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Applications of diverse nanoparticles in agriculture

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Abstract
Agriculture is a critical pillar of the global economy and it is facing various challenges such as climate change, soil contamination and increasing food demands due to population growth. Nanotechnology offers immense potential to modernize agriculture by introducing nanomaterials (NMs) like nanoparticles (NPs), nanotubes, etc. Their dimensions range between 1-100 nm and possess unique physicochemical properties like large surface area to volume ratio, increased sensitivity and better detection limits making them valuable for precision agriculture. Synthesis of NPs can be achieved by physical, chemical and biological methods like green synthesis of NPs. The uptake of nanomaterials in plants depends on plant physiology, property of the NMs and their interactions with plant systems. Thus, comprehensive understanding of these interactions and optimization of delivery methods can enhance their utility in sustainable agricultural practices. Different types of NPs exhibit different responses in plants like promotion of seed germination, elongation of roots, increased nutrient uptake, etc. Many metal oxide NPs like TiO_2, SiO_2, etc can even alleviate stress caused by drought, salinity, heat and oxidative damage. Nano pesticides like nanoherbicides, nanoinsecticides and nanofungicides are eco-friendly, prevent runoff and ensure slow release for prolonged action. Nano fertilizers can tackle nutrient deficiencies or low yields, offering controlled release and enhanced nutrient use efficiency (NUE). Nanosensors offer real-time monitoring of crop growth, pollutants and plant disease detection. This review focusses on the immense application of nanotechnology in the field of agriculture, highlighting its potential as an alternative to traditional agricultural practices ensuring sustainable agriculture with increase in crop yield. Nanomaterials are beneficial to plants at certain optimal levels, but pose the risk of phytotoxicity, bioaccumulation and risk to the ecosystem. Further research is pivotal to understand safer concentration, effects on our food chain, biosynthesized alternatives and measures to reduce toxicity.
Keywords: *Nanomaterials, Nanoparticles, Green synthesis, Nano pesticides, Nano fertilizers, Nanosensors, Sustainable agriculture*

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I. Introduction

The issue of food security has become a worldwide concern today with the exponential increase in human population along with the ongoing climate crisis. Predictions show that food demand is likely to rise from 59 to 98 % for the world population, reaching 9 billion by 2050 (Duro et al., 2020). The conventional approach for the improvement of crop productivity to sustain the growing population is through the application of bulk chemical fertilizers, synthetic, inorganic and mineral fertilizers, as well as pesticides. However, it has been established that only a small percentage of the chemical fertilizers and pesticides applied contribute to crop production (Raliya et al., 2018). Even though bulk use of chemical fertilizers might offer potential yield enhancement, it changes soil chemical properties and affect the richness, diversity or abundance of soil microbial communities, which are normal indicators of fertile soil (Dincă et al., 2022).

Recently, the use of nanotechnology in agriculture appears as an emerging alternative to conventional bulk chemical fertilizers and pesticides used in agriculture (Kalwani et al., 2022). It is possible to potentially introduce nanofertilizers and nanopesticides due to the large surface area to volume ratios, mass transfer abilities as well as slow, controlled and targeted delivery of nanomaterials even at lower nutrient or pesticide concentrations to enhance crop productivity if used appropriately (Hussain et al., 2023).

For sustainable farming, scientists have come up with a whole range of nanoparticles (NPs) such as AgNPs, AuNPs, CuNPs, ZnONPs, and Fe_3O_4NPs, among many others. There are other NPs that are crucial in the drive for sustainable agricultural practices through the improvement of efficiency and productivity in the agricultural sector, including quantum dots (QDs), silica nanoparticles (SiNPs), carbon nanotubes (CNT), polymeric nanoparticles and liposome-based NMs. There are different types of methods for synthesis of NPs; green synthesis method presents an ecofriendly and cheaper way for NP production, compared to the physical and chemical methods. Benefits, such as higher tolerance to biotic and abiotic stresses, improved plant germination, enhanced growth and nitrogen fixation will lead to healthier crops with higher yields. Besides that, these NPs also play a great role in improving soil characteristics for a sustainable and balanced ecosystem.

Although most NPs are used without any chemical coatings, these surface coatings have an impact on their physicochemical characteristics such as solubility, degradation, endocytosis and fate once inside the plant cells. Coatings enhance NP stability, improve targeted delivery to cells and reduced toxicity, thereby promoting safer applications. This highlights a growing focus on tailoring NP coatings for agricultural purposes. (Cartwright et al. 2020). However, inappropriate dosages of NPs or their formulations have been found to produce negative effects in plants, either in the form of toxicity or poor growth. Hence, one requires careful application methods and dosage for achieving their full potential without having disastrous effect on plants. This indeed equates very well on how the correct method of application of NPs depends on the type of NPs applied on plants for achieving better utility and finally attain sustainable agriculture (Fig. 1).

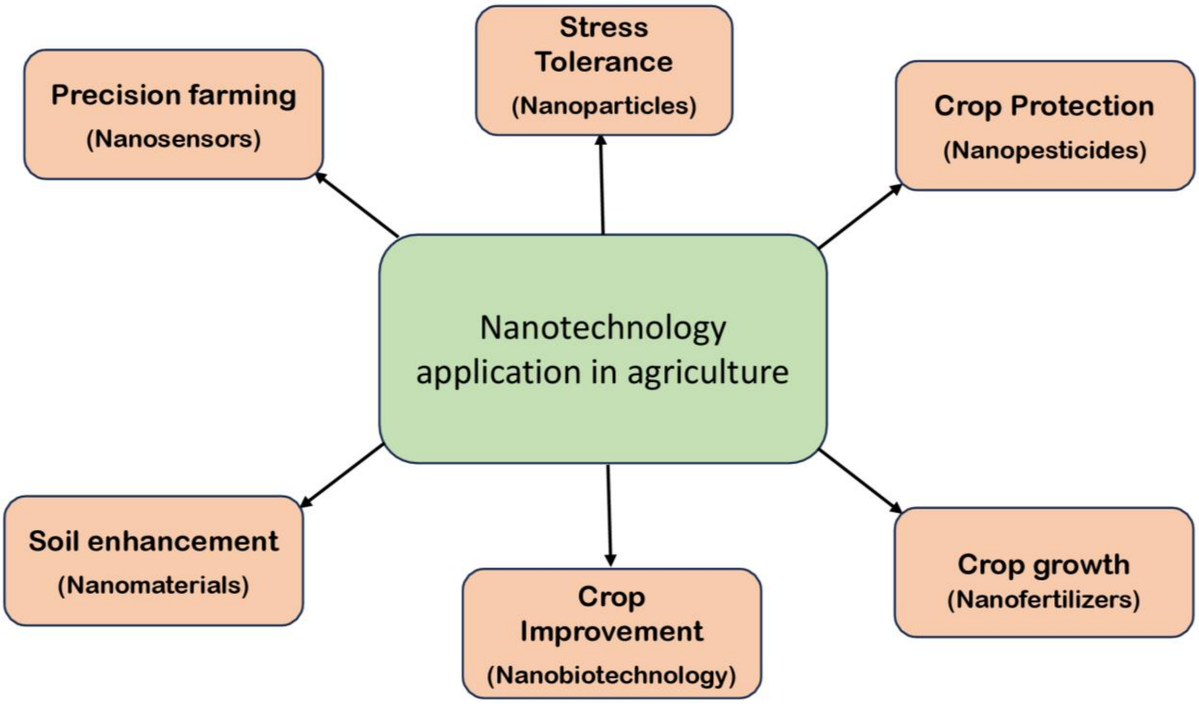

Fig. 1: Various applications of nanotechnology in agriculture

1. Synthesis of NPs

Metal NPs can be synthesized using physical, chemical or biological methods through bottom-up or top-down approaches. These techniques include precipitation, microemulsion, ball milling, ultrasound, laser ablation, sputtering, sol-gel, mechanical milling, biosynthesis, etc. Despite such dynamic approaches, physical and chemical methods often face challenges like NP stability and size uniformity in addition to being expensive, resource-intensive and environmentally hazardous due to emission of toxic chemicals (Kaningini et al. 2022).

1.1 Physical methods

Physical methods for NP synthesis involve mechanical, thermal or electrical energy to create uniform monodisperse NPs or NPs avoiding solvent contamination, but they generate significant amount of waste. Techniques include high-energy ball milling (HEBM), inert gas condensation (IGC) and physical vapor deposition (PVD), such as sputtering, electron beam evaporation and pulsed laser deposition (PLD). Other methods include laser pyrolysis, flame spray pyrolysis, melt mixing, etc (Dhand et al. 2015).

1.2 Chemical methods

Chemical methods for NP synthesis include sol-gel processing, microemulsion techniques, hydrothermal synthesis, polyol processes, chemical vapor synthesis (CVS) and plasma-enhanced chemical vapor deposition (PECVD). Among these, the sol-gel method and microemulsion techniques are most commonly used due to their simplicity, scalability and ability to produce uniform NPs. Hydrothermal synthesis is cost-effective and suitable for large-scale production, while polyol processes creates uniform metal and oxide NPs. CVS and PECVD are specialized methods for high-purity and doped NPs in advanced applications (Dhand et al. 2015).

1.3 Green Synthesis of NPs

Biosynthesis of NPs using plant extracts or green synthesis is a rapid, eco-friendly and non-toxic method leveraging plant biometabolites as reducing and stabilizing agents (Dhand et al. 2015). It is a part of green chemistry that brings together plant sciences with nanotechnology for the synthesis of NPs at neutral pH, room temperature and at a minimal cost (Kaningini et al. 2022). This approach minimizes environmental hazards, provides sustainable applications and offers versatility in tailoring NP properties (Dhand et al. 2015). The synthesis of metal nanoparticles (MNPs) involves three key components: reducing agents, stabilizing agents and a solvent medium which is generally an aqueous method. In plant extract-mediated MNP synthesis, phytochemicals in the extracts function as both reducing and stabilizing agents. As diverse phytochemicals are used in plant extracts, it becomes challenging to identify specific bioreducing and stabilizing agents, responsible for MNP synthesis. Polyphenols like flavonoids, phenolic acids, terpenoids, organic acids and proteins play important roles in reducing and stabilizing MNPs (Ovais et al. 2018). Plants, bacteria, fungus and algae substrates are being used extensively as alternatives to chemical solvents and stabilizers that diminishes the toxicity of the product and the synthesis process. These synthesized NPs can be either carbon-based or metal-based of which metal-based NPs are the most commonly used (Kaningini et al. 2022).

II. Metal NPs

2.1 Zinc oxide NPs

Zincite has gained importance and used in several industrial sectors. ZnO NPs have been used in many devices like gas sensing, solar cell preparation, electrical devices, chemical absorbents, hydrogenation catalysts, photocatalytic degradation and optical devices. ZnO NPs also possess antimicrobial activity against many microbes (Kaningini et al. 2022).

2.1.1 Synthesis of ZnONPs

Zinc oxide nanoparticles (ZnONPs) can be synthesized through many routes including chemical, physical or biological methods. Physical methods for synthesizing ZnONPs include laser ablation, vapor deposition, arc plasma, ultrasonic irradiation, thermal evaporation, etc. Laser ablation, known for its simplicity and purity depends on factors like ablation time, fluence and wavelength. Thermal evaporation, a cost-effective and catalyst-free method produces various ZnO morphologies like nanorods, nanotubes etc (Król et al. 2017). Chemical methods include sol-gel synthesis, precipitation, hydrothermal techniques, etc which are used widely. Sol-gel synthesis uses a zinc precursor salt that can be nitrate, sulphate or chloride and a chemical reagent for maintaining the pH of solution and avoiding the precipitation of $Zn(OH)_2$. The solution is subsequently exposed to thermal treatment to obtain the ZnONPs (Bandeira et al. 2020). Capping agents and stabilizers like polyethylene glycol, tetraethyl ammonium bromide, etc are used for controlling the size of the NPs and preventing agglomeration (Naveed Ul Haq et al. 2017).

2.1.2 Green synthesis of ZnOPs

The process is largely dependent on the precursor materials such as alkaloids and phenolic compounds. Green synthesis of ZnO NPs suggests that these compounds present in the plant extracts react with zinc salts to reduce the metal or form complexes. A possible mechanism is that antioxidants like flavonoids, limonoids and carotenoids chelate zinc (II) ions and form a metal-coordinated complex which is subjected to thermal treatment and finally degrades to form zinc oxide (Bandeira et al. 2020). ZnO NPs have been synthesized using extract of *Trifolium pratense* (red clover) flower and using the milk latex of *Carica papaya* to form variable-shaped ZnO nanoflowers with antibacterial activity (Ahmed et al. 2017). ZnO NPs from *Euphorbia prolifera* leaf extract was effective in waste water treatment as it was able to degrade dyes like methylene blue and congo red (Momeni et al. 2016). *Carissa edulis* ZnONPs were capable of 97% photocatalytic degradation of congo red dye (Fowsiya et al. 2016), while those synthesized from *Nephelium lappaceum* L. peel extract exhibited photocatalytic activity against methyl orange (Karnan and Selvakumar 2016). ZnONPs from *Aloe barbadensis* leaf extract showed strong antibacterial activity, demonstrating potential as highly effective nano-antibiotics (Ali et al. 2016b). Leaf extract from *Azadirachta indica*, *Vitex negundo* and flower extract from *Anchusa italica* or *Jacaranda mimosifolia* produced ZnONPs that also showed strong antimicrobial activity, while extracts from *L. leschenaultiana* produced ZnONPs that were effective in killing *Rhipicephalus microplus*. *Polygala tenuifolia* root extract yielded ZnONPs with antioxidant and anti-inflammatory properties (Ahmed et al. 2017). Sunlight-driven synthesis using mangrove plants (*Heritiera fomes* and *Sonneratia apetala*) produced ZnONPs with biomedical potential (Thatoi et al. 2016). The biosynthesis of ZnONPs using microbial cultures occurs through either extracellular or intracellular mechanisms where extracellular synthesis remains the preferred route for production due to its simplicity and efficiency (Bandeira et al. 2020). In extracellular synthesis, enzymes and proteins secreted by microorganisms reduce metal ions and stabilize NPs, preventing agglomeration. *Bacillus licheniformis* produces enzymes that stabilize ZnONPs formed from zinc acetate and sodium bicarbonate (Tripathi et al. 2014), while ureolytic bacteria

like *Serratia ureilytica* use ammonia to create zinc hydroxide and zinc-ammonia complexes which are thermally decomposed into ZnONPs (Dhand et al. 2015). Intracellular synthesis involves microorganisms internalizing metal ions which are reduced by cellular proteins and enzymes to form NPs (Hulkoti and Taranath 2014).
Fungal biomass or culture is also used for production using a similar mechanism to bacterial biosynthesis. *Aspergillus fumigatus* has been used to synthesize ZnONPs with the help of the proteins and enzymes secreted by the fungus (Raliya and Tarafdar 2013); *Aspergillus niger* cell-free filtrate has been used for extracellular biosynthesis of ZnONPs (Kalpana et al. 2018).
Algae contain certain phytochemicals with functional groups such as hydroxyl and carboxyl groups that contribute to their antioxidant activity and used as reducing and stabilizing agents in the green synthesis of ZnONPs. The mechanism of ZnONP formation in algae is similar to that of plants (Bandeira et al. 2020).

2.1.3 Application of ZnONPs

The application of ZnONPs has shown immense potential in enhancing plant growth and yield. ZnONP treatments on peanut seeds showed signs of improved germination, root and shoot growth, dry weight and pod yield. This implies that such application of nanoscale nutrients via seed dressing or foliar application can achieve desired outcomes even at very lower doses (Jayarambabu and Rao 2019). In gram and mung seedlings, ZnONPs was seen to promote root and shoot growth and when applied at optimal concentration increase in biomass production was observed. These treatments with ZnONPs ensured the maintenance of normal root architecture with no adverse effects on structural development (Mahajan et al. 2011). The generation of reactive oxygen species (ROS) in plants is measured through the levels of H_2O_2 and it varied with different concentrations of ZnONPs used. FeZnONPs reduced H_2O_2 levels in roots, indicating reduced stress levels in green pea roots, while only ZnONPs caused an increase in H_2O_2 production in leaves. The doped ZnONPs thus showed lesser stress compared to bare ZnO NPs which may be due to lesser Zn bioaccumulation inside the plant tissues. Moreover, FeZnONP treatments in stems and leaves did not affect H_2O_2 generation (Mukherjee et al. 2014; Jayarambabu and Rao 2019). ZnONPs act as growth promoters in cotton (*Gossypium hirsutum L.*). Some ZnONPs carrying phycomolecule ligands act as novel growth enhancers, improving crop productivity and holding significant role in agriculture applications. Such treated plants showed increased levels of carotenoids, chlorophyll a, superoxide dismutase (SOD) and peroxidase (POX) but decreased levels of catalase (CAT) and malondialdehyde. These effects may be due to increased activity of antioxidant defense enzymes that reduced the levels of reactive oxygen species (ROS) (Venkatachalam et al. 2017).

Studies have highlighted the effects of ZnONPs on plant growth and development like improved fresh weight and dried weight in *Cicer arietinum* seedlings (Kaningini et al. 2022) and significantly enhanced the viability and growth of tobacco plants (Balážová et al. 2020). At higher concentrations like 2000 ppm, the NPs showed toxic effects on growth and yield of peanut plant but no such impact was seen in *Cucurbita pepo* (Prasad et al. 2012). Improved seed germination and root development along with increase in plant growth was observed in plants like *Trigonella foenum-graecum* and *Brassica juncea*. In *Zea mays L.*, it increased protein content that improved photosynthesis and plant development (Kaningini et al. 2022). Concentration of 1000 ppm speeded up early plant development by increasing seed germination and seedling vigor as seen from early flowering and increased chlorophyll concentration in leaves (Prasad et al. 2012).

2.2 Silver NPs

Silver NPs (AgNPs) are versatile and extensively used in nanotechnology due to their broad range of bioactivities finding application in various fields such as agriculture, textiles and medicine. They possess optical, electrical and thermal properties, high conductivity, etc and are used in composite fibers, cryogenic superconductors, and food packaging and electronic devices due to their chemical stability and catalytic efficiency. They also possess antimicrobial properties and can be potentially used in combating resistant pathogens and boosting resistance to fungal, bacterial and nematode attacks. They are also seen to improve seed germination, thereby finding potential applications in agriculture (Ahmed et al. 2016) (Kaningini et al. 2022).

2.2.1 Synthesis of AgNPs

Physical methods such as evaporation-condensation and laser ablation approaches are some major methods utilized for synthesizing AgNPs. These methods avoid the problem of solvent contamination and ensure uniform distribution of NPs. Another method known as laser ablation in liquids produces pure, uncontaminated metal colloids without the requirement of any chemical reagents. Another method is arc discharge which can produce AgNPs (size ~ 10 nm) in deionized water without the use of surfactants and metal sputtering technique that produces uniformly dispersed NPs (size ~ 3.5 nm) (Iravani et al., 2014).

In chemical reduction method, silver ions (Ag^+) are reduced to metallic silver (Ag^0) using chemicals like sodium citrate and sodium borohydride, forming colloidal silver particles. Stabilizers such as polyvinyl alcohol and polyvinylpyrrolidone prevent agglomeration while processes like precursor injection and hyper-branched polymers are employed for controlling the size (Iravani et al, 2014). In microemulsion method, the reactants are spatially separated into two immiscible phases and the NPs form at the interface. This approach ensures controlled size and stabilization of AgNPs (Zhang et al. 2008). Electrochemical reduction enables precise control over NP size and distribution by controlling electrolysis parameters and electrolyte composition (Chen et al. 2014). Photoreduction techniques use UV irradiation to reduce silver salts in the presence of stabilizers such as polyvinylpyrrolidone or citrate (Iravani et al, 2014). Another method of synthesis is photoinduced reduction where light is used to generate NPs in polymer films or emulsions and form complex nanoprism arrays (Sato-Berrú et al. 2009). Electrochemical methods enable synthesis of NPs by adjusting electrolysis parameters and stabilizers like poly N-vinylpyrrolidone. Nanoparticles (1–30 nm) are synthesized using liquid-liquid reduction, irradiation using UV or gamma rays and microwave-assisted techniques for applications in sensing and antimicrobial applications (Iravani et al, 2014).

2.2.2 Green synthesis

Various plant parts such as peel, seed, fruit, bark, flower, stem and root have been utilized to achieve green synthesis. Leaf extracts of *Eugenia jambolana* are used to synthesize AgNPs by the activity of alkaloids, flavonoids, saponins and sugars present in it. Bark extract of *Saraca asoca* has hydroxylamine and carboxyl groups that are crucial for NP formation. Leaves of *Rhynchotechum ellipticum* contribute polyphenols, terpenoids and steroids. Extracts from fruits like *Malus domestica* and *Vitis vinifera* have also been used as reducing agents. Some other reducing agents like pepper leaf extract and combinations of various plant sources are also used. Non-plant-based reducing agents like polysaccharides, starch and natural rubber further broaden the methods of synthesis (Ahmed et al. 2016).

Bacteria-mediated synthesis of AgNPs is eco-friendly, thus gaining importance. The site of synthesis can be intracellular or extracellular. AgNPs were synthesized intracellularly using *Rhodococcus sp.* NCIM 2891 (Otari et al. 2015) while extracellular biosynthesis was achieved using *Bacillus subtilis*. Despite its advantages, challenges like contamination, lengthy procedures and limited control over size of NPs persist (Kannan and Subbalaxmi 2011). Microscopic planktonic algae to large macroscopic forms have been utilized for the green synthesis of AgNPs. Microalgal species such as *Chaetoceros calcitrans, C. salina, Isochrysis galbana* and *Tetraselmis gracilis* have been used for synthesis due to their repertoire of natural biomolecules that act as reducing and stabilizing agents (Merin et al. 2010). Synthesis using *Cystophora moniliformis,* which is a marine algae is an eco-friendly and sustainable method of synthesis (Prasad et al. 2012). Fungi also play an important role in the extracellular synthesis of AgNPs and the process is relatively cost effective and suitable for large-scale production. They are sometimes preferred over bacterial synthesis due to their superior tolerance to metals and better bioaccumulation ability (Ahmed et al. 2016).

Novel methods use DNA as an innovative reducing agent in the synthesis of AgNPs. DNA have a strong affinity for silver ions due to its guanine bases and phosphate groups that behave as a template stabilizer for NP formation. Calf thymus DNA was also experimented for this purpose. Along with DNA, silver-binding peptides have been identified for NP synthesis. These peptides stabilize and control NP formation in a unique way that is eco-friendly (Ahmed et al. 2016).

2.2.3 Applications

AgNPs are known to exhibit remarkable optical, thermal and electrical properties like high electrical conductivity along with antimicrobial and catalytic capabilities. Biosynthesized AgNPs exhibit antimicrobial activity to combat phytopathogens (Paul and Roychoudhury 2021). AgNPs in agriculture have shown improved crop productivity, better seed germination, plant growth, photosynthetic efficiency and better water and fertilizer utilization (Kaningini et al. 2022). AgNPs are valued for their chemical stability, conductivity, catalytic efficiency and notable antibacterial, antiviral, antifungal and anti-inflammatory properties (Ahmed et al. 2017). When applied to plants, silver ions released by AgNPs affect plant morphology and physiology, increasing resistance to fungal, bacterial and nematode infections (Gruyer et al. 2014). In *Trigonella foenum-graecum* (fenugreek), AgNP treatment showed enhanced seed germination and increase in biomass, while in *Brassica juncea* and cowpea, specific concentration of AgNPs showed improved growth, fresh weight and root nodulation. They also served as bactericides and fungicides due to their ability to attach to microbial cells. DNA-directed AgNPs on graphene oxide showed antibacterial activity against *Xanthomonas perforans* which is a pathogen for tomato plants (Kale et al. 2021). Common bean and corn plants treated with AgNPs showed different growth patterns that pointed towards a concentration-dependent NP uptake with maximum effect observed at 60 ppm. This study was instrumental in defining a modulating role of the HO/NO signal system in mitigating stress induced by AgNPs or $AgNO_3$ during inhibition of seed germination in *Brassica nigra*. It also highlighted the up regulation of mRNA HO-1 expression along with increase in NO production that is seen to improve tolerance towards AgNP or $AgNO_3$ induced stress (Falco et al. 2015).

Biogenic NPs are known to promote germination across many plants with AgNPs showing a significant increase in rate of germination in *Boswellia ovalifoliolata*. AgNPs can create pores in the seed coat that makes it easier for influx of nutrients and stimulation of embryo, thereby promoting faster germination and seedling growth. At 25–50 ppm concentration of AgNPs, studies have reported increase in root length, shoot length and vigor index in *Phaseolus vulgaris*. AgNPs can also enhance germination, early seedling growth and biochemical properties in *Triticum aestivum* seeds *(*Jayarambabu and Rao 2019*)*.

2.3 Copper NPs

Copper oxide NPs exist mainly in two forms, viz., copper (II) oxide (CuO) and copper (I) oxide (Cu_2O). They possess certain unique properties such as high temperature superconductivity, spin dynamics, electron correlation, etc and thus suitable for using in gas sensing, energy storage, solar energy conversion and field emission (Ren et al. 2009). These NPs have high surface-to-volume ratio and renewable surface properties that make CuO NPs good catalysts; their antimicrobial properties make them valuable tools in medicine and wastewater treatment (Kaningini et al. 2022). Other applications span across various fields like optics, electronics and manufacturing along with their use as lubricants, nanofluids and in conductive films (Din and Rehan 2017).

2.3.1 Synthesis of CuNPs

CuNPs have been synthesized using both physical and chemical techniques. Physical methods include laser ablation, radiolysis and aerosol techniques and these need expensive equipment and high energy consumption, limiting their practicality. Among chemical methods, microemulsion technique is the most widely used, but it requires high concentration of surfactants that further adds to the cost. Another approach consists of synthesis via microwave irradiation without a stabilizing agent. Such NPs are formed by the reduction of copper oxide by ascorbic acid. Surfactants like polysorbate 40 and 60 help in micelle formation for copper ion diffusion and controlling particle size and shape. These methods generate byproducts that are hazardous to the environment (Din and Rehan 2017).

2.3.2 Green synthesis

CuNPs are synthesized from various plant sources. CuNPs from *Artabotrys odoratissimus* extract have sizes ranging from 109–135 nm at 95°C . *Nerium oleander* and L-ascorbic acid are used as reducing and stabilizing agents (Umer et al. 2014; Din and Rehan 2017). *Datura metel* leaf extract can be used for synthesis by using potato starch as a stabilizing agent at room temperature and L-ascorbic acid and NaOH acted as catalysts (Din and Rehan 2017). The bark extract of *Terminalia arjuna* has been used to synthesize 23 nm CuNPs, while leaf extract of *Magnolia* served as a reducing and stabilizing agent (Yallappa et al. 2013). Other methods employed $CuSO_4$ as a precursor compound and curd, milk, soap nut, lime juice and tamarind juice acted as capping agents in acidic solutions (Din and Rehan 2017). *Pseudomonas stutzeri* produced spherical NPs. They were isolated from wastewater and formed cubic NPs used in electroplating (Varshney et al. 2012). *Morganella* was used in an aqueous environment to form polydispersed CuNPs (Din and Rehan 2017). Fungi like *Aspergillus* species were capable of forming CuNPs. Other species isolated from soil like *Penicillium vaksmanii*, *Penicillium aurantiogriseum* and *Penicillium citrinum* were used for synthesis. Certain factors like pH, monodispersity and concentration dictated NP morphology (Din and Rehan 2017).

2.3.3 Applications

CuONPs have high surface-to-volume ratio and other catalytic properties and thus find application in medicine and wastewater treatment due to their antimicrobial activity against microorganisms like *Bacillus subtilis* (Jayarambabu and Rao 2019). CuONPs showed positive effects on the growth of soybean and chickpea seedlings and optimal growth was observed at certain specific concentrations of 100 ppm and 60 ppm, respectively. Beyond these optimum concentration, growth was seen to be hindered (Jayarambabu and Rao 2019). Cu-chitosan NPs have a stable and porous structure and was observed to promote tomato seed germination, growth of seedlings and increase in biomass. It also exhibited strong antifungal activity against *Alternaria solani* (early blight), *Fusarium oxysporum* (wilt) in tomatoe and *Citrus black rot* (Alternaria citri) with synergistic effects when combined with ZnONPs (Lasso-Robledo et al. 2022). Pot experiments also revealed its potential for effective fungal disease management in agriculture (Saharan et al. 2015). The interaction of CuONPs with rice plants showed their penetration into root tissues not via casparian strips, but through lateral roots that acted as an alternate pathway for their translocation into the stele. CuONPs were also transported to leaves and chemically modified with ligands like cysteine, citrate, etc (Peng et al. 2015). Copper-based NPs show minimal immediate impact on soil, but may affect ammonia-oxidizing microbes with repeated use. More field studies are needed to confirm such long-term effects. Cu-based NPs combined with growth enhancers like kinetin showed potential impacts on the nutritional value of crops like common beans (Lasso-Robledo et al. 2022).

CuONPs have shown potential as nanofertilizers for root and tuber crops like sweet potato, but require further research under natural soil conditions to optimize their usage (Bonilla-Bird et al. 2020). The response to CuNPs differs across plant phenotypes and environment. Studies with foliar applications in plants like mustard and soybean was observed. Cu uptake and plant responses depend on surface coatings and phenotypic traits such as anthocyanin content (Lasso-Robledo et al. 2022). The response of seed-producing plants like soybean and common bean to CuONP exposure is different compared to vegetatively propagated plants like sugarcane. Additives such as silicon and NaHS have shown potential in mitigating oxidative stress induced by CuONPs in plants like rice (Rawat et al. 2018). Cu NPs have shown promise in increasing Cu content in plant tissues and seeds but their effects on photosynthesis and nutrient profiles vary and further studies are essential to establish the desired and consistent outcomes (Lasso-Robledo et al. 2022).

2.4 Iron oxide NPs

Iron exists in three main forms in nature namely, magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (Fe_2O_3). Magnetite and maghemite NPs are more prominent among these due to properties like low toxicity, superparamagnetic properties and ease of separation. Thus, they are highly valuable for biomedical applications like protein immobilization, thermal therapy and drug delivery (Ali et al. 2016a).

2.4.1 Synthesis of iron oxide NPs

The thermal decomposition method involves breaking down precursors such as iron pentacarbonyl under high temperature in the presence of surfactants or solvents. It produces crystalline NPs with controlled size and magnetic property (Cheng et al. 2012). Microemulsion technique uses a transparent system formed by mixing an oil phase and an aqueous phase with ionic surfactants and medium-chain alcohols (C_5-C_{10}). This method allows precise control over NP size and morphology and is particularly suitable for synthesizing NPs with more even distribution and less structural defects (Campos et al. 2015). In the co-precipitation method, magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) NPs are mainly produced which involves precipitation of a stoichiometric mixture of Fe(II) and Fe(III) salts in a basic (aqueous) medium. The size and surface properties of the NPs is dictated by the type of salts used, Fe^{2+}/Fe^{3+} ratio, pH, ionic strength and temperature. In the sol-gel method, hydrolysis and condensation of metal alkoxides take place to create oxide particle dispersions, yielding nanomaghemite (γ-Fe_2O_3) particles after heat treatment at 673 K. Agglomeration and oxidation are avoided by coating with polymers like polyvinyl alcohol or inorganic materials like silica and carbon (Campos et al. 2015).

2.4.2 Green synthesis

The plant-mediated synthesis of iron oxide nanoparticles (IONPs) utilize various plant extracts that are abundant in diverse bioactive compounds that act as reducing agents. Extracts from *Solanum trilobatum*, *Ziziphora tenuior*, *Persia americana*, *Abutilon indicum*, *Azadirachta indica*, *Camellia sinensis*, green tea leaves, banana peels and pruned tea leaves have been used. The process of synthesis involves many steps from washing, drying and grinding the plant material into powdered form which is finally mixed with solvents like distilled water, ethanol, etc and heated under controlled conditions (Priya et al. 2021). IONP synthesis through bacterial systems is eco-friendly and cost-effective. Several bacterial strains including *Actinobacter sp*., *Thermoanaerobacter sp.*, *Bacillus subtilis*, *Lactobacillus casei* and *Lactobacillus fermentum* have been used for both intracellular and extracellular synthesis. Some bacteria such as *Geothrix fermentans* and *Shewanella oneidensis* reduce Fe^{3+} ions by secreting redox compounds that act as electron shuttles for NP synthesis (Priya et al. 2021). Lactic acid bacteria (LAB) are more preferred for NP synthesis due to their non-pathogenic nature and ability to produce diverse enzymes (Mohd Yusof et al. 2019).

Fungal-mediated synthesis of IONP employs the use of fungal biomass, cell-free filtrates (CFF) or fungal homogenates. Examples include *Aspergillus niger* BSC-1 that yields orthorhombic crystalline magnetite NPs with superparamagnetic properties (Chatterjee et al. 2020), while *A. oryzae* TFR9 produced spherical IONPs (Raliya and Tarafdar 2013). Brown (Phaeophyceae), Red (Rhodophyceae) and Green (Chlorophyceae) algae are widely used for FeNP synthesis. Brown algae such as *Sargassum muticum*, *Padina pavonica* and *Dictyota dicotoma* are the most commonly used sources for biosynthesis, while *Kappaphycus alvarezii* (red algae) is also used. Microalgal species like *Chlorococcum* sp., *Chlorella* sp. and *Anabaena flos-aquae* have been used to synthesize small FeNPs ideal for catalytic applications and environmental remediation (Taghizadeh et al. 2020).

2.4.3 Applications

Iron is an essential element required for enzyme reactions, photosynthesis, translation, RNA synthesis, auxin activity, etc., all of which are instrumental in optimal plant growth. Iron containing minerals are limiting in nature and thus NPs offer a solution to address iron deficiency and help in the improvement of crop production even under adverse conditions (Kaningini et al. 2022). Mycorrhizal plants respond to metal NPs like FeO and Ag NPs at varying concentration; FeO NPs significantly affect overall growth and yield. It can improve dry pod and leaf weight at optimum concentration. These observations point towards the possibility of using FeO NPs to increase crop productivity by boosting pod and leaf biomass (Jayarambabu and Rao 2019). In *Solanum lycopersicum*, seeds coated with Fe_2O_3 NPs were germinated and grown in hydroponic solutions. On monitoring, NP deposition was found in roots and aerial parts. This indicates preferential deposition in root hairs and tips along with biomineralization, suggesting applications in agriculture (Shankramma et al. 2016). Foliar spraying of Fe_3O_4 NPs was able to enhance *Moringa oleifera* growth parameters such as plant height, leaf number, biomass etc along with photosynthetic pigments and auxin content. Antioxidant enzyme activities was observed to increase, thus reducing hydrogen peroxide and lipid peroxidation levels. This treatment helped alleviate salinity stress and promoted growth in the plant (Tawfik et al. 2021). Chitosan stabilizes FeNPs by preventing aggregation through electrostatic and steric barriers improving its stability and better nutrient delivery. It has been seen that chitosan-coated FeNPs are responsible for improvement in plant growth, delivery of nutrients and also safe for environment. On the other hand, silica-coated FeNPs are preferred for their chemical stability and compatibility with many functional groups which is desirable for agricultural application. Polyvinylpyrrolidone (PVP) is an effective capping agent for FeNPs that reduces the chances of aggregation by steric hindrance and enables strong interactions between functional groups and the surface of the NP (Nurfarwizah Adzuan Hafiz 2024).

2.5 CeO_2 NPs

Cerium oxide (CeO_2) nanoparticles (CeNPs) have unique redox and catalytic properties due to which they can switch between trivalent (Ce^{3+}) and tetravalent (Ce^{4+}) states. They are valuable in medicine, industry and environmental applications. Superoxide dismutase (SOD) and catalase (CAT)-like functions are influenced by Ce^{3+}/Ce^{4+} ratio and oxygen vacancies. Higher levels of Ce^{3+} increase SOD activity, while more levels of Ce^{4+} drives CAT activity. Surface modification techniques like metal doping increase the redox sites and enhance their catalytic potential (Vazirov et al. 2018).

2.5.1 Synthesis of CeO_2 NPs

CeO_2 NPs can be synthesized using various methods like the precipitation method and microemulsification method which employs aqueous and oil phases with surfactants to create NPs. The hydrothermal method uses high-temperature conditions to produce diverse morphologies such as cubes, rods and octahedra, with sizes ranging from 3–53 nm. Other techniques like solvothermal method, sol-gel method, ball milling and frame-spray pyrolysis, etc are also used (Nyoka et al. 2020).

2.5.2 Green synthesis

Hibiscus sabdariffa flower extract was used to synthesize CeO_2 NPs of size 3.9 nm with a low Ce^{3+}/Ce^{4+} ratio. Similarly, fresh egg white served as a capping agent to produce spherical CeO_2 NPs of 25 nm by using amino acid rich proteins present for particle stabilization and distribution. *Acalypha indica*, fructose, glucose and lactose were also used for making spherical NPs (Nyoka et al. 2020).

2.5.3 Applications

Nano-CeO_2 treatment affected cucumber, alfalfa, tomato and corn seedlings but their effects varied as the NP uptake depended on concentration. At high concentrations (4000 mg/L), there was substantial Ce accumulation in the plant tissues, but the effect on biomass varied. The biomass of alfalfa decreased at lower concentration of CeO_2 NPs but increased at higher levels, while corn biomass consistently declined across both low and high concentration. The effect on root and shoot growth varied and cucumber root growth was enhanced at moderate concentration levels but showed inhibition at lower concentrations (Jayarambabu and Rao 2019). Stress responses in corn showed increased ascorbate peroxidase (APX) and CAT activity in specific plant parts, depending on the concentration. These findings indicate that the impact of these NPs was dependent on concentration, influencing plant growth and physiology (Zhao et al. 2012). In cucumber and cilantro, low concentration of CeO_2 NPs increased CAT activity, while higher concentrations led to a decrease. The activity of dehydroascorbate reductase (DHAR) increased in rice stems and roots at moderate concentration of CeO_2 NPs. Capped CeO_2 NPs enhanced root biomass production and reduced Ce uptake and toxicity, as indicated by lower Ce levels in plant tissues; thus, capping of NP reduces potential toxicity (Jayarambabu and Rao 2019). Exposure to CeO_2NPs in plants occurs majorly through root or foliar pathways. They accumulate in various plant tissues including roots, shoots and fruits as observed in *Solanum lycopersicum*, *Raphanus sativus* and radish. The physicochemical properties of CeO_2NPs influence their uptake and translocation; negatively charged CeO_2NPs showed higher accumulation in wheat leaves compared to other forms. Coating agents like citric acid could reduce Ce uptake and toxicity and increase the rate of photosynthesis under optimal conditions. At high concentration, it can cause chlorophyll reduction, disrupt electron transport chain and reduce germination as seen in *Cucurbita pepo*, *Zea mays* and *Solanum lycopersicum* while *Medicago sativa* remained unaffected. Studies have revealed that CeO_2NPs can alleviate abiotic stresses like salinity and oxidative stress via ROS scavenging, aided with more antioxidant enzyme levels. Excessive concentration may lead to growth inhibition, reduction in photosynthesis, etc. Thus, further research is needed to better understand the mechanisms of uptake and effects on environment (Prakash et al. 2021).

2.6 TiO_2 NPs

Titanium dioxide (TiO_2) is the oxide form of titanium and naturally occurs in three mineral forms: anatase, rutile and brookite. They are widely produced and used in cosmetics, sunscreens, food production and drug delivery systems because of their excellent properties like ultraviolet light absorption and high refractive index, making them highly versatile in their applications (Kaningini et al. 2022). Fungal-mediated synthesis of titanium NPs has been studied in several earlier works (Roychoudhury et al. 2023).

2.6.1 Applications

Treatment of canola seeds with TiO_2 NPs at higher concentration improved germination with plumule and radicle growth, pointing towards their potential in agriculture as canola is vital for livelihoods in many regions. Application of TiO_2 NP at appropriate concentration improved germination and vigor of aged spinach seeds highlighting its ability to improve productivity and seed quality (Jayarambabu and Rao 2019). Wheat seedlings treated with TiO_2 NPs also showed signs of better growth and yield. They play an important role in agriculture as antimicrobial and growth-regulating agents and help in the prevention of food intoxication and elimination of various pathogens affecting plants and fruits. They facilitate the breakdown of residual pollutants, pesticides and organic compounds in hydroponic systems and controlled environment. Similarly, TiO_2 NP application to *Zea mays* increased its potential to absorb micro and macro nutrients, but excessive concentration negatively influenced dry biomass production (Kaningini et al. 2022).

2.7 SiO_2 NPs

Silicon dioxide nanoparticles ($nSiO_2$) can enhance seed germination and associated parameters making them a valuable tool in modern agriculture. The application of $nSiO_2$ improved germination percentage, average time of germination, seed germination and seed vigor index in *Lycopersicum esculentum*. They also increase fresh and dry weight of seedlings. Such enhanced germination and seedling performance may be attributed to its ability to improve water absorption, nutrient availability and stress tolerance during early plant development. These properties make $nSiO_2$ an effective soil amendment or foliar fertilizer for improving crop growth under different agricultural conditions (Siddiqui and Al-Whaibi 2014).

2.8 Gold NPs

Gold NPs are spherical with size range of 20–50 nm in size. They have shown significant ability in enhancing mitotic cell division and pollen germination. Their synthesis can help in promoting cell division and improving pollen viability particularly useful for rare and endangered plant species (Jayarambabu and Rao 2019).

2.9 Calcium carbonate NPs

Calcium carbonate ($CaCO_3$) NPs are affordable, less toxic, biocompatible and eco-friendly. These NPs are utilized across various industries such as plastics, paper, rubber, textiles, food, etc. $CaCO_3$ play a crucial role in biomineralization and help in the formation of bones, teeth and shells. In the medical field, it is applied in biosensors, bone replacement and drug delivery systems (Jayarambabu and Rao 2019).

2.9.1 Synthesis of $CaCO_3$ NPs

They can be synthesized through various methods like aqueous precipitation, mechano-chemical treatment without heat, lysine biomineralization. Plant-based sources like *Myrtus communis* are also used (Jayarambabu and Rao 2019).

2.9.2 Applications

It is used as drug carriers for cancer treatment due to its affordability and safety (Maleki Dizaj et al. 2015). It is also effective in pest control such as California red scale (*Aonidiella aurantii*) and Oriental fruit flies (*Bactrocera dorsalis*) when applied on to *Citrus tankan* leaves (Hua et al. 2015). A study on soybean crops showed that on combining calcium carbonate with hydroxyapatite NPs under full irrigation conditions, there was an increase in crop yield (Kaningini et al. 2022).

2.10 Magnesium oxide

Magnesium oxide (MgO) NPs exhibit unique properties such as a high refractive index, corrosion resistance, thermal conductivity and flame resistance. These characteristics make them ideal for use as a catalyst support, additive and as promoter in various chemical reactions (Jayarambabu and Rao 2019).

2.10.1 Applications

The application of MgO NPs on to peanut seeds enhanced their germination, growth and production of photosynthetic pigments (Jhansi et al. 2017). In *Vigna radiata* (green gram), application of NPs caused increase in germination rate, seedling growth and more seedling vigor index and acted as a nanopriming agent (Vijai Anand et al. 2020). Similar increase in germination was observed in mung seeds. MgO NPs are used in semiconductors, catalysis, pollutant sorption, biosensors, photocatalysis and refractory materials. They possess antibacterial, anticancer and antioxidant properties and thus effective against bacteria, fungi, etc. They are non-toxic for both plants and humans and thermally stable making them efficient for plant protection and for boosting agricultural productivity (Jayarambabu and Rao 2019).

III. Phytotoxicity of metal NPs

Metal NPs have diverse impacts on plants and phytotoxicity of any NP is largely influenced by its shape, size chemical composition and composition of coating material. ZnO NPs and their toxicity effects have been thoroughly studied which reveal that their toxicity mechanisms mainly involve particle dissolution, releasing ionic zinc, favoring ROS production and photo-induced toxicity under UV radiation. They affect growth of plant, elongation of roots and oxidative stress with changes in gene expression in species like soybean, maize and Arabidopsis. Additionally, ZnO NPs disrupt rhizobium-legume symbiosis, thereby inhibiting root nodulation and early nodule senescence in peas. Bioaccumulation studies reveal that ZnONPs adhere to root cell walls and translocate within plants, disrupting plant-microbe interactions. Research on γ-Fe_2O_3 and nano zerovalent iron (nZVI) NPs shows that γ-Fe_2O_3 reduces root conductivity and nutrient uptake in plants like *Helianthus annuus* and *Solanum lycopersicum* while nZVI has minimal impact. FeOx NPs stimulate root growth at low concentration but inhibit it at higher levels. γ-Fe_2O_3 also affects phytohormone level and enzyme activity emphasizing the need for careful use of iron nanomaterials to minimize plant health risks. (Ruttkay-Nedecky et al. 2017). CuO NPs induce oxidative DNA damage in radish and ryegrass while TiO_2 and ZnO NPs trigger distinct stress gene expression changes in *Arabidopsis*. CeO_2 NPs show minimal toxicity but enhance antioxidant enzyme activity in wheat and pumpkin. Ag NPs show toxicity, dependent on size and concentration along with oxidative stress like in *Lemna gibba*. Au NPs are toxic to rice and accumulate in aerial plant parts. These findings highlight the complex phytotoxicity of metallic NPs that is driven by both particle and ionic properties (Li et al. 2015).

IV. Carbon nanotubes (CNT)

Carbon nanotubes (CNTs) are among the most versatile nanomaterials and possess a unique cylindrical structure formed by rolled-up graphene sheets. CNTs can be classified into two types: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs are made of a single layer of graphene with diameters ranging from 0.4 to 2 nm along with varying length. They have unique crystal-like structures and are classified based on chirality, wrapping style and configurations such as zigzag or armchair forms. MWCNTs are composed of multiple concentric layers of graphene with outer diameters of 2–100 nm and inner diameters of 1–3 nm. MWCNTs have strong mechanical strength due to their layered structure and exhibit superior tensile strength and Young's modulus compared to SWCNTs (Safdar et al. 2022).

4.1 Applications

CNTs are innovative agricultural tools that act as fertilizers that slowly release their nutrients and have growth enhancer qualities. They have the potential of targeted and regulated delivery of agrochemicals while improving the uptake of water and nutrients like nitrogen, phosphorus and potassium from the soil. Nano-carbon-coated fertilizers can improve yield of crops and reduce water pollution (Safdar et al. 2022). CNTs when applied to tomato plants, can enhance flowering and increase Bacteroidetes and Firmicutes while reducing Proteobacteria and Verrucomicrobia in the soil. It has no significant impact on bacterial diversity (Khodakovskaya et al. 2013). Multi-walled carbon nanotubes can significantly influence gene expression in tomato seedlings especially in roots and leaves. Exposure to CNTs is seen to activate stress-related genes, water channel proteins that improves germination and overall plant development. Water-soluble MWCNTs exhibit concentration-dependent effects on wheat, maize, peanut and garlic seedlings. At lower concentrations, CNTs can easily penetrate thick seed coats, improving water uptake and better root water content, leading to higher biomass production (Jayarambabu and Rao 2019). Carbon nanotubes reduce pesticide residue uptake in zucchini, corn, tomato and soybean. MWCNTs lowered chlordane and DDT accumulation across plant parts, while CNTs were responsible in promoting root growth in onion, cucumber and ryegrass with slow release of pesticides (Husen and Siddiqi 2014). Onion and cucumber plants when treated with functional SWCNTs were observed to show root elongation and formation of carbon nanotube sheets. On the contrary, some studies show that there is increased germination due to more water uptake into the seeds (Jayarambabu and Rao 2019).

V. Fullerenes

Icosahedral fullerene (nC_{60}) is the most common form of fullerene. Other smaller forms of fullerenes like C_{28} and C_{36} as well as larger spherical conformations also exist. Fullerenes and their derivatives such as fullerols [$C_{60}(OH)_{20}$] possess powerful anticancer, antioxidant and antiviral properties that can suppress superoxide accumulation, lipid peroxidation and help in scavenging of free radicals. It is shown to have minimal toxicity and neuroprotective effects in vivo (Husen and Siddiqi 2014).

5.1 Applications

Fullerenes are versatile and used in optical devices, quantum computing, contaminant removal, molecular switches, medicine, drug delivery systems, etc. Treatment of bitter melon seeds with fullerene was observed to increase biomass, fruit yield and phytomedicine content. Excessive concentration was detrimental as it reduced its effectiveness. Fullerol can possibly enhance crop yield and phytomedicine levels in cereal and fruit crops. The environmental impact of fullerenes must be thoroughly assessed before their broad application in agriculture (Husen and Siddiqi 2014; Jayarambabu and Rao 2019).

VI. Adverse effects of carbon nanotubes and fullerenes

Carbon-based nanomaterials such as SWCNTs, MWCNTs and fullerenes have shown potential adverse effects on plants. SWCNTs induced ROS formation in Arabidopsis that led to cell death, while MWCNTs were responsible for causing growth inhibition. ROS production and necrotic lesions was seen in red spinach. Fullerene C_{70} caused delay in blossoming of rice followed by reduced seed-setting rates. Water-soluble fullerenes inhibited growth, disrupted gravitropism due to auxin disruption, caused shortening of roots and abnormal cell division. Fullerene C_{60} persisted in soils and increased the bioaccumulation of pollutants like dichlorodiphenyldichloroethylene in crops like zucchini and soybean. Thus, more research is needed to reduce these concerns regarding their long term environmental impact (Li et al. 2015).

6. Quantum dots

Carbon quantum dots (CQDs) are a class of nanomaterial, also known as zero-dimensional, because of particle size being less than 10 nm. It has gained much interest because of its biocompatibility, low toxicity, antioxidant and antimicrobial activities along with UV shielding capabilities and being eco-friendly. Such properties point out the potential of CQDs in agricultural purposes as an eco-friendly alternative towards increasing crop productivity and food accessibility.

CQDs are applied to plants via seed/root soaking, foliar spraying or soil application. Seed/root soaking allows uptake through roots, while foliar spraying delivers CQDs directly to leaves for rapid and targeted photosynthesis enhancement. Soil application is a newer method that allows uptake during germination. CQDs enhance plant growth and photosynthesis by improving plant height, root and shoot length and biomass. Studies show significant increases in growth parameters, including a 48% rise in lettuce biomass, a 39.6% increase in weight of maize grain and improved photosynthesis rates by higher stomatal conductance, RuBisCo activity and chlorophyll content. It also enhances stress tolerance, nitrogen content and photosynthetic efficiency. Optimal CQD concentration to be applied vary by plant type and may potentially offer promising applications in sustainable agriculture (Chowmasundaram et al. 2023).

6.1 Toxicity of QDs and need for future research

Studies show that QDs can inhibit seed germination, cause DNA damage, suppress cell proliferation, induce oxidative stress and lead to cell death. Additionally, their environmental transport and interactions with plants can cause adverse effects including leaf senescence and inhibited root growth. The complex physical properties of metal-based QDs necessitate thorough toxicity evaluations especially given their industrial applications (Li et al. 2015). Although most studies of CQD has taken place at the laboratory level, the uptake and translocation of CQDs in plants, application methods, their role in the plant growth and photosynthesis and toxicity effects need further focus. Nevertheless, there are barriers concerning scalability, cost-effectiveness, safety and practicality which serve as the basis for work to be done in the future to further enhance the agriculture application of CQDs (Chowmasundaram et al. 2023). Table 1 presents the beneficial applications of different kinds of nanomaterials in plants.

Table 1: Beneficial applications of different kinds of nanomaterials in plants

Nanomaterial	Impact on plant development and yield	Reference
Zinc oxide NPs	Improved root and shoot growth and germination in peanut, gram seeds and mung seeds, *Trigonella foenum-graecum, Brassica juncea*;reduced stress level in green pea roots, promotes growth in cotton, improved fresh and dry weight in *Cicer arietinum* seedlings, enhanced growth in tobacco, improved photosynthesis and growth in *Zea mays* L, antioxidant and antiinflamatory properties.	(Jayarambabu and Rao 2019), (Kaningini et al. 2022), (Mukherjee et al. 2014), (Balážová et al. 2020), (Venkatachalam et al. 2017), (Ahmed et al. 2017)
Silver NPs	Enhanced seed germination, increase in biomass in *Trigonella foenum-graecum*, *Triticum aestivum*, improved growth, fresh weight and root nodulation in *Brassica juncea* and cowpea, antibacterial activity in tomato, enhanced germination in *Boswellia ovalifoliolata,* increased root and shoot length in *Phaseolus vulgaris.*	(Kale et al. 2021), (Jayarambabu and Rao 2019)
Copper NPs	Antimicrobial activity against *Bacillus subtilis* (waste water treatment), increased growth of soybean and chickpea seedlings, promote germination in tomato, antifungal activity against early blight and wilt in tomatoes and citrus black rot, act as nanofertilizers for sweet potatoes.	(Jayarambabu and Rao 2019), (Lasso-Robledo et al. 2022), (Bonilla-Bird et al.

		2020)
Iron oxide NPs	Increased crop productivity in mycorrhizal plants, increased plant height, biomass, leaf number, photosynthesis and auxin content in *Moringa oleifera.*	(Jayarambabu and Rao 2019), (Tawfik et al. 2021)
Cerium oxide NPs	Varied root and shoot growth and biomass in cucumber, alfalfa, tomato, corn, increased APX and CAT activity against stress response in corn, enhanced CAT activity in cucumber, cilantro, increased DHAR activity in rice, alleviate abiotic stresses	(Jayarambabu and Rao 2019), (Zhao et al. 2012), (Prakash et al. 2021)
Titanium dioxide NPs	Improved germination, plumule and radical growth in canola and spinach seeds, better growth in wheat seedlings, antimicrobial and growth regulating agents, breakdown of pollutants, pesticides, increased nutrient absorption in *Zea mays*	(Jayarambabu and Rao 2019), (Kaningini et al. 2022)
Silicon dioxide NPs	Improved seed germination, seed vigor index, fresh and dry weight in seeds, soil improvement , foliar fertilizer for better crop growth	(Siddiqui and Al-Whaibi 2014)
Gold NPs	Enhanced mitotic cell division and pollen germination	(Jayarambabu and Rao 2019)
Calcium carbonate NPs	Pest control in *Citrus tankan* against California red scale and Oriental fruit flies, increased crop yield in soybean	(Kaningini et al. 2022)
Magnesium oxide NPs	Increased germination, seedling growth in peanut, *Vigna radiata and* mung seeds, biosensors, antibacterial, anticancer and antioxidant properties	(Jhansi et al. 2017), (Vijai Anand et al. 2020), (Jayarambabu and Rao 2019)
Carbon nanotubes (CNT)	Nanofertilizers, improved uptake of water and nutrients in wheat, maize, peanut and garlic seedlings, improved crop yield and less water pollution, enhanced flowering in tomato, increased expression of stress related genes in tomato seeds, less pesticide residue uptake in zucchini, corn, tomato and soybean, less chlorane and DDT accumulation and root growth in onion, cucumber and ryegrass	(Safdar et al. 2022), (Khodakovskaya et al. 2013), (Jayarambabu and Rao 2019), (Husen and Siddiqi 2014)
Fullerenes	Increased biomass, fruit yield and phytomedicine content in bitter melon seeds, better crop yield in cereal and fruit crops	(Husen and Siddiqi 2014), (Jayarambabu and Rao 2019)
Quantum dots (QDs / CQDs)	Antioxidant, antimicrobial properties, increased crop productivity and food accessibility, enhanced photosynthesis and nitrogen content, improved plant height, root and shoot length, increased lettuce and maize biomass, stress tolerance	(Chowmasundaram et al. 2023)

VII. Uptake of NPs by plants

NPs are absorbed by plant surfaces and can enter through natural nanoscale openings like stomata, hydathodes and root junctions (Fig. 2). Above the ground, the lipophilic shoot surfaces and structures like trichomes promote deposition of NPs. The uptake into plant tissues occur via multiple pathways (Fig. 2) governed by the size and surface properties of NPs. Smaller lipophilic NPs can easily penetrate the plant cuticle which contains apolar and polar pathways for uptake while larger particles often bypass the cuticle and instead enter through the stomata, hydathodes or through the stigma of flowers. Roots and tubers develop suberin layers that act as barriers to NP penetration. Exodermis and endodermis contain suberin and prevent apoplastic flow but lateral root development creates openings through which NPs can bypass these barriers and enter the vascular system. Transpiration increases the ratio of apoplastic to symplastic flow that guides the movement of NPs into the xylem. Additionally, mechanical injuries like herbivore activity and lateral root junctions provide alternate pathways for NPs, similar to what they do for bacteria. These entry points in combination with natural plant structures highlight the diverse and complex mechanisms by which NPs are taken up and transported within plants (Dietz and Herth 2011). Assessing the toxicity of NPs requires understanding their uptake in plants which remain inconclusive due to the lack of quantitative methods for measuring NPs in plant tissues. Studies suggest that NPs smaller than 5 nm can efficiently traverse intact cell walls, as seen in the accumulation of carbon-based nanomaterials like fullerene metal-based NPs and C_{60} in plant tissues. Several techniques, such as optical emission spectroscopy, X-ray absorption spectroscopy and transmission electron microscopy (TEM) have been used to observe NPs in plants. Carbon nanotubes penetrate cell membranes via direct penetration or endocytosis. Additionally, carrier-mediated transport mechanisms help in NP trafficking through subcellular membranes. SWCNTs can localize passively in the lipid envelopes of chloroplasts enhancing photosynthetic activity and electron transport rates. These findings indicate that NP uptake depends on the specific properties of the NPs and thus multiple mechanisms may operate simultaneously in plant systems (Li et al. 25).

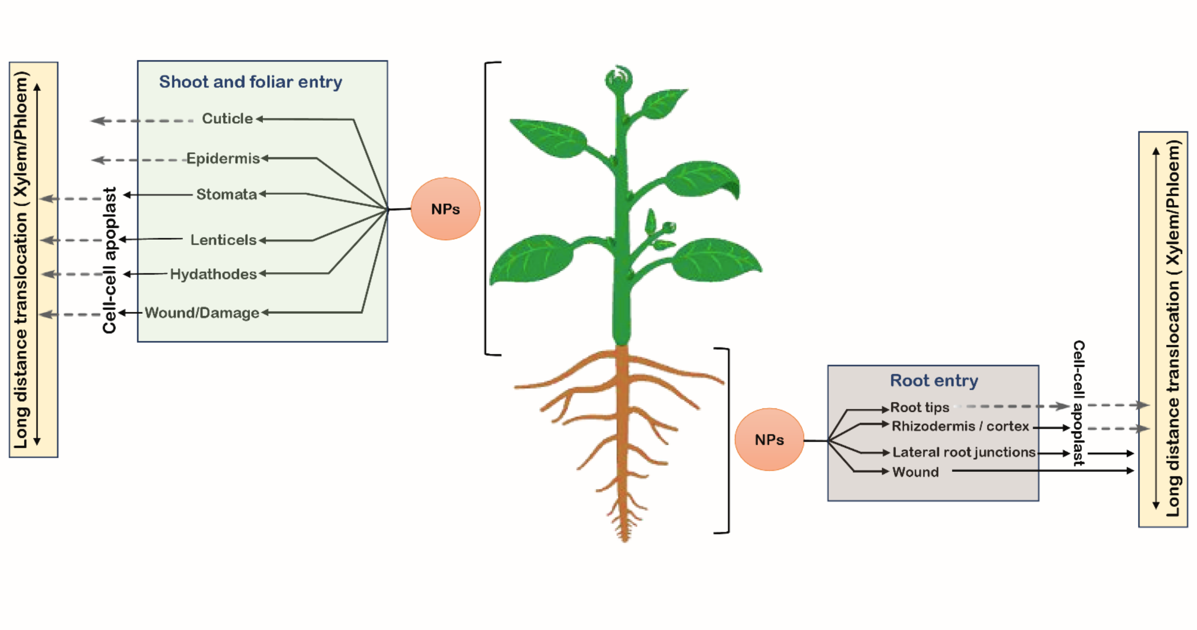

Fig. 2: Different pathways of NP uptake and translocation in plants via shoot and root

8. Nanoparticles in combating abiotic and biotic stress

Nanoparticles have been suggested as promising for alleviating the damage caused by abiotic and biotic stress. (Paul et al. 2023). In recent studies, metallic NPs have shown many applications in plants. Silica NPs have been reported to enhance plant growth and induce plant resistance against biotic stress. Silicon NP and maghemite NP application in rice improved tolerance to fluoride stress by refining the agronomic traits and modulating the ionome and physiome (Banerjee et al. 2021a, b). Likewise, the incorporation of copper, zinc oxide, and selenium NPs as nano-fertilizers showed satisfying outcomes [Wang et al. 2022]. Chitosan NPs also have the potentiality to mitigate abiotic stress in plants (Roychoudhury et al. 2022). Chitosan NPs releasing nitric oxide were found to be effective against salt stress in maize [Oliveira et al. 2016]. Another study underscored the enhancement in soybean growth under copper stress as a result of chitosan NP-mediated release of nitric oxide [Gomes et al. 2022]. Likewise, keeping in mind the biocompatibility as well as the antibacterial activity of silver and copper, the corresponding NPs have gained popularity in the management of a variety of biotic stress factors [El-Abeid et al. 2024].

Biogenic NPs have a tremendous potentiality in developing abiotic stress-tolerant plants (Chakraborty et al. 2022) and in the remediation of environmental contaminants or xenobiotics (Singh and Roychoudhury 2022; Roychoudhury and Bhowmik 2023). Recent attempts suggest the role of NPs in enhancing stress tolerance by acting as antioxidants or strengthening the antioxidative system [Rasheed et al. 2022]. Studies undertaken have also justified the use of NPs for alleviating stress caused due to ROS accumulation through enhancement of antioxidant system. These include AuNPs in wheat, ZnONPs in pea, tomato and okra, CeO_2 and CuO NPs in maize, corn and soybean, $Ca_3(PO_4)_2$ in bean, AgNP in pearl millet, biochar NP in wheat, zeolite NPs in potato, chitosan NP in bitter melon, graphene oxide NPs in wheat and SiO_2 NPs in pea [Gui et al. 2023]. Arsenic bioaccumulation and toxicity in plants can also be mitigated using NPs (Samanta and Roychoudhury 2021). The various NPs and their applications on crop have been highlighted in **Table 2**. Thus, it could be assumed that low concentration of NPs triggers detoxification of ROS and activates antioxidant enzymes by up regulating the signaling genes [Dayem et al. 2017].

Table 2: Applications of various NPs on abiotic and biotic stress tolerance

A Abiotic/Biotic Stress	N Nanoparticles (NPs) used	I Impact on crops	R References
Drought (Abiotic)	ZnO, Fe_2O_3, TiO_2, Si, Zn, zeolite	Reduced lipid peroxidation; increased biomass yield and number of seeds (**ZnO** - Rice; Safflower), increased carotenoids and chlorophyll content, decreased levels of H_2O_2 and enhanced activity of SOD, peroxidase (POD) and CAT (**Fe_2O_3, TiO_2** - Linseed), improved photosystem II, water use efficiency, leaf chlorophyll and transpiration rate (**Si, Zn, zeolite -** Coriander)	Mazhar et al. 2022, Ghiyasi et al. 2023, Aghdam et al. 2016, Mazhar et al. 2022, Mahmoud et al. 2023
Salt (Abiotic)	SiO_2, Fe_3O_4, K_2SO_4, Ag, Si	Improved phenolics, chlorophyll and phenylalanine ammonia lyase (PAL) activity (**SiO_2** – Tomato), Decreased MDA, H_2O_2, lipid peroxidation (**Fe_3O_4** - Drumstick tree), Decreased electrolyte leakage, Improved antioxidant activity, increased proline (**K_2SO_4** – Alfalfa), Improved chlorophyll content and osmolyte levels (**Si** – Cauliflower)	Pinedo-Guerrero et al. 2020, Tawfik et al. 2021, El-Sharkawy et al. 2017, Anwar et al. 2023
Heavy metal toxicity, i.e., Pb, Cd, As and Cr (Abiotic)	Fe_3O_4, Ti, ZnO	Increased activity of SOD and POD to combat Pb, Cd toxicity (**Fe_3O_4** – Wheat), Induced expression of CAT and SOD, up regulation of antioxidant related genes to combat As toxicity (**Ti**– Moong bean), Increased activity of APX, CAT, POD and SOD to combat Cr toxicity (**ZnO** – Wheat)	Noman et al. 2020, Katiyar et al. 2020, Ahmad et al. 2022
Fusarium oxysporum (Biotic)	ZnO	Increased antioxidant activity and activation of SOD, POD and CAT (Chickpea)	Farhana et al. 2022
Bipolaris sarokiniana (Biotic)	Se	Increased chlorophyll content, membrane stability index, leaf surface area, root length (Wheat)	Shahbaz et al. 2023
Fusarium andiyazi (Biotic)	Chitosan	Upregulation of *PR* genes, activation of SOD and related antioxidant genes (Tomato)	Ansari et al. 2023
Puccinia striiformis (Biotic)	TiO_2	Downregulation of proteins involved in the production of ROS (Wheat)	Satti et al. 2022

9. Nanoparticles Promote Nutrient Metabolism, Seed Germination, Plant Development and Yield

It is proven by many researchers that NPs have improved the quality of plant products better than the traditional pesticides. Nanoparticles have important functions in plant growth and plant quality improvement through nutrient enhancement, improvement of photosynthesis activity and metabolism [Shebl et al. 2019]. Zinc oxide NPs have been found to be involved in the biosynthesis and photosynthesis of chlorophyll as well as the formation of starch, thus elevating the concentration of soluble carbohydrates [Bala et al. 2019]. ZnONPs can enhance the antioxidant activity and chlorophyll content of cotton with increased number and weight of bolls per plant and the quality parameters of cotton fiber like uniformity and strength of fibers [Vaghar et al. 2020]. ZnO NPs, acting on tomato plants, improved tomato yield by enhancing nutrient uptake by the plant through phosphorus and zinc. Fe_3O_4 NPs can improve plant biomass and productivity through an increase in protein, nutrient and carbohydrate content in plants [Faizan et al. 2021].

As an efficient environment-friendly photocatalyst, TiO_2 NPs improved light absorption by improving the energy conversion of the light system, and have antibacterial activity after surface chemical modification, which can reduce the half-life of pesticides and promote seed germination and seedling growth [Mingyu et al. 2009]. TiO_2 NPs could improve the photosynthetic efficiency of spinach, promote wheat growth and yield. Another experiment showed that TiO_2 NPs stimulate germination and significantly decrease the mean time to germination for wheatgrass [AZIMI et al. 2013].

Non-metallic NPs like multiwalled carbon nanotubes (MWCNTs) may also activate germination for various crops by improving water uptake by the seed. Upon applying MWCNTs in soybean, barley and corn seed by using air spray, seed germination efficiency was increased by at least 25% more than the control. Further experiments showed that MWCNTs penetrated the surface of the seed. The relative expression of several water-channel-related genes in soybean, barley and corn seeds sprayed with MWCNTs increased significantly. Additionally, NPs such as Ag NPs, ZnO NPs, TiO_2 NPs, silica NPs and MWCNTs could stimulate the growth, photosynthesis and yield of various crop species, including spinach, cotton, maize, soybean and barley [Lahiani et al. 2013]. NPs primarily accelerate plant growth via their action on crop antioxidant enzyme activity, for example, ZnO NPs treated to cucumber enhanced plant chlorophyll content together with leaf fresh/dry weight. Antioxidant-related enzyme activities, including SOD and CAT increased in all the treated leaves of cucumber, compared with those untreated controls [Li et al. 2021]. NPs also affect plant cell morphology and enhance the amount of protein and organic compounds inside the cell. The growth of maize due to silica NPs incorporated in soil was significantly increased compared to the control, thereby increasing plant height and root length. Moreover, differences in plant morphology may be associated with the cell wall thickness. In silica-NP-treated plants, the cell wall was thicker and the number of silica bodies in root cells was higher than in the control plant. The protein content in silica-NP-treated plants was also higher than that in the bulk-silica-treated one. Organic compounds like phenols, aldehydes and ketones were less abundant in silica-NP-treated plants [Suriyaprabha et al. 2012]. NPs tend to induce gene expression related to nutrient assimilation and growth regulation [Wan et al. 2019].

NPs also have the potential to regulate plant hormone balance. Foliar application of Ag NPs to two varieties of common bean (Bronco and Nebraska) induced gene expression, related to the auxin signaling pathway, leading to a high content of auxin in plants [El-Batal et al. 2016]. Due to their structural and surface reactivity properties, NPs can cause intracellular oxidative stress and genetic damage which resulted in reduced crop yield and physiological disorders when high concentrations of NPs were applied [Maroufpoor et al. 2019]. As mentioned above, metallic NPs always have side effects on organisms due to the toxicity of metal elements. Based on this property, NPs can be an appropriate material for nanopesticides, but it is also expected to restrict plant growth and development.

10. Role of NPs in Nitrogen Fixation

Nanoparticles are found to modulate some important biochemical pathways involving the nitrogenase enzyme complex, which has been found to directly interact with the nitrogen fixation process in legumes. It includes two proteins: Fe-protein, which is responsible for electron transfer to nitrogenase, and MoFe-protein, which carries out nitrogen reduction. The process is a major component of biological nitrogen fixation (BNF) in leguminous plants. Nanoparticles, particularly metal-based NPs, such as iron oxide (Fe_2O_3) and zinc oxide (ZnO), have been used to affect the nitrogenase activity by association with its metal co-factors, for example, Fe_2O_3 NPs provide a bioavailable source of Fe needed to maintain integrity for the catalytic action of Fe-S clusters in the nitrogenase complex [Gehlout et al., 2022]. Such interaction might boost up the electron transport required for nitrogen reduction, thereby boosting the efficiency of nitrogen fixation in total.

Further, NPs can act directly upon the nitrogenase enzyme and can also modify the production of ATP, which is the energy currency of both biological processes in most organisms and utilized in the nitrogen fixation process. [Ullah et al., 2024]. Nanoparticles, such as TiO_2 NPs, have been observed to elevate the photosynthetic activity, thereby making ATP accessible for nitrogen fixation. Light capture and electron transfer enhancement by TiO_2 NPs within the chloroplasts lead to efficient ATP synthesis. The additional energy obtained is targeted to nitrogenase activity to enhance nitrogen fixation. On the other hand, it is stated that ZnO NPs can help improve root development and uptake of nutrients that would strengthen the ability to synthesize ATP needed for nitrogen fixation under varying conditions [Faizan et al., 2021].

Another significant mechanism by which NPs regulate nitrogen fixation is in the management of ROS and in the enhancement of protective antioxidant activity. Nitrogenase is sensitive to oxygen and excessive ROS damage at its active sites would inhibit nitrogen fixation [Baig et al., 2024]. Examples include zinc oxide (ZnO) and magnesium oxide (MgO), which can induce increased antioxidant activity of enzymes such as SOD and CAT, responsible for scavenging ROS and protecting nitrogenase enzyme from oxidative damage. Indeed, NPs keep nitrogenase activity unperturbed, by developing low oxygen scenarios within root nodules and by preventing ROS-induced deleterious effects. Some of the key roles of NPs in nitrogen fixation have been mentioned in the following **Table 3**.

Table 3: Role of NPs in nitrogen fixation

Nanoparticles	Key role in nitrogen fixation	References
ZnO	Enhances zinc availability for enzyme activity	Munir, *et al.,* 2024
CuO	Enhances copper availability for enzyme cofactors	Ummer *et al.,* 2023
Fe_2O_3	Enhances iron availability for Fe-S clusters in nitrogenase	Cao *et al.,* 2022
TiO_2	Enhances light absorption for photosynthesis	Kamyab *et al.,* 2023
CeO_2	Potential role in electron transfer modulation	Lijun et al. 2024
Ag	Antimicrobial protection against pathogens	Kim *et al.,* 2023
CNT	Improves nutrient transport and root elongation	Kráľová and Jampílek, 2023,
Fullerenes	Protects nitrogenase from oxidative damage	Shafiq et al. 2021

11. Different applications of nanotechnology

11.1 Application of NPs in medicine

Pharmaceutical nanotechnology holds revolutionary opportunities to fight against a number of diseases. These NPs have long-acting and brain-targeted properties with minimal adverse effects and motor complications. It helps in detection of diseases like cancer, neurodegenerative diseases and diabetes mellitus and detecting viruses and microorganisms associated with infection. It also covers the development of nanomedicine, nanorobots, tissue engineering, biomarkers and biosensors. It also has scope for material improvement [Chan et al. 2021]. Further, NPs in medical applications deal with emerging new technologies in developing customized solutions for drug delivery systems. The delivery systems of drugs affect the rate of distribution, absorption, metabolism and excretion of the drug or other chemical substances in the body. The delivery system of drugs has to ensure that the drug binds to the receptor at its target point to influence the activity of a receptor and its subsequent signalling. Nowadays, polymeric biodegradable NPs have attracted attention as potential drug delivery devices with prospects of their applications in drug release controlling, their ability to target tissues and organs, as carriers of oligonucleotides in DNA in gene therapy and antisense therapy in their ability to distribute proteins [Jayawardena et al. 2021]. In addition, many metal NPs can be used as alternative antibiotics, such as NPs of silver oxide, zinc oxide, titanium dioxide and copper oxide where they have shown strongly effective antimicrobial activity in opposition to many types of microorganisms [Surendiran et al. 2009; Roychoudhury and Singh 2024]. These approaches can give us a chance to replace antibiotic-based drugs with highly safe treatments. Nanoparticles as antimicrobial agents reduce many types of bacterial resistance through the microbicide effect since the nature of the NPs is produced through direct contact with the particular bacterial cell wall, without the need to probe inside the cell. Green synthesized copper oxide NPs have been studied as antimicrobial agents against different bacterial and fungal pathogens in an experiment where the antimicrobial activities of copper oxide NPs were compared against standard antibiotics norfloxacin and amphotericin B. Results indicated that CuO-NPs provide highly antimicrobial activities against the selected pathogens [Alavi and Rai, 2019].

The cytotoxicity of such nanomedicines to animal tissues confirmed the potential of commercially available copper/silver NPs and their combination in the decrease in the viability of mastitis-borne pathogens without toxic effects on mammary gland tissues [Abdussalam-Mohammed, 2020]. Another medical area in which the achievements of nanotechnology could be witnessed is in creating artificial organs, cells and tissues. Artificial cells are being actively used for the replacement of defective organs and cells, especially those related to metabolic functions. This includes the production of smart nanocomposite materials, fluorescent NPs like quantum dots, magnetic NPs for stem cell tracking and carbon nanotubes and graphene for enhancing the properties of the material [Zhao and Castranova, 2011].

11.2 Nanofertilizers

Based on recent investigations, nanotechnology has potential applications in revolutionizing the agricultural systems. It provides a platform for advanced delivery systems for agrochemicals, which are safe, target-bound, and preferably an easy mode of delivery. Since nanofertilizers have a very high surface area to volume ratio, these also prove to be far more effective than most modern polymeric-type conventional fertilizers. Their nature can also allow the slow release that is necessary for imparting improved nutrient uptake efficiency by the crop. Thus, this emerging technology provides the avenue for novel and sustainable nutrient delivery systems utilizing the nanoporous surfaces of plant parts in the plant surface. With encapsulated NPs, nanoclays and zeolites, there is improvement in the efficiency of interactively applied fertilizers, rehabilitation of soil fertility and plant health and reduction of environmental pollution and agroecology degradation [Manjunatha et al. 2016]. Some components of nanofertilizers include ZnONPs, silica, iron and titanium dioxide NPs, ZnS/ZnCdSe core–shell quantum dots (QDs), InP/ZnS core–shell QDs, Mn/ZnSe QDs, gold nanorods, Al_2O_3, TiO_2, CeO_2 and FeO NPs [Prasad et al. 2017]. Besides the kind of vegetation, the effective implementation of nanomaterials as fertilizers in plant growth entirely lies on some other factors such as their size, biological activity, concentration, composition and chemical properties of the inorganic nanomaterials [Thakur et al. 2018].

Nanomaterials have unique properties due to very small particle size, slightly big surface to volume ratio, and fantastic optical properties. Some of these properties and the potential opportunities that nanofertilizers have in plant development and proper nutrition security for diverse farm practice enable them to be of use in several aspects of health benefits. Just after an early revolution of the application of nanotechnology in the 21st century, there are ever-new applications of this great science to make different kinds of products in various fields of endeavour. Human population keeps on increasing, so that crop production must also be fortified. Improved forms of fertilizers can be developed into nanofertilizers using nanotechnology. Traditional fertilizers do not comprise all needed nutritional elements required for plant growth and nutritional aspects. Therefore, active nature of nanoparticulate materials makes them an attractive venture to engineer materials to produce nanofertilizers that address the nutrient problems and the related environmental issues associated with fertilizers [Dimkpa and Bindraban, 2017].

Nanofertilizers shall act as a boon by tripling the efficiency of the nutrients and combining lesser amounts of chemical fertilizers to make the crops more drought- and disease-resistant as well as able to survive with less environmental hazard. Mostly because of the high surface area-to-volume ratio, they are readily absorbed. Sizes and morphologies of NPs, however, are much more crucial determinants that can determine bio-accessibility levels by the plants from the soil. The NPs may not be activated instantly for uptake by the plants, but instead they would undergo certain reactions that may range from oxidation and recombination to provide the required micronutrients for the plants. Specific deficient nutrients could be included in engineered nanofertilizers for plants. This is because differential typical properties would be derived resulting from their specific atoms, shaped on to the surfaces of nanomaterials.

There are a number of disadvantages associated with conventional fertilizers as it is losing much of their nutrients with leaching, and further, they pollute the underground water aquifers. In other words, chemical fertilizers are associated with environmental problems such as greenhouse gas emissions as well as hypoxia, to be taken care of urgently, which have led to the search for alternatives like the nanofertilizers [Suppan 2013]. With nanofertilizer, there is slow release of the nutrients, which minimizes leaching of the nutrients, among other interesting properties. According to Li et al. (2016), metals and anionic NPs are absorbed by porous materials or and hence become overly available for use as food nutrients or as contaminants when not required. Recently, some researchers have invented and patented a nanofertilizer popularly known as "Nano-Leucite Fertilizer" that promises an eco-friendly process while lessening nutrient loss into food and increasing overall production of crops and food. These nanofertilizers would, indeed, be the best item in agricultural revolution as it might enhance soil fertility in nutrient deficient soils. Some of the approved nanofertilizers and their compositions are further tabulated in **Table 4**.

Table 4: Different kinds of nanofertilizers with their manufacturers (Prasad et al. 2017; Azam 2002)

Nanofertilizers	Constituents	Name of Manufacturer
Nano Green	Extracts of corn, soybean, potato, coconut and palm	Nano Green Sciences, Inc., India
Nano Micro Nutrient (EcoStar) (500) g	Zn, 6%; B, 2%; Cu, 1%; Fe, 6%+; EDTA Mo, 0.05%; Mn, 5%+; AMINOS, 5%	Shan Maw Myae Trading Co., Ltd., India
TAG NANO (NPK, PhoS, Zinc, Cal, etc.) fertilizers	Proteino-lacto-gluconate chelated with micronutrients, vitamins, probiotics, seaweed extracts and humic acid	Tropical Agrosystem India (P) Ltd., India
Nano Max NPK Fertilizer	Multiple organic acids chelated with major nutrients, amino acids, organic carbon, organic micro nutrients/trace elements, vitamins and probiotics	JU Agri Sciences Pvt. Ltd., Janakpuri, New Delhi, India
Nano Ultra-Fertilizer (500) g	Organic matter, 5.5%; Nitrogen, 10%; P_2O_5, 9%; K_2O, 14%; P_2O_5, 8%; K_2O, 14%; MgO, 3%	SMTET Eco-technologies Co., Ltd., Taiwan
Nano Capsule	N, 0.5%; P_2O_5, 0.7%; K_2O, 3.9%; Ca, 2.0%; Mg, 0.2%; S, 0.8%; Fe, 2.0%; Mn, 0.004%; Cu, 0.007%; Zn, 0.004%	The Best International Network Co., Ltd., Thailand

11.3 Nanopesticides

Many efforts have been made for agricultural improvement like producing high-yielding varieties, synthetic pesticides and genetically modified (GM) crops to improve food security, but still issues like environmental pollution and risks to non-target organisms persist. With pests developing resistance, innovative solutions like nanopesticides show promise for sustainable crop protection and global food security (Priyanka et al. 2019). Nanopesticides are nanostructures with sizes ranging between 1 to 200 nm and can carry agrochemical ingredients (AcI). They are formulated using nanomaterials to enhance their efficiency and find various applications in agriculture. Such formulations can be either fixed on hybrid substrates, encapsulated in matrices or as nanocarriers. Materials like polymers ceramics silica, lipids, metals and carbon serve as bases for nanopesticide development. The nanoscale properties help to improve pesticide activity by enhancing water solubility, bioavailability, protection against environmental degradation and thus improved control over pests, weeds and pathogens (Chaud et al. 2021).

Type 1 nanopesticides are comprised of metal-based nanopesticides (like Ag, Cu, Ti) that exhibit strong antimicrobial properties against pathogens like *Escherichia coli*, *Staphylococcus aureus*, *Candida* and *Fusarium* through adhesion, dissolution, oxidative stress (ROS) and genotoxicity. Type 2 nanopesticides consist of nanocarriers with active ingredients (AI) encapsulated in them such as polymers (chitosan, cellulose, etc) and clays providing stimuli-responsive systems that are biocompatible and cost-effective. These nanocarriers help in the delivery of AIs like insecticides (e.g., avermectin) and herbicides (e.g., atrazine, glyphosate) (Wang et al. 2012).

Encapsulation is the process where a biologically active ingredient is surrounded with a protective layer that is designed to release the core active ingredient under certain specific conditions or external stimuli. This mechanism of controlled release can occur either through chemical bond cleavage or by physical diffusion (Chaud et al. 2021). Nano-microcapsules and nanospheres are created through processes like encapsulation, embedding, adsorption and coupling that protect the active ingredients present, improve their stability, ensure controlled release along with reducing odours and volatility. These formulations can improve spray coverage and adhesion, making them more effective and eco-friendly options (Huang et al. 2018).

Lipid-based nanocarriers such as nanoemulsions, micellar and vesicular systems are designed for controlled release of pesticides. These systems use specific lipids and surface modifiers for targeted delivery and improve the solubility, stability and bioavailability of the pesticides. Emulsified carriers have high surface area and biocompatibility and thus can successfully control pests and weeds while reducing environmental impact (Chaud et al. 2021). Pickering emulsions (PE) are lipid colloidal dispersions without surfactants that are stabilized by polymer or inorganic particles. They have stimuli-responsive behavior and can transition between stable and unstable forms based on changes (Chen et al. 2017). Liquid crystals particularly lyotropic liquid crystals are another type that are used for pesticide delivery as they can enhance tissue penetration, increase bioadhesion to plant leaves and reduce detrimental effects on environment (Bisset et al. 2019). Functionalized liposomes are vessel-like nanocarriers that protect active ingredients from thermal and photodegradation (Chaud et al. 2021).

11.3.1 Applications

An amphiphilic chitosan nanocarrier with octadecanol glycidyl ether as the hydrophobic group and sulfate as the hydrophilic group was prepared using a reverse-micelle approach to encapsulate rotenone while polylactide nanocarriers of varying sizes were designed to encapsulate avermectin for insecticidal activity (Wang et al. 2012). Liposomes, carrying α-cypermethrin and etofenprox along with chitosan, was used to create a depot system and extend the delivery period of the active ingredients (Chaud et al. 2021). Anisotropic silica nanoparticles grafted with alginate were developed as environmentally responsive carriers for pesticides like λ-cyhalothrin (Chen et al. 2017). Phytantriol used in emulsions with lyotropic liquid crystals have better structural stability and show effective transport of hydrophobic herbicides for improved application (Bisset et al. 2019). Encapsulation of neem oil and citronella oil in nanoemulsions showed fungicidal activity that could effectively transport and deliver hydrophobic pesticides against fungal diseases (Osman Mohamed Ali et al. 2017). A green oil-in-water nanoemulsion with surfactant like alkyl polyglycoside and polyoxyethylene could enhance the bioavailability of β-cypermethrin. Similarly, a nanoemulsion containing *Manilkara subsericea* fruit extract showed effective removal of *Dysdercus peruvianus* which is a pest of cotton. Nanocapsules with an inner cavity of polymer coating were utilized to encapsulate lansiumamide B for nematicidal activity (Priyanka et al. 2019).

Nano-SiO_2 gel significantly reduced *Tuta absoluta* infestation in tomato compared to conventional SiO_2 gel. Nano-chitosan was able to maintain high locust mortality under laboratory conditions and Poly(e-caprolactone) nano-capsules with atrazine showed herbicidal activity by adhering to mustard leaves and penetrating through the stomata to mesophyll tissue. Nano-atrazine could reduce the growth of target weeds and was equally effective as conventional formulations even at dilute concentration. Nanoparticles like nano-Ag, nano-FeO and nano-ZnO also serve as broad-spectrum antibacterial and antifungal agents. Nano-Ag composites were able to eliminate *Botrytis cinerea* in strawberries. Nano-FeO inhibited 60–80% of fungal pathogens such as *Rhizoctonia solani* and *Fusarium oxysporum* while nano-ZnO was highly effective against tobacco blue mold at low concentration compared to bulk ZnO. Such examples highlight the potential of nanotechnology to revolutionize pest and disease control and ensure sustainability in agricultural practices (Xin et al. 2020). The application of nano-calcium carbonate pesticides results in increase in calcium content in plants while $Cu(OH)_2$ nanopesticides applied to maize increase potassium and phosphorus levels. Lettuce treated with nanopesticides showed improved potassium and copper concentrations while foliar application on spinach increases the content of elements like aluminium, iron and silver (Priyanka et al. 2019). Some nanopesticides with their activities are listed in Table 5.

Table 5: Some different kinds of nanopesticides used and their effects

Name of Pesticide	Effects observed	References
Nano-Rotenone (Amphiphilic nanocarrier)	Insecticidal	(Wang et al. 2022)
Nano-Avermectin (Polylactide nanocarriers)	Insecticidal	(Wang et al. 2022)
Neem oil, Citronella oil (nanoemulsion)	Fungicidal	(Osman Mohamed Ali et al. 2017)
Lansiumamide B (Nanocapsules)	Nematicidal	(Priyanka et al. 2019)
Nano-SiO_2 gel	Reduced *Tuta absoluta* infestation in tomato	(Xin et al. 2020)
Nano-chitosan	High locust mortality	
Nano-atrazine	Herbicidal, reduce weeds	

Nano-Ag	Eliminate *Botrytis cinerea* in strawberries	
Nano-FeO	Inhibit fungal pathogens (*R. solani* and *F. oxysporum)*	
Nano-ZnO	Fungicidal (tobacco blue mold)	
Nano-calcium carbonate pesticides	Increase in calcium content	(Priyanka et al. 2019)
$Cu(OH)_2$ nanopesticides	Increase potassium and phosphorus levels in maize	

11.3.2 Safety issues of nanopesticides

Nanopesticides are generally composed of biodegradable and non-toxic pesticide compounds, NPs and polymers. Green pesticide compounds can target pests via absorption through gut, while NPs can penetrate membranes and disrupts proteins, enzymes or DNA, resulting in apoptosis. Polymers are used to ensure slow release and long-term stability, thereby reducing side effects. Though biopolymer-encased nanopesticides are relatively safe, proper precautions must be ensured during field application to avoid exposure to operator. Nanopesticides pose toxicity risks to humans and animals along with the environment. As they are of nanoscale size, they can penetrate cell membranes and cause respiratory issues through inhalation and even cross the blood-brain barrier. They can harm the environment due to long-term accumulation in air, water, soil and the food chain. Collaborative research is important to deal with their long-term impacts on health and ecosystem (Priyanka et al. 2019).

11.4 Nanobiosensors

Nanobiosensors are advanced sensors that integrate nanotechnology with biological probes to detect target analyte molecules and possess exceptional sensitivity and specificity. A typical nanobiosensor consists of a transducer, a biologically sensitized probe and a detector that converts analyte signals into quantifiable data. Probes consist of receptors, enzymes or nucleic acids that detect analytes and transmit signals to the transducer which in turn converts them into measurable electrical outputs. The detector analyses these signals via a microprocessor generating precise data. These sensors that include optical, mechanical and nanowires offer a high surface-to-volume ratio, remarkable sensitivity and atomic-scale functionality, making them extremely useful in agriculture and food technology (Shawon et al. 2020).

11.4.1 Applications

Traditional pesticide detection techniques like high-performance liquid chromatography, enzyme-linked immunosorbent assays and gas chromatography-mass spectrometry are expensive time-consuming and not perfectly suitable for on-site detection. Thus, optical nanosensors that are made of enzymes, antibodies and aptamers with nanomaterials offer enhanced sensitivity, specificity and rapid detection of pesticides. They are cost-effective and good alternatives for pesticide residue monitoring (Sharma et al. 2021). Nanosensors are used for NP detection, e.g., microcavity sensors are used to detect NPs. Whispering gallery resonators identify particles that bind to the microcavity surface, resulting in changes in optical properties. These changes generate a wavelength shift that helps monitor the interactions of particles and their size in real-time (Lu et al. 2011). Split-mode microcavity Raman lasers are optical sensors which are highly sensitive and detect individual NPs by observing changes in beat frequency and can even detect particles as small as 20 nm (Li et al. 2014).

Nanosensors also find their application in detecting pathogens while wireless nanosensors are instrumental in detecting pesticides in both food and environment, for example, nanobiosensors with Au electrodes modified by Cu NPs efficiently detect salicylic acid levels in plants such as in oilseeds affected by fungal pathogens. Electrochemical nanobiosensors with carbon nanotube electrodes and Au NP coatings could detect triazophos in postharvest crops, while Ag and Au NPs could identify organophosphorus pesticides as well. In addition, surface-enhanced Raman scattering (SERS) using Ag NP monolayers has enabled better detection of pesticides like methylparathion in agricultural samples (Shawon et al. 2020).

Bacterial receptors, antibodies and lectins are widely used in biosensors for pathogen detection, while aptamers are cheap and stable alternatives despite their preparation challenges. The "chemical nose" approach uses diverse receptors to generate unique response patterns for identifying pathogens. This method trains sensors with bacterial samples to create a reference database for pathogen identification. The size and surface composition of NPs are tailored to respond distinctly to different classes of bacteria, thereby providing precise detection. Multichannel nanosensors can detect bacterial species and strains in biofilms within minutes. AuNP-based multichannel sensor could identify six biofilms by their physicochemical properties while another hydrophobically functionalized AuNP sensor was able to detect three *E. coli* strains. Gold nanorod-based plasmon resonance immunosensors effectively identified specific plant viruses while Fe_3O_4/SiO_2 immunosensors were designed to detect a range of plant pathogens with high sensitivity (Sharma et al. 2021).

CNTs demonstrated greater sensitivity in detecting low levels of ammonia, compared to conventional probes along with herbicide fenclorim in soil, while nano-Au immunosensors efficiently detected Karnal bunt disease in wheat and chlorosis virus in bell peppers. Biofunctionalized nano-Fe_3O_4 identified *L. monocytogenes* in milk powder and lettuce. Another type is the quantum dot-based biosensors that are used for detection of organo-phosphorus pesticides even at low concentration. Similarly, ZnO quantum dots sensed low concentration of pesticides like aldrin and atrazine that are commonly used (Xin et al. 2020).

Nanosensors and nanobiosensors enhance agricultural productivity by monitoring factors like temperature, soil health, moisture and nutrients in real-time. They also detect pesticide residues, heavy metals, pathogens, toxins, etc that allow timely interventions to prevent crop losses. The development of broad-spectrum nanosensors, capable of detecting multiple targets and innovative nanomaterials, will further bring advancements to the field. Integrating nanotechnology with agricultural science and plant diagnostics is a key step towards achieving sustainable development goals ensuring environmental preservation and safety (Sharma et al. 2021). Some nanosensors with their application are listed in Table 6.

Table 6: Some different kinds of nanosensors and their applications

Nanobiosensor	Applications	References
Nanobiosensors with Au electrodes modified by Cu NPs	Detect salicylic acid levels in oilseed affected by fungal pathogens	(Shawon et al. 2020)
Electrochemical nanobiosensors, with carbon nanotube electrodes and Au nanoparticle coatings	Detect triazophos in postharvest crops	
Electrochemical nanobiosensors, with carbon nanotube electrodes and Ag and Au NP coatings	Identify organophosphorus pesticides	
Surface-enhanced Raman scattering (SERS) using Ag NP	Detection of pesticide like methylparathion	
AuNP-based Multichannel nanosensors	Detect bacterial species and strains like *E. coli* strains in biofilms within minutes	(Sharma et al. 2021)
Gold nanorod-based plasmon resonance immunosensors	Identified specific plant viruses	
Fe_3O_4/SiO_2 immunosensors	Detect range of plant pathogens	
Nano-Au immunosensors	Detect Karnal bunt disease in wheat and chlorosis virus in bell peppers	(Xin et al. 2020)
Biofunctionalized nano-Fe_3O_4 sensor	Identified *Listeria monocytogenes* in milk powder and lettuce	
ZnO quantum dot biosensor	Sensed low concentrations of pesticides like aldrin and atrazine	

11.5 Nanotechnology in plant genetic engineering

Challenges such as population growth, climate change and plant diseases jeopardize food security and plant-based systems. To address these issues, molecular farming and genetic engineering have emerged as transformative solutions. Traditional approaches which were used during the Green Revolution helped to improve yields and nutritional quality of crops but were low throughput, less specific and more dependent on natural genetic pools. Modern advancements like *Agrobacterium tumefaciens*-mediated transformation and biolistic delivery systems have expanded plant genetic engineering applications, which however still remain species-specific and labour demanding. Nanotechnology offers an alternative path with precise scalable tools for better molecule delivery and genetic transformation (Squire et al. 2023). CRISPR-Cas system revolutionized genetic engineering, although the technique faces challenges in terms of delivery system. Nano-mediated strategies, including sgRNA-nanocarrier attachment and small endonucleases like Cas14 offer potential solutions for non-biolistic and regeneration-independent editing. Early efforts in nano-delivery faced challenges due to the lack of design frameworks but the Lipid Exchange Envelope Penetration (LEEP) model provided insights into how NP size and charge influenced its cellular uptake. Innovations like organelle-targeting peptides such as RuBisCo subunits for chloroplasts enable precise and specific subcellular delivery. Nanocarriers including carbon-based and gold NPs enable species-independent delivery of DNA and RNA, thus achieving subcellular targeting of organelles like chloroplasts and mitochondria. These advancements have laid the foundation for efficient and scalable genetic engineering in plants.

Still, challenges remain in enabling direct germline editing, delivering large DNA plasmids and proteins and improving reproducibility in pollen transformation. Nano-mediated delivery of hormones and transcription factors show promise in enhancing regeneration efficiency and broadening species compatibility like in recalcitrant crops. Future research efforts should focus on optimizing nanocarrier design, leveraging cell-penetrating peptides for large cargo delivery and refining the hormone transport mechanisms to overcome regeneration barriers and help in more improvement in plant genetic engineering (Squire et al. 2023).

12. Conclusion and future perspectives

Nanotechnology has shown great potential in agriculture for enhancing plant growth, improving crop yield and strengthening defense mechanisms against diseases. However, unintended release of NPs into the environment can pose risks to both aquatic and land plants by inducing oxidative stress, disrupting plant growth and enzyme activity. The method of production of NPs also influence its toxicity and so plant-derived NPs are considered more safer and environment friendly. The indiscriminate use of agrochemicals and pesticides has serious environmental and health concerns that highlight the need for safer alternatives. Nanotechnology offers a promising solution by enabling the precise delivery of nutrients, fertilizers and pesticides. Nano-encapsulation techniques improve the effectiveness and safety of such applications by reducing human exposure and ensuring more controlled delivery; however, there are challenges like understanding the compatibility of encapsulation materials with active ingredients and producing cost-effective formulations that are competitive with conventional products. On the other hand, biosensors coated with NPs like Au and Ag can enhance the sensitivity of diagnostic tools for detecting plant infections. In disease management, nanomaterials can be used either directly as antimicrobial agents or by encapsulating antimicrobial chemicals to improve their delivery and release. Nanotubes and nanocapsules enable efficient transport and controlled release of active ingredients that can target and eliminate plant pathogens. However, concerns regarding NP accumulation, phytotoxicity and mammalian toxicity remain unsolved and must be addressed before their widespread commercial use in mitigating plant diseases. Nanoparticles offer promising benefits for nutrient delivery and crop growth enhancement but further research is needed to ensure their safe and sustainable application in agriculture. There are emerging opportunities in the field of nano-based plant biotechnology to further advance plant genetic engineering.

Author contributions

UC and DC drafted the manuscript. ARC supervised the overall work, provided critical comments and made modifications wherever necessary.

Conflict of interest

There is no conflict of interest in publishing this manuscript

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