







Potential nano strategies in insect pest management: synthesis, applications and plant interactions

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Abstract

Global crop production is significantly affected by biotic stress, typically managed with conventional chemical agents. However, these methods can have detrimental effects such as the development of resistance, pest resurgence, unwanted effects on human health and environment. Nanotechnology offers an alternative approach to crop pest management that can help alleviate these issues. It is a multidisciplinary strategy for plant protection that includes nano-based pesticide formulations and nano carrier based biopesticides. Nanoparticles have distinct physical and chemical characteristics due to their tiny size, measured in nanometers. Various nanoparticles, including polymeric, metal, metal oxides and silica nanoparticles have been synthesized and utilized to combat various insect pests and aid in pest control. Nano silica (SiO₂) and other metal oxide nanoparticles like silver (Ag), copper (CuO), titanium (TiO₂), zinc oxide (ZnO), gold (Au) and aluminum (Al₂O₃) have been found to be effective against stored pests and crop pests, as well. However, more studies are needed in the future to understand how these particles affect non-target species that coexist in the same habitat as the target species. While nanoparticles offer promising solutions for pest management, their potential risks such as toxicity to beneficial organisms, environmental persistence, regulatory challenges and high production costs must be addressed in the future by developing eco-friendly, biodegradable formulations and establishing regulatory frameworks to ensure their safe and sustainable application. This review explores the effectiveness of nanoparticles and nano-based formulations in managing insect pests and also outlines future research directions on the impact of nanoparticles on beneficial fauna.

Keywords: insect pests; management; nanoformulations; nanoparticles; synthesis

Introduction

Plant pests cause up to 40 % yield losses globally, threatening food security and economic stability. As a result, there is a growing need for innovative solutions that minimize environmental impact while addressing pest-related challenges. One such promising advancement is nanotechnology, a novel and multidisciplinary field that focuses on the synthesis and development of nanoparticles at the molecular level on a nanoscale (1). Nanotechnology has the potential to revolutionize the agricultural and food industries (2).

Nanoparticles, which range in size from 1 - 2 nm, are engineered with specific shapes, sizes and structural properties, allowing them to be used as carriers for precise and controlled pesticide release through techniques such as adsorption, conjugation and encapsulation (3, 4). Their positive effects on crop growth, enhancement of germination potential, along with increased resilience to both abiotic and biotic stresses, make nanomaterials a viable alternative to traditional chemical pesticides in crop production (5, 6).

Furthermore, nanoparticles synthesized from various plants exhibit strong insecticidal and pesticidal properties (7). A range of nanotechnology-based products have been developed, including nano-pesticides, nano-herbicides, nano-fungicides and nano-fertilizers, which address pests, weeds, diseases and nutritional deficiencies, respectively.

Abiotic and biotic stresses significantly reduce agricultural productivity, with diseases, weeds and insects negatively impacting crop yields. Insects, which account for nearly two-thirds of all known species, feed on a wide variety of plants and also infest stored products, causing direct and indirect damage. Recent advances in nanotechnology have enabled precise control at the nanoscale, offering new possibilities for enhancing crop protection (8). The use of nanoparticles can help mitigate biotic stresses while also providing protection against abiotic stresses. Various nanoformulations developed using metal nanoparticles such as silver (Ag), copper oxide (CuO), zinc oxide (ZnO), aluminum (Al), titanium dioxide (TiO₂), selenium (Se) and silica dioxide (SiO₂), have shown a wide range of applications in plants.

Silica nanoparticles (SiO₂), in particular, have been found to alleviate insect pests by promoting plant growth and strengthening plant resistance (9).

Recently, nano-pesticide formulations such as polymeric nanocapsules, nanoshells, nanogels and micelles have been developed to address the challenges associated with traditional pesticide use. Polymeric nanoparticles, for instance, can act as carriers for biocontrol agents and help manage biotic stresses in plants (10, 11). Exposure to nanoparticles enhances the plant's ability to activate antioxidant enzymes, scavenge free radicals and modulate mRNA expression. Nanoparticles also influence detoxifying enzyme activities and consequently increasing insect mortality (12).

Nanocapsules offer additional benefits by making pesticides more stable and allowing them to remain on plant surfaces for longer periods. They shield the active ingredients from sunlight and UV rays, reducing the frequency of insecticide applications (13). Despite the advantages of pesticides, their use can lead to negative consequences such as food contamination, harm to beneficial organisms, environmental disruption and the development of pesticide resistance (14). To address these issues, biological nanoparticles and biopesticides have been introduced as eco-friendly alternatives to chemical insecticides (15). Moreover, nanoformulations of conventional insecticides have the potential to enhance their toxicity against target insect pests by up to 10 times (16).

This review aims to explore the recent scientific advancements in crop pest management using nanoparticles, with a focus on the role of various nano-based formulations in controlling insect pests and their impact on natural enemies.

Synthesis of nanoparticles

Nanoparticles can originate from either natural or synthetic sources and they display distinct properties at the nanoscale. Their synthesis follows 2 main approaches: top-down and bottom-up processes, each employing different preparation techniques (Fig. 1).

Top-down approach

Physical method: The top-down approach reduces bulk materials into nano-sized particles (17). Nanoparticles synthesized through top-down methods commonly utilize techniques such as mechanical milling, laser ablation, laser pyrolysis, thermal decomposition, sputtering, nanolithography and the pulsed wire discharge method (Fig. 2).

In mechanical milling, shear ball mills with a milling chamber and small balls are used to break down solid particles into nanoparticles, making it a highly economical method for producing particles ranging from 2 - 20 nm in size (18). In laser ablation technique, the process of creating plasma involves directing a high-power pulsed laser beam into a vacuum chamber containing the targeted material. This method has been used to synthesize a wide range of nanomaterials, including carbon nanomaterials, oxidecomposites and metal nanoparticles (19).

Laser pyrolysis, in which an intense laser beam breaks down reactant gases like argon or helium, produces nanoparticles whose distribution and size are influenced by gas pressure (20). In sputtering, nanoparticles are deposited onto a surface by causing ions to collide with particles (21). Nanolithography achieves precise shapes and structures on light-sensitive materials by selectively removing material from individual nanoparticles and it is a cost-effective technique (22). In the pulsed wire discharge method, a metal wire is subjected to a pulsating current that causes it to evaporate into vapor, which then cools in an ambient gas to form nanoparticles (20). While these techniques may be costly and impractical for large-scale production, they are effective for in-vitro research purposes.

Bottom-up approach

Chemical method

Bottom-up techniques utilize small physical or chemical forces to assemble basic building blocks into more complex structures. The chemical method, also known as solution-phase or wet synthesis, includes techniques such as sol-gel processing, chemical vapor deposition (CVD), co-precipitation

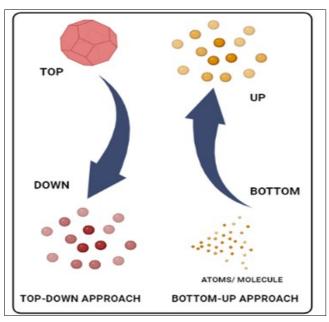


Fig. 1. Approaches on the synthesis of nanoparticles.

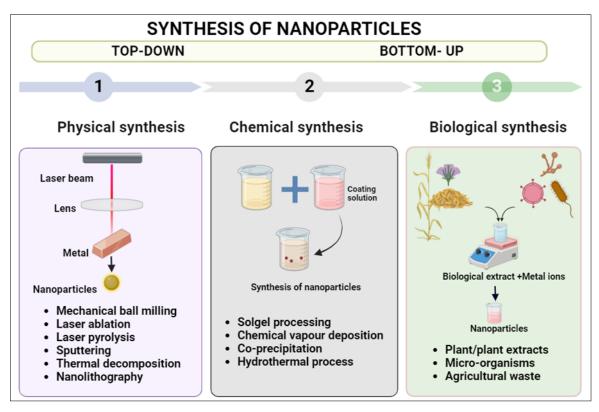


Fig. 2. Synthesis of nanoparticles using various methods.

and hydrothermal processing (17). Among these, the sol-gel method is the most commonly used for generating nanoparticles. In this method, a sol is a liquid-phase colloidal system, while a gel is a solid macromolecule dispersed in a liquid. Precursor chemical solutions, such as metal oxides and chlorides, are agitated to disperse them evenly throughout the host liquid, creating a system with both solid and liquid phases (23). The nanoparticles are then recovered through phase separation techniques, such as filtration, sedimentation and centrifugation.

In chemical vapor deposition (CVD), the interaction between a heated substrate and gas forms a thin layer on the substrate's surface, from which high-quality nanoparticles are produced (24). In the co-precipitation process, solvents like ethanol, acetone, or hexane rapidly diffuse into a non-solvent polymer phase, leading to nanoparticle formation (20, 25). Hydrothermal synthesis allows for the creation of nanoparticles across a broad temperature range, from room temperature to very high temperatures and is used to produce various nanomaterials such as nanosheets, nanospheres,

nanorods and nanowires (21, 26). Chemical methods are advantageous over physical methods because they do not require complex or expensive equipment. However, they may pose environmental risks due to the use of hazardous chemical agents.

Biogenic synthesis: Compared to chemical and physical methods, the biological approach offers a more sustainable means of synthesizing nanoparticles. Biogenic methods are simpler, cost-effective, eco-friendly and easier to characterize than traditionally synthesized nanoparticles. Biogenic nanoparticles can be synthesized using various biological systems, including bacteria, fungi, yeast, viruses, plants and plant-derived products (Table 1).

In bio-based nanoparticle production, a bottom-up approach is employed, wherein molecules derived from biological organisms act as reducing and stabilizing agents that facilitate the synthesis process. The synthesis of nanoparticles using biological systems involves 3 primary steps: selecting an appropriate solvent medium, choosing a reliable and environmentally friendly reducing agent and

 Table 1. Biogenic synthesis of nanoparticles employed in pest management

Biomaterial to synthesize NP's	Nanoparticles	NP's shape/ structure	Size	Target insect pest	Reference
Ocimum tenuiflorum (Leaf extract)	Ag NPs	Spherical	10 - 65 nm	Larvicidal effect against <i>H. armigera</i>	(92)
Sargassum wightii (Leaf extract)	Zn NPs	Spherical	20- 62 nm	Insecticidal effect on H. armigera	(93)
Punica granatum (Peels extract)	Cu NPs	Spherical	40 nm	Insecticidal activity against green peach aphid	(94)
Pongamia pinnata (Leaf extract)	ZnO NPs	Hexagonal	21.3 nm	Pesticidal effect on Callosobruchus maculatus	(95)
Beauveria bessiana (Fungi)	Ag NPs	Spherical	3-25 nm	Significant mortality against Lipaphis erysimi	(96)
Aspergillus niger (Fungi)	CuO NPs	Spherical	14.0 - 47.4 nm	Insecticidal activity against Rhyzopertha dominica and Sitophilus granarius	(97)
Bacillus thuringiensis (Bacteria)	Ag NPs	Spherical	18.24 nm	Inhibition of survival, growth and reproduction of <i>Tribolium castaneum</i>	(98)
Pseudomonas fluorescens (Bacteria)	Cu NPs	Spherical	48. 07 nm	Excellent insecticidal activity against Tribolium castaneum	(62)
Spirogyra hyalina (Algae)	Ag NPs	Spherical	52.7 nm	Insecticidal activity against <i>Tribolium</i> castaneum	(99)

selecting a non-toxic substance to serve as a capping agent to stabilize the generated nanoparticles. This approach yields nanoparticles with distinct and improved qualities, making them valuable for biomedical and other related applications (27).

Multifaceted applications of nanoparticles: Advancements across various fields

In past few years, nanotechnology have witnessed an abrupt rise in interest because of its substantial applications in various fields including medicine, agriculture, environment, food, biotechnology, pharmaceuticals, energy and materials (Fig. 3). A few examples are waste water treatment, environmental monitoring, food additives with functional properties and antimicrobial agents (17).

Employing nanoparticles (NPs) in agriculture will promote higher crop yields, alleviate the negative effects of agriculture on the environment, while improving the safety and quality of food products (17). One of the most significant applications of NPs in agriculture is, utilizing them as an agrochemical input delivery system, which enables more precise application and thereby aids in minimisation of dosages and lowers the risk of environmental contamination (28). Nano based fertilizers are found to be superior to conventional fertilizers, because of its controlled nutrient release property and that eventually improves the plant's nutrient uptake efficiency. Nano biochar derived from agro waste materials has the worth of sustainability in agriculture, as they aid in soil amelioration, enhancement of crop growth and plant protection as well (29). Moreover, application of nanoparticles on crops have assisted in managing various biotic (insect pests, diseases, nematodes) as well as abiotic stresses (drought, salinity, heavy metals, flooding), of which the significance of various NPs in alleviating insect pests is comprehensively reviewed below. Regarding food safety, NPs can detect and

destroy the pathogenic microbes in food products, consequently lowering the risk of foodborne illness (30).

Nanoparticles are increasingly attractive for their diverse applications in the environmental field. They serve as bioremediators for polluted ecosystems, sensors for monitoring pollutants and catalysts in environmental remediation processes. NPs facilitate the removal of pollutants from wastewater, while materials such as carbon nanotubes, fibers, metal oxides and nanoscale zeolites are employed to remediate contaminated soil and water (30). In the fields of medicine and pharmaceuticals, NPs are utilized in diagnostics, drug delivery, cancer therapy and tissue engineering (31). Additionally, NPs find applications in the food industry, defense sector, as well as in electronics, energy and materials science (17). Despite their wide range of applications, NPs face several challenges, particularly in their development and synthesis, as well as their environmental impact.

Nanoparticles in insect pest management

Insect pest management primarily relies on use of pesticides which are potentially harmful to the ecosystem and also, they pose greatest threat to crop yields. Nanoparticles have emerged as a promising alternative in the agricultural sector due to their biocompatibility, eco-friendliness and biosafety. Advanced "smart" delivery systems for controlled release of active agents have been influenced by techniques such as encapsulation, covalent bonding, adhesion and adsorption. These systems are crucial for protecting bio-actives applied in the field from environmental challenges, including UV degradation, rain, evaporation and temperature fluctuations, offering an alternative to traditional chemical pesticides and resistant plants (3). In recent years, the use of nanoparticles and nano-based formulations in pest management has gained traction. Nano-based pest management reduces pesticide costs through targeted delivery and slow-release

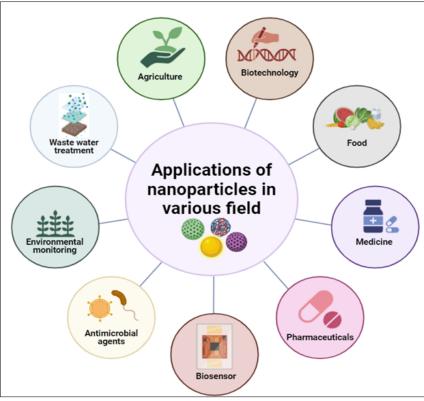


Fig. 3. Applications of nanoparticles across various field.

formulations, thereby minimizing input expenses for farmers. They boost crop yields, improve market value and and offer long-term savings by reducing environmental impact and pesticide resistance. Various nano-formulations, depending on their structure and chemical composition, have been reported to be effective against different insect groups, including sucking pests, defoliators and borers.

Role of nanoparticles in insect pest management

Sucking pests

Sucking pests are among the most notorious insect pests, causing significant damage to crop plants. Numerous studies have reported the successful application of nanoparticles for managing these pests. In a greenhouse experiment, spraying faba bean leaves with silica (SiO₂) nanoparticles resulted in 100 % mortality against 3 distinct aphid species: Acyrthosiphon pisum, Aphis craccivora and Myzus persicae at a concentration of 500 ppm (32). Application of iron oxide (FeO) and ZnO nanoparticles in cotton cultivation led to a complete reduction in thrips populations (33). Additionally, suppression of thrips in Capsicum species under greenhouse conditions was primarily attributed to the use of silver (Ag) and copper (Cu) nanoparticles (34). Ag nanoparticles synthesized from neem extracts showed impressive efficacy against 3rd instar nymphs and adults of Bemisia tabaci at a concentration of 1200 ppm (35). Furthermore, application of fluorescent silica nanoparticles in rice at 5 mg/L increased lignin content and facilitated silica precipitation in cells, thereby creating a mechanical barrier that enhanced resistance against the brown planthopper, Nilaparvata lugens (36).

Defoliators

Insect defoliators cause significant leaf damage to crop plants, disrupting the plants' photosynthetic efficiency. The primary insect defoliator in crop ecosystems is lepidopteran caterpillars. Various nano-based pesticide formulations have been evaluated for their effectiveness against different defoliators. For instance, when 2nd instar larvae of the cotton leaf worm, Spodoptera littoralis, were exposed to 2 types of nanoparticles-one functionalized mercaptopropyltriethoxysilane and the other with thiolcapped silica nanoparticles at a concentration of 0.125 mg/ cm²-mortality rates of 58 % and 64 % were observed respectively (37). Additionally, tomato plants treated with 300 and 350 ppm of nano silica exhibited increased resistance against S. littoralis (38). The application of silica nanoparticles for agricultural pest management is logically supported by silicon's potential to enhance plant resistance to both biotic and abiotic stresses.

Moreover, the application of zinc oxide (ZnO) nanoparticles resulted in significant decrease in fecundity, hatchability and oviposition of *Spodoptera frugiperda* (39). In a laboratory bioassay, larvae of the diamondback moth, *Plutella xylostella*, exhibited elevated mortality when treated with silicon dioxide nanoparticles due to body wall abrasion, spiracle blockage and desiccation. Among the 4 bioassay techniques-leaf dipping, dust spray, solution spray and larva dipping-the dust spray method resulted in increased mortality of up to 85 % after 72 hr of treatment at a rate of 1 mg/cm² (40). Interestingly, there is a beneficial insect

defoliator, the mulberry silkworm, *Bombyx mori*, which primarily feeds on mulberry leaves. Silver nanoparticles (Ag NPs) at a lower concentration of less than 400 mg/L promoted larval growth and increased cocoon weights in *B. mori*, while higher concentrations exceeding 800 mg/L resulted in larval mortality (41).

Borers

This category of pest bores into the shoots, fruits, buds, stems and roots of various crop plants, causing devastating yield losses. Titanium dioxide (TiO₂) nanoparticles derived from the leaf extract of Moringa oleifera demonstrated a promising insecticidal effect on the red palm weevil, Rhynchophorus ferrugineus, with mortality rates increasing as the concentration of nanoparticles rose (42). Silver nanoparticles synthesized from Aristolochia indica extract exhibited 100 % mortality against 3rd instar larvae of the American bollworm, Helicoverpa armigera, at a concentration of 50 mg/mL, highlighting their potent larvicidal activity (43). Moreover, the insecticidal activity of silver nanoparticles mediated by Ficus benghalensis inhibited midgut protease activity in H. armigera, significantly reducing both larval weight and survival rates (44). Silica nanoparticles of size 20 nm showed notable insecticidal effects against the tomato pinworm, *Tuta* absoluta (45). Higher mortality rates of 93 - 100 % were observed in subterranean termites, Reticulitermes flavipes, when exposed to wood treated with nano zinc oxide, in contrast to zinc sulfate (46). This indicates that nanoparticles can be effectively recommended for termite management as well (Table 2).

Nanoparticles in storage pest management

Primary pests of storage

Internal feeders: Buildup of insects in stored grains leads to both quantitative and qualitative losses, rendering the food products unfit for human consumption. Traditionally, synthetic insecticides have been used to manage stored grain pests. However, repeated use of these chemicals has led to the development of pesticide resistance. In recent years, nanoparticles have garnered significant attention for their role in agricultural pest management. In particular, inorganic nanoparticles have been extensively studied for controlling storage grain pests. Additionally, plant-mediated nanoparticles have gained interest due to their ease of production and environmentally friendly nature, compared to chemically fabricated nanoparticles (47).

In storage pest management, inorganic inert dust serves as an ecologically sound alternative to chemical pesticides. These inert dusts, such as synthetic silica (SiO₂), natural silica (diatomaceous earth), kaolinite and silica gel, eliminate storage pests by removing or adsorbing the epicuticular lipid layers, resulting in excessive water loss through the cuticle. There is evidence suggesting that nano silica can serve as a viable substitute for commercially available inert dusts. An investigation on impact of nanoparticles, including nano silica, nano clay and nano alumina, on the rice weevil (*Sitophilus oryzae*) in stored maize revealed that nano silica at 500 ppm/kg proved to be the most effective among others, inducing immediate mortality and halting adult emergence of *S. oryzae* (48). In another study,

Table 2: An overview of different NPs employed in insect pest management

Nanoparticles	Size, Shape	Concentration of NPs	Target pests	Impact on target pests	Reference
Silver nanoparticles (Ag NPs)	61.70 nm, spherical	2000 ppm	H. armigera	93.33 % larval mortality at 2000 ppm	(100)
	50.2 nm, hemispherical	64 ppm	Diaphorina citri	High insecticidal activity on 2 nd instar nymphs	(101)
Titanium dioxide	36.4 nm, spherical	900 µg/mL	Spodoptera litura	Increase in detoxifying enzymes	(102)
Zinc oxide nanoparticles (ZnO NPs)	80-100 nm, irregular spherical	200 ppm	H. armigera	Reduction in longevity and fecundity	(103)
	60.82 nm, hemispherical	343.4 ppm	Spodoptera frugiperda	Alteration in larval body morphology, necrotic and mummified bodies	(104)
Silica nanoparticles	4 nm, round-shape	250 ppm	Callosobruchus maculatus	Decreased adult longevity and their emergence rate	(105)
Selenium nanoparticles (Se NPs)	3 to 15 nm, spherical	25 ppm	Agrotis ipsilon	Decrease in antioxidant activities and also exhibited larvicidal activity	(106)
Iron oxide nanoparticles (Fe NPs)	3.8- 11.95 nm, irregular in shape	100 μg/mL	Tuta absoluta	Strong insecticidal activity	(107)
Copper nanoparticles (Cu NPs)	38 nm-size, flake-like- shaped	150 µg/10 µL/ larva	Galleria mellonella	Reduction in mitotic haemocytes and increase in apoptotic and necrotic haemocyctes	(108)

increased concentrations of silica nanoparticles led to 100 % mortality and reduced fecundity in the groundnut bruchid (*Caryedon serratus*) in stored groundnuts (49). Nano silica particles outperformed coarse silica in terms of insecticidal efficacy against the pulse beetle, *Callosobruchus chinensis* (50). Moreover, treatment of green gram seeds with *Bacillus thuringiensis*-coated zinc oxide nanoparticles at 25 μ g/mL resulted in 100 % mortality of *C. maculatus*, with decreased inhibition of detoxifying enzymes such as cysteine protease, mid-gut α -amylase, glutathione transferase (GST) and α -glucosidase activity (51).

Insecticidal potential of ZnO nanoparticles as an efficient and sustainable control agent against the Angoumois grain moth (*Sitotroga cerealella*) and rice weevil (*S. oryzae*) was also explored with increasing mortality and reduced progeny in both the species (52). Biogenic silver nanoparticles (AgNPs) demonstrated higher contact toxicity against *S. oryzae* compared to *Tribolium castaneum* (53). Silicon dioxide (SiO₂) nanoparticles proved more effective against the lesser grain borer (*Rhyzopertha dominica*) than against *Tribolium confusum* in wheat and barley (54). Nano silica particles also caused larval mortality in the potato tuber moth (*Phthorimaea operculella*) (55). Thus, nano silica not only offers an outstanding management option for coleopteran

storage pests but also demonstrates its potential in tackling lepidopteran storage pests (Fig. 4).

External feeders: These pests feed on the outer portions of grains, including the endosperm and germ, leading to significant damage. Silica nanoparticles have shown high efficacy against the rice moth, Corcyra cephalonica, resulting in increased mortality rates (56). Green nanoparticles, such as silica, copper and zinc, synthesized from paddy husk, tulsi and spinach leaves respectively at 1500 ppm, were also effective in increasing the larval and pupal mortality of C. cephalonica (57). Development of an essential oil nanoemulsion from Pimpinella anisum enhanced its insecticidal activity against Tribolium castaneum (58). In the case of the khapra beetle, Trogoderma granarium, silver nanoparticles (AgNPs) synthesized from the alkaloids of Peganum harmala seeds significantly reduced adult emergence and greatly affected the growth and development of 2nd instar grubs when they were fed grains treated with AgNPs (59). Moreover, these nanoparticles exhibit additional benefits such as antimicrobial activity, electrical conductivity and enhanced chemical stability in pest management. Compared to conventional pesticides, nanoparticles deliver a higher concentration of active chemicals to target species.

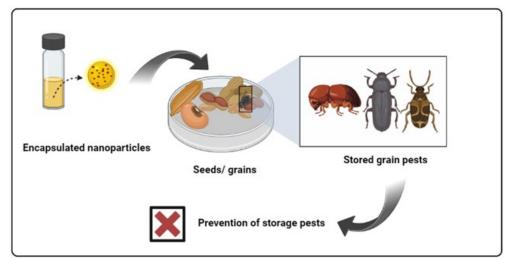


Fig. 4. Role of nanoparticles in storage pest management.

Secondary pests of storage

Secondary pests can infest stored grains following the primary feeders. Nanoemulsions developed from sweet orange essential oil exhibited effective repellent activity and successfully controlled the flat grain beetle, *Cryptolestes ferrugineus* (60). Additionally, the insecticidal activity of nanostructured alumina, when mixed with seeds of *Phaseolus vulgaris* at a concentration of 400 mg/kg, resulted in 80.64 % mortality in the saw-toothed grain beetle, *Oryzaephilus surinamensis* and 79.41 % mortality in the rust red flour beetle, *T. confusum* (61).

Impact of nanoparticles on insect structure and function

External damage: The chemical characteristics of nanoparticles significantly influence insect morphology. nanoparticles (CuNPs) have been shown to affect pest management through multiple mechanisms, including physical damage, desiccation, water loss and cuticle disruption (62). In general, nanoparticles bind to insect cuticles and subsequently cause lipid and wax physicosorption, thereby leading to insect dehydration. Application of TiO₂ NPs to H. armigera caused slugglish larval mortality and leakage of internal body fluids and apparently resulted in the larval mortality (63). Exposure of T. castaneum to P. anisum nanoemulsion led to severe cuticle damage, including pigment alterations, muscle breakdown, hindered cell regeneration and necrosis in the epidermis (58).

Silica nanoparticles (SiO₂) also inflict damage on insects' exoskeletons. When *Callosobruchus maculatus* was exposed to these nanoparticles, it resulted in abrasions and splits in the elytra, ultimately leading to death by desiccation (64). The use of silica nanoparticles as a dust spray on *P. xylostella* caused enhanced mortality by damaging the water barrier, leading to dehydration (40).

Internal Damage: When ingested or inhaled, nanoparticles can cause internal damage to insects, altering their metabolic activity. Nanoparticles are capable of inhibiting detoxifying enzymes such as cytochrome P450 monooxygenase (P450), carboxylesterase (CarE) and glutathione S-transferase (GST) (65). Along with the suppression of detoxifying enzymes, the levels of biochemical parameters like total lipids, proteins and carbohydrates in the midgut of cotton leafworm larvae decreased after exposure to AgNPs (66). In Callosobruchus maculatus, detoxification mechanisms were rendered ineffective by Bacillus thuringiensis-coated zinc oxide nanoparticles (51). Additionally, biosynthesized AgNPs led to a marked reduction in extracellular enzyme production and gut microflora (67). Protease activity in H. armigera was also diminished due to the binding of silver nanoparticles to the substrate binding site (44). Furthermore, the application of silica nanoparticles significantly reduced fecundity and adult emergence in C. maculatus (64). These findings underscore the role of nanoparticles in disrupting the internal defense systems of insects, making them highly effective in insect pest management.

Nano formulations in insect pest management

Nano-based formulations in plant protection demonstrate significant potential to enhance the efficacy and safety of active ingredients compared to conventional formulations. These nanoformulations come in various types, including nanoencapsulations, nanosuspensions, nanoemulsions, nanogels, nanomicelles, nanospheres and nanocapsules. Nanoemulsion consists of a mixture of water and oil, which can be either water-in-oil or oil-in-water, with droplet sizes ranging from 20 - 200 nm. This formulation offers excellent dispersity and stability, effectively preventing rapid degradation of the active ingredient (68). Conversely, nanosuspension is a combination of solid (the dispersed phase) and liquid (the dispersion medium) with particle sizes less than 100 nm, making it particularly effective for water-insoluble compounds. For example, colloidal suspension of nanoparticles loaded with Azadirachta indica achieved 100 % mortality against the larvae of P. xylostella while enhancing the stability of the neem extracts (69).

Nanoencapsulation involves encasing various forms of nanoparticles (referred to as the core) in a secondary material (the matrix or shell) to create nanocapsules. Various nanomaterials, including those based on polymers, solid lipid nanoparticles and inorganic porous materials, have been used in encapsulation (70). Polymeric nanoparticles (PNPs), which range in size from 1 - 1000 nm, can carry active chemicals that are either adsorbed onto the polymeric core or trapped inside. These polymeric nanoparticles have attracted considerable attention in agriculture due to their remarkable stability and targeted release of active ingredients at specific plant locations. These formulations offer advantages such as biodegradability and biocompatibility, enhanced targeting and absorption, slow release and minimized chemical losses, thus improving overall efficacy (71). They also facilitate prolonged adhesion and absorption, enhanced photostability and reduced soil leaching (72). Various polymeric nanostructures, including nanomicelles, nanocapsules and nanospheres have been synthesized and utilized across diverse domains. In crop protection and growth, PNPs are being investigated for their potential to deliver fungicides, herbicides, insecticides and plant growth promoters. Polymeric nanocapsules have been developed using biodegradable polymers such as chitosan, alginate, poly (εcaprolactone) (PCL), polyethylene glycol (PEG) and zein (71). Among these, chitosan is the most widely used biopolymer in agricultural applications due to its biocompatibility, biodegradability and cost-effectiveness (Table 3).

Recently, nanoparticles have emerged as efficient carriers for RNAi-based biopesticides, revolutionizing insect pest management. RNA Interference (RNAi) is a sequence-specific, post-transcriptional gene silencing technology that targets insect pests through the exogenous application of double-stranded RNA (dsRNA). However, various challenges have limited its field applicability. Nanoparticle-mediated dsRNA delivery enhances its stability, protects it from enzymatic degradation and ensures efficient uptake by insect pests, thereby improving gene silencing efficiency (73, 74).

Plant's response to nanoparticles

Phyto hormone response

Plant hormones are essential for the growth and development of plants, as well as for regulating resistance mechanisms. Hormones such as ethylene, salicylic acid and jasmonic acid play significant roles in defense reactions. The

Table 3: An overview of different nano formulations in insect pest management

Nanoformulation ty	pe	Size (nm)	Active ingredient (A.I)	Target insect pest	Outcomes	Reference
Nano-encapsulation	Chitosan/gum arabic NPs	220 nm	Geraniol	Bemisia tabaci	Protection of geraniol from UV degradation. Significant attraction effect was observed which could be utilized for designing traps.	(109)
with Chitosan	Chitosan nanocomposite fabricated with metabolites	50-85 nm	Insect metabolites from <i>Nomuraea</i> <i>rileyi</i>	Spodoptera litura	Enhancement of larvicidal activity against <i>S. litura</i> larval instars.	(110)
Nano-encapsulation with Zein nanopartic	les	100 nm	Curcumin and carvacrol (co-loaded)	Tetranychus urticae, Spodoptera frugiperda, S. cosmioides, S. eridania and Helicoverpa armigera	Higher repellency and acaricidal activity against <i>T. urticae</i> . Significant increase in larval mortality of <i>S. cosmioides</i> and <i>S. eridania</i>	(111)
Nano-encapsulation	with Alginate	150 nm	Imidacloprid	Amrasca biguttula biguttula	Improved efficacy against the pests over longer duration (9- 15 days).	(112)
Nano-encapsulation	with PCL	450-465 nm	Essential oil from Zanthoxylum rhoifolium leaves	B. tabaci	Reduction of eggs and nymphal population of whitefly.	(113)
Nano-encapsulation	with PEG	230 nm	Essential oil from garlic	T. castaneum	Insecticidal activity was improved when compared to the un-encapsulated A. I	(114)
Nano-encapsulation	with Si NPs	-	Azadirachtin	B. tabaci	Resulted in cent percent mortality of adult whiteflies.	(115)
Nano emulsion		50-70 nm	Essential oil from sea fennel seeds	S. litura	Enhancement of toxicity, adult insect fecundity and longevity also affected.	(116)
		116 nm	Cell-free supernatant from <i>Photorhabdusl</i> <i>uminescens</i>	S. frugiperda	Exhibited significant insecticidal activity with 80% larval mortality.	(117)
Nanosphere		106.7 - 129.2 nm	Essential oil from Zanthoxylum riedelianum fruit	B. tabaci	Exhibited insecticidal and oviposition deterrent activity as well.	(118)

quantity and activity of these hormones are critical indicators of toxicity in plants. Nanoparticles have been shown to alter the synthesis of jasmonic acid (JA) and salicylic acid (SA) in the shoots of rice, thereby strengthening the plant's defenses (75). This underscores the substantial impact of nanoparticles on the synthesis of plant hormones (Fig. 5).

Biochemical response

To mitigate the damage caused by reactive oxygen species (ROS), plants activate antioxidant mechanisms to protect their systems. The application ZnO and CuO nanoparticles on cucumber plants at a concentration of 100 mg/L exhibited a significant increase in catalase (CAT), superoxide dismutase (SOD), peroxidase (POD) activities (76). In rice seedlings, exposure to silver nanoparticles resulted in elevated ROS levels and a decrease in sugar content (77). Foliar application of chitosan nanocarrier loaded with salicylic acid in maize boosted the production of defense compounds such as MBOA, DIMBOA, DIMBOA-Glc, DIBOA, DIBOA-Glc, DIM2BOA-Glc and HDM2BOA-Glc. This treatment also reduced oxidative stress induced by *S. frugiperda*, leading to increased antioxidant enzyme activity (POD, SOD and CAT) (78).

In a novel approach, using gibberellic acid (GA3) as a reducing agent to synthesize copper and silver oxide nanoparticles and applying them to rice plants resulted in enhanced volatile profiles and defense systems, ultimately causing mortality of brown planthopper, *N. lugens* (79). In addition to various biochemical responses, some studies suggestes that nanoparticles may also induce molecular-level responses. For instance, the expression of microRNAs (miRNA)

395, miRNA 397 and miRNA 398) significantly increased when tobacco plants were exposed to 1 % aluminum oxide nanoparticles, thereby improving the plants' ability to with stand environmental stress (80).

Plant secondary metabolite response

Nanoparticles play a significant role in promoting plant growth and enhancing their quality by improving photosynthetic activity and metabolism. In maize, silica nanoparticles have been shown to elevate phenolic content, resulting in silica accumulation in the leaf epidermis, which serves as a physical barrier and enhances the resistance (81). Similarly, plants treated with chitosan nanoparticles demonstrated higher levels of phenolic compounds, attributed to increased activity of phenylalanine ammonia lyase (PAL) (82). Moreover, the soil application of silica nanoparticles in Hordeum vulgare led to a significant increase in carotenoid and chlorophyll content in the leaves (83). In terms of bioactive compounds in tomatoes, the application of copper nanoparticles at a concentration of 250 mg/L significantly increased the levels of total phenols, flavonoids, vitamin C and lycopene, thereby enhancing fruit quality (84). This illustrates that nanoparticles can induce and regulate plants' secondary metabolites, potentially aiding in their resistance to insects' pests.

Impact of nanoparticles on natural enemies

The advancement of the agricultural sector significantly affects non-target organisms. In crop ecosystems, natural enemies, such as predators and parasitoids, play a crucial role in managing insect pests, making it essential to protect them from chemical pesticide exposure. However, the use of nano

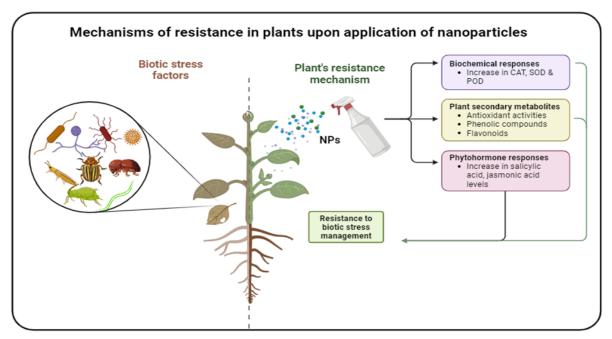


Fig. 5. Mechanisms of resistance in plants upon application of nanoparticles.

pesticides has had some impact on these beneficial organisms. For instance, the emergence potential of the green lacewing, *Chrysoperla zastrowi* was drastically reduced when exposed to various doses of silica nanoparticles, with the emergence rate dropping to just 29.41 % at 20000 and 15000 ppm (85). Remarkably, citrate-coated silver nanoparticles at lower concentrations were found to affect the survival, behavior and reproduction of dragonflies in prey- predator interaction (86). Conversely, silver nanoparticles synthesized from *Datura metel* enhanced the predatory potential of dragonfly naiads (87). These contrasting findings suggest that nanoparticles can have both positive and negative effects on predators, highlighting the need for further research to fully understand their impact on natural enemies.

On the other hand, nanoparticles seem to have more positive effects on parasitoids. Members of the family Trichogrammatidae, which are effective egg parasitoids of insects across more than 8 orders, have shown promising responses. For example, nanoemulsion of hexanal had minimal impact on the adult emergence of the egg parasitoid, *Trichogramma chilonis* (88). Parasitization rates and adult emergence of *T. chilonis* and *Trichogramma pretiosum* on *Corcyra* eggs treated with hexanal nanoemulsion were significantly increased, with parasitization rates of 97.65 % and 96.12 and adult emergence rates of 96.40 % and 94.29 respectively (89).

Future directions

Global crop productivity is significantly hindered by biotic stresses. In agriculture, biotic stress remains a major contributor to yield loss, with insect pests and diseases accounting for over 20 - 40 % of crop losses (90). A cutting-edge, multidisciplinary approach such as nanotechnology holds immense potential to address these challenges and provide sustainable solutions. Nanoparticles (NPs), with their exceptional physical and chemical properties and diverse applications, can play a crucial role in managing the key pests that affect crop plants. To ensure their practical implementation, cost-effective production approaches, such as eco-friendly synthesis using plant or

microbial sources and nano-encapsulation for controlled release, can enhance affordability, efficiency and large-scale adoption in agriculture. However, several challenges and obstacles associated with NPs must be addressed in the near future. Firstly, it is essential to standardize the concentration and dosage of NPs delivered to the plant system, as higher doses may lead to phytotoxicity and negatively impact non-target organisms and the environment. Secondly, the adoption of NPs and nano-based products against insect pests at the field level remains relatively low. Most research is conducted in laboratory and greenhouse settings, making it critical to assess the efficacy of NPs in real-world field conditions. Thirdly, evaluating the safety of NPs for the environment, as well as for human and animal health, requires thorough long-term studies on their impacts. Ecotoxicological research on nanomaterials and the establishment of a regulatory framework for their use in largescale agricultural production are vital steps in this process (91). Furthermore, implementing a global regulatory framework for biosafety assessments is crucial, including adherence to OECD (Organization for Economic Co-operation and Development) guidelines for safety testing. Consideration of these recommendations in future research endeavors would be highly beneficial.

Conclusion

Nanotechnology represents an exciting and highly promising approach for sustainable agriculture, particularly in enhancing plant growth under biotic stresses. Although chemical pesticides have historically been effective in pest control, they have also caused significant harm to ecosystems and the environment. The application of nanoparticles in pest management marks a paradigm shift from broad-spectrum chemical control to precision-targeted, sustainable strategies. Their small size, large surface area and efficient penetration enable nanoparticles to enter plants via extracellular and intracellular sites. They also stimulate various physiological processes in plants; including growth, yield and productivity, while regulating defense-related activities. However, the effects

of these compounds on humans, animals and the environment necessitate thorough investigation. Future research should focus on how nanoparticles impact earthworms, pollinators, insect parasitoids and predators. Additionally, challenges associated with the application of nanoformulations for pest management need to be addressed. Currently, there is substantial research on storage pests and in vitro studies, yet there are only a limited number of investigations concerning the use of nanoparticles in managing insect pests that affect field crops. More information is also needed regarding the safety of nanoparticles on beneficial insects in real-world agricultural settings. With advancements in regulatory frameworks and industrial scalability, nanopesticides are set to transform crop protection, promoting sustainable agriculture and safeguarding global food security amid climate challenges and growing ecological concerns. In conclusion, nanoparticles have the potential to serve as a viable alternative to conventional pesticides for managing insect pests in crop protection.

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Authors' contributions

JJ drafted the manuscript. MS contributed to conceptualization, writing and editing the review paper. MM, SKR, DJSS and PJ were involved in manuscript editing. All authors read and approved the final manuscript.

Compliance with ethical standards

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