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Review

Recent progress of nanomaterials in sustainable agricultural applications

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ABSTRACT

Nanomaterials have shown immense potential for their versatile applications in various sectors like medicine, healthcare, food sector, environment, agriculture, electronics, and pharmaceutics due to their unique and tunable physicochemical properties attributed to their small sizes. Recently nanomaterials have garnered foremost interest in agricultural applications due to constructive results of various studies showing significantly better crops growth/yield as compared to traditional fertilizers and pesticides. Besides, nanomaterials have shown encouraging results to deal with problems associated with conventional fertilizers, such as low nutrient usage efficiency and unregulated nutrient release with no precise control on the nutrients delivery. Moreover, nanomaterials have positively impacted plants growth attributing to higher chlorophyll content in leaves, increased root/shoot lengths, and better stress tolerance. Furthermore, nanomaterials are extremely capable of disease detection in plants and soil remediation. In this review, we have attempted to provide the readers with a complete overview of nanomaterials in agriculture by implementing the ideas of precision farming. Hereby, we have deliberated the development of nanomaterials in agriculture in the form of nanofertilizers, nanopesticides and nanosensors for sustainable growth in crops productivity, quality and protection. We have also illuminated the possibility of integrated farm management via soil remediation using nanotechnology. Finally, we have explicated limitations and possible improvements of nanomaterials for sustainable agricultural applications.

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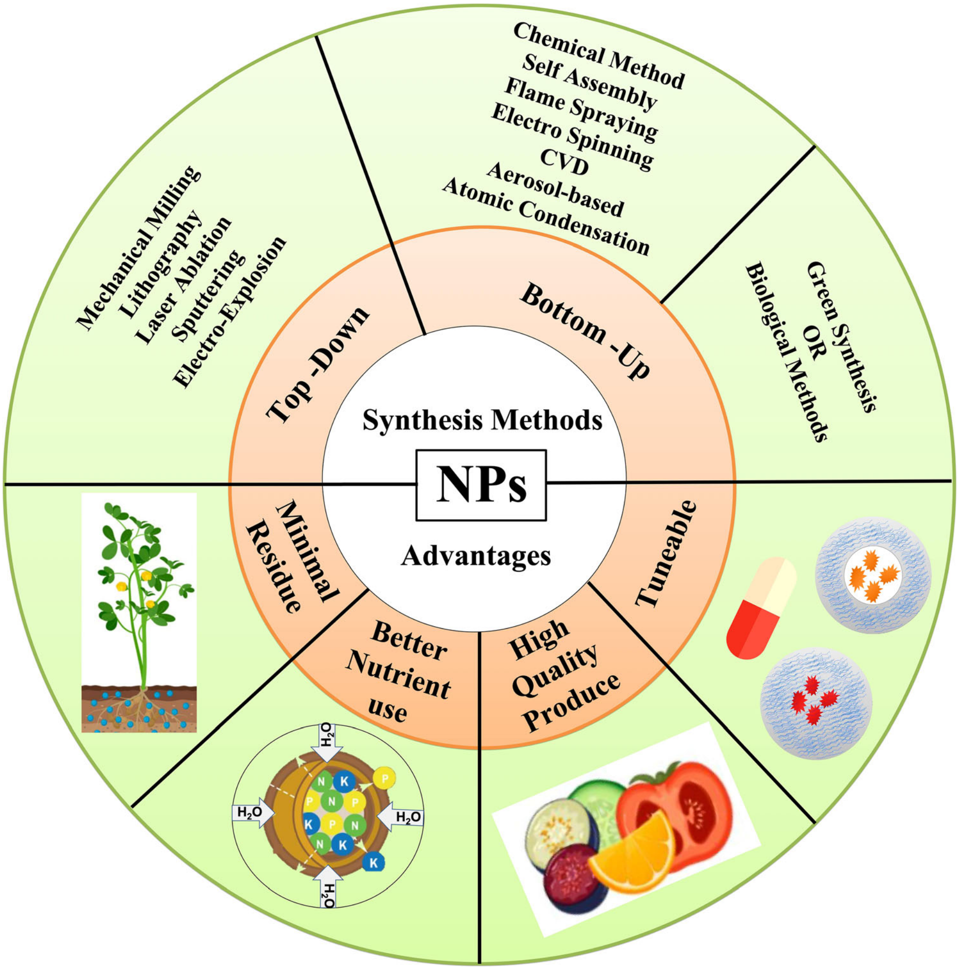
GRAPHICAL ABSTRACT



Abbreviations

NPs	Nanoparticles
MONPs	Metal oxide nanoparticles
CNTs	Carbon nanotubes
CVD	Chemical vapor deposition
MOCVD	Metal–organic chemical vapor deposition
ALE	Atomic layer epitaxy
VPE	Vapor phase epitaxy
PECVD	Plasma enhanced chemical vapor deposition
MRSA	Methicillin-resistant staphylococcus aureus
ATCC	American type culture collection
CNMs	Carbon nanomaterials
HANs	Hydroxyapatite nanoparticles
^{31}P NMR	Phosphorus -31 nuclear magnetic resonance
CMC	Carboxymethyl cellulose
CuO NPs	Copper oxide nanoparticles
TiO_2	Titanium dioxide
LDH	Layered double hydroxide
DDT	Dichloro diphenyl trichloroethane

Introduction

Agriculture has traditionally been the backbone of developing nations, a significant part of their economy depends on agriculture and is a major sector for labor employment. Several challenges plaguing the agricultural sector include lower productivity which is further aggravated due to climate change and the rampant usage of fertilizers that cause ecological imbalance and deterioration of soil and water resources. The ever-rising human population also brings forth the challenge of achieving food security. While several factors contribute to food shortages, pests and crop weeds are one of the most common causes and have been extensively studied [1]. Fertilizers are relevant because the amount of nutrients present in the soil does not always meet the requirement for optimum plant growth and yield, so they must be externally supplied to crops. The "Green Revolution" successfully increased crop yields worldwide, using synthetically produced fertilizers and pesticides [2, 3]. However, as awareness regarding the environmental aspect of intensive fertilizer farming grew, investigations on the impact of fertilizers have revealed that such increased crop productivity comes at the cost of deteriorated soil and water resource quality. The excessive use of chemical fertilizers causes depletion of the micronutrients and microflora in the soil and increases the salinity, thereby further reducing crop yield and nutrient quality [4].

The widely acknowledged limitations of conventional fertilizers include low bioavailability and higher losses due to leaching and runoffs, consequently deteriorating the soil and water resources. The inefficiency of nutrient-delivering fertilizers has been one of the significant drawbacks associated with them, leading to more wastage and making them unsustainable in the long run [5]. While environmental aspects related to synthetic fertilizer usage are important, the productivity of the crops cannot be compromised. With the impacts of climate change already being felt, there is an increased need for strategies that enable expedited adaptation of plants to climate change factors, such as extreme temperatures, salinity, alkalinity, water deficiency, and environmental pollution with toxic metals without threatening existing sensitive ecosystems. The agricultural sector is under immense pressure to meet the needs of a growing population, as it lags innovative solutions at its disposal to achieve sustainable growth without causing severe detrimental effects to the soil and the environment [6].

As agriculture faces several challenges, the concept of precision farming is gaining traction to improve current farming techniques by utilizing nano-products such as nanofertilizers, nanopesticides, and nanosensors, to change the current scenario of agricultural practices, which is largely unsustainable [7–10]. Besides, the use of nanomaterials for advanced farm applications can be highly beneficial in increasing yield, lowering farms input costs, enhancing stress resistance in plants, and improving the nutrient quality of the yield [8]. Due to their small size, nanomaterials have a large surface area to volume ratio, which leads to higher surface activity/reactivity. Therefore, nanomaterials have been massively investigated in various sectors, particularly in agriculture, because of their unique/tunable properties. Nanomaterials have great potential to be used as nanofertilizer and nanopesticides with targeted action and higher efficiency, as nanosensors for effectively monitoring the crop requirements, and also as catalysts/adsorbers in soil remediation. In the current scenario where there is a need to achieve maximum crop productivity and quality with minimum environmental impact, we believe nanomaterials can significantly improve the traditional farming practice and act as an alternative tool for sustainable intensive agriculture.

Synthesis of nanomaterials

The mode of synthesis is a crucial aspect to be considered for the production of nanomaterial-based products as these significantly impact their physicochemical properties, which in turn majorly control the effects of their interaction with living cells. The targeted impact of nano-based products can be achieved by selecting a suitable synthesis method based on the intended use. The different techniques used for nanoparticle synthesis, which include physical, chemical, and biological processes, are briefly discussed in this section. These methods are broadly classified into bottom-up and top-down approaches.

Bottom-up method

In this approach, smaller constituents like atoms, and molecules, are added as a building block to form nanoparticles. This technique mainly involves a chemical reaction, which leads to nuclei (atomic clusters), followed by the growth of the nanoparticles with fewer defects and enhanced homogeneous chemical composition. There are several methods included in this approach, as mentioned below.

Chemical methods

Chemical methods are the most flexible and straightforward approach for the synthesis of nanoparticles. This method gives us the freedom to select different attributes, such as precursors, reductants, surfactants, and concentrations. The variations in these parameters affect the shape, size, composition, and structure of nanoparticles. So desired morphology of nanoparticles can be obtained by making specific changes in synthesis parameters [11]. Co-precipitation [12], thermal decomposition [13], solvothermal decomposition [14], sonochemical method [15], self-assembly using template [16], pyrolysis [17], electrospinning [18, 19], chemical vapor deposition [20, 21], atomic or molecular condensation [22] and photochemical methods are all included in the chemical methods. The electrochemical synthesis method involves the reaction between the electrodes at different poles, as shown in Fig. 1. The nanoparticle formation takes place at the electrode–electrolyte interface [23]. By varying the electrochemical parameters, nanoparticles of different shapes and sizes can be obtained.

Green synthesis or biological method

Reducing chemicals such as hydrazine hydrate, Lithium aluminium hydride, and Sodium Borohydride is commonly used to reduce the metal precursors for nanoparticle synthesis. The problem with them has associated toxicity which makes them harmful to the environment. In order to combat the

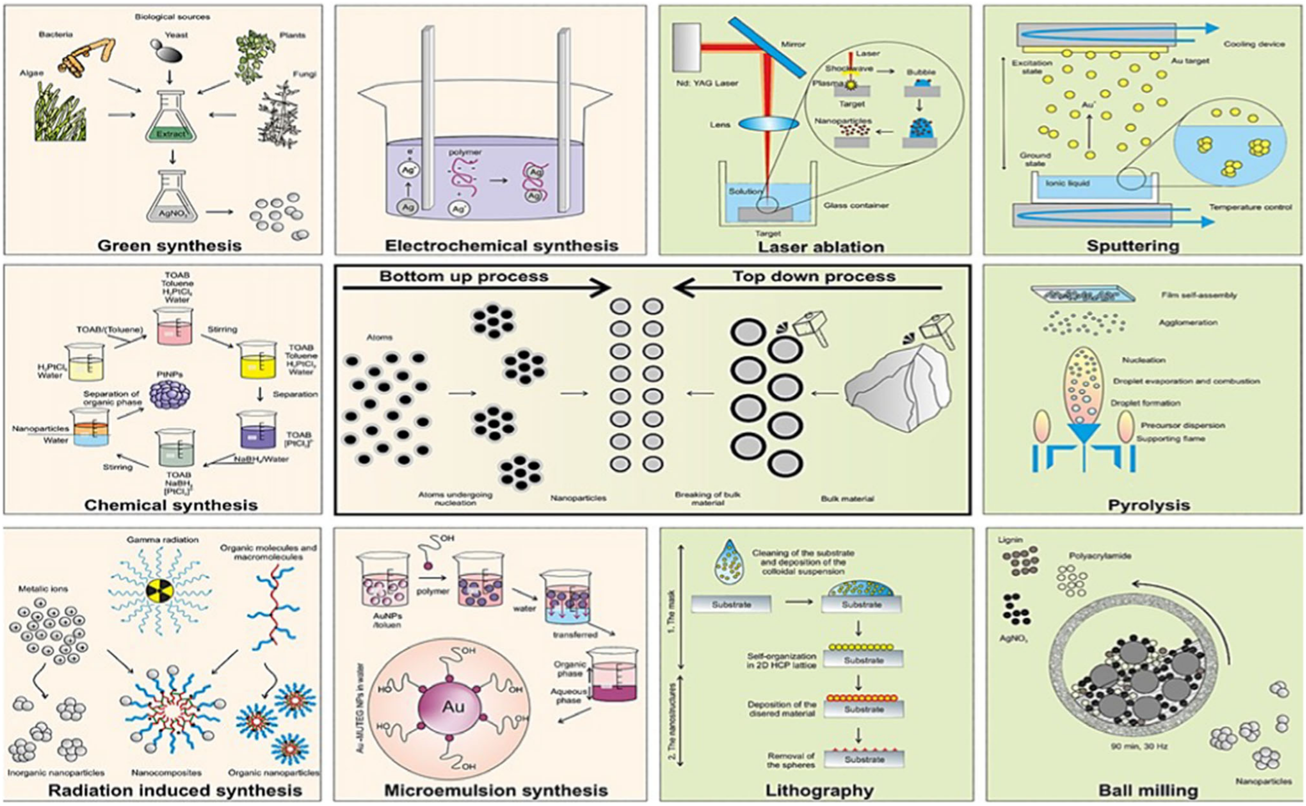


Figure 1 Various methods of nanomaterial synthesis via bottom-up and top-down approaches [24]. Synthesis methods are important because they impact the physicochemical characteristics of the nanoparticles.

problem of toxicity, a greener and safe method of nanoparticle synthesis are used. The green or biological method utilizes plant extracts and micro-organisms like bacteria, fungi, algae, and viruses, which are readily available alternatives to toxic chemicals [25]. Hence, these methods are cheaper and eco-friendly. Plant extracts contain various natural components such as sugars, proteins, flavonoids, and polyphenols, which act as reducing agents and capping agents during nanoparticle synthesis. Many metals, metal oxide, and zero-valent nanoparticles can be synthesized using plant leaf extracts [26–28], plant seed extracts [29, 30], and algal extracts [31]. Micro-organisms internalize and accumulate the precursor salts and the various reductase enzymes, which helps them reduce and detoxify the metal precursors. They have multiple enzymes, proteins, and metal-resistant genes, which act as reducing and capping agents. The synthesis of nanoparticles in micro-organisms may be intracellular [32, 33] or extracellular [34–36].

Top-down method

The top-down approach is a destructive type of method where it merely relies on techniques where bulk materials are crushed down or chopped down into smaller particles of nanometer range. The oldest and simplest top-down method is the mechanical method, where tungsten carbide, carbide steel, or iron balls are used for the milling process [37, 38]. Apart from this, techniques like lithography [39–42], laser ablation [43], sputtering [44–46], and electro-sputtering [47–50] are also included in the top-down approach.

Characteristics of nanoparticles

Antimicrobial properties

Several nanoparticles have been investigated to be used as antimicrobial agents due to their antimicrobial activity. For example, Silver nanoparticles have been employed for wound dressings due to their antimicrobial activity for centuries. Many medical instruments are also made of silver nanoparticles as they play a vital role in preventing infections. The antimicrobial activity of the silver nanoparticles is due to their ability to damage the outer bacterial membrane [51, 52]. Moreover, they disrupt the metabolic process by interacting with the disulfide group of enzymes, which leads to cell death [52, 53]. Colloidal silver nanoparticles synthesized using different honey or β-d-glucose demonstrate excellent antimicrobial activity against microbes like *Bacillus cereus, Bacillus subtilis, Escherichia coli,* and *Staphylococcus aureus* [54]. Zinc oxide (ZnO) nanoparticles have also been reported to have antimicrobial properties [55].

Hydroxyapatite coated with peppermint essential oil showed good antimicrobial activity against methicillin-resistant *Staphylococcus aureus* (MRSA) 388, *S. aureus* ATCC 25,923, *S. aureus* ATCC 6538, *E. faecium* DSM 13,590, *Escherichia coli* ATCC 25,922, *E. coli* C5, *P. aeruginosa* ATCC 27,853, *P. aeruginosa* ATCC 9027 and *Candida parapsilosis* compared to that of hydroxyapatite nanoparticles [56]. Similarly, magnesium incorporated hydroxyapatite nanoparticles have larvicidal activity against *Aedes aegypti*, *Anopheles stephensi*, and *Culex quinquefasciatus* [57].

Selenium nanoparticles synthesized from various bacterial strains like *Escherichia coli*, *Pseudomonas aeruginosa*, MRSA, and *Staphylococcus aureus* show excellent antimicrobial activity by reducing the bacterial growth of *Staphylococcus aureus* and *Escherichia coli* with no cytotoxicity effect against human dermal fibroblasts[58]. Titanium dioxide (TiO_2) nanoparticles are also widely used as additives in various commercialized cosmetic products. TiO_2 nanoparticles synthesized using aqueous leaf extract of *Trigonella foenum-graecum* have good antimicrobial activity against *Y. enterocolitica*, *E. coli*, *S. aureus*, *E. faecalis*, and *S. faecalis* by using the disc diffusion method as reported in the literature [59].

Optical properties

Metallic nanoparticles are widely investigated in various detection techniques due to their biocompatibility and unique tunable optical properties in the near-infrared region [60, 61]. For instance, optical tuning of gold nanoparticles can be achieved by altering their shape and size, and hence they are extensively used for biomedical applications, particularly in theranostics [62, 63]. Moreover, gold nanoparticles are used to develop colorimetric detection assays to detect various constituents present in the environment, biotoxins in food, and many biological samples, due to their simple, quick, and sensitive colorimetric sensing strategy [64]. Apart from this, bimetallic nanoparticles are also investigated due to their superior optical tunable properties like localized surface plasmon resonance that are easily tunable by changing the size, shape, and composition of nanoparticles [65, 66]. The application of pesticides in large amounts pollutes the soil and water, which possesses harmful effects on living beings. Novel nanosensors are developed to detect pesticides, heavy metal ions, and dyes from the water [67–71].

Effect of size and shape of nanomaterials in agriculture

Nanomaterials have unique electrical, mechanical and optical properties. The distinct properties imparted to nanomaterials are the effects of quantum confinement and the local energy disorder of surface atoms [72]. Nanomaterials provide significant advantages over their bulk counterparts, such as high chemical bioactivity, better cellular/tissue/organ penetration capability, and significantly higher bioactivity, which can be exploited in applications. These physicochemical properties of nanomaterials are highly dependent on size and shape. This provides flexibility to optimize the nanoscale properties to produce various nanostructured materials with customized properties to meet different requirements by altering the morphology of the nanoparticles [73]. Nanoparticles can have different structures such as nanowires, nanorods, nanoshells, nanocages, nanoprisms, cubic, spherical, nanobars, flower-shaped, to name a few. The nanoparticle's wide range of shapes and sizes depends upon several reaction parameters such as precursor quality, concentration, nature of reactants, pH of the solution, heating rates, stirring conditions, and reaction time. The control over the morphology of nanoparticles is crucial, which is generally achieved by varying the synthesis methods, the reducing agents, and stabilizers involved in the production of nanoparticles [74].

The variations in the shape and size of nanoparticles impart characteristic colors and properties to them [75]. Extensive studies have been carried out to understand the dependence of size on the required properties of the nanoparticles. For instance, studies on the antibacterial activity of different metal nanoparticles, such as silver colloids, have shown that the smaller the nanoparticles' particle size, the higher their antibacterial activity [76]. Studies on the catalytic activity of nanoparticles have also shown dependence on their size and shape besides depending on other parameters such as structure and chemical-physical environment [77]. The optical and magnetic properties are also dependent on the shape and size of the nanoparticles [78, 79]. The size and shape of the nanoparticles affect the delivery rate and site-specificity of the nanoparticles in the delivery system.

Moreover, using nanoparticles, shape-based preferential interaction with proteins is also possible [80]. The optimal size depends on the intended action required in the specific location. The designing of nanoparticles for applications that involve interaction with living cells requires extensive testing. It is necessary to consistently prepare the nanoparticles of a precise size, as cellular uptake is affected by their shape and size. Even minor differences in the size of particles can result in a wide variety of actions, consequently undermining the advantage of nanoparticles to produce targeted action [81]. The toxicity of nanoparticles is also dependent on their shape and size [82].

Applications of nanomaterials in agriculture

Nanofertilizers

As the human population was booming to meet the surplus demand for food "Green Revolution" was introduced in the 1950–60 s; this brought in the concept of wide-scale usage of fertilizers in the agricultural sector. Fertilizers are nutrients supplied to the crops externally, majorly in the form of chemical compounds. Chemical fertilizers improve crop productivity, and hence they are extensively used through different modes of application [83]. The minerals present in the chemical fertilizers are utilized by the crops, whereas the remaining minerals get leached, leading to water and soil pollution [84]. Such leaching of minerals into the soil by continuous application of chemical fertilizers leads to a decrease in soil fertility and an increase in the concentration of salts, which directly affects soil fertility. For increasing crop productivity and its quality, it is essential to develop nanofertilizers that can effectively release nutrients in a slow and controlled manner [83].

Nanofertilizers are highly effective in enhancing plant growth attributes and crops yield. This is mainly due to their unique small size, higher surface area, better solubility, and higher surface energy. Nanofertilizers have several advantages over conventional fertilizers and are meant to replace conventional fertilizers [85, 86] eventually. They help enhance the bioavailability, reduce losses due to leaching, and improve nutrient delivery and usage efficiency, as shown in studies conducted in labs and the limited number of field trials, thereby giving significantly better yield quality and quantity. Besides, nanofertilizers can be formulated to possess high stability, better solubility, and time-controlled release with enhanced targeted activity at effective concentration providing better delivery and disposal. Nanofertilizers can also be made environmentally responsive to control nutrients' release [87]. Various nanoparticle-based nanocarriers have been explored for the controlled release of nutrients without affecting the soil, unlike conventional fertilizers [88], which are called smart fertilizers [89, 90]. Nanofibers have also been studied to achieve controlled release of nutrients in soil. One such study has reported poly (butylene adipate-co-terephthalate) nanofibers loaded with Zn; the results showed nutrients were released in a slow, controlled manner with increased nutrient availability in soil [91]. Metal and metal oxide nanoparticles (MONPs) [92], carbon-based nanomaterials, polymeric nanoparticles, nanoclays, hydroxyapatite nanoparticles, and mesoporous silica have been used as nanocarriers of nutrients.

Nanofertilizers positively impact plant growth attributes when administered at a lower concentration. For instance, metallic nanoparticles such as gold and silver nanoparticles have been explored to improve the number of leaves, leaf area, plant height, chlorophyll content, and sugar content leading to better crop yield [93]. Zinc oxide (ZnO, 4500 mg/hectare), when administered to the brinjal plant along with 25% (by quantity) of the regularly used nitrogen phosphorus potassium (NPK) fertilizer, increases the yield by 91% [94]. Similar results are reported on field trials conducted on rabi crops using 50% less quantity of regularly used NPK fertilizer and two sprays of Nano nitrogen, which resulted in considerably increased crop yield [95]. We can infer from these results that the employment of nanofertilizers along with a lower amount of conventional fertilizers can have significant economic benefits [93–95]. ZnO is also known to impact coffee plants positively [96], whereas previous studies have shown its positive impact on allium and maize crops. The effect of various nanofertilizers on crops has been illustrated in Fig. 2. We have summarized the impact of some of the nanoparticles applied to plants along with the mode of application in Table 1 [97–107].

Nanoclays are bi-dimensional layered silicates with nanoscale thickness and several micrometers in length with broad applications in the field of food-beverage packaging [108], agriculture [108], and drug delivery [108]. Nanoclays (e.g., zeolites, kaolinite, and montmorillonite) are widely used as carriers for nutrients like nitrate [109] and phosphate [110, 111]. Carbon nanomaterials (CNMs) have shown great potential in drug delivery. However, it has not received much attention in the agricultural application in the form of fertilizers. CNMs have several positive and negative effects on the plants and soil microbes associated with the plants [112]. These effects range from acute cytotoxicity to crop yield and depend on the concentration of CNMs used. It is reported that water uptake and transport, seed germination, photosystem and antioxidant activities, activation of water channel proteins, and nutrient absorption are enhanced at low concentrations of CNMs. However, curtailment and toxicity are observed when used at higher concentrations [113]. CNMs include nanodots, nanotubes, nanodiamonds, nanobeads, nanohorns, fullerenes, and nanofibers. The most often produced CNMs for various applications include fullerenes (C_{60}), graphene, carboxyfullerenes, fullerols, carbon nanoparticles, carbon nanodots, graphene oxide, carbon nanofibers, and carbon nanotubes (CNTs). The effect of C_{60} shows no adverse effect on the growth of aquatic and terrestrial plants [114]. When treated with CNTs and graphene via the foliar and drench method, Tomato seedlings show an increased dry weight of the roots [115]. With the increase in the concentration of CNMs, the protein content, phenols, flavonoids, ascorbic acid, glutathione, photosynthetic pigments, and the activity of the enzyme's ascorbate peroxidase, glutathione peroxidase, catalase increase. Carbon nanofibers have been investigated to achieve slow release of micronutrients. Carbon nanofibers loaded with Cu–Zn in a polymeric formulation have shown increased pea plant length by more than 80 percent against the

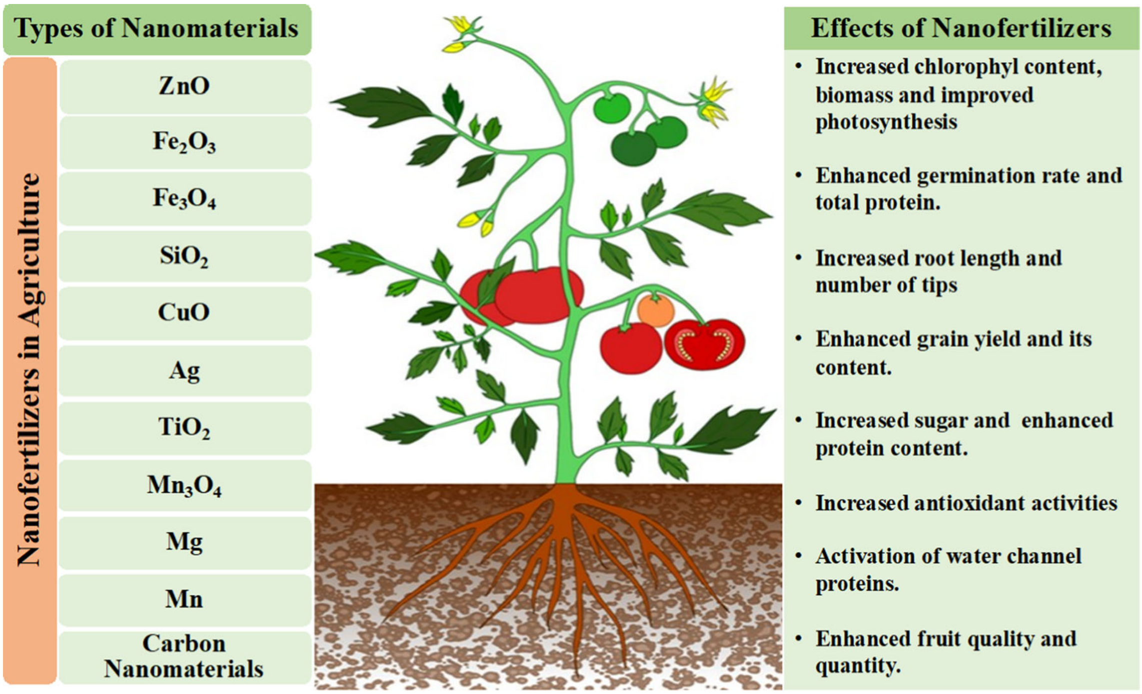


Figure 2 Different types of nanomaterials used as nanofertilizers and their effects in agriculture are summarized in this figure. Nanofertilizers affect plants in different ways based on their composition, structure/morphology/concentration, and physicochemical characteristics which can have significant impact on plants/crops productivity and quality.

control plant that did not receive the nanoformulation [116].

Mung bean is extensively consumed in many countries. The application of CNMs shows a systematic effect on the growth and development of mung beans [117]. Furthermore, it is mentioned that the application of both types of chiral carbon dots (L-CD and D-CD) increases the activity of the Rubisco enzyme and increases the photosynthesis and carbohydrate content in mung bean plants. Similar results are obtained when carbon dots are used on rice crops and show a 14.8% increase in total rice yield and resistance to rice plant diseases [118]. CNTs are widely used in various applications due to their excellent mechanical, electrical, optical, and thermal properties. CNTs help detoxify chemical fertilizers and pesticides, improve disease resistance, help in plant growth [119], and cadmium/lead uptake in seeds [120, 121]. Nanofibers are also being used as carriers to deliver various nanoparticles as nanofertilizer [116]. The investigators have prepared polymer film (PVAc-starch) with carbon nanofibers, acting as a Cu–Zn nanoparticles delivery vehicle. This complex enhances the growth of chickpea, and the scavenging activity of Zn is observed. Besides scavenging, ZnO nanofertilizers improve crop productivity in terms of dry weight and net photosynthetic rate compared with the other conventional zinc salts [96]. Zn-chitosan nanoparticles increase grain yield from 20.5 to 39.8% and enrich the grain with Zn micronutrient from 41.27 to 62.21 µg/g dry weight [122].

Hydroxyapatite nanoparticles (HANs) have enormous potential to be used as nanofertilizers and have gained substantial interest in nutrient delivery in plants. HANs are naturally occurring, biocompatible, and is chemically identical to the mineral constituent present in humans [123, 124]. Braidot, E. et al. studied carboxymethyl cellulose stabilized HANs affecting root elongation, as seen in *Solanum lycopersicum* L. [125]. They have revealed no phytotoxicity in tomato plants grown in hydroponics containing HANs and conclude that it can be used as phosphate and other element delivery vehicles. Kottegoda, N. et al. also revealed the effect of HANs on the slow release of nutrients [126]. They have studied the impact of urea-hydroxyapatite nanohybrid on tea fields located in three distinct climatic zones. They have concluded that the increment of 10–17% and 14–16% of annual nitrogen requirement compared to the conventional recommendation. Apart from this, the number of

Table 1 Different types of metalmetal oxide and silicon-based nanoparticles, their synthesis methods, mode of application, and their impacts on various plants [97–107]

Nano particles used	Synthesis method	Particle size/ shape	Types of plant	Mode of applications	Effects/impacts	Ref.
Mn_3O_4	Microwave-assisted hydrothermal method	20–60 nm, Diamond-shaped	Squash plant	Foliar application	Improved vegetative growth characteristics of the fruits, yield Increased photosynthetic pigments	[97]
Fe_2O_3	Microwave-assisted hydrothermal method	20–60 nm, Diamond-shaped	Squash plant	Foliar application	Higher content of organic matter, protein, lipids, and total energy (K cal/g) in fruits	[97]
ZnO	Procured	12–50 nm average, quasi-spherical	Capsicum chinense, coffee, pomegranate	Foliar application	Increased fruit yield and biomass accumulation Improved seed germination Improved production quality	[98, 100]
Si-NPs	Solvent extraction method along with Sol–gel method	15–91 nm, 202 nm, spherical	Rice, wheat, tomato	Soil application, spraying, or seed soaking	Protects plants against heavy metal toxicity, UVB stress, salinity stress, dehydration Plant growth promoter Mitigates toxicity of arsenic Increased production of photosynthetic pigments and improved enzymatic activity	[99, 101–103]
TiO_2	Laser-ablation method, procured	19.5–20 nm, spherical	coriander plant, Rice	Foliar Spraying, Soil application	Increased shoot and root dry biomass Increased amino acids, total sugars, total phenols and pigments Increased palmitic acid and glycerol content in grains of rice grown in Phosphorus deficient soil	[104, 105]
Cu-NPs and CuO-NPs	Procured	NA	Barley plant	Seed soaking	Improved seed germination rate Increased root and shoot length Increased fresh and dry biomass Improved antioxidant activity	[106]
Ag-NPs	Biological method (dates extract)	50 nm	Lavender	NPs added to the growth media	Increase in number of shoots per explant Increased pigment content at low doses	[107]
Si-NPs	Procured	10–20 nm	Lavender	NPs added to the growth media	Induced root formation on explant Dose dependent enhancement effects on roots/explant and length of longest root Enhanced chlorophyll a, b and carotenoid content in dose dependent manner	[107]

fertilizer applications is reduced to 50% using urea-hydroxyapatite nanohybrid, and it shows high phosphorus in soil and nitrogen in leaves.

A similar study is carried out on rice crops to evaluate the effect of urea-HANs in seed germination and transportation of essential nutrients into the soil. Urea-HANs can be an alternate source of nitrogen and phosphorus fertilizers. The hydroxyapatite nanoparticles are synthesized using the sol–gel method, and urea is loaded into the hydroxyapatite nanoparticles [127]. The urea hydroxyapatite nanoparticle enhances the fresh weight, dry weight, and seedling growth compared to hydroxyapatite nanoparticles alone. Urea-HANs show two-fold efficiency compared to the average Nitrogen and Phosphorous fertilizers, and it shows no toxicity even at higher doses.

Phosphorous plays an essential role in the growth and development of crops. The storage and release of nutrients depend on the acidity of the medium, this makes nutrient availability for plants highly dependent on the soil pH. To address this problem, in one study, researchers [128] synthesized HANs and stored them in thermoplastic biodegradable starch: pectin sachets, improving solubility and increasing phosphorous release due to acidic pH. The result also suggests that the release of HANs is independent of size, shape, and crystallinity. Similarly, nanohydroxyapatite is reported to be more effective than the conventional phosphorous source when applying hydroxyapatite to the lettuce (*Lactuca sativa* L.) plant [129]. Another study on using hydrotalcite-like Layered Double Hydroxide (LDH) structure for the controlled release of phosphorus is reported. Researchers [111] have studied the efficiency of hydrotalcite-like LDH structure and its dynamics in the soil. It is reported that the release of phosphorus in water is ten times higher for a more extended period, maintaining the availability of phosphorus in the soil, and the same level of phosphorus is released compared to that of Potassium dihydrogen phosphate. Apart from this, the interaction of phosphorus with the LDH matrix is analyzed by ^{31}P NMR, which reports the interaction of phosphorus with Fe^{3+} and Al^{3+} [111]. At the same time, Al^{3+} does not restrict the movement of nutrients in soil application [111]. Table 3 summarizes some commercially available nanofertlizers [130–136].

Nano pesticides

Pesticides like herbicides, insecticides, bactericides, fungicides, and nematicides are commonly used to target weeds, pests, plant pathogens, nematodes, and microbes that are harmful to standing crops [137] can be seen in Fig. 3. Similar to nanofertilizers, nanopesticides have garnered significant interest in replacing conventional pesticides due to their effectiveness against various pests and opportunities for targeted

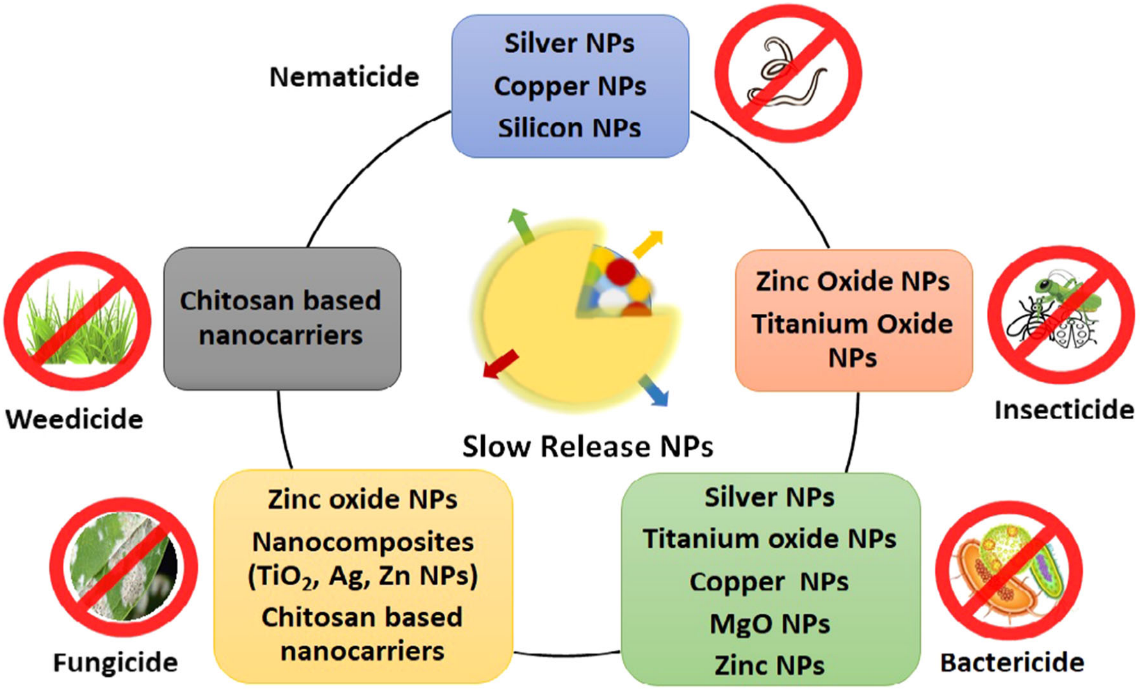


Figure 3 Different types of nanomaterials based nanopesticides in agriculture applications. Various nanomaterials have been investigated for their action against crop hampering organisms that include nematodes, fungi, bacteria, insects, and weeds.

action reducing possibilities of leakage to the environment.

Coffee is one such constituent widely used worldwide gets affected by *Colletotrichum* sp., a causative agent of anthracnose. In a study, the effect of the ZnO nanoparticles on the causative agent of anthracnose is explored by exposing them to the fungus at different concentrations [138]. In this study, cyproconazole is used as a positive control, and the fungus is grown as a negative control. The study concludes that the concentration of 15 mmol L^{-1} shows 96% fungal growth inhibition and formation of vacuoles-like structure and a decrease in cytoplasmic space. Similar work has demonstrated the effect of ZnO nanoparticles synthesized via the chemical and green method (using garlic extract) on *Mycenacitricolor* and *Colletotrichum* sp., and concludes that the nanobiohybrids show ~ 97% and ~ 93% growth inhibition of *Mycenacitricolor* and *Colletotrichum* sp. respectively [139]. We have attempted to summarize the impact of various nanoformulations on target pathogens in Table 2 [55, 140–149].

Chitosan-based nanoparticles/nanoformulations are extensively studied due to their biodegradability and biocompatibility [150, 151]. Zinc nanoparticles associated with chitosan strengthen plant immunity by increasing antioxidant and lignin content in maize crops to elevate disease control [122]. Chitosan loaded with spinosad and permethrin is checked for its anti-pests activity at different concentrations using *Drosophila melanogaster* as a model organism. It reveals that the chitosan loaded with spinosad and permethrin is more effective than the individual spinosad and permethrin, indicating that the nanoformulations may be used for pest management control [152]. More efforts to synthesize nanoparticles from plants and micro-organisms are given as they are more compatible and less toxic than the chemical route, where toxic chemicals are used for the synthesis purpose. Silver nanoparticles synthesized from red seaweed extract showed antibacterial and antifungal activity, making them suitable for nano-pesticide formulation [153]. Nanocapsules are also used to release fertilizers as well as pesticides or fungicides. Various plant extracts have antimicrobial activity and are thereby used as antimicrobial agents. The release of eucalyptus extract, which has a pesticide effect, has been carried out using urea-formaldehyde eucalyptus extract nanocapsule [154].

Similarly, azadirachtin, the main active ingredient of neem oil extracted from *Azadirachta indica*, is mainly used as biopesticides at the commercial level. Neem oil-loaded zein (corn protein) nanoparticles are studied for pesticide effect and toxicity against *Allium cepa* and *Caenorhabditis elegans* [155]. The authors have concluded that the neem oil does not alter the number of genes of *C.elegans*, which is responsible for the production of nitrogen fixation enzymes, thereby making it safe to be used as an alternative to chemical pesticides. In Table 3, we have summarized some of the commercially available nanoproducts as shown in Table 3 [130–136, 156–164].

Nanosensors

Depending upon the use, various sensors are manufactured for monitoring purposes. For practicing precision farming, it is essential to monitor factors such as plant growth, plant diseases, soil nutrition, ambient temperature, and humidity conditions. Various nanomaterials are being developed to manufacture nanosensors for utilization in agriculture and related biotechnology industries; some are documented in Table 3 [157, 160, 162, 164]. Nanomaterials-based nano biosensors can play an essential role in quantifying various chemicals samples and micro-organisms such as fungi, bacteria, and viruses in plants [7]. Numerous nanosensors have been tested on plants, such as carbon-based electrochemical sensors, antibody nanosensors, nanowire nanosensors, and fluorescence-based nanosensors. In *Arabidopsis thaliana* single-walled CNTs have been used for nitric oxide monitoring, and gold nanoparticles have been used for detecting the bacterium *Pseudomanas syringae* [165, 166]. MoS_2 (Molybdenum disulfide)-based sensors have widely been reported to detect heavy metal ions, pesticides, nitrates, and other pollutants [167].

Many nanomaterials are used in electrochemical sensing in which electrodes modified with nanoparticles work as electrocatalysts, thereby increasing the sensitivity and electron kinetics. Platinum nanoparticles (Pt NP) are used in electrochemical sensing, but such high sensitivity is not required every time, so they are utilized in combination with other metals. The electrode made from Pt NP and iron shows good electrocatalytic activity in terms of sensitivity and selectivity toward detecting hydrogen peroxide, formaldehyde, and glucose [168]. Carbon

Table 2 Different nanomaterials based nanopesticide used on target pathogens and their mode of applications, and impacts on various plants [55, 140–149]

Nano particles used/Synthesis method	Type of plant + diameter + shape	Surface coating/capping agents	Mode of applications	Target pathogen	Effect/impact	Ref.
Lignin based nano Carriers/Ultra homogenising followed by ultrasonication and drying	Grapevine + 200–300 nm + NA	Sodium Dodecyl sulfate (SDS)	Trunk Injections, in vitro by calculating Minimum Inhibitory Concentration	*Phaeomoniella chlamydospora* and *Phaeoacremonium minimum*	Highly efficient encapsulation of hydrophobic fungicides shows fungal growth inhibition	[144]
Biosynthesized Zn NPs/ Hydrothermal method	Sugar beet plants + 30 nm + Spherical to hexagonal	*M.nigra* and *G.robusta* Plant extracts	Spraying method	Cercospora leaf spot disease-causing fungus *Cercospora beticola*	Reduction of Cercospora leaf spot (CLS) disease severity Enhances sucrose content	[55, 145]
Biosynthesized CuO NPs/ Hydrothermal method	Tobacco seedlings + 40–80 nm + NA	*C. papaya* L. leaves extract	Non injured root injection method via root irrigation	Bacterial wilt disease-causing *Ralstonia solanacearum*	Results in decreased bacterial motility and disturbed ATP production in bacterial cells Greater efficacy in controlling bacterial wilt under greenhouse conditions	[146]
Thiamine-Chitosan NPs/ Magnetic stirring method	Chickpea + 10–60 nm + NA	Sodium tri polyphosphate	Foliar application	Wilt causing fungus *Fusarium oxysporum*	Positively impacts growth of chickpea seedlings by inducing defense enzymes in leaves and roots Enhanced seed germination tenfold increase in auxin levels	[147]
Neem-oil nanoemulsion/ Homogenizing method	Rice Kernal and Broken wheat grain + 208–507 nm + NA	Alkylpolyglucoside or polysorbate 80, Deionised water	Food impregnation method	Adult *Sitophilus oryzae* and *Tribolium castaneum*	Application (2.0 mL/kg azadirachtin) causes 100% mortality in *S. oryzae* adults after 24 h exposure via food impregnated method also shows efficacy against *T. castaneum*	[149]
Copper-Chitosan NPs/ Hydrothermal and Magnetic stirring	Finger millet plant + 20–30 nm + spherical	Acetic acid, acetone	Foliar, (seed + Foliar)	Blast disease-causing *Pyricularia grisea*	Significantly improved immune response observed in finger millet plant resulted in effective suppression of blast disease (up to 75% protection) and increased yield	[140, 141]

Table 2 continued

Nano particles used/Synthesis method	Type of plant + diameter + shape	Surface coating/capping agents	Mode of applications	Target pathogen	Effect/impact	Ref.
Silver NPs/ Chemical method	NA + 9 nm spherical and 21 nm Quasi- spherical	Luteolin tetraphosphate	–	*F. oxysporum, A. nidulans, Penicilliumitalicum, C. gloeosporioides, C. freundii, E. coli, L. monocytogenes, C. freundii*	Effective inhibition of a variety of fungi Effective inhibition of bacteria Lower cytotoxicity	[142]
Chitosan NPs/ Procured	Tomato + NA + NA	–	Spray Coating method	Wilt disease-causing *Fusarium andiyazi*	Antifungal effect and enhanced biotic stress tolerance Better seedling germination percentage, Growth-promoting impact on tomato seedlings	[148]
Biosynthesized Ag NPs/Using plant fruit extract (Ginkgo fruit)	NA + 8–24 nm + spherical		–	Leaf blight causing *Bipolaris maydis*	It shows the best antifungal effect at a concentration of 200 μg/mL,	[143]
Fruit extract of ginkgo fruit					Synergistic effects when used along with fungicides	

Table 3 Some of the commercially available nanoproducts and their composition, form of agricultural applications, and corresponding unique selling point [130–136, 156–164]

Product name/manufacturer	Composition	Form of agricultural applications	Unique selling point	Ref.
Prathista NPK/Prathista Industries Ltd., India	Proteino-lacto-gluconates with nitrogen, phosphorous and potash mobilizing/solubilizing bacteria as Nanotechnology formulation	Nanofertilizer	Eco-friendly fermentation process as raw material inputs	[130]
IcON Suspensions/ Sonic Essentials, Australia	Essential secondary and trace elements (zinc, copper, calcium, manganese, and magnesium) as suspension concentrates	Nanofertilizer	Research and development in collaboration with universities and independent research organisations	[131]
Nano-5/UNO Fortune Inc., Taiwan	Natural mucilage organic fertilizer contains G-protein	Nanofertilizer	Apart from growth promoting, effects on pathogenic bacterias can be seen within 20 s of coming in contact	[132]
Nano-Gro/Agro Nanotechnology Corp., USA	Growth regulator and immunity enhancer Zeolite based	Nanofertilizer	It acts as immune responder and does not make alteration at gene level	[133]
NovaL and Nano-Mn,Cu,Fe,Zn,Mo,N/ Land Green & Technology Co, Taiwan	Nanoparticles contain microelements (Mn, Cu, Fe, Zn, Mo, N) for plant growth	Nanofertilizer	Increases harvest by 20–70% and follows the moto of rebirth of healthy plantations	[134]
Nubiotek Hyper Fe + Mg/Bioteska, Mexico	Contains Iron as Nanoparticle/Nanopowder, Magnesium as Nanocapsule	Nanofertilizer	Carries active ingredients in stomata which opens for three femtoseconds	[135]
Nasco Sudarshan/Nano Agro Science Co-operative Society Ltd., India	Organic, combination of various plant nutrition, value-added natural mineral source, botanical rich elements, and bio stimulants in a nano powder form	Nanofertilizer	Ecofriendly and biobased formulations focussing on "Quit Poison and save Nature"	[136]
Cruiser MaXX/ Syngenta, Switzerland	Ingredient-Thiamethoxam, Mefenoxam, Fludioxonil	Nanopesticide	It helps in early-season diseases with its unique formulations against broad spectral diseases	[163]
PRIMO Maxx/ Syngenta, Switzerland	Active ingredient -Trinexapac-ethyl	Nanopesticide	It helps to mitigate different stresses like heat, drought, disease and traffic	[158]
Karate Zeon/Syngenta, Switzerland	Encapsulated Lambda-Cyhalothrin Insecticide	Nanopesticide	Strong adhesion to the target site and protection of active ingredients against UV by encapsulation	[161]
Kocide 3000/Certis USA LLC	Copper Hydroxide NPs (Fungicide/Bactericide)	Nanopesticide	Pioneer in the field of biobased pesticides	[156]
Banner MAXX/ Syngenta, Switzerland	Propiconazole concentrate emulsion	Fungicide	Fast Uptake, Action and Result	[159]
RipeSense/Ripesense Limited, New Zealand	Intelligent sensor label that changes color to indicate the ripeness of fruit	Nanosensor	Expertise in delivery of the right product to consumer as per their need	[164]
Nanodetect/TTZ Bremenhaven, Germany	Monitor contaminants such as Pathogenic micro-organisms, Mycotoxins, drug residues in the food chain	Nanosensor	–	[157]

Table 3 continued

Product name/manufacturer	Composition	Form of agricultural applications	Unique selling point	Ref.
Cantilever based Biosensor/NA	Placed in the soil to measure the soil content by chemical reaction with the fertilizers, also used to measure temperature and humidity	Nanosensor	–	[160]
FRET-based sensors/ NA	Studying intracellular concentration of any metabolite *in-vivo*/*in-vitro*		–	[162]

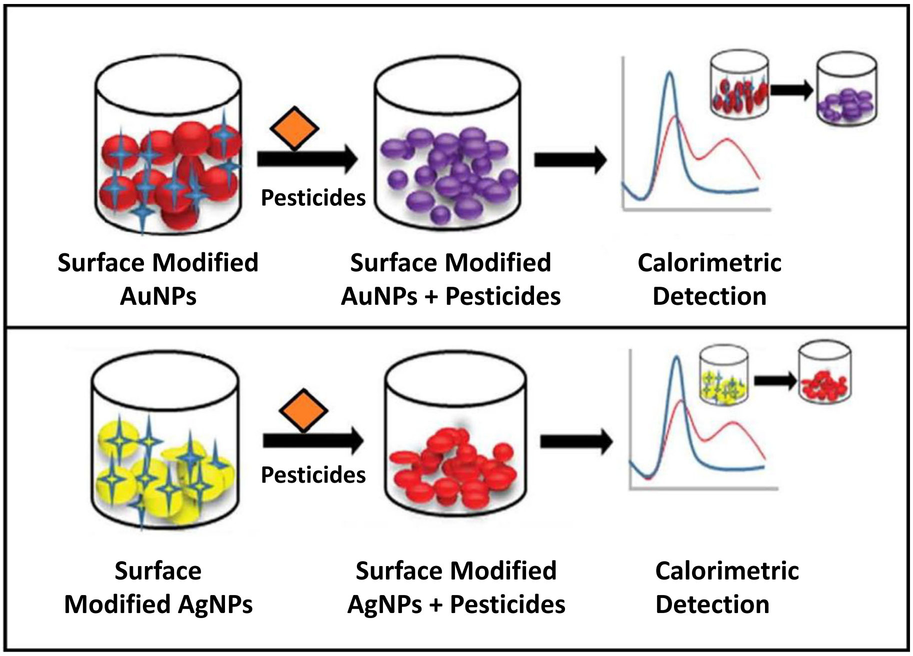
nanomaterials are also used in electrochemical sensing [169]. They are used for multiple applications such as bioimaging, nanomedicines, photo/electrocatalysis, and bio/chemical sensing due to their unique properties such as high surface area, nontoxicity, biocompatibility, high porosity, and absorption capability [169].

Fluorescence is another technique used in the detection system that works with the help of fluorophores by producing measurable changes when it comes in contact with the analytes. Nanoparticle-based fluorescence techniques are excellent compared to conventional fluorescence techniques [170]. As a result, the inorganic nanoparticles are used with fluorophores, which offer tremendous potential in the optical sensing of various analytes. Also, many inorganic nanoparticles show promising results in colorimetric detection techniques to make them simple, faster, and more sensitive [171]. Metal nanoparticles show different colors depending on the size of the nanoparticles. When coming in contact with the pesticides (analyte), these metal nanoparticles agglomerate and reveal color change within a few minutes of reaction, as seen in Fig. 4.

Soil remediation

In agriculture, the status of the soil in terms of fertility, pH, and water holding capacity plays an important role, and the crop yield is directly related to the soil grade. Though chemical agents like insecticides, fungicides, and herbicides, collectively known as pesticides, prevent crop wastage by protecting plants against pests, however, over time, these chemical agents get accumulated, thereby making the soil unfit for agriculture. Soil degradation due to contamination has been a cause of significant concern worldwide [172]. Consumption of foods grown on bioaccumulated soil and biomagnified by such pollutants can significantly risk health. Various nanotechnology-based products are currently used in the remediation of soil. Nanoparticles like ZnO, titanium oxide, fullerenes, and other stabilized nanoparticles have been investigated for use in soil remediation [173]. The large surface area of the nanomaterials makes them the right candidate for great adsorbents [174, 175] for soil remediation either by detoxification or transformation of the pollutants present in the soil [176]. Aerosols generated due to the combustion of fossil fuels in the paper, pulp, dye industries, and textile mills may lead to the deposition of heavy metals such as arsenic, chromium, cadmium, mercury, lead, and tin causing soil contamination [177, 178]. Crops are grown in such heavy metal polluted soil resulting in the reduction of chlorophyll content which indirectly hinders plant's growth and development [179].

Nanoscale zero-valent iron is the most widely studied nanoparticle for soil remediation. The authors have reported [180] that the nanoscale zero-valent iron successfully reduces the concentration of arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), and zinc (Zn) in the soil. The study also reveals that at 10% of nanoscale zero-valent iron, the concentration of As, Cr, and Pb decreases by more than 82%, whereas, for Zn, it is in the range of 31–75%. The lowest decrease in the concentration is seen for Cd in 13–42%. Hexavalent chromium [Cr(VI)] is one of the toxic contaminants present in the environment. It has been revealed that synthetic iron sulfide nanoparticles stabilized with carboxymethyl cellulose (CMC) can remediate the soil and groundwater contaminated by hexavalent chromium [Cr(VI)] [181]. A study carried out by Huijie Su, and co-workers [182] reveals that the biochar-supported zero-valent iron nanoparticles (nZVI@BC) synthesized can decrease



Figuer 4 Colorimetric detection technique using nanosensors. Gold and silver nanoparticles interacted with analyte and agglomerate to give specific color changes enabling easy detection. (reproduced from [171]).

the hexavalent chromium [Cr(VI)] contaminant from the soil by using 8 g of (nZVI@BC) per kg of soil for 15 days. The study also reveals that the synthesized biochar-supported zero-valent iron nanoparticles (nZVI@BC) can increase the fertility of the soil and decrease the phytotoxicity caused by Cr(VI).

Pesticides and persistent organic pollutants (POP) pose a significant risk to the health of the food chain due to bioaccumulation and biomagnification. POP are lipophilic compounds that accumulate in human beings' fatty tissues, thereby affecting their health in complex ways [183]. Nanoparticles are also investigated in removing or degrading these pollutants. These pesticides and POP are degraded into more harmless and simple forms like H_2O, CO_2, and N_2 by photocatalysis with the help of ZnO [184] and TiO_2 nanoparticles [184, 185]. A study [186] reveals the effect of two types of nanoscale zero-valent iron (nZVI) (type B made using precipitation with borohydride and type T produced by gas-phase reduction of iron oxides under H_2) on persistent organic pollutants like Dichlorodiphenyltrichloroethane (DDT), the eco-toxicity effect of soil and water on barley and flax plants, earthworms, ostracods, and bacteria. Both types of nZVI effectively degrade DDT in water and have a negative impact on tested organisms. The degradation of aged DDT in the soil is less, and nZVI-T has the most negligible adverse effects on tested organisms. Similarly, the researchers [187] have reported using nanomaterial and metal–organic framework complex to remove pesticides from the soil. Apart from this, nanomaterials in association with plants help remove the soil pollutants, leading to phytoremediation, as shown in Fig. 5. The nanomaterials adsorb the soil pollutants onto their surface, which are then internalized by the plants and get accumulated in various plant parts, thereby removing the pollutants from the soil [188].

Limitations

The toxicity studies of different nanomaterials on plants are of utmost importance and must be assessed thoroughly before applying them to agriculture. Plants tend to absorb the non-essential components besides the essential nutrients/elements [189]. This may have a lethal effect on organisms that are dependent on plants as a source of nutrition once these non-essential components get accumulated in the plants beyond a threshold level. There are significant practical chances that such toxic elements

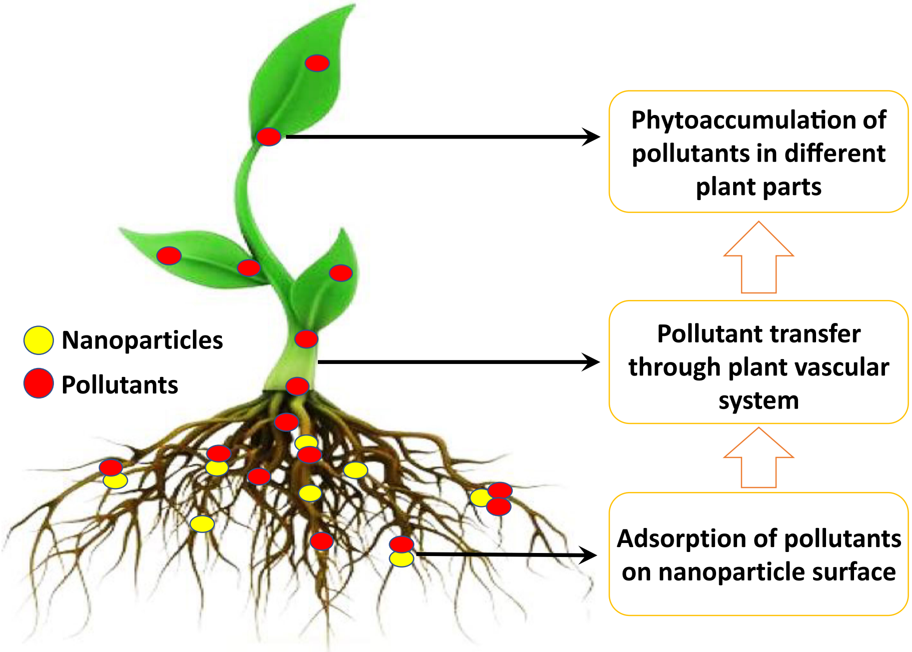


Figure 5 Soil remediation using nanoparticles via phytoremediation. This figure illustrates the process of accumulation of soil pollutants in different plant parts achieved with the aid of nanoparticle that enables preferential uptake (reproduced from [188]).

may enter the food chain of the organisms ingesting such crops. Recently CNTs have been widely investigated for their usage in agriculture; most of the studies have shown that they can positively impact cell growth and development [190, 191], whereas some other studies showed a reduction in plant growth and development [192]. Thus, these conflicting results raise questions regarding the safety of CNTs. Besides, CNTs can have a detrimental effect on the environment and health when they are applied in association with other nanoparticles [113, 193]. Moreover, many MONPs have been shown to reduce germination rate, root/shoot length, transpiration rate, and number or size of stomata, chloroplasts, thylakoids, plastoglobules, along with the decrease in chlorophyll content, including chlorophyll-a, chlorophyll-b, carotenoids, and an increase in the number of genes responsible for chlorophyll synthesis [194–196].

Furthermore, studies have also shown that titanium oxide NPs increase the overall amino acid accumulation, whereas CuO NPs decrease the essential amino acid concentration [197]. The transgenerational effect on the treatment of radish plants (*Raphanus sativus*) with ZnO and CuO NPs negatively impacts progeny root and shoot lengths. The accumulation of copper and zinc elements from the parent plants is also reported [198]. Moreover, MONPs such as CuO and Al_2O_3 applied with tomato plants (*Solanum lycopersicon*) showed variations in plant growth properties such as foliage surface area, chlorophyll, and proteins [199]. In addition, the accumulation of copper and aluminum in root/shoot is also reported. However, the effects of nanoparticles on non-target ecosystems have been a significant concern. Therefore, long-term mesocosm studies have been reported using intensified eutrophication in aquatic ecosystems and altered ecosystem productivity [200]. The impact on exposures of copper (II) hydroxide [$Cu(OH)_2$] as nanopesticides on the soil and sediment biodiversity of terrestrial and wetland ecosystems show limited effects on the terrestrial soil communities.

In contrast, significant changes in the sediment communities of the wetland mesocosms are reported. Similarly, the soil biodiversity of terrestrial ecosystems has limited effects on exposure to nanoparticles, whereas non-target aquatic communities show significant impacts [201]. From the above studies, it is evident that the effect of nanomaterials on crops depends on their concentration and the immediate environment to which (i.e., terrestrial or aquatic region) they are applied. Hence, studying the nanomaterial's full effect and the life cycle is essential to avoid future detrimental effects. This needs serious attention from manufacturers, researchers, and policymakers to study the interaction of nanomaterials with the environment.

Though nanoparticles have shown promising results in small-scale agriculture studies, extensive data on field trials are required to ascertain their safety, which is currently unavailable. Similarly, while going through published literature, we have observed that there is not much data on the long-term effects of the nanoparticles and their fate after being exposed to the ecosystem. The amount of information regarding the nanoparticle's effect on the crops is currently limited. Therefore, we firmly believe that the delivery systems for nanoparticles need to be improved, keeping in mind their ecotoxic effects. As a combination of different factors affects the final impact of nanomaterials on the yield and quality of crops, it would be convenient to have a consolidated source to select the best possible attributes for the usage of nanoparticles. Thus, a central database can be created with information on the morphology and impacts of the individual nanoparticles and potential toxicity based on different attributes such as dosage, concentration, and physical characteristics. Besides, toxicity in the practical scenario cannot be ascertained based on just a single generation's yield, and hence more studies need to be conducted. Likewise, bioaccumulation of nanoparticles in the food web is a possible scenario that can be pretty severe. Therefore, studies on determining the life cycle of the nanoparticles, their wear and tear with time, and final fixation when placed in the environment of their activities need to be further considered. Moreover, apart from the chemical synthesis mode, nature-derived nanoparticles or nanoformulations that are biocompatible and biodegradable could undoubtedly lower the concerns regarding their effects on the ecosystem. However, as mentioned earlier, minor changes in the morphology of nanoparticles can significantly impact their efficacy in agricultural applications. Hence, appropriate methods need to be adopted for manufacturing similar-sized nanoparticles consistently and economically. Nevertheless, we have also found a lack of legislation and public awareness on the usage of nanoparticles that needs to be immediately addressed.

Conclusion and future perspective

The role of nanomaterials in agriculture can bring a revolution in increasing the quality and quantity of crops. Nanoparticles-based fertilizers and pesticides can ultimately replace conventional fertilizers/pesticides. The results reported by various investigators on their utilization have been quite encouraging. Moreover, nanosensors can significantly help implement precision farming to achieve sustainable growth in crop productivity and quality. Besides improving stress tolerance in plants to external environment conditions, nanoparticle administration also provides an alternative to genetically engineered plants needed to adapt with constantly changing climatic factors as a result of global warming. Soil remediation is another aspect to which nanoparticles have been applied, and results have shown that they can significantly improve the prospects for sustainable farm management. Although there are significant advantages associated with the usage of nanomaterials-based products in agriculture; however, there are still some gaps that need to be addressed, and thereby further investigations are required. Additionally, the potential toxicity is a major concern impeding the wide-scale adoption of nanoparticles-based fertilizers/pesticides, and sensors, primarily focusing on the trans-generational impact of nanomaterials to ascertain their safety aspect.

Furthermore, based on the positive impact of nanomaterials in lab-scale studies and limited field trials, the implementation of such commercially available nanoproducts is bound to increase in the future. Although applications of nanomaterials in agriculture are very promising; however, it brings a daunting task of educating the end-user regarding their usage, especially in developing, agri-intensive countries like India. Nevertheless, to bring a transition from conventional fertilizers and pesticides to nano-fertilizers/-pesticides in the agriculture sector, the end-user must be educated regarding the importance of nanoproducts while strictly adhering to dosage limits to overcome their side effects. Otherwise, the purpose of using nanotechnology to achieve sustainable development in the agriculture sector will be defeated.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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