Exposure of engineered nanomaterials to plants: Insights into the physiological and biochemical responses-A Review

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38 **Abstract**

39 Recent investigations show that carbon-based and metal-based engineered nanomaterials
40 (ENMs), components of consumer goods and agricultural products, have the potential to build up
41 in sediments and biosolid-amended agricultural soils. In addition, reports indicate that both
42 carbon-based and metal-based ENMs affect plants differently at the physiological, biochemical,
43 nutritional, and genetic levels. The toxicity threshold is species-dependent and responses to
44 ENMs are driven by a series of factors including the nanomaterial characteristics and
45 environmental conditions. Effects on the growth, physiological and biochemical traits,
46 production and food quality, among others, have been reported. However, a complete
47 understanding of the dynamics of interactions between plants and ENMs is not clear enough yet.
48 This review presents recent publications on the physiological and biochemical effects that
49 commercial carbon-based and metal-based ENMs have in terrestrial plants. This document
50 focuses on crop plants because of their relevance in human nutrition and health. We have
51 summarized the mechanisms of interaction between plants and ENMs as well as identified gaps
52 in knowledge for future investigations.

53 **Keywords:** Engineered nanomaterials, Toxicity, Uptake, Accumulation, Crop plants, ROS
54 production

55 **Abbreviations:** n, prefix to denominate “nano”; μ , prefix to denominate “micro”; NP,
 56 nanoparticle; NM, nanomaterial; ENP, engineered nanoparticle; ENM, engineered nanomaterial;
 57 ppm, parts per million (mg/kg; mg/L); ZVI, zero-valent iron; CNT, carbon nanotube; SWCNT,
 58 single walled carbon nanotube; SWCNH, single walled carbon nanohorn; MWCNT, multi-
 59 walled carbon nanotube; OD, outer diameter; ID, inner diameter; NS, nutrient solution; MS,
 60 Murashige and Skoog; JPL, Jouanneau and Péaud-Lenoël; DNA, deoxyribonucleic acid; RAPD,
 61 random amplified polymorphic DNA; ROS, reactive oxygen species; H_2O_2 , hydrogen peroxide;
 62 ABA, abscisic acid; ADH, alcohol dehydrogenase; APX, ascorbate peroxidase; CAT, catalase;
 63 GDH, glutamate dehydrogenase; GS, glutamine synthetase; GPT, glutamic-pyruvic transaminase;
 64 IAA, indole-3-acetic acid; MDA, malondialdehyde; POD, peroxidase; SOD, superoxide
 65 dismutase; PSII, photosystem II; NOM, natural organic matter; wt, weight; TEM, transmission
 66 electron microscope; EC_{50} , half maximal effective concentration; IC_{50} , inhibition concentration,
 67 response reduced by half.

1. Introduction

The “Nano-era” began in the early 2000s when more than 35 countries initiated research programs in nanotechnology, leading to a steady increase in production of engineered nanomaterials (ENMs) (Roco, 2003). Special characteristics of ENMs such as higher surface area to volume ratio and reactivity, compared with equivalent bulk materials, have allowed their utilization in different technologies. Manufacturing, electronics, communications, medicine, water and wastewater treatment, personal care, agriculture and food packaging technologies are using ENMs, including carbon-based (fullerenes, graphene, and carbon nanotubes (CNTs)) and metal-based (quantum dots, metal and metal oxide) ENMs (Klaine et al., 2008; Peralta-Videa et al., 2011; Roco et al., 2011; Bandyopadhyay et al., 2013). The intensive use of ENMs has raised concerns about their possible build up in ecosystems and food supply. Concerns are greater in agriculture, where soils are intentionally exposed to products containing ENMs, irrigated with raw wastewater, or amended with ENM-loaded biosolids (Shah et al., 2010; Lu et al., 2012; Colman et al., 2013; Hong et al., 2013; Gardea-Torresdey et al., 2014).

Plants, primary producers in terrestrial ecosystems, have evolved in environments that have a high load of naturally occurring nanomaterials such as in the vicinity of active volcanoes (Rico et al., 2011). However, agricultural regions have higher risk of exposure to ENMs than to naturally occurring nanoparticles (NPs), since thousands of tons of ENMs are predicted to be released into air, water, and soil (Keller and Lazareva, 2014). Quantum dots (QDs), carbon-based, and metal-based ENMs have been shown to produce different effects on plants (Rico et al., 2015b). These include accumulation, effects on the growth, physiological and biochemical traits, production, and quality of food, among others (Gardea-Torresdey et al., 2014). Quantum dots have been studied for cell imaging in living plants (Müller et al., 2006; Hu et al., 2010) given their fluorescent properties (Al-Salim et al.,

2011). While mercaptoacetic acid (MAA)-coated CdSe/ZnS QDs had “very little” toxicity in maize seedlings (Hu et al., 2010), pristine cadmium/tellurium (Cd/Te) QDs have been found to cause fracture of chromatin, destruction of mitochondria and growth inhibition in green gram sprouts (*Phaseolus radiatus*) (Song et al., 2013).

A good understanding of the interactions between ENMs and plant systems is of paramount importance for assessing the NMs’ toxicity and their possible trophic transport (Gardea-Torresdey et al., 2014). Variation in accumulation and biotransformation, perturbation of agronomic and physiological traits, and detoxification ways have been reported (Ma et al., 2015). A few studies have also shown that ENMs impact seed quality in some plant species (Rico et al., 2014; 2015a; Majumdar et al., 2015). In addition, Rico et al. (2015b) reviewed the effects of metal-based ENMs on plants’ antioxidant defense, while Ma et al. (2015) reviewed recent advances in ENMs’ detoxification pathways in higher plants. In this review we analyze the most recent advances in the physiological and biochemical responses of higher plants to ENMs exposure. The reviewed literature covers the most used carbon-based and metal-based ENMs (ordered by their appearance in the periodic table, followed by stable metal oxides) and studies performed in model wild plants and crop plants.

2. Carbon-based nanomaterials

Carbon-based nanomaterials started in 1985 with the detection of the first fullerene, which was called “Buckminsterfullerene or the buckyball” (Kroto et al., 1985; Klaine et al., 2008). The CNTs are fullerene derivatives that appeared in 1991, while graphene was isolated in 2004 (Novoselov et al., 2004; Klaine et al., 2008). The three members of the CNT family have been found to interact with living organisms in different manners. Readers

interested in the bioaccumulation and ecotoxicity of CNTs in aquatic microorganisms,
 pelagic invertebrates and vertebrates, and terrestrial invertebrates will find abundant
 information in the review by Jackson et al. (2013). Literature shows that, in plants, single
 walled carbon nanohorns (SWCNHs), SWCNTs, and multi-walled carbon nanotubes
 (MWCNTs) affect the physiology and biochemistry in diverse ways. Single-walled carbon
 nanotubes (SWCNTs) affect root growth in a species-dependent manner (Cañas et al., 2008).
 Besides the effects on plant growth (Khodakovskaya et al., 2013), research points towards
 the fact that all carbon-based ENMs All carbon based ENMs could potentially modify the
 expression level of genes involved in responses to stimuli. For instance, SWCNHs impact the
 expression of genes involved in stress responses in tomato, a feature that can be controlled to
 regulate plant development (Lahiani et al., 2015). However, more studies especially related
 to food quality are required before recommending SWCNHs or other carbon based NMs to
 be safely used in crop production. On the other hand, CNTs have shown to modify DNA
 structure in plant tissues. While MWCNTs prompted chromosomal aberrations in *Allium*
cepa roots, which resulted in differential expression of genes involved in cellular division
 and apoptosis (Ghosh et al., 2011), the proximity of SWCNT to DNA led to the unzipping of
 the strands, impairing the normal matching of the nucleobases in rice DNA (Katti et al.,
 2015).

Other biochemical changes induced by carbon-based ENMs include redox modifications
 in certain ions like Fe^{2+} or Fe^{3+} or cationic exchange in the maize (*Zea mays*) cell wall matrix
 (Tiwari et al., 2014). A previous compilation of the literature on carbon-based ENMs was
 published by Husen and Siddiqi (2014). Table 1 provides a summary of compelling data on
 the biochemical and physiological effects produced by carbon-based ENMs in plants. As

seen in Table 1, most of the studies have been performed with MWCNTs. These nanotubes have been exposed to several plants such as zucchini, corn, tomato, and soybean with no apparent toxic effects (De La Torre-Roche et al., 2013). Similar results were reported by Lin and Xing (2007) in rape (*Brassica napus*), radish (*Raphanus sativus*), ryegrass (*Lolium perenne*), lettuce (*Lactuca sativa*), corn (*Zea mays*), and cucumber (*Cucumis sativus*). However, in rice (*Oryza sativa*), these nanotubes delayed flowering by 1 month, affecting seed formation (Lin et al., 2009), upregulated stress-related genes in tomato (*Solanum lycopersicon*) plants (Khodakovskaya, 2011), and increased peroxidase (POX) activity in *Onobrychis arenaria* seedlings (Smirnova et al., 2012).

3. Metal-based nanomaterials

The properties that make NPs unique could adversely affect crop plants or favorably transform agriculture and food production. The literature provides diverse, and often contradictory, results on the plant responses to NPs. Some of the factors driven the results are shown in Tables 2 - 8. This review comprises commercial metal-based nanomaterials. Nano-sized Fe, Cu, and Zn are included as bare metal and as their derivative forms such as zero valent iron nanoparticles (nZVI) and FeOx. Also, Ag and Au are presented only as plain metals and at last, the oxides CeO₂ and TiO₂ are discussed.

3.1 Fe-based nanomaterials

Although iron and iron oxides are environmentally ubiquitous materials, nowadays the utilization of iron-based nanomaterials (nFeOx) is being widely studied (Afkhami et al., 2010; Mohapatra and Anand, 2010; Pan et al., 2010; Dias et al., 2011; Gómez-Pastora et al.,

2014; Martínez-Fernández et al., 2016b). The easy and cost-effective synthesis of highly reactive nanogoethite (α -FeOOH), nanohematite (α -Fe₂O₃), nanomaghemitite (γ -Fe₂O₃), nanomagnetite (Fe₃O₄), and nano zero-valent iron (nZVI) makes them readily available from the academic community and industrial producers. Their nano-size and magnetic characteristics involve an increased specific surface area and modified surface structure, which strongly affect their reactivity and chemistry (Deliyanni et al., 2004; Waychunas et al., 2005; Mohapatra and Anand, 2010; Mueller et al., 2012). It has been demonstrated that nFeOx are important scavengers of the most toxic forms of As(III), Cr(VI), Cd(II), Cu(II), Pb(II), and Zn(II) (Chen and Li, 2010; Nassar, 2010; Zhang et al., 2010; Chomoucka et al., 2012; Lin et al., 2012; Roy and Bhattacharya, 2012; Tuutijarvi et al., 2012; Xu et al., 2012; Jiang et al., 2013; Akhbarizadeh et al., 2014; Komárek et al., 2015). For that reason, environmental engineering has used nFeOx for environmental remediation purposes, especially for the removal of metal/metalloids from contaminated waters and soils, or their stabilization therein (Gómez-Pastora et al., 2014; Martínez-Fernández et al., 2016b). During the remediation of contaminated soils, nFeOx can be used as a permeable wall in the soil and in porous media, applied directly as nFeOx or in the form of their precursors (i.e. nZVI) (Komárek et al., 2013). They are considered to be of low mobility and are assumed to remain where they are applied due to the insolubility of nFeOx and their preferential adherence to soil particles. In the resulting iron-enriched walls, flowing contaminations can be broken down chemically because of their adsorption capacities. In this way, the *in situ* immobilization of contaminants limits the potential leachability of pollutants, which prevents their transport into deeper soil layers and groundwater (Gil-Díaz et al., 2014).

Due to their potential cost-efficiency, compared to conventional methods, it is expected that nFeOx will be increasingly used as widespread remediation amendment. nFeOx can also be easily separated and recovered, because these NPs are magnetic (Gómez-Pastora et al., 2014). In fact, researchers are also investigating nFeOx to be used in medical imaging and treatments as “magic bullets,” since their iron core can guide the delivery of a drug by the use of a magnetic field to a particular region of patient bodies (Lin et al., 2007).

Naturally occurring iron oxides are ubiquitously found in the environment and the amounts of engineered nFeOx administered are usually small. In general, nFeOx are considered to be non-toxic to the environment mainly because nFeOx are scarcely taken up by organisms. The recorded effects of nFeOx on plants indicate lack of uptake, insignificant translocation to the shoots (Zhu et al., 2008; Corredor et al., 2009; Wang et al., 2011; Ma et al., 2013; Martínez-Fernández et al., 2016b), and that nFeOx are not transported across the plasma membranes given that NPs larger than 20 nm are considered to be unable to penetrate through the cell walls (Rico et al., 2013; Martínez-Fernández et al., 2016a). Uncoated nFeOx behave similarly to naturally occurring iron-based nanoparticles and agglomerate to a certain degree due to Van der Waals forces and other interactions, forming aggregates too large to be transported within the xylem tissues. Both the nFeOx and their aggregates adhere to the negatively-charged root surface by electrostatic attraction and binding to cation exchange sites (Trakal et al., 2015).

The effects of nFeOx on plants have been related to particle aggregation on the surface of the roots. The clogging effects of nFeOx reduce the root hydraulic conductivity by inhibiting the adequate water uptake (Ma et al., 2013; Martínez-Fernández et al., 2015). Martínez-Fernández et al. (2016a) found a reduction of macronutrients (Ca, K, Mg and S) in

sunflower's shoots. They suggest that this was due to the water blocking effects of nFeOx, which altered the dissolved nutrients in water. In this way, even internal symptoms in the plants (Table 2) can be explained by mechanical disruption of membranes and root cell walls during nFeOx exposure, which disturbs the interactions of the plant with the external medium. For example, the increase in the antioxidant enzyme activities in plants treated with nFe₃O₄ has been suggested to be more related to disruption of the mineral uptake than to direct effects of nFe₃O₄ (Trujillo-Reyes et al., 2014). The increase in lipid peroxidation has also been attributed to nFe₃O₄ blockage of the aquaporins and disturbance of the respiration rate in the root (Wang et al., 2011). In a similar way, nFeOx generally reduce the accumulation of chlorophylls in the leaves, but this effect is also related to the reduction of the root hydraulic conductivity and the transport of dissolved nutrients, especially for Mg since this nutrient is associated with the synthesis of chlorophylls (Ma et al., 2013; Trujillo-Reyes et al., 2014; Martínez-Fernández et al., 2016a). With this in mind, nFeOx are not toxic to plants, but their potential adherence to the root surface causes adverse effects in plants when administered in relatively high concentrations. According to the literature published to date, the recorded effects of nFeOx fall into all possible classes because the toxicity threshold is species-dependent—being negative, nil, or positive at the physiological, biochemical, nutritional, and genetic levels—but the complete causes of all of them are not clear enough yet.

3.2 Cu-based nanomaterials

Copper is an essential element for plant nutrition (Yruela, 2005). On average, one kilogram of dry plant tissue contains 10 mg of Cu (Baker and Senef, 1995). Extensive studies

have been performed regarding insufficient or excessive amounts of Cu in plants (Yruela, 2005). However, there is limited information about the effects of copper-based nanomaterials in plants.

Research on plant exposure to Cu based nanomaterials (Table 3) includes metallic nano-copper (nCu), nano-CuO (nCuO), and composite nanoparticles of a Cu center coated with CuO. Besides the NPs, researchers usually include a treatment of soluble Cu (a salt that most likely dissociates into Cu^{2+} ions) in order to discriminate between the effects of ions and particles. For example, Lee et al. (2008) grew mung bean and wheat seedlings for two days in agar and attributed the toxicity (seedlings' length decrease) to Cu NPs and not the Cu ions. They suggest that Cu NPs can cross the cell membrane, since Cu aggregates were observed in root cell vacuoles of both species. However, Aruoja et al. (2009) exposed microalgae to micro-sized (bulk) CuO and CuO NPs. Even though CuO NPs seemed to be more toxic than bulk CuO, they concluded that the growth inhibition was attributed to the released Cu ions, and not the NPs. Similarly, Perreault et al. (2014) observed that the inhibition of photosynthetic activity of duckweed exposed to CuO NPs was due to the Cu^{2+} ions released from NPs.

Cell walls are the principal zone of interaction through which NPs could get access inside plants (Masarovičová and Král'ová, 2013). Wang et al. (2011) described that CuO NPs enter into prokaryotic alga cells by endocytosis without affecting the phospholipid bilayer integrity. Even though the mechanisms of Cu-based NP entrance into higher (vascular) plants are not yet completely understood, Le Van et al. (2016) proved that Bt-transgenic cotton internalizes nCuO into leaves' cells through endocytosis, while conventional cotton retained the nCuO on the outmost cell layer. In the roots, most of the CuO clusters remained

in the epidermis, but some CuO was also detected within intercellular spaces of both cotton types (Le Van et al., 2016). Wang et al. (2012) localized the CuO NPs in maize seedlings' epidermal cell walls. These researchers also reported that maize translocate nCuO from roots to shoots through the xylem and from shoots to roots via phloem. Likewise, Andreotti et al. (2015) found that the salt marsh plant *Phragmites australis* can relocate Cu from roots to shoots. Although they observed that a similar species (*Halimione portulacoides*) retained Cu in the roots. CuO NPs can trigger the formation of reactive oxygen species (ROS) (Nair and Chung, 2014; Nair et al., 2014) causing oxidative stress (Dimkpa et al., 2012; Shaw and Hossain, 2013) and DNA damage (Shi et al., 2011; Atha et al., 2012).

Other molecular changes induced by the presence of NPs include modifications in the amount of hormones. For example, exposing cotton and Bt-cotton to CuO NPs resulted in significant alterations of the concentrations of indole-3-acetic acid (IAA) and abscisic acid (ABA) (Le Van et al., 2016). In addition, plants activate antioxidant enzymes as part of detoxification mechanisms (Shaw et al., 2014). For example, Trujillo-Reyes et al., (2014) found that in roots of lettuce exposed to Cu/CuO NPs, the activity of catalase (CAT) increased, while that of ascorbate peroxidase (APX) decreased. Other researchers also found changes in enzymatic activities after exposure to Cu NPs (Table 3) Exposure to Cu-based NPs can also affect the balance of nutritional elements' content in plants (Dimkpa et al., 2015). In addition, the effects seem to be species-dependent. Hong et al. (2015) reported that Cu-based NPs increased P and S in alfalfa shoots, while decreased Fe and P and in lettuce shoots. Similarly to the effects in lettuce, P contents decreased in cilantro shoots exposed to several Cu based NMs (Zuverza-Mena et al., 2015).

Cu based NPs also affect the amount of photosynthetic pigments. In mung bean plants, carotenoids remained unchanged and chlorophyll reduction began at 100 mg/L CuO NPs (Nair et al., 2014), while in soybean, carotenoids content diminished at 400 mg/L CuO NPs, but chlorophyll started decreasing at 400 mg/L (Nair and Chung, 2014a). However, in mustard, CuO NPs reduced carotenoids and chlorophylls (Nair and Chung, 2015) and in cilantro, Cu-based NPs did not affect chlorophyll production (Zuverza-Mena et al., 2015). Overall, the effects of Cu-based NPs in plants appear at different levels of exposure and conditions depending on the NPs characteristics and plant species.

3.3 Zinc oxide nanoparticles (nano-ZnO)

Zinc oxide (ZnO) NPs hold a vast area of applications due to their unique properties such as optical, antimicrobial, wide band gap, increased catalytic efficiency and surface area (Kołodziejczak-Radzimska and Jesionowski 2014). Inconsistent results are commonly found in reports about the interaction of ZnO NPs with plant systems. For instance, Prasad et al. (2012) exposed *Arachis hypogaea* L. to a 1000 mg ZnO NPs/L suspension for 3 h and reported an increase in germination and seedling vigor. On the other hand, corn kernels incubated for 2 h in a suspension of ZnO NPs at 2000 mg/L showed germination inhibition (Lin and Xing, 2007). The gene profile of *Arabidopsis thaliana* exposed to ZnO NPs compiled by Landa et al. (2012) shows alterations in the plant's genome, including down regulation of genes associated with protein synthesis and biogenesis. Other physiological and biochemical responses of plant exposed to ZnO NPs are, to some extent, consistent in the literature (Table 4). Different media including hydroponics, agar and soil have been used. Exposure of pea (*Pisum sativum*) to nZnO had an impact on root length, decreasing the

number of first- and second-order lateral roots (Huang et al., 2014). Exposure to ZnO NPs also resulted in shorter root length of radish (*Raphanus sativus*), rape (*Brassica napus*), ryegrass (*Lolium* sp.), lettuce (*Lactuca sativa*), corn, and cucumber seedlings (Lin and Xing 2007). Additionally, Yoon et al. (2014) reported similar results using soil as growth media and a ZnO NPs concentration of 500 mg/kg. Kumari et al. (2011) concluded that there was a higher toxicity of ZnO NPs when compared to the Zn^{2+} ion, based on a hydroponic study in onion (*Allium cepa*), suggesting a higher release of reactive oxygen species as the possible toxicity mechanism. Nevertheless, Wang et al. (2013) reported that in soil amended with either ZnO NPs or Zn^{2+} , cowpea (*Vigna unguiculata*) showed no difference in plant growth, accumulation or speciation between the ion and the ZnO NPs treatments. This difference in results between hydroponic and soil experiments emphasizes the importance of the growth matrix when investigating NPs-plant interactions.

Recently, a study found that soil amended with ZnO NPs increased plant height on *Solanum lycopersicum* at concentrations up to 250 mg/kg. Above that concentration, the plant root length was affected (Raliya et al., 2015). Foliar application of ZnO NPs to *Cyamopsis tetragonoloba* L. and *S. lycopersicum* has also shown a positive response in terms of biomass, chlorophyll, and total soluble leaf protein content (Raliya et al., 2013; Raliya et al., 2015).

The interactions of NPs in the rhizosphere are of great interest due to the potential effects they could have on the roots-bacteria symbiosis. Studies have found that the presence of ZnO NPs in the environment is potentially hazardous to the Rhizobium–legume symbiosis system (Huang et al., 2014), and this interaction is an important factor for plant growth and crop productivity, since it provides bio-available nitrogen to the plants. The presence of nZnO in

the rhizosphere affected the early interactions between rhizobia and the host plant as well as nodule development, and subsequently delayed the onset of nitrogen fixation (Huang et al., 2014).

The analyzed literature suggests that it is essential to understand the physiological and biochemical responses of plants to ZnO NPs' exposure to assess their potential role in agriculture and the environment. The response of numerous plants to ZnO NPs is summarized in Table 4.

3.4 Silver nanoparticles

Nanosilver (silver nanoparticles, nAg) is a zero-valent silver (Ag^0) (Schluesener and Schluesener, 2013; Ivask et al., 2014) which possesses stronger, longer-term, and broader spectrum antimicrobial activities compared with its bulk counterpart (bulk silver). This is mainly due to its high specific surface area and the silver ion (Ag^+) release from nAg dissolution (Kittler et al., 2010; Xiu et al., 2012; Yu et al., 2014; Kooti et al., 2015). In fact, stability tests of nAg indicated a 7% decrease in the presence of Ag as nanoparticles three months after its synthesis (Galazzi et al., 2016). As a result of its biocidal activity, nAg has become one of the most commonly applied ENMs worldwide, being used for drinking water disinfection and wastewater treatment (Ahmed et al., 2014; Lalley et al., 2014; Loo et al., 2015), food preservation (De Moura et al., 2012; Llorens et al., 2012), medical/clinical uses (Dos Santos et al., 2014; Ge et al., 2014), and in numerous consumer products (Sharma, 2014; Wen et al., 2016; Zhang et al., 2016). The nAg is commonly synthesized through chemical reduction methods (Zhang et al., 2016) and green synthesis (Klaus et al., 1999; Dhand et al., 2016) that yields different morphologies such as spheres, rods, and cubes.

The production of nAg was estimated to be 3-20 tons per year in the U.S. (Hendren et al., 2011) and 5.5 tons per year in Europe (Piccinno et al., 2012), with approximately 800 megatons of global use per year (Geisler-Lee et al., 2014). Inevitably, nAg washes out of products and it is released into the environment (Colman et al., 2013; Sharma, 2013) with dramatic effects. For example, Ag^+ is viewed as one of the most toxic metal ions in fresh water environments (Griffitt et al., 2012). In fact, wastewater streams represent the primary entry pathway into the environment for nAg (Mueller and Nowack, 2008; Gottschalk et al., 2009), but its fate and toxicity are governed not only by the primary particle released from products, but also to a large degree by its transformation products like nAg_2S (Doolette et al., 2015).

Studies of the toxicity in plants due to nAg agree that silver nanotoxicity is positively concentration-dependent, negatively size-dependent, and more acute with a long exposure time (Gubbins et al., 2011; Lee et al., 2012; Geisler-Lee et al., 2014; see Table 5). Although the phytotoxicity of nAg has been related to the uptake of nAg by plants and to the presence of dissolved Ag^+ ions, the phytotoxic effect could not be explained solely by the dissolution as Ag^+ . When the roots of plants are exposed to nAg, alterations in the cell morphology and a notable change in color appear in the root tip (the cap and columella), attributed to the adsorption of the nAg—either by itself or in conjunction with cell wall materials or even with secondary metabolites produced by the root tips (Ma et al., 2010; Geisler-Lee et al., 2014). Some claim that most of the nAg aggregates on the root surface (Wen et al., 2016), and when nAg is bound to roots it may serve as a source of Ag^+ ions under toxic conditions, through the oxidation of zero-valent Ag (Dobias and Bernier-Latmani, 2013).

Regardless of whether the nAg particles are aggregated or not, once nAg is in the vascular tissues it can be taken up (mainly through root pathways) and then transported to the leaves through long-distance transport (Ma et al., 2010a; Dietz and Herth, 2011; Geisler-Lee et al., 2014). Moreover, aggregated nAg has been found in plasmodesmata and in the cell wall (Geisler-Lee et al., 2013). This suggests that there would be wall leakage and blockage of intercellular communication due to the mechanical presence of nAg at these sites (Geisler-Lee et al., 2014), affecting the function of nutrient transporter proteins and intercellular transport. Higher ascorbic acid levels were induced in *Asparagus officinalis* exposed to nAg (An et al., 2008), related to the modulation of antioxidant status in plants. In fact, ROS response has been documented under nAg exposure in *Brassica juncea* (Sharma et al., 2012), *Spirodela polyrhiza* (Jiang et al., 2014), and recently reported in *Arabidopsis thaliana*, with also higher total amino acid concentrations (Wen et al., 2016). As Table 5 shows, exposure to nAg seems to have many physiological and biochemical consequences in plants (transpiration, oxidative stress, genotoxicity, etc.), but until the causality of silver nanotoxicity (particle or ion) is disentangled, contradictory results will be common (reduction or increment in the chlorophylls content, inhibition or stimulation of growth, etc.).

3.5 Gold nanoparticles

In 1857, Michael Faraday discovered gold nanoparticles (nAu) and described them as fine “colloids” of gold which are “very minute in their dimensions”, thus founding what later would become modern nanotechnology (Thompson, 2007; Das et al., 2011). The nano-size of nAu has dramatic consequences for its physical and chemical properties, compared with bulk Au, for example, lower melting point, red color, and a larger proportion of atoms at its

surface, which allows the nAu to catalyze some reactions (Schmid and Corain, 2003). These Au NPs possess controllable size dispersity, stability, stronger adsorbing capacity, and excellent optical properties (Lee et al., 2010). As a result of their properties and economic interest as a precious metal, the synthesis of nAu has been widely investigated including simple and “green methods” for extraction using plants (Gardea-Torresdey et al., 2002; Elia et al., 2014; Megarajan et al., 2016). Currently, nAu synthesis is the most studied among all metal-based nanomaterials. Moreover, nAu are considered as chemically inert and have greater biological compatibility due to their non-cytotoxicity (Moaveni et al., 2011; Tomar and Garg, 2013). The versatile surface chemistry of nAu allows them to be coated with small molecules, polymers, and biological recognition molecules, thereby extending their range of application to medicine (diagnosis of diseases, targeted chemotherapy, drug delivery) and industrial uses (pollution-control technologies, colorimetric sensory probes, electronic conductors) (Schmid and Corain, 2003; Dykman and Khlebtsov, 2012). This industrial potential of nAu has led to the hazard of disposal of the related materials in the environment, imposing biomagnifications from primary producers to primary consumers and risks for ecosystems (Rayavarapu et al., 2010; Judy et al., 2011). However, the mechanisms of uptake of nAu by the primary producers, the plants, are far from being determined.

The terminal functional groups and surface charge greatly affect the nAu uptake into plant tissues. Positively charged nAu are the most readily taken up (Zhu et al., 2012; Koelmel et al., 2013). Since nAu behave conservatively inside plants and do not dissolve and form gold ions (Zhai et al., 2014), their effects are related to their accumulation and potential aggregation in the cells. As seen in Table 6, this accumulation in plant tissues is species- and size-dependent, with interference in plant growth. The mechanical disruption caused by

aggregates of nAu can influence the transport of nutrients and other materials when they lodge in the plasmodesmata (Zhai et al., 2014) and vascular tract (Koelmel et al., 2013). Similarly, the interference of nAu has been related to the increase in fluorescence quenching of chlorophylls, attributed to the enhanced electron transfer from excited chlorophyll molecules to nAu (Barazzouk et al., 2005; Falco et al., 2011; Rico et al., 2015).

Normally, plants are exposed to very small amounts of nAu, which are generally non-toxic and only exceptionally high concentrations—resulting from biomagnification—can be problematic (Judy et al., 2011). Even though the catalytic activity of bulk particles is zero, and it is greater for nAu, the effects of Au NPs seem to be mainly caused by mechanical and physical actions on plants, and gold nanotoxicology is a crucial factor regarding the use of nAu.

3.6 Titanium dioxide nanoparticles

According to recent estimates, nano-TiO₂ (nTiO₂) is the most abundant ENM released to the environment, with a high probability of reaching bodies of water (Keller et al., 2013). As a result, nTiO₂ will be in wastewaters and could be taken up by crop plants from biosolid amended agricultural soils (Gottschalk et al., 2009). Although there is no evidence of nTiO₂ aggregation, these NPs can remain in the soil due to their low solubility, and can be taken up by roots in nanoparticulate form, affecting the plants in different manners (Larue et al., 2012). The most recent studies suggest that the effects on plants are mainly caused by the NPs and not by ionic Ti (Du et al., 2011; Conway et al., 2015). Contradictory effects on seed germination have been reported for nTiO₂ (Zheng et al., 2005; Castiglione et al., 2011; Feizi et al., 2012). Zheng et al. (2005) reported that nTiO₂ (5 nm, 0.25-4%) increased water

absorption of spinach seeds, resulting in acceleration of germination. On the other hand, Feizi et al. (2012) did not find changes in germination of wheat grains exposed to nTiO₂ (20 nm, 1–500 mg/L); however, these researchers reported reduction in germination time of seeds exposed to 10 mg/L. Conversely, Castiglione et al. (2011) found delayed germination of *Vicia narbonensis* seeds exposed to nTiO₂ (<100 nm, 0.2–4.0%). Besides the effect on seed germination, nano-TiO₂ have been shown to affect plant growth. The presence of nTiO₂ in plant cells or accumulation on root cell walls of wheat (Figure 1a) changed the biochemical conditions in the area of contact, affecting the availability of nutrients and consequently, plant growth (Du et al., 2011).

Although the results of different studies are controversial, nTiO₂ have been shown to affect the electron transfer and absorption of water and light, consequently impacting the photosynthetic process. The effects on photosynthesis are attributed to the photocatalytic and thermal conductivity properties of this NM (Rezaei et al., 2015; Rico et al., 2015b). Perturbations in the photosynthetic activity result in oxidative stress, with a subsequent response of the antioxidative defense system (Rico et al., 2015b). In spinach leaves, nTiO₂ increase the Hill reaction and chloroplast activity by enhancing light absorption in chlorophyll *a*, electron transfer, and oxygen evolution rate (Hong et al., 2005; Su et al., 2007; Zheng et al., 2007a, 2007b; Wang et al., 2008; Monica et al., 2009). As such, the application of nTiO₂ for suppressing crop disease and enhancing yield should proceed with caution. A detailed description of the effects of nano-TiO₂ in plants is shown in Table 7.

3.7 Cerium dioxide nanoparticles

The annual global production of nano-CeO₂ (nCeO₂) was estimated to be 1000 tons/year by 2012 (Piccinno et al. 2012), which suggests significant amounts of nCeO₂ entering to the environment with a high potential to impact plants (Keller and Lazareva 2014; Hong et al., 2016). A modeling study predicted that nCeO₂ could enter agricultural soils through biosolid amendment (Keller et al., 2013; Keller and Lazareva 2014). These ENPs have been found to be very stable and with limited dissolution in soil (Cornellis et al., 2011; Priester et al., 2012; Zhang et al., 2012;; Hernandez-Viezcas et al., 2013). This suggests that nCeO₂ have the potential to interact with crop plants, perhaps for more than one generation. However, root exudates could enhance the solubility of nCeO₂ (Schwabe et al., 2015), leading to significant accumulation of Ce in plant tissues. Reports of Ce accumulation in the edible portion of plants include cilantro (*Coriandrum sativum*) leaves (Morales et al., 2013), tomato fruits (Wang et al., 2012), rice (Rico et al., 2013a) and cucumber fruit (Zhao et al., 2013; Hong et al., 2016). Barrios et al. (2015) reported that Ce was mostly retained in the soil and relatively low Ce contents were found in tomato plants grown in soil amended with nCeO₂. An analysis of the tomato fruit revealed that, although Ce was below the detection limit of the ICP-MS, nCeO₂ altered the concentration of essential elements (Barrios et al., 2016).

Exposure concentrations and plant species are factors that can modulate the physiological responses of plants to nCeO₂ exposure. Majumdar et al. (2015) found an increased yield of kidney bean seeds exposed to nCeO₂ at different concentrations. However, these researchers also observed a down regulation in phaseolin and lectins, proteins related to nutrient reserves and carbohydrate metabolism, respectively. As summarized in Table 8, nCeO₂ toxicity has been linked to ROS generation followed by a response of the antioxidative defense mechanisms in plants.

4. Conclusions and future work

Given the lack of experimental standardization and the divergent responses, even within similar plant species, it is challenging to conclude what the effects of ENMs are in plants. Per the reported literature, the effects depend on the concentration of the NPs, exposure media, and plant species. In addition, there is the need for deeper interpretation on the neutral or positive effects that NPs have on plants, as they are often not emphasized nor discussed in comparison to the adverse effects reported for photosynthetic organisms. Another important aspect that, in some way prevents generalizations, is that most of the results come from laboratory or greenhouse experiments, performed under controlled conditions. Thus, it is difficult to predict if the response will be the same under field conditions.

The current knowledge suggests that more studies are needed in order to fully understand the physiological and biochemical effects of ENMs in plants. Future studies should address the following issues: (1) There is a new generation of ENMs (coated NPs) whose effects have been less studied. (2) Very little is known about their effects on food quality. (3) There is, practically, no information on threshold concentrations. (4) Only few studies have explored the genotoxicity and generational effects of ENMs. (5) Since most of the reported studies have been performed in hydroponics, potting soil, or standard synthetic soil, almost nothing is known about the interactions of ENMs with plants in soils with different physico-chemical properties. (6) Finally, information about the effects of weathered ENMs on plants has not been published yet.

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Figure legends

Figure 1. TEM images of wheat root tips (a-d) and chloroplast in leaves (e, f) from plants grown without nanoparticle (c, e) (modified from Du et al. 2015), with 90 mg/kg nTiO₂ (a) (modified from Du et al. 2011), and with 400 mg/kg nCeO₂ (d, f) (modified from Du et al. 2015) in soil. O, outside; cw, cell wall; cy, cytoplasm; n, nucleus; ch, chloroplast; th, thylakoids; arrows point particles on cell wall.

Figure 2. General trends of effects for ENMs in plants, based and adapted from Martínez-Fernández et al. (2016b). The matrix has been created using the plant responses under ENMs exposure from the literature compiled in Tables 1 to 8. Contradictory responses have been detected (two colors in the same box), denoting that their effects depends on the specific kind of ENM, their concentration, and the plant species.

Figure 3. Interactions between a transverse cross section of the root absorption zone and ENMs, their uptake and translocation pathways in plants. The differential ENMs behavior can shed light on the environmental consequences of nanotechnology, but the research on ENMs toxicity needs to be improved.

Table 1. Summary of the interactions of carbon-based engineered nanomaterials with plants.

ENM	Particle size	Concentration	Growth media	Mode of exposure	Exposure time	Plant species	Physiological/bio chemical effects	Reference
MWCNTs C ₆₀ fullerenes	MWCNTs Outer diameter (OD):13–18 nm Inner diameter (ID): 5–10 nm Length:10–30 µm	0, 500, 1000, or 5000 mg/kg	Soil/vermiculite irrigated with 10% Hoagland's solution	NPs within growth media	28 days	Zucchini, corn, tomato soybean	No effects on zucchini and tomato development. Reduced biomass on corn and soybean exposed to C ₆₀ at 500 mg/kg	De La Torre-Roche et al., 2013
Fullerol [C ₆₀ (OH) ₂₀]	Hydrodynamic size 1.5 ± 0.2 – 5.0 ± 0.7 nm	0.943, 4.72, 9.43, 10.88, 47.2 nM	After seed treatment, plants grown in potting mix	Seeds exposed to fullerol solutions	48 hrs	Bitter melon	Fullerol found within root, stem, petiole, leaf, flower and fruit. Promoted plant development, enhanced fruit yield and growth.	Kole et al., 2013
MWCNTs	Diameter: 10–20 nm, Length: 1–2 µm	2000 mg/L	Aqueous media – Petri dish	NPs within growth media	5 days	Rape, radish, ryegrass, lettuce, corn cucumber,	Germination not altered. Root growth not affected significantly	Lin and Xing, 2007
Graphene	Length × breadth from 0.5 × 0.6 to 1.5 × 6.5 µm	500 to 2000 mg/L	Wetted filter paper with graphene solution at 25°C for germination test. Modified Hoagland medium for seedling evaluation.	Seed were soaked in solution with different concentrations of graphene overnight at 25°C	4 days for germination test and 20 days for seedling evaluation	Cabbage, tomato, red spinach and lettuce	Inhibition of plant growth and reduction of biomass Concentration-dependent ROS production and cell death. No effects on lettuce	Begum et al., 2011

Single bilayer graphene oxide sheet	05 – 5 μm	100, 200, and 1600 mg/L	Seeds were soaked in 4 ml of solutions	Petri dishes with Whatman No. 1 paper filter Incubated in the dark at 23 ± 2 °C until germination	Germination period	Faba bean	Stress in plant development and growth. Reduction on POD enzymes activity	Anjum et al., 2014
Graphene	10 to 500 nm	40, and 80 mg/L	Jouanneau and Peaud-Lenoel (JPL) medium	Cells cultured at 22°C under continuous shaking 120 rpm and illumination with white fluorescent lamps	7 days	Arabidopsis	Fragmented nuclei, membrane damage, and mitochondrial dysfunction	Begum and Bunshi, 2013
Non functionalized and functionalized SWCNTs	Not specified	0, 9, 56, 315, and 1,750 mg/L	Nanotubes functionalized with poly-3-aminobenzenesulfonic acid	Seeds incubated in Petri dishes	0, 24, 48 hours	Carrot, cabbage, cucumber, lettuce, onion, tomato	Functionalized SWCNTs inhibited root growth in tomato, enhanced it in onion and cucumber. Nonfunctionalized SWCNTs inhibited lettuce root growth.	Cañas, 2008
Single-walled carbon nanohorns (SWCNHs)	50-100 nm	0.025, 0.050, and 0.10 mg/L	Murashige and Skoog (MS) medium	Seeds exposed to nanotubes in Magenta boxes	10 to 20 days	Barley, corn, rice, soybean, switchgrass, tomato and tobacco cell culture	Activate seed germination and enhance seedling growth. Increase growth of tobacco cells by 78%, compared to control	Lahiani et al., 2014

Multi walled carbon nanotubes (MWCNTs)	Diameter: 10-30 nm; Length: 5-15 μm	20 mg/L	Cells cultured in Murashige and Skoog medium (MS)	Cells were subcultured once a week. MWCNT studies in cells on their exponential growth phase	6 days	Rice cells	ROS increase and cell viability decrease. Cell with individual MWCNTs at the wall prevent pathogen growth	Tan et al., 2009
MWCNTs	OD: 40-70 nm; ID: 5-40 nm; Length: 0.5-2 μm	2.5-800 mg L^{-1}	MWCNTs suspended in natural organic matter (NOM) solution of 1000 mg/L in Milli-Q water	Seeds incubated in Petri dishes	2 weeks	Rice	Flowering delaying by at least one month. Seed setting rate reduced by 10.5%, compared to controls. Weight of 100 reduced by 11.2 at 400 mg L^{-1} MWCNTs-NOM suspension	Lin et al., 2009
MWCNTs	NA	1,10,100, or 1000 mg/L	Hoagland solution at 25%.	Hydroponic	15-17 days	Zucchini	MWCNTs affect biomass production and transpiration	Stampoulis et al., 2009
MWCNTs	Diameter: 110-170 nm Length: up to 9 μm	100 $\mu\text{g/mL}$	Hydroponic systems bulked with 4 mm glass beads	Hydroponic solution	96 h intervals	Wheat	MWCNTs were observed attached to the wheat root cell walls and promoted the transport of phenantrene into the living cells.	Wild and Jones, 2009
MWCNTs	10-60 nm	0.01%, 0.1 % and 0.5% (w/w)	Sewage sludge and MWCNTs mixture	Sewage sludge with inert material (Standard OECD soil)	3 days	Garden cress, sorghum, tomato, radish , and cucumber	Influenced seed germination and root growth depending of the type of sewage sludge	Oleszczuk et al., 2011

Oxidized MWCNTs	20 nm	2.3×10^{-3} mg/L	Oxidized MWCNTs solution	Seed were stirred frequently in the solution	4 h	Mustard	Shorter germination time, enhanced root growth, and seedling stem development	Mondal et al., 2011
MWCNTs	44 – 800 nm	10,20, and 50 μ g/ml	MWCNT were suspended in filter sterilized double distilled water and were sonicated on ice for 20 minutes	Seed were exposed dampened with the suspension	24h	Onion	Chromosomal aberrations, DNA fragmentation and apoptosis in root cells	Ghosh et al., 2011
SWCNTs, MWCNTs, few-layer graphene	MWCNTs OD: 10-35nm L: 6 μ m SWCNTs OD: 0.86 - 2.22 nm Graphene thickness 2-25 nm and diameter: 100-120 nm	50 μ g/mL Gene expression analysis only with MWCNTs at 50, 100 and 200 μ g/mL.	Agar - Murashige and Skoog medium (MS)	Carbon-based NMs present within growth media	10 days	Tomato	Seedling development not significantly affected by graphene. MWCNTs upregulated stress-related genes	Khodakovskaya, 2011
MWCNTs	10 -12 nm	40 to 2,560 mg/L	Agar medium Petri dishes	MWCNTs within agar medium	7 days	Alfalfa and wheat	Germination and seedling root elongation was enhanced	Miralles et al., 2012b
MWCNTs	Length (L): 2 μ m OD: 20-70 nm ID: 5-10 nm	100 and 1000 mg/L	MWCNTs suspended in distilled water	Seeds were deposited in filter paper dampened with 5 ml of suspension and incubated in Petri dishes	10 days	Onobrychis	Stimulated the growth of roots and stems, and enhanced the POD activity	Smirnova et al., 2012
MWCNTs	D: 20 nm Length: 500	0.005-0.500 mg/L	MS agar medium	Callus culture	30 days	Tobacco cells	Enhanced cell growth; Regulate	Khodakovskaya, 2012a

	nm to 1 μ m.						cell division and plant growth through activation of water channels and cell division and extension	
MWCNTs	Mean OD: 41 nm	100 mg/L	Sand soaked with Hoagland solution	15 day old seedlings transferred to MWCNT suspension	7 days exposure	Seeds of wheat and rapeseed	Less than 0.005% of the applied MWCNTs was taken up by plant roots and translocated to the leaves	Larue et al., 2012a
MWCNTs	OD: 13 nm, and length: 1 μ m.	0, 20, 200, 1000 and 2000 mg/L	Hydroponic	300 mL Modified Hoagland Media	15 days	Red spinach, lettuce, rice, cucumber, chili, lady's finger, and soybean	Growth retardation. Root and shoot length of spinach and lettuce significantly affected at 1000 and 2000 ppm.	Begum et al., 2012a
CNTs	OD ~ 11 nm, ID ~4 nm, 1 μ m length	0, 125, 250, 500, 1000 mg/L	Hydroponic	Modified Hoagland's solution	15 days	Red spinach	Growth inhibition, changes to tissue structure.	Begum et al., 2012b
MWCNTs	OD 6-9 nm	5,10,20,40,60 mg/L	Bacteriological agar (BA) and Agarose.	Seeds were implanted into the set gel substrates in Petri dishes sealed with a tape. Incubated at 23-25°C, RH: 71.5%, photoperiod 16h/8h	7 days	Sweet corn	At low concentration enhance the germination and seedling growth but depressed it at higher concentration	Tiwari et al., 2014
MWCNTs, Fullerol [C ₆₀ (OH) ₂₀]	MWCNT: 223.08 $\pm$ 38.72 nm Fullerol: 1.17 $\pm$ 0.36 nm	50 mg/L	Suspension of agarose gel amended with Rhodamine B	Double exposure effects (Sonicated and followed non	60 min sonication 9 to 10 h 5 days for germination	Tomato	Seed coat permeability disrupted. Increase in germination and	Ratnikova et al., 2015

				sonicated seeds soaked in the same suspension)	test		seedling length	
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Species name in order of appearance in the table: zucchini, *Cucurbita pepo*; corn, *Zea mays*; tomato, *Solanum lycopersicum*; soybean, *Glycine max*; Bitter melon, *Momordica charantia*; rape, *Brassica napus*; radish, *Raphanus sativus*; ryegrass, *Lolium perenne*; lettuce, *Lactuca sativa*; cabbage, *Brassica oleracea*; red spinach, *Amaranthus dubius*; faba bean, *Vicia faba*; arabidopsis, *Arabidopsis thaliana*; carrot, *Daucus carota*; onion, *Allium cepa*; barley, *Hordeum vulgare*; rice, *Oryza sativa*; switchgrass, *Panicum virgatum*; tobacco, *Nicotiana tabacum*; wheat, *Triticum aestivum*; garden cress, *Lepidium sativum*; sorghum, *Sorghum saccharatum*; mustard, *Brassica juncea*; alfalfa, *Medicago sativa*; squash, *Cucurbita pepo*; onobrychis, *Onobrychis arenaria*; chili, *Capsicum annuum*; lady's finger, *Abelmoschus esculentus*.

Table 2. Summary of the effects of iron-based nanomaterials in plants.

ENM	Particle size (nm)	Concentration (ppm)	Growth medium	Mode of exposure	Exposure time	Plant species	Physiological/biochemical effects	Reference
Carbon coated nFe	5–200	Not specified	Germinated <i>in vitro</i> , grown in polyethylene bag system	Injected through stem petiole	24, 48 and 72 h	Pumpkin	Nanoparticles found within extracellular spaces and inside cells.	González-Melendi et al., 2008
Carbon-coated nFe	46	Not specified	Polyethylene bag system	Injected and sprayed	24, 48, 168 h	Pumpkin	NMs anomaterials move to remote positions, through the vascular system. Particles larger than 46 nm were not transported.	Corredor et al., 2009
nFe/ Fe ₃ O ₄	50-60	10, 20 mg/L	Hydroponics	NPs within aqueous growth media	15 days	Lettuce	Increased the antioxidant enzyme activities related to the changes in the mineral composition, reduced root size, lowered chlorophylls accumulation, particle aggregation on the root, affected water entrance.	Trujillo-Reyes et al., 2014
nFe ₂ O ₃	20–100	50, 100 mg/L	Perlite substrate, then hydroponics	After 20 days, NPs included in growth medium	5 days	Sunflower	Lack of uptake and translocation. Reduction of the root hydraulic conductivity	Martínez-Fernández et al., 2016a
nFe ₂ O ₃	22–67	4 mg/kg (72 mM)	Agar	NPs within agar	0, 7, 12, 18, 56 days	Arabidopsis	Less chlorophylls, lower plant biomass	Marusenko et al., 2013
nFe ₂ O ₃	Not specified	0, 0.25, 0.5, 0.75, 1 g/L	In field	Sprayed	Sprayed at different stages until maturity	Soybean	Increased leaf and pod dry weight, 48% increase in grain yield	Sheykhabglou et al., 2010
nFe ₂ O ₃	246	1000 mg/L	Aqueous - Petri dishes	NPs within growth medium	3 days	Lettuce, radish, cucumber	Tendency to adsorb on seed surfaces	Wu et al., 2012

nFe ₃ O ₄	7	116 µg/mL	Not specified	Not specified	7 days	Cucumber, lettuce	Low to nil toxicity on germination	Barrena et al., 2009
nFe ₃ O ₄	<50	0.01, 0.1, 0.5 and 4 mmol/L	Aqueous media	NPs in growth media	7 days	Garden cress and garden pea	Root accumulation due to its strong adsorption	Bystrzejewska-Piotrowska et al., 2012
nFe ₃ O ₄	6	0.67 mg/mL	Not specified	NPs in growth media	5 days	Lettuce, radish, cucumber, spinach, tomato, leek, peppers	Total inhibition of germination	García et al., 2011
nFe ₃ O ₄	25	30, 100 and 500 mg/L	Hydroponics	NPs in growth media	18 days	Ryegrass, pumpkin	No uptake, increased root elongation, block of aquaporins, oxidative stress	Wang et al., 2011a
nFe ₃ O ₄	20	0.5 g/L	Aqueous medium	NPs added to growth media after appearance of 3 rd leave	< 20 days	Pumpkin	Translocation throughout the plant tissues, NPs detected in stem and leaves. Accumulation on the root surface.	Zhu et al., 2008
nZVI	1-20	0, 100, 250, 500, 1000, 2000, 5000 mg/L or mg/kg	Petri dishes - Soil or aqueous media	NPs within growing media	4 weeks	Flax, ryegrass, barley	Seed germination inhibition varied by plant species, exposure concentration and soil type.	El-Temsah and Joner, 2012
nZVI	54	0.1 g/L agar; 0.5 g/kg in soil	Hydroponic, soil	½ strength MS (agar)	10 days, 3 weeks	Arabidopsis	nZVI triggered high plasma membrane H ⁺ -ATPase activity, stomatal opening.	Kim et al., 2015
nZVI	25	10 g/L	Petri dish	NPs within aqueous growth media	72 h	Garden cress, white mustard, sorghum	No significant phytotoxicity.	Libralato et al., 2015
nZVI	300–400	0, 25, 50, 200, 500, 1000 mg/L	Hydroponic	NPs within aqueous growth media (freshly replenished each week)	4 weeks	Cattail	Minimal upward transport to shoots, reduced transpiration, penetration into several layers of epidermal cells	Ma et al., 2013a

Species name in order of appearance in the table: pumpkin, *Cucurbita pepo*; lettuce, *Lactuca sativa*; sunflower, *Helianthus annuus*; arabidopsis, *Arabidopsis thaliana*; soybean, *Glycine max*; radish, *Raphanus sativus*; cucumber, *Cucumis sativus*; garden cress, *Lepidium sativum*; garden pea, *Pisum sativum*; spinach, *Spinacia oleracea*; tomato, *Solanum lycopersicum*; leek, *Allium porrum*; ryegrass, *Lolium perenne*; pumpkin, *Cucurbita mixta*, *Cucurbita maxima*; flax, *Linum usitatissimum*; barley, *Hordeum vulgare*; white mustard, *Sinapis alba*; sorghum, *Sorghum saccharatum*; cattail, *Typha latifolia*.

Table 3. Summary of the effects of copper-based nanomaterials in plants.

ENM	Particle size (nm)	Concentration (ppm)	Growth medium	Mode of exposure	Exposure time	Plant species	Physiological/biochemical effects	Reference
nCuO	<50	0, 20, 50, 100, 200, 400, 500 mg/L	Agar	1/2 strength Murashige and Skoog	14 days	Mustard	Reduced shoot growth, root shortening	Nair and Chung, 2015
nCuO	<50	0, 0.5, 1, 2, 5, 10, 20, 50, 100 mg/L	Agar	1/2 strength Murashige and Skoog	21 days	Arabidopsis	Plant biomass reduction, root growth retardation, excess ROS generation	Nair and Chung, 2014
nCuO	<50	0, 50, 100, 200, 400, 500 mg/L	Agar	1/2 strength Murashige and Skoog	14 days	Soybean	Diminished fresh weight and root size. Enhanced root lid lignification.	Nair and Chung, 2014a
nCuO	10-50	0, 20, 50, 100, 200, 500 mg/L	Agar	1/2 strength Murashige and Skoog	21 days	Mung bean	No changes in carotenoids. Chlorophyll reduced above 100. Root length and biomass reduction at all concentrations, H ₂ O ₂ and lipid peroxidation increased. Increased ROS with increases in NPs concentration. Modulations in gene expression (roots' CuZn SOD, CAT and APX genes)	Nair et al., 2014
nCuO	<50	10 ppm	Sediment elutriate	Growing media doped with 10 ppm, regardless of original Cu content	8 days	<i>Halimione portulacoides</i> , <i>Phragmites australis</i>	No metal translocation Cu in roots of <i>H. portulacoides</i> . Less Cu accumulation in roots when Cu available in the form of NP, Cu translocation varies from species to species. Cu can form aggregates, reducing SA and thus decreasing Cu availability.	Andreotti et al., 2015
nCuO	30 ± 10	0, 10, 200, 1000 mg/L	Basic nutrient solution	NPs within NS	10 days	Transgenic cotton (Bt-29317) and conventional cotton (Jihe 321)	Hormones IAA and ABA were significantly affected, modified the amount of nutritional elements content (diminishes, Mo, Mn, Mg, Zn and Fe), plants biomass and height not affected at 10 ppm CuO exposure, plant growth significantly diminished at other concentrations.	Le Van et al., 2016

nCuO	20 – 40	2, 5, 10, 20, 30, 40, 50, 100 mg/L	Hydroponic ¼ strength nutrient solution	Treatment started when seedlings had grown three leaves. Solution with NPs replenished every 3 days	15 days	Corn	Cu reduction from (II) to (I), no effects on germination, larger seedlings observed at 2 ppm, At 100 ppm chlorosis and inhibition of seedling growth occurred.	Wang et al., 2012
nCu	>100	0, 200, 400, 600, 800, 1000 mg/L	Agar	Exposure started after 1 day germination	2 days	Mung bean and wheat	No adverse effect observed below 200 ppm	Lee et al., 2008
nCuO	30	100 mg/L	Algal growth medium	Glass incubation vials	3 days	Microalgae (<i>Pseudo-kirchneriella subcapitata</i>)	100% growth inhibition at < 1 ppm CuO NPs, no effects at 0.42mg/L for nCuO. At 72 hrs, CuO NPs EC ₅₀ = 0.71 mg Cu /L	Aruoja et al., 2009
nCu	Not specified	130, 660 mg/kg	Soil	NPs within soil	11 days	Lettuce	No effects when seeded the same day soil was amended. Shoot/root length ratio increased in seeds sown after 15 days of NPs incubation.	Shah and Belozeroval, 2009
nCu	< 50	0, 100, 500 mg/L	Hydroponic	¼ Hoagland NS with or w/o humic acid. Plants were grown for two weeks before exposure.	14 days	Squash	Growth and transpiration reduced by 60 - 70 % (same bulk and nCu) Higher ionic Cu found in media amended with bulk Cu than nCu, humic acid increased ionic Cu in suspensions amended with nCu.	Musante and White, 2012
nCu, nCuO, Cu(OH) ₂	nCuO, 10-100; nCu, 100-1000; Cu(OH) ₂ , >10 ⁴ .	0, 5, 10, 20 mg/L	Hydroponic	Hoagland's NS, plants were two weeks old before exposure.	15 days	Lettuce, alfalfa	Lettuce root growth reduction, P and Fe decreased in shoot, APX increased in roots. In alfalfa, root length decreased, Cu, P, and S increased in shoots, reduced CAT both shoots and roots and APX increased in roots.	Hong et al., 2015
nCu, nCuO, Cu(OH) ₂	nCuO, 10-100; nCu, 100-	0, 20, 80 mg/kg Cu from various compounds	Soil	NPs within soil	30 days	Cilantro	nCuO reduced germination, nCu at 80mg/L did not affect germination, but reduced shoot elongation.	Zuverza-Mena et al., 2015

	1000; Cu(OH) ₂ , >10 ⁴ .							
nCuO	30–40	0.68 ± 0.06, 1.04 ± 0.12, 2.08 ± 0.34 and 4.51 ± 0.95 g/L	Freshwater inorganic culture medium	Exposure in 24-well plate	2 days	<i>Lemna gibba</i>	Effect due to release of Cu ²⁺ ions, CuO bioaccumulation observed	Perreault et al., 2014
nCuO	<50	~40, 80, 120 mg/L	Aqueous media	Seeds exposed to NPs suspension. Experiment started after germination. Suspension with NPs replenished as needed	14 days	Rice	Decreased root and shoot growth, weight and germination yield	Shaw and Hossain, 2013
nCuO	<50	~40, 80, 120 mg/L	½ strength Murashige and Skoog medium	Seeds exposed to NPs suspension. Experiment time started counting after germination	20 days	Barley	Induce the release of ROS, membrane damage, decrease in shoot and root growth, overall enzymatic activity not enough to cope with stress at 20 day exposure. Does not alter significantly the PSII (photosynthetic Fv/Fm alteration	Shaw et al., 2014
nCuO, nCuO:nZn O	<50	100, 250, 500 ppm Cu from CuO	Sand	NPs within sand	7 days	Bean	Growth inhibition, metal nutrition imbalance in shoots. Na increased, Fe, Mn, Zn and Ca decreased (500 ppm CuO)	Dimkpa et al., 2015
nCuO	<50	500 mg/kg	Sand	NPs within sand	14 days	Wheat	Growth inhibition (roots and shoots) and oxidative stress possibly due to Cu released from NPs, Cu bioaccumulates.	Dimkpa et al., 2012
Cu/CuO	20 – 30	0, 10, 20 mg/L	Hoagland's nutrient solution	NPs within growth media	15 days	Lettuce	More Cu accumulation from NPs than ionic Cu treatment, nutrients content, dry biomass, water content and seedlings' growth were impaired. more Cu,	Trujillo-Reyes et al., 2014

							Al and S but less Mn, P, Ca, and Mg	
nCuO	<100	10, 100, 500, and 1000 mg/L	Aqueous media	NPs within growing media	6 days	Radish, grasses	DNA damage, growth inhibition	Atha et al., 2012
nCuO	10-15	1.0 mg/L	½ strength Hoagland's nutrient solution	NPs within growing media	9 days	<i>Landoltia punctata</i>	Decreased chlorophyll content, inhibits growth, Cu conc. higher in fronds than roots, promotes oxidative stress, damages in membrane and DNA.	Shi et al., 2011
nCuO	43 ± 9	0, 100, 200, 500, 1000 mg/L,	Hydroponic s, nutrient solution	Seedlings grown for 21 days before treatment	14 days	<i>Elsholtzia splendens</i>	Growth inhibition, EC ₅₀ = 384 mg Cu/L. Plant stayed alive even at 1000 mg/L. Inside tissues, Cu found mainly as CuO.	Shi et al., 2014
nCuO	25-80 avg. = 55	*20, 200; **5, 10, 50, 100, 200 mg/kg	Agar	* desorption experiment ** exposure treatment	*1 day	Wheat	* Adsorbed NPs better removed with Na ₄ EDTA **Uptake increases with increasing concentrations.	Zhou et al., 2011
nCuO	< 40	0.5 mg/L	Modified BG11, natural and distilled water	NPs in growth media with or without organic matter.	5 days (cell viability)	<i>Microcystis aeruginosa</i>	Cu in plant mainly as Cu ₂ O. Apparently internalization does not affect membrane. Suwannee river fulvic acid (SRFA) increases CuO NPs toxicity	Wang et al., 2011
nCuO	30	0.025, 0.25, 0.5, 1.0, 5.0 mg/L	nCuO suspension	Plant incubated in nCuO suspension	3 days	<i>Elodea densa</i>	Increased SOD activity, higher lipid peroxidation effect than ionic treatment. nCuO increased CAT at 0.5 ppm and POD at 0.25, but decreased as nCuO increased. Photosynthesis at 1.0 mg/L was negatively affected.	Nekrasova et al., 2011
nCu, nCuO	32± 4.2 (metal) 76±10.6 (metal oxide)	0, 10, 50, 100, 500, 1,000 mg/L	Hydroponic	½ strength Hoagland's NS, plants grown for four weeks before treatment	5 days	Cucumber	nCuO increases SOD, CAT and POD, at 1000 ppm nCuO decreases seedlings' biomass by 75% and nCu by 30%. IC ₅₀ was higher for NPs than Cu ions (nCu 333 mg/L; nCuO, 376 mg/L; Cu ²⁺ ; 14 mg/L)	Kim et al., 2012

Species name in order of appearance in the table: mustard, *Brassica juncea*; arabidopsis, *Arabidopsis thaliana*; soybean, *Glycine max*; mung bean, *Vigna radiate*, *Phasesolus radiates*; corn, *Zea mays*; wheat, *Triticum aestivum*; microalgae, *Pseudokirchneriella subcapitata*; lettuce, *Lactuca sativa*; squash, *Cucurbita pepo*; alfalfa, *Medicago sativa*; cilantro, *Coriandrum sativum*; rice, *Oryza sativa*; barley, *Hordeum vulgare*; bean, *Phaseolus vulgaris*; radish, *Raphanus sativus*; grasses, *Lolium perenne*, *Lolium rigidum*; cucumber, *Cucumis sativus*.

Table 4. Summary of the effects of zinc-based nanomaterials in plants.

ENM	Particle size (nm)	Concentration (ppm)	Growth medium	Mode of exposure	Exposure time	Plant species	Physiological/biochemical effects	Reference
nZnO	10	250,500,750 mg/kg	Soil	NPs within growth media	30 days	Alfalfa	Root biomass reduction by 80%	Bandyopadhyay et al., 2015
nZnO	44.4	400,2000,4000 mg/L	Agar	½ strength MS, NPs within growth media	18 days	Arabidopsis	Inhibitory effects on seed germination. Inhibitory effects on root elongation and in the total number of leaves.	Lee et al., 2010a
nZnO	<100	100 mg/L	MS medium	NPs added to growth media of 6 week old plants	7 days	Arabidopsis	Plant biomass reduction by 81.4%. Inhibitory effects on seed germination. 660 up regulated genes and 826 down regulated genes.	Landa et al., 2012
nZnO	1.2 – 6.8	10 mg/L	Soil	Foliar	28 days	Guar bean	Improvement of 27% in plant biomass. Increased chlorophyll (276%) and total soluble leaf protein content (27%).	Raliya et al., 2013
nZnO	10	200 – 800 mg/kg	Soil	NPs within growth media	28 days	Corn	Increased Zn in roots and shoots when compared to control. Zn internalization through apoplastic pathway.	Zhao et al., 2012
nZnO	< 100	25 mg/L and 500 mg/kg	Hydroponic and soil	NPs within growth media	80 days	Cowpea	No difference in growth, accumulation or speciation of Zn, when nZnO and soluble Zn ²⁺ were compared	Wang et al., 2013
ZnO and Fe@ZnO	10 – 22	125,250,500 mg/kg	Soil	NPs within growth media	25 days	Garden pea	Doped ZnO NPs were less toxic based on ROS (H ₂ O ₂) and chlorophyll content.	Mukherjee et al. 2014
nZnO	10	0.1-1000 mg/L	In vitro	Seeds grown in NPs suspension	6 – 7 days	Corn and cabbage	On both plants, germination and root elongation results showed lower NPs toxicity compared to free ions.	Pokhrel and Dubey 2013
nZnO	10	400 – 800 mg/kg	Soil	NPs within growth media	53 days	Cucumber	ZnO NPs had no impact on growth, gas exchange or chlorophyll content.	Zhao et al., 2013
nZnO	90	800 mg/kg	Soil	NPs within growth media	8 weeks	Corn	Growth inhibition and Arbuscular mycorrhizal fungi	Wang et al., 2016

							inhibition	
nZnO	10	2000-4000 mg/Kg	Hydroponic	NPs within growth media	15 days	Mesquite	Increased reactive oxygen species	Hernandez-Viezcas et al., 2011
nZnO	10	0-4000 mg/L	In vitro	Seeds grown in NPs suspension	4,6,7 days	Palo verde, mesquite, tumbleweed	Germination was not significantly affected in any of the three plant species	de La Rosa et al., 2011
nZnO	<100	25, 50, 75, and 100 µg/mL	Hydroponic	Bulbs of 2-3 cm in root length were exposed to NPs suspension	4 h	Onion	Results showed the NPs to be a clastogenic/genotoxic and cytotoxic agent.	Kumari et al., 2011
nZnO	50	5,10 and 20 mg/L	Hydroponic	Bulbs of 1.3 - 1.5 cm in root length were exposed to NPs suspension	3 days	Onion	Results showed a reduction in root growth at all concentrations.	Ghodake et al., 2011
nZnO	25	1000 mg/L	Soil	Seed inoculation	3 h	Peanut	Seed germination and seedling vigor were promoted	Prasad et al., 2012
nZnO	20	2000 mg/L	In vitro	Seed inoculation	2 h	Rapeseed, radish, ryegrass, lettuce, corn and cucumber	Germination inhibition was observed in <i>Zea mays</i> . Root growth inhibition was observed in all plant species.	Lin and Xing., 2007
nZnO	<100	10,100,500, 1000 mg/L	In vitro	Seed inoculation	1, 2 and 3 days	Rice	No effect on seed germination was observed. Root length and number was reduced.	Boonyanitipong et al., 2011
nZnO	20	10 – 1000 mg/L	Hydroponics	NPs added to growth media	One week old plants exposed for 12 days	Ryegrass	Biomass was reduced. Lower translocation factors when compared to Zn ion treatments.	Lin and Xing., 2008
nZnO	25	0, 1, 10, 20, and 50 mg/L	Hydroponics	NPs added to growth media	One week old plants exposed for 7 days	<i>Salvinia natans</i>	SOD and CAT activities were increased and photosynthetic pigments were reduced. Plant growth was not significantly affected.	Hu et al., 2014
nZnO	10	500 mg/kg	Soil	NPs within growth media	~ 48 days	Soybean	Above mass yield was not affected. Conversely, belowground biomass was	Priester et al., 2012

							increased.	
nZnO	<50	500mg/kg	Soil	NPs within growth media	57 days	Soybean	Roots and shoots were shorter and had smaller surface area and volume. In addition, plants did not form seeds.	Yoon et al., 2014
nZnO	8	0, 500, 1000, 2000, 4000 mg/L	Aqueous media (in Petri dish)	Direct seed contact to suspension	5 days	Soybean	No effects on plant germination. Genotoxicity observed at 4000 mg/L: a new band in the roots RAPD profile	López-Moreno et al., 2010a
nZnO	10	0-500 mg/kg	Soil	NPs within growth media	48	Soybean	Fe was significantly reduced at all treatments. Mg and K were decreased at 500 mg Zn/kg treatment.	Peralta-Videa et al., 2014
nZnO	8	1600 mg/L	In vitro	NPs within aqueous growth media	12 -13	Alfalfa, Cucumber, tomato	Cucumber germination increased 10%, while tomato and alfalfa were reduced by 20 and 40% respectively	de la Rosa et al., 2013
nZnO	<50	100-1000 mg/L	In vitro and culture media	Foliar spray	7, 20	Garden pea	No impact on germination. Root length was affected. Root nodulation was affected.	Raliya et al., 2015
nZnO	25	0-1000 mg/L	Soil	Soil amended with NPs	14	Tomato	24% increase in plant height at 250mg ZnO/kg. Increased root length in foliar sprayed plants with 250mg ZnO/L. Concentrations above 250mg ZnO/kg affected root length in both methods of application.	Raliya et al., 2015
nZnO	<100	50mg/kg	Soil	NPs within soil	7 months	Wheat	Biomass of wheat was reduced	Du et al., 2011
nZnO	<100	500mg/kg	Sand	NPs within sand	14	Wheat	Root growth was reduced. There was an increased production of reactive oxygen species.	Dimkpa et al., 2012
nZnO	<10	1000mg/L	Hydroponic	NPs within aqueous media	15	Zucchini	No Phytotoxicity observed. 78-90% biomass reduction.	Stampoulis et al., 2009

Species name in order of appearance in the table: alfalfa, *Medicago Sativa*; arabidopsis, *Arabidopsis thaliana*; guar bean, *Cyamopsis tetragonoloba*; corn, *Zea mays*; cowpea, *Vigna unguiculata*; garden pea, *Pisum sativum*; cabbage, *Brassica oleracea*; cucumber, *Cucumis sativus*; mesquite, *Prosopis juliflora-velutina*; palo verde, *Parkinsonia florida*; tumbleweed, *Salsola tragus*; onion, *Allium cepa*; peanut, *Arachis hypogaea*; rapeseed, *Brassica napus*; radish, *Raphanus sativus*; ryegrass, *Lolium perenne*; lettuce *Lactuca sativa*; rice, *Oryza sativa*; soybean, *Glycine max*;tomato, *Solanum lycopersicum*; wheat, *Triticum aestivum*; zucchini, *Cucurbita pepo*.

Table 5. Summary of the effects of silver-based nanomaterials in plants.

ENM	Particle size (nm)	Concentration (ppm)	Growth medium	Mode of exposure	Exposure time	Plant species	Physiological/biochemical effects	Reference
nAg	5-50	800 mg/kg	Soil	NPs within soil	5 weeks	Faba bean	Declined germination, retarded the process of nodulation, early senescence of root nodules, decreased shoot and root length	Abd-Alla et al., 2016
nAg	20	100 mg/L	Coating solution	submerged	25 days	Asparagus	Higher ascorbic acid and total chlorophyll contents	An et al., 2008
nAg	20-80	67-535 mg/L	Hydroponic	irrigated	2 weeks	Arabidopsis	Brown tips in the roots, transported to the internal root tissue	Geisler-Lee et al., 2013
nAg	20	75 µg/L	Soil	irrigated	42 days	Arabidopsis	Loss of belowground function of the primary root meristem	Geisler-Lee et al., 2014
nAg	20, 100	5 µg/L	Aqueous medium	NPs added to the aqueous medium	14 days	<i>Lemma minor</i>	Inhibition of plant growth was dependent of NP size and this became more acute with longer exposure time	Gubbins et al., 2011
nAg	6-20	0.5-10 mg/L	In vitro	NPs were added to 10% Hoagland's solution	72 h	<i>Spirodela polyrhiza</i>	Oxidative stress, affected chloroplast structure	Jiang et al., 2014
nAg	5-25	0, 5, 10, 20, 40 mg/L	Artificial soil	NPs and soil mixed	5 days	Mung bean, Sorghum	Growth inhibition	Lee et al., 2012
nAg	< 100	0, 100, 500 mg/L	Hydroponic	¼ Hoagland NS with or w/o humic acid. Plants were grown for two weeks before exposure.	7 days	Squash	Reduced biomass, reduction of transpiration by 66–84%	Musante and White 2012
nAg	190-1100	0, 25, 50, 100, 200 or 400 mg/L	Aqueous medium	MS medium supplemented with NPs	7 days	Mustard	Increase in root length, improved quantum efficiency of PSII, modulation antioxidant status	Sharma et al., 2012
nAg	10–15	0, 100, 1000 mg/L	Hydroponic	NPs in Hoagland soln.	6 days	Tomato	Significant decreases in root growth, decreased chlorophyll	Song et al., 2013

nAg	100	50-100 μ M	In vitro	NPs added to the medium	10 days	Arabidopsis	Aminoacid accumulation and ROS response	Wen et al., 2016
nAg	2	0, 125, 250, 500 mg/L	In vitro	Aqueous media	5 days	Radish	Germination not affected, diminished water content, root and shoot length. At 125 ppm, Ca, Mg and Zn remain unchanged	Zuverza-Mena et al., 2016

Species name in order of appearance in the table: Faba bean, *Vicia faba*; asparagus, *Asparagus officinalis*; arabidopsis, *Arabidopsis thaliana*; mung bean, *Phaseolus radiates*; sorghum, *Sorghum bicolor*; squash, *Cucurbita pepo*; mustard, *Brassica juncea*; tomato, *Lycopersicon esculentum*; radish, *Raphanus sativus*.

Table 6. Summary of the effects of gold-based nanomaterials in plants.

ENM	Particle size (nm)	Concentration (ppm)	Growth medium	Mode of exposure	Exposure time	Plant species	Physiological/biochemical effects	Reference
nAu	10-20	0, 10, 25, 50 and 100 mg/kg	Field conditions	Foliar spray	50 and 70 days	Mustard	Enhanced growth, increased number of leaves per plant, total sugar contents increased, improved the redox status	Arora et al., 2012
nAu	5, 10, 20	0, 3.6, 7.2, 10.6, 14.0, 17.3 μ M	Soil	Seed inoculation	>2 weeks	Soybean	Decreased quantum yield in PSII	Falco et al., 2011
nAu	10	to 10 μ g/mL	Hydroponic	colloidal solution	2 weeks	Barley	Decreased root growth	Feichtmeier et al., 2015
nAu	4-18	250 μ g/L	Suspensions	colloidal solution	24 h	<i>Myriophyllum simulans</i> , <i>Egeria densa</i> , <i>Azolla caroliniana</i>	Root uptake was size and species dependent	Glenn et al., 2012
nAu	50	0, 100, 200, 300.00, 400 mg/L	MS media	NPs in growth media	10 days	Mustard	Increase in free radical stress and proline, increased root length	Gunjan et al., 2014
nAu	5, 10, 15	100 mg/L and 30 mg/L	Hydroponic	NPs in growth media	7 days	Tobacco	Evidence for biomagnification	Judy et al., 2011
nAu	10, 30, 50		Hydroponic	NPs in growth media	3-7 days	Tobacco, wheat	Accumulation is species dependent.	Judy et al., 2012
nAu	1-3	1.6 - 0.14 mg/L	Hydroponic	NPs in growth media	5 days-3 months	Rice	NPs found in the mesophyll and in the vascular tract of the middle sheath	Koelmel et al. 2013
nAu	0.1–1000	30–60 μ g/ml	Growth media with agar	Mixed with culture medium	7, 14 and 21 days	Rice	Affected and damaged cell wall, shoot growth.	Mirzajani et al., 2013
nAu	20	6×10^{-6} – 1.8×10^{-5} M	Aqueous medium	NPs added to the aqueous medium	24-28 days	<i>Ceratophyllum demersum</i>	20% of the shoots died	Ostroumov et al., 2014
nAu	3.5 18	NPs of 3.5 nm at 48 mg/L, NPs of 48 nm at 76 mg/L	Hydroponics, ½ strength Hoagland's solution	NPs added to aqueous growth media	14 days	Tobacco	Uptake was size selective, leaf necrosis	Sabo-Attwood et al., 2012

Species name in order of appearance in the table: mustard, *Brassica juncea*; soybean, *Glycine max*; barley, *Hordeum vulgare*; tobacco, *Nicotiana tabacum*, *Nicotiana xanthi*; wheat, *Triticum aestivum*; rice, *Oryza sativa*.

Table 7. Summary of the effects of titanium dioxide-based nanomaterials in plants.

ENM	Particle size (nm)	Concentration (ppm)	Growth medium	Mode of exposure	Exposure time	Plant species	Physiological/biochemical effects	Ref
nTiO ₂	5	0.25%	Soil	Pre-treated seeds and subsequent foliar spray at “four leaf” stage	Seeds exposed for two days, plants sprayed once.	Spinach	Less O ₂ ^{·-} and H ₂ O ₂ accumulation and consequently less lipid peroxidation in spinach chloroplasts	Zheng et al., 2008
nTiO ₂	6.22	0.1%-0.4%	Soil	Suspensions sprayed on two year-old seedling leaves	One month	<i>Ulmus elongata</i>	Net photosynthetic rate was reduced. Promoted Cu accumulation in leaves. Increase in carbohydrates and lipids	Gao et al., 2013
nTiO ₂	7-40	2–10 mg/kg	Soil	Seeds exposed to nTiO ₂ suspensions, seedlings transplanted to soil. Leaves sprayed with nTiO ₂ suspensions at 12 th and 16 th days	21 days after germination and 9 and 5 days after spray	Chickpea	5 mg/kg treatment caused reduction in electrolyte leakage and MDA content	Mohammadi et al., 2013
nTiO ₂ core coated with Al(OH) ₃ and polydimethylsiloxane	10 × 50	5, 25, and 50 mg/L	Aqueous media	Seedlings were grown four days in Hoagland solution spiked with the nTiO ₂	2 days	Faba bean	No lipid peroxidation was observed. However, in roots, there was a reduction of glutathione reductase activity at 50 mg/L and APX activity at 5 and 25 mg/L	Foltête et al., 2011
nTiO ₂	5-10	0, 10, 50, 100, 200, 1,000, 2,000 mg/L	1/10 Modified Steinberg	Media spiked with NPs.	30 day old plants, 7 days	<i>Lemna minor</i>	Increased enzymatic activity SOD, CAT and POD	Song et al., 2012

			medium		exposure			
nTiO ₂	27 ± 4	0, 250, 500, 750 mg/kg	Sandy loam soil	NPs in soil	150 days	Cucumber	Enhanced CAT activity in cucumber leaves. Enhanced P and K availability in cucumber fruit.	Servin et al., 2013
nTiO ₂	20–160	20 mg/kg supplied at least once per week	Soil	NPs in soil	~ 130 days	Tomato	Did not affect Ca, K, Mg, Na, P, S in roots, enhanced contents of Ca, Mg, P, S in stems and P, S in leaves.	Antisari et al., 2015
nTiO ₂	4–6	0.25%	2 days pretreated seeds in nTiO ₂ , then grown in Hoagland's NS	Sprayed once when seedlings showed two leaves	Harvested at 45 days	Spinach	Beneficial effects on spinach growth. Increased glutamate dehydrogenase (GDH), glutamine synthetase (GS), and glutamic-pyruvic transaminase (GPT) activity.	Yang et al., 2006
nTiO ₂	Not specified	0, 0.01%, 0.02%, 0.03%	Soil	Spray supplied NPs. 240 ml per square meter at "stem elongation" and "flowering" stages.	Harvested at the end of the growing season	Wheat	At 0.02% the agronomic parameters increased.	Jaberzadeh et al., 2013
nTiO ₂	Not specified	0, 0.01%, 0.03%, 0.05%	Soil	Foliar application. Sprayed during "vegetative" or "reproductive" stages	Harvest at plant maturity	Soybean	0.05% increases height and dry weight of soybean.	Rezaei et al., 2015
nTiO ₂	<100	~ 91 mg/kg	Loamy clay soil (lysimeters)	NPs in soil	Seven months	Wheat	Biomass reduction, NPs found mainly adhered on roots' surface	Du et al., 2011
nTiO ₂	< 25	0, 0.1, 1, 2.5, 5 %	Agar	Murashige and Skoog, NPs in growth media	~ 21 days	Tobacco	Germination inhibition, root length and biomass reduction. Upregulation of ADH and APX.	Frazier et al., 2014

Species name in order of appearance in the table: spinach, *Spinacia oleracea*; chickpea, *Cicer arietinum*; faba bean, *Vicia faba*; cucumber, *Cucumis sativus*; tomato, *Lycopersicon esculentum*; wheat, *Triticum aestivum*; soybean, *Glycine max*; tobacco, *Nicotiana tabacum*.

Table 8. Summary of the effects of cerium dioxide nanomaterials in plants.

ENM	Particle size (nm)	Concentration (ppm)	Growth medium	Mode of exposure	Exposure time	Plant species	Physiological/biochemical effects	Ref
nCeO ₂	8 ± 1	0, 62.5, 125, 250, 500 mg/L	Aqueous media (Petri dish)	Direct seed contact	4 days	Rice	No changes in seed germination rate or seedling growth in rice. Chlorophyll ratio increased, but chlorophyll content decreased. Changes in grains' fatty acids and starch.	Rico et al., 2013b
nCeO ₂	20 ± 1.9	0.1, 1.0, 10 mg/kg	Soil (potting mix)	Pretreated seeds, seeded in potting mix, irrigated with NP suspension	70 days	Tomato	Germination not affected, 10 ppm enhanced plant growth and fruit yield, Ce detected in fruit.	Wang et al., 2012
nCeO ₂	7	0, 500, 1000, 2000, 4000 mg/L	Aqueous media (in Petri dish)	Direct seed contact to suspension	5 days	Soybean	Genotoxicity observed by the appearance of new bands in RAPD profile of soybean roots at 2000 and 4000 mg/L	López-Moreno et al., 2010a
nCeO ₂	7	0, 500, 1000, 2000, 4000 mg/L	Aqueous media (in Petri dish)	Direct seed contact to suspension	Various, 6-9 days	Alfalfa, corn, cucumber, tomato	At 2000 ppm reduced seed germination of corn, tomato and cucumber, promoted root elongation of corn and cucumber, reduced root growth of alfalfa and tomato	López-Moreno et al., 2010b
nCeO ₂	8	62.5, 125, 250, 500 mg/kg	Soil	NPs within soil	96 – 102 days	Bean	At 62.5 and 125 mg/kg, upregulation of stress-related proteins, down regulation of phaseolin and lectins as nanoceria increased.	Majumdar et al., 2015
nCeO ₂	7.2 ± 0.7	2000 mg/L	Aqueous media (in Petri dish)	Direct contact with NP suspension	Pretreat seeds 2 hrs in water or NP followed by 5 days	Radish, Rapeseed, tomato, wheat, cabbage, cucumber, lettuce	nCeO ₂ at 2000 had no effect on root elongation of radish, rape, tomato, wheat, cabbage or cucumber, but reduced root elongation of lettuce	Ma et al., 2010b

					incubation in water or NP			
nCeO ₂	10-30 nm	1000, 2000 mg/L	Agar	NPs in half strength Murashige and Skoog NS	25 days	Arabidopsis	Decreased chlorophyll content. Increased growth at 250 ppm, decrease in biomass 500-2000 ppm.	Ma et al., 2013
nCeO ₂	8 ± 1	0, 400, 800 mg/kg	Mixture of loam sand soil, sand, organic soil	NPs within solid growth media	53 days	Cucumber	No impact on photosynthesis (regarding chlorophyll and gas exchange). At 400 ppm, no changes in biomass, no changes in yield. Reduced fruit yield at 800 ppm.	Zhao et al., 2013
nCeO ₂	8 ± 1	0, 400, 800 mg/kg	Soil	NPs in soil	84 days	Corn	No impact on photosynthesis (regarding chlorophyll and gas exchange)	Zhao et al., 2015
nCeO ₂	8 ± 1	0, 100, 400 mg/kg	Soil (lysimeter field station)	NPs in soil substrate	~210 days (7 months)	Wheat	Changes in microstructure of leaf cells, swollen chloroplasts (Figure 1f), squeezed nuclei (Figure 1d), bent and loosely arranged thylakoids (Figure 1f), decreased chlorophyll content. Protective cellular response induced by the radical scavenging ability of nCeO ₂ . Changes in protein content.	Du et al. 2015
nCeO ₂	10 ± 3.2	0, 100, 500 mg/L	Nutrient solution	Growth media spiked with NPs	~ 30 days	<i>Bacillus thuringiensis</i> - transgenic cotton	Swollen and destructed chloroplasts. Reduced Zn, Mg, Fe and P levels in xylem sap of cotton	Nhan et al., 2015
nCeO ₂	8 ± 1	0, 62.5, 125, 250, 500 mg/L	Aqueous (Petri dish)	Direct seed contact	4 days	Rice	Alters enzymatic activity, increases H ₂ O ₂ at 500 ppm nCeO ₂ , highest membrane damage at 125 ppm. No visible signs of toxicity at <62.5 mg L ⁻¹ .	Rico et al. 2013c
nCeO ₂	8 ± 1	0, 125, 250, 500 mg/L	Soil	Yoshida nutrient solution	48 days after treatment	Barley	Enhanced Ca, K, Zn, Mg, Cu, Al, Fe, P and S in barley grains.	Rico et al., 2015a

					(DAT) - Agronomic parameters and yield evaluation) Spikes harvested 169 (DAT)			
nCeO ₂	50-105	20 mg/kg	Soil	Irrigation with NP suspension	130 days	Tomato	Enhanced concentrations of Ca, K, Mg, P in roots; increased Ca, Mg in stems, but decreased contents of Na in stems and K, Na, P and S in tomato leaves	Antisari et al., 2015
nCeO ₂	8 ± 1	0, 125, 250, 500 mg/L	Soil	Yoshida nutrient solution	94 days	Wheat	Changes the amounts S and Mn in grains, amino acid composition and linolenic acid contents.	Rico et al., 2014

Species name in order of appearance in the table: rice, *Oryza sativa*; tomato, *Solanum lycopersicum*, *Lycopersicon esculentum*; soybean, *Glycine max*; alfalfa, *Medicago sativa*; corn, *Zea mays*; cucumber, *Cucumis sativus*; bean, *Phaseolus vulgaris*; radish, *Raphanus sativus*; rapeseed, *Brassica napus*; wheat, *Triticum aestivum*; cabbage, *Brassica oleracea*; lettuce, *Lactuca sativa*; arabidopsis, *Arabidopsis thaliana*; barley, *Hordeum vulgare*.

Figure 1

			Germination	Uptake	Translocation	Water balance	Nutrition	Oxidative stress	Photosynthesis	Genotoxicity	Shoot growth	Root growth	Seed production
NPs	nm												
Fullerenes		1	+	+	+	+	+	+	+	+	+	+	+
SWCNTs		D:10-170	+	+	+	+	+	+	+	+	+	+	+
MWCNTs		L: 50-800	+	+	+	+	+	+	+	+	+	+	+
nFe*		5-400	+	+	+	+	+	+	+	+	+	+	+
nCu*		1-50	+	+	+	+	+	+	+	+	+	+	+
nZn*		5-100	+	+	+	+	+	+	+	+	+	+	+
nAg		10-50	+	+	+	+	+	+	+	+	+	+	+
nAu		10-50	+	+	+	+	+	+	+	+	+	+	+
nTiO ₂		4-50	+	+	+	+	+	+	+	+	+	+	+
nCeO ₂		7-100	+	+	+	+	+	+	+	+	+	+	+

* based materials + Effect/ stimulation - Effect/ inhibition No effect Unknown

Figure 2

Figure 3

CONTRIBUTION

J. Gardea-Torresdey and J. R. Peralta-Videa generated the idea, designed the manuscript, and revise the final version and additional material. N. Zuverza-Mena worked the Cu-Based NPs, completed table information, and coordinated the writing process of the manuscript. D.

Martínez-Fernández and M. Komárek contributed the Ag, Au, iron-based NPs' material and the two diagrams. W. Du analyzed the literature about CeO₂ and TiO₂ and contributed Figure 1. J.A. Hernandez-Viezcas wrote about ZnO. N. Bonilla-Bird worked on carbon nanotubes, and M. Lopez-Moreno collaborated in table preparation and introduction.