahmed et al. 2016a; Bennur

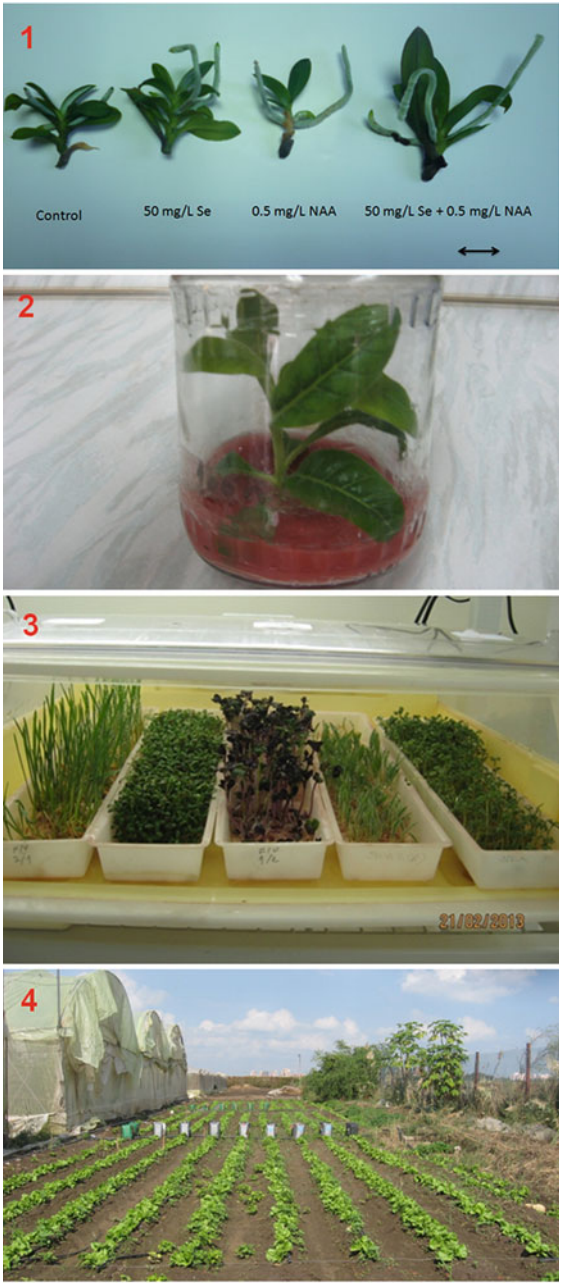

Fig. 4.1 Some experiments using nanoparticles in plant nutrition including *in vitro* trials (*photo 1*: nano-Se and in a very hard rooting moth orchids plant – *Phalaenopsis spp*. – unpublished data; whereas *photo 2*: nano-Se and tobacco plant growth), microfarm (*photo 3*: nano-Se and some sprouts production) and field experiments (*photo 4*: using of nitrogen nanofertilizer in lettuce growth). All photos by El-Ramady except no.1 by Elmahrouk; a kind permission from Dr. Mohamed Sharaf for *photo 4*; the bar in *photo 1* represents 2 cm

et al. 2016; Kuppusamy et al. 2016a, b; Sodipo and Abdul Aziz 2016; Singh et al. 2016), nanosensors (Priyadarshini and Pradhan 2016), oil lubrication (Dai et al. 2016), the dynamics and effects of metal oxide nanoparticles (Joo and Zhao 2016; Mustafa and Komatsu 2016; Rizwan et al. 2016b), biomedical applications (Durán et al. 2016; Karimzadeh et al. 2016; Jones et al. 2016; Zarschler et al. 2016), and antimicrobial purposes (Ahmed et al. 2016b; Samiei et al. 2016; Ambika and Sundrarajan 2016).

It is well known that, nanoparticles can (in homogeneous or heterogeneous) interact with soil, air, sediment, and plants and release into different previous environmental compartments. Several studies concerning the beneficial and negative effects of nanoparticles on plants have been reported (Rizwan et al. 2016b; Wang et al. 2016a, b). Definitely, these effects were controlled by plant and nanoparticles characterization including the source, type, the duration of exposure to plants and size of these nanoparticles as well as the plant species (Rico et al. 2014; Bandyopadhyay et al. 2015; Lalau et al. 2015; Cox et al. 2016; Du et al. 2016; Mustafa and Komatsu 2016). On the other hand, the factor of environmental media is also significant in orientation the interaction between nanoparticles and plants including *in vitro* (Domokos-Szabolcsy et al. 2012, 2014; El-Ramady et al. 2014c; Gomez-Garay et al. 2014; Homaee and Ehsanpour 2015; Castiglione et al. 2016; Kumari et al. 2016; Sarmast and Salehi 2016), micro-farm (El-Ramady et al. 2014a, b, c; El-Ramady et al. 2015a, b; El-Ramady et al. 2016a, b), pots (Alidoust and Isoda 2013; Sri Sindhura et al. 2014; Rico et al. 2015a; Gogos et al. 2016; Moll et al. 2016), hydroponic (Schwabe et al. 2013; Haghighi et al. 2014; Zhang et al. 2015a, b; López-Moreno et al. 2016; Tripathi et al. 2016) and field experimentation (Suriyaprabha et al. 2012).

In the early 2000s, the *nano-era* began when more than 35 countries have been initiated research programs in nanotechnology, resulting in a steady increase in engineered nanomaterials production (Zuverza-Mena et al. 2016). The release of engineered nanomaterials in the environment is considered an important issue (Nowack et al. 2013, 2014, 2015; Keller et al. 2013, 2014; Wigger et al. 2015; Conway and Keller 2016; Caballero-Guzman and Nowack 2016; Nowack et al. 2016; Park et al. 2016; Tolaymat et al. 2016). It has been resulted from the rapid proliferation of nanoproducts use increasing in the exposure to humans through different environmental systems (e.g. water, air, sediments and soils). Regarding the exposure to nanomaterials, it could be happened directly through the unintentional release during both use and consumption of nanoproducts and through remediation purposes for polluted sites (Nowack et al. 2013). The indirect pathway for nanomaterials can be occurred *via* the sewage treatment plants and landfills as well as incineration plants (Park et al. 2016; Caballero-Guzman and Nowack 2016).

There are several metal/metalloid oxide nanoparticles (e.g., TiO_2, ZnO, CeO_2) can be release into the aquatic environments through both wastewater discharge and runoff (Osmond and McCall 2010). It is reported that, ZnO and TiO_2 nanoparticles have been extensively used in the production of skincare products, with more than 33,000 tons of sunscreens produced containing up to 25% of ZnO nanoparticles as well as at least 25% of the sunscreen used (~4000–6000 tons/ year) was released in reef areas (Joo and Zhao 2016; Caballero-Guzman and Nowack 2016). Concerning the uptake pathway by plants and translocation of metal nanoparticles, two confirmed pathways in plant system have been reported including the uptake from the soil application (root to leaves or fruits) or from the foliar application (leaves to roots) (Ma et al. 2015; Du et al. 2016). Due to the existence of metal nanoparticles and their interaction with plant system, several physiological, agronomical, photosynthetic parameters and antioxidant activities have been reported (Du et al. 2016; Reddy et al. 2016; Rizwan et al. 2016b; Zuverza-Mena et al. 2016).

It is reported that, fertilizers are an important outputs in enhancing the agricultural production but its problem includes the environmental pollution from overuse and the low use efficiency (only 30–40% from the total applied fertilizers, whereas the rest is lost form the agroecosystem through leaching or evaporation or degradation) (Panpatte et al. 2016). Therefore, using the nanofertilizers or nanonutrients will increase the efficiency use of nutrients as well as reducing the possibility for environment pollution if nanofertilizers will be used in proper amounts. On the other hand, nanofertilizers can be mainly produced from the encapsulation of fertilizers within a nanoparticle. Concerning the main techniques for encapsulating fertilizers within nanoparticles, it is reported according to Rai et al. (2012) that, these techniques include (1) encapsulating the nutrients inside nano-porous materials, (2) coating with thin polymer film and (3) delivering nutrients as particle or emulsions in nanoscale dimensions (Panpatte et al. 2016).

Nanofertilizers can be defined as fertilizers contained within nano-structured formulations which can be delivered to targeted sites to allow release of active ingredients keeping the plant nutrient demands (Wang et al. 2016a, b). Therefore, among different agricultural inputs, nanofertilizers can be quite considered promising in enhancing the growth, nutrition and then productivity of crops as well as regulating the release of nutrients and improving efficiency use of nutrients under controlled environmental conditions (Yuvaraj and Subramanian 2015; Subramanian et al. 2015, 2016). Different crops have been fertilized using nanonutrients or nanofertilizers as presented in Table 4.2. These studies include fate and behavior of these nanonutrients in different agroecosystem compartments (soil, water and soil micro-biota), and evaluation of the potential mechanism for toxicity of nanonutrients and their tolerance in both soil–micro-biota and plants (Anjum et al. 2015). It is found that, the manufactured nanoparticles are not always more toxic than other chemical species containing the same elements. For example, CuO nanoparticles are slightly more toxic comparing with other Cu ions, whereas ZnO nanoparticles have a similar toxicity of Zn ions but in case of manganese and iron oxide nanoparticles the toxicity were less than their ionic counterparts as well as significant enhancement the growth of lettuce seedlings by 12–54%, respectively (Liu et al. 2016). That means nanoparticles of Mn and Fe can be considered effective nanofertilizers in increasing the agronomic productivity (Liu et al. 2016).

Therefore, it could be summarized that, the global food production suffer from several challenges including climate changes, pollution, poverty, the wrong agricultural practices, tenure, and low soil fertility. To save the enough and safe food for all people, new strategies in the agricultural production should be performed particularly using the applications of technology in agriculture. These applications include the precision farming and nanofertilizers or nanonutrients. A part from the great advantages of nanofertilizers including the high use efficiency, saving in costs

Table 4.2 A list of some important articles published recently on plant nano-nutrition

Focus area of the study	References
The effects of uncoated and coated cerium oxide nanoparticles with citric acid, bulk cerium oxide, cerium acetate on the nutritional quality of tomato fruits	Barrios et al. (2016)
Physiological and biochemical response of plants to engineered nanomaterials and their levels in the environment including the interactions with the plants, soil microorganisms and potential accumulation in the food chain	de la Rosa et al. (2016)
The interaction between metal oxide nanoparticles with higher terrestrial plants including the physiological and biochemical aspects	Du et al. (2016)
Selenium and nano-selenium in plant nutrition including different nano-fertilizers of selenium	El-Ramady et al. (2016a)
Synthesis, using and characterization of nano-zeolite and nano–composite as an environment friendly slow release fertilizer	Lateef et al. (2016)
Study of the phytotoxicity of ionic ($FeCl_3$), micro- and nano-sized zerovalent iron in three macrophyte plants (*Lepidium sativum*, *Sinapis alba* and *Sorghum saccharatum*)	Libralato et al. (2016)
Study the effects of stabilized nanoparticles of oxide Cu, Zn, Mg, and Fe in low concentrations on lettuce seed germination to establish and know these nano-toxicants or nanonutrients	Liu et al. (2016)
Effects of soil organic matter contents on cerium translocation and different physiological processes in kidney bean plants exposed to cerium oxide nanoparticles increasing the antioxidant enzyme activities in the aerial tissues of plants	Majumdar et al. (2016)
Toxicity of heavy metals and metal-containing nanoparticles on plants including different strategies for plant tolerance mechanisms and transport through cell wall and plasma membrane and the vacuole	Mustafa and Komatsu (2016)
The next generation technology for nanoparticles and its application in nanofertilizers in frame of the sustainable agriculture	Panpatte et al. (2016)
Different lessons learned from nanotechnology including the toxicity of engineered nanomaterials to terrestrial plants	Reddy et al. (2016)
The next steps for understanding engineered nanoparticle exposure and risk in frame of nanotechnology in agriculture	Servin and White (2016)
Using of nano-TiO_2 particles in removal and bioaccumulation of cadmium in soybean plants cultivated in contaminated soils	Singh and Lee (2016)
Selenium nanoparticles as a nutrition supplement including different methods for synthesis of Se-nanoparticles	Skalickova et al. (2016)
Nano zerovalent iron from synthesis to environmental applications including the impacts on living organisms, microorganisms, aquatic and soil, plants and its toxicity assessment	Stefaniuk et al. (2016)
The role of nano-silicon and its foliar application on heavy metals accumulation in different rice cultivars	Wang et al. (2016c)
Exposure of different engineered nanoparticles (metal oxide of iron, copper, zinc, etc) to plants including the physiological and biochemical responses	Zuverza-Mena et al. (2016)
Different copper nano-scales and its fate in the soil–plant system including the toxicity and its potential mechanisms	Anjum et al. (2015)

(continued)

Table 4.2 (continued)

Focus area of the study	References
The applications of nanotechnology in agriculture sector including the controlled release of different agrochemicals	Aouada and de Moura (2015)
The using, applications and perspectives of nanoparticles in sustainable agricultural crop production	Ditta et al. (2015)
The potentials of engineered nanoparticles as fertilizers in increasing the agronomic productions	Liu and Lal (2015)
The emerging contaminants and opportunities for risk mitigation from both nanopesticides and nanofertilizers	Kah (2015)
The strategic role of nanotechnology in fertilizers sector including their potential and limitations	Mastronardi et al. (2015)
Nano-fertilizers and their smart delivery system including the comparison between conventional and nano-fertilizers	Solanki et al. (2015)
Nano-fertilizers and their using for balanced crop nutrition including synthesis of nanofertilizers, characterization, uptake by plants	Subramanian et al. (2015)
Implications of nanotechnology on plant productivity including nanofertilizers and its rhizospheric environment	Thul and Sarangi (2015)
Using silicon nanoparticles in alleviating chromium (VI) phytotoxicity in pea (*Pisum sativum* L.) seedlings	Tripathi et al. (2015)
The role of foliar application with nano-silicon in alleviating cadmium toxicity in rice seedlings	Wang et al. (2015)

and time, a lot of problems are still need solution and further researches. These problems include the nanotoxicity, ecotoxicity, genotoxicity for all environmental compartments.

4.6 Plant Nano-nutrition

The using of nanoparticles or nanomaterials in plant nutrition could be defined as the plant nano-nutrition. It includes using these nanofertilizers or nanonutrients in supplying cultivated plants with the essential nutrients for their growth and productivity (e.g., ZnO, SiO_2, iron oxide, CuO, Mn oxide, phosphorus, nitrogen nanoparticles, etc.). That means simply the source of different nutrients for plants will be through the applied nanonutrients or nanofertilizers as well as the release of nutrients will be also slowly and steadily for a long time (more than 30 days) creating a new approach in improving the nutrient use efficiency (Kah 2015; Mastronardi et al. 2015; Subramanian et al. 2015). Globally, the use of nanofertilizer in a large scale is still limited, although the customized fertilizers have a significant role in sustaining the farm productivity (Subramanian et al. 2015).

As mentioned before, nanonutrients are nutrients in nano-dimensions ranging from 30 to 40 nm having the capability in holding of many nutrient ions because of their high surface area; the release of nutrients is slowly and steadily in commensuration with crop demands (Subramanian et al. 2015). It is also reported about the effects of nanonutrients on the nutritional quality of crops by a few researchers (e.g., Peralta-Videa et al. 2014; Barrios et al. 2016; Reddy et al. 2016; Servin and White 2016). These effects include in general beside different positive effects on plant defense and growth aspects improving the nutritional quality of edible crops. The previous effects definitely depend on the type, concentration and size of metal/metalloid nanoparticles or nanonutrients, plant species, soil and its characterization and climatic conditions. The nutritional quality of edible crops has been become one of the most important issues in plant nano-nutrition, which many studies focused on it (e.g., Rico et al. 2013, 2014, 2015a; Reddy et al. 2016; Servin and White 2016). Many previous studied have been shown effects of nanoparticles on the nutritional quality of some crop plants exposure to CeO_2 nanoparticles such as wheat (Rico et al. 2014), rice (Rico et al. 2013), barley (Rico et al. 2015a), soybean (Lopez-Moreno et al. 2010; Hernandez-Viezcas et al. 2013; Peralta-Videa et al. 2014), tomato (Wang et al. 2013; Barrios et al. 2016) and cucumber (Zhao et al. 2014).

Therefore, plant nano-nutrition is a branch of plant nutrition dealing with the nutrition and development of plants using nanonutrients or nanomaterials. These nanonutrients have a positive effects in plant growth as well as the nutritional quality of crop plants. Definitely, there are some gaps in plant nano-nutrition particularly in the use of these nanonutrients on the large scale and the global level. The different interactions between nanonutrients or nanomaterials with different agroecosystem compartments is still not fully understood and needs further more researches.

4.7 Conclusion

No doubt that, metal/metalloid nanoparticles have a vital role in the emerging nanotechnological sectors but the progress in researches related to the impact of these nanoparticles on the terrestrial environments is still not fully understood. In general, the concentration of nanoparticles less than 50 mg kg^{-1} thought to be beneficial for plant growth, whereas the higher concentrations will be inhibited as well as toxic. Therefore, more in depth studies should be carried out on the plant cell level including gene expression, production of reactive oxygen species, signal transduction etc. (Reddy et al. 2016). Studies of omics in the nanotoxicology should be also considered (Costa and Fadeel 2016; Hu et al. 2016) as well as the plant physiology and biochemistry resulted from nanonutrients exposure (Barrios et al. 2016; de la Rosa et al. 2016; Zuverza-Mena et al. 2016). More researches are also needed in investigating the response of the terrestrial ecosystems to the combined metal nanoparticles and the interaction between nanoparticles and pollutants under different climatic conditions including the arid, flooding, etc. (Du et al. 2016). More investigations in the rhizospheric region are required in order to evaluate the interaction among nanonutrients besides their properties and different soil characterization as well as plant species (Majumdar et al. 2016; Zuverza-Mena et al. 2016). It is worth to mention that, an urgent need is also wanted concerning development of a framework in measuring the availability and total soil contents of nanoparticles or nanonutrients as well as their extraction (Rodrigues et al. 2016).

The safe and enough food production were and will still the global emerging issue. To produce these enough amounts of food, it should focus on the plant nutrition science and how develop its applications to achieve this global target. Plant nano-nutrition can be considered one of the most important tools that help us in performing a high use efficiency of nutrients saving their amount and time. A global regulation for use these nanonutrients or nanofertilizers should be established as soon as possible.

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