

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



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**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 CO<sub>2</sub> 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.,  $\text{HS}^-$  and  $\text{H}_2\text{S}$ , 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  $\text{CaSO}_4$  and  $\text{CaCO}_3$  along with elements like iron oxides. Nonetheless, physical and chemical processes, like weathering, precipitation, and dissolution of carbonates influenced by  $\text{CO}_2$ , intermediate hydrocarbonate ( $\text{HCO}_3^{3-}$ ) 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  $\text{Ag}^+$ ,  $\text{Au}^{3+}$ ,  $\text{S}^{2-}$ , and  $\text{SeO}_3^{2-}$ , 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  $\mu\text{m}$  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.  $\alpha$ -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<sup>+</sup> 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<sup>(0)</sup> leading to the generation of gold NPs. Varying the concentration of HAuCl<sub>4</sub>, 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, –NH<sub>2</sub>, –OH, and –COOH as binding sites that facilitate the bioreduction of Au<sup>3+</sup> 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 Fe<sub>3</sub>O<sub>4</sub>-NPs can be intracellularly generated by *Magnetospirillum magneticum* using FeCl<sub>3</sub> 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 Fe<sub>3</sub>O<sub>4</sub>NPs 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*, *Ferroplasma 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 µg/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 ( $\text{SeO}_3^{-2}$ ) into elemental Se and accumulate granules in cell cytoplasm or extracellular spaces. In addition, *Enterobacter cloacae*, *Desulfovibrio desulfuricans*, and *Rhodospirillum rubrum* can reduce  $\text{SeO}_3^{-2}$ , 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  $\text{SeO}_3^{-2}$ . 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 ( $\text{Se}^0$ ). 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  $\text{Se}^0$  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 ( $\text{Se}^0$ ) 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  $\gamma$ -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 CdSO<sub>4</sub>, 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. Pd<sup>0</sup> NPs (PdNPs) can be biorecovered by *Enterococcus faecalis*, electron donor, and sodium formate. Successful Pd<sup>2+</sup> 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 Pd<sup>2+</sup> 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<sup>+</sup>) 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- $\alpha$  (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 ( $\text{Fe}_3\text{O}_4$ ) and maghemite ( $\text{Fe}_2\text{O}_3$ ) 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  $\text{Fe}_3\text{O}_4$  magnetic NPs are used for dibenzothiophene desulfurization [28]. The PdNPs synthesized by *Enterococcus*

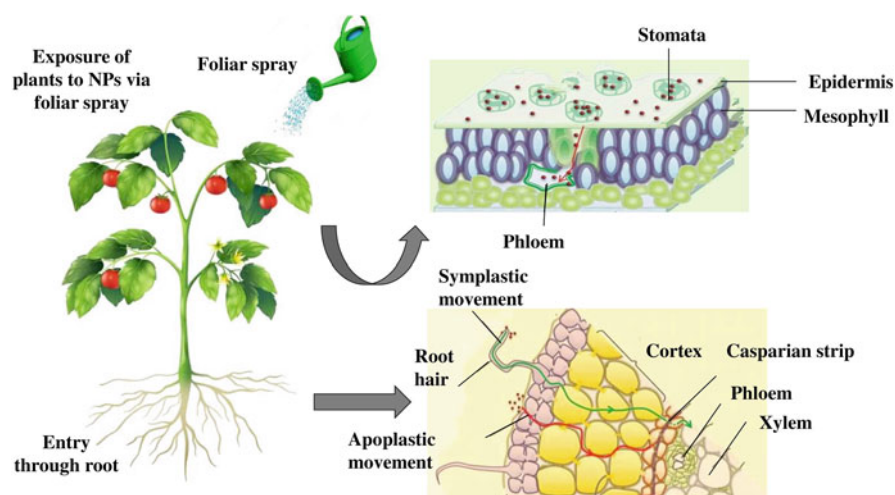
*faecalis* could readily catalyze the complete reduction of chromate [44]. Certain biologically synthesized NPs can readily remove pollutants like heavy metals, pesticides, synthetic dyes, etc. from the environment by acting as catalysts. Palladium NPs obtained from bacterial biomass are used as a catalyst 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]. Fe<sub>3</sub>O<sub>4</sub> 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, SiO<sub>2</sub>, TiO<sub>2</sub>, 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 <sub>2</sub>	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 <sub>2</sub> and bTiO <sub>2</sub>	nTiO <sub>2</sub> —less than 50 nm and bTiO <sub>2</sub> —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 <sub>2</sub> and TiO <sub>2</sub>	SiO <sub>2</sub> : 5–15 nm TiO <sub>2</sub> : 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 <sub>2</sub> and TiO <sub>2</sub> NPs and NaCl	SiO <sub>2</sub> : 10–15 nm TiO <sub>2</sub> : an average of 24.5 nm	SiO <sub>2</sub> and TiO <sub>2</sub> 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 $\mu\text{M}$ Chitosan: 10, 50, and 100 $\mu\text{M}$	<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 <sub>3</sub>	–	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 $\mu\text{g/L}$ 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 <sub>2</sub> ) and citric acid-coated cerium oxide (nCeO <sub>2</sub> +CA)	nCeO <sub>2</sub> : 8 $\pm$ 1 (primary size) and 231 $\pm$ 16 (in deionized water) nCeO <sub>2</sub> +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)

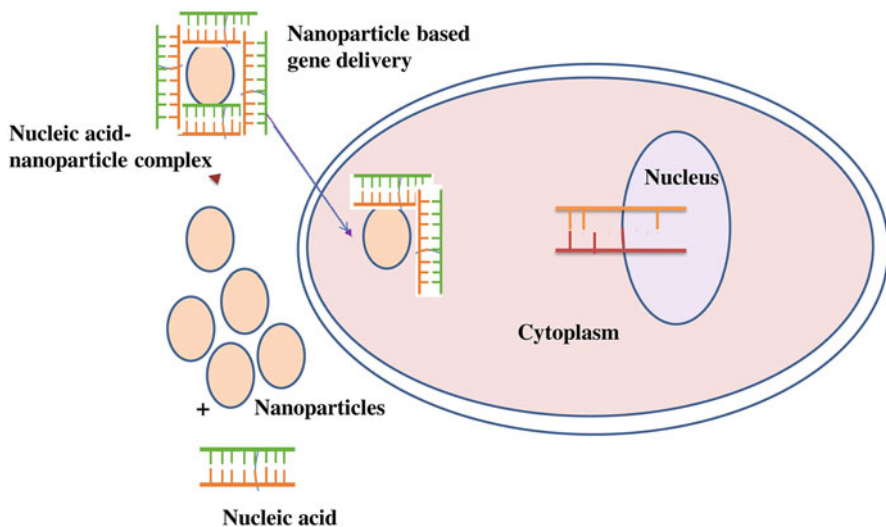
**Table 1** (continued)

Nanoparticles	Size	Conc.	Plant	Tissue	Effects	References
Cu	40 nm	0, 200, 400, and 800 mg/kg	<i>Cucumis sativus</i>	Fruit	Augmentation of leucine, threonine, fructose, valine glycine, proline, benzoic acid, isoleucine, glutaric acid, tyrosine, caprylic acid, linolenic acid, xylose, and imidazole. Decrease of lysine and methionine	[87]
Cu absorbed on chitosan hydrogel	-	100 mg/kg 0.3, 0.15, 0.06, 0.03, and 0.015 g/L	<i>Solanum lycopersicum</i>	Seedlings, fruits, and leaves	Inclined lycopene, titratable acidity, and catalase activities	[88]



## 5.2 Nanoparticles and Plant Genetic Engineering

Genetic engineering in plants has enhanced the quality of crops as well as the fundamental biology of plants [89, 90]. But the presence of cell walls in plant cells acts as a hurdle in the delivery of foreign genetic material to the nucleus of the target cell. For this purpose, gene gun and *Agrobacterium*-based transfer mechanisms are widely used. But there are some disadvantages of using these methods like gene gun technology that can have destroying impact on the tissue and the *Agrobacterium*-based transformation in host-specific. So, there must be some other safe method that can be used for delivering purpose, and one such method is nanoparticle-mediated gene transformation (Fig. 2) [91]. This method has been used commonly in the case of animal cells. And now the researchers are experimenting with nanoparticle-based genetic engineering in plant cell culture too. Silicon carbide-mediated transfer of DNA in cotton plants is one such example [92]. Another successful genetic transformation using magnetic nanoparticles (MNPs) has also been reported in the case of cotton plants. During this transformation, the reported gene, GUS ( $\beta$ -glucosidase), was complexed with MNP, and the complex thus formed was infiltrated by the magnetic force into pollen grains of the plant, without having any effect on the pollen viability. Then by pollination of these magnetofected pollens, cotton transgenic plants with successful incorporation of exogenous DNA into the genome occur [93]. Another study documents the application of mesoporous silica nanoparticles (MSNs) in delivering Cre recombinase in immature embryos of maize plant that carries Lox sites incorporated in the chromosomal DNA. After the application of modified MSN, the lox p was found to recombine specifically, thus resulting in successful genome editing in maize plants [94].



**Fig. 2** Model depicting nanoparticle-mediated gene transfer in case of plants

## 6 Nanoparticles as Frontiers in Agriculture

Nanotechnology upholds a great position in the agriculture industry due to its extraordinary characteristics and novel strategies of nutrient acquisition, precision agricultural practices, and pathogen recognition [95]. Research is consistently being focused on discovering nano-structured catalysts that boost the competence of fertilizers, pesticides, or herbicides for their minimal use. Nonetheless, through the use of nanosensors, the farming protocols induce agricultural productivity and yield by providing accurate information about weather, soil properties, and other factors that enable the farmers in agricultural practices. For instance, the equipment could be utilized for measuring the plant health before they cause any severity. These devices may further be potent in responding to various stressful conditions and remediating them [96]. Nanotechnology paves us with novel strategies without impairing the environment through the usage of nanomaterials coated on chemical fertilizers or biofertilizers to boost their effectiveness. They possess the ability to slowly and sustainably release fertilizer that is further taken up by plants, preventing their nutritional losses along with avoidance of non-wanted nutrient associations with microbial communities [97]. Silicon nanomaterials coated on fertilizers form a film over microbial cells to prevent infections along with improvement in plant resistance mechanisms against diseases [64]. Apart from this, silicon nanoparticles improve germination rate and promote root development in plants. Moreover, few nanoparticles also enhance water retention ability in soil, for example, *Bacillus subtilis*, *Pseudomonas fluorescens*, *P. elgii*, etc. are used as biofertilizers when augmented with nanoparticles and enhance plant growth and metabolism [1]. All these positive characteristics of nanoparticles make them capable to be used as bio-nanofertilizers that are the most effective and feasible alternative of the agriculture sector [98].

### 6.1 Nano-farming: Novel Window in Crop Production

Nanoparticle engineering is the most recent technology and innovation that determines the distinctive targeted features with utmost efficiency. It is quite evident that nanotechnology has made its recognized place in various disciplines, yet the idea of nanoparticles in agriculture is latest and technological advancement and research and is still going on for its progression [99, 100]. The novel discoveries in nanoparticle fabrication of various types, shapes, and sizes with numerous applications in medicine, food sciences, chemical sciences, agriculture, and environment have been studied. Throughout history, the agriculture sector has always been benefited from such innovative approaches [8]. Alongside, agriculture also faces abundant and unprecedented issues or challenges such as reduction in crop productivity due to stressed conditions or by a mineral deficiency in soil and the presence of environmental pollutants. Therefore, nanotechnology has proved to offer propitious



**Fig. 3** Applications of nanotechnology in agriculture

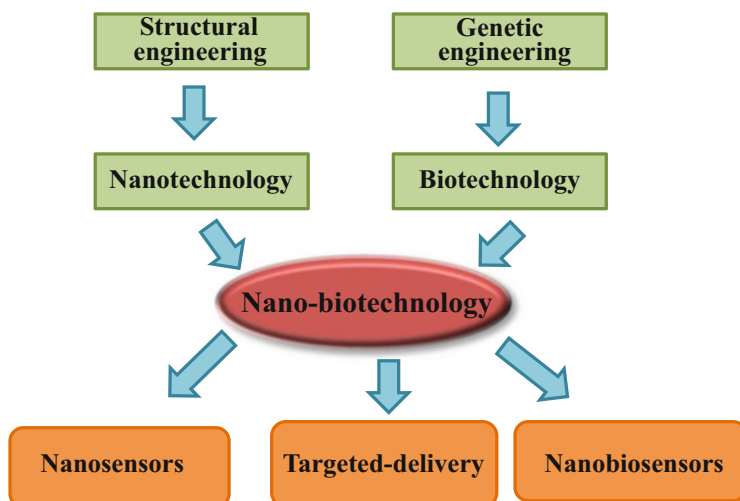
applications in precision agricultural practices (Fig. 3). The term precision farming has been found to evolve in the last few years with the involvement of wireless networking and the use of miniature sensors to monitor, examine, and regulate agricultural practices. Especially, it is associated with site-specific regulation with a plethora of production strategies in agriculture starting from horticulture to field crops [55]. More recently the role of tissue engineering and engineering of nanoparticles by using a targeted delivery system based on clustered regularly interspaced short palindromic repeats (CRISPER)/Cas (CRISPER-linked proteins) mRNA and sRNA for transgenic crops is a remarkable achievement in agriculture [101, 102]. Apart from this, nanotechnology also provides an excellent approach for coping with various environmental challenges. To illustrate, nanosensors have broader prospects in evaluating environmental stresses along with the potential to protect them against diseases [103]. Thus, such consistent innovations in

nanotechnology with specific features of identifying the problem and exploring them in sustainable agriculture provide them noteworthy potential and equitable benefits.

## ***6.2 Nanoparticle-Mediated Delivery System: New Avenue in Sustainable Agriculture***

Nanotechnology is the most prominent strategy of the twenty-first century with the latest sustainable agricultural practices and with the power to regulate agriculture by following conserved tactics to minimize agricultural wastes [104]. The delivery process of agrochemicals, as well as organic molecules such as DNA or oligonucleotides within the plant cells, is substantial for precise farming and sustainable agriculture [105]. While in case of traditional methods, the agrochemicals are directly sprayed onto crops that usually result in nontargets. A very limited supply of chemicals reaches the target site that is quite low in concentration that is required for plant growth. This further results in chemical leaching, degradation due to photolysis, microbial degradation, or hydrolysis [106]. While applying fertilizers in the fields, special care should be taken toward nutrient bioavailability through chelation, microbial degradation, evaporation, run-off, or overapplication of chemicals [99]. During pesticide application, the efficacy could be enhanced by spray management [107]. For successful eco-friendly agricultural methods, the nanotechnology-mediated synthesis of fertilizers, pesticides, fungicides, and herbicides is extremely important, and extra attention should be paid to this aspect [108]. Gradually, nanotechnology has moved out of lab trials toward practical field investigations and proved its efficacy. The main motive of controlled delivery systems means to release the specific quantities of agrochemicals over a specific period to get complete biological competence with minimal losses and adversities [109]. Nanoparticles provide us the effective agrochemical delivery due to their huge surface area, fast mass transfer, and ability to get easily attached to the surfaces [108]. Owing to this, micronic or sub-micronic particles are penetrated within agrochemicals by various methods such as capsulation, absorption, ionic bond attachments, or entrapment within nano-matrix [5]. The capsulation of  $\text{KNO}_3$  by graphene oxide usually protracts from the release of fertilizer. This process is cost-effective and is used for large-scale production purposes [110]. The nanomaterial coating enhances the agrochemical stability and protects them from being degraded and released into the ecosystem that further induces its effectiveness and lowering the agrochemical quantity.

Nevertheless, the combinatorial role of nanotechnology and biotechnology also designs new kits of molecular transporters for gene modification and the production of new organisms (Fig. 4) [111]. To elucidate, nanobiotechnology offers nanoparticles, nanocapsules, and nanofibers for carrying out foreign DNA along with chemicals to facilitate the modification of target genes. At the time of genetic material delivery, viral vectors face many challenges due to limited host range, size



**Fig. 4** Schematic representation of nano-biotechnology. The combination of nanotechnology and biotechnology gives birth to nano-biotechnology, which entails the understanding of genetic as well as structural engineering. This field has emerged as a novel for various sectors, especially agriculture with the emergence of smart approaches in farming such as nanosensors, targeted delivery systems of genetic material, and pathogen identification through nanobiosensors

of genetic material, and transport across cell membrane along with trafficking within nuclei [107]. Contrastingly, the recent quantum leap in nano-biotechnology provides many advancements to replace the genetic material completely by others [112]. Genetic engineering offers different types of nanoparticles for delivering DNA sequences in the target plant species without causing any side effects [113]. Additionally, the nanoparticle delivery system is useful in breeding programs for developing resistant varieties of crops. For example, DNA-coated nanoparticles are useful as bullets in the gene gun method for tissue and cell bombardment for transferring desirable genes at targeted locations in different plants [111]. Moreover, the recent development of the chitosan nanoparticle entrapped siRNA delivery system has attained a remarkable position in the field of crop improvement that enables target-specific control of pathogens. This is because chitosan has high binding properties with RNA along with its penetration ability across cell membranes [114]. The contemporary technological advancements in nanomaterial-mediated delivery of CRISPER/Cas9 RNA have formed a breakthrough in genetic engineering. CRISPER/Cas9 constitutes CRISPER repeat spacers along with Cas proteins, which form RNA-directed defensive strategy and are being continuously used in genome editing of plants [102]. Though, the limited delivery is still a barricade of this application and many studies are still being conducted for understanding their applicability. Strikingly, nanomaterials minimize the target changes through improvising the specificity of CRISPER/Cas systems. Like in the case of cationic arginine, AuNPs congregated Cas9En (E-tag)-RNP delivery of RNA and

showed nearly 30% of efficient cytoplasmic and nuclear gene editing effectively, which would have a great impact on crop production and development [115].

### ***6.3 Nanofertilizers: Effectual Crop Nutrition***

It is unequivocally sensed that crop productivity is directly proportional to fertilizers and their efficiency. Generally, the application of mineral elements improves crop fertility and productivity; henceforth the fertilizers are considered to be the predominant prerequisites for promoting sustainable agriculture [116]. In the pool of conventional fertilizers, the majority of chemicals leach into the soil and cause environmental pollution, thereby affecting plant growth. However, the role of engineered nanoparticles for sustainable agriculture has paved a new path to overcome these uncertainties [117]. The revolution in green nano-biotechnology has played a vital role in the global agricultural canvass where nanoparticles have emerged as promising agents to meet the future projections of crop production. Nanoparticles help in the alleviation of macro- and micronutrient deficiencies by enhancing mineral use efficiencies for overcoming environmental problems of eutrophication [118]. Nanofertilizers are unique and are mainly developed as plant nutrients possessing higher absorption and utilization efficacy with the minimal losses that make them best for facilitating nutrient uptake in plants. The studies conducted by Abdel-Aziz et al. [119] observed the remarkable properties of nanochitosan-based nitrogen, potassium, and phosphorus-based fertilizer in wheat plants in terms of boosting their sugar levels and potential to grow in varied soils. Similarly, peanut crops when treated with zinc oxide nanoparticles enhanced seed germination, yield, flowering, and chlorophyll content, revealing their significance in promoting morpho-physiological characteristics [120]. Nanofertilizers are designed with a special intention to properly regulate the crop requirement along with minimizing losses, for example, nitrogen fertilizers are lost by leaching or evaporation, but their nano-formulations synchronize their release as per the crop demand [121]. They prevent the losses through direct internalization followed by avoidance of nutrients interacting with soils, microbes, water, or soil [55]. To illustrate, the supplementation of porous nanomaterials like zeolites, chitosan reduced the nitrogen loss by targeted release and enhances the uptake process of the plant [122]. Moreover, ammonium zeolites also increase phosphate nutrients and availability, while graphene oxide carbon nanomaterial enhances  $\text{KNO}_3$  release to extend the release time and prevent leaching [123]. Furthermore, Sabir et al. [124] depicted that the nanocalcite combined with nano-silicon oxide, magnesium oxide, and iron oxide enhanced Ca, Mg, and Fe uptake along with improving Zn, Mn, and P uptake.

Based on different characteristics, nanofertilizers can be defined as slowly released fertilizers, magnetic fertilizers, controlled fertilizers, nano-composite fertilizers, and nano-device combined fertilizers, respectively [108]. They are produced through the encapsulation of minerals with nanomaterials (produced by top-down/

bottom-up approaches). This includes encapsulation with nano-porous material with a thin coating of polymer and delivered as emulsions of nanoscale or surface modification of anionic nutrients [108]. Overall agricultural yield is boosted by the use of nano-formulated fertilizers. Studies depicted that chitosan-NPK fertilizer enhances harvest index, crop index, and mobilization index along with overall crop productivity and yields. Moreover, nanomaterials also enhance other facets like root and shoot development due to their porous state that enables effective nutrient uptake [119]. Moreover, they also facilitate complex formation with molecular transporters and root exudates by generating new pores, ion channels, and endocytosis, respectively [125]. The size of nanoparticles also affects the nutrient ion adsorption/desorption process depending upon their surface charge to mass ratios; therefore they ensure a balanced amount of nutrition throughout the plant growth cycle [126]. Nanotechnology is a promising field to earn profit in agriculture by stimulating crop productivity. They also play a vital role under nutrient-deficient conditions by maintaining the nutrient balance for effective soil and plant health. Like in the case of Zn-deprived soils, zinc oxide nanoparticles at lower doses influence physiological plant processes [71, 127]. The technological and scientific advancements have benefited human welfare, where plant scientists aimed to restore the genomic diversities of various crops and reduce the chemical fertilizers without compromising the crop yields as well as sustainability. In this regard, “controlled fertilizers” are being promoted that have been engineered only to reduce pollution as well as enhance agriculture by forming a nano-networking [128]. This considerably works in a way where encapsulated fertilizer in a soil network is bound by hydrogen bonds, molecular attractions, and surface tension. As a consequence, their spatial movement allows them to be blocked by soil filtration and get attached around the plant roots in the soil for facilitating nutrient acquisition in plants throughout their growth phases [129]. However, further investigations are still carried out for exploring such promising techniques.

#### ***6.4 Nanomaterials in Modulating Crop Production, Quality, and Yield***

Nanoscience is a novel field with enormous developments with broad nanotech applications in agri-tech for inducing plant processes such as seed germination, vigor index, growth, and adaptation toward varied environmental conditions. Seed germination is a very sensitive stage of plants that induces seedling formation, growth, and survival. Yet the germination is very much affected by environmental, genetic, and edaphic factors [130]. NPs have, however, played an essential role in plant growth, development, and yield. For example, the use of carbon nanotubes had a huge impact on the germination of various plant species like tomato, potato, soybean, wheat, garlic, etc. [131]. Also, silicon NPs, titanium NPs, and zeolite have a positive impact on germination [130]. Another study conducted on iron and



silicon NPs showed an improved germination rate in maize and barley plants. Despite a handful of studies conducted on the positive role of NPs on plants, the exact mechanism by which they stimulate growth and yield is still unclear. A very few studies determined that NPs penetrate the seed coat to boost their absorption and water retention for the proper function of enzymes to regulate germination and growth [132].

Additionally, NPs, namely, zinc oxide NPs, titanium oxide NPs, iron oxide NPs, and zinc/iron/copper oxide NPs, are reported to mediate the crop productivity and development of plants [123, 133]. The carbon nanomaterials like fullerenes show positive effects on plants in terms of stimulating hypocotyl growth, cell division, fruit number, size, yield, and bioactive ingredients (cucurbitacin B, lycopene, and inulin) [134]. Moreover, the studies conducted by Yousefzadeh and Sabaghnia [135] determined that nano-iron fertilizers induced agronomic traits of *Dracocephalum moldavica* along with their oil content. Similar to this, zinc and boron nanofertilizers enhanced fruit yield, quality, soluble sugars, and maturity index of *Punica granatum* [136]. All these investigations on NPs stimulated crop yield and quality product, but the exact underlying mechanisms are still unclear. However, it has been explained that NPs have a higher absorption capacity to absorb nutrients and water content for enhancing vigor index as well as enzymatic activities [137]. Along with this, the research carried out on the regulated release of nutrients to prevent the loss of nanofertilizers has also inferred that the availability of nutrients is essential for plants in terms of flowering, germination, fruiting, etc. [138]. Furthermore, hydroxyapatite NP coated on urea fertilizer controls the nitrogen release, thereby implicating their positive impact on crops [139]. Table 2 summarizes the reports depicting the role of NPs in mediating crop production in plants.

## 6.5 Nanoparticles in Stress Management and Plant Protection

The food demand is quite challenging to be fulfilled for the sky-rocketed population due to scarcity of resources and climate change all over the world. Climate change means the alteration of climate over some time such as temperature, water deprivation, low temperature, salinity, heavy metal pollution, etc. Hence, the matter of concern is to enhance the adaptation of plants without harming the ecosystem to strive to counteract environmental stressors [6]. For the accomplishment of this approach, it is imperative to strengthen the plant's enzymatic system, hormonal synthesis, stress genes and proteins, and regulation of stressed conditions through a shortening life cycle. Apart from this, NP engineering shows that nano-fertilizers are best for crop production in extreme environmental conditions (Fig. 5).

For example, silicon oxide NPs enhance seed germination, growth parameters, pigment levels, and proline synthesis in plants under saline conditions [158]. A similar study conducted by Torabian et al. [159] found that iron sulfate NPs



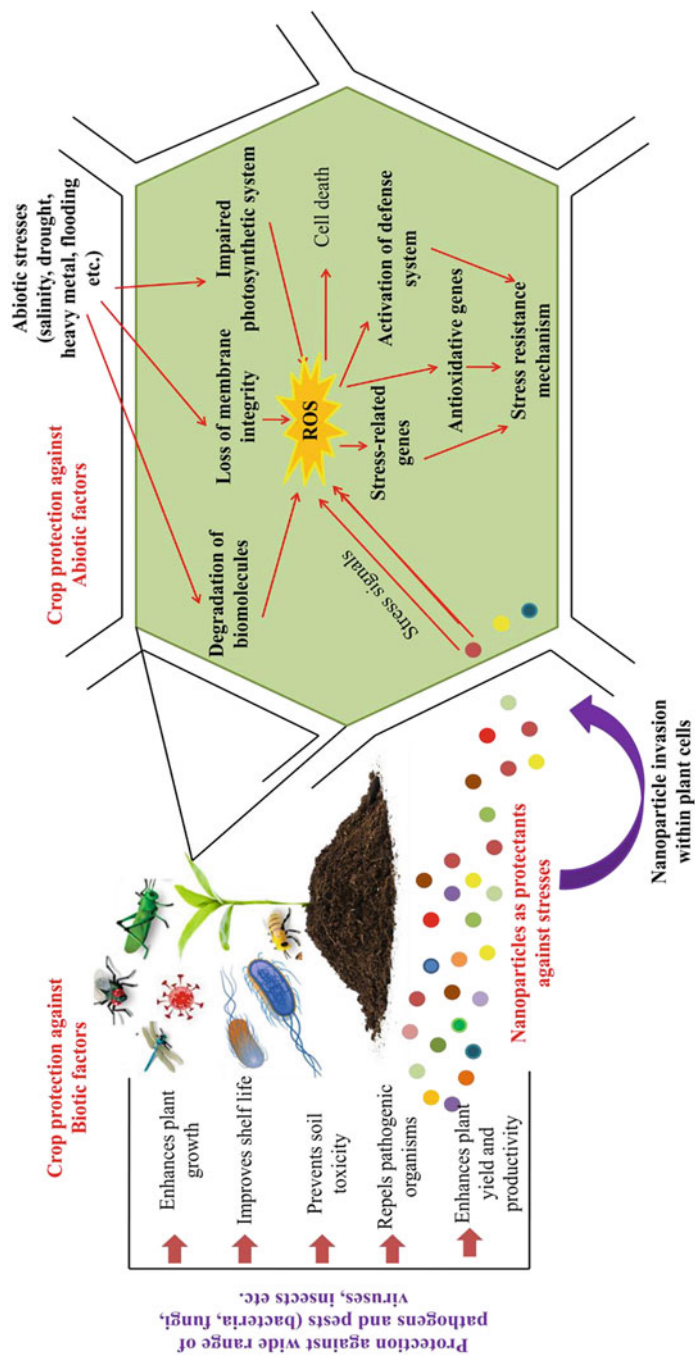
**Table 2** Role of nanoparticles in crop production

S. No	Nanoparticles	Conc.	Plant	Response in plants	References
1.	Zero-valent iron (ZVI), Fe <sub>3</sub> O <sub>4</sub> , and Fe <sub>2</sub> O <sub>3</sub> NPs	50, 500 mg/L	<i>Oryza sativa</i>	Induced growth parameters (biomass, root/shoot length), pigments, phytohormones along with mitigation of oxidative stress	[140]
2.	Hydroxyapatite nanoparticles (HANPs)	10,000 mg/L	<i>Raphanus sativus</i>	Stimulated shoot and root elongation, dry biomass, soluble protein, and indoleacetic acid (IAA) content	[141]
3.	ZnO NPs	100 and 500 mg/L	<i>Datura stramonium</i>	Enhanced Zn bioaccumulation and induced phenylalanine ammonia-lyase, catalase, and peroxidase activities	[54]
4.	AgNPs	25, 50, 75, 100 and 150 µM	<i>Nicotiana tabacum</i>	Improved germination rate, photosynthetic efficiency, pigments, and growth rate	[142]
5.	Fe <sub>3</sub> O <sub>4</sub> NPs	2000 mg/L	<i>Phaseolus vulgaris</i>	Enhanced morphological characters, nitrogenase activity, iron content, and nitrogen fixation	[143]
6.	SiNPs	200 mg/L	<i>Tagetes erecta</i> L.	Higher plant biometrics, physiology, flowering (number, diameter, fresh, and dry masses)	[144]
7.	Fe <sub>3</sub> O <sub>4</sub> -NPs	50 and 100 mg iron/L	<i>Glycine max</i>	Higher root surface, shoot weight, chlorophyll content, and antioxidants	[145]
8.	AgNPs	5–100 µg/mL	<i>Allium cepa</i>	Improved plant growth and physiological responses	[146]
9.	ZnO NPs	20 and 100 mg/L	<i>Solanum lycopersicum</i>	Higher chlorophyll content, photosystem II activity with upregulated expression of genes encoding nutrient element transport, carbon/nitrogen metabolism, secondary metabolism, antioxidative enzymes, transporters, sugars, and amino acids	[147]
10.	Ceria nanoparticles (NPs)	50, 100, and 200 mg/kg	<i>Phaseolus vulgaris</i>	Modulated levels of antioxidants, nutrient quality, the flavor of pods, and mineral content	[148]
11.	CeO <sub>2</sub> NPs	0–2000 mg/L	<i>Fragaria</i> × <i>ananassa</i> Duch.	Improved the plant growth and colonization of plant growth-promoting rhizobacteria	[149]
12.	α- and γ-Fe <sub>2</sub> O <sub>3</sub> NPs	100, 200, and 400 ppm	<i>Citrullus lanatus</i>	Promoted plant growth characteristics and nutritional qualities	[74, 150]

(continued)

Table 2 (continued)

S. No	Nanoparticles	Conc.	Plant	Response in plants	References
13.	Fe <sub>2</sub> O <sub>3</sub> NPs	10–100 mg/L	<i>Hordeum vulgare</i>	Stimulated plant growth, and formulations can be best used as nanofertilizers	[151]
14.	MnO <sub>x</sub> /FeO <sub>x</sub> NPs	2 mM	<i>Lactuca sativa</i>	Promoted plant growth, germination rate, root growth, fresh weight, and used as micronutrient nanofertilizer	[133]
15.	Poly(vinylpyrrolidone) (PVP) stabilized platinum nanoparticles (Pt:PVP)	1 mM	<i>Pisum sativum</i>	Improved yield and modification of growth regulatory hormones or biochemicals	[152]
16.	Al <sub>2</sub> O <sub>3</sub> and NiO NPs	50, 100, 1000 and 2500 mg/L	<i>Nigella arvensis</i> L.	Enhanced biomass, antioxidants such as ascorbate peroxidase, catalase, superoxide dismutase, and peroxidases, total antioxidant capacity, reducing power, iridoid content, saponin content, and total phenolic content	[153]
17.	Fe <sub>3</sub> O <sub>4</sub> NPs	50 and 500 mg/kg	<i>Zea mays</i>	Promoted morphological attributes and dehydrogenase enzyme activity	[154]
18.	TiO <sub>2</sub> NPs	50, 100, 200, and 400 mg/L	<i>Coriandrum sativum</i> L.	Higher shoot K, Ca, Mg, Fe, Mn, Zn, and B accumulation along with improved antioxidant defense system to alleviate oxidative stress	[155]
19.	Ag NPs	100–1000 mg/L	<i>Zea mays</i>	Reduced phytotoxicity and oxidative stress	[156]
20.	CuO NPs	0.2 and 300 µg/mL	<i>Lactuca sativa</i> L.	Promoted plant growth and enhanced nitrite and S-nitrosothiol levels in radicle with involvement in nitric oxide signaling	[157]



**Fig. 5** Mechanistic role of nanoparticle-mediated stress tolerance in plants

mediated salinity tolerance in sunflower along with stimulating other characteristics such as leaf surface area, the assimilation rate of CO<sub>2</sub>, pigment content, photosynthesis, etc. It has also been reported that silicon oxide NPs mitigate UV stress in wheat, while nano-zeolite enhances nutrient acquisition, germination rate, and plant growth [160]. Studies also found that the usage of NPs reduced the plant life cycle with enhanced yield in contrast to traditionally used fertilizers. This feature proves to be effective during agricultural practices in drought or flood-prone areas where the short life cycle of the plant is quintessential for sustainable agriculture [119]. Several reports encompassing the role of NPs in plants during stress tolerance against different biotic/abiotic stressors are summarized in Table 3.

NPs are also imperative for remediating or detoxifying heavy metals. Like in the case of Cd-stressed rice plants, silicon NPs enhanced Cd accumulation [89, 179]. Interestingly, these NPs were effective in curbing Pb, Cu, Zn, and Cd pollution, respectively [180]. Along with this, certain biotic agents like pathogens, pests, and insects also impede crop production [181]. Pesticides have been used to control this obnoxious agent, but they are against environmental health and sustainability. The use of NPs successfully minimizes the pathogen attack and improves the crop yield from such hazards. For instance, silver NPs synthesized from cotton stem extract showed a strong potential against bacterial diseases, respectively [182]. Certain metal oxide NPs (Cu, Zn, Mg) also inhibit various soil- and plant-borne diseases caused by pathogenic fungi such as *Alternaria alternate*, *Fusarium solani*, *Botrytis cinerea*, *Verticillium dahliae*, *Colletotrichum gloeosporioides*, *Phytophthora infestans*, etc. respectively [89, 179, 183–185]. The judicious use of NPs can therefore prove beneficial in the field of plant protection with higher efficiency and accuracy. The silver combined with chitosan NPs along with fungicide Antracol induced the antifungal properties, and *Bacillus thuringiensis* comprising NPs enhances efficiency and pesticide shelf life [184, 186]. Various reports of NPs in plants against stress management are tabulated in Table 2. The probable mechanism of NP effectively toward crops is mainly due to the NP-mediated enhanced activity of enzymatic systems (superoxide dismutase, catalase, peroxidase, ascorbate, glutathione, nitrate reductase, etc.), accumulation of metabolites (sugars, proline, amino acids), and nutrient and water uptake that imparts the defensive properties to plants for coping the stressed conditions [89, 179]. Microarray assay also revealed the gene expression of different genes in response to NPs and found that genes upregulated were concerned with oxidative stress such as cytochrome P-450-dependent oxidase, peroxidase, catalase, superoxide dismutase. Various genes subjected to pathogenic attack, hormones, systemic resistance, auxin regulation, and ethylene signaling were downregulated [132]. Therefore, further research should be carried out for assessing signaling responses and gene regulatory pathways related to NPs in plants.

**Table 3** Role of nanoparticles in plants during stress resistance against various stressors

S. No	Nano-particles	Conc.	Plant	Stress	Response in plants	References
Biotic stress						
1.	CuNPs	0.1, 0.25, 0.5, 0.75, and 1.0 mg/mL	<i>Solanum lycopersicum</i>	<i>Fusarium oxysporum</i>	Induced plant growth and chlorophyll content and acted as potential fertilizer	[161]
2.	MgO NPs	25, 50, or 100 ppm	<i>Vigna unguiculata</i> L.	<i>Meloidogyne incognita</i>	Lowered nematode fecundity and galls and stimulated plant growth, chlorophyll, carotenoid, seed protein, and root/shoot nitrogen content	[162]
3.	Alginate-chitosan nanoparticles (CNPs)	–	<i>Capsicum annuum</i>	<i>Sclerotium rolfsii</i>	High IAA synthesis, nitrogen-fixing capacity, 1-aminocyclopropane-1-carboxylic acid (ACC) deaminase production, and antifungal activity	[163]
4.	SeNPs	100 ppm	<i>Solanum lycopersicum</i>	<i>Phytophthora infestans</i>	Plant growth promotion with an accumulation of lignin, callose, and hydrogen peroxide and elevated activities of lipoxygenase (LOX), phenylalanine lyase, $\beta$ -1,3-glucanase, and superoxide dismutase as a cellular defense mechanism	[131]
5.	Chitosan-coupled copper nanoparticles (Ch-CuNPs)	0.2%	<i>Vigna unguiculata</i> , <i>Solanum lycopersicum</i>	<i>Rhizoctonia solani</i> and <i>Pythium aphanidermatum</i>	Acted as fungicide and growth promoter, and alternative to pesticides	[164]
6.	Ag NPs	50 mg/L	<i>Lycopersicon esculentum</i>	<i>Alternaria solani</i>	Higher antioxidant enzyme activity, along with enhanced plant growth attributes and lowered fungal infection	[165]

(continued)

Table 3 (continued)

S. No	Nano-particles	Conc.	Plant	Stress	Response in plants	References
7.	Fe <sub>3</sub> O <sub>4</sub> NPs	100 µg/mL	<i>Nicotiana benthamiana</i>	<i>Tobacco mosaic virus</i>	Induced plant biomass and antioxidants and upregulated SA synthesis along with the expression of SA-responsive PR genes (i.e., <i>PR1</i> and <i>PR2</i> ), to enhance plant resistance	[166]
8.	S-NPs	0.1 mL	<i>Rosmarinus officinalis</i>	<i>Meloidogyne javanica</i>	S-NPs displayed nematocidal activity and mortality of second-stage juveniles	[167]
9.	Graphene oxide (GO), ZnO NPs	0.05 and 0.10 mg/mL	<i>Daucus carota</i>	<i>Pectobacterium carotovorum</i> , <i>Xanthomonas campestris</i> pv. <i>carotae</i> , <i>Meloidogyne javanica</i> , <i>Alternaria dauci</i> , and <i>Fusarium solani</i>	Improved plant growth, chlorophyll, carotenoid, and proline content with declined galling, nematode multiplication, and disease indices	[168]
10.	TiO <sub>2</sub> and ZnO NPs	0.25 and 0.50 mL/L	<i>Beta vulgaris</i>	<i>Pectobacterium betavasculorum</i> , <i>Xanthomonas campestris</i> , <i>Pseudomonas syringae</i>	Augmented plant growth, chlorophyll, carotenoid, proline, antioxidant activities, proline, and H <sub>2</sub> O <sub>2</sub> contents and decreased MDA content and disease indices	[169]
Abiotic stress						
11.	Chitosan nanoparticles (CSNPs)	1%	<i>Catharanthus roseus</i>	Salinity	Enhancement in the activities of catalase, peroxidase, and glutathione reductase along with alleviation of oxidative stress	[170]
12.	Chitosan nanoparticles (CSNPs)	1%	<i>Catharanthus roseus</i>	Drought	Alkaloid and proline accumulation and higher activities of catalase and ascorbate peroxidase with induced gene expression of deacetyl-vindoline-4-O-acetyltransferase, strictosidine synthase, peroxidase 1, and	[171]

13.	ZnO NPs	25, 50, 100 mg/L	<i>Triticum aestivum</i>	Cd	geissoschizine synthase and reduced H <sub>2</sub> O <sub>2</sub> and malondialdehyde (MDA) accumulation Increased leaf chlorophyll content, leaf superoxide dismutase, and peroxidase and decreased oxidative stress	[172]
14.	Fe <sub>3</sub> O <sub>4</sub> NP	2 mM	<i>Oryza sativa</i>	As	Significant increase in germination, root/shoot length, and As stress mitigation	[173]
15.	Zero-valent iron nanoparticles (nZVI)	5 mg/L	<i>Solanum lycopersicum</i>	Cr	Increased chlorophyll and carotenoid levels with effective Cr remediation	[174]
16.	Zn, B, Si, and zeolite NPs	20, 12, and 15 ppm	<i>Solanum tuberosum</i> L.	Salinity	Enhanced morphological characters, photosynthetic rate, stomatal conductance, chlorophyll content, tuber yield, proline, gibberellins, proteins, carbohydrates, and antioxidant enzymes	[175]
17.	ZnO-NPs	50 mg/L	<i>Lycopersicon esculentum</i>	Cd	Stimulated plant height, fresh and dry weight, leaf area, chlorophyll, photosynthetic attributes, (net photosynthetic rate, transpiration rate, internal CO <sub>2</sub> concentration, and stomatal conductance), protein content, and activities of nitrate reductase and carbonic anhydrase	[176]
18.	Si NPs	25, 50, and 100 mg/kg	<i>Triticum aestivum</i> L	Cd	Dwindled oxidative stress by reducing hydrogen peroxide, electrolyte leakage, and malondialdehyde, with an increase in growth,	[69, 70]

(continued)

**Table 3** (continued)

S. No	Nano-particles	Conc.	Plant	Stress	Response in plants	References
19.	Ag NPs	5 ppm	<i>Allium cepa</i>	Salinity	photosynthesis, superoxide dismutase, and peroxidase activities Stimulated proline, flavonoids, sugars, chlorophyll, and carotenoid content	[177]
20.	TiO <sub>2</sub> NPs	50, 100, and 200 mg/L	<i>Dracocephalum moldavica</i> L.	Salinity	Improved agronomic traits, highest essential oil content, and increased antioxidant enzyme activities with lowered H <sub>2</sub> O <sub>2</sub> concentration	[178]



## 7 Conclusions and Future Perspectives

Agriculture is the only proprietor for the survival of the human race, and with the increasing population, there is a need to establish novel techniques and strategies to accelerate the production rate especially in developing countries. The green revolution has enhanced crop production worldwide but the use of massive chemical-based fertilizers dilapidates the ecosystem. The use of eco-friendly methods in plant growth promotion and maintaining the ecosystem has developed a better agriculture pattern. The latest techniques of using agro-nanofertilizers in contrast to chemical fertilizers have proved to be environment-friendly inputs to implement sustainable agriculture by the use of NPs. Nanotechnology enhances crop production along with maintaining the quality standards and proves to be an enrichment technique in farming systems. The surfacing of NP engineering and their actions in sustainable agriculture have revolutionized the global agriculture canvass with its novelty, enormous growth, and effectiveness to meet the global food demands. This also upholds the process to protect the environment from hazards, and NPs have emerged with the assurance to regulate and conserve the environment for plant production. NPs provide a new green revolution to the farmers by taking into account all the risks and mitigation practices. However, there is still an enormous information lacking about NPs in terms of their uptake, permissible limits, and ecotoxicology. Henceforth, many other investigations are on the way to untangle the behavior of NPs in the soil and its fate along with their interactions in the living systems.

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