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The foliar applications of engineered nanoparticles have been widely explored. NPs have promising potential, or may be even used already, in actual agricultural production. Foliar application is a more efficient and effective way of providing nutrition or disease/pest protection in plants when barriers (e.g., leaf surface properties, NPs characteristics, environmental factors) are overcome. However, negative impacts of NPs on plants (genotoxicity and phytotoxicity) as well their accumulation and potential human exposure still require more studies.

Foliar application of nanoparticles: Mechanisms of absorption, transfer, and multiple impacts

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Abstract

Foliar spray of engineered nanoparticles (NPs) as nanofertilizer, nanopesticides, nanosensors, and nanocarriers is increasingly being employed in the agricultural industry. Foliar spraying of NPs improves the effectiveness of plant protection technologies compared to traditional soil-root application. Foliar sprayed NPs mainly enter the leaves through stomata, and transported to different plant parts via apoplastic and symplastic pathways. Foliar NPs enhance defenses and resistance against pests and diseases, and improve the yield and quality of crops. However, the mechanisms of damage caused by foliar NPs need further elucidation. Moreover, important factors limiting foliage uptake of NPs such as wax deposits on leaf surfaces, environmental factors (e.g., light, temperature, and humidity), and physical and chemical properties of NPs should be investigated to further improve this technology.

Keywords: Efficacy; Human exposure; Nanofertilizer; Nanofungicide; Plant toxicity

Introduction

The innovation in nanotechnology greatly promotes the research on foliar application of engineered nanoparticles (NPs) as nanofertilizers, nanocarriers, and nanosensors on wide range of fields of agricultural industry. NPs have an average size <100 nm with high surface to volume ratio and high reactivity which are useful in many industrial processes.[1-4] NPs have good catalytic activity,[5] and can carry various types of functional groups that increase their cellular uptake.[6] Therefore, scientists have studied various applications of NPs, such as mitigation of environmental pollution and prevention of pests and pathogens,[7] antibacterial nanoagents,[8] nanofertilizers,[9] nanosensors for monitoring plant health in real-time,[10] nanomaterials for genetic engineering,[11] and usefulness as fuel additives.[12]

Foliar applications of NPs have been widely studied and valuable information on this technology has been obtained (Supporting Information Table S1). The advantages of foliar NPs include reduced production of reactive oxygen *in vivo*, improved seed germination,[7] increased shelf life of agricultural produce,[13] improved absorption and assimilation of foliar fertilizer,[14] controlled release of NPs at targeted locations,[15] and reduced damage by abiotic stresses[16]. Foliar applications of single or multiple NPs have been reported to synergistically reduce plant absorption of heavy metals (Cd, Pb), which has been attributed to the stimulation of antioxidative enzyme activity and increased resistance to stress.[17-20]

Plants absorb foliar NPs usually through stomata, cracks or water pores, ion channels, protein carriers, endocytosis, stigma, wound and trichomes.[9, 21-24] Stomata permeation and epidermal adsorption and internalization are the main ways in which foliage absorbs metals. NPs also enter plants through root tissues, lateral root development zones, and root damaged sites.[25, 26] Studies have shown that most inorganic metals can enter the plant through leaf stomata, and gets transported to the root through xylem and phloem. There are some surface modification methods of NPs such as coating or encapsulation technologies that alter the adhesion, lipophilicity, or hydrophilicity of NPs to aid NPs entry into the leaves.[23] It should be noted that the effect of NPs is complex and affected by many factors, such as dosage,[12, 27] plant species,[28] rhizosphere and foliage microorganisms,[29] particle size, shape, and charge of NPs,[14, 30, 31] and soil pH, and soil matrix.[32]

Agricultural crops actively, or passively, absorb NPs in the environment. NPs can come from the use of nanofertilizers, exhaust gases from vehicles or industry, fine particulate matter from incineration, accidental leakage, and nanofungicides.[13, 33] High demand for these materials can release pollutants into water, soil and even the atmosphere.[34] Nano-scale metal pollutants in atmosphere (e.g., Pb which has high toxicity to organisms) can accumulate in plants through the leaves which cause leaf surface necrosis, affect plant growth, and induce potential harm to human health.[35] However, the mechanisms of accumulation and responses in plants through foliar exposure is currently not understood.

This review summarizes the foliar application of NPs, the mechanisms of absorption and transport, and the influence of plant physiology and abiotic environment on NPs impacts in plants. The differences between foliage and root exposures were compared to understand the beneficial and adverse effects of foliar NPs, and to analyze the causes of damages and the corresponding measures to prevent or reduce those damages. Foliar application of NPs is a promising alternative technology compared to traditional soil-root application, and has economic and environmental protection benefits that cannot be ignored. However, there is still a big knowledge gap on how plant species or structural properties of NPs affect the efficacies of foliar NPs. Long-term field experiment, technological measures to prevent harmful effect of foliar NPs, and methods development to effectively quantify NPs transfer in plants also need further studies.[23]

1. Types of nanomaterials and their applications as foliar spray

Foliar NPs is expected to be a novel way to solve prominent production challenges in agricultural system. The uses of NPs in agriculture include soil monitoring, disease control, nutritional supplements, and slow release nanofertilizers and nanofungicides.[36] NPs can also be used as nanocapsules to carry and release herbicides, fertilizers, or genes to specific plant target sites to achieve the desired effects.[37, 38] Spraying proper amount of micro/macronutrients on foliage can mitigate damage caused by traditional soil-root application methods.[21] There are also other ultrafine particles, including particulate matters and heavy metals, discharged into the environment through various human activities (e.g., waste incineration, transportation, smelters) that may deposit on foliage and may have serious impacts on agricultural production.[35 39] Therefore, it is particularly important to understand and adjust the physical, chemical, biological, and photocatalytic properties of NPs in production applications to reduce or eliminate toxicity.

1.1 Types of nanoparticles

In general, agricultural plants are exposed to two types NPs: synthetic NPs or natural NPs (which are mainly formed from industrial production, volcanic eruptions, and fossil fuel combustion).[40] Synthetic NPs can be further divided into four categories: inorganic NPs (metal oxides, metal-based, inorganic non-metals), organic NPs (biopolymers, liposomes), carbon-based NPs (fullerenes, carbon nanotubes), and organic-inorganic hybrid NPs (metal-organic combined with NPs).[41-43] These synthetic NPs have been studied in agricultural applications. For example, inorganic NPs can be applied as nanopesticide and nanofungicides to prevent disease or pest occurrence in plants,[2, 44, 45] carbon-based NPs can be used as coatings for slow release nanofertilizers to improve plant biomass in agriculture,[46] and organic NPs can serve as nanocarriers of nutrient elements (e.g., iron and magnesium) to treat acute malnutrition in crops.[47, 48]

Figure 1 shows the classification and common uses of NPs. There are physicochemical, biological, and hybrid methods to synthesize NPs applied in agriculture. Physical and chemical syntheses are more commonly used; however, their biological applications are extremely limited due to toxic chemical components.[26] Therefore, researchers gradually explored green synthesis of agriculture-friendly NPs.[49-51] Green synthesis uses unique environmentally friendly solvents, renewable materials, and non-toxic chemicals to synthesize NPs.[52] Green synthesized NPs induce significant improvement on germination of seeds,[53] production of photosynthetic pigments, and activation of antioxidant enzymes.[54]

Chitosan is another non-toxic, biodegradable, and biocompatible biopolymer that can be used as nanocarrier for various elements. Chitosan NPs also adsorb easily on leaves that it can be used as coating for slow release fertilizer and pesticide.[55] Its structure is also suitable for encapsulating metal ions that chitosan NPs have been shown to increase the antibacterial efficacy of metal ions.[56] The stability of chitosan as nanocoating protects the surface stability of large particles, reduces the dissolution of fertilizer, and promotes more effective absorption of nutrients by plants. In this way a chitosan nanocoating can be employed to reduce fertilizer waste and environmental damage.[57] For example, zinc complexed with chitosan NPs can be applied as micronutrient to mitigate the problem on zinc deficiency in soil.[56]

Carbon-based NPs are also showing potentials in foliar applications of NPs. These types of NPs serve as vehicle for DNA delivery because of their ability to penetrate cell membranes and cell walls.[58] Nanocomposites can be used as effective way to regulate and transport nutrients in seeds.[59] Natural polymer NPs such as arabic gum materials can coat NPs and reduce the impact on crop health.[60] The high stability and biodegradability of a biopolymer NPs make biopolymer-mineral nanofertilizer effective at reducing toxicity to agricultural crops.[58]

1.2 Foliar application of NPs

Foliar applied NPs are often used in agriculture as herbicides, fertilizers, plant nutritional supplements, post-harvest preservatives, and biosensors.[34, 61] Due to rainfall and adsorption on soil complexes, the utilization rate of soil-applied fertilizers by plants is low, resulting in increased application of chemical fertilizers which leads to eutrophication.[62] Fertilizers with low solubility cause plants to grow poorly because they cannot absorb enough trace elements.[63] Additionally, some plant nutrients may precipitate or bind with soil colloids and organic matter that further reduce their availability to plants.[58] Biodegradable natural macromolecules such as chitosan, kaolinite, mesoporous silica, and carboxyl methyl cellulose polymers have been used to develop slow release nanofertilizers.[58] There is also report on EDTA-coated ferroferric oxide (Fe_3O_4) NPs as plant fertilizer.[1]

Compared with traditional soil-applied fertilizers, foliar applied nanofertilizers have advantages of being quickly absorbed by plants, more cost-effective, and minimally impacting soil health.[64] Foliar application can provide vitamins and some elements lacking in soils.[21] Researchers have shown that slow release nanofertilizers enhanced plant uptake of nitrogen, phosphorus, and potassium.[65] Mesoporous silica NPs prevented premature volatilization of nutrients and reduced environmental impacts of nanopesticide.[66] Foliar NPs can also provide nutrients lacking in crops, achieve biofortification in a short period of time, and reduce the deficiency of certain essential nutrients in crops.[56, 67] Study showed that foliar spraying of ZnO NPs promoted zinc augmentation in plants.[68] Relevant studies revealed that foliage spraying of nano-scale fertilizers can release the metal ions required by the plant at low concentration without causing serious toxicity.[63] Another study demonstrated that foliar application of fullerene NPs can improve plant's response to drought stress through additional water storage, which provides protection by relieving oxidative stress caused by drought.[69]

Studies also show antibacterial activity of foliar NPs. Silver has antibacterial properties that it can be used as major component of spray products and detergents to control plant diseases caused by fungi and mold.[60] Silver NPs are widely used as fungicides,[70] and some biologically prepared NPs (e.g., silver NPs synthesized by bacteria isolated from soil) exhibit high antimicrobial activity.[45] Inorganic metal-based NPs, such as CuZn bimetallic nanoparticles, also possess antibacterial properties that they are often used as insecticides and antibacterial agents.[71] In recent years, inorganic antibacterial agents such as bimetallic type and mixed ions type have broad research prospects, and studies showed that the antibacterial effects of different metals combined are superior to those used alone.

The foliar application of NPs has been well documented.[72] However, the specific mechanisms need to be further studied. Results demonstrated that efficacy of foliar nanofertilizer depends on identifying the nutrients needed by plants.[21] Leaf absorption needs to meet several conditions: NPs should have sufficient residence time, able to penetrate the epidermis to reach the target organ, and be in a form that can be utilized by the plant. Depending on the ion concentration gradient, diffusion into the leaves is a possible way for NPs to penetrate the epidermis.[63]

2. Absorption, transfer, and effects of foliar NPs

Foliar NPs can enter plants through leaf epidermis or stomata, and then translocate via the apoplast or symplast pathways.[22, 73] The xylem and phloem also play important role in transport of NPs[62] while vacuole and cell wall serve as the main accumulation sites of NPs.[74, 75] Many factors affect the absorption, transport, and accumulation of NPs:[72] these include abiotic factors (humidity and temperature), NPs properties (size and shape), and plants physiological characteristics. Foliar applied NPs are proving to be more efficient and soil environment friendly compared with root or soil exposure.[58, 76] Figure 2 summarizes the different factors (plant characteristics, environmental conditions, and NPs properties) that influence the uptake and transport of foliar-applied NPs.

2.1 Factors affecting uptake and transport of foliar NPs

Plant species (e.g., monocotyledons and dicotyledons) strongly influence the accumulation and biotransformation of foliar NPs.[77] Study showed that the absorbed multiwalled carbon nanotubes are easier to migrate in dicotyledons, wherein their accumulation was 1.5-3.0 folds higher than in monocotyledons.[36, 73] The difference in uptake could be attributed to the distribution of stomata in dicotyledons which was uneven and about 1.4 times more on the abaxial than on the adaxial leaf surface than in monocotyledons.[72] Another study noted that plants with large leaf surface areas, hard shoots, depressed leaves vein, and short petiole can accumulate more atmospheric NPs.[74] It has also been reported that NPs can increase plant uptake of external substances by affecting gene expression or metabolism.[78] Related reports showed that potassium deficiency in leaves affects stomatal regulation which affects NPs uptake.[35, 79] The life cycle and growth stage of plants determine the absorption, accumulation and transport of particulate matter by leaves,[80] therefore the amount NPs absorbed by plants on the leaf surface varies at different growth stages.[81, 82]

Leaf hair and cuticular wax could prevent absorption of foliar NPs, and their ability to block entry is affected by particle size, epidermal structure, leaf area, and growth stage.[77, 83] Cell walls and waxes can act as physical barriers to prevent the penetration of foreign substances such as NPs and provide certain degree of detoxification.[55, 70] The characteristic lipophilicity of leaf epidermal wax promotes the adsorption of hydrophobic or lipophilic NPs and high repellency to nanosuspensions.[23, 72] In this way, epidermal wax also protects plant by preventing leaf cell necrosis and genotoxic effects caused by excessive deposition of metal particles.[79] The thickness of the waxy layer, the density of the pores and trichomes,[84] and the structure and chemical composition of the leaf epidermis affect the absorption of NPs sprayed on the leaf surface. For example, cuticle contains a large amount of pectin which promotes NPs penetration,[85] the shape of the trichomes of different plants affect NPs absorption,[86] and species affect toxicity threshold of plants to metal NPs.[87]

Moreover, studies revealed that organic and inorganic compounds released by phyllosphere microbes have the ability to acidify, reduce, and chelate NPs, and affect NPs entry into the leaves.[83] Once inside the leaves, the transport of NPs in plants may be affected by factors such as cell wall pore size, liquid flow rate, and pore size limitations of plant membrane structures.[72] Plant cell wall lignification is another mechanism that helps plant to cope with stresses caused by foliar NPs.[88] Once inside the leaves, NPs could be accumulated in vacuole to slow down absorption and transfer in plants.[74, 89] For example, metal and carbon-based NPs may be sequestered in the vacuole by binding with thiol-containing compounds present in the vacuoles. Lastly, the casparian strip serves as the ultimate barrier that could hinder the penetration of NPs into the xylem.[36]

Environmental conditions affect the penetration of foliar NPs. Abiotic factors such as shading, high temperature, and low humidity cause the plant leaf epidermis to shrink and close the stomata thereby preventing the foliar absorption of NPs. High relative humidity affects osmotic potential of the leaf surface, which increases the penetration of metal NPs.[74] Abiotic factors such as light and temperature affect the development of leaf epidermis, which affects leaf absorption of NPs.[90-92] Report showed that light (which affects photosynthtic efficiency) and root temperature influence leaf surface absorption of NPs.[85] Similarly, rainfall washes away foliar sprayed NPs and reduce their absorption.[21]

The properties of NPs and the amount and method of application also affect the accumulation and migration of foliar NPs.[62] Small size NPs are easily transferred within the tissue and may have a higher level of accumulation and toxicity; therefore the right dosage of appropriate size of NPs promotes absorption by plants.[56] Crystallinity, redox potential, porosity, charge, catalytic activity, and aggregation all affect NPs penetration in plant leaves. In addition, high surface activity may accelerate the release of metal component of NPs.[93] By controlling the concentration of the mixed NPs on the foliar spray, the competing inhibition of absorption and transport between the elements can be alleviated.[94] The physical adsorption, lipophilicity or hydrophilicity of the particles, and electrostatic attraction can affect the agglomeration of NPs on the surface.[58] Studies have shown that negatively charged particles may be transported through vascular tissues, while positively charged particles may cross the cell membrane by endocytosis. Researches showed that negative charge is more favorable for transport, while positive or neutral charge is more favorable for accumulation on plant vascular system and therefore not transported.[72]

Surface modifications of NPs with various substances (such as fluorescein isothiocyanate, aminopropyl triethoxysilane, citrate,[58] iron, humic acid,[95] polyvinylpyrrolidone,[36] polyethylene glycol,[96] natural organic matter[72]) increase the chance of leaf absorption. For example, protein-encapsulated NPs are more stable on leaf surface,[49] and a hydrophilic protective sheet allowed NPs to be better absorbed by leaves.[1] Protective nanocarrier can ensure the transport of nutrients in cells such that foliar applied nano-liposomes can penetrate and translocate in the leaves.[47] Organic macromolecules such as chitosan alters the physical and chemical properties of NPs which enhance the stability of NPs and reduce their agglomeration that makes them easily enter through leaf epidermal cells.[55] The surface charge of NPs can be modified by coating, which contributes to the transport of NPs.[31, 72] Report showed that surface coating material prevents blocking of stomata by reducing the excessive accumulation of NPs,[97] thus increasing the probability of NPs being absorbed in the leaves. In addition, the use of surfactants and functional groups can enhance adhesion of NPs on leaf surface and therefore improve the bioavailability of NPs.[2, 98] For example, hydroxyapatite can be applied to modify NPs surface to reduce their aggregation and increase leaf absorption.[95]

2.2 Mechanisms of absorption and transfer of foliar NPs

Stomata penetration may be the main absorption pathway on leaf surface since absorption through the epidermis is very limited due to its small pore size.[83] It has been reported that particles larger than 20 nm are limited when passing through cell wall pores.[21] Generally, stomata are located only on the lower surface of leaves, but there are stomata on the upper surface of leaves in some species, which increases the possibility that NPs can be absorbed on the leaf surface. In addition, young leaves usually have higher ability to absorb nutrients compared to more mature leaves because new leaves have thinner wax and are still poorly developed physiologically to hinder metal absorption.[74] This has been observed in developing seeds which absorb nutrients through young leaves because of lack of well-developed leaf wax.[99]

Atmospheric NPs may settle and accumulate on the leaf surface which can be taken up eventually by the plants.[13] Large particles usually stick to the leaf surface wax, but fine particles penetrate and enter the leaves through leaf trichomes and get transported further to other plant tissues. Studies have demonstrated intact NPs in the mesophyll, epidermis, and vascular tissues of leaves sprayed with Ag NPs, while other reports showed the transfer of NPs from the foliage to other sites such as roots and newly formed leaves.[35, 70] Reports also showed that gold NPs (spherical, 30-90 nm) in aerosol form can enter the plant stomata via gas uptake, albeit on limited capacity.[100] Related study compared foliar spray between suspension and aerosol NPs: foliar spraying of suspension delivered 60-70% NPs but spraying of aerosol supplied 3.3-5.0% NPs on leaf surface.[72] However, the corresponding NPs absorption rate need to be further studied.

NPs uptake into plant cells through stomata and their subsequent transfer are largely dependent on particle sizes.[101] Leaf pores have diameter of about 100 nanometers but waxy hydrophobic stomata has a smaller pore size, which can block large particles.[72] Large particles (50-200 nm) are mainly transported through the apoplast, while small particles (10-50 nm) are transported mostly via the symplast. NPs that are further internalized by plants are transported through the vasculature of the phloem.[58, 62] For example, zinc is transported to the vascular bundle after being absorbed by the epidermal cells and then transported to the grain organ through the phloem. Studies have reported that small-sized NPs can be better absorbed through leaf pores, resulting in greater amount of NPs getting into the plants.[56]

NPs can enter plant cells by endocytosis, ion or water molecular pathways, formation of carrier protein complexes, physical damage, or binding with organic matter.[9] When NPs are taken up by plants, redox and other reactions may occur resulting in changes in NPs morphology. Studies have shown that some foliar NPs can induce formation of new pores in the cell wall that is conducive to NPs entering the cells.[13] Iron NPs may be more easily absorbed by plants through pores or foliar cracks, and there could be enzymes and chelating agents that contribute to iron transport within the plant.[93] It has been reported that foliar sprayed NPs are mainly absorbed by the pores through a hydrophilic pathway, whereas absorption via lipophilic pathway is less likely because NPs may be wrapped and absorbed by the epidermal wax before entering the tissue.[102] Endocytosis is another mechanism by which plant cells absorb NPs. NPs that enter through the cell wall can reach the phloem by endocytosis and can be transported to plants roots.[66, 89] Foliar NPs can enter the plant through the base of trichomes, and then further transferred to other tissues.[103] Studies have shown that foliar sprayed NPs were translocated down to the roots through the phloem or transferred upwards to other parts of the aboveground tissue through the xylem.[36]

A related study provided interesting insights on the migration and transformation of NPs in aquatic environment. Metal oxide NPs may undergo two processes of dissolution and sulfidation after being absorbed by algae, but the specific mechanism of transformation still needs to be studied.[104] The mechanism of aqueous solution penetrating into plant leaves through stomata is complex and influenced by many factors, such as surface tension of liquid, contact angle between liquid and leaf surface, and shape of pore wall.[80]

2.3 Comparison between foliar and root uptake

The physiological functions of leaves and roots are different that NPs absorption varies between these organs. Roots release exudates that inhibit absorption of NPs, while leaves can isolate NPs in cell wall after spraying on leaves. Plants exposed to metal NPs (e.g., Ag and ZnO NPs) through the leaves or roots exhibit different degrees of uptake and toxicity[70, 105] Foliar applied nutrients are transported downwards and further distributed to other parts of the plant.[85] Similarly, NPs sprayed on the leaves increased NPs content in the root system, which helped root cells absorb nutrients and improve their disease resistance.[98] However, there are also reports showing that metal NPs may not be transported to the roots by foliar application or transferred to plant shoots by root absorption.[102]

Plant stomata have a faster rate of nutrient absorption than root cells. Therefore, compared with soil fertilization, foliar application of nanofertilizers can be employed to correct nutrient deficiency in plants more quickly by accumulating the applied nutrient.[21, 77] Foliar application can also be used as an effective method to supplement special nutrient elements required for plant growth without affecting the soil environment.[106] For the same type of NPs, root or foliar application methods may have opposite effects because soil applied NPs have slower response than foliar applied.[70] Moreover, they have different bioavailability because root absorption has certain environmental constraints such as soil adsorption, desorption, transport, and transformation.[100, 107]

3. Effects of foliar NPs on plants

In recent years, the demand for food has increased but the efficiency of fertilizer use is generally poor.[72] NPs have positive effects on plants such as increased yield and quality, reduced oxidative stress, and improved disease resistance,[95, 108, 109] but sometimes high concentrations have adverse effects on crops.[34] For example, zinc deficiency can cause growth retardation,[56] but excessive zinc inhibits seedling growth.[94] Spraying Zn NPs on leaves can be an effective means for plant fertilization, but many aspects need to be considered in real life application.[21] Figure 3 shows the adverse and positive effects of foliar spraying of NPs on plants.

3.1 Beneficial effects of foliar NPs

Foliar application of NPs has beneficial effects in plants. In general, foliar NPs provide sufficient nutrient elements for plant growth,[82] help plants fight diseases or pathogens,[110] replenish nutrients quickly in nutrient deficient plants and provide essential elements that are difficult to absorb in the root,[21] supplement elements (e.g., iron and zinc) that are hard to obtain from deficient soil,[111] and provide micronutrients (such as zinc, iron, manganese, copper) that play important roles in plant metabolism.[63]

3.1.1 Foliar NPs promote plant growth

Foliar NPs exhibit positive effects in plants by enhancing resistance against pests and diseases, increasing biomass and yield, enhancing nutrient content, and improving crop quality.[108, 112] For example, carbon nanotubes promoted growth and seed germination of a variety of agricultural crops, which may be related to their ability to increase water absorption.[69] Foliar application of aerosolized ZnO, CuO and TiO_2 NPs was an efficient way to increase chlorophyll content, improve photosynthetic rate, and enhance resistance to diseases in tomato (*Lycopersicon esculentum*)[98, 100] Foliar application of Fe_3O_4 NPs increased ferritin content, reduced lipid peroxidation, and maintained iron homeostasis in maize (*Zea mays*).[113] Similarly, foliar application of Mn (square-shaped, 20 nm), Fe_2O_3 (sphere, 10-20 nm), and Mo (100-250 nm) nanofertilizers increased crop yields in plants.[58, 66, 114] The foliar application of Cu NPs enhanced vitamin content, fruit firmness, and antioxidant enzyme activity, thus improving fruit quality and freshness in tomato.[88] Likewise, foliar TiO_2 NPs improved plant tolerance to abiotic stresses such as drought, salinity, and submergence,[41] promoted water and fertilizer uptake, and enhanced photophosphorylation and yield in barley (*Hordeum vulgare*).[59] It also showed significant enhancements on phenols, carotenoids, total sugar, indole and amino acid contents in maize and coriander (*Coriandrum sativum*).[115, 116] Related reports also showed good germicidal activity and anti-pathogen activity of foliar applied TiO_2 NPa.[57] It is noteworthy that foliar spray of

NPs improved elemental contents in plants: ZnO NPs enhanced phosphorus and zinc uptake in tomato,[18, 100] Fe_3O_4 in improved iron and calcium contents in maize seeds,[113] Mg NPs increased copper and zinc contents in wheat (*Triticum aestivum*),[49] and TiO_2 NPs improved potassium, phosphorous, and magnesium accumulation in grapevine (*Vitis vinifera*).[117]

3.1.2 Foliar NPs improve food safety

Foliar application of NPs has been explored to reduce heavy metals toxicity in plants.[18] Studies showed that foliar application of ZnO NPs (spherical, 2-64 nm in size) effectively reduced the absorption of Cd and Pb in *Leucaena leucocephala* seedlings by enhancing the activities of various antioxidant enzymes.[118] Similarly, foliar TiO_2 NPs (near spherical shapes, average diameter of 68 nm) decreased the uptake and accumulation of Cd probably due to increased chlorophyll b content and enhanced antioxidant enzymes (CAT, SOD) activity.[17] Similarly, foliar application of ZnO NPs reduced the phytotoxicity of Cd by increasing the protein content and enhancing nitrate reductase and carbonic anhydrase activities which resulted in higher photosynthetic activity and biomass in tomato.[18] Similar findings in maize under Cd stress have been reported wherein foliar spraying of ZnO NPs (20-30 nm) mitigated oxidative stress that resulted in lower Cd accumulation.[119] Another study demonstrated that foliar ZnO NPs (20-30 nm) improved the tolerance of wheat to heavy metal toxicity by reducing Cd uptake (30-77%) and simultaneously increasing the absorption of Zn in grains.[120] Foliar application of graphene oxide NPs (0.8-1.2 nm thickness) in lettuce (*Lactuca sativa*) reduced the accumulation of Cd in leaves and roots and effectively reduced the damage of Cd to plant organelles.[19] Another study on heavy metal (Cd, Pb) exposure in rice (*Oryza sativa*) demonstrated that Se NPs (mean diameters of 12.26 ± 2 nm) and Si NPs (mean diameters of 18.04 ± 3 nm) reduced the accumulation of these metals in rice, and that the effect of combined application was better than that of single application of either NPs.[121] In the same manner, foliar SiO_2 NPs (spherical particles, 97.8 ± 2.8 nm) significantly decreased As accumulation in rice grains,[122] reduced Cd toxicity in rice,[58] improved resistance to diseases,[57] prolonged the storage time of grains and fruits,[88] and reduced disease rate in harvested crops and improve the quality of fruits.[108] Therefore, foliar application of NPs is a promising strategy to reduce the hazards (such as yield reduction, low soil utilization rate, and heavy metal accumulation) caused by heavy metal stress and improve nutrient content in agricultural crops (especially vegetables). Foliar application provides a new way to improve food quality and mitigate safety concerns from heavy metal exposure of agricultural crops. However, the foliage application of NPs should be done cautiously, and more field experimental data are needed to demonstrate the suitability of its wide application.

The use of foliar NPs has many benefits, however their application in agriculture is bound to raise food safety issues and concerns. The potential hazards of food safety should be taken seriously especially that there are reports showing NPs could induce cancer and genotoxicity in human cells.[79] It should be noted that even NP-loaded vegetables, fruits, and plant-based products such as feed, processed food, and seed oil can also impose toxicity risks.[74] For example, cesium oxide (Cs_2O) NPs may be transmitted through the food chain by being absorbed by plants and delivered to higher trophic levels, which can ultimately affect human health. Although humans may naturally digest and excrete NPs,[81] their accumulation in human body and their toxic side effects cannot be ignored.[63] Therefore, the widespread use of NPs requires more in-depth research to further assess NPs potential risks.

3.2 Adverse effects of foliar NPs on plants

Foliar NPs may cause unknown toxicity which limits their use in agriculture.[103, 123] The foliar application of high concentrations of metal NPs to vegetables has significant effects on gene expression,[79] and can cause electrolyte leakage and membrane damage, decrease photosynthetic pigment content, and induce oxidative stress.[107] Both CuO and Ag NPs may adversely affect the structure and function of photosynthetic machineries in plants. Foliar CuO NPs may limit the growth of roots and shoots, and there are symptoms of stomata closure after foliar application. Foliar application of TiO_2 NPs has negative effects on crops; these NPs induced genotoxicity, decreased biomass, and reduced enzyme activity.[117] Foliar application of nanofertilizers can cause foliar burns, which reduces photosynthetic efficiency, or blocking of pores due to aggregation of NPs, which hinders gas exchange and photosynthesis. Blocking of pores may also result in reduced absorption of some important elements.[85, 124]

The dosage has a great influence on the toxicity.[34, 125] Once the applied amount of zinc or copper exceeds the critical value, it will be toxic to plants, resulting in growth retardation and leaf chlorosis. Likewise, excessive use of iron and manganese NPs can cause necrosis.[63] Copper deficiency can cause young leaf dysplasia, but excessive use can cause toxicity to plants.[37] Also, it is worth noting that the application of NPs to foliar surfaces may have adverse effects on plant offspring, even though on the initial crops it exhibits positive effects.[93] For example, contrary to the first generation, the second generation showed a decrease in yield and protein and chlorophyll contents after exposure to foliar iron NPs. It may have a lot to do with the iron threshold since residual iron NPs inhibit seed development and excessive accumulation of iron NPs induces toxicity.[93] This may be the first generation of iron NPs that are passed through the seed to the next generation.

NPs adhered on leaf surface are difficult to remove by simple washing, which poses a certain degree of threat to the trophic level particularly humans.[87] Intentional use or accidental release of NPs can potentially contaminate food crops.[70] Because of its high reactivity, it is possible that these NPs produce toxic products.[81] The foliar application of NPs may also cause plants to absorb and accumulate toxic substances and produce adverse reactions in the next trophic level.[100, 104] Whether foliar spraying of NPs will cause harm to pollinators such as birds and bees or the next trophic level needs further studies.[58]

3.2.1 Causes of damage of foliar NPs and mitigation measures

NPs may cause plant damage in several ways: induce oxidative stress and produce excessive reactive oxygen species, promote mechanical damage such as stomata blockage promoted by particles physical properties, dissolution of NPs and release of their component toxic metal ions, damage DNA, protein and other biomacromolecules, and interfere with normal cell metabolism.[26, 66] Reactive oxygen species (ROS) is a metabolic by-product of aerobic metabolism that can induce detrimental effects in plants.[36] NPs induce the accumulation of ROS, causing damage to lipids and proteins.[126] Oxidative stress is caused by the inability to balance between the generation and elimination of reactive oxygen, and it damages genetic material, inhibits important enzymes, and induces lipid peroxidation.[127] Most particles exhibit solubility that they can release the component metal ions; foliar Ag NPs could release silver ions and induce toxic responses in plants (e.g., destroy electron transport, cause inactivation of respiratory-related enzymes, membrane permeability, and gene mutation and cytolysis).[57, 70] The production of OH radicals is a possible cause of copper phytotoxicity in leaves, which influences macromolecular metabolic pathways and further triggers genotoxicity.[79] NPs can undergo chemical changes in plants, such as redox and valence transformation, which can cause damages to plants.[9, 128] The interaction between NPs and cells may cause some mechanical damage to the cell structure, such as blocking the ducts, cell wall pores, and stomata, resulting in obstruction of nutrient uptake and transport.[5, 87]

Some measures can be taken to mitigate the biological damages caused by NPs. The coating method can effectively reduce the release of toxic ions. For example, the phytotoxicity of ZnO NPs is reduced due to the iron coating, and the modified NPs do not show adverse effects on chlorophyll content and germination.[95] NPs surface modification may have a certain effect on decreasing plant toxicity of mixed NPs (CuO NPs + ZnO NPs).[95] Studies have shown that NPs encapsulated by macromolecule polymers have reduced toxicity.[58] Plants can produce proteins to cope with various external adverse stresses. Root exudates contain organic acids and natural reducing substances that can decrease the effect of NPs in plants. Foliar application and root pathways can work together to reduce plant damage and improve utilization of nutrients.[81, 102] In addition to enzymes that can eliminate reactive oxygen, plants also have non-enzymatic substances that reduce damage caused by reactive oxygen species.[7, 129] High doses of NPs lead to an increase in ROS,[130] and activate plant's own defense mechanisms including increased production of antioxidant compounds such as ascorbic acid, lycopene, glutathione, and flavonoids.[88] Since sulfur helps maintain ascorbic acid and glutathione supply, sulfur supplement can improve plants performance against biotic and abiotic stresses.[99] Appropriate supplement of flavonols are conducive to protect leaf photosynthetic machinery due to their ability to resist reactive oxygen species.[117, 131] Accelerating the accumulation of proline in plants is a method to be considered because proline has the effect of maintaining stable subcellular structure, regulating penetration, and scavenging free radicals.[132] Furthermore, it is worth noting that the accumulation of heavy metals, pesticides, and antibiotics in plants is significantly reduced when metal-based or carbon-based NPs are applied.[36]

Deposition of atmospheric NPs on foliage can serve as an efficient filter by adsorbing air particles and heavy metal particles in industrial dust. Leaves and rinds can be considered for removal of NPs especially that even after washing there are still NPs adhering to the plants.[107] Therefore physical barriers, such as plastic greenhouses to reduce the adsorption of atmospheric particulate matter by plants, cultivating tall shrubs and plants that can block and accumulate pollutants in high-polluted areas can be an alternative mitigating measures to reduce potential accumulation and risks of NPs in plants.[35, 39, 89]

3.3 Physiological, biochemical, and molecular mechanisms of effects of foliar NPs on plants

Foliar application of NPs has positive or negative effects on plants at the physiological, biochemical, and molecular levels. The final impact is affected by many factors, such as the physical and chemical properties of NPs, plant species, applied concentration, and others.[27, 90] Foliar application of NPs can promote growth, biomass production, and yield in some agricultural crops,[22, 41]and can cause nutrient deficiency, retard root elongation, and delay flowering in others.[14, 94]

NPs can affect plant growth by releasing toxic ions, hindering biochemical processes, and inducing imbalance in reactive oxygen species (ROS).[130] Appropriate amount of

ROS plays a key role in plant development, cell division, and gene expression.[133] However, excessive production of ROS in plants will cause the reduction of protein content, DNA damage, lipid peroxidation, and lead to plant death eventually.[12, 129] Malondialdehyde (MDA) is the end product of polyunsaturated fatty acid oxidation, which directly reflects the degree of lipid damage caused by oxidative stress.[99] The significant increase of MDA level indicates that the degree of lipid peroxidation is intensified, and membrane damage may exist. Foliar application of NPs can activate the defense system of plant to cope with the adverse stress. This can be mainly reflected in the content of antioxidant molecules, various enzyme activities, hormone levels, and other changes. Study showed that plants can scavenge excessive free radicals by adjusting the molecular level of alcohol glycoside (salicin) and phenol glycoside (arbutin) in plants.[134] Besides sugar polyols, the accumulation of aromatic compounds (4-hydroxyquinazoline, 3-hydroxybenzoic acid, 1,2,4-benzenetriol and pyrogallol) also can be regarded as a defense mechanism for plants to eliminate excessive ROS.[134] Studies have shown that foliar application of NPs may positively or negatively affect the hormone level, the content of soluble total protein and leaf fatty acid, and the activity of nitrate reductase in plants.[7, 35] For example, salicylic acid (SA) is a plant hormone, and up-regulating its level to activate defense response is a common defense behavior in plants.[74]

Some studies have shown that the photosynthetic related processes of plants are inhibited after foliar application of NPs, which includes decreased photosynthetic activity, damaged chloroplast membrane and decreased of gas exchange capacity,[9, 90] and destroyed chlorophyll machineries that resulted in leaf chlorosis, necrosis, and senescence.[35, 135] Related study has measured chlorophyll breakdown through the significant accumulation of phytol, which is a major product of chlorophyll degradation.[134] However, phytol is used for the biosynthesis of tocopherol (an effective lipid soluble antioxidant) that molecular changes cause by chlorophyll degradation may be a strategy for plants to resist stress.[136] In addition, the carbon fixation, water absorption and transport can also be inhibited.[5, 28] On the other hand, some literatures have shown that foliar spray of TiO_2 NPs can increase the photosynthetic rate by stimulating enzyme activity and accelerating the photolysis of water.[17, 27] Study showed that glycine and serine are two essential amino acids which were formed during photorespiration, and their ratio is usually used as an indicator for photorespiration activity and leaf senescence. Glycine can also be used to synthesize a wide range of defense molecules including glutathione.[134] In addition, the application of NPs may change the activities of starch degrading enzyme, starch phosphorylase, and sucrose phosphate synthase in plants, thus inducing the change of carbohydrate content in plants.[9, 133]

Amino acids are important components of plant primary metabolism and they play an important role in the synthesis of defense related metabolites. For example, proline can reduce the absorption of heavy metals, provide osmotic adjustment, and maintain the redox state of cells under external stress.[69, 99] However, the application of NPs on leaves may result in the oxidation of several amino acids (such as lysine, methionine, proline, threonine, etc.) to form free carbonyl groups, which will inhibit the activity of protein.[127, 133] Tyrosine and phenylalanine are precursors of alkaloids, glucosinolates and other secondary metabolites, when these two amino acids are up-regulated they can be an indicator of activated defense response.[134] Foliar application of NPs can activate the production of non-enzymatic (proline, phenolic compounds) and enzymatic antioxidant (CAT, POD, SOD) to alleviate stress.[14, 74, 130] Study also showed that the nitrogen-containing compound 4-aminobutyric acid, which is a non-protein amino acid, plays an important role in signal transduction and stress defense.[137]

It should be noted that NPs in plant can destroy the normal biochemical process by interfering with RNA and DNA metabolism, ATP synthesis, phospholipid metabolism, chromosome aberration, oxidative phosphorylation, and glycolysis.[7, 11, 130, 138] NPs can stimulate plants to change the properties of cell membrane by affecting the content of fatty acids. For example, arachidonic acid is an unsaturated phospholipid fatty acid, and pentadecanoic acid is a component of phospholipid bilayer. After foliar application of NPs, plants may increase their content to reconstruct or repair damaged cell membranes.[134] And when the contents of linolenic acid, which is one of the main components of plasma membrane, decrease significantly also indicate that the cell membrane is destroyed.[134, 136] The tricarboxylic acid pathway, the expression of glycolysis related enzymes, such as glucose-6-phosphate isomerase and glyceraldehyde-3-phosphate dehydrogenase may also be up-regulated after foliar application of NPs.[136] Although there are many studies on the physiological, biochemical and molecular effects of NPs on plants, more research is needed regarding its deep mechanism.

Conclusions and future perspectives

Foliar spraying of NPs can be effective in providing slow release nanofertilizers, fungicides, herbicides, and preservatives. Foliar sprayed NPs can enter the leaves through stomata, endocytosis, and direct absorption, but particle size plays a critical role on leaf absorption. Leaf wax and cell wall can hinder the absorption of NPs, and once taken up most NPs are accumulated in the vacuoles. Absorption and transport are affected by many factors, the most important of which are plant characteristics, NPs physical properties, and environmental conditions. The effect of foliar NPs on plants is still widely debated. Advantages such as improving yield and disease resistance, reducing pollution and waste; and disadvantages such as toxicity and genotoxicity to plants are reported in the literature. Foliar application of NPs, which has many advantages not available in traditional methods, is a research direction with great potential in agro-industry. If the adverse effects of foliar application are overcome, it will definitely be an advantageous technology beneficial to the society. Therefore, studying the essential mechanism of adverse effects and how to overcome them is the primary research direction needed to promote foliar application of NPs.

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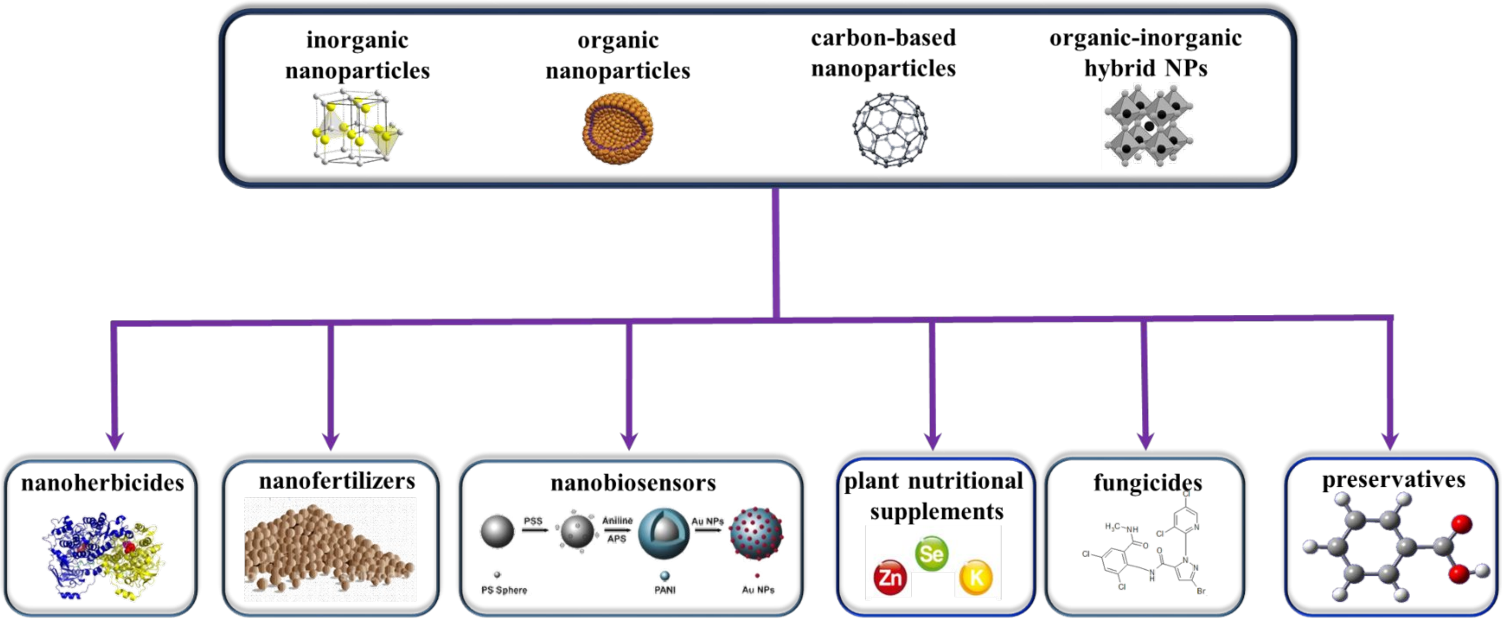

Figure 1. Classification of engineered nanoparticles and some of their agricultural applications.

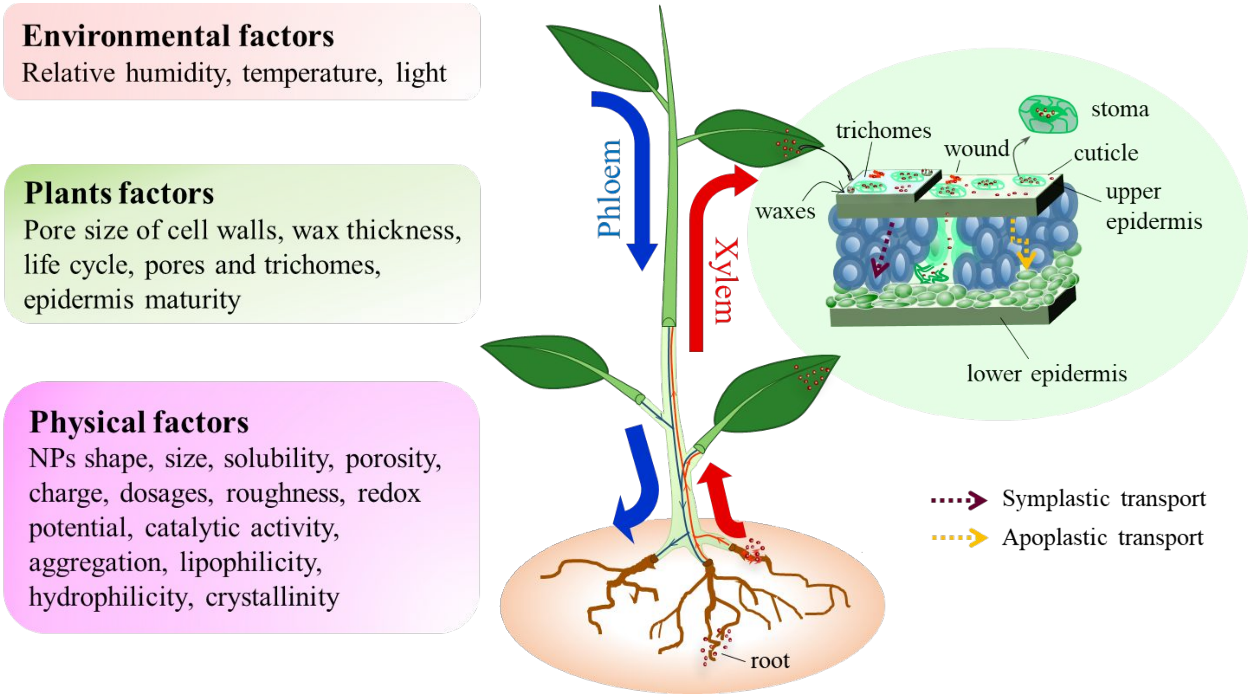

Figure 2. Factors affecting the plant uptake and transport of engineered nanoparticles by foliar application.

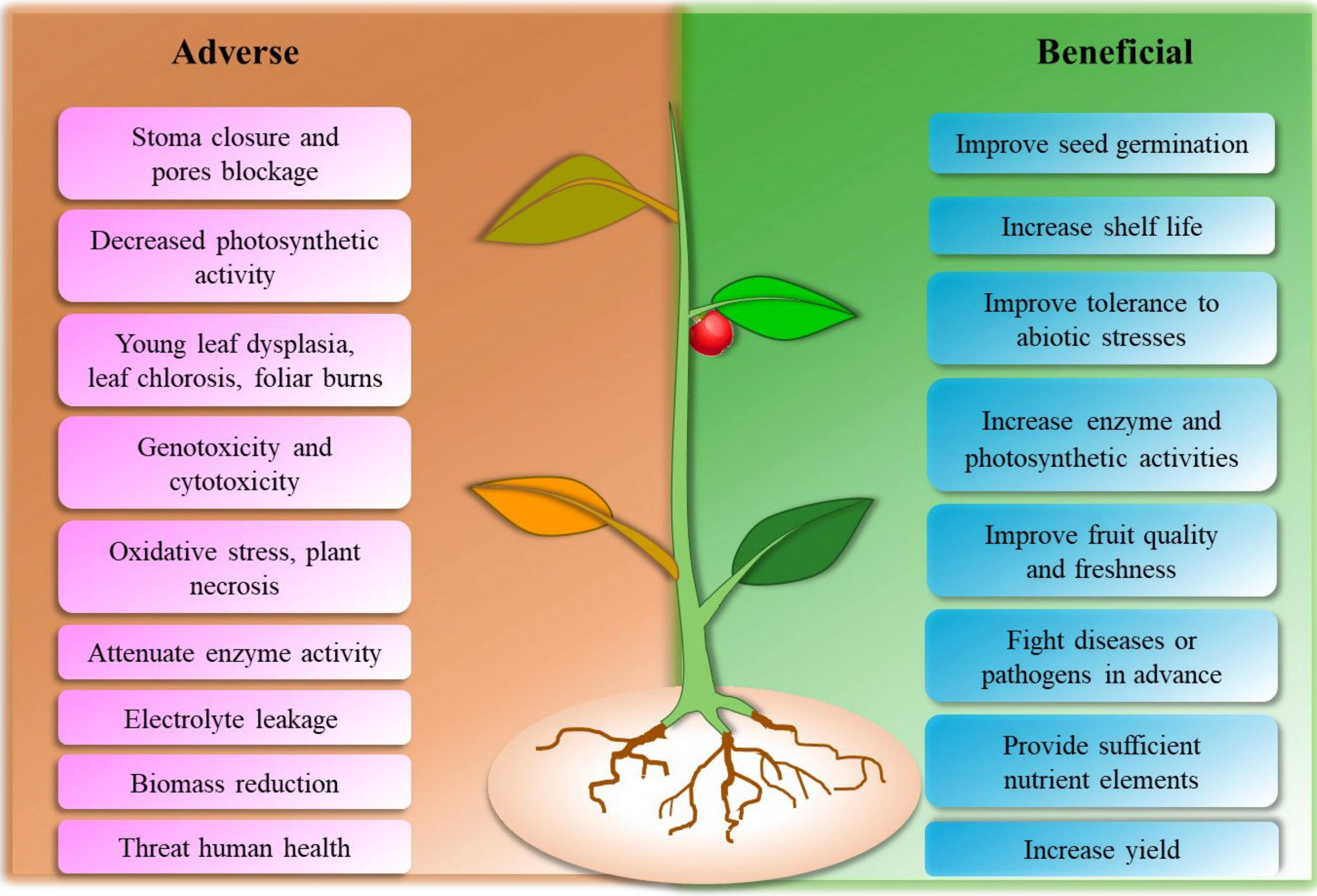

Figure 3. The adverse and beneficial effects of foliar applications of engineered nanoparticles.