Insecticidal Activity of Nanoparticles and Mechanism of Action

12

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Abstract

The growth of population in the world and the requirement for food have urged the need to optimize the agriculture practices with minimal loss on fields. This can be achieved by the application of insecticides and pesticides. However, long-term application of these compounds has encountered serious environmental concerns of insecticide and pesticide resistance in plants and environmental deterioration. This has led to the ban of numerous deadly pesticides. However, this problem could be overcome with the development of various biological pest control agents. In recent years, nanotechnology has picked up prevalence at a fast pace in various field and disciplines with special mention in environmental and agricultural systems. In this regard, application of various nanoparticles has attracted many researchers worldwide to investigate and test their toxic potential against various insects and pests. Owing to the advantages, that is, affordability, availability, and easy synthesis, numerous inorganic and organic nanoparticles/composites, namely, titanium, gold, silver, silica, titanium dioxide, zinc oxide, iron and carbon, etc., have been successfully targeted against extensive range of noxious arthropods and agricultural pests and vectors. Therefore, the present chapter deals on different nanobased formulations employed against insects and pests, along with their mechanism of action. Based on many research reports,

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nanoparticles have been recognized as excellent candidates to combat insects and pests with their proven toxicity against mosquitoes and ticks. In addition, they are capable of exhibiting their toxicity at different stages of insects and pests. However, implementation of nanotechnology in agriculture, particularly in pest control, needs to be carefully evaluated to benefit the agricultural sector and the public health concerns of nanotoxicity.

Keywords
Nanoparticles · Insecticidal · Pesticidal · Agriculture · Environment · Mechanism

12.1 Introduction

Agriculture contributes to the crucial development toward the rise of sedentary human lifestyle. The production of crop for human consumption by agriculture began thousands of years ago. However, present-day agriculture faces huge loss in terms of crop and finance due to various biotic and abiotic factors. Biotic factors include pest invasion and resistance, whereas abiotic factors include water inadequacy or excess during growing season, extreme temperature changes, high or low irradiance and biotic stressors, and nutrient supply (Oerke 2006). Thus, the farmers had to compete with biotic factors such as plant pathogen (bacteria, virus, fungi, weeds, and chromista) and animal pathogens (mites, rodents, insects, nematodes, snails, and slugs) that are together specified as pests. Unlike abiotic factors, biotic factors are caused mostly due to anthropogenic activities of excess usage of synthetic pesticides and insecticides, due to which the crop is expected to gain resistance. Insects are the common creatures found in almost all the environment, occupying slightly more than 2/3rds of animal's space, globally. Insects feed all the types of plants, namely, medicinal plants, crop plants, weeds, and forest trees. They too exhibit the capability of infesting food products and stored grains in godowns, bins, packages, and huge storages leading to massive loss in food quality and investments (Rai and Ingle 2012). Wheat, maize, rice, barley, potatoes, coffee soybeans, and cotton are crops that face major loss due to pests and diseases (Oerke 2006).

In general, insects causing <5% damage are not categorized as pests. If the destruction is between 5% and 10%, they are termed as minor pests and with damage more than 10% are termed as dominant pests (Dhaliwal et al. 2010). According to Pimentel (2009), globally, an estimated loss of 14% was caused by insect pests and 13% loss due to plant pathogens and weeds, with a crop loss estimate of US$ 2000 billion per year. For example, the annual yield loss of potatoes ranges from 5 to 96% in France, 100% for cotton in Thailand, and 24 to 41% in Asia. Over the decades, global crop loss due to insect pest invasion varies with different crops. However, such losses are scarcer in perennial crops. Yield losses on apples and other stone fruits are much less compared with coffee yield loss in Brazil that ranged from 13 to 45% and 5% in Netherlands. However, most developing countries do not have accurate estimation of the loss caused by the invasion of insects and noninsect pests, affecting main crops (Culliney 2014). The scarcity of crop loss quantifications and their causal analysis is mainly related to the difficulty of their evaluation.

Pest and disease attacks are quite common even during preharvest and postharvest (storage) stages, that greatly affects the crop yield along with its quality and quantity. Additionally, financial returns are also been threatened due to low production and quality that reflects in poor customer satisfaction. The most outstanding efforts taken during the last 20 years focused on the quantification of relative yield losses due to pests and diseases only by experiments and surveys. However, control or reduction of pest-associated crop losses will accelerate the agricultural production and allow us to march one step forward to accomplish the global Sustainable Development Goals (SDGs) to curb hunger, poverty, and malnutrition.

12.1.1 Emergence of Pesticides

In Ancient Roman times, sulfur was used to kill pests, and weeds were controlled with salts, ashes, and bitters. Honey/arsenic mixture was used in the 1600s to control ants. Farmers in the United States started to use certain chemicals for field-related posts such as sulfate, nicotine, sulfur, and calcium arsenate in the late 1800s. Different types of pest control agents are illustrated in Fig. 12.1. Colorado potato beetle was controlled by arsenic, and an impure form of copper, in the United States in 1867. During and after World War II, a quantum leap in the pesticide development had arisen that eventually led to the synthesis and production of numerous effective and cheap pesticides/insecticides (Mahmood et al. 2016). 2,4-D, Dieldrin, DDT, BHC, Aldrin, Endrin, and Chlordane were discovered in 1939. However, due

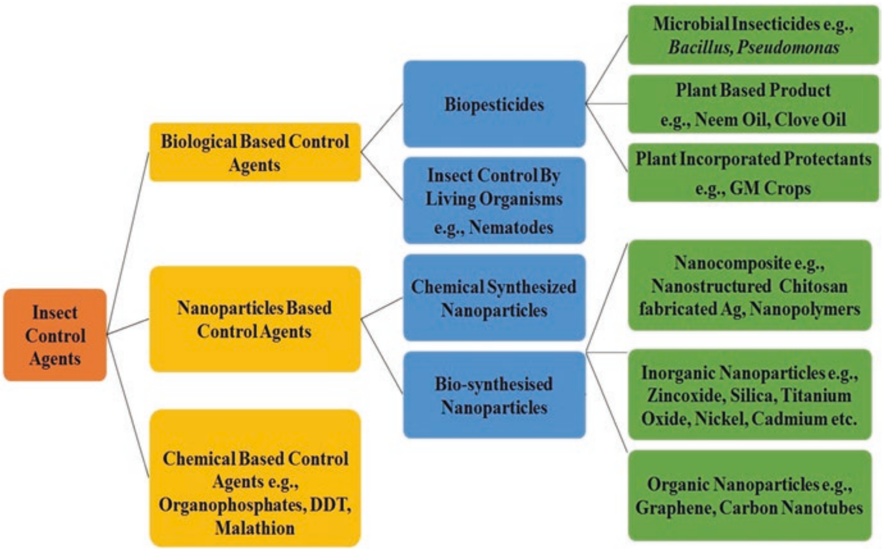

Fig. 12.1 Different types of pest control agents

to primitive application methods, most of the efforts were unsuccessful (Delaplane 2000). Despite this fact, usage of pesticides has reached its peak, worldwide in the year 1961 with 48,000 tons usage in Germany, 1.7 million tons in China, 24,000 tons in Poland, over 18,000 tons in The Great Britain, and 62,000 tons in Italy. However, in the year 1962, pesticide usage was sharply declined due to the public awareness of environmental hazards and health effects related to indiscriminate the use of chemical pesticides. This paved to a new area of "integrated pest management" (IPM) from late 1960 onwards.

12.1.2 Need for Pesticide

A pesticide is a general term which refers to herbicides, insecticides, rodenticides, fungicides, nematicides, molluscicides, and growth regulators. Pyrethroids, neonicitinoids organochlorines, carbamates, and organophosphates are the most common and widely used pesticides (Theerthagiri et al. 2017). These toxic chemical compounds are employed to kill/control/destroy rodents, weeds, fungi, insects, and other harmful pest populations, that challenge the crop production. Pesticides work primarily by attracting the pests, then seduce them, and finally destroy or mitigate them. According to Alavanja (2009), billions of kilograms of pesticides are used annually to reduce such yield losses. Over the past few decades, the practice of pesticides application has increased several folds. According to an estimate, the use of pesticides was found to be approximately 5.2 billion pounds globally per unit area/annum.

It is estimated that 90% of the pesticides will be lost during or after the application (Ghormade et al. 2011). In addition, chemical insecticides are often nonspecific and hence can affect nontarget organisms too. As a result, there is increased need to develop high-performance, sustainable, and cost-effective pesticides that are less harmful to the environment.

12.1.3 Effect of Conventional Pesticides/Insecticides

In India, pesticides are primarily used for cash crops such as cotton, paddy, and wheat to improve their production in terms of quality and quantity (Choudhary et al. 2018). Pesticides/insecticides are used not only in agricultural farmland but also in household as powders, sprays, and poisons to control cockroaches, fleas, ticks, mosquitoes, rats, and other pests and insects (Murugan et al. 2018). However unexpectedly, the risks combined with their usage have exceeded their beneficial effects. Due to continuous application, few traces of chemical pesticides are commonly detected in our food commodities, water, soil, and even in air (Murugan et al. 2017). On environmental degradation, the metabolites of the pesticides were reported to be equally harmful as the active ingredients of the pesticides. Owing to their ill effects, carcinogenicity, and roles in ozone depletion, many widely used pesticides has been banned in many countries (Rajendran and Sriranjini 2008). According to a report on 19 March 2019 by "Directorate of Plant Protection Quarantine & Storage", Govt. of India, and USEPA

(United States Environmental Protection Agency), various chemical pesticides such as aldrin, chlordane, endosulfan, lindane, DDT, DDD, etc., have been completely banned in India and throughout the world (Web sources 2019). In particular, many governments have prohibited the use of pesticides to protect stored products too. Due to continuous application, most of the pests/insects become resistant and worsen the pest management practices. Various resistance mechanisms include penetration resistance, altered target-site resistance, metabolic resistance, and behavioral resistance (Benelli 2018). Therefore, this has urged the worldwide researchers to develop new eco-friendly and sustainable options of insecticide for plant protection.

12.1.4 Nanobased Pesticide/Insecticide

A nanoparticle (NP) refers to ultrafine particle subclass with distinctive dimensions ranging from 1 to 100 nm, which seems to be uncommon with non-nanoscale particles of same chemical composition. Nanotechnology offers numerous applications in many fields such as medical, industrial, environmental, nanobiosystems, parasitology, among others. A wide number of nanomaterials, including carbon, metal oxides, metals, polymers, proteins, dendrimers, ceramics, semiconductor quantum dots (QDs), emulsions, lipids, and silicates, have been synthesized by chemical or biological means (Puoci et al. 2008). Physical characteristics such as, shape, size (irregular, rods, tubes, sphere), crystal phase (crystalline/amorphous), chemical configuration (e.g., carbon, metallic, organic, polymeric, inorganic), and surface-to-volume ratio are the vital parameters that define the outstanding characteristics of these nanomaterials and aids in determining their applications in various fields (Athanassiou et al. 2018).

Over the past decades, nanotechnology is a rapid growing and highly attractive research field among worldwide researchers. This field has shown remarkable potential for the use of nanomaterials towards food protection and crop. A variety of metal NPs, metal oxide NPs, and polymer-based nanocomposites have been developed for crop pest management. Different research attempts have been successfully reported on new approaches of constructing nanoscale materials, active insecticidal ingredients, formulation, and delivery which can be referenced as “nanopesticides” (Ragaei and Sabry 2014). The evolution of nanopesticides has been one of the most recent discoveries that address the application of nanomaterials for crop protection through nanotechnology. It includes broad research contribution that aids in the fundamental understanding of the formulation of the active ingredients into nanoemulsions, interaction between nanoscale materials and insects, and effective delivery options. Development of new formulations of nanopesticides employing nanomaterials as active insecticidal tool for delivery is collectively referred to as nanocarriers (Benelli et al. 2017). As agricultural nanotechnology develops, there will be a significant upsurge in the application prospective of the nanoparticles to provide a new generation of pesticides and other plant disease management options. Different nanobased insecticides along with their insecticidal effects are schematically shown in Fig. 12.2.

Many common economic advantages of nanobased insecticide formulations include (1) enhanced solubility of the insoluble insecticide components; (2) high

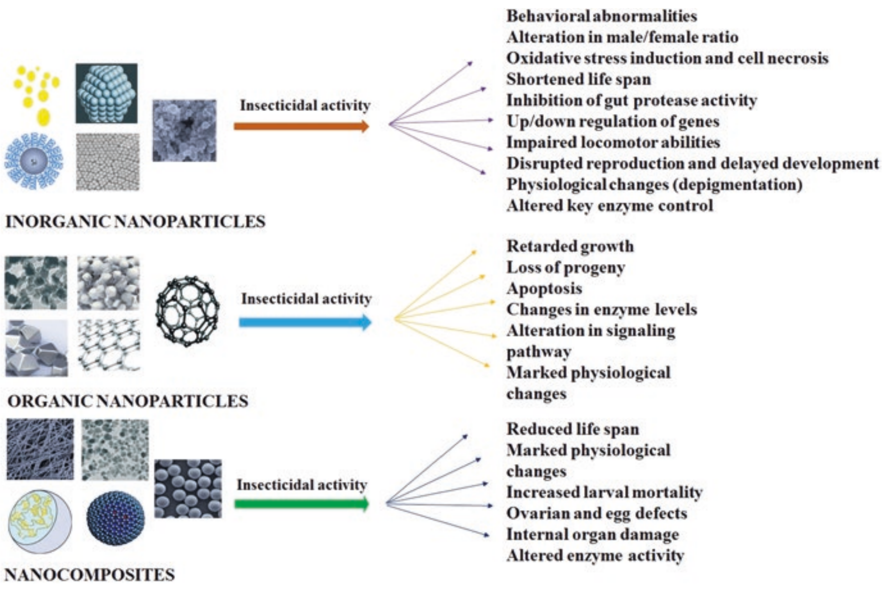

Fig. 12.2 Different nanobased insecticides along with their insecticidal effects

formulation strength; (3) active expulsion of toxic organic solvents than the conventional pesticides; (4) sustained release options; (5) improved resistance to degradation; (6) high mobility and enhanced insecticidal action, due to its small particle size; and (7) prolonged longevity, due to large surface area (Sasson et al. 2007). Additional nanocarrier benefits include increased activity efficacy and stability of the nanopesticides under extreme environmental conditions (UV and rain) and reduced toxicity and costs (Worrall et al. 2018). Using of NPs and its composites has various advantages than the other control strategies, namely, being cost-effective, exerting no adverse effects toward nontarget pests/insects, and use of low temperature, less pressure, and energy (Jayaraman et al. 2018; Arun Prasad et al. 2018; Barabadi et al. 2019). In particular, inorganic NPs, metals, metal oxides, and nanocomposites synthesized by green methods were reported to be highly efficient against various economically important pests and insect vectors.

The use of nanoparticles for plant protection was reported to be implied via two different mechanisms (Worrall et al. 2018). One way is by direct use of nanoparticles to provide crop protection, and the other one is by using nanoparticles as carriers for existing pesticides or other active ingredients. Adapting the second option ensures the application of pesticides specifically to seeds, foliar tissue, or roots by spray application or drenching/soaking. Torney et al. (2007) reported on the concept of effective delivery of NPs directly into biomolecules of plants. This concept was later expanded by other researchers too (Martin-Ortigosa et al. 2012). The available report specifies that a minimum number of NPs may be used by plant cells (Yasur and UshaRani 2013). However, the physical characteristics of the NPs were reported to play a major role in exhibiting its application. Stadler et al. (2010) reported on the insecticidal activity of the alumina NPs toward two species of stored grains, namely, *Rhyzopertha dominica*o*ryzae* and *Sitophilus oryzae.* Goswami et al. (2010) assessed the controlling effect on *S. oryzae* using various NPs, namely, titanium/aluminum oxide NPs (ANP), SiO_2 NPs (SNPs), TiO_2 NPs (TNP), and ZnO NPs (ZNP). By comparison, ANP and SNP showed superior activity than TNP and ZNP. In addition, based on the different spherical SNPs functionalized on their surface, they exhibited different insecticidal effects, thus confirming the significance of the physical characteristics of the NPs. Another study by Debnath et al. (2012) also pointed out that the amorphous structured nanosilica (SNP) effectually killed the larvae of *Spodoptera litura* at 0.5 mg/cm concentration. These studies evidenced the nanobased pesticide/insecticide that could surely serve the agricultural sector with huge benefits.

12.2 Inorganic Nanoparticles-Based Insecticides

Insecticides are most likely to emerge in the upcoming years with new nanoformulations of existing insecticide's active ingredients (AIs). Most of the agrochemical nanoformulations that are in use today contain structures of nanometer-sized range depending upon specific applications including nanopesticide development. Applications of inorganic NPs have been extensively reviewed over the past 20 years, for pharmaceutical formulations Benelli (2016). Nanoformulations are mostly the combination of solid inorganic NPs in the form of nanoemulsions, liposomes, and polymer NPs that provide simple production, higher loading capability, more responsive release, low cost, and better stability (Sujitha et al. 2017; Small et al. 2016). Despite these advantages, the availability of less reports toward the development of advanced pesticide delivery systems using inorganic NPs is quite surprising. Future studies of other nanoformulation combinations and AIs are in urgent need, with a particular objective of achieving longer durability on application to soil.

12.2.1 Silver Nanoparticles (AgNPs)

Silver nanoparticles (AgNPs) were considered as a primary target of a green method possessing larvicidal, pesticidal, antimicrobial, viral, inflammatory, angiogenesis, and platelet properties. These properties have found applications in various fields such as medicine, biology, plant management, pest control, and agriculture (Chhipa 2017). Many studies demonstrating the inscecticidal activity of the AgNPs were reported by researchers worldwide. A concentration of 5–25 mg/L of adult hematophagous flies, *Hippobosca maculate*, and cattle ticks, *Rhipicephalus (Boophilus) microplus*, was reported to be killed by AgNPs (Santhoshkumar et al. 2012). The synthesized AgNPs (form of nanocorns) from *E. prostrata* were reported to be effective against pests and insects, *S. oryzae* (Zahir et al. 2012). Nair and Choi (2011) reported on the insecticidal effect of AgNPs in *Chironomus riparius* (Meigen), an aquatic midge, at a concentration of 0.2, 0.5, and 1.0 mg/L. The results of the above study demonstrated the nanomaterial's impact on the genetic expression of glutathione S-transferase enzyme, that are associated with the induction of oxidative stress in the pest/insect. Similar study on AgNPs nanomaterial induced oxidative stress against two lepidopteran species, *Spodoptera litura* (*Fabricius*), the Asian armyworm, and *Achaea janata* (L.), the castor semilooper was also reported (Yasur and Usha-Rani 2015).

AgNPs synthesized from *Manilkara zapota* were also reported to exhibit dose-dependent activity (concentration 1.25–20 mg/L) against the *R. microplus* larvae (Rajakumar et al. 2012). The insecticidal effect of nanosilver colloid and ethanol-based colloid sulfur nanosilver at a concentration of 20 ppm was reported to show almost massive mortality against case-making clothing moth, *T. pellionella* (L.) larvae, affecting wool fibers within 14 d of treatment (Ki et al. 2007). AgNPs from the aqueous extracts of *Eclipta prostrata* exhibited larvicidal activity to control the *C. quinquefasciatus* and *Anopheles subpictus Grassi* mosquitoes (Rajakumar et al. 2011). The nano-formulated AgNP biopesticide synthesized from *H. coronarium* and its rhizome extract was reported to show and pupicidal and larvicidal activity against *A. aegypti* and the adults of *Mesocyclops formosanus,* the nontarget copepod, within an exposure time of 24 h. Significant histological changes, targeting the midgut epithelial cells of mosquitoes, were also reported (Kalimuthu et al. 2017). The systemic effect of AgNPs obtained from the aqueous extracts of *Cassia fistula L* was tested against the fourth instar larvae of *A. albopictus* and *Culex. pipiens.* The study was supported by enzyme assays too (Fouad et al. 2018). Green synthesized AgNPs was reported to be active against *A. aegypti* and few human pathogens (Ezhumalai et al. 2019). The survival of the *Drosophila melanogaster* flies was found to be compromised with pathophysiological abnormalities due to the exposure of AgNPs at higher concentrations (Armstrong et al. 2013). AgNPs synthesized from the leaf extracts of *Ficus religiosa* and *F. benghalensis* were reported to exhibit insecticidal activity against *H. Amigrate.* They reported an inhibition of Ha-Gut protease by 50% and 70%, respectively, due to the activity of AgNPs (Kantrao et al. 2017).

12.2.2 Nickel Nanoparticles (NiNPs)

Nickel nanoparticles (NiNPs) synthesized from methanolic extract of *C. nucifera* exhibited pesticidal activity against the agricultural pest, *C. maculates*, with 97.31% mortality and larvicidal activity against *A. aegypti* larvae (Elango et al. 2016). Rajakumar et al. (2013) reported on 5–10 mg/L nanoparticles of this metal were active against the larvae of two species of cattle ticks, namely, *Rhipicephalus microplus* and *Hyalomma anatolicum*, and against three species of mosquitoes, namely, *A. subpictus*, *C. gelidus,* and *C. quinquefasciatus*. Phytochemically synthesized bimetallic NPs, Ni-Pd, were found to exhibit larvicidal activity against *A. aegypti*, and phyto-synthesized Ni-Pd NPs were showed antifeedant and ovicidal effect against *C. maculatus* and *C. maculatus* eggs (Ganesh et al. 2016).

12.2.3 Cadmium Nanoparticles (CdNPs)

Though CdNPs exert significant biotoxicity, not much work, they have not been much explored in pest control application. In a study by Sujitha et al. (2017), nano-CdS exhibited high toxicity against young malarial instars of *A. sundaicus* and *A. stephensi* after 16 d of exposure. In another study, marigold petal extract synthesis of CdNPs showed complete mortality (100%) toward mosquitocidal larva after an incubation period of 72 h with 10 ppm of CdNPs in comparison with that of rose petal extracts (Hajra et al. 2016).

12.2.4 Gold Nanoparticles (AuNPs)

Reports on exploration of AuNPs against insect control are less abundant as compared with research attempts of AgNPs (Benelli 2018). The biosynthesized AuNPs from *Jatropha curcas* L. *latex* showed serum trypsin inhibition in different species of insects, including *A. Aegypti*, beetles, and pests of mealybug (Patil et al. 2016). In another study, AuNPs disrupted the reproduction and development in German cockroaches, *Blattella germanica* (L.) (Small et al. 2016). Larvicidal effects of AuNPs synthesized from the zein biopolymer (Ze-AuNPs) were tested against *A. aegypti,* a Zika virus vector. Histopathological results showed remarkable physiological changes such as complete abdominal disintegration (midgut and caeca), caudal hair loss in antenna, lower, lateral, and upper head (Suganya et al. 2017). Similar study of AuNPs synthesized from the leaf extracts of *Artemisia vulgaris* L. was found to exert larvicidal effect against third and fourth instars of *A. Aegypti* (Sundararajan and Kumari 2017). They too have observed marked physiological damage in epithelial cells, cortex, and midgut along with AuNPs deposition in the midgut region.

12.2.5 Silica-Based Insecticides (SiO_2 NPs)

Silica NPs are one of the most interesting inorganic NPs employed as pesticide delivery nanocarriers, for the application of fungicides, bioinsecticides, growth, promoters, and pheromones. Silicone has already been recognized long since enhancing plant tolerance and acting against stress (biotic and abiotic) responses. It has naturally been considered as potential candidates that can offer increased protection over a wide range of agricultural insects/pests (Barik et al. 2008). Song et al. (2012) showed that the new compounds of silica NPs had previously been reported for delayed release of growth promoters and chlorfenapyr. Field testing of such nanoformulation had showed that the silica NPs-related insecticidal activity was twice as large as microparticular or particulate-free chlorfenapyr. The mechanism involved is distinct from the mixtures of insecticides without NPs, and the greater efficacy observed is possibly associated with the slow and sustained release (up to 10–20 weeks), that provided high regionalized target activity over a long time period. The effect of hydrophobic nanosilica toward *C. quinquefasciatus, A. aegypti,* and *A. stephensi* was studied by Barik et al. (2012). The lethal and sublethal side effects of commercially available Ludox TMA silica NPs were tested against a terrestrial pollinator, *B. terrestris L.*, via a dietary exposure of drinking sugar water (Mommaerts et al. 2012). The insecticidal potential of silica NPs against various insects, namely, *Bombus terrestris, Callosobruchus maculatus, P. xylostella,* and *Lipaphis pseudobrassicae* has also been reported (Mommaerts et al. 2012).

Debnath et al. (2011) reported on higher incidence of mortality of the weevils (*Sitophilus oryzae*), affecting *Oryza sativa* grains (kept in storages) on using nano form of silica NPs, of size ranged from 15 to 30 nm than the bulk silica of size that ranged from 100 to 400 nm. On the one hand, they too have attempted the surface modification in silica NPs using hydrophobic and hydrophilic coatings and tested against the same pest and reported on fewer deaths of weevils on using bulk silica. On the other hand, no new progeny of weevils was found after the treatment of *O. sativa* grains with silica NPs. As an additional advantage, silica NPs may release silicate ions in very small quantities, which exhibit insecticidal effect that may not involve the pests, but the grain itself. It exerts this property by strengthening the cell wall by depositing solid silica on it and by promoting the biosynthesis of defense compounds (Epstein 2009). The factors such as temperature, pH, and shell thickness were found to influence the release rate of these molecules. The release profile of the encapsulated avermectin showed a multistage pattern that interrupted the AI in various parts of the particles (i.e., internal core, porous channel, and external structures) (Liu et al. 2006). According to a report, lab trials were conducted to determine the insecticidal potential of silica NPs and AgNPs on the larvae and the adults of *C. maculatus*, affecting cowpea seed which showed 100% and 83% insect mortality (Rouhani et al. 2012). A study showing evidence of silica NPs sprayed at a concentration of 3200 mg/Lwas found to show lack of phytotoxicity in several plants (Park et al. 2006). This confirmed the urge of following permissible or optimized concentration of NPs in a strict manner, in order to achieve the targeted applications.

12.2.6 Alumina Nanobased Insecticides (Al_2O_3 NPs)

Many laboratory bioassays have already evidenced the insecticidal properties of the nanobased alumina structures that were proved effective against insect pests affecting stored products. It also has the advantage of involving electrostatic and physical phenomenon in their mechanism of action. Owing to these properties, nanoalumina was reported to an effective alternative to conventional organic synthetic insecticides (Sabbour et al. 2015). The insecticidal action of nanostructured alumina on *Sitophilus oryzae* (L.) showed the binding of nanoalumina to the cuticle of the beetle due to tribo electrical forces that sorbs its waxlayer, resulting in insect dehydration (Stadler et al. 2017). Stadler et al. (2010) demonstarted the insectical property of the nanoformulated alumina against two species, *S. oryzae* L. and *R. dominica* (F.). These two are regarded as the common insect pests that affect the world's stored food supplies. However, both the species were found to experience critical fatality after 3 d of continuous exposure to the nano-treated wheat. Buteler et al. (2015) too studied the insecticidal activity of nanoalumina dust of varying size and morphology against the above said two pests that affect the stored food supplies. Though they observed greater mortality rates, they concluded that reducing the size of the particle and increasing the surface area were not the only dominant factors that influence the effectiveness of insecticides.

12.2.7 Titanium Dioxide Nanobased Insecticides (TiO_2 NPs)

The insecticidal activity of TiO_2 NPs was reported to be the causative agent for the deaths of *R. microplus* larvae and *Haemaphysalis bispinosa* adults (Marimuthu et al. 2013). An increased insecticidal activity was noted with an increase in the concentration (4–20 mg/L) of NPs. Philbrook et al. (2011) too reported on the effect of TiO_2 and AgNPs (concentrations ranging from 0.005 to 0.05%) against the fruit fly, *D. Melanogaster*, that resulted in major progeny loss and decreased success in insect development. Sabbour (2012) demonstrated entomotoxicity testing of TiO_2 and Al_2O_3 NPs against *S. oryzae,* both under lab and sored conditions. TiO_2 NPs activity against the *Bombyx mori L.* (silkworms) was found to stimulate the biosynthesis of 20-hydroxyecdysone. This resulted in shortened time for insect growth and decreased molting period (Li et al. 2014). This study has enabled the researchers to claim and explore the potential sericulture benefits in using TiO_2 NPs. The insecticidal activity of TiO_2 NPs synthesized from extracellular *Trichoderma viride* was evaluated for their pupicidal, larvicidal, and antifeedant effect against *H. armigera.* They reported on complete 100% mortality on the first and second instar and 92.34% on third instar larvae at a concentration of 100 ppm (Chinnaperumal et al. 2018). The larvicidal activity of TiO_2 NPs against *Bombyx mori* has been much explored by various researchers (Tian et al. 2016; Xue et al. 2018).

12.2.8 Zinc Oxide Nanobased Insecticides (ZnO NPs)

Zinc oxide nanoparticles (ZnO NPs) exhibit remarkable physical, optical, and antimicrobial properties that can be used to enhance agriculture. Synthesis of ZnO NPs can be achieved by various chemical and biological methods. However, the plant extract-based biogenic synthesis of ZnO NPs is most often used in crop-pest control practices. *L. leschenaultiana*-encapsulated ZnO NPs showed 100% mortality of *A. Aegypti*. They too reported on significant morphological defects such as abdominal shrinkage, thorax shape changes, mid-parent damage, loss of lateral hair, brushes and anal gills, and deposition of ZnO NPs in thorax and abdomen (Banumathi et al. 2017). Similarly, ZnO NPs synthesized from exopolysaccharides (EPS) extracted from *Bacillus licheniformis* Dahb1 (EPS-ZnO NPs), the probiotic strain showed complete mortality (100%) against third instar larvae of *Aedes* mosquito species even at lowest doses. Histolopathological studies too confirmed the cellular and tissue damages in the midgut of the nano-treated mosquito larvae (Abinaya et al. 2018). Another insecticidal study of *U. lactuca*-fabricated ZnO NPs showed complete mortality (100%) of the fourth instar larvae of *A. aegypti* at 50 μg/mL within 1 day with marked morphological and histological changes inthe larva (Ishwarya et al. 2018). Different concentrations of ZnO NPs synthesized via precipitation route was exposed to the *Trialeurodes vaporariorum* (greenhouse whitefly), a major pest affecting ornamental and horticultural plants and reported with a maximum mortality of 91.6% (Khooshe-bast et al. 2016). Surface coating of ZnO NPs with *B. thuringiensis* was found to act against *Apis mellifera* and *Callosobruchus maculatus* (Milivojevi et al. 2015; Malaikozhundan et al. 2017). Another study to test the efficiency of zinc oxide, aluminum oxide, and aluminum-doped zinc oxide NPs against *Cx. quinquefasciatus* larvae showed a maximum mortality of 96%. The tested NPs were found to be attached in the cuticle of different body parts of the dead larvae (Mostafa et al. 2018).

Apart from the above-discussed NPs, other inorganic metal oxide NPs and sulfide based compounds have been reported from our group too. The toxicity of bismuth oxyiodide nanoflakes was investigated and reported for the first time against *A. stephensi* and *Plasmodium berghei*. They have compared their results with malarial drug, chloroquine, via animal testing and reported on excellent antiplasmodial experiments against *P. berghei* with a prominent chemosuppression after 4 d of treatment with of BiOI (300 mg/kg/day) (Murugan et al. 2018a). Green and chemical-fabricated nano-ferric and ferrous oxide NP-based composites produced from *Ficus natalensis* were tested against larvicidal and pupicidal experiments on *Cx. Quinquefasciatus* and reported on enhanced toxicity of the iron-based composites on the mosquito vectors (Murugan et al. 2018b). Profound mosquitocidal activity of flower such as copper sulfide nanocrystals was reported against the *A. stephensi* instar larvae and plasmpodium parasites (Theerthagiri et al. 2017).

12.3 Organic Nanobased Insectides

12.3.1 Carbon Nanobased Insecticides (CNPs)

Low toxicity and readily available characteristics make carbon NPs a much preferred option in a variety of biomedicine and research developments. In addition, they exhibit good mechanical properties, extraordinary electrical conductivity, and heat conductivity. Since they are made of pure carbon, they show high stability, low toxicity, good conductivity, and environment-friendly properties (Street et al. 2007). Moreover, carbon NPs synthesized by environmentally sustainable methods were reported to be highly effectual against the arthropod pests that are economically important (Athanassiou et al. 2018). Nonetheless, most of the studies concentrated on mosquitoes with only few NPs tested on pests (Murugan et al. 2017). Martins et al. (2019) demonstrated the enduring effects of the diet containing two classes of carbon NPs of different dimensions (i.e., oxidized form of multiwalled carbon nanotubes (MWCNT), 1D-MWCNT, graphene oxide (GO), and 2D-GO) fed to the insect *Spodoptera frugiperda (Lepidoptera: Noctuidae*). They have observed many critical influences that affected the general behaviour, fertility, nutritional physiology, and changes in enzyme activities in the moth. Similar work by Liu et al. (2009) demonstrated that a diet-fed fruit fly larvae, *D. melanogaster* coformulated with single-walled or MWCNT carbon black, fullerene C60, had no considerable effect on insect development and survival, despite the presence of carbon nanostructures in tissues of fruit fly. However, fruitfly adults exposed to dry forms of carbon-based NPs were found to strongly adhere to the flying parts of the fly, resulting in diminished motor activities and less mortality. Recently, Sultana et al. (2018) reported on the *Solanum tuberosum* L. that served as carbon-dot precursors source-based synthesis of carbon-dot silver nanohybrid was tested against the larval and pupal stages of the two mosquito vectors, *A. stephensi liston* and *Culex quinque fasciatus,* and found to be highly toxic to both the species that led to their death due to cellular-level nano-Ag toxicity. Dziewięcka et al. (2016) demonstrated the GO NP toxicity (0.1 μl/100 mg) on insertion into the hemolymph of Cricket fly, *Acheta domesticus L,* caused oxidative stress with increased activity of catalase, glutathione peroxidase, total antioxidants, and heat shock proteins (HSP 70) release.

12.3.2 Nanocomposites-Based Insecticides

Nanocomposites have wide applications in many areas such as disease diagnosis, drug delivery system, energy storage, food processing, pest detection and control, water treatment, and agricultural productivity. Among all, the potentiality of nanocomposites has been effectively employed in plant growth and plant pest management. In the present era, the role of nanocomposites in agriculture is expected to reduce the burden of chemical pesticides and fertilizers (Gupta 2018).

12.3.3 Chitosan-Fabricated AgNPs-Based Insecticides (Ch-AgNPs)

In a recent study, chitosan (using male crab shells)-synthesized silver nanoparticles (Ch-AgNPs) was tested against *A. sundaicus* vector larvae and pupae. They also evaluated the predatory activity of the mosquito's natural enemy, *C. auratus,* under lab conditions and found significant improvement after treating with sublethal dosages of Ch-AgNPs. Similar report on testing the efficiency of Ch-AgNP against the pupae and larvae of *A. stephensi,* a malarial vector with observed LC_{50} value range of 3.18–6.54 ppm (pupae) was also reported (Murugan et al. 2016). In another study, cumulative mortality was noted for larval instars of *S. litura,* thus confirming the insecticidal activity of chitosan nanocomposite. In addition, biochemical changes of midgut and hemolymph constituents evidenced the enhanced pesticidal activity of the nanocomposite against all stages of larva with high mortality rate (Namasivayam et al. 2018).

12.3.4 Nanopolymer-Based Insecticides

In recent years, polymer-based nanoformulations are gaining popularity among many researchers to employ them as plant protection molecules (mainly pesticides). Pesticide formulation prepared using polyethylene glycol (PEG) in water was found to show controlled and slow released activity that lasted for several weeks than commercial pesticides, such as betacyfluthrin, carbofuran, thiamethoxam, imidacloprid, and thiram (Kaushik et al. 2013; Pankaj et al. 2012). Few reports on bioassay research too confirm the potentiality of some of these formulations based on PEG being more effective than commercial insect and nematodes control products (Pankaj et al. 2012). Essential garlic oil loaded on PEG-coated polymer-based NPs was used to control red flour beetle adults, *Tribolium castaneum (Herbst)* (*Coleoptera: Tenebrionidae*). They too reported on the sustained efficacy of PEG-coated polymer NPs <80% after 5 months (Yang et al. 2009). Film preparation of high-density polyethylene (HDPE) fabricated with two NPs (ZnO/Ag) was reported to shield stored food supplies from the insect/pest invasion. The outcomes of the present study showed the non-penetration of *Sitophilus granarius* adults into the loaded NPs and the γ-irradiated HDPE films (Eyssa et al. 2018). Polymer-based nanoformulations were found to exhibit greater effectiveness to commercial mixtures over relatively long time period (30 d), owing to their slower release capability instead of increased absorption by the nanoformulation uptake by the target organisms of the released pesticide. However, their very slow release (in some cases) has been considered as a disadvantage of polymer-based nanoformulation as it can lead to decreased environmental flexibility, high production expenses, and high energy involving methods of preparation (Torchilin 2006). Argemone mexicana-based synthesis of TiO_2, capped with poly(styrene sulfonate)/poly (allylamine hydrochloride) was reported to exhibit both larvicidal and pupicidal activities against Zika virus vector, *A. aegypti* (Murugan et al. 2017).

12.4 Smart Delivery Systems of Nanopesticides

NPs are employed as a common delivery tool in medical therapies. Likewise, a similar "pesticide delivery system" for pest control has also been established. The nano-based deliveries are much preferred for their physical properties and specificity. The idea of nanobased formulations as effective delivery systems is adapted from its application in medical field. Many researchers believe that these nanocarrier systems can strengthen/enhance the pesticide properties and activities such as mobility, stability, solubility, dispersion, and targeted delivery. In addition, they possess the capacity to provide highly flexible loading because of the installation of single carriers, wider surface area, many distinct pesticide compounds, and an extremely rapid mass transfer toward the targeted pest (Zhao et al. 2017). Many conceptual ideas

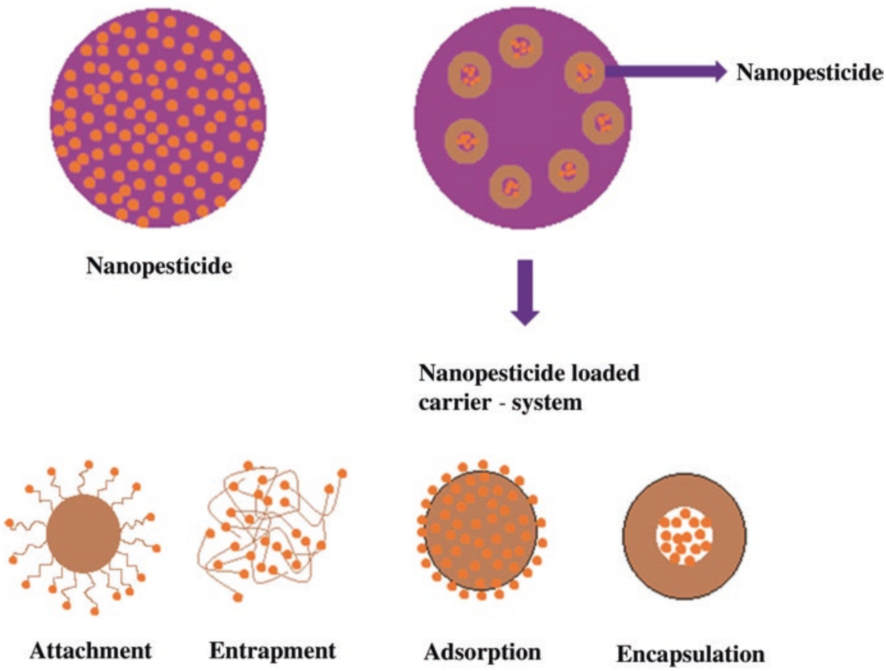

Fig. 12.3 The delivery systems of nanopesticides

were reported so far for the loading of active pesticide compounds on NPs, namely, surface adsorption, nanoparticulate polymer shell encapsulation, covalent binding by various ligands, and nanopolymer matrix entrapment (Jia et al. 2014). The delivery systems of nanopesticides are illustrated in Fig. 12.3. Of all, nanoencapsulation was reported to be an effective strategy that can be used safely to deliver pesticides with less exposure to the environment (Qian et al. 2011). Other reports on the use of mesoporous NPs such as porous hollow silica, activated carbon, and nanoclay were also found to be ideal delivery systems with controlled release options for both polar and nonpolar pesticides. These NPs were found to possess good biocompatibility, high drug-loading capacity, low toxicity, and multistage release patterns (Wang et al. 2012). According to Yu et al. (2017), the strength of the adhesion depended heavily on the size distribution and the surface functional groups on the NPs and hence can easily be controlled by varying the size and functional groups. Among all NPs, silica-based NPs had generated much interest among the researchers to employ as an effective agent for plant-based agrochemical application. This is attributed to their flexible structure that allows to form numerous shapes and sizes of NPs, as well as their ability to form pores that aid in effective loading of the biomolecules.

12.5 Mode of Action of Nanobased Insecticides

Though enormous literature is discussed on nanotoxicity to selected pests and vectors, reliable data about the possible mode of insecticidal action is lacking (Athanassiou et al. 2018). As discussed earlier, nanobased formulations possess specific morphological characteristics compared with traditional pesticide formulations, which could effectively enhance pest coverage, adherence, and permeability (Zhao et al. 2017). Owing to the influence of the size, shape, and charge of the AgNPs, various in vitro and in vivo studies have been reported on the cytotoxicity and genotoxicity using bacterial and other biological models. However, only a few research has focussed on the mechanism of action against mites and insects (Santo-Orihuela et al. 2016). In addition, their toxicity may also be due to the penetration of NPs into the exoskeleton. Few nanobased formulations were found to act similar to traditional pesticides. Basically, the mode of action would be by activating insect-target alteration pathways and triggering stomach poisons release. Pesticide ingestion in pests primarily affects its digestive system. The other way of entry is through inhalation or contact with the poisonous fluids from the host (Zhao et al. 2017). Based on the other reports, the nanobased formulations enhanced the function of stomach and contact poisoning by improving the dispersal and permeability which in turn increased the rate of pesticides entering the pest (Yang et al. 2017). Enhanced transport and conductivity of the nanobased formulations was reported to improve the insecticidal efficiency by accelerating the pesticide poisoning, pesticide efficacy, bioactivity, and dose effect. Possible mode of action of nanoinsecticides is shown in Fig. 12.4.

12.6 Future Research Challenges

By reducing the use of chemical-based crop protectants, nanotechnology is expected to make agriculture more eco-friendly and highly profitable. Despite a slow progress, nanobased technologies appear to have a great future not only in the agricultural sector but also in other sectors (Athanassiou et al. 2018). In the past few decades, NPs have gained huge prospects for their wide applications in agricultural field that will surely interest the researchers to develop safer and more efficient pest control formulations. Undoubtedly, intensive research could possibly lead to many revolutionary formulations based on nanopesticides such as nanoemulsions, nanodispersions, etc., in the near future (Murugan et al. 2015). However, research pertaining to insecticidal mechanism or mode of action remains lacking for many nanobased insecticides. Apart from very few studies of Ag, copper. and chitosan NPs, many key classes of NPs are yet to be investigated in terms of entomological and parasitological research. Likewise, there is an urgent need for a comprehensive understanding of different routes that lead to the toxic effects of chronic NPs on the vertebrate population (Benelli 2018). Similarly, experiments performed on polymer-based nanoinsecticides remain at nascent stage due to lack of knowledge on the unique characteristics of nanocomposites behavior in soil and agriculture. Hence, more studies are required to extend this concept for various commercial crop

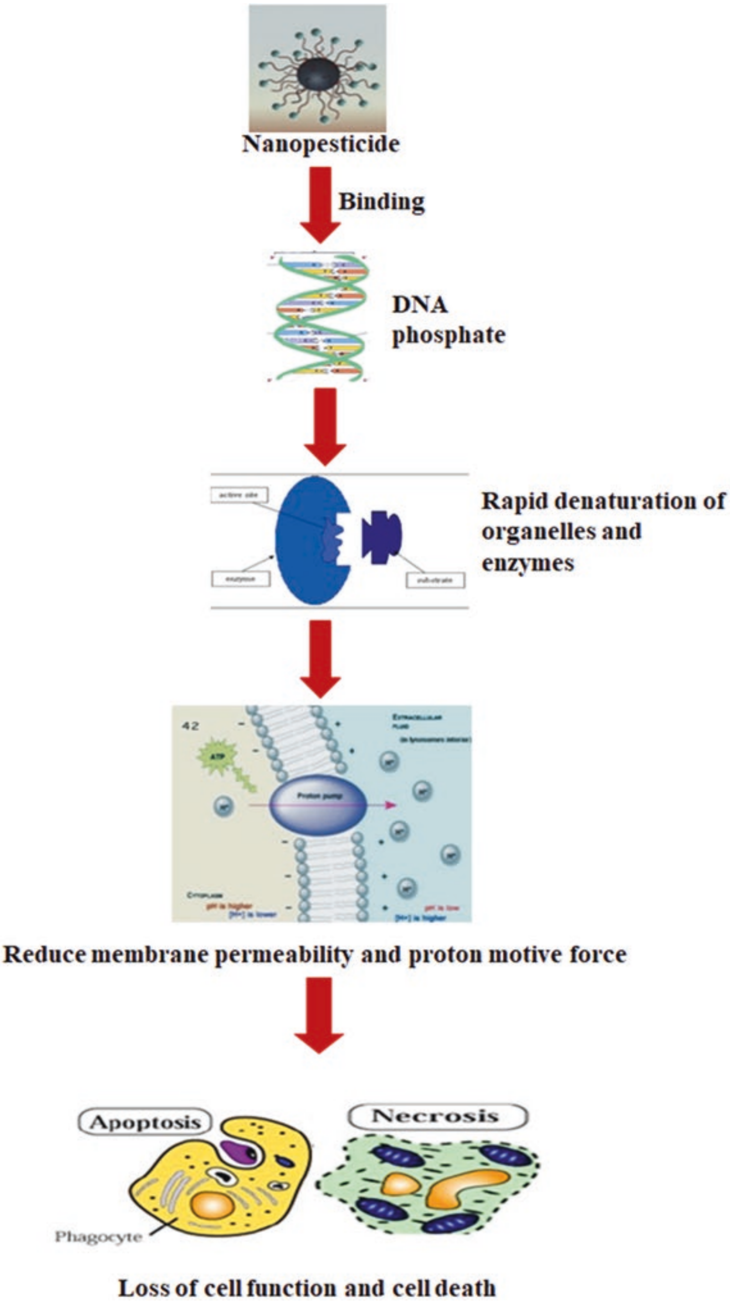

Fig. 12.4 Possible mode of action of nanoinsecticides

applications. Before the implementation of in situ pest management practices, a huge amount of work is still required on formulations of nanopesticides by integrating analytical methods which can detect, characterize (in terms of size, surface area, nature, or shape), and quantify the main ingredient and formulations of the insecticides (Athanassiou et al. 2018). Additional research efforts toward the development of smart nanodevices as effective delivery tools, that aid in the development of smart fertilizers, pesticides, and growth regulators are also of high need. Development of nanosensors for real-time monitoring of crop growth, pest invasion, soil conditions, and disease development will surely place nanotechnology in greater heights. Similarly, the development of nanocapsules for controlled and systemic release of herbicides through proper implementation means will also greatly increase their options to use against parasitic plants (e.g., contact herbicide-based mode of implementation) (Shahzad and Manzoor 2019). Therefore, intensive research on the above said issues is much needed to target the pests more precisely for the implementation of sustainable advanced agricultural nanotechnology.

12.7 Limitations of Nanopesticides

Considerable knowledge on the possible toxicity of NPs and nanoformulations toward both the target and nontarget species is one of the key issues that need to be addressed before their extensive use. More alarming is that, in many cases, the NPs claimed to be synthesized using "green" methods are not at all "green" (P'erez-de-Luqu et al. 2009). It is also equally important to notice that not all NPs pose similar toxicity risks. Serious evaluation of biocompounds is much needed to be chosen to develop less hazardous nanoformulations. In this regard, it was reported that the nanocapsules and liposomes formulated using natural organic compounds such as chitin and lipids are considered to be less toxic than those NPs formulated using heavy metals (P'erez-de-Luqu et al. 2009). Another important for nanocarrier development is the scale of production and costs. Till date, large quantities of many NPs that can be used in agriculture cannot be produced, owing to their prohibitive costs. Nonetheless, the implementation of nanotechnology for crop protection and agricultural pest combats needs to be carefully evaluated to serve public health and livestock science. Unfortunately, there are almost no data on the final destiny of nanoparticles, particularly those that have not reached their goal and leaked away from the agricultural fields. However, few researchers believe that agricultural nanotechnology research is not reaching its maximum potential due to the scarcity of commercial applications. Worrall et al. (2018) reported that out of the 84 papers investigating pesticides, herbicides, fungicides, or loaded with nanoparticles (published until October 2018), only two papers have attempted field trials. In addition, only 24 papers addressed environmental issues such as soil leaching and nontarget toxicity, and only 46 papers inspected the formulations developed against the target pest.

12.8 Conclusions

Nanobased insecticidal formulations exhibit many benefits over conventional formulations such as highly targeted delivery, high efficiency, smart controlled release options, and environment friendly. Due to technological advancements, large-scale application of nanopesticides in crop production is quite possible, nowadays. Based on many research reports, various NPs, namely, AgNPs, SiO_2, TiO_2, ZnONPs, etc., were recognized as excellent candidates for fighting against many insects and pests with their proven toxicity against mosquitoes and ticks. They were also found to display their toxicity at various stages of insects and pests. Nano-encapsulation-mediated nanocomposites loaded with herbicides, fungicides, fertilizers, nutrients, and target-specific plant site are regarded to achieve desired results. However, these nanocomposites are to be carefully evaluated, as they might pose certain health hazard and disturbances in the ecosystem. In conclusion, formulations of nanobased pesticides bring beneficial improvements to the behavior and properties of the traditional pesticides such as dispersion, solubility, controlled release of active ingredients, delivery targeting, and of course, stability. Additionally, it could not only enhance the efficiency but also improve the bioavailability properties and minimize the nontarget toxicity against wildlife, food, and environmental residues.

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