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Fabrication of Nanomaterials and Their Potential Advantage for Sustainable Agriculture

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1.1 Introduction

The current global population is anticipated to be 8.12 billion and is increasing day by day. The developed countries with highly advanced economies and highly developed technological infrastructure grow food in surplus, while developing countries, because of unawareness of farming technology and harsh environmental impacts, lead to food crises. To overcome this food shortage or to feed such a huge population, there's no other way than intensifying the growth of agricultural products and improving food processing and distribution. Earlier, traditional or chemical fertilizers were used in agriculture for optimizing crop growth and productivity. Fertilizers, once indispensable for boosting food, fodder, and fuel production, have become a double-edged sword in modern agriculture, contributing to environmental challenges (Bhardwaj et al. 2022). The excessive and prolonged use of conventional fertilizers has led to severe environmental hazards, such as emission of greenhouse gases, groundwater contamination, eutrophication of water bodies, soil degradation, and harmful for the beneficial organisms (Meena et al. 2017; Chaitra et al. 2021). The inefficient utilization of fertilizer nutrients by plants hampers the pursuit of sustainable agriculture practices. The rapid release of nutrients from chemical fertilizers often exceeds plant uptake, leading to nutrient losses and reduced bioavailability. To address the environmental consequences of traditional fertilizers and improve nutrient use efficiency, there is a critical need for innovative, eco-friendly fertilizer solutions with minimal leaching potential (Alkhader 2023; Van Eerd et al. 2018). This can be achieved by introducing new technologies in the field of agriculture. Among several modern technologies (biotechnology, industrial, information, nanotechnology [NT], etc.),

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NT, although an evolving one, is the one with immense potential to transform the system of food production. With having some unique properties, such as small size and high surface area to volume ratio, enhanced physical strength, improved electrical conductance, distinctive optical characteristics, stability, heightened reactivity, and notable magnetic properties, nanoparticles (NPs) are currently offering interesting innovative solutions for sustainable agricultural production, such as nanopesticides, nano-fungicides, nanofertilizers (NFs), and nanosensors, to enhance crop growth, quality, and protection (Periakaruppan et al. 2023). The development of NPs through green synthesis methods using plants and microorganisms has emerged as a more sustainable and eco-friendly approach, as fabricated NPs through physical and chemical methods have had an adverse impact on the ecosystem and enhanced input efficiency in agriculture (Gupta et al. 2023). These NPs, including nanosensors and nanobarcodes, have significantly contributed to modern agricultural practices by elevating crop yield, nutrient utilization, and disease resistance, along with minimizing waste production (Bhandari et al. 2023; Yasmine et al. 2023). By utilizing NT in agriculture, we can deal with the challenges caused by population explosion, environmental damage, and food security concerns, paving the way for a more efficient and sustainable agricultural system (León-Silva et al. 2018). Hence, NT offers a promising approach to enhance horticulture crop production by utilizing NFs, nanopesticides, and nano-biofertilizers to support overall plant growth via higher uptake and bioavailability and lower rain-fastness. These innovative solutions address the growing food demand while promoting sustainability through reduced resource consumption and environmental impact (Feregrino-Perez et al. 2018).

1.1.1 Shortcomings of Conventional Agriculture

The soil microbiome supports multiple ecosystem processes. Plant growth-promoting bacteria (or PGPB), such as *Azospirillum, Bacillus*, and *Rhizobium*, as well as soil fungal communities, including mycorrhizal fungi and super-parasites, can be found in the rhizosphere, on the root surface, or associated with it. They stabilize the soil microbiome and aid in biogeochemical cycles and bioremediation. They are also capable of enhancing the growth of plants by processes such as biological nitrogen fixation, phosphate solubilization, and stress alleviation, including countering salt stress in crops through the modulation of 1-aminocyclopropane-1-carboxylate (ACC) deaminase expression and production of phytohormones and siderophores, while also protecting them from diseases and abiotic stresses (Frąc et al. 2022; Del Carmen Orozco-Mosqueda, Glick, and Santoyo 2020). In walnut trees, it has been observed by Bai et al. (2020) that the use of chemical fertilizers for long duration results in excess ammonium–nitrogen and available phosphorus. The excess of NH_4^+ causes soil acidification and altered bacterial communities, while available phosphorus diminishes fungal diversity. In contrast, nonfertilized soils have higher organic matter, nitrate-nitrogen, total nitrogen, pH, and total phosphorus levels than fertilized soils, and naturally grown walnut trees foster beneficial bacteria like *Burkholderia, Nitrospira*, and *Pseudomonas*, along with fungi such as *Trichoderma, Phomopsis*, and *Chaetomium*, which enhance nutrient mobilization and plant growth (Bai et al. 2020). Lin et al. (2024) investigated the presence and diversity of antibiotic resistance genes (ARGs) in the soil and rhizosphere of maize and found that chemical fertilization led to lower but more diverse ARGs compared to straw-return while promoting mobile genetic elements (MGEs) in the rhizosphere. Metagenomic analysis identified *Pseudomonas, Bacillus*, and *Streptomyces* as key biomarkers for ARG accumulation. A total of 509 isolates belonging to these three genera from the rhizosphere showed high multiresistance, especially in *Pseudomonas*. The co-occurrence of specific ARGs and class I integrons (LR134330, LS998783, CP065848, and LT883143) in *Pseudomonas* sp. contigs suggests a complex link between chemical fertilization and antibiotic resistance. Overall, the chemical fertilizers may influence the resistance of the maize rhizosphere, potentially increasing the risk of multidrug-resistant bacteria that could impact animal and human health.

Pesticides play a critical and indispensable role in agriculture to enhance crop production and controlling weeds and pests. They are classified as fungicides, insecticides, herbicides, and rodenticides. However, pesticide use has created environmental contamination in the long term as their residues can persist in the environment and agricultural crops through processes like leaching, adsorption, and runoff. These pesticide residues can disrupt the stability of ecosystems and produce potential health risks to humans and animals. For example, dichlorodiphenyltrichloroethane (DDT), an organochlorine compound, known for their high toxicity, bioaccumulation, and slow degradation, build up in the tissues and also harm the different ecosystems. The contaminants of soil and water resources, chlorpyrifos and its metabolites such as TCP (3,5,6-trichloropyridinol), pose potential health risks to human health, especially as endocrine disruptors (Tudi et al. 2021). Pesticides also impact agrobiodiversity as less than 1% of them reach their target pests, while most target nontarget organisms like honeybees, earthworms, parasitoids, and predators, crucial to the functioning of agricultural ecosystems (Elhamalawy, Bakr, and Eissa 2024). The use of chemical pesticides and fertilizers on a large scale for better yield and productivity in agriculture has put tremendous pressure on the environment, questioning its sustainability in the near future. The synthetic fertilizers and pesticides can enhance crop yields in the short term, but in the long term, they may degrade soil and water, disrupt local ecosystems, impact human health, and also contribute to the development of pesticide-resistant pests, creating a cycle of dependency on them.

1.2 Fabrication Techniques for Nanomaterials

NPs can be fabricated by different methods, such as biological, chemical and physical techniques (Figure 1.1). These methods come under two prominent approaches (Top-down and Bottom-up) utilized for the synthesis of nanomaterials. The top-down approach downscales bulk material into nano-sized material mechanically. The physical methods are termed as top-down approaches. The bottom-up approach self-assembles themselves to create nano-sized material. Biological and chemical methods are some methods of bottom-up approach (Mabrouk et al. 2021).

1.2.1 Top-down Approaches

The top-down/physical/destructive methods reduce the larger bulk molecule into the smaller molecule. These smaller molecules are further fragmented to form NPs. Some of the techniques of top-down/destructive methods are mechanical milling or ball milling, laser ablation, sputtering, thermal decomposition methods, lithography, and arc-discharge methods (Mekuye and Abera 2023).

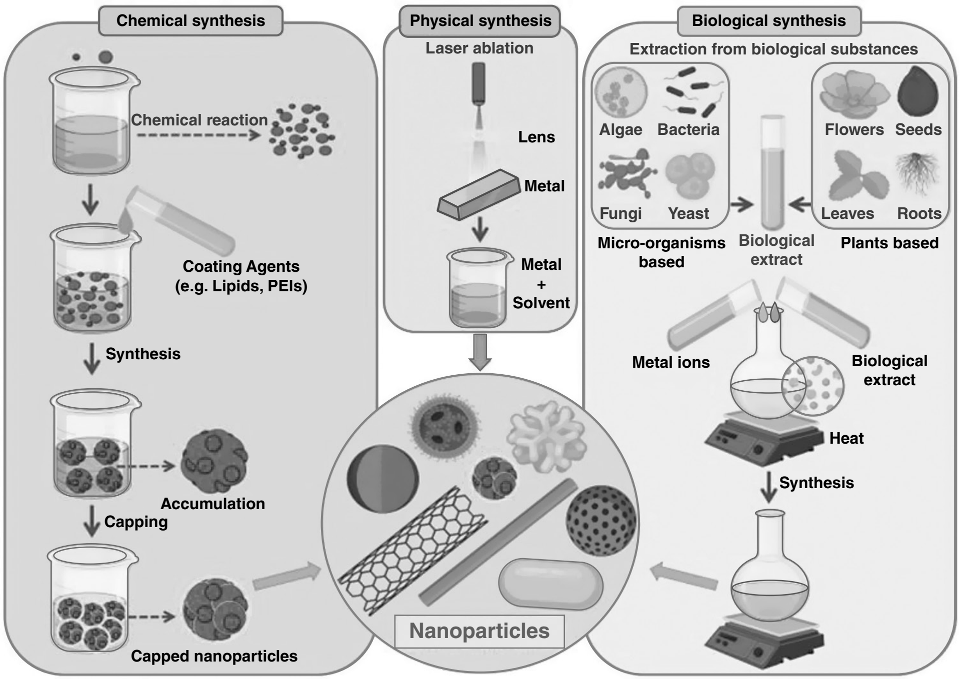

Figure 1.1 Different approaches (chemical, physical, and biological) for synthesis of nanomaterials.

1.2.1.1 Mechanical Milling or Ball Milling

Mechanical milling is the most inexpensive and simplest mechanical method for producing nano-metric scale particles from bulk materials. The purpose of milling is to break particles into smaller sizes and allow their blending in next phases. The efficiency of the milling and alloying process hinges on the energy transferred from the ball to powder particles. The energy transferred is influenced by various parameters, such as type of mill, milling speed, dry or wet milling, the powder used, temperature, and duration of milling (Baig, Kammakakam, and Falath 2021).

The predominant factors like cold-welding, plastic deformation, and fracture play a key role in high-energy ball milling process. In the deformation stage, the particle's shape is changed. The cold-welding initiates an increase in size, while fracture causes decrease in the particle's size. The three-staged process results in the making of alloying particles, which are finely dispersed in a grain-refined matrix. The mechanical milling method is leveraged in the synthesis of different types of oxide, aluminum/copper/magnesium/nickel-based nanoscale alloys, aluminum alloys strengthened by oxide and carbide particles, wear-resistant spray coatings, and numerous types of nano-composite materials (Namakka et al. 2023; Ratso et al. 2021; Liu et al. 2023). Carbon nanomaterials formed through the ball milling technique are utilized in environmental remediation, energy storage, and conversion (Kovalev, Kochetov, and Chuev 2021). Nagesha et al. ball milled powder of iron, nickel, and cobalt with an impact of 48% speed of ball milling (Nagesha et al. 2023). The mechanical/ball milling is a simple, eco-friendly, cost-effective, and high yield method (Wang et al. 2023).

1.2.1.2 Nanolithography

Nanolithography is another fabrication method utilized for creating nano-metric scale structure. Lithography on the basis of use of mask/template is categorized into two types. One is mask lithography, which utilizes mask/templates/molds to transfer nano-patterns over exposed large surface areas of wafers, resulting in the synthesis of high-throughput devices. Some of the examples of mask lithography are nanoimprint lithography and photolithography (Sharma et al. 2022; Salem et al. 2022). Another is maskless lithography, which creates nano-patterns without using masks. Such methods generate patterns in a serial manner. It causes ultrahigh-resolution patterning of different shapes having feature size smaller than a few nanometers. Nevertheless, the amount of material passing through this system is limited due to its leisurely serial nature. In maskless lithography, a small area of wafers is exposed in one step resulting in low throughput. And this low throughput removes any possibility of mass production. Some examples of maskless lithography are scanning probe, focussed ion beam, and electron beam lithography (EBL; Sharma et al. 2022; Paras et al. 2022). Panikar et al. (2023) assembled 30 nm Au NPs using simple stamping method upon EBL substrate. McMullen et al. developed a 5–40 nm wide electrode pair using a single step of EBL (McMullen, Mishra, and Slinker 2022). Nanosphere lithography is one of the recent advancements in the world of interfacial technology. Recently, using nanosphere lithography, polystyrene nanoscale meshes were created (Sharma et al. 2023). The meshes were shaped in honeycombed structures. Maskless lithography is inexpensive and easy to use (Brady et al. 2019).

1.2.1.3 Laser Ablation Method

Laser ablation technique of top-down approach synthesizes nanomaterial by utilizing laser beams as an energy source. In laser ablation, a high-intensity laser beam is focused on target material. This high-intensity laser beam increases the temperature of the irradiated spot, and the target material or precursor gets vaporized, resulting in the formation of plasma (Altammar 2023). This laser-induced plasma is produced because of haphazard collisions among nearby molecules, clusters, and atoms (Kim et al. 2017). The laser ablation technique does not use any toxic or hazardous chemicals or stabilizing agents (Ijaz et al. 2020). This method is used to produce different kinds of NPs, such as metallic NPs, metallic oxide NPs, semiconductor quantum dots, nanowires, and nanocarbons (Su and Chang 2017; Baig et al. 2021). Laser ablation is a simple, laboratory safe, and environmentally friendly method and has the ability to synthesize nanomaterials with complex stoichiometry, high purity (~90%), and uniform size distribution (Meidanchi and Jafari 2019).

1.2.1.4 Thermal Decomposition

Thermal decomposition method is an endothermic process in which the chemical bond of the molecule is decomposed by heat (Zeng, Xuan, and Li 2023). The temperature at which the molecule gets fragmented or decomposed is termed as decomposition temperature (Ealia and Saravanakumar 2017). The rate at which chemical bonds of the molecule get decomposed for NP production is measured by thermogravimetric analysis (Odularu 2018). Ahab et al. (2016) used thermal decomposition technique and synthesized NPs of gadolinium oxide. Zinc dehydrate acetate, along with ethylene glycol, was thermally decomposed at a temperature of 500 °C for 240 minutes to fabricate 35.4 nm-sized NPs of

ZnO_2, as reported by Rathore and Kaurav (2022), and its fabrication was confirmed by conducting X-ray diffraction (XRD), energy dispersive X-ray spectroscopy, and field emission scanning electron microscopy analyses. Tomar and Jeevanandam (2022) used thermal decomposition method and synthesized NPs of zinc ferrite ($ZnFe_2O_4$). Che et al. (2022) fabricated NPs of 99.92% pure CuO. The thermal decomposition technique is favorable for the fabrication of NPs used in cancer treatment (Odularu 2018), the utilization and storage of solar energy (Zeng et al. 2023), and the formation of nanoscale electrodes and catalysts (Yu et al. 2023), among others.

1.2.1.5 Sputtering Method

Sputtering is a nanofabrication method, in which tiny clusters of atoms are expelled off from the target surface by bombarding with high-energy gas or plasma particles (Inoue et al. 2023; Wirecka et al. 2022). The deposition of nanoscale particles is followed by the process of annealing. Substrate, temperature, thickness of layer, and annealing time help in determining the shape and size of nanoscale particles (Ijaz et al. 2020). Pleskunov et al. (2021) employed single-step plasma-based method for the fabrication of NPs. For the production of tantalum oxynitride NPs, direct current (DC) reactive magnetron sputtering techniques were used. The structural characteristics of platinum layer were modified using conventional magnetron sputtering technique at varying argon pressure (0.3–3.2 Pa; Sandhya et al. 2021). Sputtering technique is fascinating because it is cheaper than EBL and also because the sputtered nanomaterials' make-up is akin to the target material and has less impurity (Baig et al. 2021).

1.2.1.6 Arc-discharge Method

Arc-discharge is the classical method of fabrication of NPs. This is one of the most fascinating methods to develop carbon-based NPs, such as few-layer graphene, carbon nano-horns, fullerenes, and carbon nanotubes (CNTs; Kafle 2019; Zhang et al. 2019). In this method, carbon rod vaporization is produced by an electric arc between two graphite rods. The graphite rods are enclosed in a closed chamber filled with helium. The pressure of helium in the enclosed chamber is maintained as availability of oxygen prevents fullerene formation (Baig et al. 2021). The yield of nanoscale material fabricated is greatly influenced by the factors such as the distance between the graphite rods, its diameter, and the medium in which the rods are immersed. Other than these factors, pressure, temperature, voltage, and current also affect the yield of the synthesized nanomaterial (El-Khatib et al. 2018). As the growth mechanism of carbon-based nanomaterials differs from each other, their position of collection is different in the arc-discharge method. Karpov et al. (2019) studied the effectiveness on residual stress by the technological parameter during the fabrication of NPs and also established its correlation with voltage of arc plasma generator and NP magnetization on gaseous mixture pressure. They developed a single-step process in low-pressure arc-discharge to synthesize copper oxide NPs. Utilizing the arc-discharge methods, 19.60 and 32.97-nm-sized nanoscale particles of copper and argon were formed and analyzed using XRD, transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDX) methods (El-Khatib et al. 2018). Tseng et al. (2018) developed Ag^+ and AgO nanoscale particles by submerged arc-discharge method.

1.2.2 Bottom-up Approach

The Bottom-up approach, also termed as constructive method, progressively builds atoms into clusters and subsequently to NPs. This method includes both chemical and biological/green synthesis methods. Some of the chemical and biological methods are sol–gel method, spinning method, hydrothermal method, chemical vapor deposition (CVD), and biological synthesis by plant.

1.2.2.1 CVD Method

CVD method involves congealment of a thin coating of gaseous reactants on the surface of substrate in a reaction chamber. At an ambient temperature, chemical reaction ensues when combining gas and heated substrate collide with each other (Ijaz et al. 2020). The thin coating of the product accumulated on the substrate as a result of the reaction, was recovered, and then used. The substrate temperature greatly affects the CVD process. Lumen et al. (2021) utilized CVD method for the synthesis of porous silica NPs. This method circumvents the requirement of a highly pure monocrystalline silicon substrate as an initial material. In case of CVD-based synthesis of graphene, multilayer graphene is produced using Co and Ni catalysts, whereas monolayer graphene is produced by Cu catalyst (Baig et al. 2021). Ideal CVD precursors are volatile, pure, stable, inexpensive, nonhazardous, and long-lasting. CVD is a fascinating approach as it fabricates high-quality pure nanoscale particles that are homogeneous and stiff (Machac et al. 2020).

1.2.2.2 Sol–Gel Method

Sol–gel method is a simple, eco-friendly, and most preferred wet-chemical method for fabrication of NPs (Won et al. 2023; Solunke et al. 2023). In the word "sol–gel," sol is a colloidal dispersion consisting of solid particles suspended within a continuous liquid phase and gel is a dispersion of liquid within a solid matrix. In the sol–gel method, metal alkoxide and chloride used as precursors results in a stable solution that is thermally decomposed, condensed, and hydrolyzed (Altammar 2023). The precursor is distributed uniformly in host liquid by sonication, shaking, or stirring. The resultant solution is carried out and phase separation is performed by utilizing different techniques like filtration, sedimentation, and centrifugation (Ijaz et al. 2020). The morphology and size of nanoscale particles are controlled by optimizing the process parameters like solution pH, gelation/calcination temperature, and precursor concentration (Alabada et al. 2023). The flexibility in adjusting morphological characteristics makes sol–gel synthesis a highly effective technique for synthesizing photocatalysts (Habte et al. 2019). This method, processed at low temperature, provides uniform quality NPs and easily produces complex nanomaterials (Araoyinbo et al. 2018).

1.2.2.3 Spinning Method

The fabrication of nanoscale particles, using the spinning method, is processed by utilizing a spinning disc reactor (SDR). A rotating disc, consisting of stainless steel or copper with smooth and polished surface, is housed within a chamber/reactor where temperature, rotation speed, and other physical parameters can be regulated (Mekuye and Abera 2023). SDR is capable of continuous production of commercial amounts of the solid product. The morphological characteristics of nanoscale particles fabricated via SDR are influenced by several parameters, including disc surface properties, liquid-to-precursor ratio, disc rotation speed, feed location, and flow rate of liquid (Ijaz et al. 2020). The key factors that make SDR technology successful and more efficient are optimal heat and mass transfer, exceptional liquid–liquid mixing facilitating efficient micro-mixing, the ability to operate continuously, and suitability for gas–liquid reactions (Chianese, Picano, and Stoller 2021).

1.2.2.4 Hydrothermal Method

Fabrication of NPs by hydrothermal technique is the most widely used solution-reaction-based method. The synthesis of NPs by hydrothermal process is carried out at a wide range of temperature, i.e. from room temperature to significantly elevated temperature and pressure (Gan et al. 2020). The size and morphology of the NP synthesized by the hydrothermal process are maintained by controlling variable parameters such as pH, pressure, reactant concentration, temperature, and additives (Li et al. 2016). Chang et al. (2020) synthesized versatile nanostructures of ZnO like one-dimensional nanorods, two-dimensional nanoplatelets, and three-dimensional multi-branched flower-like particles utilizing hydrothermal processes and maintaining the pH of the precursor. Fabricated ZnO NPs were analyzed using selected area electron diffraction (SAED), XRD, and TEM. Zhongguan et al. (2023) fabricated graphene oxide by one-pot hydrothermal process. Okada, Kuno, and Yamada (2023) using microwave-assisted hydrothermal technique fabricated monoclinic vanadium dioxide (VO_2). Hydrothermal techniques serve as a versatile tool for enhancing other fabrication techniques (Yaghoobi, Asjadi, and Sanikhani 2023) and producing magnetite (Silva et al. 2023). There are several advantages of this process that makes it more attractive: less hazardous, environment friendly, low cost, use of simple equipment, etc.

1.3 Green Synthesis of Nanomaterials

In recent years, there has been a surge in research to develop eco-friendly methods for the synthesis of well-characterized NPs. Green/biological synthesis is one such method. The NP fabrication technique "green synthesis" employs biological entities, such as prokaryotes, complex eukaryotes, organic acid, primary or secondary metabolite, and enzymes, to reduce metallic ion to their elemental form (Kumari, Dhand, and Padma 2021; Parveen, Banse, and Ledwani 2016). This method is favored over conventional physical and chemical NP fabrication methods owing to its economic viability, reduced environmental impact, and enhanced safety for humans and the environment. It's also inexpensive, eco-friendly (Jiang et al. 2022), and prevents the use of toxic and hazardous chemicals. Besides, it has several other advantages: it's readily adaptable to mass production, produces highly stable products, and reduces processing time (Malhotra and Alghuthaymi 2022).

1.3.1 Nanomaterial Synthesis Using Microorganism

Biological synthesis of green NPs using microorganisms, like bacteria, fungi, and yeast, have emerged as prominent platforms. Due to certain properties like rapid growth rate, ease in cultivation, and ability to adapt in ambient conditions made these microorganisms a potential source of green synthesis (Ali et al. 2020). The wide variety of microorganisms can act as potential biofactories for the synthesis of several metallic NPs, such as copper, zinc, silver, gold, and iron. NPs prepared by Magnetotactic bacteria (found on the ocean floor) are specialized for synthesis of Magnetic NPs (10 to 20 nm). However, synthesis of Au NPs by photosynthetic bacteria, and Ag NPs by Fusarium oxysporum are some of the examples of green nanomaterial fabricated using microbes (Mekuye and Abera 2023).

1.3.2 Nanomaterial Synthesis Using Bacteria

In recent times, the primary focus of research has been on utilizing prokaryotes for metallic NPs production (Omran 2020). The synthesis of nontoxic, biologically derived NPs by utilizing bacteria is gaining attention due to their unique and superior properties, such as ubiquity, adaptation to harsh environments, ease of growth, ease of cultivation, and inexpensiveness, which make them ideal for biomedical applications. Nanomaterial synthesized by bacteria can utilize extracellular or intracellular methods (Marooufpour et al. 2019).

The extracellular mechanism involves the nitrate reductase synthesis method. This nitrate reductase enzyme is either secreted by the cell or is present in the cell wall and is responsible for the reduction of metal ions (Yusof et al. 2019). Nicotinamide adenine dinucleotide (NADH)-dependent reductase catalyzes the bioreduction of silver ions into Ag NPs. Electrons donated by NADH are oxidized to NAD^+ during the process. The enzyme undergoes simultaneous oxidation as silver ions are reduced to nanosilver (Prathna et al. 2010). Some of the bacterial species, such as *Bacillus subtilis, Bacillus licheniformis, Ochrobactrum anthropi, Pseudomonas stutzeri*, and actinobacter, are utilized for the production of Ag NPs (Dikshit et al. 2021). Rauf et al. (2017) in their study stated that *Staphylococcus aureus* via extracellular biosynthesis mechanism can produce ZnO NPs. The bacterial electrokinetic potential and alkalinity of the solution play a key role in the reduction of metal ions. For the reduction of metal ions, several extracellular enzymes act as electron shuttles. *Mycobacterium paratuberculosis, Geobacter fermentans*, and *Shewanella oneidensis* are some bacteria that release such enzymes, which act as electron shuttles and reduce Fe^{3+} ions (Priya et al. 2021).

The intracellular mechanism for the synthesis of nanomaterial is different from the extracellular mechanism of microorganism. The production of NPs through an intracellular mechanism involves three steps: trapping, bioreduction, and capping. The intracellular synthesis of nanomaterial involves the targeted transport of specific ions through negatively charged cellular environments. This process is influenced by biomolecules, enzymes, and coenzymes, which facilitate the reduction of metal ions into NPs (Slavin et al. 2017). Król et al. (2018) produced ZnO nanocomposite via intracellular biosynthesis mechanism utilizing *Lacticaseibacillus paracasei* bacterial strain and precursor Zn nitrate. Magnetite NPs were produced intracellularly by sulfate-reducing bacterial strain *Desulfovibrio magneticus*, which grows and respires in the presence of fumarate. Gold NPs were fabricated via an intracellular mechanism using *Lactobacillus kimchicus* $DCY51^T$ (Markus et al. 2016).

1.3.3 Nanomaterial Synthesis Using Actinomycetes

Actinomycetes, while understudied, have emerged as a promising group of organisms for metal NP synthesis (Golinska et al. 2014). It has the ability to produce varieties of secondary metabolites during their saprophytic existence. Actinomycetes synthesize NPs characterized by good polydispersity, excellent stability, and broad-spectrum antimicrobial properties (Mabrouk, Elkhooly, and Amer 2021). It can serve as bio-nanofactories for the fabrication of various NPs (Aswani, Reshmi, and Suchithra 2019). Species of *Streptomyces* like *Streptomyces zaomyceticus* and *Streptomyces pseudogriseolus* by both extracellular and intracellular mechanisms produces CuO NPs of size 78 and 80 nm, respectively (Hassan et al. 2019). Silver NPs of size 30 and 60 nm were synthesized using strains of *Streptomyces rimosus* and *Streptomyces chrestomyceticus* for the control of phytopathogens (Zwar et al. 2022). Some of the actinomycetes, such as *Nocardia farcinica, Streptomyces viridogens, Streptomyces hygroscopicus, Rhodococcus* sp., and *Thermoactinomycetes* sp., were identified for producing silver NPs.

1.3.4 Green Synthesis of NP Using Fungi

Mycotechnology is another biological approach, which is used in the synthesis of various NPs. Fungi are considered as an ideal organism for synthesizing metal and sulfide-based NPs due to their abundant intracellular enzymes, mycelial structure, potential for large-scale cultivation, ease of handling, superior tolerance of heavy metal, and economic viability benefits (Ahmed et al. 2022). It was observed that Ag^+ ions are trapped on the mycelial surface via electrostatic interaction with anionic carboxyl groups, facilitated by enzymes present in the mycelial cell wall (Altammar 2023). These enzymes then further reduced the trapped Ag^+ ion to Ag^+ bionanomaterial. Fungus-based nanomaterials can be synthesized both via extracellular and intracellular mechanisms. It was observed that the fabrication of NPs by fungi was influenced by several factors. The age of the culture affects the count of NPs, change in pH results in change in the shape of nanomaterial, and increase in temperature results in higher growth rate and accumulation of NPs of gold (Ma et al. 2017). Silver NPs of size 20–55 nm were produced extracellularly by different strains of *Penicillium aculeatum*. This fungal strain can be used as a potential bioresource for eco-friendly and cost-effective production of silver NPs. Chatterjee et al. (2020) fabricated 20 to 40 nm-sized superamagnetic Fe_3O_4 NPs by utilizing *Aspergillus niger* isolated from mangroves. Vijayanandan and Balakrishnan (2018) used the strain of *Aspergillus nidulans* and developed NPs of cobalt oxide. Another species of *Aspergillus, A. niger* with excellent antimicrobial properties were used in the synthesis of zinc oxide NPs. Researchers have observed varieties of filamentous fungal strains for the production of metallic NPs, such as AuO, AgO, and FeO of required shape, size, and ionic charge. Some of these observed fungal species are *Hormoconis resinae, Humicola* sp., *A. niger, F. oxysporum, Phoma* sp. *Phanerochaete chrysosporium, Pestalotiopsis* sp., *Trichoderma* sp., and *Penicillium* sp. (Rai et al. 2021).

1.3.5 Nanomaterial Synthesis Using Plant Extract

NPs can also be synthesized using different parts of plants, like roots, leaves, barks, flowers, shoots, fruits, and their extracts (Aboyewa et al. 2021; Mekuye and Abera 2023). Plants are the most eco-friendly resource and inexpensive to grow as well as available in abundance. The synthesis involves combining plant extracts and metal salt solution at room temperature to create NPs. The plant extract contains several phytochemicals, such as organic acids, quinones, and flavones, which work as natural reducing agents in the synthesis of NPs. NPs of palladium and platinum were fabricated using plant extracts of various plants, such as *Ocimum sanctum, Curcuma longa, Pulicaria glutinosa, Anogeissus latifolia, Glycine max*, and *Diospyros kaki* (Siddiqi and Husen 2016). Utilizing the extracts of *Pelargonium graveolens* and *Medicago sativa*, different shapes of gold NPs were fabricated (Mekuye and Abera 2023). Armendariz et al. (2004) were the first to report the biosynthesis of rod-shaped NPs using biomaterials. They characterized the Au NPs synthesized from wheat biomass using a 0.3 mM potassium tetrachloroaurate solution at pH levels ranging from 2 to 6 and at room temperature. Ag NPs of approximately 58 nm were fabricated from leaves of *Polyalthia longifolia* (Kumar et al. 2016). Gardea-Torresdey et al. (2002, 2003) first documented the intracellular biosynthesis of Au and Ag NPs within living plants. The extracts of sunflower (*Helianthus annuus*) and *Brassica juncea* were used to fabricate Co, Zn, Cu, Ni, and Ag NPs. Rate of synthesis of NPs from plants is influenced by several factors, such as plant extract type, its concentration, metal salt concentration, temperature, pH, and reaction duration (Ali et al. 2020).

1.4 Nanomaterials as Controlled Delivery System for Actives and Sustainable Agriculture

NT has revolutionized the agriculture sector by offering sustainable solutions for precision agriculture and providing us eco-friendly and resource-efficient technologies. Nanomaterials have immense potential to deal with crop productivity, the requirement of nutrients and fertilizers, soil health, plant disease, detection of pathogens and pests responsible for the disease, pesticide delivery, etc. by synthesizing the essential nanomaterials. Nanomaterials fabricated in the range of 1–100 nm are utilized for sustainable agriculture in the form of NFs, nanocides (nanopesticides, nano-bacteriocides, etc.), nanosensors to improve land and crop productivity, to detect and cure pathogenic disease, to site-specific and controlled release of fertilizers and pesticides, to improve soil health, etc. This section deals with NPs used in the form of NFs, nanocides, and nanosensors for improved, efficient, and productive agriculture.

1.4.1 Carrier-based Nanomaterials

The current methods of biomolecule delivery systems in agriculture and plants face various limitations, like low delivery efficiency, complex procedures, and dependence on specific plant species. In order to address challenges related to environmental and global food security issues, NT has revolutionized genetic engineering in plants and agricultural sectors (delivery of active biomolecules [herbicides/insecticide], including proteins, RNA, and DNA into plants) with improved delivery efficiencies, biocompatibility, and plant regeneration (Zhang, Ying, and Ping 2021).

A man-made, spheroidal nanomaterial known as “Dendrimer” has gained attention due to its multifunctional, three-dimensional structure, typically ranging from 1 to 10 nm in size. These dendrimers can be mathematically designed and synthesized (Figure 1.2). Structurally, they consist of a central core, an interior cavity, and surface functional groups.

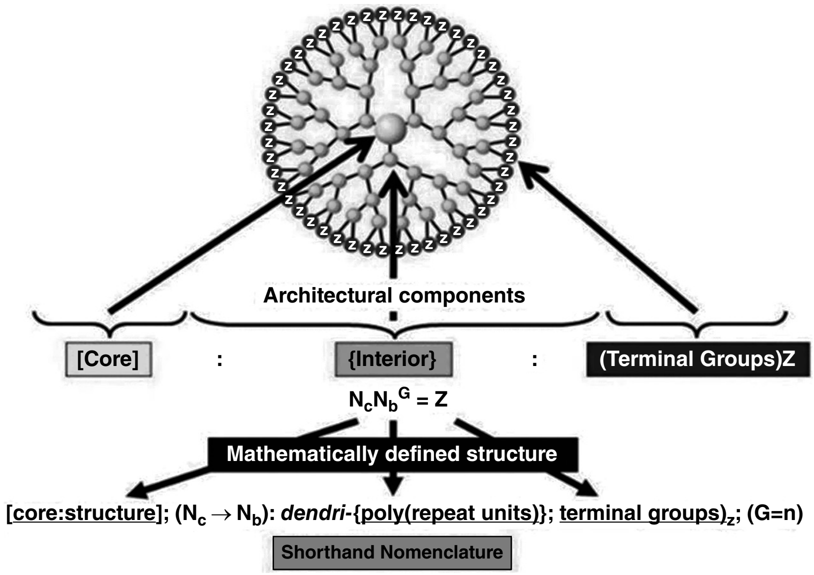

Figure 1.2 Architectural three-dimensional components of PAMAM dendrimer. *Source:* Graphic provided by NanoSynthons (i.e. Dendrimer Nanotechnology Company located in Mount Pleasant, MI, USA).

The interior cavity is capable of entrapping guest molecules, while the surface groups offer customizable sites for various physical or chemical interactions allowing for tailored applications across fields, such as medicine, biotechnology, materials science, and agriculture. Historically, Tomalia-type poly(amidoamine) (PAMAM) dendrimers are recognized as the first dendrimer family to be synthesized and become commercially available (https://www.sigmaaldrich.com).

However, a second commercial family of dendrimers was developed by Tomalia (2005), while managing Starpharma's Dendritic Nanotechnologies Inc. (DNT) at Mount Pleasant, Michigan, USA. This family is called Priostar® dendrimers; Starpharma further enhanced the water solubility of various crop protection actives (herbicides) like trifluralin and 2,4-dichlorophenoxyacetic acid that is used to kill weeds and regulate plant growth. The formulation of Trifluralin with dendrimer enhanced its aqueous solubility by 25,000 folds from 0.22 mg/L to 5.43 g/L. Meanwhile, the dendrimer also provided another benefit related to improving the shelf-life of products and greater stability in the field, leading to improved control of pests. However, with 2,4-dichlorophenoxyacetic acid, these dendrimers provided numerous benefits over commercially existing products, such as improved weed control, increased seedling density, and reduced environmental impact. Again, glyphosate, a well-known broad-spectrum systemic herbicide and crop desiccant, was formulated with these dendrimers resulting in a 150–250% improvement in rain-fastness in glasshouse trials (i.e. making the active more resistant to being washed away in poor weather when compared to a non-dendrimer control glyphosate formulation). Other glasshouse studies with these dendrimers have successfully witnessed the role of dendrimers in improving the efficacy of an active and systemic control of a fungicide. Amazingly, this dendrimer has also been successful in confirming the enhanced soil permeability of a well-known insecticide (i.e. imidacloprid) and making it more effective at targeting pests and diseases that current formulations cannot control due to poor soil permeation. These dendrimers-based imidacloprid study confirms the potential of dendrimers to elevate the soil permeation up to 7.5 cm, as compared to only 2.5 cm without dendrimers. However, native imidacloprid could reach only 10% at the bottom, whereas dendrimer-based imidacloprid showed significant accumulation, up to 40%, in the depth of the soil. Thus, dendrimer technology can be explored as nano excipients in the area of agriculture-related crop protection (https://starpharma.com).

Furthermore, other NT-based carriers (Figure 1.3) demonstrate a unique opportunity to manipulate some beneficial plant traits and allow natural resistance to pests and disease, as well as enhanced production of crop yields with longer shelf lives. In the past decade, mesoporous silica nanoparticles (MSNs) arranged in a honeycomb-like structure have attracted more and more attention for their potential use for specific delivery within plant organelles. Due to porous nature, MSNs provide a high surface area that can be easily modified with functional groups, thanks to the presence of exposed silanol groups. Silica particles with their high biocompatibility and inertness, as well as chemically and thermally stable mesoporous structures with variable pore sizes (2–10 nm in diameter), make MSNs suitable for hosting a diverse range of guest molecules, including those necessary for gene and chemical delivery (Miyamoto and Numata 2023; Law, Miyamoto, and Numata 2023).

CNTs, cylindrical or tube-like structures of carbon allotropes, possess distinctive physicochemical qualities. CNTs as microtubes inside the plant body can improve seed germination by aiding in water uptake and also act as a plant growth stimulator, increasing dry biomass and lengths of root/shoot. As a growth promoter and slow-release fertilizer, CNT is emerging as a new nano-carbon fertilizer in agriculture (Vithanage et al. 2017).

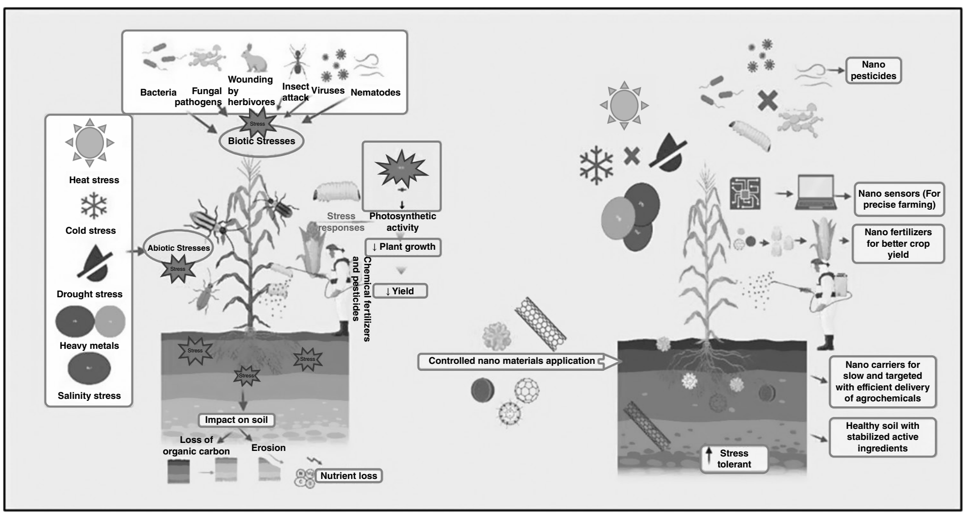

Figure 1.3 Nanomaterials as controlled delivery systems for nutrients, herbicide, insecticide, and sustainable agriculture.

An ornamental plant, Lily (*Lilium* spp.), has inefficient traditional genetic transformation methods. The highest germination percentage (88.32%) of *Lilium* regale pollen was observed while using nanomagnetic beads. Pollen magnetofection utilizes magnetic MPs as gene carriers to directly produce transgenic seeds without the need for tissue culture. The green fluorescent protein (GFP) activity reached an average of 69.66% in transformed pollen. A significant β-glucuronidase (GUS) activity, with a transformation efficiency of 56.34%, was also observed in transgenic seedlings, demonstrating that pollen magnetofection is effective in plant breeding transformation (Zhang et al. 2023).

1.4.1.1 Nanopesticides

The development of pesticide nanoformulations incorporating polymers, copolymers, silica, nanocarriers, and metal NPs is a rapidly expanding field within the pesticide industry. The main objective of nanopesticides development is to enhance pesticide efficacy, prolong its action, and minimize environmental impact, revolutionizing pests and disease management in crop production (Pérez-de-Luque and Rubiales 2009). Nanopesticides are categorized as follows: polymer-coated organic molecules and carrier-less inorganic molecules, on the basis of formulation of nanopesticides (Zhang et al. 2019). Polymer-coated pesticides are often used in the field of agriculture because of its features like targeted delivery, enhanced stability and solubility, etc. (Nair et al. 2010; Zhang et al. 2019). Huang et al. (2018) fabricated light-responsive nanopesticides by encapsulating pesticides within a PEO-PMAA copolymer matrix. Bhan, Mohan, and Srivastava (2014) demonstrated enhanced larvicidal efficacy of polyethylene glycol (PEG)-encapsulated temephos and imidacloprid nanopesticides compared to conventional formulation. Against a wide variety of phytopathogens, such as *Fusarium culmorum, Botrytis cinerea, Magnaporthe grisea, Bipolaris sorokiniana, Pythium ultimum*, and *Trichoderma* sp., silver NP encapsulated nanopesticides exhibit antimicrobial activity (Park et al. 2006; Sharon, Choudhary, and Kumar 2010). Porous silica nanomaterials offer a promising platform for controlled pesticides' delivery, as exemplified by the successful encapsulation and controlled release of validamycin (Liu et al. 2006). Copper NPs exhibit potent broad-spectrum antimicrobial activity against both Gram-positive and Gram-negative bacteria, as well as a range of fungal pathogens, including *Fusarium* sp., *Xanthomonas oryzae, Phytophthora infestans*, and others (Cioffi et al. 2005; Giannousi et al. 2014). Polymeric nanocapsules coated with both fungicides and herbicides mitigate environmental impact, applied and demonstrated by Campos et al. (2015) and De Oliveira et al. (2015), respectively. Both studies reported superior performance of nanoformulations compared to conventional products. A diverse range of nanopesticide formulation have been developed, including nanosphere, mesoporous metal oxide NPs, nanocapsule, nanosuspension, nanoemulsion, and solid lipid NPs (Ayoub et al. 2018; Zhao et al. 2017). Abamectin nanoemulsion demonstrated superior wettability and rapid penetration on cabbage leaves, characterized by a low contact angle (Feng et al. 2020). Nanocapsule delivery system demonstrated superior efficacy against *Rhizoctonia solani* compared to conventional formulation, highlighting the synergistic benefits of this approach (Cui et al. 2020). Thorough environmental risk assessment and regulatory compliance are essential prerequisites for the commercialization of nanomaterials. To mitigate potential environmental risks, comprehensive nanopesticides regulations should be implemented at the federal level.

1.4.1.2 Nanofertilizers

NFs are formulated by coating nutrients within active materials, enabling controlled and gradual release into the soil. NFs can mitigate nutrient loss through leaching and volatilization, enhancing nutrient use efficiency and soil fertility. This ultimately leads to improved crop productivity and long-term soil health (Rautela et al. 2021). NPs act like an adjuvant by conjugating easily with the plant because of having large surface area. NFs have the potential to significantly enhance crop growth by enhancing seed emergence, metabolism of nitrogen, photosynthesis, and production of carbohydrates and protein, while also improving stress tolerance (Rop et al. 2018). Leveraging their unique properties, NFs demonstrate superior efficacy compared to traditional polymer-coated slow-release fertilizers (Duhan et al. 2017). While NFs offer several benefits, there are also some challenges associated with their use. These NFs containing microelement when administered in high dose may result in phytotoxic effects. According to several literature, silver-containing NFs have detrimental effects on plant growth, primarily through root epidermal damage. This disruption inhibits root development, leading to overall plant weakness and reduced yield (Goswami, Yadav, and Mathur 2019; Izadiyan et al. 2020). NFs are typically produced by encapsulating fertilizer components within a NP matrix. This can be encapsulated through three techniques: by encapsulating nutrients within nonporous structure, by coating with a thin layer of polymer film, and by delivering it in the form of nanoscale particles or emulsion (Rai, Acharya, and Dey 2012). These NFs are further classified into two types based on nutrient availability which is further described as: (i) micronutrient NFs and (ii) macronutrient NFs. Some of the NFs fabricated and used in the agriculture sector are listed in Table 1.1.

1.4.1.3 Nanosensors

Nanosensors are accurate, efficient, and cost-effective devices that are revolutionizing farming by identifying pathogens, pesticides, pollutants, heavy metal ions, and more, along with monitoring humidity and temperature. They are helpful in monitoring precise crop progression, optimizing planting and harvesting schedules, and also detecting crop diseases efficiently. Biofilms, which are sessile and complex bacterial communities, can be detected by nanosensors optically with high sensitivity and spatial resolution, aiding in disease prevention (Pu et al. 2020). Sheikh et al. (2024) reported nanosensors' role in managing biotic and abiotic stresses in plants, diagnosing diseases, and providing accurate detection methods. Yin et al. (2021) developed a nanosensor platform for monitoring soil moisture levels using gold NPs, aiding in precision irrigation and water conservation. To promote healthier crops, integration of nano-functionalized materials, like hydrogels, will help in enhancing water retention and nutrient delivery (Das et al. 2024).

1.4.1.4 Stimuli-responsive Nanocarriers

Designing controlled stimuli-responsive nanomaterials (NFs, nanopesticides, etc.) in response to biotic and abiotic stimuli (e.g. enzymes, light, pH, redox conditions, and temperature) has been researched and developed in the past decade. These nanocarriers achieve controlled release through structural changes triggered by external stimuli or by breaking chemical or hydrogen bonds between the nanocarrier and the pesticide or nutrient-active ingredient.

Table 1.1 List of nanoformulations (nanofertilizers, nanocides, and nanosensors) fabricated with plant species and their critical impact on crops.

Nanoformulations with particle size (nm)	Plant species	Impact on crops	References
Nanofertilizers			
CaB (80 nm)	*Lactuca sativa* and *Cucurbita pepo*	Boosts productivity of plant and enhances root and shoot dry weight	Meier et al. (2020)
CaO (~69.9 nm)	*Arachis hypogaea*	Boosts root growth and augments Ca deposition in plant	Deepa et al. (2014)
NPK chitosan (26.2–30.6 nm)	*Triticum aestivum*	Reduces life cycle of crop and enhances yield and vegetative growth	Abdel-Aziz et al. (2016)
N (biosynthesis; 1–2 nm)	*Pennisetum americanum*	Boosts biomass production and augments soil microbes responsible for P and N metabolism	Thomas, Rathore, and Tarafdar (2016)
MgO	*Solanum lycopersicum*	Prevents wilt outbreak	Imada et al. (2015)
Mg	*Vigna unguiculata*	Enhances growth and yield and promotes photosynthesis	Delfani et al. (2014)
S (20 ± 4 nm)	*Cucurbita pepo*	Promotes stem and root growth	Salem et al. (2015)
Urea HAP (~18 nm)	*Oryza sativa*	Maintains sustained release of nitrogen; enhances N and K content and increases yield	Kottegoda et al. (2017)
P (15.8 ± 7.4 nm)	*Glycine max*	Enhances plant growth, biomass, and yield	Liu and Lal (2014)
Mo (100–250 nm)	*Cicer arietinum*	Minimizes K leaching and enhances biomass yield	Taran et al. (2014)
ZnO (35 nm)	*S. lycopersicum*	Enhances root and shoot growth	Faizan et al. (2018)
ZnO (90 nm)	*Lactuca sativa*	Enhances biomass production and photosynthesis efficiency	Xu et al. (2017)
ZnO (23 nm)	*Vigna radiata*	Improves photosynthetic efficiency and plant height	Raliya, Tarafdar, and Biswas (2016)
ZnO (16–35 nm)	*Abelmoschus esculentus* L. Moench	Enhances photosynthetic pigments and reduces soluble sugar and proline concentration	Alabdallah and Alzahrani (2020)
SiO_2 (12 nm)	*S. lycopersicum*	Promotes seed germination	Siddiqui and Al-Whaibi (2014)

Nanoformulations with particle size (nm)	Plant species	Impact on crops	References
SiO_2 (12 nm)	*Cucurbita pepo* L.	Produces enhanced proline, chlorophyll content, and transpiration rate	Siddiqui et al. (2014)
SiO_2 (10–20 nm)	*Fragaria* × *ananassa*	Enhances absorption of K, Ca, Mg, Fe, Mn, and Si. Limits biochemical and anatomical behavior due to salt stress	Avestan et al. (2019)
SiO_2 (20–30 nm)	*Hordeum vulgare*	Enhances carotenoid and chlorophyll II content	Ghorbanpour, Mohammadi, and Kariman (2020)
SiO_2 (20–40 nm)	*Musa acuminata*	Promotes shoot development and photosynthesis; balances Na^+ and K^+	Mahmoud et al. (2020)
TiO_2 (10–25 nm)	*Linum usitatissimum*	Enhances chlorophyll and carotenoid concentration and reduces H_2O_2 level	Aghdam et al. (2015)
TiO_2 (30–50 nm)	*Triticum vulgare* L.	Enhances Zn, P, N, and Cu content	Dağhan et al. (2020)
TiO_2	*Spinacia oleracea*	Promotes N_2 fixation and enhances dry weight of plant	Zheng et al. (2005)
TiO_2 (30–50 nm)	*S. lycopersicum*	Enhances chlorophyll II content and photosynthetic efficiency	Tiwari et al. (2017)
TiO_2 (10–25 nm)	*Triticum aestivum*	Increases seed dry weight, chlorophyll, and carotenoid content and enhances transpiration rate and antioxidative enzyme activity	Faraji and Sepehri (2020)
Fe_2O_3 (20 nm)	*Arachis hypogaea*	Enhances chlorophyll II content, biomass, and plant growth	Rui et al. (2016)
Fe_2O_3 (50 nm)	*Spinacia oleracea*	Enhances plant biomass	Jeyasubramanian et al. (2016)
Fe_2O_3 (27.3–34.62 nm)	*Mentha piperita* L.	Deduces level of malondialdehyde (MDA) and proline	Askary, Amirjani, and Saberi (2016)
Fe_2O_3 (6 nm)	*O. sativa*	Improves root growth	Alidoust and Isoda (2013)

(Continued)

Table 1.1 (Continued)

Nanoformulations with particle size (nm)	Plant species	Impact on crops	References
Fe_3O_4 (13 nm)	*Hordeum vulgare* L.	Enhances plant growth and improves chlorophyll II and protein content	Tombuloglu et al. (2019)
Fe_3O_4 (40–53 nm)	*Fragaria* × *ananassa* Duch.	Improves growth parameters of plantlets	Mozafari, Havas, and Ghaderi (2017)
CuO (20–40 nm)	*S. lycopersicum*	Enhances sugar and chlorophyll concentration and root length	Singh et al. (2017)
CuO (10 nm)	*Zea mays*	Improves biomass and seed growth	Saharan et al. (2016)
CuO (<50 nm)	*Zea mays*	Enhances plant growth	Adhikari et al. (2015)
AgNPs (20 nm)	*Trigonella foenum-graecum*	Enhances seed dry weight and germination rate	Hojjat and Kamyab (2017)
AgNPs (47 ± 7 nm)	*Arabidopsis thaliana*	Promotes root growth and mitotic cycle metabolism	Syu et al. (2014)
AgNPs (25 nm)	*Populus deltoides*	Promotes root growth	Wang et al. (2013)
AgNPs (20 nm)	*S. lycopersicum*	Enhances root growth and promotes germination of seed and its dry weight	Almutairi (2016)
AgNPs (21 nm)	*Trigonella foenum-graecum*	Enhances plant growth	Jasim et al. (2017)
AgNPs (15–29 nm)	*Triticum aestivum*	Promotes leaf growth and enhances proline and soluble sugar concentration	Mohamed et al. (2017); Iqbal et al. (2017)
Au (10 nm)	*Cucumis sativus*	Promotes root growth	Lin and Xing (2007)
Au, Ag, Cu, etc. (14–35 nm)	*Pennisetum glaucum*	Promotes seed germination and growth	Parveen at al. (2016)
Selenium and nano-selenium (N-Se; 8–15 nm)	*Lycopersicum esculentum*	Enhances shoot growth and dry weight and enhances root diameter, volume, and dry weight	Haghighi, Abolghasemi, and Da Silva (2014)
Se-NP (10–40 nm)	*Sorghum bicolor* L.	Augments membrane integrity and antioxidant system	Djanaguiraman et al. (2018)
Nanocides (nanopesticides, nano-bacteriocides, etc.)			
Ag-based NPs coated with chitosan (50 nm)	*Prunus persica*	Reduces bacterial canker disease caused by *Pseudomonas syringae*	Shahryari, Rabiei, and Sadighian (2020)
Ag-based NPs	*Punica granatum*	Controls blight disease caused by *Xanthomonas axonopodis*	As et al. (2018)

Nanoformulations with particle size (nm)	**Plant species**	**Impact on crops**	**References**
AgNPs (5–100 nm)	*Nicotiana tabacum*	Prevents infection by *Phytophthora parasitica* and *Phytophthora capsici* and enhances antibacterial efficiency	Ali et al. (2015)
Si-based NPs (<50 nm)	*Zea mays*	Protects plant from severe damage by *Sitophilus oryzae, Rhyzopertha dominica*, and *Tribolium castaneum*	El-Naggar et al. (2020)
Si NPs with or without chitosan coating (36 nm)	*Citrullus lanatus*	Suppresses disease severity caused by *Fusarium* wilt	Buchman et al. (2019)
$TiO_2/Cu_2(OH)_2CO_3$ NPs (20–50 nm)	Various crops	Prevents crop diseases caused by *Escherichia coli* and *Fusarium graminearum*	Liu et al. (2020)
Cu NPs/Thiophanate methyl (25 nm)	Greek orchards	Suppresses growth of benzimidazole-resistant *Monilinia fructicola*	Malandrakis, Kavroulakis, and Chrysikopoulos (2021)
Star polymer (SPc; 17.4–144.6 nm)	*Solanum tuberosum*	Activates endocytosis pathway and effective against potato late blight disease	Wang et al. (2021)
Polylactic acid/ dinotefuran/avermectin co-delivery nanoparticles (245.7 nm)	*Pyrus communis* L.	Increases bioactivity at lower concentration and is more effective against *Grapholita molesta* Busck	An et al. (2022)
Phyto-fabricated ZnO (20–30 nm)	*Brassica*	Is effective against Alternaria blight disease caused by *Alternaria brassicae*	Dhiman et al. (2021)
Metarhizium anisopliae–chitosan NPs (75.83 nm)	*Brassica oleracea*	Decreases the pathogenicity of *Plutella xylostella*	Wu et al. (2021)
Neem oil-zein NPs (198 nm)	*Phaseolus vulgaris* L.	Is highly effective against the disease caused by *Acanthoscelides obtectus*	Pascoli et al. (2020)
ZnO NPs (76.2–183.8 nm)	*S. officinarum*	Shows larvicidal efficacy against *Holotrichia* sp. (white grubs)	Shukla, Gaurav, and Singh (2020)
TiO_2/Fe_2O_3 NPs (20/40–100 nm)	*Nicotiana benthamiana*	Suppresses viral infection caused by *Turnip mosaic* virus	Hao et al. (2018)

(Continued)

Table 1.1 (Continued)

Nanoformulations with particle size (nm)	Plant species	Impact on crops	References
Cymbopogon martinii essential oil-chitosan (100 nm)	*Zea mays*	Shows antifungal and anti-mycotoxin activities and reduces the growth of *F. graminearum*	Kalagatur et al. (2018)
Azadirachtin-zinc oxide and chitosan (33.1 and 78.8 nm)	*Arachis hypogaea* L.	Growth of *Caryedon serratus* was successfully controlled	Jenne et al. (2018)
Mg $(OH)_2$ NPs (100 nm)	*S. lycopersicum*	Prevents growth of *E. coli, P. syringae*, and *X. alfaalfae*	Huang et al. (2018)
Nanosensors			
Au NPs-based (20 nm)	*S. tuberosum*	Detects bacterial wilt *R. solanacearum*	Khaledian et al. (2017)
TiO_2-Acetylcholinesterase (29 nm)	*Zea mays, Anacardium occidentale, O. sativa*	Detects pesticide dichlorvos causing toxic effects on humans and the environment	Cui et al. (2018)
Cd and Au NPs-quantum dots (27 and 4 nm)	Citrus plant	Detects the infection caused by *Citrus tristeza*	Safarnejad et al. (2017)
ZnO NPs-multiwalled carbon nanotubes (23 and <10 nm)	–	Detects *E. coli* and Gram-positive and Gram-negative bacteria	Meraat et al. (2020)
Primer-mediated asymmetric PCR-Au NPs (15 nm)	*S. tuberosum*	Detects *Phytophthora infestans* which cause potato late blight disease	Zhan et al. (2018)

In agriculture, soil pH influences the nutrient and pesticide fate and efficacy. A pH of 7.0 and above can reduce nitrogen loss from applied urea fertilizers to agricultural soil due to volatilization. Also, optimization and release of pesticides at a specific pH level that matches pest or infected crop conditions can improve its efficacy. pH-responsive nanofertilizers and pesticides often use natural and synthetic polymers with carboxyl or amino groups that react to pH changes. Carboxyl groups, at a pH below their pKa, remain protonated (–COOH) and form hydrogen among these groups and with other functional groups, such as hydroxyls, hindering the nutrient or pesticide-active ingredients release from the polymer matrix. When the pH exceeds the pKa, carboxyl groups become predominantly deprotonated (–COO–) causing swelling, which provides pore channels for accelerated release due to electrostatic repulsion.

1.4.2 Carrier-free Nanomaterials

The rapid development and expansion of carrier-free nanomaterials composed of pure active material can be directly used in crops or soil without the need for a secondary carrier substance, as discussed above (i.e. Dendrimers, CNTs, MSNs, etc.). In contrast to conventional carrier-based nanomaterials, the active materials are often entrapped, encapsulated, or chemically attached with carriers to improve stability and delivery. However, a carrier-free nanomaterials bypass this extra component, making the active material itself responsible for the intended function.

1.4.2.1 Micronutrient NFs

Micronutrient NFs represent advanced agricultural inputs that enhance nutrient delivery efficiency compared to conventional methods. Micronutrient NFs offer numerous advantages for plant health, including enhanced nutrient absorption, increased productivity, and improved resilience to biotic and abiotic stresses. These are required in trace amounts, but their deficiency can significantly disrupt plant physiological processes. Some of the micronutrients required by the plants are boron, zinc, copper, nickel, iron, manganese, and titanium (Yadav, Yadav, and Abd-Elsalam 2023).

Zinc is a vital micronutrient for the growth and development of all living organisms. Zinc functions as a crucial cofactor for numerous enzymes in plants, playing a pivotal role in protein synthesis, carbohydrate production, auxin biosynthesis, and overall plant defense mechanisms (Noreen et al. 2018). Awan et al. (2021) developed ZnO-NFs (zinc oxide NFs) using a green synthesis approach involving zinc sulfate solution and black seed (*Nigella sativa* L.) extract. On introducing ZnO NFs into broccoli, they observed significant enhancement in seed germination, seedling weight, root and shoot growth, leaf number, plant height, etc. Mattiello et al. (2015) studied enhancement in shoot growth and yield of cucumber when cultivated in a nutrient solution containing rubbery nanosuspension of zinc. In a recent study, *Citrus aurantium* fruit treated with 20 mg/L of zinc oxide NPs showed an increase in biochemical composition and growth parameters (Punitha et al. 2023).

Boron, an essential micronutrient, plays a vital role in plant growth and development by contributing to cell wall formation, pollen development, and nutrient translocation (Davarpanah et al. 2016). Boron-based NFs are produced by encapsulating borates within a NP matrix composed of material like humic acid. These formulations can be applied in both liquid and solid forms for both soil and foliar applications. Their unique properties enable the penetration of plant cells for direct nutrient delivery (Gehlout et al. 2022). Foliar application of zinc and boron, applied at optimal concentration (i.e. high concentration of Zn and low concentration of B), significantly increased pomegranate fruit yield (*Punica granatum* cv. Ardestani; Shang et al. 2019). While studying the effect of boron NPs on mung beans, Ibrahim and Farttoosi (2019) observed an enhancement in plant length, productivity of seed, and the number of pods.

Iron is a critical micronutrient that plays a pivotal role in plant metabolism, supporting processes, such as RNA synthesis, enzyme function, and photosynthesis (Mushtaq et al. 2020). It exhibits low soil availability due to limited solubility. Iron in reduced or excess quantities negatively impacts plant growth and development by disrupting essential metabolic processes (Palmqvist et al. 2017). Iron oxide and sulfide NPs represent the simplest form of iron fertilizers. Their small size enables superior soil penetration and plant uptake compared to conventional iron fertilizers. To enhance stability and longevity, iron NPs can be encapsulated within a protective biopolymer or lipid coating. Iron NFs offer a sustainable approach to enhance agricultural productivity by boosting crop yields, restoring soil health, reducing contamination, mitigating the effect of acid rain, and safeguarding water quality (Pitambara, Archana, and Shukla 2019; Cui et al. 2017). Dola et al. (2022) observed that foliar application of Fe_3O_4 NPs on *G. max* effectively enhanced the drought stress tolerance, deducing the loss caused by it. The application of Fe_3O_4 also promotes the productivity, quality, and growth of the plants.

Copper NPs outperform bulk copper in nutrient delivery, enhancing plant growth. As a vital micronutrient for protein and enzyme function, copper is efficiently delivered to plant cells via these NPs, ensuring rapid and effective nutrient uptake. Copper NFs offer a safe and efficient method for improving plant health and productivity (Yadav, Yadav, and Abd-Elsalam 2023; Khatri and Bhateria 2023). Van Nguyen et al. (2021), in their study, highlighted the efficacy of copper NP priming in mitigating drought stress in maize. The study demonstrated a reduction in reactive oxygen species (ROS) accumulation, suggesting an upregulation of ROS scavenging enzymes. Kasana et al. (2017) demonstrated the antimicrobial efficacy of biosynthesized copper NPs, but emphasized the need for further research to assess their yield-enhancing potential in field conditions. These copper NPs exhibit antimicrobial and antifungal properties, enhancing plant resistance to pests and disease.

Silicon, the second most abundant element on Earth, plays a vital role in plant health and development. Silica NPs mitigate salt stress, which is one of the biggest hurdles in enhancing crop production in agriculture, by enhancing K uptake and reducing Na uptake (Rizwan et al. 2015). Chitosan-Si NFs exhibited sustained Si release, promoting maize growth and yield. These NFs, when applied through foliar spray, activate antioxidant defense mechanisms by balancing oxidative stress through improved oxygen and hydrogen peroxide levels (Kumaraswamy et al. 2021). Tereshchenko et al. (2017) observed enhanced plant resistance to various stresses, while studying the impact of silicon dioxide NPs on hulless oat (monocotyledons) and lucerne (dicotyledons) under field conditions. Fatemi, Pour, and Rizwan (2020) studied the effect of silicon NPs on *Coriandrum sativum* L. They applied Si NPs through foliar spray on coriander plants and observed reduction in lead, malondialdehyde, flavonoid, and vitamin C concentration.

Titanium dioxide, known for its photocatalytic properties, is commercially used as pigment in cosmetics, paints, and other industries. Titanium dioxide NFs protect plants against several pests and diseases because of its antimicrobial properties. When treated with 0.01% $nTiO_2$, significant rise in plant growth parameters, including length of root and shoot, leaf area, and biomass accumulation were observed, compared to alkaline condition (Pitambara et al. 2019). TiO_2-based NFs successfully applied to enhance the growth of various crops like lettuce, tomato, spinach, watermelon, millet, lemna minor, wheat, and bean. These studies consistently reported a rise in germination rate, photosynthetic efficiency, chlorophyll content, biomass, and nutrient uptake (Zahra et al. 2015). TiO_2 NPs synthesized using *Citrus medica* L. were applied through foliar spray on *Capsicum annuum* L. As a result of utilization of TiO_2 NPs, the plant becomes resistant to disease and shows enhancement in growth parameters such as yield, biomass, and productivity (Prakashraj et al. 2021).

1.4.2.2 Macronutrient NFs

The essential micronutrients like calcium, magnesium, nitrogen, potassium, phosphorus, hydrogen, and sulfur have been encapsulated in nanomaterials to create NFs and capable of precise nutrient delivery to crops, resulting in the enhancement of plant growth (Chhipa 2016;

Ditta and Arshad 2016). These macronutrient-based NFs mitigate eutrophication, offer superior nutrient absorption and leaching resistance, and enhance crop yield and quality (Mejias et al. 2021; Sharma et al. 2022; Sarkar et al. 2022).

Nitrogen is a critical macronutrient essential for plant growth and development. As a key component of chlorophyll, it plays a pivotal role in photosynthesis. Nitrogen deficiency leads to chlorosis, characterized by yellowing of plant leaves. The nitrogen molecules encapsulated with various NPs like metal oxide, graphene, and nanotubes enhance the nitrogen availability in the soil and make the plant more accessible to nutrients (Erisman et al. 2008). The controlled release of nitrogen from these fertilizers minimizes nutrient leaching and runoff, reducing environmental risk in aqueous ecosystems. The nitrogen-encapsulated NFs sustain nutrient availability for approximately 1200 hours compared to the 300–350 hours duration of traditional fertilizer. Manikandan and Subramanian (2016) suggested that zeolite-encapsulated NFs enhance the efficiency of nitrogen. A novel nitrogen NF was developed using urea-coated hydroxyapatite nanorods for targeted and sustained nutrient release (Kottegoda et al. 2017).

Like nitrogen, phosphorus is also critical macronutrients essential for growth and development of plants. Phosphorus NFs offer a sustainable and efficient approach to nutrient management, surpassing traditional fertilizers in delivering essential nutrients to crops. Employing slow-release phosphorus NFs can optimize phosphorus utilization throughout the crop lifecycle, thereby conserving this essential resource (Saraiva et al. 2022). Nano-rock phosphate demonstrated comparable phosphorus utilization efficiency to superphosphate while offering cost-benefits in maize cultivation (Adhikari et al. 2014). For the synthesis of fungal-mediated P-NPs, tricalcium phosphate was utilized as a precursor by Tarafdar, Raliya, and Rathore (2012). Phosphorus NFs derived using natural phosphorite, produced using ultrasonic dispersion, demonstrate effective seed treatment benefits (Sharonova et al. 2015). Hydroxyapatite NPs coated with spherical carboxymethyl cellulose significantly enhanced soybean growth and yield by improving phosphorus availability compared to conventional soluble phosphate fertilizers (Liu and Lal 2014). Research on Ca-phosphate-based phosphorus fertilizers has highlighted the influence of ionic strength, pH, calcium-to-phosphorus ratio, and NP size on hydroxyapatite solubility (Tang and Fei 2021) and nearly doubles the nutrient use efficiency.

Magnesium also plays a crucial role in photosynthetic processes, activation of enzymes, and in synthesizing protein. Chlorophyll, the green pigment essential for photosynthesis, incorporates magnesium as a key component (Liao et al. 2021). Some of the Mg-based NFs, like Mg-oxide and Mg-sulfate, effectively enhance the growth and productivity of crops, nutritional values of vegetable and fruits, and bolster natural defenses against disease and pests. Anand et al. (2020) investigated the potential of magnesium oxide NPs to enhance mung bean seed germination. MgO NFs release free radicals. The antioxidant enzymes neutralize the free radicals and protect the chloroplast membrane (Cai et al. 2018). Delfani et al. (2014) conducted a factorial experiment involving three replications to evaluate the interactive effects of varying iron and magnesium concentrations. They observed the significant enhancement in yield, Fe content in leaves, Mg content in stem, chlorophyll content, and membrane integrity. Varamin et al. (2018) studied the impact of chitosan and Mg-based NFs under stress condition on sesame plants and observed significant enhancement in chlorophyll, proline, protein, soluble sugar, and carotenoid level, while also boosting enzyme activity.

Sulfur is also a vital macronutrient essential for numerous plant processes, including protein synthesis, activation of enzymes, vitamin production, and hormone regulation. Like Mg, sulfur also enhances plant defense against pests and disease (Ingenbleek and Kimura 2013). There are several sulfur-based NFs. Some of these are produced by encapsulation of elemental sulfur or sulfur compounds like urea and potassium sulfate within a nanomaterial matrix (Li et al. 2019). Sulfate-based NFs enhance the uptake and utilization of sulfur in groundnut, leading to improved root, shoot, kernel, and shell development as compared to conventional sulfur sources. Thirunavukkarasu et al. (2018) observed that when applied sulfur-encapsulated NFs, uptake of sulfur by root, kernel, and shoot was more compared to that of traditional fertilizer.

The microscopic size potassium nanofertilizers, often called nano potassium, allows for deeper soil penetration, facilitating direct nutrient delivery to plant roots. This results in enhanced absorption rate, leading to faster and more efficient nutrient delivery to plants compared to traditional fertilizers. Other than these, potassium-encapsulated NFs exhibit superior leaching resistance and water solubility compared to traditional potassium fertilizers, ensuring efficient nutrient retention within the soil (Sheoran et al. 2021). Foliar application of monopotassium significantly enhanced chlorophyll biosynthesis in peanuts.

1.4.2.3 Nano-biofertilizers

Biofertilizers are microbial formulations that enhance soil fertility by fixing atmospheric nitrogen, producing growth hormones, and solubilizing phosphorus. Hence, the integration of biofertilizers with NT has led to the development of nano-biofertilizers (Kumari and Singh 2019; Simarmata et al. 2016). Biofertilizers offer a sustainable and eco-friendly alternative to traditional chemical fertilizers by providing essential plant nutrients through microbial activity. The synergistic interaction between microbes and NPs, along with their controlled release and transport properties, are three crucial determinants of nano-biofertilizer efficacy. Biofertilizers encompass diverse microbial groups, including mycorrhizal fungi, phosphorus-solubilizing bacteria, nitrogen-fixing bacteria, and plant growth–promoting rhizobacteria (PGPR), but PGPR, like rhizospheric and endophytic bacteria, have been primarily explored in this domain (Ali et al. 2021) as it enhances plant growth by improving nutrient uptake, bolstering stress tolerance, and activating plant defense mechanism against pathogens (Castro et al. 2018; Redman et al. 2002; Batista et al. 2018; Waller et al. 2005). Nano-biofertilizers are fabricated by encapsulating nutrients or growth-promoting bacteria within a polymer matrix through nanoencapsulation methods to optimize nutrient uptake and minimize losses. Chitosan and Zeolite are commonly used encapsulating agents (Iqbal 2019). Gahoi et al. (2021) engineered a nanocomposite biofertilizer by encapsulating bacterial endospores and iron–carbon nanofibers coated with homoserine lactone within an activated carbon matrix and applied on legumes and nonlegumes plants. After 30 days of the experiment, significant enhancement in biomass, length of root, chlorophyll content, and protein accumulation was observed. In an investigation, *Pseudomonas putida*, when applied to gold NPs coated with PGPRs, showed no observable changes on the plant because of their harmful effect (Duhan et al. 2017) on microorganism. However, enhancement of growth parameters in *B. subtilis, Paenibacillus elgii*, and *Pseudomonas fluorescens* was noticed (Shukla et al. 2015). The emulsified hydro-repellent silica nanoscale particles have demonstrated enhanced biofertilizer delivery and extended cell longevity by preventing moisture loss (Kaushik and Djiwanti 2017). Due to the large size of microbe compared to NPs, macroscopic filters constructed from multiwalled CNTs are used for adsorption and capture of *Escherichia coli* (Srivastava et al. 2004). Gatahi et al. (2016) observed that *Ralstonia solanacearum*, a wilt pathogen, infected tomato plant when treated with nano-biofertilizers, and the infected plants exhibited enhanced wilt resistance. The fungal and nematode infectious rabi crops can be recovered by applying nanoclay-coated biofertilizer encapsulated with *Pseudomonas* sp. and *Trichoderma* sp. They also enhance the plant tolerance to abiotic stress. Nano-biofertilizer formulations leverage the unique surface chemistry of NPs, characterized by a net negative charge with both positive and hydrophobic domains (Kurdish 2019). These properties influence NP aggregation and binding to bacterial cell membranes, primarily through hydrophobic interactions (Hayden et al. 2012). Bacterial-NP interactions involve not only electrostatic force but also surface chemical reactions, including interactions with the phospholipid membrane (Palmqvist et al. 2015). Smart seeds, encapsulating specific bacterial strains, offer enhanced crop performance by reducing seeding rates. These seeds can be evenly distributed across fields and programmed to germinate under optimal environmental conditions (El-Ramady et al. 2018; Chinnamuthu and Boopathi, 2009). Nano-biofertilizer offers distinct advantages over conventional biofertilizers: (i) nanoformulation significantly enhances the longevity of biofertilizers; (ii) it also enhances biofertilizer resilience to desiccation, heat stress, and ultraviolet (UV) radiation; (iii) nano-biofertilizers offers precise control over nutrient delivery and release; (iv) nanoformulation enhances rhizosphere bacterial activity, leading to improved soil condition; (v) improves plant resistance against abiotic and biotic stresses; (vi) retains soil hydration; and (vii) enhances siderophore production (Shukla et al. 2015; Malusá, Sas-Paszt, and Ciesielska 2012).

1.5 Challenges and Future Outlook

Despite the benefits of NT, there are some demerits too, influenced by different factors, such as shape, size, chemical composition, and doses. Nanomaterials interact with organic matter and particles in soil, like altering its structure and nutrient cycling processes (Sun et al. 2021). Some studies have shown that while these nanomaterials improve nutrient delivery and promote plant growth, certain NPs, like silver and copper NPs, can have adverse effects on beneficial soil earthworms, aquatic organisms, and microbes, potentially disrupting ecological balances and negatively impacting biodiversity in agricultural ecosystems. Also, there are concerns regarding the potential accumulation of NPs in the environment and food chain, posing risks to nontarget organisms, ecosystems, and human health (Francis et al. 2024; Parada et al. 2018). In lettuce leaves, the accumulation of copper NPs negatively impacts the plant growth and photosynthesis, affects antioxidant system activity, and increases ROS accumulation (Xiong et al. 2021). Similarly, Yusefi-Tanha et al. (2024) observed size-dependent toxicity of soil-applied nCuO (copper oxide NPs) in soybean (*G. max* L.). The smaller nCuO exhibited higher inhibitory effects on photosynthetic pigments, seed yield, and nutrient accumulation, with increased root and seed Cu bioaccumulation leading to oxidative stress. Structural alterations in seed oil bodies and protein storage vacuoles were also observed during TEM analysis. In zebrafish embryos, developmental abnormalities have been observed due to oxidative stress when administering gold NPs at concentrations of 1 mg/L (Strungaru et al. 2018). Similarly, silver NPs have been found to reduce the reproduction rates and survival of *Lumbriculus variegatus* at concentrations of 1098 mg/kg (Francis et al. 2024). Another NP, CNT, can enhance seed germination and plant growth, but they may also form ROS that can potentially harm plant tissues, consequently leading to cell death. Overtime, CNT accumulation in soil also impacts the microbial diversity, population, and composition in soil (Vithanage et al. 2017). The judicious release of nanomaterials into the ecosystems and understanding their sustainability and biodegradation in environmental fate will definitely benefit all its stakeholders in the long term and will mitigate the ecological imbalances with robust risk management strategies (Wahab et al. 2024).

1.6 Conclusion

NT has emerged and exhibits great potential towards each and every aspect of modern agriculture practices and food industries. To ensure food security, various NT modalities have been developed as sustainable tools for agriculture production. This chapter discusses the drawbacks of conventional agriculture practices and advantages of NT for sustainable agriculture. Further in the preceding major sections, this chapter provides a plethora of nanomaterial fabrication techniques and subsequent utilization of these advanced nanoscale materials like NFs, nanocides, and nanosensors to ensure slow and sustained delivery of active agents, endorsing soil permeability, low rain-fastness, and higher nutrient uptake. Apart from the beneficial aspect, there are some issues also associated with NT in agriculture. Difficulty in scalability during nanomaterial synthesis is one of them. Owing to their higher reactivity, nanomaterials may also pose phytotoxicity and bioaccumulation in target crops or nearby other flora and fauna. However, as compared to controlled studies in a laboratory set-up, the physicochemical behavior of these nanomaterials in an open ecosystem are poorly investigated. Although green nanotechnologies described in this chapter are advantageous in agriculture, in few cases, synthesized nanomaterials using green methods are not green at all. As far as ecosystem health is concerned, nanotoxicity linkage with populations including humans must also be considered. All these aforementioned possible facts must be considered while designing and developing nanoscale materials for agricultural application. Additionally, cost-effective NT is the need of the hour for sustainable development in the field of agriculture, and these developing NT shall be thoroughly tested for the benefits and risks associated with their sustainability and biodegradability in the environment.

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