

Jen-Tsung Chen *Editor*

Plant and Nanoparticles



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About the Editor

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Emerging Trends of Nanoparticles in Sustainable Agriculture: Current and Future Perspectives



Kanika Khanna, Nandni Sharma, Puja Ohri, and Renu Bhardwaj

Abstract Nanotechnology in agriculture is emerging at an escalating rate, owing to its excellent properties in plant growth and development. In the present era where climate change is most commonly observed, the global patterns of agriculture are observing unprecedented challenges. For achieving food quality and yields, nano-engineering is a novel tool that maintains sustainable crop production. Due to the disastrous effects of chemical fertilizers, there is a need to switch to safer alternatives. Nano-technology enables safe crop production by improving efficiency and reducing losses. This technology has been predominantly entered into wider areas of fertilizers and pesticides for synthesizing agrochemicals based-nanoparticles. Because of their critical and direct/indirect approach in management and regulatory inputs (herbicides, pesticides, fungicides, etc.), nanotools like nano-biosensors also support avant-garde agriculture farms. Therefore, plant biology and nanotechnology together have a great impact on the environment due to their innovative characteristics in agriculture, to meet the urgent needs of food with environmental sustainability. In this chapter, we have mainly focused on nanoparticle interactions among plants, their uptake, mobilization, and metabolic actions. Moreover, the bioactive compounds in plants possess many functions that are also modulated by nanoparticles. Therefore, nanoparticles function as elicitors in the plant's secondary metabolism. We have envisaged the multidisciplinary actions of nanoparticles with plant nanotechnology, biotechnology, genetic engineering and pushed it towards agriculture sector, as well as plant research. In particular, we have depicted the role of nanoparticles in enhancing bioactive compounds of plants, thereby improving crop productivity through boosting the nutraceutical and nutrients of plants. Here, we have also reviewed the nanoparticle abilities toward plant protection and stress management against numerous adverse conditions. This chapter will enable the researchers to understand the nanotechnology blend in agriculture, thereby

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designing the specific nanoparticles according to the agriculture needs as well as standards for promoting sustainable agriculture.

1 Introduction

Agriculture is the main source of livelihood in various developing countries, and nearly two-thirds of the world's total populace is dependent on it. The enormous agricultural demand leads to huge pressure for formulating novel agricultural techniques that enhance the yield and productivity of the crops by lessening the impact of chemical fertilizers on soils. The fertilizers are imperative for enhancing the agricultural yields, though their excessive levels alter the soil ecology and area for crop production. For meeting the rising demands of food, agriculturalists tend to use chemical-based fertilizers, and it has become an integral factor in farming systems. These are mainly classified into three types such as nitrogenous, phosphate, and potassium fertilizers. But certain complexities and other climatic or edaphic factors cause the mineral elements to immobilize within the soil, thereby hindering its availability and uptake by plants [1]. Consequently, their utilization creates significant drift on human as well as environmental health [2]. The indiscriminate usage and improper maintenance have made our focus oriented toward biofertilizers from chemical-based fertilizers. However, the use of farmyard manure, animal waste, compost, etc. has been promoted that stimulates the production in appropriate proportion. Sustainable agriculture necessitates the minimal usage of agrochemicals to protect and conserve them for posterity. To tackle the challenges for sustainable agriculture and food demand in agriculture, various technological advancements and novelties in the past few years should be explored [3]. The most important concern here is to make more efficient use of these fertilizers by substituting nanoparticles (NPs). Nanotechnology has the potential for providing an effective strategy for agricultural problems. It is a great solution to bridge the gap between bulk materials and NPs. Decades ago, noteworthy research on nanotechnology has been carried out with a special emphasis on agriculture [4]. NPs have remarkable physicochemical properties with minute size, larger surface area to mass ratio, reactivity, ionizing power, chemical stability, enhanced absorbability, pH resistance, and thermal stability. Owing to these abundant characteristics, nanomaterials combined with fertilizers enhance the potential growth and development of the plants.

Nanofertilizer using efficiency is escalated by penetrating the NPs into agrochemicals *via* different modes or methods such as encapsulation, ionic charges, hydrogen bonding, absorption, entrapment into nanomatrix, etc. [5]. Sidewise, there are numerous sectors for globally commercializing the NPs fertilizers. For example, other factors like NP absorption capacity, behavior in soil, root/shoot uptake, chemical stability, xylem/phloem loading and unloading, and interaction with other biomolecules such as protein, RNA, and DNA, respectively, also play a critical role [1]. Interestingly, the NPs improve the plant productivities by enhancing the agricultural inputs for facilitation of site-targeted regulated delivery of nutrients, to

ensure the minimal usage of agri-inputs. Indeed, nanotechnology has reformed as an avant-garde technique in plant protection, and its popularity is increasing on an exponential phase with a surety for higher production levels. Besides, the important aspect in agriculture practices is to induce plant adaptation toward changing climatic conditions such as temperature, water deprivation, salinity, freezing, water logging, and heavy metal pollution without hampering the ecosystem [6, 7]. Furthermore, the formulation of nanosensors in farming for proper monitoring of crops, soil activities, pathogens, invasion of agrochemicals, and environmental pollutants ensures sustainability in terms of soil and plant health. Subsequently, it maintains quality and safety assurance for successfully mediating sustainability and environment systems [8]. Nano-engineering is a cutting-edge technology that enables the formation of high-technological aids and offers broad areas of research for agricultural systems. Henceforth, nanotechnology coordinates with sustainable agriculture practices with innovations and fixing various problems and concerns regarding modern agriculture. The present chapter summarizes the types, applications, and role of nanotechnology in agriculture for maintaining sustainability and standards.

2 Sources of Nanoparticles

2.1 Natural Sources of NPs

NPs occur naturally in all “spheres” of our planet, covering the biosphere, atmosphere, lithosphere, and hydrosphere. These particles are formed by various photochemical, chemical, thermal, mechanical, and biological processes occurring either separately or in amalgamation [9]. The natural occurrence of metallic NPs and their sulfides/oxides in hydrothermal vents, ore deposits, waters, wastewaters, and mining regions is largely controlled by the environmental conditions, such as the temperature, pH, light, oxic/anoxic conditions, and the characteristics and concentration of the naturally occurring organic matter [10]. The NPs present in the hydrosphere and the atmosphere occur at concentrations of up to 106–107 particles/mL and impose a major effect on biota because of their close association and contact with the biota.

The major processes resulting in the formation of natural NPs are entirely inorganic including nucleation, mechanical, thermal, and biological processes. Nucleation and inorganic phases in the hydrosphere, atmosphere, and the lithosphere occur purely based on inorganic reactions or may also originate from organic matter. Reactions occurring in hydrothermal vents and surface water often contribute to NP release into the environment and may advance *via* photochemical, thermal, and nonthermal processes. The presence of Fe(II) facilitates the development of ferrihydrite NPs, stabilized by silicon ions. Similarly, different NPs containing Cu, Mn, Ba, Cr, and Pb are also formed in chilly CO₂ seeps. The mechanical processes involved in NP formation include aeolian erosion resulting from desert winds, unvegetated farmlands, deforested lands, and the particles emanating during events like earthquakes. Biomass combustion such as the forest fires, mainly occurring in

the equatorial regions of the earth, exemplifies the involvement of thermal processes in the generation of NPs [11]. And lastly, biomineralization, carried out by microbes, generates inorganic nanomaterials through various biological processes. Such inorganic particles include silicon and iron-based nanominerals, magnetite, calcium phosphate, and calcium carbonate [12].

2.1.1 Volcanic Eruptions and Forest Fires

The ash emitted by volcanic eruptions frequently reaches above 1400 °C and possesses a complex composition of liquid and solid particulate matter lifted in the atmosphere by hot gas currents. After ashes diffuse in the atmosphere, the temperature of the gas lowers down, and its composition changes, resulting in the accumulation of particles [13]. Volcanic eruptions result in the release of a gigantic amount of fine particles and aerosols with sizes of up to micrometers to nanometers, into the atmosphere. Ash clouds formed from volcanic eruptions contain an array of polydispersed nano- and microparticles with sizes ranging between 100 and 200 nm. About 30 million tons of NPs are emitted in the form of ash in a single volcanic eruption. Chemically these particles are composed of iron and silicate compounds which are easily suspended in the air. Volcanic eruptions also release bismuth oxide NPs in the stratosphere. These particles remain suspended in the air and may result in respiratory disorders once inhaled [14]. Volcanic ash on reaching the upper troposphere and stratosphere can readily spread worldwide affecting different regions of the globe for years. In the upper atmosphere, the nanoparticulate debris of the ash blocks and scatters sun radiation. While some effects of volcanic ash are seen throughout the world, the maximum levels of nanomaterial released are present in areas within 10 km of the volcano [15].

Lightning and anthropogenic activities are largely responsible for grass and forest across the globe. The smoke and ash released by these fires can extend over larger areas and increase the number of nanosized particulate matter, thus distressing the ambient air quality. In the inorganic sphere, fire is one such chemical process that eventually results in the formation of nanoscopic particles [14]. Numerous fires are known to occur throughout the world, in North America, Europe, Asia, Africa, Brazil, and Australia [15]. The fire smoke carries soot and black carbon in huge quantities as Asian brown clouds have been deposited over the Himalayan glaciers. The deposited particles have resulted in amplified absorption of heat from the sun, thus accelerating glacial melting. Many reported cases of forest fire reveal transportation of micro- and nanosized particulate matter through ash and smoke and are held responsible for respiratory ailments in animals and humans. Smoke containing nanosized particles can worsen cardiopulmonary problems in patients [16].

2.1.2 Water Bodies

Oceans and seas, covering the largest area on the surface of the earth, emit sea salt aerosols in huge amounts. These aerosols are created by evaporation of water and by ejection of waterdrops into the atmosphere by waves. The size of these particles ranges from 100 nm to up to several microns. Water bodies can also form NPs through precipitation resulting from evaporation and temperature changes in patients [16]. The water of Lake Michigan contains large amounts of calcium carbonate which remains dissolved in cold water, for most of the year, but when summer is about to end, the temperature of the water increases considerably, thus reducing calcium carbonate solubility in the lake water. This results in the precipitation of calcium carbonate out from the water, generating clouds of nanosized particles [14]. Inorganic sulfide, i.e., HS^- and H_2S , is an essential component of the biogeochemical sulfur cycle occurring in mining water, hydrothermal vents, and sediments under anaerobic conditions. Sulfur and metals present in the ocean are often emitted from hydrothermal vents, and they can readily react with one another, serving as a source of metal-containing sulfide NPs [11].

Also, the drinking water from underground sources and freshwater streams contains nanoscopic and microscopic materials, chemically originating from CaSO_4 and CaCO_3 along with elements like iron oxides. Nonetheless, physical and chemical processes, like weathering, precipitation, and dissolution of carbonates influenced by CO_2 , intermediate hydrocarbonate (HCO_3^{3-}) formation, and the dawdling iron oxide precipitation, can readily generate nanosized particles [14, 15].

2.1.3 Dust Storms and Cosmic Dust

Deserts on the earth's surface are the largest permanent major source of NPs, and the dust storms originating from them are responsible for the long-distance migration of not only mineral dust but also anthropogenic pollutants, which are lifted in the atmosphere by the air currents [13]. Nearly 50% of the atmospheric aerosols in the troposphere are originated from deserts. The particle size produced by dust storms varies between 100 nm and several microns. Satellite imagery reveals the dynamics of dust migration on large scale across continents, demonstrating that the NPs generated in one region of the globe by important environmental events affect regions that are present thousand kilometers away. For instance, the dust storms stirring up during spring in the Gobi desert every year strongly influence the air quality in North America and Asia [15]. However, the composition of the dust varies with a specific place and the human actions in the adjoining areas from where the wind currents generally cross.

Throughout the universe, different kinds of nanomaterials are present which are sorted, mixed, and tailored into various forms. Electromagnetic radiations, dramatic temperatures, pressure gradients, shock waves, and physical collisions help in stimulating and generating NPs in outer space [16]. Astronomical observations

along with direct analysis of stardust during space expeditions and meteorite collections affirmed the presence of a vast array of carbon, nitride, oxide, silicate, carbide, and organic nanomaterials as major stardust components [17]. The presence of nanosized diamond in Murchison meteorite exemplifies the origin of nanoparticulate matter in planetary structures other than the stars. The lunar dust when compared to terrestrial is fine grain and comprises substantial amounts of magnetic NPs that often cling to astronauts' suits which have electrostatically charged surfaces [15].

2.1.4 Biogenic Production

Nature provides an insight into the synthesis of nanomaterials. Biological systems act as “bio-laboratory” or “bio-factory” for the fabrication of metal oxide particles and pure metals at nanometer scale employing a biomimetic approach [10]. Many uni- and multicellular can generate nanoparticulate inorganic matter through intra- and extracellular processes. In microbial environments, NPs are constantly being formed indirectly *via* redox reactions related to metabolic processes [11]. On exposure to inorganic salts such as those containing Ag^+ , Au^{3+} , S^{2-} , and SeO_3^{2-} , certain bacteria like *Pseudomonas aeruginosa*, *Stenotrophomonas*, *Serratia*, and *Thiobacillus* species employ an oxidizing or reductive detoxification pathway which forms nanosized elemental particles [14]. Nanobacterium synthesizes a calcium phosphate shell around itself, resembling an inorganic particle. The size of the shell ranges between 20 and 300 nm [15]. Fungi also contain enzymes that can synthesize NPs of different shapes and sizes. They have been known for generating various NPs such as silver, gold, and even alloys [16].

However various organisms can also naturally produce NPs. Plants utilize the macro- and micronutrients present in soil/water for their development and growth leading to the amassment of these minerals in nano-forms. Small insects and animals use nanostructures for protection from predators. In some insects, the lightweight wings are protected by nanowax coatings. Even humans possess organs, e.g., bones, primarily constructed by nanosized structures. Enzymes, antibodies, proteins, and DNA are also composed of nanostructures [16]. It is apparent from the aforesaid that NPs are generated in the form of aerosols, colloids, and dust, as constituents of sediments and soils, chemical or hydrothermal deposits, mineral nuclei, and lamellae. In most cases, NP formation occurs through a combination of different processes, e.g., weathering is a mechanical process that combines with precipitation or dissolution, and colloid formation in volcanic activity and rivers results from explosive eruptions expelling tephra along with rapid cooling of fumes. Based on chemical composition, naturally occurring NPs include an array of elements such as metal hydroxides/oxides, metal alloys, silicates sulfides, halides, carbonates, etc. [18].

2.2 *Anthropogenic Sources*

Anthropogenic NPs are created by humans and often lead to incidental exposure. Man-made NPs are intentionally or unintentionally released into the environment due to mechanical and industrial practices. These anthropogenic NPs are heterogeneous in nature and fall under two categories. The first category of NPs displays undefined chemistry and does not have a predetermined size. This includes combustion particulates, welding fumes, coal fly ash, and diesel exhaust. The second category includes the engineered NPs which exhibit a specific size, ranging between 1 and 100 nm, and are pure particles displaying controlled surfaces. These include carbon nanotubes, fullerenes, dendrimers, quantum dots, silver and gold NPs, etc. [9, 19]. The man-made particles are either produced by stationary or mobile sources, and their generation may or may not be deliberate.

Accurate estimation of the annual discharge of NPs in the environment is impossible. However, there is a strong increase in their production volumes every year. The exhaust gases produced from diesel engines contain huge quantities of NPs resulting from incomplete fuel combustion. Similarly industrial processes, liquid or solid waste from manufacturing units, gas boilers, oil, and coal account for the unintentional release of tons of NPs. The advancement of nanotechnology and industrial processes has led to the manufacturing of NPs on large scale, and their use in related products results in the unavoidable release of these engineered NPs into the air, soil, and water, both knowingly or unknowingly [9].

2.2.1 *Mobile Sources*

Due to urbanization and industrialization, automobile exhaust is the major source of atmospheric NPs. Among different kinds of automobile exhaust, diesel engines release particles in the environment with sizes range between 20 and 130 nm, whereas gasoline engines release particles of 20–60 nm size. Besides, carbon nanotubes and fibers are also liberated during the diesel combustion process as by-products. Over 90% of the carbon NPs that occur in the atmosphere are an outcome of diesel fuel combustion [16]. These particles are hydrocarbons or sulfates generated by nucleation reactions. The accumulation mode NPs from diesel exhaust are mainly sooty carbonaceous aggregates. NPs from diesel exhaust are primarily composed of lubricating oil and unburned fuel. Also, sulfuric acid which accounts for a small percentage plays a crucial role as nuclei providing for condensation of the organic particles. The nanosized diesel exhaust comprises about 95% unburned lubricating oil. In diesel engines, the lower emission standards often decrease particle mass emissions, but the concentration of NPs tends to increase due to the reduced availability of surfaces providing for condensation. Both leaded and unleaded gasoline engines emit particles with an average diameter of about 45 nm. Liquid petroleum gas is considered a cleaner fuel. However, in comparison to unleaded gasoline, it leads to more emission of NPs [20]. Thus, the pollution caused

by vehicles is the main root of nanoparticulate contamination in the urban atmosphere.

2.2.2 Industrial and Stationary Sources

A spectrum of industrial settings has an immense potential to create ultrafine particles, yet to be investigated, including milling, printing, plasma cutting, powder coating, cooking, and baking. The ultrafine particles released during industrial processes include fumes produced by hot processes like welding and smelting, fumes from incomplete fuel combustion processes, and bioaerosols. Industrial setups mainly provide favorable conditions such as high temperature, the occurrence of vaporizable material, and large temperature gradient along with rapid cooling processes [20]. Ultrafine-sized particles from gas, coal, and oil-fired stationary in the size range of 15–25, 40–50, and 70–100 nm are generated on combustion of natural gas, sulfur-containing bituminous coal, and No. 6 fuel oil, respectively. The composition of used fuel largely determines the production of the end product. Industrial effluents contain carbon nanotubes, silver-, gold-, zinc oxide-, and titanium oxide-based nanoparticles normally, which are released among the wastewater effluents as well as through the chimneys. Once released into the environment, these NPs are deposited in sediments, landfills, soil, and water bodies [21].

2.2.3 Engineered NPs

Currently, many consumer products contain NP ingredients, such as paints and sunscreens (nanostructured zinc oxide and titanium dioxide), tire additives (carbon fibers, fumed silica and nanotubes), polishing slurries and lubricants (nanosized silica), and detergents and shampoos (nanosized alumina). With the advent of nanotechnology, the usage of NPs is considerably increasing [20]. These particles are often synthesized employing chemical, physical, biological, and hybrid methods. Nanomaterials such as titanium oxide NPs, carbon NPs, and hydroxyapatites occur in sporting goods, cosmetics, toothpaste, and sunscreens [16]. Through several pathways, these NPs present in consumer products enter the environmental surroundings either mechanically from the product or upon their disposal [20]. Bundschuh et al. [21] proposed that engineered NPs gain entry into our surroundings through three emission scenarios, i.e., (1) discharged during fabrication of nano-enabled products and raw material, (2) release during usage, and (3) release during waste handling of products containing NPs. These emitted nanosized particles ultimately deposit in surface water bodies and on land [18]. ZnO NP, primarily used in electronics, medicine, and cosmetics, amass in sediments, urban and natural soil, and landfills. Similarly, 90% of carbon nanotube production accumulates in landfills, soils, sediments, and air [20]. However, at times, certain kinds of NPs are intentionally released into the environment for their application. Examples include nanosized metal particles for dechlorination of

groundwater, nanoenergetic explosives/materials and highly obscured nanoflakes, and application of nanopesticides and nanonutrients in agricultural fields [22].

2.2.4 Miscellaneous Sources

Besides the abovementioned sources, several human activities are responsible for the formation of NPs. Cigarette smoking releases a complex of about 100,000 compounds in the atmospheres that are nanosized, ranging between 10 and 700 nm [15]. Cooking practices like frying contribute to an indoor source of ultrafine particles. It has been reported by Wallace et al. [23] that >90% of the particulate matter produced during cooking was contributed to the ultrafine fraction exhibiting a primary and secondary peak at 60 nm and <10 nm, respectively. Heating elements of an electric stove or even a gas burner result in ultrafine particle generation at concentration levels of $1.1 \times 10^5 \text{ cm}^{-3}$. Candles, incense, mosquito coils, residential wood, coal combustion, and tobacco smoke also add to indoor NP levels [20]. Micro- and nanoparticulates of size smaller than 10 μm are often released in the environment upon demolition of large buildings. Along with the building debris, respirable asbestos fibers, glass, lead, and various toxic particles belonging to the nanometric scale are released from household materials at the demolition site [16]. NPs are employed in the fabrication of an array of products that are used on regular basis. Their production, usage, and disposal lead to continuous emission of these particles into the atmosphere.

3 Types of Nanoparticles

The NPs synthesized by a biological source such as microbes prove to be highly effective in terms of their applicability [24]. The NPs are characterized and designed in various shapes and sizes in contrast to other sources. Owing to its eco-friendly nature, low cost, and high effectiveness, the microbial sources are considered to be the best resource for manufacturing metal NPs. Various types of NPs have been discussed below.

3.1 Silver NPs

Silver NPs are frequently applied in the biomedical field (drugs/coatings, bandages, and implants), agriculture, clothing, water purification, and as antibiotics. They possess antimicrobial potential with high efficiency. Musarrat et al. [25] reported AgNPs synthesis of around 5–27 nm by *Amylomyces rouxii* strain KSU-09, screened from *Phoenix dactylifera*. They confirmed that water extracts of 72-h suspended mycelia facilitated the generation of stable, monodispersed, spherical NPs from

1 mM silver nitrate. The results were confirmed by UV-visible spectroscopy, AFM, XRD, and TEM. The fungal proteins present in the extracts revealed by infrared spectrum attributed toward NP stability. The bioreduction process of NP synthesis involves enzymes that are known to transfer electrons from donors to positively charged metal ions, thus stabilizing the end product. Certain *Bacillus* sp. synthesizing AgNPs enzymatically control the size of the NPs. α -amylase enzymes generated by these bacteria are held responsible for the same [26].

Synthesis of AgNPs extracellularly by microbes often involves a mechanism mediated by nitrate reductase [27]. Fungi like *Fusarium oxysporum*, *Verticillium*, and *Aspergillus flavus* have been employed for the synthesis of AgNPs in solutions or surfaces of fungal cells and even in the form of a film [28]. Moreover, Mishra et al. [29] reported that *Stenotrophomonas* sp. BHU-S7 could extracellularly biosynthesize spherically shaped AgNPs with an approximate diameter of 12 nm. They suggested that extracellular enzyme nitrate reductase, which appeared in the cell supernatant, facilitated the transfer of electrons to Ag⁺ ions leading to the formation of AgNPs. Besides, they also proposed the role of carbonyl groups of certain enzymes and proteins in stabilizing the NPs by attaching them to the NP surfaces.

Cell-free culture supernatants of various bacteria such as *Phaeocystis antarctica*, *Bacillus cecembensis*, *Pseudomonas meridiana*, *Pseudomonas proteolytica*, *Arthrobacter gangotriensis*, *Arthrobacter kerguelensis*, and *B. indicus* can also biosynthesize stable AgNPs in the size range of 6–13 nm. The biosynthesis and stability of AgNPs often depend upon pH, temperature, or the bacterial species from which the supernatants are collected [30].

3.2 Gold NPs

In medicine, NPs offer an alternate choice to antimicrobials, since they do not lead to multidrug resistance in bacteria. Gold NPs (AuNPs) hold promising deals in the field of antimicrobials, tumor therapy, diagnostics, and targeted gene delivery systems. In general, AuNPs exhibit negligible cell membrane permeability, except cancer/tumor cells that show enhanced uptake, permeation, and retention effect. When AuNPs are capped with proteins, their uptake is enhanced even more, since the protein cap not only stabilizes the NPs in their colloidal state but also provides a docking site for drugs'/genes' delivery [31]. Besides, gold NPs are biocompatible and nontoxic and have unique catalytic, optical, and biomedical properties [32].

In addition, cell-free extract of *Rhodopseudomonas capsulata* can synthesize gold NPs. This bacterium secretes a cofactor NADH along with NADH-dependent enzymes. The bioreduction of gold ions activates by electron transfer from NADH via NADH-dependent reductase acting as an electron carrier. After receiving the electrons, gold ions get reduced to Au⁽⁰⁾ leading to the generation of gold NPs. Varying the concentration of HAuCl₄, different shapes of NPs can be obtained. Low concentration of Au ions in the aqueous solutions (pH of 7) generate spherical gold

NPs, whereas higher concentrations (pH of 4) generate networked gold nanowires. The diameter of these gold nanowires ranged between 50 and 60 nm [33]. Basu et al. [34] reported the extracellular synthesis of protein-coated polydispersed AuNPs by mycorrhizal, edible fungi, *Tricholoma crassum* within a size range of 5–25 nm and possessing different shapes. Spectroscopic analysis revealed that at higher pH, blue shift of absorption maxima was observed indicating inhibition of enzyme reaction involved in NP synthesis. However, substrate concentrations, temperature, and precursor concentrations largely determined the amount of AuNPs. The produced NPs even displayed antimicrobial activity against pathogenic organisms such as *E. coli*, *A. tumefaciens*, and *M. oryzae*. At higher doses, these particles induced apoptosis in eukaryotic cells, confirming its putative role in cancer therapy.

Even biomolecules obtained from different microbial species have also been employed for NP synthesis. Protein extracts of *Deinococcus radiodurans* generated AgNPs by providing functional groups like –SH, –NH₂, –OH, and –COOH as binding sites that facilitate the bioreduction of Au³⁺ to AuNPs. Furthermore, these proteins also encapsulated the newly formed AuNPs, as capping agents, to prevent them from aggregating, thus stabilizing the NPs [26].

3.3 Magnetic NPs

Magnetic NPs possess exclusive micro-configuration, superparamagnetic properties, and tremendous coercive force and, therefore, show broad application in the field of biomedicine, DNA analysis, gene therapy, and cancer treatment [28]. Gram-negative magnetotactic bacteria synthesize magnetic NPs of varied morphology and often occur in fresh and marine water sediments. These bacteria can synthesize magnetosomes, which act as magneto receptors. Magnetotactic bacteria can produce membrane-bound, intracellular magnetite, greigite, and pyrrhotite [12, 35]. They can synthesize magnetic nanoparticles made up of iron sulfides (FeS), iron oxide (FeO), or both intracellularly. Fe(III), an oxidant present in natural and contaminated areas, influences the geochemistry of aquatic sediments by increasing the concentration of dissolved iron, manganese, phosphate, and trace metals. Sulfate-reducing bacteria can readily produce magnetic iron FeSNPs that adsorb radioactive metals because of their increased surface area and thus can be used for bioremediation [28, 30]. Because of the superparamagnetic nature of Fe and FeONPs, they are extensively used in the biomedical field (tissue repair, cell labeling, magnetic resonance imaging, and drug delivery) [10].

Magnetic Fe₃O₄-NPs can be intracellularly generated by *Magnetospirillum magneticum* using FeCl₃ precursor. The magnetosome organelles of *M. magneticum*, present intracellularly, play a pivotal role in the creation of these NPs. Ferritin, a globular protein complex, encapsulates the magnetosomes, thus enabling the storage of Fe in bacteria in nontoxic soluble form. This protein attributes to the generation of Fe₃O₄NPs and their nucleation [26]. Bhargava et al. [36] were able to achieve FeONPs employing *Aspergillus japonicus* strain AJP01.

The fungus could hydrolyze the precursor (iron cyanide) salt solution, under suitable conditions releasing ferric and ferrous ions. These ions co-precipitated under the influence of fungal proteins and underwent controlled nucleation, ultimately leading to the formation of FeONPs. Analysis of TEM, SAED, EDS, and X-ray diffraction results verified the mycosynthesis of these cubical shaped crystalline NPs respectively (60–70 nm).

Iron(Fe)-reducing thermophilic bacteria can also substitute metals like cobalt, nickel, uranium, manganese, and chromium into biosynthesized magnetite crystals. Different bacterial species, such as *Desulfovibrio* sp., *Thermoanaerobacter ethanolicus*, *Magnetospirillum* sp., and *Pelobacter* sp., and fungal species like *Verticillium* sp. and *Fusarium oxysporum* are reported for their high efficiency in producing magnetic NPs involving different metals [12, 30]. Certain non-magnetotactic bacteria such as *Leptospirillum ferrooxidans*, *Ferropasma thermophilum*, and *Acidithiobacillus ferrooxidans* produce only a few magnetosomes, thus exhibiting a weak magnetic field. These are present in freshwater, seawater, trash, sulfur springs, and soil and are also employed in the production of magnetosomes owing to their easy mass cultivation [12].

3.4 Zinc NPs

Zinc oxide NPs (ZnONPs) and zinc sulfide NPs (ZnSNPs) have recently gained popularity in the scientific world because of their photocatalytic, electronic, optical, and antibacterial properties and dermatological properties and are extensively used in photocatalysis, memory resistors, chemical sensors, and photovoltaics. One-dimensional ZnONPs are recognized as major photonic materials in the UV region because of their huge exciton binding energy, broad direct band gap, and high surface-to-volume ratio. ZnO nanopowder also finds its commercial application in products including ceramics, glass, plastics, cement, lubricants, paints, rubber, pigments, foods, batteries, personal care products, fire retardants, etc. [37].

Aeromonas hydrophila, a reproducible bacterium, can synthesize ZnO NPs following a simple low-cost procedure. These particles have a size of approximately 57 nm and are spherical to oval in shape as confirmed from atomic force microscopy. The crystalline nature of these particles was revealed by X-ray diffraction. At the concentration of 25 $\mu\text{g/mL}$, these ZnONPs exhibited strong antifungal and antibacterial activity against *Aspergillus flavus* and *Pseudomonas aeruginosa*, respectively [38]. Moreover, Malarkodi et al. [39] reported the formation of ZnSNPs by *Klebsiella pneumoniae* from zinc sulfate. The spherical NPs of 65 nm size are generated extracellularly in the presence of zinc sulfate. The structural (XRD) and morphological (SAED and TEM) analysis along with spectroscopic techniques (FTIR and UV-Vis spectrophotometer) affirmed the role of bacteria in the stabilization of ZnS NPs. These NPs also exhibited strong fungicidal and bactericidal activity against *Candida albicans*, *Streptococcus* sp., and *Lactobacillus* sp.

3.5 Selenium and Tellurium NPs

Selenium because of its semiconducting and photo-optical properties finds its application in electronic circuit devices and photocopiers [30]. Also, Se compounds are used in anticancer therapy since they can lower the risk of cancers like mammary, prostate, liver, lung, and colon cancers. Researchers have suggested that the redox potential, the concentration of Se compounds, and chemical species are crucial for an anticancer response. Generally, high dosages of Se compounds exhibit substantial anticancer activity, but such high doses pose toxicity concerns. Se nanostructured particles offer an alternative for removal of Se toxicity and have been employed in cancer treatments owing to their anticancer activity along with lesser toxicity in comparison to organic and inorganic Se compounds [40]. *Stenotrophomonas maltophilia* can easily transform selenite (SeO_3^{-2}) into elemental Se and accumulate granules in cell cytoplasm or extracellular spaces. In addition, *Enterobacter cloacae*, *Desulfovibrio desulfuricans*, and *Rhodospirillum rubrum* can reduce SeO_3^{-2} , both intercellularly and extracellularly, to selenium NPs exhibiting different morphologies like fibrillar, granular, and spherical [30].

In another report by Dwivedi et al. [41], monodispersed, spherical, and stable Se NPs (average size 21 nm) were biosynthesized employing bacterial isolate of JS-11 strain of *Pseudomonas aeruginosa*. The bacteria displayed considerable tolerance to SeO_3^{-2} . The supernatant of the bacterial culture at 37 °C exhibited the potential to reduce colorless and soluble and colorless selenite into red elemental insoluble selenium nanospheres (Se^0). Phenazine-1-carboxylic acid, a metabolite secreted from strain JS-11, and NADH and NADH-dependent reductases (redox agents) were responsible for this biomimetic reduction. The authors suggested the use of red-colored Se^0 nanospheres as a biosensor for assessing nanotoxicity assessment. Similarly, Ahmad et al. [40] reported the bioreductive ability of *Streptomyces bikiniensis* Ess_amA-1 strain for the biosynthesis of Se nanorods. The strain in the presence of selenium oxide displayed a time-dependent color change from gray to red, of the liquid culture medium in which it was grown. The appearance of red-brick color after 48 h of incubation indicated the biogenic ability of the strain in reducing selenite ions into elemental Se (Se^0) insoluble form. The yield of Se nanorods was about 7.74 mg/100 mL of culture medium. The strain produced aromatic amino acids that helped in the adherence of biological macromolecules on nanorods' surfaces. These biological molecules are attributed toward reduction, nucleation growth, and stabilization of the biosynthesized Se nanorods as revealed by FTIR spectroscopy.

Different fungal isolates of *Aspergillus* were screened for their capacity to reduce potassium tellurite into elemental tellurium and generate NPs (TeNPs) in the process. *Aspergillus welwitschiae* (KY766958) was reported to be the most efficient species depending upon their enzymatic production of NPs. DLS, TEM, and FTIR techniques characterized the produced TeNPs and revealed that the spherical and oval particles that were formed had an average size of about 60.80 nm. TeNPs showed antimicrobial activity against pathogens, *Staphylococcus aureus* and *Escherichia coli*, when applied at 25 mg/mL concentration. Exposure of the fungus

in culture medium to γ -irradiation enhanced TeNP production [42]. Similarly, *Sulfurospirillum barnesii* and *Bacillus selenitireducens* can also produce NPs within size <50 nm and 10 nm diameter [27]. Generally, tellurium resistance in microbes requires either reductive precipitation or volatilization of tellurite. Generation of TeNPs involves NADH-dependent tellurite reductase which is liable for tellurite detoxification [26].

3.6 Cadmium NPs

Cadmium sulfide nanoparticles (CdSNPs) are well-known wide band gap semiconductors, and because of their optical properties, they are employed as fluorophores. Owing to their smaller size, generally 1–10 nm, they are also referred to as quantum dots. These cadmium nanocrystals are regularly used in laser technology, optoelectronics, and biomedicine [43]. Microbes like *Moorella thermoacetica*, *Klebsiella aerogenes*, *Schizosaccharomyces pombe*, *Candida glabrata*, *Coriolus versicolor*, and *Flagellospora curta* synthesize cadmium sulfide NPs [26, 30].

Klebsiella pneumoniae strain MAA in the presence of cadmium sulfate reduced sulfate into sulfide, readily synthesizing spherically shaped CdSNPs after 24-h incubation period of the bacterial biomass with CdSO₄, as observed from the appearance of white color in the reaction mixture [39]. The authors outlined the mechanism involved in the synthesis of these NPs and suggested that firstly the sulfate ions present in the extracellular nutrient medium are taken up by the bacteria and in the presence of ATP sulfurylase get reduced to adenosine phosphosulfate, which is then phosphorylated into 3′phosphoadenosine phosphosulfate. Next, 3′phosphoadenosine phosphosulfate gets reduced, resulting in the formation of sulfite ions in the presence of enzyme phosphoadenosine phosphosulfate reductase. The enzyme sulfite reductase reduces these sulfite ions to sulfide ions. The sulfide ions thus formed a couple with inorganic cadmium ions present in the extracellular environment and forms NPs of CdS.

3.7 Palladium NPs

Palladium (Pd) is considered a scarce natural resource that has increasing demand in industrial applications. Pd⁰ NPs (PdNPs) can be biorecovered by *Enterococcus faecalis*, electron donor, and sodium formate. Successful Pd²⁺ reduction led to the generation of PdNP, 10 nm, either inside the cell or at the membrane surface, as revealed by TEM. The process occurred under optimal conditions of at 40 °C temperature, pH 3.0–3.5, with 25 mM sodium formate concentration, 1.2 g/L bacterial biomass, and 210 mg/L Pd²⁺ respectively [44].

4 Applications of Nanoparticles

The synthesis of metal-based and inorganic NPs has augmented the development of interlinkage of new fields/disciplines of science. The development and designing of affordable novel techniques for the production of NPs have provided a fascinating field of study and also address the escalating human needs in terms of health security and environmental problems. In modern times, industries utilize nanomaterial, and it is progressively being adopted anonymously and will soon replace the toxic and harmful chemicals used during traditional times. This is possibly due to NPs and their nanocomposites offering a comparatively better alternative [35]. Microbially synthesized NPs offer applications in various fields like medicines, agriculture, bioremediation, biosensing, catalysis, etc. and are briefly discussed in this section.

4.1 Biomedical Applications

Nanotechnology in medicine and healthcare has emerged as a promising deal, owing to its deployment in gene and drug delivery, biosensors, treatment of human diseases, detection of pathogens, tumor destruction, DNA analysis, and various phagokinetic examinations finds its applications in plethora of fields. The microbe-synthesized metallic NPs hold immense potential in their usage in formulating antimicrobial agents, in drug delivery, in imaging/diagnostics, and in biosensor development [45].

4.1.1 Nanomedicine

Microbial NPs exhibit strong antimicrobial activities. NPs attach to the cell membrane and penetrate the cell by communing with DNA, thus obstructing DNA replication and also even attacking pathogenic respiratory processes. In certain cases, they cause structural damage to the cell membranes resulting in pit formation accompanied by degradation and deterioration of the cellular components, ultimately leading to their death [46]. AgNPs obtained from *Bacillus cereus*, an endophytic bacteria, display bactericidal properties against certain pathogenic bacteria's such as *Klebsiella pneumonia*, *Escherichia coli*, *Salmonella typhi*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus* [47]. It is suggested that silver ions (Ag⁺) of the AgNPs get discharged and adhere to the thiol (-SH) group present on the pathogen's cell membrane and interrupt its function, thus displaying antimicrobial potential [48].

Spherical-shaped AuNPs, produced from the protein extract of *Streptomyces platensis*, display inhibitory response against *S. aureus* and *B. subtilis*. Gram-positive bacteria possess a thick peptidoglycan layer to which the NPs adhere and disrupt the bonds in the cell membrane, thereby gaining entry into the

microorganism [10]. Fungi-generated AgNPs show bactericidal activity against Gram-negative/-positive bacteria. They adhere and invade bacterial cell walls and modulate signaling pathways in the cells by dephosphorylating major peptide substrates present on tyrosine residues. Extracellularly synthesized AgNPs, using *Trichoderma* sp. and *Fusarium oxysporum*, can be integrated into materials like textiles. The fabrics implanted with AgNPs are antibacterial and can safely be employed in hospitals to minimize/prevent infection of certain pathogenic bacteria like *Staphylococcus aureus* [45]. Copper oxide NPs synthesized by *Bifurcaria bifurcata*, brown algae, also exhibited significant antibacterial activity against pathogenic bacteria, *Enterobacter aerogenes* and *Staphylococcus aureus* [49]. Besides, certain cobalt NPs obtained from *Bacillus thuringiensis* display larvicidal activity against dengue- and malaria-causing vectors, *Aedes aegypti* and *Anopheles subpictus*, respectively [50].

Nanomedicine has been effectively employed for the detection of tumors, site-specific drug delivery, and cancer treatment [51]. The biologically biosynthesized NPs, because of their intrinsic benefits, can readily cross biological barriers and assist molecular interactions without distressing healthy cells. Biosynthesized AgNPs affect apoptosis induction and endocytic activity of cancer cell lines. The efficacy of particles is reported to be directly proportional to the endocytic activities of the cancer cells. Silver NPs formed by *Cryptococcus laurentii* demonstrated effective antitumor activity against cancer cell lines [52]. Platinum NPs biosynthesized by *Saccharomyces boulardii* exhibit anticancer activity against MCF-7 and A431 cell lines [31]. Selenium nanorods with an average particle size of 17 nm, synthesized by *Streptomyces bikiniensis* Ess_amA-1 strain, induced cell death of MCF-7 and Hep-G2 human cancer cells at a lethal dose ($LD_{50\%}$) of 61.86 and 75.96 $\mu\text{g/mL}$, respectively [40]. Similarly, selenium nanorods and gold NPs have also been successfully employed against cancer cells, owing to their ability to stimulate mitochondrial apoptosis, DNA impairment, and cytokinesis detention in cancer cell lines [46]. PEG-coated gold NPs maximize tumor damage in comparison to TNF- α (tumor necrosis factor-alpha), a cytokine with anticancer activity [10].

4.1.2 Targeted Drug Delivery

An important application of NP is the targeted or localized delivery of biomolecules and drugs in the cells and tissues. These nanosized particles, acting as delivery vehicles, protect the biomolecule or the drug from degradation, successfully transport them to the targeted cells/tissues, and sustainably release the delivered molecules. Besides, a significantly higher cellular uptake efficiency of the bioactive molecules is observed for NPs in comparison to microparticles [53]. NP drug carriers such as AgNPs are often referred to as drug conveyors and, owing to their minute size, can easily bypass the skin's rigid epithelial junctions and blood-brain barrier that often impede drug delivery at the preferred target site. Due to the high surface/volume ratio, these nanocarriers exhibit enhanced biodistribution and pharmacokinetics of the therapeutic agents, thus minimizing toxicity at the desired site. They not

only enhance the solubility of hydrophobic compounds but also make them pertinent for parenteral administration [54]. Additionally, these NPs augment the stability of therapeutic agents such as oligonucleotides and peptides. Toxicokinetics can easily be controlled in cases where the drug readily conjugates with NPs either by encapsulation or by linker molecules. Toxicity of the drug carrier systems is lowered ensuring the drug's therapeutic effects in the patients [46].

Magnetic NPs such as magnetite (Fe_3O_4) and maghemite (Fe_2O_3) are biocompatible and are extensively used in site-specific cancer treatment, guided drug delivery, stem cell manipulation and sorting, DNA analysis, and gene therapy and MRI scanning [28]. *Rhodococcus pyridinivorans*-synthesized ZnO NPs laden with anthraquinone, displayed cytotoxicity towards HT-29 colon carcinoma cells in a concentration-dependent manner, thus revealing its role during drug delivery carrier for cancer treatment [37]. NP-targeted drug delivery systems are anticipated to significantly cut down the dose of anticancer drugs with low toxicity, better specificity, and enhanced efficacy [28].

4.2 Biosensors

NPs exhibit optical and electronic properties and thus find their application in biosensing techniques. They are frequently used for sensing different biological analytes such as DNA, proteins, and small molecules like glucose. In biosensing techniques, specific receptors bound to the NP surface interact with an explicit biological analyte, and this recognition event is then translated into a detectable magnetic, optical, or electrochemical signal [53]. Ag-Au alloy NPs biosynthesized from yeast cells are used for fabricating an electrochemical sensitive vanillin sensor. This vanillin sensor can successfully determine vanillin content from vanilla tea and vanilla bean samples, suggesting its practical application in vanillin tracking systems [28]. AuNPs are utilized as biosensor labels, for curing hyperthermia, for determining glucose content in glucose injections fabricated commercially, for staining biological tissues, and for estimating biomolecules [54]. In comparison to macro-scale biosensors, the NP-based biosensors exhibit low detection limits and increased sensitivity, endorsed to NPs' high surface to volume ratio which results in greater density of specific receptors/unit volume of NP [53].

4.3 Catalytic Applications

Owing to their larger surface area and certain special characteristics, NPs have found their application in improving reaction rates, either as reductants or as catalysts. Magnetic NPs are employed for improving rates of microbiological reactions. Cells of *Pseudomonas delafieldii* coated with Fe_3O_4 magnetic NPs are used for dibenzothiophene desulfurization [28]. The PdNPs synthesized by *Enterococcus*

faecalis could readily catalyze the complete reduction of chromate [44]. Certain biologically synthesized NPs can readily remove pollutants like heavy metals, pesticides, synthetic dyes, etc. from the environment by acting as catalysts. Palladium NPs obtained from bacterial biomass are used as a catalyst to produce hydrogen, using hypophosphite as substrate [26]. AuNPs biosynthesized using *Trichoderma* sp. cell-free extract (20–30 nm) along with anisotropic planar shapes are useful in optoelectronics and photonics [45]. Fe₃O₄ NPs can proficiently adsorb crystal violet dye, a model pollutant, thus offering an alternative for the removal of water pollutants. PdNPs from *Chlorella vulgaris* act as a catalyst in Mizoroki-Heck cross-coupling reaction [10].

4.4 Agriculture

Nanotechnology aims at improving agricultural practices by escalating input efficiency and reducing production losses. NPs provide a broad surface area for pesticides and fertilizers. Besides, nanomaterial-based agrochemicals facilitate targeted delivery of mineral elements along with augmented crop protection [55]. Nanonutrient/nanopesticide application to plants in the form of aerosol sprays is considered superior as compared to traditional sprays. Also, the loss of nanonutrient/nanopesticide during spray is lesser (15%) as compared to natural sprays (33%). Using particles of 20 nm or less is generally considered more beneficial [9]. Inorganic NPs like ZnO, SiO₂, TiO₂, Cu, CaO, MnO, MgO, and AgNPs play a pertinent role in plant protection against pathogens and pests [55]. Owing to distinct properties such as sensitivity and performance, NPs can also be used as biosensors for detecting crop pests and physiological stresses like drought stress and soil analysis, thereby, employing global positioning systems using field satellite images. NPs display excellent transduction properties owing to which they are explored for agricultural products. Several nanoscale carrier molecules can thus be utilized for delivery of herbicides, pesticides, fertilizers, plant growth regulators, etc. in small amounts and improved and extended management in the agriculture sector [45].

5 Nanoparticle-Plant Interactions

Plants are the fundamental and most important biotic component of the ecosystem. They play an imperative role in maintaining equilibrium *via* the transportation of nutrients across the food chain and food web of the ecosystem. These biotic components work in coordination with other abiotic components of the ecosystem like water, soil, etc. These abiotic components make a path for different components like nanoparticles (NPs) *via* specified routes [56]. So, there are different ways through which NPs interact with the plants like direct application, accidental release,

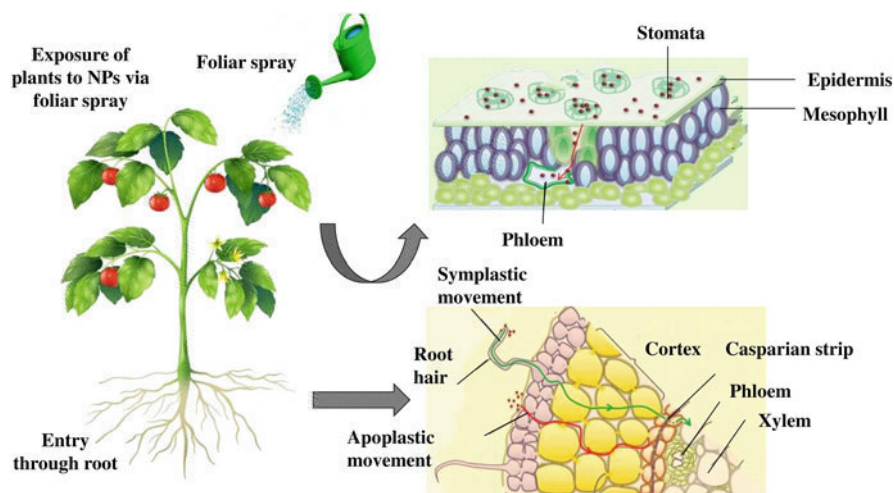


Fig. 1 Model depicting the uptake and transportation of NPs in plants

and presence in the soil as contaminants in the soil or atmosphere. A schematic overview of plant-NP interaction is given in Fig. 1. After reaching the soil-plant zone, NPs interact with plants in a non-partial manner, thus influencing the physiological processes of plants and enhancing the food security and thus ultimately the management of agronomy fields. But researchers have also documented the toxic effects of NPs on the environment and its components. The toxicity of NPs depends directly on their interaction with the specific substrate where they have been applied. In a nutshell, the phytotoxicity of NPs is based on their uptake, transport, and accumulation in plants.

5.1 Uptake and Translocation Mechanism

The researchers have reported two methods of NPs exposure to plants, i.e., root exposure and exposure to the vegetative part, especially leaves.

5.1.1 Uptake of NPs Through Root

During the encounter of NPs with plants, NPs enter the plant cell by crossing the cell wall and cell membrane of the root epidermal cells, and this penetration is followed by a cascade of events that ultimately results in the entry of NPs to the vascular tissue. Once inside the plant tissue, NPs take up either symplastic or apoplastic modes of transportation to migrate from one plant part to the other. With the help of

apoplastic mode of transportation, NPs invade the vascular system of the plant and ultimately to the other parts of the plant.

Whereas, in case of symplastic transportation, NPs move through plasmodesmata and cell sieves. In both, modes, water, and nutrient molecules also play a significant role [57]. After passing *via* the symplastic route, NPs can move to other parts of plants and perform their functions (Fig. 1) [58, 59]. However, the whole process of uptake and translocation of NPs is considered to be size-specific [60]. It has been reported that the basic criterion for entering into the plant tissue and cell is the size that NPs exhibit. As per the studies, penetration and translocation of NPs having sizes 40–50 nm are smooth [61]. Besides size, other factors play a critical role in the uptake and accumulation process like the chemical composition of NPs, their morphology, and type of coating material [62, 63]. Furthermore, the type of plant, environmental conditions, microflora, etc. also serve as important factor that can affect the uptake of NPs.

5.1.2 Uptake of NPs via Foliar Spray

In the case of uptake *via* foliar spray in plants, the primary hurdle is the waxy protective layer present in the leaves, i.e., cuticle which prevents excess water loss and also controls the exchange of solutes [57]. Researchers have reported two possible pathways through which the NPs can penetrate the waxy cuticle, i.e., polar solutes can penetrate through the hydrophilic pathway, and nonpolar solutes can enter *via* lipophilic pathways that include permeation and diffusion [58, 64]. Moreover, the studies have also revealed that the uptake of hydrophilic substances can also occur through stomatal apertures. But in the case of stomatal uptake, the major influencing factors are the morphology of leaf and size and density of stomata [65]. After entering the apoplast of the leaf, the most possible route that NPs follow must be the conductive tissue or the vascular system, usually phloem, because in phloem, the flow of substances is from top to bottom, i.e., from shoot to root (Fig. 1). Thus, the NPs translocated during the foliar spray may be exudated into the phyllosphere and influence the microbial community in the phyllosphere.

Researchers have well documented the role of NPs as potential abiotic elicitors. The NPs are known to induce bioactive metabolites in plants [66]. Furthermore, researchers have constantly examined the potency of NPs in modulating the expression of genes encoding biomanufacturing of the secondary active metabolites [67]. It has been reported that apart from inducing secondary signaling cascade, NPs also induce the level of various ROS in the plant cells, which further triggers oxidative stress and thus influences the levels of primary and secondary metabolites [68]. Several studies that document the role of NPs in secondary metabolite production in plants are enlisted in Table 1.

Table 1 Role of nanoparticle-mediated secondary metabolic profiles in plants

Nanoparticles	Size	Conc.	Plant	Tissue	Effects	References
Mesoporous silica in combination with amines and TiO ₂	165 nm	1, 10, 100 µg/mL and 1, 2.5 mg/mL	<i>Solidago nemoralis</i>	Hair root culture	Enhanced level of flavonoids, continued synthesis of flavonoids after harvest	[69, 70]
Ag	40 nm	30, 60, and 90 µg/L	<i>Caralluma tuberculata</i>	Callus culture	Increment in the levels of flavonoids, total phenols, phenylalanine lyase, superoxide dismutase, catalase, and ascorbate peroxidase	[71]
ZnO	–	100 and 150 mg/L	<i>Zataria multiflora</i> , <i>Thymus vulgaris</i> , <i>T. aenensis</i> , <i>T. kotschyanus</i>	Callus culture	Enhanced contents of thymol and carvacrol	[72]
ZnO and NaCl	10–30 nm	NaCl—0.50 and 100 mM	<i>Camelina sativa</i>	Shoot-root	Decreased antioxidant capacity, total flavonoid content. Induced total phenol, anthocyanins, carotenoid calcium, zinc, and phosphorus content	[73]
		ZnO—0, 20, 40, 80 mg/L				
Se	50–78 nm	5 mg/L	<i>Apium graveolens</i> L.	Stems-leaves	Enhanced flavonoids, total phenols, chlorophyll, total proteins, soluble sugars, and various amino acids	[74]

(continued)

Table 1 (continued)

Nanoparticles	Size	Conc.	Plant	Tissue	Effects	References
Ag	10, 40, and 100 nm	0.5, 1.0, 5.0 mg/L	<i>Arabidopsis thaliana</i>	Seedlings	Increase in the contents of glutathione disulfide, sinapoyl malate, kaempferitrin, G(8-5)FA dihexoside, G(8-0-4)G hexoside, G(8-0-4)G(8-0-4)G hexoside, coniferyl aldehyde hexoside, 4-glucosyloxy-benzoate, 6-MeO-ICOOH, sinapic acid, 4-hydroxyglucobrassicin, and camalexin. Decreased of 4-glucosyloxy-benzoate, pinoresinol hexoside, and kaempferol-3-O-glucoside	[75]
nTiO ₂ and bTiO ₂	nTiO ₂ —less than 50 nm and bTiO ₂ —68 nm	200 and 800 mg/kg mixed in potting soil	<i>Abelmoschus esculentus</i> L.	Roots, leaves, and fruits	Enhanced seed germination, increment in the content of chlorophyll	[76]
SiO ₂ and TiO ₂	SiO ₂ : 5–15 nm TiO ₂ : an average of 25 nm	5, 10, and 20 ppm after 15 days of incubation	<i>Argania spinosa</i>	Callus culture (leaves)	Increased tocopherol content	[77]
SiO ₂ and TiO ₂ NPs and NaCl	SiO ₂ : 10–15 nm TiO ₂ : an average of 24.5 nm	SiO ₂ and TiO ₂ NPs: 25 and 50 mg/L NaCl: 0.3 M	<i>Tanacetum parthenium</i> L.	Leaves	Enhanced level of genes that are used in the biosynthesis of parthenolide and β-caryophyllene	[78]
Ag	–	0, 0.25, 0.5, 1, 1.5, and 2 mg/L	<i>Isatis consstricta</i>	Plantlets	Increased indigo and tryptanthrin	[79]

ZnO NPs, jasmonate, and chitosan	–	ZnO: 20, 60, and 100 ppm Jasmonate: 100, 250, and 500 μ M Chitosan: 10, 50, and 100 μ M	<i>Momordica charantia</i> L.	Shoot	Upregulation in the activities of antioxidant enzymes, enhanced level of phenolic compounds, carotenoids, and proline content	[80]
ZnO and CuO	ZnO: 20–30 nm CuO: 25–30 nm	0, 2, 20, 200, and 2000 mg/L	<i>Stevia rebaudiana</i>	Shoot	Enhanced contents of phenolic compounds, total reducing sugars, and increased antioxidant activity	[81]
AgNPs and AgNO ₃	–	0.5, 1.0, and 2.0 mg/L	<i>Cucumis anguria</i> L.	Hairy root	Increased levels of total phenols	[82]
Ag	30–50 nm	0, 2.5, 5, and 10 ppm	<i>Corylus avellana</i> L.	Hazel cells	Rise in taxanes content (taxol and baccatin III)	[83]
Ag, Au, and naphthalene acetic acid (NAA)	–	30 μ g/L of each NPs in ratios of Ag:Au: 1:2; 1:3; 2:1, and 3:1 with NAA	<i>Prunella vulgaris</i> L.	Calli cultures	Enhanced biomass, total phenols and flavonoids, and DPPH-radical scavenging activity	[84]
CuO	–	1 ppm	<i>Withania somnifera</i> L.	Shoots and roots	Elevated polyphenols (total phenol content, flavonoid content) and antioxidant activities	[85]
Cerium oxide (nCeO ₂) and citric acid-coated cerium oxide (nCeO ₂ +CA)	nCeO ₂ : 8 \pm 1 (primary size) and 231 \pm 16 (in deionized water) nCeO ₂ +CA: 12.4 nm (primary size) and 189 \pm 2 (in deionized water)	0, 62.5, 125, 250, and 500 mg/kg	<i>Solanum lycopersicum</i>	Fruits	Increment in the content of lycopene	[86]

(continued)