# Chapter 3
# Effects of Surface Coating on the Bioactivity of Metal-Based Engineered Nanoparticles: Lessons Learned from Higher Plants

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**Abstract** Characteristics such as size, surface-to-volume ratio, and surface chemistry, among others, convey uniqueness to engineering nanoparticles (ENPs). The surface chemistry determines the stability and aggregation of ENPs and also constrains their applications, environmental fate, and interaction with living organisms. To avoid aggregation and improve stabilization, the surface chemistry of numerous ENPs has been modified through coating with several agents. However, the coating also changes their biointeractions. In this chapter we discuss literature concerning the uptake, translocation, accumulation, and physiological effects of surface-coated ENPs in economically important plants. We discussed existing information based on the type of ENP, coating agent, and species of plant. Negative and positive effects are discussed.

**Keywords** Nanoparticles · Surface chemistry · Crop plants · Uptake · Stress

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## 3.1 Introduction

Contemporarily, nanomaterials are profusely used in many applications including products for personal care, communications, manufacture, food packaging, medicine, imaging, and remediation of soil and water, among others [1, 2]. In addition, there are strong evidences that agricultural activities like pest control and fertilization are becoming nano-enabled [3]. This suggests that nanomaterial production, which by 2010 was estimated at 260,000–309,000 t [4], will continue growing at a very rapid pace. The global production includes several metal-based ENPs, being the most produced silica, titanium dioxide, alumina, and iron and zinc oxides [4]. A side effect of the huge production and use of ENPs is the discharge into the environment after end-user applications. Estimates for the 2010 production indicated that 20,800–86,520 tons ended up in soils, 1040–21,630 in bodies of water, and 260–4635 in the air [4].

Since it seemed evident that ENPs were accumulated in the environment, the scientific community started to investigate their effects on living organisms. Different research facilities with controlled environments have been used to study the effects of ENPs in mammals, microorganisms, insects, and plants. Investigations with plants have received much attention. A simple search in ScienceDirect.com (August 20, 2016) using the keywords "effects of nanoparticles in plant growth" shows that the number of papers describing the interactions of ENPs with plants has increased exponentially during the last 12 years (Fig. 3.1).

The first publications showed effects on seed germination [5] and photosynthesis [6, 7]. In subsequent works, researchers started to explore biochemical effects [8], effects on plant growth [9–11], and molecular expression [12]. The literature covering uptake, accumulation, biotransformation, and toxicity piled up very fast. In a very popular review, Rico et al. [13] analyzed most of the existing literature produced in the first decade, concerning the effects of nanoparticles in crop plants. Five years later, several review articles analyzed different aspects of the interaction of ENPs with plants [14–16]. Some of the recent reports indicate that the interaction of the ENPs with plants is modulated by several factors including soil conditions,
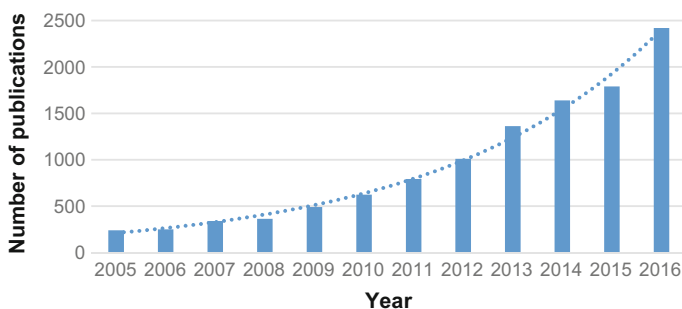


**Fig. 3.1** Number of publications about the effects of nanoparticles in plants in the last 12 years
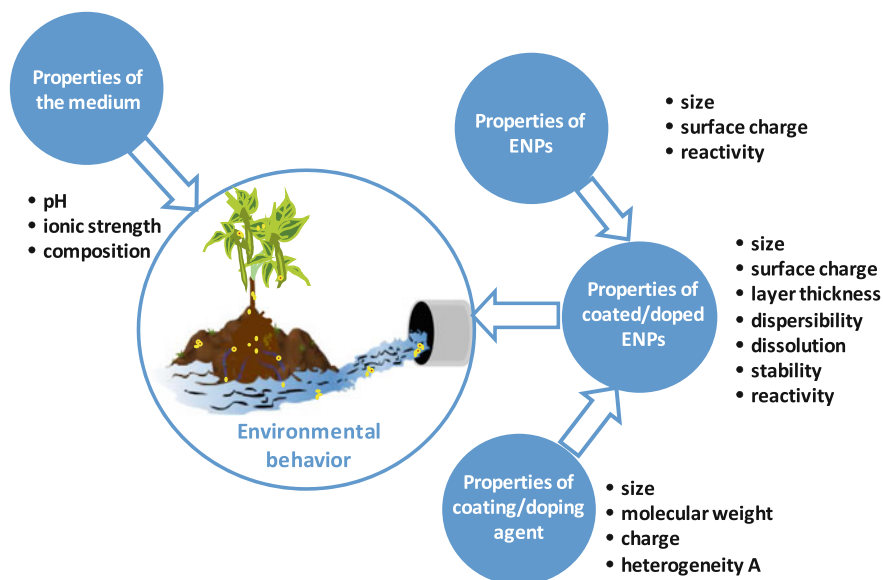
**Fig. 3.2** Environmental behavior of ENPs with changes in the surface properties. Adapted from Louie et al. [18]

plant species, particle size and type, ion release from the nano forms, and surface properties [17]. Figure 3.2 shows some of the factors that can modulate the environmental impacts of ENPs. As it can be observed in Fig. 3.2, the incorporation of natural or engineered macromolecules into the surface of the nanomaterials may affect their toxicity and reactivity, as well as the way they interact with the environment, including plants [18].

Although the volume of information regarding the effects of uncoated ENPs in plants is growing very fast, very little is known about the interaction of coated/doped ENPs with them. This chapter is devoted to analyzing the effects of surface coating on the interaction of silver, gold, zinc oxide, cerium oxide, and copper oxide ENPs with plants. Effects on physiological, biochemical, and phenotypical traits are discussed. Table 3.1 summarizes the effects of surface-modified metal-based ENPs in higher plants.

## 3.2 Metallic ENP

### 3.2.1 Silver Nanoparticles (Ag ENPs)

Silver (Ag) is known to have effective antimicrobial properties and it is among the most widely used metals in the world. Prevalence applications of Ag ENPs in medical, cosmetics, and textile industries has significantly increased the release of

**Table 3.1** Summary of reports about effects of surface-modified metal-based engineered nanoparticles in higher plants

| Engineered nanoparticle and surface modification | Enhanced properties after modification | Plant | Uptake, translocation, and physiological effects | | | | Ref. |
|---|---|---|---|---|---|---|---|
| | | | Root | Stem | Leaf | Fruit | |
| Gum Arabic coated Ag NPs | • Increased dissolution and greater release of Ag from AgNP | Lolium multiflorum | ✓ | ✓ | N/A | N/A | [19] |
| | | | Decreased root growth rate and distortion of root morphology and cell structure | | | | |
| Citrated-coated Ag NPs | • Functionalization to induce a positive charge | Mung bean (Phaseolus radiatus) | ✓ | ✓ | N/A | N/A | [20] |
| | • Lower release of Ag | | Concentration-dependent growth inhibition of the plant and morphological distortion of the root | | | | |
| | | Sorghum (Sorghum bicolor) | ✓ | ✓ | N/A | N/A | |
| | | | Concentration-dependent growth inhibition of the plant and morphological distortion of the root | | | | |
| | • Electrostatic stabilization of AgNPs | Maize (Zea mays) | ✓ | ✓ | N/A | ✓ | [21] |
| | • Minimized dissolution of Ag | | Growth suppression; abnormal root morphology and structures at developmental stage | | | | |
| | • Lower release of Ag | Cabbage (Brassica oleracea var. capitata) | ✓ | ✓ | N/A | ✓ | |
| | | | Growth suppression; abnormal root morphology and structures at developmental stage | | | | |

**Table 3.1** (continued)

| Engineered nanoparticle and surface modification | Enhanced properties after modification | Plant | Uptake, translocation, and physiological effects | | | | Ref. |
|---|---|---|---|---|---|---|---|
| | | | Root | Stem | Leaf | Fruit | |
| Au NPs coated with TTMA[a] | • Functionalization to induced a positive charge | Rice (Oryza sativa) | ✓ | ✓ | ✓ | N/A | [22] |
| | Functional group coating affected Au uptake. Highest Au uptake observed in TTMA in root tissues | | | | | | |
| Au NPs coated with TEGOH | • Functionalization to induce a neutral charge | | ✓ | ✓ | ✓ | N/A | |
| | LA-ICP-MS reveals heterogeneous distribution of Au ions in leaf tissues | | | | | | |
| Au NPs coated with TEGCOOH | • Functionalization to induce a negative charge | | ✓ | ✓ | ✓ | N/A | |
| | Au concentration highest in shoots treated with TEGCOOH | | | | | | |
| Au NPs coated with citrate | • Coated to simulate low molecular weight organic acids in soil | Tobacco (Nicotiana tabacum) | ✓ | ✓ | ✓ | N/A | [23] |
| | Accumulation of Au in leaf | | | | | | |
| | | Wheat (Triticum aestivum) | ✗ | ✗ | ✗ | N/A | |
| | No evidence of Au accumulation in any tissues | | | | | | |
| Au NPs coated with tannate | • Coated to simulate low molecular weight organic acids in soil | Tobacco (Nicotiana tabacum) | ✓ | ✓ | ✓ | N/A | [23] |
| | Au uptake between 2 and 50 mg/kg | | | | | | |
| | | Wheat (Triticum aestivum) | ✗ | ✗ | ✗ | N/A | |
| | No evidence of Au accumulation in any tissues | | | | | | |

**Table 3.1** (continued)

| Engineered nanoparticle and surface modification | Enhanced properties after modification | Plant | Uptake, translocation, and physiological effects | | | | Ref. |
|---|---|---|---|---|---|---|---|
| | | | Root | Stem | Leaf | Fruit | |
| Au NPs capped with citrate | • Functionalization to provide electrostatic stabilization | Onion (*Allium cepa*) | N/A | N/A | N/A | N/A | [24, 25] |
| | | | Oxidative stress increased with increasing concentration and particle size | | | | |
| Aluminum-doped ZnO | • Broadening of optical band gap | Green pea (*Pisum sativum*) | ✓ | ✓ | ✓ | ✓ | [26, 27] |
| | | | Increased weight of fresh plant tissues at 1000 mg/kg. Chlorophyll and carotenoids increased at 250 mg/kg. Nutrient content and carbohydrate profile (sucrose) changed | | | | |
| Iron-doped ZnO | • Reduced dissolution<br>• Reduced toxicity to bronchial and macrophage cells<br>• Stabilization of material crystal structure | Green pea (*Pisum sativum*) | ✓ | ✓ | ✓ | ✓ | [28, 29] |
| | | | Chlorophyll content and $H_2O_2$ production decreased. Doped ZnO ENPs resulted less toxic than uncoated ZnO ENPs | | | | |
| ZnO coated with γ-aminopropyltriethoxysilane (KH550) | • Functionalization with organic groups<br>• Improved dispersibility and shape<br>• Improved UV absorption | Green pea (*Pisum sativum*) | ✗ | ✓ | ✓ | ✓ | [27, 30, 31] |
| | | | Increased weight of fresh plant tissues at 1000 mg/kg | | | | |
| Alginate-coated $CeO_2$ | • Better interactions in water/soil environment | Corn (*Zea mays*) | ✓ | ✓ | | N/A | [32, 33] |
| | | | Different behavior of alginate-coated $CeO_2$ ENPs with the plant and soil when compared to uncoated ENPs | | | | |

**Table 3.1** (continued)

| Engineered nanoparticle and surface modification | Enhanced properties after modification | Plant | Uptake, translocation, and physiological effects | | | | Ref. |
|---|---|---|---|---|---|---|---|
| | | | Root | Stem | Leaf | Fruit | |
| Citric acid-coated $CeO_2$ | • Hydrophilic characteristics with a carboxylic group that can be further functionalized <br> • Less agglomeration <br> • Better interactions with the environment | Radish (*Raphanus sativus*) | Seedlings ✓ | [34] | | | [34–36] |
| | | | Citric acid-coated $CeO_2$ ENPs at 1:7 molar ratio showed increased root biomass, water content, and reduced Ce uptake | | | | |
| | | | Decreased toxicity when compared to uncoated ENPs | | | | |
| | | Tomato (*Solanum lycopersicum*) | ✗ | ✗ | ✗ | ✗ | |
| | | | Increased chlorophyll | | | | |
| | | | Enhanced catalase activity and reduced ascorbate peroxidase activity | | | | |
| | | | Carbohydrates affected | | | | |

the element into the environment [37–39]. In the last decade, several studies have shown that Ag NPs have a wide variety of applications [16]. In addition, these ENPs, at the appropriate concentration, are considered nontoxic and non-carcinogenic [U. S. EPA, www.epa.gov/IRIS/subst/0099.htm].

Various forms of Ag ENPs, with diverse physical and surface properties, portend contamination of the ecosystem [40]. Thus, there is a need to understand the stability, mode of interaction, translocation, aggregation, and effects of this important nanomaterial at various levels of ecosystems [38]. Silver ENPs are synthesized by several methods but the synthesis is generally done in organic solvents or by the use of capping agents to avoid its aggregation [41–53]. Organic coating of Ag ENPs primarily stabilizes them against aggregation, while the capping agent, concomitantly, reduces $Ag^+$ ions to $Ag^0$.

Various sizes and shapes of Ag ENPs have been synthesized by several methods. Shapes, as shown in Fig. 3.3, include quasi-spheres, nanotubes, rods, discs, cubes, prisms, octahedral, and triangular nanoplates [54–57]. Capping agents such as citrate, polysaccharides, surfactants, proteins, polymers, and natural organic matter can be used in the synthesis of Ag ENPs [56–61]. Ag ENPs can also be synthesized by using inorganic ligands such as borate, carbonate, chloride, and sulfide to produce inorganic-coated Ag ENPs [62, 63]. The fate of Ag ENPs in the ecosystem is determined by size, shape, as well as the core shell surrounding the Ag atom [64].

There are few reports describing the response of plants to surface-coated Ag ENPs. A study showed negative effects of gum Arabic (GA)-coated Ag ENPs on *Lolium multiflorum*. There was a significant decrease in the growth rate of the root
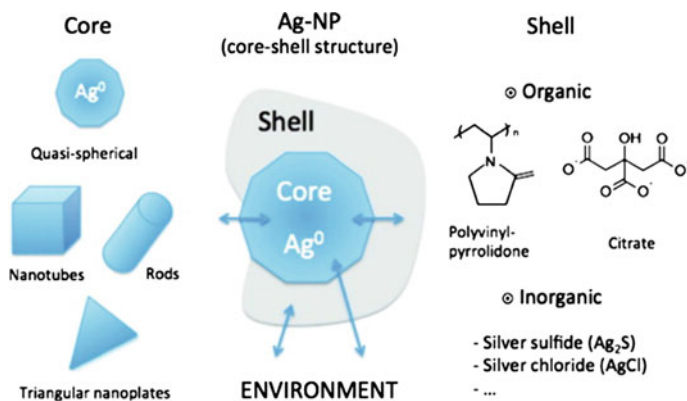


**Fig. 3.3** Typical core–shell structure of an Ag ENP that might be released in the environment. *Double arrows* represent the reactions that might occur between the shell or the core with the environment and also at the interface between core and shell. Note that the shell is usually not a continuous impermeable layer but rather is a discontinuous layer allowing the interaction between the core and the surrounding environment. The discontinuity arises from steric and electrostatic forces between the macromolecules attached to the surface. Reprinted with permission from Levard et al. [55]. Copyright 2012 America Chemical Society

and a distortion in the root morphology and cell structure [19]. At a concentration of 40 mg/L of GA-coated Ag ENPs, light microscopy revealed that the seedling growth was inhibited, the root hair failed to develop, the cortical cells were highly vacuolated, and the epidermis and root cap were collapsed. Compared with exposure to equivalent concentrations of ionic silver, the seedlings showed no such effects. There was a significant decrease in root growth rate and distortion of root morphology and cell structure [19]. Seedlings exposed to ionic Ag did not show such effects. Since the effects were observed at high concentrations of Ag ENPs over a short period of time, it is not known if the plants recovered at longer developmental stages. Moreover, by comparing cysteine binding GA-coated Ag ENPs and supernatant components of the GA-coated Ag ENP suspension, it was demonstrated that the toxicity of GA-coated Ag ENPs might not be only due to the released Ag from the ENPs [19]. The Ag concentration in the root might result from the Ag ions adsorbed to the root surface, while the concentration in the shoot could result from the adsorption of Ag ENPs and the translocation of both the ENPs and Ag ions, similar to plants treated with $CeO_2$ [19, 65]. The root growth inhibition and cell damage may result from the nanomaterial itself, the Ag ions released from the ENPs, or both [19].

Phytotoxicity studies of citrated-coated Ag ENPs were performed in *Phaseolus radiatus* and *Sorghum bicolor*. Experiments were carried out in both agar and soil media. Transmission electron microscopy (TEM) images showed that Ag ENPs were spherical in shape (Fig. 3.4a) and evenly distributed in the agar medium (Fig. 3.4b). TEM images also showed that the plants took up the ENPs from both media but the growth rate was inhibited in both plants only in the agar medium, in a dose-dependent manner. At the higher concentration, the citrate-coated Ag ENPs inhibited the growth of seedlings in agar medium; however, none of the concentrations affected soil grown seedlings.
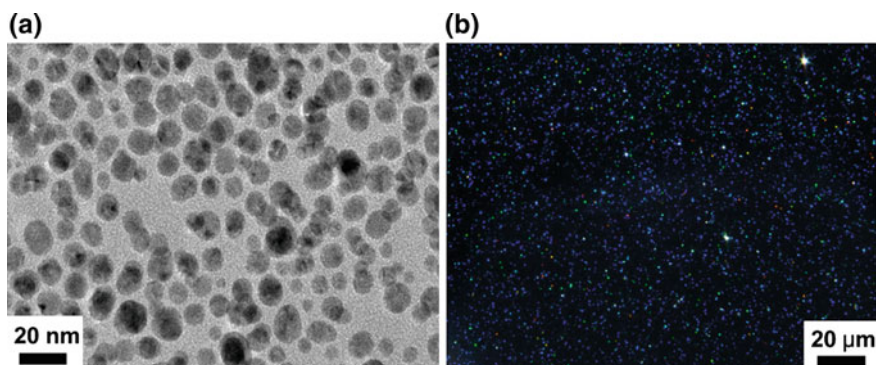


**Fig. 3.4** **a** Transmission electron micrograph of silver nanoparticles; **b** high-resolution microscopic image of silver nanoparticle distributed in agar medium of 40 mg/L. Reprinted from Lee et al. [20]. Copyright 2011, with permission from Elsevier
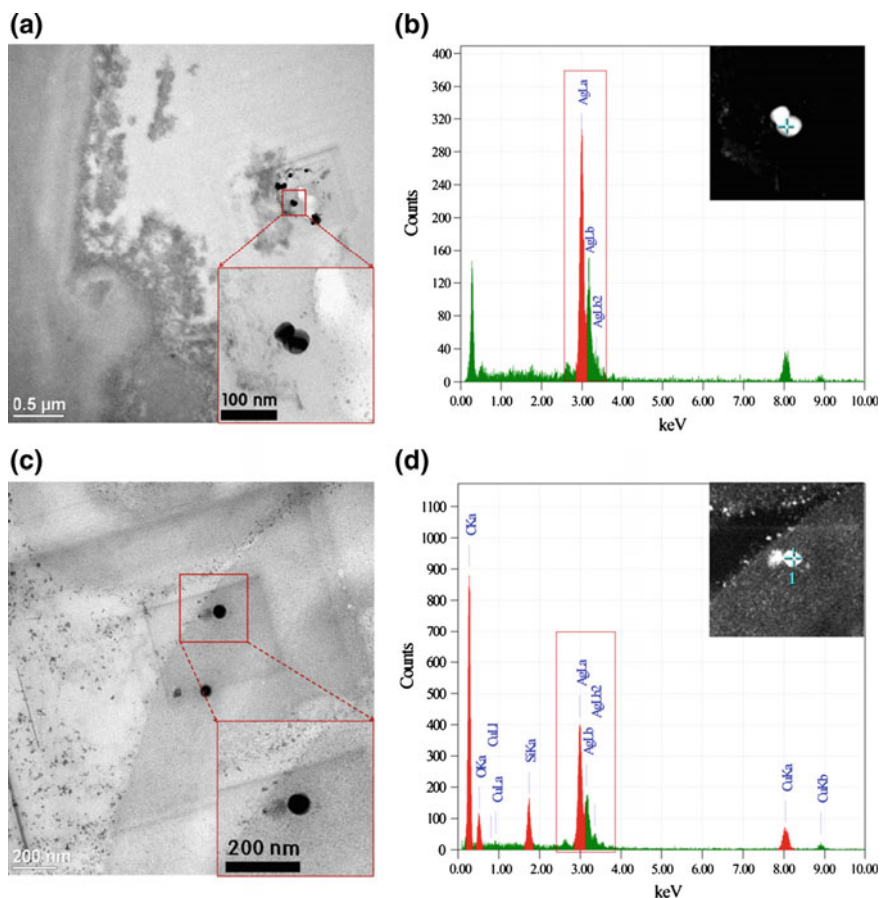
**Fig. 3.5** Transmission electron micrographs of the roots of *Phaseolus radiatus* and *Sorghum bicolor* exposed to Ag NPs in agar medium of 100 and 40 mg/L, respectively: **a** *Phaseolus radiatus*, **b** spectrum of energy-dispersive spectroscopy (EDS) of dense spot for TEM scan in (**a**), **c** *Sorghum bicolor*, and **d** spectrum of EDS of dense spot for TEM scan in **c**. Reprinted from Lee et al. [20] Copyright 2011, with permission from Elsevier

Figure 3.5 shows further TEM and energy-dispersive spectroscopy (EDS) images of the root tissue of *P. radiatus* and *S. bicolor* exposed to Ag ENPs in agar medium at 100 and 40 mg/L. The EDS scan showed the penetration of particulate Ag into the root [20]. The study showed that toxicity was species dependent, since *P. radiatus* and *S. bicolor* showed 13 and 26 mg/L $EC_{50}$ values, respectively. It is noteworthy that citrate, at 3 mg/L, may have no significant effect on the growth of *P. radiatus* [66]. Pokhrel and Dubey [21] reported that citrate-coated Ag ENPs imposed toxicity to the early growth and development of both maize (*Zea mays* L.) and cabbage (*Brassica oleracea* var. capitata L.). The toxic potential of Ag ENPs was more pronounced in both plants than the

corresponding ionic salts. Both plants revealed abnormal root morphology and structures under exposure to citrate-coated Ag ENPs. However, germination and root elongation were less affected by the ENPs, compared to free ions [21]. In addition, maize absorbed less Ag from citrate-coated Ag ENPs, compared with $AgNO_3$ [21].

### 3.2.2  Gold Nanoparticles (Au ENPs)

Although many coatings are currently being utilized on Au ENPs [67–72], research investigating the implications of their exposure to agricultural crops is extremely lacking. Koelmel et al. [22] explored the effects of Au ENPs coated with thioalkyl tetra(ethyleneglycol)ated trimethylammonium (TTMA), tetraethylene glycol (TEGOH), and tetraethylene glycol acetic acid ligand (TEGCOOH). These coatings gave the ENPs a positive, neutral, and negative charge, respectively. Hydroponically grown rice (*Oryza sativa*) plants were studied by using a laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) to track the uptake of the coated ENPs and determine how surface charge affected the spatial distribution of Au [22]. LA-ICP-MS analysis revealed that functional groups on the Au ENP coatings did affect uptake, with roots showing a preference for the positively charged TTMA coating, followed by the neutral TEGOH coating, and then the negatively charged TEGCOOH coating. Gold concentrations were highest in the shoots with the TEGCOOH (–) coating. Examination of rice leaves revealed heterogeneous distribution of Au based on charge/surface coating. Leaves from rice treated with Au ENPs and coated with TEGOH (neutral) contained higher concentrations of gold on the left side of the blade, while rice treated with TEGCOOH (–) showed gold concentrated in the midsection of the leaf.

The effects of Au ENPs coated with citrate and tannate have also been evaluated [23]. Both tobacco (*Nicotiana tabacum*) and wheat (*Triticum aestivum*) were grown hydroponically and exposed to Au ENPs coated with either citrate or tannate at sizes of 10, 30, or 50 nm. At the 30 mg/kg treatment concentration tested, the authors found no gold uptake in wheat with any of the size/coating combinations. In addition, synchrotron micro X-ray fluorescence (μ-XRF) analysis revealed no uptake of gold into the root tissues. Gold uptake in tobacco was measured between 2 and 50 mg/kg at all treatments. Synchrotron experiments indicated the accumulation of gold from 30-nm citrate-coated Au ENPs in the mid-rib of tobacco leaves. However, with the exception of the above-mentioned treatment, the majority of tobacco leaves tested contained Au concentrations below the μ-XRF detection limit of 1 mg/kg.

A recently published study examined the biological effects of Au NPs capped with citrate in onion (*Allium cepa*) [24]. These researchers measured the generation of reactive oxygen species (ROS) in roots exposed to increasing concentrations of capped Au ENPs at sizes of 15, 30, and 40 nm. The authors found that generation of $O_2^-$, $H_2O_2$, and $^-OH$ radicals increased with increasing nanoparticle exposure, but

the trend decreased with increased nanoparticle size. This trend was mirrored with the production of malondialdehyde (MDA) production, with the most MDA production occurring in onions treated with 15 nm Au ENPs at the highest concentration.

It is clear from the number of published articles, and from the scope of these studies, that research into the effects that coatings may have on Au ENPs is still in its infancy. Research in this area must intensify, if it is to keep pace with the demand for Au ENPs with a seemingly endless list of coatings.

## 3.3   Metal Oxide ENPs

### 3.3.1   Zinc Oxide Nanoparticles (ZnO ENPs)

Among the ENPs, zinc oxide is subjected to surface modification to enhance its properties, including conductivity, dispersion, shape, photoluminescence, and reflectance, among others. The growing application in electronics and optics has increased the number of coated/doped ZnO ENPs. However, their release into the environment is unquantified and its implications are still unknown. Table 3.1 shows literature reports on the synthesis of surface-modified ZnO nanoparticles whose biocompatibility with plants has been studied.

To the best of the authors' knowledge, there are only a couple of studies evaluating the effects of coated/doped ZnO ENPs in plants. Mukherjee et al. [29] performed a soil study in green pea (*Pisum sativum* L.) plants exposed to iron-doped ZnO ENPs (Fe@ZnO) and uncoated ZnO ENPs. Plants were grown in soil amended with either 10% Fe@ZnO or uncoated ZnO at 0, 125, 250, and 500 mg/kg. Root and stem Zn was enhanced after exposure to the Fe-doped ENPs, but the Fe absorption remained unaffected after comparison to control treatments. In addition, chlorophyll content and production of $H_2O_2$ decreased. Authors concluded that Fe@ZnO ENPs resulted less toxic than uncoated ZnO ENPs. In a further study, Mukherjee et al. [27] exposed green pea for 65 days to soil amended uncoated ZnO, 2 wt% alumina ($Al_2O_3$)-doped ZnO, and 1% KH550-coated ZnO at 250 and 1000 mg ENP/kg. Results showed increased weight of fresh plant tissues at 1000 mg/kg. Higher concentrations of Zn were found in roots and seeds under aluminum-doped ZnO at 1000 mg/kg, compared with other ZnO ENPs and macrosized ZnO. Authors attributed the result to the high positive surface charge due to Al doping as well as high $Zn^{2+}$ dissolution. Increased seed Zn was found in both doped and coated ZnO treatments at 250 mg/kg, attributed to the alumina doping and the negative surface charge of the KH550-coated that promotes Zn uptake due to the repulsion from the negatively charged root surface. Chlorophyll and carotenoids were increased by the alumina-doped treatment at 250 mg/kg, compared to the rest of the treatments. The seed quality was affected the most by the doped NPs at 1000 mg/kg, where nutrient content and carbohydrate profile

(sucrose) changed. Alumina-doped particles had larger size (15 nm) than bare-ZnO ENPs (10 nm); authors hypothesized this had greater effects on plant and seed quality. The authors highlighted the importance of the surface modification in the behavior of ENPs in edible plants, since the aluminum-doped ZnO showed more negative effects in green pea plants than KH550-coated and uncoated ZnO ENPs.

### 3.3.2 Cerium Dioxide Nanoparticles (CeO$_2$ ENPs)

One of the first studies on the effects of coated CeO$_2$ ENPs in plants was reported by Zhao et al. [32]. Alginate-coated CeO$_2$ ENPs interaction with corn (Zea mays) plants was evaluated in natural (sandy loam) and organic (1:1 natural soil:commercial potting soil) soils at concentrations of 100, 200, 400, and 800 mg/kg, and compared to uncoated CeO$_2$ ENPs. Alginate was selected as a coating agent, since it is naturally produced by algae and some bacteria found in soil [33]; thus, the interaction between alginate and the ENPs can occur naturally in water or soil environments. Authors reported that the surface coating modified the interaction of CeO$_2$ ENPs with the plant and soils. Authors also stated that the behavior of the coated ENPs depends on the type of soil and its organic matter content. In this specific study, Ce content increased in plants grown in organic soil amended with uncoated and coated CeO$_2$ ENPs at concentrations of 400 and 800 mg/kg, compared with plants grown in natural soil under the same conditions. This confirms that the behavior of both uncoated/coated ENPs is highly dependent on the medium properties.

Trujillo-Reyes et al. [34] modified CeO$_2$ ENPs with a surface coating of citric acid (CA) at molar ratios of 1:2, 1:3, 1:7, and 1:10 CeO$_2$:CA. Citric acid was previously reported as a coating agent for silver [73] and iron oxide [74] ENPs. Citric acid was added as a coating material due to its biocompatibility with Fe$_2$O$_3$ ENPs and its adsorption onto the ENPs surface [74]. Coating with CA also adds to the surface at least one carboxylic group exposed (that can be even further functionalized), gives hydrophilic characteristics to the ENPs, and avoids agglomeration [74]. In addition, similarly to alginate, CA can be naturally found in the environment, representing a potential path of interaction with ENPs. In the study performed by Trujillo-Reyes et al. [34], they evaluated the toxicity of CA-coated and uncoated CeO$_2$ ENPs into radish (Raphanus sativus) seedlings at concentrations of 50, 100, and 200 mg/L. Water and CA at 100 mg/L were used as controls. The results did not show any changes in seed germination. However, at all concentrations, CA-coated CeO$_2$ ENPs at 1:7 molar ratio showed increased root biomass, water content, and reduced Ce uptake. According to the authors, citric acid coating decreased the toxicity of CeO$_2$ ENPs.

CA-coated CeO$_2$ ENPs were also evaluated in tomato (Solanum lycopersicum L.) plants, along with uncoated CeO$_2$, micron-sized CeO$_2$, ionic Ce (cerium acetate), and citric acid. Barrios et al. [36] exposed tomato plants for 210 days to commercial potting soil amended with each of the five different chemicals at concentrations of

62.5, 125, 250, and 500 mg/kg. None of the treatments increased stem and leaf Ce, but CA-coated $CeO_2$ ENPs reduced the Ce uptake by roots and increased levels of chlorophyll, in comparison to control. Neither uncoated nor coated particles affect the accumulation of micro and macronutrients in roots, stems, and leaves. However, at 500 mg/kg, CA-coated $CeO_2$ enhanced catalase activity, which represents the plant's response to modifications in the environmental conditions [75]. Additionally, both coated and uncoated $CeO_2$ ENPs reduced the activity of ascorbate peroxidase, enzyme responsible for hydrogen peroxide and hydroxyl radicals scavenging, which could damage cell constituents [76].

Finally, Barrios et al. [35] performed a nutritional assessment in the fruit obtained from tomato plants exposed to the previously mentioned materials. The study included quantification of elements (Ce, Al, B, Ca, Cu, Fe, K, Mg, Mn, P, and Zn) along with total and reducing sugars, starch, and lycopene. The authors concluded that all Ce compounds (macrosized, uncoated, and coated nano $CeO_2$) affected the physiology and nutrient composition of the tomato fruits. However, it was evident that the surface coating plays an important role in the effects of the ENPs on the biochemistry of the plant, since the uncoated $CeO_2$ ENPs affected mainly the nutritional elements, while the CA-coated $CeO_2$ ENPs disturbed the carbohydrates.

### 3.3.3 Copper Oxide ENPs

Although the scope of this chapter is limited to higher plants, a comprehensive search yielded no published work dealing with terrestrial vascular plants. However, some work has been done looking at polymer coated CuO in duckweed and green algae. Saison et al. [77] investigated the effects of polystyrene(poly (styrene-co-butyl acrylate)-coated CuO nanoparticles (CS-CuO ENPs) on ROS generation in green algae. Measurements of lipid peroxidation indicate a 350% increase in ROS production in algae treated with CS-CuO ENPs at 20 mg/L, compared to control. There was no significant increase in ROS observed in algae treated with bare CuO or with polystyrene alone. The authors attributed high ROS production to photocatalytic processes induced by CuO semiconductor properties and light exposure, as plants treated with CS-CuO ENPs in the absence of light produced low levels of ROS. Chlorophyll content decreased by half and photosynthesis II (PS II) electron transport was significantly reduced, after six hours of exposure to CS-CuO NPs. These results were supported by a later study that found CS-CuO ENPs produced a 390% increase in ROS generation, and caused a reduction in PS II activity to 13% of control levels [78]. In the same study, green algae treated with uncoated CuO ENPs saw ROS levels of only 160% of controls, while PS II activity remained at 78% of controls.

Perreault et al. [79] recently conducted studies looking at CS-CuO ENPs, this time using duckweed instead of green algae. CS-CuO ENPs were found to be 10 times more toxic than bare CuO. The coated CuO also reduced duckweed's growth

rate by 50%, while the bare CuO ENPs required over 10 times the concentration to achieve the same effect. Perreault et al. [78] also reported that ROS generation was 400% higher in CS-CuO ENPs compared to CuO ENPs, citing unique characteristics caused by the surface coating, as the polymer alone did not produce similar results.

## 3.4  Conclusions

Although the number of reports concerning the effects of surface-coated ENPs on plants is limited (a dozen of species), they have covered growth stages from germination to fruit production and, in the case of Au NPs [22], the compartmentalization of particles as affected by the type of surface coating. Practically, no effects have been observed in germination; however, some effects have been shown in root growth and ROS production [20, 24]. Attempts have also been made to evaluate the effects of surface modification on the quality of seeds [27] and fruit [35]. Alumina-doped ZnO ENPs increased chlorophyll, carotenoids, and seed Zn in green pea [27], while citric acid-coated $CeO_2$ disturbed carbohydrates in tomato [35]. The above information clearly shows that more studies are needed in order to generalize the effects of surface coating in the interaction of NPs with plants. Very few long-term studies have shown possible effects of seeds and fruits. Only a study has evaluated the tissue distribution of coated NPs [22] and there is no idea about the effects on trophic transfer. Only one report has evaluated the interaction of coating × soil properties [32]. This suggests that future research has to be performed in soils with different properties and with plants of different species. In addition, future studies have to determine the biotransformation of surface-coated ENPs within plants, possible trophic transfer and the transgenerational effects. In summary, there is a long way to run in order to have a clear idea about the environmental effects of surface modification of ENPs.

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