Chapter 9
What It Takes to Control Plant Pathogenic Fungi Using Chitosan and Chitosan-Based Nanoparticles in the Twenty-First Century

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Abstract The use of nanoparticles is a safe approach that offers a novel control method against different fungal pathogens affecting plants. The negative impacts of chemical fungicides worldwide have compelled the utilization of new strategies to manage plant diseases. The use of nanoparticles in plant protection offers target delivery, strong efficacy, and unique mechanisms of action with low toxic impacts. Chitosan has attracted attention as a result of its desirable qualities and antimicrobial activities. Chitosan nanoparticles alone or when coupled with other compounds (active ingredients) provided a great effect against plant pathogenic fungi. It gives two benefits (disease control and improving the defense mechanisms in the host). Because of the need for natural antimicrobial agents that could minimize the negative effects of chemical pesticides. This work aimed to explore the unique properties of chitosan and the antifungal potentialities of chitosan-based and chitosan nanoparticles alone against several fungal phytopathogens. In addition, the mechanisms of

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action against different fungal pathogens and biosafety are also extensively discussed. The use of chitosan and chitosan-based nanotechnological approaches has been promising for the management of fungal pathogens affecting varieties of plant species; this method is considered safe for the environment and the host plants.

Keywords Biosafety · Disease control · Chitosan · Fungi · Mode of action · Nanotechnology

9.1 Introduction

To lessen reliance on synthetic pesticides, there is a significant interest in creating an alternative plant disease control method. Without a doubt, the most valuable organism for plant growth destruction is the pathogenic fungi of plants. Among the many approaches, inventions supported by nanotechnology have produced desired data mostly by using nanofungicides (Cho et al. 2010; El-Mohamedya et al. 2019). Chitosan is a biopolymer derived from the alkaline deacetylating of chitins (Fig. 9.1). The majority of the protective cuticles of crustaceans including shrimp, crabs, prawns, and lobsters are derivative of chitin, a homopolymer made of β-(1,4) linked N acetylglucosamine. It is extensively used in the domains of agriculture, medicine, pharmaceuticals, and the environment (Abd El-Aziz et al. 2018; Mahmoud et al. 2018). Due to its excellent antifungal effect, broad spectrum in use, and low toxicity for human cells, chitosan offers a number of benefits over other forms of molecules (Youssef et al. 2019).

The need for a safe alternative to manufactured pesticides spurs research into natural antifungal substances like chitosan. The most essential substance in agricultural nanotechnology is chitosan which is non-toxic, antifungal, and biodegradable. According to studies (Meng et al. 2010), chitosan has an antifungal property in nature due to its cationic amino groups which form the biological constituents and its functions. However, its insolubility in water and reduced fungicidal efficacy are the reasons why chitosan molecule has not been mainly used as an antifungal substance (Youssef et al. 2018).

Chitosan's physicochemical properties are being modified to increase its antifungal effectiveness (Meng et al. 2010). O-hydroxy phenylaldehyde thiosemicarbazone chitosan and triethylene diamine dithiocarbamate chitosan are two chemically modified forms of chitosan that have greater antifungal properties than chitosan (El-Mohamedya et al. 2019; Meng et al. 2010). Due to their high permeability to the biological membrane, biodegradability, cost efficiency, wide antifungal potentialities, and non-toxicity to humans, chitosan nanoparticles are preferred for usage in a variety of industries. Due to modified physicochemical qualities like surface area, size, active functional groups, cationic nature, and increased encapsulation potentialities, chitosan nanoparticles have a wide range of biological functions, etc. alone or in combination with other elements (Saharan et al. 2013). Few publications are known on the utilization of chitosan nanoparticles in plant infection control,

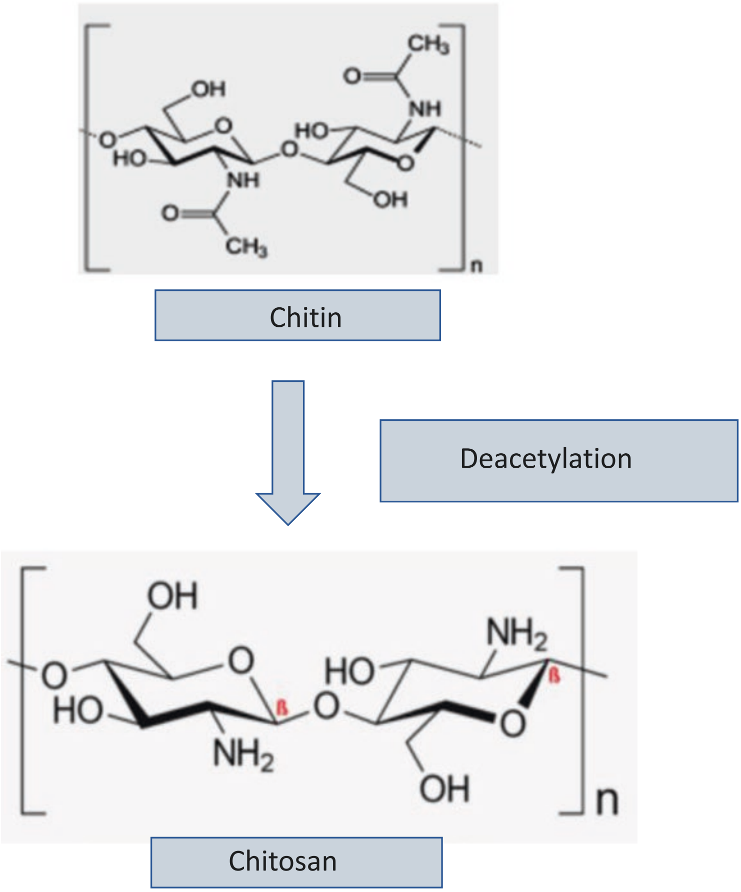

Fig. 9.1 Derivation of chitosan from chitin using the deacetylation method at a temperature of 80 °C

specifically against the fungi despite their potential uses in the agricultural sector. This chapter aimed to focus on the desired properties of chitosan and the antifungal properties of chitosan-based and chitosan nanofungicides against fungal plant pathogens and, more so, to study its overall modes of action for different plant pathogenic fungi and biosafety.

9.2 Definition and Properties of Chitosan

A few researchers have verified that chitosan's capacity to stop pathogen development, which affects spore germination, viability, and sporulation, is what causes it to work against the pathogenic fungi. By the stimulation and inhibition of numerous biochemical processes during the phytopathogenic interactions, chitosan's effect may disrupt pathogen cells or serve as an inducer of defensive responses in the plants (Hassan et al. 2022). The increased surface area, cationic nature, and small size of chitosan are what enable it to successfully carry out a variety of biological activities (Table 9.1). In addition, because they have functional groups in their structures, they easily react with various inorganic and organic compounds (Choudhar et al. 2019). In general, chitosan has been studied in both its pure and functionalized nanomaterial forms with other organic and inorganic substances because it is a highly effective antibacterial, plant elicitor, and plant growth regulator (El-Mohamedya et al. 2019; Devi et al. 2020).

Table 9.1 The fungicidal effects of chitosan alone against several fungal phytopathogens

Chitosan	Effect	Target pathogen	Sources
Chitosan	Highest inhibition (14 mm) of the fungi	*Aspergillus flavus*, *A. niger*, and *A. fumigates*	Debnath et al. (2022)
Chitosan	Complete inhibition at 5.0 g/L (in vitro)	*Alternaria solani*	Ghule et al. (2021)
Chitosan	Inhibition was highest (10.66 mm) *A. flavus*	*Rhizoctonia solani*, *Alternaria alternata*, and *A. flavus*	Shakeel et al. (2018)
Chitosan	Decrease deoxynivalenol and fumonisin formation in irradiated wheat and maize and the growth rate of the pathogens also decrease	*F. verticillioides* and *F. proliferatum*	Zachetti et al. (2019)
Chitosan	Post-emergence seedlings mortality of 7.67% where the seeds were treated with chitosan (1%)	*Colletotrichum capsici*	Akter et al. (2018)
Chitosan	In vitro antifungal activity (50%) inhibition	*Pyricularia oryzae*	Kutawa et al. (2021)
Chitosan	In vitro antifungal activity (50%) inhibition	*Ganoderma boninense*	Maluin et al. (2019a)
Chitosan	Decrease in disease severity of 42.8% and 16.60% after the application of chitosan 1.0 g/L + *T. harzianum* and chitosan (1 g/L)	*Fusarium oxysporum* f. sp. *Radicis lycopersici*	El-Mohamedy et al. (2017)
Chitosan	100% inhibition at a concentration of 5 g/L	*Fusarium oxysporum*, *F. solani*, *Sclerotium rolfsii*, *Rhizoctonia solani*, *Pythium* sp., *Phytophthora* sp., and *Macrophomina phaseolina*	El-Mohamedy et al. (2013)

9.3 Chitosan Nanofungicides for the Control of Fungal Infections in Plant

9.3.1 Antifungal Effects of Chitosan Nanofungicides Against Some Species of Fungi

Chitosan's usefulness in creating chitosan NPs either on its own or after being combined with other organic and inorganic materials has been recognized. To increase their efficacy and prevent environmental toxicity, the synthesized chitosan-based nanocomposites might enable control, targeted, protected, and systemic release of active components (Devi et al. 2020; Chouhan et al. 2017). A smart chitosan-based nano-agri input may be produced by combining chitosan with other various compounds, which might result in precision farming that is both efficient and affordable (Fig. 9.2). This section describes in detail many NMs made of chitosan that may be able to avert the effect of the plant pathogenic fungi (Table 9.2).

Chitosan nanomaterials were investigated due to their biological potentialities. They were tested against several fungi and were found effective in averting the growth of the fungi (Chookhongkha et al. 2012). Chitosan NMs at a concentration (0.6%) had inhibited the growth of mycelia for *Colletotrichum capsici*, *C. gloeosporioides*, *A. niger*, and *Rhizopus* sp. Chitosan nanoparticles have better potentialities than chitosan alone in terms of mycelial growth reduction. Moreover, chitosan combined with chickpea seeds had a good antifungal effect, and this can be based on two facts: (1) Seeds treated with chitosan yield more lignin and phenolic substances. (2) Chitosan can inhibit the growth of the mycelia (Chookhongkha et al. 2012). The chitosan nanoparticles were examined against phytopathogenic fungi (*Macrophomina phaseolina*, *Rhizoctonia solani*, and *Alternaria alternata*) at different concentrations from 0.001 to 0.1% (in vitro). The inhibitory effect of 87.6% was found against *Macrophomina phaseolina* at concentrations of 0.1%. The growth of *R. solani* fungus was inhibited by all the tested concentrations of chitosan nanoparticles (Saharan et al. 2013). In a different research work, a method of preparing chitosan nanoparticles using an anionic protein obtained from *Penicillium oxalicum* was used. These nanoparticles have greatly inhibited the growth and development of *Alternaria solani*, *Pyricularia grisea*, and *F. oxysporum* (Sathiyabama and

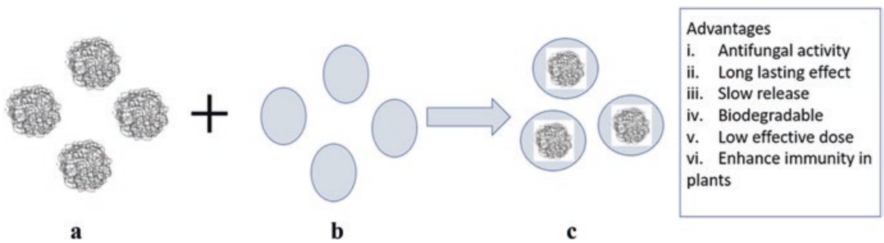

Fig. 9.2 Chitosan reacting with other bioactive compounds to form a nanomaterial with desirable properties: (**a**) chitosan, (**b**) active ingredient, (**c**) formed nanomaterial

Table 9.2 Chitosan coupled with other compounds utilized against several phytopathogenic fungi

Nanomaterials	Particle size (nm)	Polydispersity index (PDI)	Zeta potential (mV)	Effects	Sources
Chitosan dazomet	7	–	–	Antifungal effect against *Pyricularia oryzae*, *Ganoderma boninense* (in vitro)	Maluin et al. (2019a)
Chitosan NPs	89.8	0.22	−37	Antifungal effects against *Alternaria solani*, *Pyricularia grisea*, *Fusarium oxysporum.* It also enhances the germination and growth of chickpea seedling (in vitro)	Sathiyabama and Parthasarathy (2016)
Chitosan NPs	83.3	0.31	−28	In vivo and in vitro fungicidal effects against *Pyricularia oryzae*	Manikandan and Sathiyabama (2016)
Chitosan NPs	180.9	0.31	+45.6	Fungicidal effect against *Fusarium graminearum*	Kheiri et al. (2017)
Cu (II)–chitosan nanogel	220	0.20	+40	Antifungal effect against *Fusarium graminearum* (in vitro)	Brunel et al. (2013)
Cu–chitosan NPs	196.4	0.50	+88	Antifungal effects against *A. alternata*, *Rhizoctonia solani*, and *M. phaseolina* (in vitro)	Saharan et al. (2013)
Cu–chitosan NPs	2.5–25	N/A	N/A	Fungicidal effects of *F. solani*	Devi et al. (2020)
Cu–chitosan NPs	2–3	N/A	N/A	Inhibition of *Sclerotium rolfsii* and *R. solani* (in vitro)	Rubina et al. (2017)
Cu–chitosan NPs	374.3	0.33	+22.6	In vivo and in vitro fungicidal effect on *Curvularia lunata* in corn	Choudhar et al. (2019)
Chitosan–saponin NPs	373.9	1	+31	Antifungal effect of *M. phaseolina*, *A. alternata*, and *R. solani* (in vitro)	Saharan et al. (2013)

Table 9.2 (continued)

Nanomaterials	Particle size (nm)	Polydispersity index (PDI)	Zeta potential (mV)	Effects	Sources
Oleoyl–chitosan NPs	296.9	N/A	N/A	Mycelial and spore germination inhibition of *Verticillium dahliae* (in vitro)	Xing et al. (2017)
Chitosan–Zn NPs	200–300	0.22	+34	In vivo and in vitro antifungal effect of *C. lunata* in corn plants	Choudhar et al. (2019)
Chitosan loaded with salicylic acid NPs	368.7	0.1	+34.1	In vivo and in vitro fungicidal effect of post flowering stalk rot of corn incited by *Fusarium verticillioides*	Kumaraswamy et al. (2019)
Chitosan–silica NPs	110	N/A	N/A	Antifungal effects of *Phomopsis asparagi* (in vitro)	Cao et al. (2016)
Chitosan–*Schinus molle* (CS-EO) essential oil NPs	754	9.1 ± 1.74	N/A	Antifungal effects on the conidia of *Aspergillus parasiticus*	Cao et al. (2016)
Mentha piperita EO in cinnamic acid–chitosan nanogel	N/A	N/A	N/A	Fungicidal effects of *A. flavus* during the storage of tomato fruits	Devi et al. (2020)
Chitosan loaded with *Zataria multiflora* EOs nanoparticles	125–175	N/A	N/A	*Botryticidal* effects of *B. cinerea* in strawberry (in vivo and in vitro)	Mohammadi et al. (2015)
Chitosan boehmite–thyme oil and alumina nanocomposite films	N/A	N/A	N/A	*Monilinia laxa* inhibition during the storage of peach	Cindi et al. (2015)
Chitosan–*Cymbopogon martinii* essential oil	455–480	39.3–37.2	N/A	Antifungal effects of *Fusarium graminearum*, during the storage of corn grains	Kalagatur et al. (2018)
Chitosan–thymol nanoparticles	175 ± 21	37 ± 2.7	0.4 ± 0.1	Antifungal effects on the mycelia of *Botrytis cinerea* in tomato and blueberries during the storage period	Medina et al. (2019)

Parthasarathy 2016). The rate of inhibition for *Fusarium oxysporum ciceri*, *Pyricularia grisea*, and *A. solani* was 87%, 92%, and 72%, respectively (Table 9.2). A seed treatment with chitosan nanoparticles yielded a good morphological effect which included improved vegetative biomass, seed vigor index, and percent germination of chickpea seedlings. The antifungal effect of nanoparticles can be due to their size and highly permeable membrane (Devi et al. 2020; Saharan et al. 2015). Their lower PDI values, higher zeta potential, and small size make the nanoparticles efficient and stable against phytopathogens.

9.4 Chitosan Coupled with Synthetic Fungicidal Active Ingredients for Managing Plant Fungal Diseases

Maluin et al. (2019b) carried out another study in which they created nanofungicides of the three distinct types by entrapping chitosan, dazomet, and hexaconazole: chitosan combined with dazomet, chitosan combined with hexaconazole, and chitosan combined with dazomet and hexaconazole formulations (Maluin et al. 2019b). Furthermore, it was deduced from the results that the antifungal activity will be strong if the particles are tiny (Maluin et al. 2019c). The lowest EC50 for chitosan combined with dazomet and hexaconazole was discovered to be 3.5 ng/mL. The lowest EC50 for chitosan combined with dazomet and chitosan combined with hexaconazole, respectively, was 13.7 ng/mL and 4.6 ng/mL. Additionally, (Maluin et al. 2019a) observed that phenazine nanoformulation has 70.74% suppression of the growth of the fungus *G. boninense* at 1000 μg/mL (Maluin et al. 2019a).

The fungicide was intercalated in zinc–aluminum layered double hydroxide (Al-Zn-LDH) by exchange of ions to create the nanodelivery form of fungicide used by Mustafa et al. (Mustafa and Komatsu 2016). Dazomet and hexaconazole were the fungicides employed, and they were shown to be effective in the control of *G. boninense* (Maluin et al. 2019b). Hexaconazole's controlled release characteristic was achieved in H-Al-Zn-LDH, and the EC50 value was discovered to be 30.0·2.9 ng/mL. H-Al-Zn-LDH and D-Al-Zn-LDH have shown a less phytotoxic impact than traditional fungicides (Maluin et al. 2019c).

9.5 Chitosan Coupled with Natural Products for Managing Plant Fungal Diseases

9.5.1 Fungicidal Effects of Zataria Multiflora Essential Oil in Chitosan

One of the EOs that appears to be a possible natural product for managing fruit post-harvest loss is *Zataria multiflora* essential oils (ZEO). According to Sajed et al. (Sajed et al. 2013), oxygenated monoterpenes make up the majority of the hydro-distilled ZEO's constituents (about 70%), followed by monoterpenes, sesquiterpene, and oxygenated sesquiterpene. In order to preserve fruit quality and reduce fungal rot, EOs utilized volatile chemicals; however, these compounds are rapidly affected by high pressure, temperatures, oxygen, and light. Additionally, they are insoluble in H_2O, necessitating a regulated release for several applications (Devi et al. 2020; Martin et al. 2010). So, to get the most out of employing EOs as antimicrobial compounds, continuous and regulated release is essential.

These compounds' nanoencapsulation techniques may offer a workable and effective solution to some of these issues, such as physical instability. Using chitosan nanoparticles (CSNPs), Mohammadi et al. (Mohammadi et al. 2015) examined the encapsulation of ZEO to increase the stability and antifungal effect against the fungus (*Botrytis cinerea*) responsible for strawberry gray mold infection. ZEO was enclosed in CSNPs using the ionic gelation process, and the transmission electron microscope analysis revealed that the average size was between 125 and 175 nm (Devi et al. 2020). Works on the release of ZEO in vitro showed that this release was sustained and regulated for a period of 40 days. When ZEO was enclosed by CSNPs, it had greater anti-*Botrytis cinerea* activity compared to ZEO (in vitro and in vivo). After 7 days of storage at 4 °C, followed by another period of storage at 20 °C for 2–3 days, strawberries infected with *Botrytis* had dramatically reduced in terms of disease incidence and severity at 1500 ppm. These results demonstrated the use of CSNPs as an EO-controlled release method to increase the antifungal effect (Devi et al. 2020).

9.5.2 Antifungal Activity of Chitosan–Thymol Nanoparticles

The main antibacterial component of the thyme plant is thymol (2 isopropyl-5-methylphenol). Due to its capacity to bind to bacterial proteins and produce cell membrane permeability and disintegration, it has a potent antibacterial effect (Ahmad et al. 2011). Thymol interferes with energy-producing mechanisms, which prevents the cell from recovering (Ahmad et al. 2011). To increase the life span of the food, it may be used as a natural fungicidal material during the packaging of the active (Mirdehghan and Valerob 2017). By incorporating chitosan–thymol nanofungicides made by the ionic exchange process, Medina et al. (Medina et al. 2019) improved the effectiveness of chitosan–quinoa protein films on the enhancement of the life span of tomato and blueberry cherries. They were able to generate NPs with hydrodynamic diameters (175±21 nm) comparable to TEM diameters (153 42 nm). The zeta potential value was 37 2.7 mV, while the PDI value was 0.4 0.1 mV. In several dilutions applied to the PDA bearing the same amounts of active chemicals, the effects of thymol–chitosan nanoparticles (TCNPs), CNPs, and thymol–chitosan (CT) mix on the mycelial growth inhibition were assessed. While CT mix only demonstrated complete inhibition at a higher dose (50% v/v), CTNP formulations showed inhibition of 100% for all the dilutions (10, 25, and 50%) (Medina et al. 2019). At higher concentrations (50% v/v), CNP demonstrated the lowest suppression of mycelial development (74%). The treatment that showed inhibition at the least concentration (10%) was CTNPs.

9.5.3 Antifungal Activity of Thyme–Tea Tree, Thyme–Pepper Mint, and Chitosan–Thyme–Oregano Essential Oil

The management of fungal proliferation and contamination in processed food is now being aided by bio-nanocomposite-based packaging that contains EOs obtained from green plants (Hossain et al. 2017). To overcome dose restrictions and enhance the stability of active substances, EOs are more effectively employed in meals when entrapped in suitable delivery methods (Van Long et al. 2016). When EOs are encapsulated at the nanoscale, their bioactivities are improved. They do so via tissue infusion or passive mechanism which allows the EO levels necessary to ensure the antibacterial effect to be reduced (Van Long et al. 2016).

Due to the modest concentrations of the bioactive ingredient used, food flavor, natural scent, and taste remain unchanged (Lu et al. 2016). By encasing EO nano-emulsion, Hossaina et al. (Hossaina et al. 2019) developed cellulose nanocrystals coupled with chitosan (CNCs) antifungal films. For a storage period of 8 weeks at 28 °C, chitosan-based films combined with EO mixtures of oregano, thyme, peppermint, and tea tree reduced the fungal growth (*Aspergillus flavus*, *Aspergillus niger*, *Penicillium chrysogenum*, and *Aspergillus parasiticus*) by 51–77% on the inoculated rice. Thyme–peppermint, thyme–tea tree, and thyme–oregano formulations have z-averages of 69.9 nm, 76.58 nm, and 57.9 nm, respectively, as well as PDI values of 0.25, 0.21, and 0.32 and zeta-potential values of 51, 50, and 53 mV (Hossaina et al. 2019). After 24 h of inoculation, they demonstrated significant inhibition of 83.73 2.55, 75.60 1.27, 87.95, and 6.81% against the fungus *A. niger*. Over the course of 12 weeks of storage, there was a gradual release of volatile chemicals (26%), but the paddy samples wrapped with bioactive films underwent no distinct changes in flavor, odor, and color. The chitosan matrix-incorporated CNCs were crucial in maintaining the release and physicochemical characteristics of the nanocomposite film (Devi et al. 2020; Hossaina et al. 2019).

9.5.4 Antifungal Effect of Cymbopogon martinii Essential Oils Coupled with Chitosan

A tropical herb in the Poaceae family, *Cymbopogon martinii*, is often referred to as motia, Indian geranium, or rosha (Kakaraparthi et al. 2015). The chemical components of its EOs include bioactive substances including humulene, geraniol, caryophyllene, linalool, geranyl acetate, limonene, selinenes, etc. (Kalagatur et al. 2018). The antifungal efficacy of *C. martini* essential oils (CMEOs) was examined against the post-harvest *Fusarium graminearum* fungus which is responsible for causing *Fusarium* head blight infection in corn plants (Devi et al. 2020). They discovered that CMEOs had MIC of 421.7±27.14 ppm and minimum fungicidal concentrations of 618.3±79.35 ppm. Craters, vesicles, rough surfaces, and protuberances of macroconidia underwent morphological alteration when exposed to CMEOs as opposed to controls. Fungi died as a result of increased lipid peroxidation and ROS concentration (Kalagatur et al. 2018). The chitosan-entrapped CMEO nanoparticles (CeCMEONPs) had a zeta potential ranging from 37.2 to 39.3 mV and a spherical shape between 455 and 480 nm in size. The bioactive components of CMEOs were effectively conjugated with chitosan and successfully produced CeCMEONPs according to the FTIR analyses (Kalagatur et al. 2018). By gradually releasing the antifungal components of CeCMEONPs, a stable complex structure generated between CMEOs and chitosan improved the lifespan and antifungal properties of CMEOs. In a lab setting, during the course of a 28-day storage period, grains of maize have been utilized as the samples to test the antimycotoxin and antifungal potentialities of CeCMEONPs and CMEOs against *F. graminearum*. The fungal growth was inhibited by CMEOs and CeCMEONPs at 900 and 700 ppm, respectively. CeCMEONPs had superior antimycotoxin and antifungal properties compared to CMEO, which may be explained by the antifungal components of CeCMEONPs' regulated release of antifungal agents over time.

9.5.5 Antifungal Activity of Thyme Oil with Chitosan–Boehmite

Thyme oil (TO) sachets were packaged in PET punnets that were additionally packed with lidding films made of a boehmite–chitosan nanocomposite, according to Cindi et al. (Cindi et al. 2015). They discovered that brown rot severity and incidence were decreased in experimentally infected *Prunus persica* (cv. Kakawa) peach fruits when kept at 25 °C for 5 days. In addition, the incidence of brown rot infection in naturally infected fruits was decreased to 10% when kept at 0.5 °C, 90% RH for a total of 7 days. Linalool (37.6%), caryophyllene (9.47%), and thymol (56.43%) were kept inside the punnet as active substances (Cindi et al. 2015). The taste, appearance, and flavor of natural peach remain the same as such people prefer to buy the fruit packed from commercial punnet which contains thyme oil (sachet) and sealed using boehmite–chitosan film.

9.5.6 Antifungal Activity of Thiadiazole Functionalized Chitosan Derivative

Li et al. (Li et al. 2013) demonstrated that a group of water-soluble derivatives of chitosan, which are 1,3,4-thiadiazole, 2-methyl-1,3,4-thiadiazole, and 2-phenyl-1,3,4-thiadiazole, had strong fungicidal properties against the pathogenic fungi like *Phomopsis asparagi*, *Monilinia fructicola*, and *Colletotrichum lagenarium*. At 1.0 mg/mL, the inhibition was measured to be 31.6% for *C. lagenarium*. When compared to chitosan, the antifungal properties of chitosan derivative showed higher results. With inhibition of 82.5, 65.8, and 75.3% against *M. fructicola*, *P. asparagi*, and *C. lagenarium*, respectively, at 1.00 mg/mL, MTPCTS had the greatest performance among the investigated chitosan derivatives. The hydrophobic moiety and the length of the thiadiazole's alkyl substituent could influence the antifungal effects of the chitosan derivative (Li et al. 2013).

9.5.7 Chitosan Coupled with Pepper Tree Essential Oils

The pepper tree which belongs to the family Anacardiaceae also contains EOs with antibacterial qualities (Lopez et al. 2014). The pepper tree contains the chemical components of EOs like FC; - phellandrene, FC; and -pinene, limonene, phellandrene myrcene, and monoterpenes. Its EOs have been shown to be effective against *Fusarium solani* filamentous fungus (Rhouma et al. 2009). The mycelium inhibition of *A. flavus* was observed to be up to 53.5% at 500 ppm of pepper tree EOs. *A. niger*, *A. oryzae*, and *A. japonicus* were all also inhibited significantly by the antifungal agent (Alanis-Garza et al. 2007). Against *A. fumigates*, the EOs had a MIC of >1000 mg/mL (Alanis-Garza et al. 2007).

Chitosan nanomaterials were prepared by Luque-Alcaraz et al. (Luque-Alcaraz et al. 2016) and included pepper tree EOs with a zeta potential of +9.1±1.74 mV and particle size of 754±7.5 nm. They looked at how varied chitosan nanoparticle concentrations in pepper tree EO affected the conidia of *A. parasiticus*. It was discovered that, when compared to controls, all treatments decreased the vitality of the fungal conidia. According to their findings, adding pepper tree EO to chitosan nanocomposites is a substitute that maintains the fungicidal effects of both constituents while reducing the potential for EOs to volatilize and the ensuing loss of their activities (Devi et al. 2020).

9.6 Mechanisms of Action for Chitosan Nanoparticles

As a result, interference that damages the cell wall of the fungus may result in content loss and death. According to their findings, *Pyricularia oryzae* strain Gry hyphae treated with CNP exhibited swollen, cell wall damage, and aberrant structure that resulted in partial loss of contents (Ibrahim et al. 2020a; Pariona et al. 2019; Oussou-Azo et al. 2020). In contrast, *Pyricularia oryzae* strain Gry's cell walls displayed typical structural properties in the untreated control (Fig. 9.3c). Similar to AgNPs, CNPs have been discovered to exhibit antifungal effects on the cell walls of several plant fungal pathogens, including *Fusarium solani*, *F. oxysporum*, *Colletotrichum gloeosporioides*, and *Fusarium graminearum* (Oussou-Azo et al. 2020; Kriti et al. 2020).

It is well known that the conidia of pathogenic fungi play a significant part in infecting and colonizing plants (Khalil et al. 2019; Nicomrat et al. 2017). As a

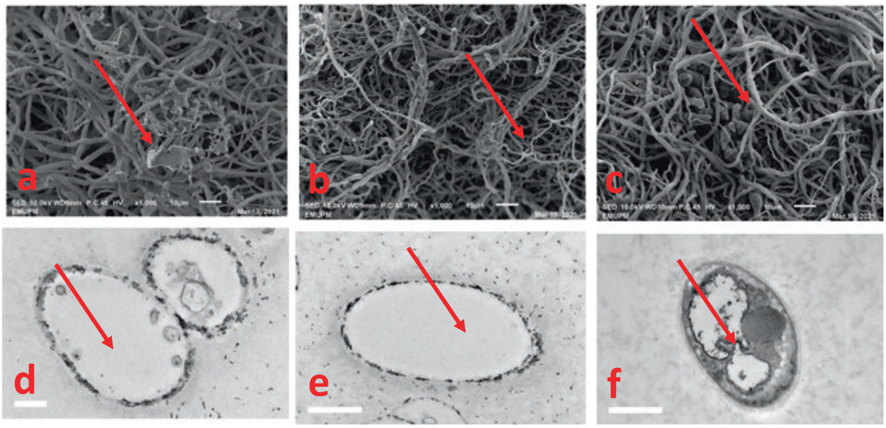

Fig. 9.3 Morphological changes of the treated rice pathogen. (**a**) Complete disruption of *P. oryzae* mycelia after being treated with chitosan hexaconazole agronanofungicides. (**b**) Shrinkage of *P. oryzae* mycelia after being treated with chitosan dazomet agronanofungicides. (**c**) Normal growth of *P. oryzae* mycelia (control). (**d**) Leakage of major cellular organelles after being treated with chitosan hexaconazole agronanofungicides. (**e**) Leakage of major cellular organelles after being treated with chitosan dazomet agronanofungicides. (**f**) The fungal cell was intact without any leakage for the control

result, slowing down the pace of conidial germination will greatly lessen the danger posed by pathogenic fungi in rice. The germ tube development and conidial germination of *P. oryzae* strain Gry could be effectively inhibited by the synthesized CNPs, and the fungicidal effects could increase with the rise in CNP concentrations. In actuality, 83% of spores germinated, whereas the length of the germ tubes in the negative control was 77.63 m (Ibrahim et al. 2020b). Furthermore, our study conducted in 2021 showed that both chitosan hexaconazole and chitosan dazomet agronanofungicides have played a role in disrupting the mycelia and conidia of *P. oryzae* isolated from rice plants (in vitro), while the control was not affected as presented in Fig. 9.3.

9.7 Conclusion and Future Perfectives

Chitosan and chitosan nanoparticles can play a significant role as nanopesticides against different fungal pathogens. Chitosan is a flexible biomaterial with outstanding fungicidal properties. It is easily manipulable using a variety of chemical and physical methods. By combining chitosan's functional groups (−NH2 and −OH), which may be functionalized with both organic and inorganic compounds to expand its range of applications, this biopolymer can serve as a special platform for the production of effective fungicides. Similarly, new fungicides that are promising and eco-friendly with lower doses can be manufactured in this way.

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Chapter 10
The Docking and Physiological Characteristics as Detectors of Nanoparticle's Role in Plant Responses to Biotic Stress

Sozan E. El-Abeid, Mohamed A. M. El-Tabakh, Ahmed Z. I. Shehata, Reham I. AbdelHamid, and Ahmed G. Soliman

Abstract Plant pathogens and other pests that feed on plants are a major cause of crop loss. Historically, many pesticides have been used to control plant pests, even though these chemicals are extremely toxic. However, these chemicals are considered fundamentals of supplying food and reducing crop loss. As a result, plant diseases are one of the biotic stresses that harm plants and productivity in general. Recently, nanomaterial has been utilized as a novel method to reduce the amount of hazardous substances released into the environment. The present chapter aims to shed light on the physiological effects of nanomaterial in terms of hormonal and enzymatic aspects as their role as exterminators for some diseases, in addition to highlighting some innovative new tools used to give a visualization of the nanomaterial-pathogen site of action, interaction, and their stability.

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10.1 Introduction

Nanotechnology has recently gained significant attention in the agricultural sector due to its potential to provide novel approaches for controlling and managing plant diseases. Nanoparticles, characterized by their size ranging from 1 to 100 nm, have distinct features that render them well-suited for diverse applications in plant disease control. This topic aims to learn how nanoparticles may be used for the prevention and treatment of plant diseases. Nanoparticles' primary function in preventing plant disease is as delivery vehicles for bioactive compounds. Nanoparticles can encapsulate and safeguard bioactive substances, including fungicides, bactericides, and plant growth regulators, augmenting their stability and effectiveness. Through encapsulation, nanoparticles can provide regulated release mechanisms, facilitating a prolonged and targeted distribution to specific diseased plant tissues (El-Abeid et al. 2020; Mosa et al. 2022).

Furthermore, nanoparticles can potentially enhance the bioavailability and absorption of these bioactive chemicals inside plants. The diminutive dimensions of these particles enable them to readily infiltrate the plant's cuticle or cell walls, enhancing the efficacy of their uptake via the roots or leaves. Improved efficacy against infections and better overall disease control result from increased absorption (El-Abeid et al. 2020). Furthermore, nanoparticles have antibacterial characteristics in addition to their role as transporters for bioactive chemicals. Several studies have shown that certain categories of nanoparticles, including silver nanoparticles, possess various antibacterial properties against diverse diseases. These substances can interfere with the cellular structures of bacteria or fungi, impeding their development and reproductive processes (Choudhary et al. 2022).

The antimicrobial properties shown by nanoparticles provide them a compelling substitute for traditional chemical pesticides, which may potentially harm human well-being and the ecosystem. In addition, nanoparticles can induce the plant's innate defensive responses against pathogens. Plants may be rendered more resistant to disease infection by the induction of systemic acquired resistance (SAR) or the activation of defense-related genes, thus enhancing their ability to combat pathogens (Abdelkhalek et al. 2022). The observed enhancement in the immune system of plants facilitates a more efficient defense against infections and diminishes their vulnerability to subsequent pathogenic assaults. One further functional aspect of nanoparticles in controlling plant diseases is their potential use in diagnostics. Nanoparticles can be functionalized by attaching ligands or antibodies that exhibit specificity toward pathogen-related compounds or antigens. Nanoparticles facilitate the development of expeditious and highly responsive diagnostic instruments, hence facilitating the timely detection and characterization of plant diseases (Benjamin et al. 2023). The early identification of diseases is of utmost importance to promptly adopt control measures and effectively mitigate their spread. In general, nanoparticles possess a diverse array of functional capacities in the regulation and administration of plant diseases. Nanoparticles possess several advantageous characteristics in contemporary agriculture, including their capacity to serve as carriers for bioactive chemicals, boost the bioavailability of these compounds, display antibacterial capabilities, activate plant defense systems, and facilitate diagnostics. Ongoing research and development endeavors in this domain exhibit significant potential for implementing sustainable and efficient disease control approaches in agricultural production.

This chapter aims to provide insights into the physiological impacts of nanomaterial in relation to hormonal and enzymatic factors, particularly their efficacy as agents for combating certain diseases (Fig. 10.1). Additionally, this chapter emphasizes utilizing novel techniques for visualizing the site of action, interaction, and stability of nanomaterials and their relation with pathogens.

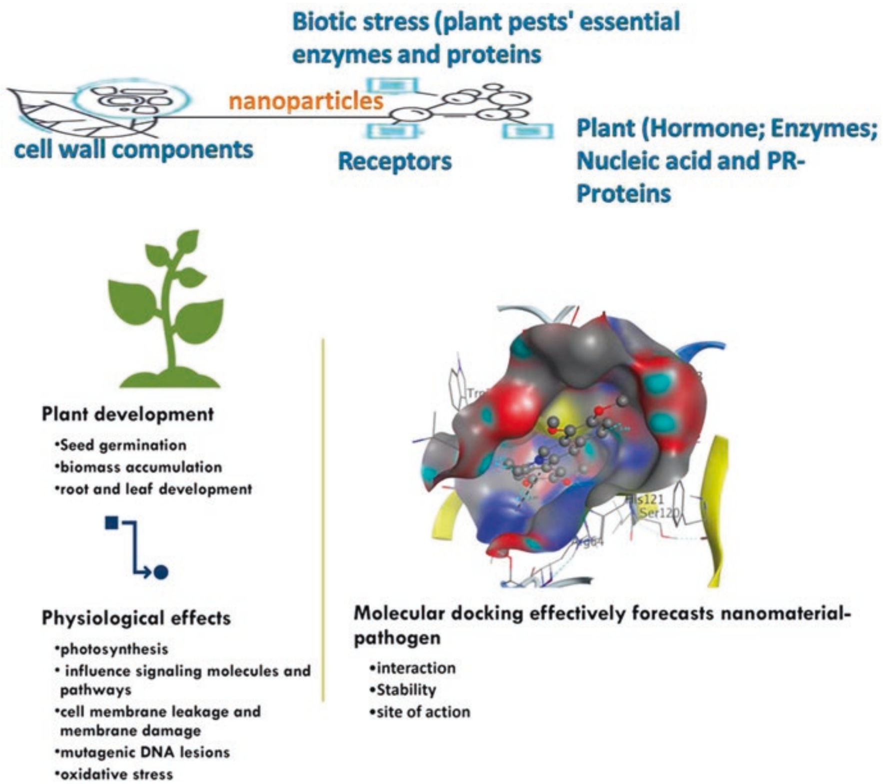

Fig. 10.1 Schematic representation to illustrate the docking and physiological characteristics as detectors of nanoparticle's role in plant responses to biotic stress

10.2 The Functional Roles of Nanoparticles in Controlling and Managing Plant Diseases

Nanoparticles possess the capacity to function as nano-scale insecticides, fertilizers, and nutrition, exhibiting the ability to selectively target specific cellular organelles within both plants and diseases. Nanoparticles have been found to enhance various physiological processes in plants, including metabolism, seed germination, plant development, and nutrient use. The utilization of nanoparticles has the potential to yield two significant advantages: a reduction in the utilization of agrochemicals and a mitigation of the environmental impact associated with current farming practices. One potential mechanism by which nanoparticles can mitigate the pathogenicity and growth of phytopathogens is their interference with many cellular processes, including membrane function, metabolism, respiration, and gene expression. Nanoparticles possess the capacity to enhance a plant's resilience to both biotic and abiotic stresses by modulating its physiological and biochemical responses. The application of nanoparticles in the identification and management of infections can be achieved by the utilization of nano-sensors, nano-carriers, and nano-biocides.

10.3 Their Role in the Regulation of Biotic Stress in Plants

1. Delivery of antimicrobial agents: Nanoparticles may transport drugs to plant infection spots. These nanoparticles can encapsulate or attach antimicrobial compounds such as fungicides, bactericides, or bio-control agents, allowing for targeted and controlled release of these agents to combat plant diseases effectively (Mosa et al. 2022).
2. Enhanced penetration and uptake: Nanoparticles can improve the penetration and uptake of antimicrobial agents into plant tissues. Since they are so small and have such a high surface area to volume ratio, they can readily pierce the plant's cuticle or cell walls, allowing antimicrobial chemicals to be delivered directly to the cells where the infections are hiding out.
3. Controlled release of active compounds: Nanoparticles can be engineered to release antimicrobial compounds in a controlled manner, ensuring a sustained and prolonged effect against plant pathogens. Modifying the surface properties or encapsulating the active compounds within nanoparticles can regulate their release rate, providing long-lasting protection against diseases.
4. Improved stability and bioavailability: Nanoparticles can enhance the stability and bioavailability of antimicrobial agents by protecting them from degradation or inactivation in harsh environmental conditions. They can shield the active compounds from UV radiation, pH variations, enzymatic degradation, or interactions with other molecules in the plant's surroundings.

5. Targeted delivery to specific plant tissues: Nanoparticles can be functionalized with ligands or antibodies that specifically recognize certain plant tissues or pathogen receptors. These allow targeted antimicrobial agent delivery to infected areas while minimizing off-target effects on non-infected tissues.
6. Induction of plant defense mechanisms: Certain nanoparticles have been found to stimulate plants' natural defense mechanisms against pathogens. These nanoparticles can trigger plant immune responses, leading to enhanced production of defense-related molecules such as phytoalexins, pathogenesis-related proteins, or reactive oxygen species that help combat diseases.
7. Enhanced nutrient uptake and growth promotion: Some nanoparticles boost nutrient intake and plant development, making plants more disease-resistant. These nanoparticles can enhance the availability and uptake of essential nutrients, stimulate root development, or modulate plant hormone levels, thereby strengthening plants' overall health and resilience against pathogens (Mosa et al. 2022; El-Abeid et al. 2020).
8. Diagnostic tools for disease detection: Nanoparticles may be used as diagnostic tools for early detection of plant diseases. Functionalized nanoparticles can specifically bind to pathogen-derived molecules or biomarkers in infected plants, enabling rapid and sensitive detection of diseases through techniques such as colorimetric assays or biosensors. Overall, nanoparticles offer promising strategies for controlling and managing plant diseases by providing targeted delivery of antimicrobial agents, enhancing their stability and bioavailability, stimulating plant defense mechanisms, improving nutrient uptake, and enabling early disease detection (Benjamin et al. 2023).

10.4 Nanoparticle Impact on Plant Growth and Development

Nanoparticles have been proven to have dual activity in preventing and treating wilt disease in common bean plants (Tortella et al. 2023; El-Sayed et al. 2023). According to Li et al. (2023a, b), these substances have the potential to function as highly targeted agents, capable of delivering herbicides, nano-pesticide fertilizers, or genes to particular cellular organelles inside plants. According to recent studies by Li et al. (2023a, b) and Wang et al. (2023), using nanoparticles has shown potential to enhance membrane integrity and plant-water connections, mitigating drought stress' effects. Additionally, these nanoparticles have shown the capacity to boost nutrient absorption in plants under drought stress. Additionally, they can provide a novel remedy for the insufficiency of nutrients in crops, stimulate plant growth and advancement, and impede plant disease proliferation (Li et al. 2023a, b; Siddiqui et al. 2015).

Moreover, previous studies have shown that silica nanoparticles (SiNPs) might positively impact the development and growth of plants, particularly the presence of both biotic and abiotic stressors. Silicon nanoparticles (SiNPs) can partially improve leaf and stem development (Mosa et al. 2022) by regulating plant hormone metabolism and soluble sugar levels. According to Li et al. (2023a, b), SiNPs can potentially enhance wheat development via direct or indirect mechanisms, such as the elevation of auxin (IAA) and fructose levels.

10.5 What Is the Mechanism Behind Nanoparticles' Effect on Plant Growth?

The unique physicochemical features of nanomaterials provide significant prospects in the agricultural domain. The physiological, morphological, and genotoxic alterations that occur when nanoparticles interact with plants are important in using nanotechnology for agriculture. The effects of nanoparticles on plant growth and development may differ depending on the characteristics of the nanomaterial, the application technique, and the type of plant used, as shown by the studies. The effects of nanoparticles on plants' physiology, biochemistry, and molecular processes have recently been studied. Particular attention has been paid to the risks and benefits of utilizing nanomaterials on economically important crops and their absorption, translocation, and biotransformation (Nair 2016). Nanoparticles have been identified as beneficial agents for enhancing plant growth, facilitating developmental processes, and providing protective effects. They confer specificity in the administration of pesticides, improve nutrition availability, manage pathogenicity, boost photosynthetic capacity, and increase the germination rate. However, there have been recorded cases of nanoparticle toxicity and bioaccumulation, leading to a number of drawbacks. Therefore, it is essential to have a clear awareness of the benefits and drawbacks of nanoparticles and to do extensive research into their varied properties.

The effects of nanoscale ZnO on peanut (*Arachis hypogaea*) plants were studied, and it was shown that 1000 ppm ZnO had a positive effect on germination, seedling vigor, plant growth, blooming, chlorophyll content, pod yield, and root development (Pawar and Laware 2018). Inhibitory effects were seen, however, at doses beyond 2000 ppm (Pawar and Laware 2018). Biocompatibility studies have shown that zinc oxide nanoparticles (ZnO-NPs) pose no harm to living organisms. ZnO-NPs have been found in previous studies to improve seed germination and boost plant growth. The antibacterial characteristics discovered in these nanoparticles may also aid in disease prevention and plant defense.

Throughout their evolution, ZnO nanoparticles (NPs) have been shown to have positive and negative effects on plant growth and metabolism, according to several studies. Specific features of the nanoparticles themselves, as well as the physiological qualities of the host plant, affect the absorption, translocation, and storage of zinc oxide nanoparticles (ZnO-NPs) by plants. It is theorized that ZnO exerts its effects by causing an increase in membrane lipid peroxidation via the production of reactive oxygen species. This, in turn, reduces cell viability by allowing reducing sugars, DNA, and proteins to flow out of the membrane. Nanoparticles have been found to have deleterious effects on vegetation. The results of this study demonstrate that nonpolar molecules (NPs) may be absorbed, transported, and accumulated inside terrestrial plant species. Some types of edible plants have been found to contain nanoparticles (NPs), which may reduce agricultural yields and pose health hazards to humans. Understanding how nanoparticles (NPs) move through plants and how they exert their toxicity is crucial for any risk assessment to be credible. Several stages of plant development, including expansion, germination, biomass accumulation, and root and leaf development, may be negatively impacted by an abundance of nanoparticles.

However, depending on the plant species, the kind of nanoparticles utilized, and their dosage, the impacts of NPs might be either helpful or destructive. The physiological effects of nanoparticles on plants led to increased seed germination rates and total biomass or grain yield. The NPs also improved the plant's resistance to biotic and abiotic stresses. The molecular-level processes are crucial to the plant's biological functions. In Ali et al. 2021, Ali and coworkers did research.

10.6 Nanoparticle-Microbe Interactions Inside Plant System

Various factors, including nanoparticle characteristics, application method, and plant species, are thought to influence how nanoparticles influence plant growth and development, as Agrahari and Dubey (2020) reported. In almost every way, nanoparticles have helped plants flourish and thrive while keeping them safe. Nanoparticles boost photosynthetic capacity and germination rate, decrease pathogen prevalence, and improve the specificity with which pesticides are delivered (2022). Rasheed et al. found that the effects of various nanoparticles on plant development were very variable (Rasheed et al. 2022).

The green pigment chlorophyll captures the light energy necessary for photosynthesis. It is found in the thylakoid membrane of chloroplasts and is the main pigment used in photosynthesis. Light is captured by chlorophyll and converted into chemical energy, which is then used to synthesize glucose from carbon dioxide and water. The process of photosynthesis may be affected positively or negatively by nanoparticles. Nanoparticles may alter the ability of plants to take in solar energy. Up-conversion nanoparticles, for instance, may transform infrared light into visible light, which solar cells can use to generate more electricity. Up-conversion nanoparticles may be used to increase the amount of energy harvested from solar panels. These nanoparticles take in infrared radiation and output visible light. Not all nanoparticles have the same impact on carotenoid levels, and the photosynthetic mechanism reacts differently when nanoparticles are present.

This compound stimulates the reaction in the plant's light-harvesting complex, and it also inhibits the electron transport system and changes the activity of RuBisCo, carbonic anhydrase, or phosphoenolpyruvate carboxylase (PEP) enzymes, all of which work together to halt metabolism (Poddar et al. 2020). Nanoparticles may have both negative (decreased chlorophyll content and electron transport rate) and positive (increased chlorophyll content, RuBisCo enzyme activity, PSII performance, CO_2 harvesting, and a broader chloroplast photoabsorption spectrum) effects on photosynthesis (Ghorbanpour et al. 2021). Researchers found that when SWCNTs were exposed to photosynthetic-pigment-protein assemblies in an aqueous environment, the steady-state chlorophyll fluorescence in the thylakoid membrane-biohybrid systems was quenched, and the average fluorescence lifetimes were shortened. The impact was unrelated to alterations in the structure and function of photosynthetic membranes at the macro level.

In photosynthetic organisms, nanoparticles may influence signaling molecules and pathways. For instance, single-walled carbon nanotubes (SWCNT) boosted the activity of plant signaling chemicals like nitric acid and facilitated the quick transit of electrons, leading to a threefold increase in photosynthetic production in the chloroplasts (Ghorbanpour et al. (2021)). Muhammad et al. (2021) thoroughly explain how the presence of various nanoparticles affects photosynthesis and how the photosynthetic process reacts to those nanoparticles.

Leakage of photosynthetic electrons toward the nanotubes, most likely at the level of the PSII acceptor site, is suggested by the reduction of the fluorescence signal in thylakoid membrane-biohybrid systems (Lambreva et al. 2023).

Titanium dioxide (TiO_2) nanoparticles increase the chlorophyll content of plants like tomatoes and oilseeds, among other beneficial benefits. Arabidopsis, spinach, and tomato all had their chlorophyll content raised, their RuBisCo (Ribulose-1,5-bisphosphate carboxylase/oxygenase) activity boosted, and their net photosynthesis stimulated by a foliar spray of TiO_2 NPs (Chen et al. 2017). TiO_2 NPs were shown to improve photosynthesis, growth rate, and solar energy absorption in spinach plants by increasing leaf chlorophyll content and influencing the thylakoid membrane (Karvar et al. 2022). Adil et al. found that chlorophyll a and b and total content concentrations rose in response to increasing concentrations of ZnO NPs, from 0.06 to 0.12 g (Adil et al. 2022). In contrast to the positive effects of ZnO NPs on seedling growth and chlorophyll and carotenoid content, Pb severely slowed their development (Hussain et al. 2021). By increasing plant growth and enhancing chlorophyll and carotenoid levels, ZnO NPs reduce Pb-induced stress (Hussain et al. 2021). Using differential modulation of photosynthesis and anti-oxidative defense mechanisms, ZnO-NPs may protect plant seedlings from Cd and Pb stress by reducing HMs-induced phytotoxicity and boosting physiochemical activity Alhammad et al. (2023).

It is unclear how nanoparticles compromise the structure and function of photosynthetic membranes. Various investigations have proven that polyvinyl chloride (PVC) nanoparticles cause cell membrane leakage and membrane damage (Li et al. 2022). An in-depth understanding of nanoparticles' interactions with chloroplast and its structural components (e.g., thylakoid membranes), signaling molecules, and pathways is necessary because increased photosynthetic efficiency is a potential impact of NPs on photosynthetic organisms of major economic and ecological significance (e.g., crops and algae).

Polyvinyl chloride (PVC) nanoparticles can cause mutagenic DNA lesions, generate reactive oxygen species, destruct cellular membranes, enhance membrane lipid peroxidation, and thus inhibit the metabolism and growth of plants (Ahmed et al. 2021). The negative effect of NPs on plant growth is mainly caused by excessive NPs (Gao et al. 2023).

DNA damage in plants caused by nanoparticles may be mutagenic. Examples include the first proof that manufactured nanoparticles may harm DNA in plant cells, published by a team from NIST and UMass Amherst (Atha et al. 2012). DNA damage from oxidative stress is the primary source of genotoxicity from NPs. Plants may experience oxidative stress due to nanoparticle production of reactive oxygen species (ROS). In addition to causing damage to DNA and RNA, ROS may also destroy proteins and enzymes inside a cell. TiO_2 nanoparticles stimulate the RuBisCo enzyme. To create reactive oxygen species (ROS), nanoparticles release metal ions and interact with water molecules (Yu et al. 2020; Abdal Dayem et al. 2017). Carbon nanomaterial, copper oxide nanoparticles, and metal-based nanoparticles, including gold, iron, cerium, copper, and titanium, may all produce reactive oxygen species (ROS) (Wen et al. 2020; Zhang et al. 2021; Sicwetsha et al. 2021).

10.7 Reducing Pathogen Infection by Affecting Their Receptors

Germline-encoded pathogen recognition receptors (PRRs) identify pathogen-associated molecular patterns (PAMPs). Macrophages and dendritic cells have these receptors, two types of immune cells. Until more specialized adaptive immunity is created, innate immunity serves a critical function as the body's initial line of defense. Therefore, reducing pathogen infection by affecting their receptors is a promising approach to combat infectious diseases. However, it is important to note that this is an active area of research, and there are no approved therapies yet that target PRRs to reduce pathogen infection (Jang et al. 2015).

Nanoparticles have been proposed as a promising approach to reduce pathogen infection by affecting their receptors. In particular, bio-receptor-functionalized nanoparticles effectively detect pathogenic bacteria and microbial biomolecules. Antibodies, oligonucleotide aptamers, proteins, enzymes, nano-zymes (chromogens), cells, antigens, microbes, bio-mimic substances, and other tiny molecules are all examples of bio-receptors that may be attached to these nanoparticles. Pathogen-associated molecular patterns (PAMPs) are recognized by bio-receptors, initiating a reaction that ultimately eliminates the pathogen (Lin et al. 2021). These nanoparticles are very useful for detecting harmful bacteria and other microbial macromolecules. Binding to target pathogens causes a change in the nanoparticles' refractive index, which in turn causes a shift in the surface plasmon resonance peak. Some research has shown that harmful bacteria and biomolecules may be detected visually, rapidly, and with a high intensity of colorimetry at a very low analytic concentration. The selectivity and specificity of a bio-receptor-functionalized nanoparticle, as well as the binding relationship displayed by the nanoparticle, bio-receptor, and analytes to create a bio-sensing complex, determine how well it functions as a detection component (Daramola et al. 2022).

It's worth noting that this is a dynamic field of study and that, yet, no medicines have been authorized that specifically target PRRs in an effort to lessen pathogen infection. There are two types of chemicals that pattern recognition receptors (PRRs) may identify: PAMPs, which are molecules associated with microbial pathogens, and DAMPs, which are molecules linked with host cell components that are produced after cell injury or death. The microbe-specific molecules that a given PRR recognizes are called pathogen-associated molecular patterns (PAMPs) and include bacterial carbohydrates (such as lipopolysaccharide or LPS, mannose), nucleic acids (such as bacterial or viral DNA or RNA), bacterial peptides (flagellin, microtubule elongation factors), peptidoglycans and lipoteichoic acids (from Gram-positive bacteria), N-formylmethionine, lipoproteins, and fungal glucans and chitin. Uric acid and extracellular ATP are damage-associated molecular patterns (DAMPs) that serve as endogenous stress signals.

PRRs are classified as localized in the membrane or the cytoplasm based on their location in the cell. The Toll-like receptors (TLRs) and the C-type lectin receptors are two examples of membrane-bound PRRs (CLRs). Many PRRs, such as NOD-like (NLRs) and RIG-I-like receptors, are in the cytoplasm (RLRs). Toll-like receptors mediate cytokine generation and release and activate other host defense processes in response to pathogen-associated molecular patterns detected either extracellularly or endosomal (Amarante-Mendes et al. 2018).

10.8 The Role of Nanoparticles in Regulating Gene Expression for Biotic Stress in Plants

It has been discovered that nanoparticles may regulate biotic stress in plants by modulating gene expression. Gene expression refers to producing a protein or other gene product from genetic instructions. In biotic stress response and defense, nanoparticles may be used to control gene expression (Kandhol et al. 2022).

The pathogenesis-related (PR) gene is an important player in plant immunity. Proteins having antimicrobial characteristics are encoded by a collection of genes called PR genes, which are activated in response to pathogen assault. These proteins are essential for preventing the proliferation of harmful microorganisms (Zribi et al. 2021; Jain and Khurana 2018).

Increased defensive responses against pathogens in plants have been attributed to nanoparticles' ability to stimulate the expression of PR genes. Silver and titanium nanoparticles, for example, have been shown in studies to stimulate the overexpression of PR genes in plants. Due to this upregulation, the enhanced synthesis of PR proteins is one factor in the plant's resistance to infections (Pérez-Labrada et al. 2020).

The precise mechanisms by which nanoparticles regulate gene expression in plants are still being investigated. However, it is believed that nanoparticles can interact with plant cell receptors and signaling molecules, triggering a cascade of molecular events that ultimately result in gene expression changes. Reactive oxygen species (ROS) produced by nanoparticles inside plant cells may serve as signaling molecules to turn on genes involved in defense (Thwala et al. 2013; Vannini et al. 2013; Jiang et al. 2017; Tripathi et al. 2017).

It's worth noting that the nanoparticle type, concentration, and length of exposure may all affect how they affect gene expression. Nanoparticle-mediated gene expression modification and its impact on plant defense against pathogens need more study to completely grasp the underlying processes. Nanoparticles may affect plant gene expression, boosting the plant's defensive response against pathogens by, among other things, upregulating genes involved in pathogenesis. One of the functional functions of nanoparticles in the management and prevention of plant diseases is the regulation of gene expression.

10.8.1 Multiple Crop Types Were Studied to See How Nanoparticles Affected Gene Expression and Plant Disease Resistance

Tomato (*Solanum lycopersicum*)

Silver nanoparticles (AgNPs) were studied for their effect on gene expression and disease resistance in tomato plants in a study by Rai et al. (2009). They analyzed the expression of important defense-related genes after treating tomato plants with AgNPs. In this study, we found that AgNP treatment induced an increase in the expression of many genes involved in plant defense against pathogens, known as pathogenesis-related (PR) genes. Increased defensive responses in tomato plants may be attributed to this upregulation. In addition, the treated tomato plants showed enhanced resistance to the early blight-causing fungus *Alternaria solani*. Disease severity was reduced, and pathogen development was stymied in plants treated with AgNP.

Sugar Beet (*Beta vulgaris*)

Khodakovskaya et al. (2012) investigated the effects of carbon nanotubes (CNTs) on sugar beet plants and their defense response against the fungal pathogen *Cercospora beticola*, which causes *Cercospora* leaf spot disease. This study revealed that applying CNTs to sugar beet plants resulted in the upregulation of defense-related genes associated with pathogen recognition and defense signaling pathways. These genes included those involved in synthesizing antimicrobial compounds and reinforcing cell walls. Moreover, CNT-treated sugar beet plants exhibited increased resistance against *Cercospora* leaf spot disease. The CNT treatment reduced disease severity and inhibited the growth and colonization of pathogens on plant leaves.

Arabidopsis Plant Studies

Vivancos et al. (2015) investigated the role of silicon nanoparticles (SiNPs) in enhancing resistance against the fungal pathogen *Fusarium oxysporum* in *Arabidopsis* plants. The researchers observed that SiNP treatment increased the expression of defense-related genes associated with the SA signaling pathway. This upregulation of defense gene expression resulted in improved resistance against fungal pathogens. This study demonstrated the potential of SiNPs to modulate gene expression and enhance plant defense mechanisms in *Arabidopsis*.

Sugarcane (*Saccharum officinalis*)

The effects of copper nanoparticles (CuNPs) on sugarcane development and disease control were studied by Elmer and White (2016). They tested the effects of CuNPs on sugarcane plants by measuring the expression of defense-related genes. Genes involved in pathogen detection and defense signaling were shown to be elevated after treatment with CuNP. The activation of plant defense mechanisms against pathogens is reflected in this increase. In addition, sugarcane plants treated with CuNP showed increased resistance to the bacterial pathogen *Xanthomonas albilineans*, the causative agent of sugarcane leaf scald disease. The severity of the sickness was lessened, and the spread of the infection was stifled after treatment with CuNP.

In summary, increased expression of defense genes involved in fending off diseases, known as pathogenesis-related (PR) genes, has been linked to plant exposure to nanoparticles. Silver nanoparticles (AgNPs), carbon nanotubes (CNTs), and copper nanoparticles (CuNPs) have all been proven in studies on tomato, sugar beet, *Arabidopsis*, and sugarcane to upregulate defense-related genes. In tomato plants, AgNP treatment led to the upregulation of PR genes and improved resistance against the fungal pathogen *Alternaria solani*. Similarly, in sugar beet plants, the CNT treatment upregulated defense-related genes associated with pathogen recognition and defense signaling pathways, resulting in enhanced resistance against the fungal pathogen *Cercospora beticola*. Silicon nanoparticles (SiNPs) applied to *Arabidopsis* plants boost the plant's resistance to the fungal disease *Fusarium oxysporum* by increasing the expression of defense-related genes linked with the salicylic acid (SA) signaling pathway, while sugarcane plants are more resistant to the bacterial pathogen *Xanthomonas albilineans*, which causes leaf scald disease, after receiving a treatment with CuNP.

The precise mechanisms by which nanoparticles regulate gene expression in plants are still being investigated. However, it is believed that nanoparticles interact with plant cell receptors and signaling molecules and generate reactive oxygen species (ROS), triggering molecular cascades that result in changes in gene expression. Overall, these studies demonstrate the potential of nanoparticles to enhance plant defense against pathogens by modulating gene expression. Further research is needed to fully understand the mechanisms underlying nanoparticle-mediated gene expression modulation and its impact on plant defense mechanisms.

10.8.2 Plant Hormone Inducers

Nanoparticles have become promising tools in plant science because of their ability to modulate gene expression and influence plant defense responses. Their interaction with plant cells at the molecular level, potentially involving specific genes and receptors, is crucial for harnessing their full potential in controlling and managing plant diseases (Khalid et al. 2022). While the exact details of nanoparticle-cell interactions in plants are still unknown, research has provided insights into the general processes involved. Nanoparticles interact with receptors on the surface of plant cells, triggering signaling cascades that can lead to changes in gene expression. These interactions can activate or mediate various signaling pathways within plant cells, such as hormone signaling or reactive oxygen species signaling (Khan et al. 2019).

Nanoparticles such as silver nanoparticles (AgNPs), titanium dioxide nanoparticles (TiO_2 NPs), and silicon nanoparticles (SiNPs) have been found to interact with plant hormone signaling pathways, potentially influencing plant growth and defense responses. The following are some general observations.

Silver Nanoparticles (AgNPs)

Auxins, gibberellins, and ethylene are only some plant hormones whose production and signaling are affected by AgNPs. These nanoparticles may affect hormone synthesis in plants, which can either increase or decrease hormone production (Tripathi et al. 2022).

Titanium Dioxide Nanoparticles (TiO_2 NPs)

Auxins and abscisic acid are two plant hormones that TiO_2 NPs might affect during biosynthesis and transduction (ABA). Increased synthesis of auxins, hormones essential for plant growth and development, has been linked to their presence (Tripathi et al. 2022).

Silicon Nanoparticles (SiNPs)

SiNPs have been reported to modulate hormone signaling pathways, including those associated with abscisic acid (ABA) and salicylic acid (SA). SiNP treatment enhances ABA signaling, which is involved in plant stress responses and drought tolerance. While these observations suggest that nanoparticles can potentially influence plant hormone signaling, it is important to note that the specific mechanisms and effects may vary depending on nanoparticle type, concentration, and plant species.

10.9 Receptor-Mediated Interactions

Nanoparticles may alter gene expression in plants by interacting with particular receptors on the surfaces of plant cells. Plant defensive responses are mediated by various membrane-bound receptors, some of which are involved in pattern recognition (Swartzwelter et al. 2021).

10.9.1 Signaling Pathways and Gene Expression

Nanoparticles can potentially activate or modulate various signaling pathways within plant cells, leading to changes in gene expression. These pathways may involve hormone signaling, reactive oxygen species (ROS) signaling, or other defense-related signaling cascades (Hasanuzzaman et al. 2021).

10.9.2 Defense-Related Genes

Exposure to nanoparticles may affect the expression of genes involved in plant defense. These genes can include pathogenesis-related (PR) genes, which encode antimicrobial proteins, genes involved in synthesizing secondary metabolites, reinforcement of cell walls, and other defense mechanisms (Khoshru et al. 2023).

10.9.3 Some Examples of Bio-receptor-Functionalized Nanoparticles

Antibody-functionalized gold nanoparticles: These nanoparticles have been shown to effectively detect and kill bacteria such as *Escherichia coli* and *Staphylococcus aureus*.

Aptamer-functionalized magnetic nanoparticles: These nanoparticles have been shown to effectively detect and kill bacteria such as *Salmonella typhimurium*.

Protein-functionalized silver nanoparticles: These nanoparticles have been shown to effectively detect and kill bacteria such as *Pseudomonas aeruginosa* (Mocan et al. 2017).

Enzyme-functionalized silica nanoparticles: These nanoparticles have been shown to effectively detect and kill bacteria such as *Staphylococcus aureus*.

Nanoparticle-based detection and killing of bacteria rely on bio-receptors functionalized on the surface of nanoparticles detecting pathogen-associated molecular patterns (PAMPs) (Mocan et al. 2017). Binding to target pathogens causes a change in the nanoparticles' refractive index, which in turn causes a shift in the surface plasmon resonance peak. This change is detected by optical sensors that can rapidly detect pathogens (Selvarajan et al. 2020).

In addition to detection, bio-receptor-functionalized nanoparticles can also kill bacteria. The bio-receptors recognize PAMPs on the pathogen's surface and trigger a response that leads to the destruction of the pathogen. For example, antibody-functionalized gold nanoparticles can bind to bacterial cells through specific interactions between antibodies and bacterial cell surface proteins or carbohydrates (Tian et al. 2021). Once bound, these nanoparticles can induce oxidative stress or generate heat, leading to bacterial cell death (Tian et al. 2021). Similarly, aptamer-functionalized magnetic nanoparticles can bind to bacterial cells through specific interactions between aptamers and bacterial cell surface proteins or carbohydrates (Tian et al. 2021). Once bound, these nanoparticles can induce mechanical stress or generate heat, leading to bacterial cell death. This is a developing field of study, and there are currently no FDA-approved medicines specifically targeting PRRs to lessen pathogen infection. Further study is required to evaluate the safety and effectiveness of these nanoparticles for clinical usage.

10.10 Effective Nanocides in Literature and the Market

Recent articles show that metal nanoparticles can be used as nanocides to control plant fungal diseases and create environmentally friendly fungicides that selectively activate their pathogen-suppressing properties only in the chosen fungal pathogen (Table 10.1). Nanocides effectively control plant fungal infection, thus providing a targeted approach to plant disease management that minimizes the impact on the surrounding environment and non-target organisms. This innovative use of nanotechnology in agriculture could revolutionize the way we protect crops from fungal pathogens, ensuring food security while maintaining ecological balance.

Nanoguard is a commercially available product that employs the usage of silver nanoparticles to effectively eradicate odor-causing microorganisms that may potentially interact with various types of fabric materials. The silver particles exhibit precision design, possess non-ionic properties, and are characterized by their non-toxic nature. The efficacy of nanoguard-treated fabrics in eradicating various bacterial strains has been substantiated by independent testing, demonstrating a 99.99% elimination rate upon contact.

Nanozymes refer to nanomaterial-based artificial enzymes that imitate the catalytic regions found in real enzymes or possess multivalent components to facilitate various reactions (Gomaa 2022). The subsequent instances illustrate the application of nanomaterials in nanozymes: Metal oxides are compounds that consist of a metal element bonded with oxygen. These chemicals are ubiquitous in the natural world and have many potential uses. Nanomaterials made from metal oxides like cerium oxide and iron oxide have been the subject of much study to mimic the activity of several naturally occurring enzymes (Wang et al. 2016). Due to their intrinsic catalytic properties, carbon-based nanomaterials such as fullerene and its derivatives,

Table 10.1 Effective nanocides against plant pathogens in literature and the market

Compound	The target	Type of nanoparticles	References
Nanoguard	Bacteria, viruses, fungi	Product-based–nano-silver	Tran et al. (2022)
Nanozyme	Enhance the effectiveness of enzyme	– Carbon quantum dots, carbon nanotubes, and graphene oxide – Au, Ag, Pt, PD, Rh, Ru, and Ir	Jeelani et al. (2020) Wong et al. (2021) Wang et al. (2023)
Nanoagri	Pesticides and fertilizers	Such as carbon, silica dioxide, iron oxide, titanium dioxide	Nazir et al. (2020), https://aradbranding.com/en/nano-agri-products-agriculture-upsc/
Chitosan-copper nanoparticles	Damping off fungi	Chitosan copper	Vanti et al. (2020)
Silver nanoparticles as a fungicide	Against *Sclerotium rolfsii* on wheat plants	Silver	Desai et al. (2022)
Copper-graphene nanocomposite	Fusarium wilt disease and Root rot	Graphene copper	El-Abeid et al. (2020)
A delivery fungicide in mesoporous silica nanoparticles	Fusarium crown and root rot in tomato	Mesoporous silica Chitosan and fungicide	Mosa et al. (2022)
ZnO nanoparticles as a nanofungicide	*Magnaporthe grisea*	ZnO	Ghamari et al. (2022)

carbon quantum dots, carbon nanotubes, and graphene oxide show great promise as non-metallic nanozymes (Wong et al. 2021). Also, gold (Au), silver (Ag), platinum (Pt), palladium (PD), rhodium (Rh), ruthenium (Ru), and iridium (Ir) are only a few of the metals that make up metallic nanozyme (Wang et al. 2023).

10.11 Molecular Docking Effectively Forecasts the Nanomaterial-Pathogen Site of Action, Interaction, and Stability

The binding interactions between ligands (nanomaterials) and targets may be predicted using a computer method called molecular docking (pathogen biomolecules). Molecular docking finds the optimal binding mode by simulating interactions between the ligand and the target in various conformations and orientations (Fig. 10.1). It employs scoring methods to assess the stability of ligand-target complexes and estimate binding affinities (Lin et al. 2020). To rationally develop and find new insecticides, understanding their biomolecular interactions by molecular docking is an interesting scaffold. Insecticide complexes' binding energy, free energy, and stability may be estimated using data gained via docking. Because it is performed before the experimental section of any inquiry, molecular docking can prove the viability of any insecticidal action. Enzymes may be used as a predictor of insecticide binding capabilities to nucleic acid, and molecular docking has transformed the study of interactions between tiny chemicals (ligands) and protein targets. This is why entomologists are often looking into the method of interaction between nucleic acid and insecticides in an attempt to demonstrate the harmful impact mechanism of insecticides at the molecular level (Mehrotra et al. 2013; Agarwal et al. 2014). The experimental methods are made accessible to determine the true binding mode of the complex if the docking algorithm predicts the indicated interaction (Dar and Mir 2017). As a result, researchers can create improved pesticides. This information may aid in identifying structural modifications to pesticides that will result in sequence-/structure-specific binding (Holt et al. 2008).

Due to their novel characteristics and possible therapeutic uses, nanomaterials have emerged as intriguing options for controlling plant pests. Understanding the molecular connections between nanomaterials and disease is crucial for developing individualized and effective treatment methods. To understand the underlying workings, interactions, and stability of nanomaterials at the nanoscale, the computational method of molecular docking is essential (Li et al. 2023a, b).

Molecular docking allows for the atomic-level study of how nanomaterials interact with plant pests' essential enzymes and proteins. It reveals unique binding locations inside timeless essential processes, which sheds light on the therapeutic potential of nanomaterials. Nanomaterials with increased affinity and specificity may be designed by docking them onto pathogen biomolecular targets, which helps discover critical residues involved in binding interactions (Krishnani et al. 2022).

The method of action of nanomaterials may be deduced from the binding poses and interaction patterns inside pathogen biomolecular targets, which are revealed by molecular docking. It sheds light on the mechanisms through which nanomaterials interfere with pathogen activity, enzymes, and cellular functions. To stop viruses from entering cells or replicating, docking studies may show how nanoparticles interact with surface proteins. Docking also reveals the binding mechanisms of nanomaterials to cell wall components or key enzymes, which may kill bacteria or prevent them from releasing virulence factors (Lokhande et al. 2023).

To create successful treatments, evaluating the stability and dynamics of nanomaterial-pathogen complexes is essential. By revealing the stability and strength of connections, molecular docking helps improve nanomaterial development. Surface changes, functionalization, and other methods may improve stability, toxicity, and targeting. The size, shape, surface charge, and functional groups of nanomaterials are all factors in their therapeutic effectiveness, and molecular docking studies help choose the best ones (Majumder et al. 2023).

Experimental validation of molecular docking results is common practice to verify predicted interactions and assess therapeutic potential. Binding affinities, kinetics, and thermodynamics of nanomaterial-pathogen interactions may be verified using surface plasmon resonance, isothermal titration calorimetry, or fluorescence spectroscopy. Nanomaterial-based therapies' effectiveness, biodistribution, and safety characteristics may be gleaned from cellular and animal research (Malla et al. 2023).

Molecular docking is useful for learning about the mode of action of insecticides such as synthetic chemical compounds, plant extracts, microbial insecticides, nanoparticles, etc., which have often been used against plant pests over many years. The order Coleoptera has been the focus of less research on the effects of pesticides on insects than any other order of insects. From this vantage point, the following examples are adequate. In Domínguez-Arrizabalaga et al. 2020, Domínguez-Arrizabalaga et al. investigated the efficacy of *Bacillus thuringiensis* as a microbial pesticide agent against many agro-forestry pest species, including Coleoptera and Lepidoptera. Insects of the Coleoptera, Lepidoptera, Hemiptera, and Hymenoptera orders, as well as mites, are killed by *Bacillus thuringiensis* because of the inclusions, called parasporal crystalline inclusions, that are formed of proteins (Cry and Cyt) (Schnepf et al. 1998). In addition, while *B. thuringiensis* is in its vegetative development phase, it secretes toxins into the medium. The vegetative insecticidal protein (Vip) and the secretory insecticidal protein (Sip) are two examples of these poisons (Sip) (Palma et al. 2014).

Since the active toxin contacts a specific receptor in the midgut epithelial cells, where an oligomeric pre-pore structure is generated, and since changes in midgut receptors are the first step in the development of insect resistance, molecular docking may shed light on the mode of action of a wide range of toxins (Jurat-Fuentes and Crickmore 2017). Most important coleopteran families, such as Chrysomelidae, Curculionidae, Scarabaeidae, Tenebrionidae, etc., have been demonstrated to be susceptible to the Cry3Aa, Cry3Ba, Cry3Bb, and Cry3Ca proteins (Domínguez-Arrizabalaga et al. 2020). Although heterologous competition assays show that each protein may bind at a different site, it has been shown that Cry3Ba, Cry3Aa, and Cry3Ca all share the same receptor (Rausell et al. 2004). Also, Cry3Bb, Cry3Ca, and Cry7Aa proteins competed in the same binding sites in sweet potato weevil, *Cylas puncticollis*; thus, the three proteins may become ineffective because of mutation in the midgut receptors (Hernández-Martínez et al. 2014). Ochoa-Campuzano et al. (2007) reported that Cry3Aa in *Leptinotarsa decemlineata* is considered a receptor of ADAM metalloprotease, and this binding interaction improves Cry3Aa pore formation.

To connect pyridylpyrazole to functional groups like alkanes, benzene rings, and heterocycles, a carboxylate group is used as a "linker." Yang et al. (2022) created new RyRs insecticides comprising an N-pyridylpyrazole moiety. The majority of the pieces came from the structures of common agricultural chemicals. Insecticidal properties against *Plutella xylostella* and *Spodoptera frugiperda* were tested after the design and synthesis of 44 new pyridylpyrazole carboxylate derivatives. The potential target of these compounds was also discussed, with compounds G34 and G35 being related to ryanodine receptors (RyRs). Crystal structures of the N-terminal domain of *P. xylostella* RyR were used to study how chemicals G34 and G35 dock with RyR. Consistency between the molecules G34 and G35 and the RyR N-terminal domain gap is possible. Both the aniline portion of G34 and the acetanilide portion of G35, which are surrounded by the residues A/Val-73, A/Arg-74, A/Asn-102, B/

Glu-155, B/Tyr-175, and A/Val-73, A/Gly-101, B/Pro-148, B/Ile-166, and B/Tyr-175, respectively, reach deep into the hydrophobic pocket. Also, residues A/Val-73, A/Gly-101, A/Asn-102, and B/Tyr-175 encircled chlorantraniliprole. One hydrogen bond was established between compound G34 and the B/Tyr-175 residue at a distance of 2.2, while three hydrogen bonds were formed between compound G35 and the A/Val-73, A/Gly-101, and B/Pro-148 residues at distances of 1.9, 3.5, and 3.0. Evidence for a possible insecticidal mechanism against *P. xylostella* is provided by the ability of compounds G34 and G35 to fix in the N-terminal domain of RyR. One possible explanation for G34's diminished insecticidal activity against *P. xylostella* is that it has less hydrogen bond interactions in its docking complex (binding energy = -5.65 kcal.mol^{-1}) than G35 (binding energy = -5.94 kcal.mol^{-1}). Chlorantraniliprole bound to the protein receptor with a lower binding energy (-7.03 kcal.mol^{-1}) than the chemical G35 (binding energy = -5.94 kcal.mol^{-1}), presumably because it established four hydrogen bonds with the receptor's A/Val-73, A/Gly-101, A/Asn-102, and B/Tyr-175 residues. This may explain why compound G35 has less insecticidal activity against *P. xylostella* than chlorantraniliprole. Due to the lack of crystal structures for cowpea aphids, *Aphis craccivora*, a docking investigation was performed using X-ray crystal structures of acetylcholine (protein AChBP) from *Lymnaea stagnalis* (PDB 2ZJU) (Alanazi et al. 2022). With an RMSD of 1.3201 and a binding energy of -8.17 kcal/mol, the cocrystallized ligand imidacloprid was redocked inside the AChBP binding area. H-bond lengths and binding energy were evaluated when the target compounds were docked within the AChBP and H-bonding amino acid residues. The binding score of Compound 9 to the AChBP site was -8.51 kcal/mol, which is quite close to that of imidacloprid. In addition, the quinoxaline moiety connected with Tyr385 through arene-H interactions, while the azomethine N created H-bonds with Trp143. In contrast, the thiazolidine quinoxaline derivative 15 formed three hydrogen bonds: (1) Trp143 with CN, (2) Thr144 with quinoxaline NH, and (3) Cys187 with thiazolidino S. This compound also exhibited arene-H interactions with the thiazolidino moiety. The thiazolidinone C=O established a hydrogen bond with Trp143, making compound 16 the most active chemical targeting cowpea aphid nymphs (with a binding score of -10.54 kcal/mol).

Another compound that affects insect acetylcholinesterase is 2, 3-dimethylmaleic anhydride. CASTp study of the projected model of AChE revealed three significant pockets, designated CP1 (CASTp Pocket 1), CP2 (CASTp Pocket 2), and CP3 (CASTp Pocket 3), against the rice weevil, Sitophilus oryzae. Most of the residues that make up the catalytic triad (SER111, GLU237, and HIS351) and the substrate binding site (GLY29, GLY30, GLY31, GLU110, SER111, ALA112, VAL115, SER266, LEU270, ASN271, VAL306, GLY352, and ILE355) of the modeled AChE can be found in CP1. Using the AutoDock 4.2 software, we performed docking analysis in two different ways: first, with the whole protein and, then, with only the region of interest. The initial docking simulations helped us identify and verify putative ligand binding locations. Cluster analysis was used to determine the resulting numerous conformations of AChE and 2,3-dimethylmaleic anhydride complexes. Four of the most populous clusters were selected for further study, denoted below as AC1, AC2, AC3, and AC4. Three of the four clusters, AC1, AC3, and AC4, were found to validate the three main CASTp pockets, CP1, CP2, and CP3, as possible ligand binding sites. The last cluster, AC2, didn't share any features with the others; therefore, it was singled out as a separate and distinct candidate for a binding site. Within CP1, a cluster of AC1 forms close to the region allocated for substrate binding. Consequently, the binding site for future study was validated jointly by considering the AC1 and CP1 sites. In addition, fresh targeted docking simulations were run on the validated binding location. The second round of docking studies yielded a docking conformation with a binding energy of 5.25 kcal/mol, and this structure was chosen as the complex's typical structure. Protein and ligand interact with one another on the level of 153 individual atomic atoms. In addition, 2,3-dimethyl maleic anhydride formed hydrogen bonds with CYS198 and GLU199 at 1.81 and 2.17, respectively, from these amino acids. Individual amino acids and the protein's collective interaction energies (IE) with the ligand were also studied. Both electrostatic (IE = −18.50 kcal/mol) and van der Waals (IE = −19.16 kcal/mol) interactions contributed equally to the IE between the protein and ligand. It was determined that the interaction energy of the established residues is less than −2.0 kcal/mol. The amino acids GLU199, GLU191, and PHE202 were identified as van der Waal interaction contributors, whereas the amino acids PHE241, PHE200, and TYR244 were identified as polar or electrostatic interaction contributors (Singh et al. 2017). Furthermore, GPI-anchored alkaline phosphatases (ALP) are also important for the Cry3Aa binding to Tenebrio molitor brush border membrane vesicles (BBMV) and are highly expressed when larvae are exposed to Cry3Aa (Zúñiga-Navarrete et al. 2013).

10.12 Advantages and Disadvantages of Docking

Molecular docking is a computational technique used in drug discovery and various other scientific fields to predict the interactions between molecules, such as small molecules (ligands) and biological macromolecules (receptors), like proteins or nucleic acids. When applying molecular docking to study interactions between nanomaterials and plant receptors, there are both advantages and disadvantages to consider:

10.12.1 Advantages

Cost-effective: Molecular docking is a cost-effective and time-saving method compared to experimental techniques. It can significantly reduce the time and resources required for the initial screening of potential interactions.

High Throughput: It allows for the screening of a large number of nanomaterials and plant receptors in a relatively short amount of time, making it suitable for virtual high-throughput screening.

Hypothesis Generation: Molecular docking can provide insights into potential binding sites, binding modes, and affinity rankings for various nanomaterials, aiding in the generation of hypotheses for further experimental validation.

Customization: The method is highly customizable, allowing researchers to adjust parameters and incorporate additional information like energy calculations, solvation effects, and flexibility of molecules to improve accuracy.

Reduction of Lab Work: By narrowing down the list of potential candidates, molecular docking can reduce the amount of experimental work required, saving time and resources (Van Dijk et al. 2005; Orihuela and Ungerfeld 2019).

10.12.2 Disadvantages

Simplification: Molecular docking relies on simplifications and assumptions, such as rigid receptor structures and static conformations, which may not accurately represent the dynamic nature of biological systems. In addition from previous work, molecular docking technique gives a low binding affinity which does not suggest the real interaction may be due to the presence of unfavorable interactions and only a few significant interactions were detected between nanomaterial and amino acid pocket (Rarey et al. 1996).

Accuracy and False Positives: Docking results can produce false positives and false negatives due to limitations in force field accuracy, scoring functions, and the neglect of important factors like water-mediated interactions and induced-fit effects (Lill 2011).

Parameter Sensitivity: The accuracy of molecular docking is highly dependent on the choice of parameters, scoring functions, and force fields, which can introduce variability in results. This limitation increases due to there is a limited number of tools that can be used to preform docking for nanomaterial in addition to the previous knowledge needed to add atom parameters to the successful docking process (Jain 2007; Befort et al. 2021).

Data Availability: The accuracy of molecular docking heavily relies on the availability of high-quality structural data for both nanomaterials and plant receptors. A lack of accurate structural information can lead to unreliable predictions.

Limited Information: Docking can only provide information about binding affinity and binding modes but cannot predict the biological activity or toxicity of nanomaterials accurately (Lin et al. 2020).

Another challenge is due to the complexity of biological systems. In the case of plant receptors, the complexity of plant signaling pathways, post-translational modifications, and allosteric effects may not be adequately captured by molecular docking alone (Sheik Amamuddy et al. 2020).

Validation: Docking results should always be validated through experimental methods, such as X-ray crystallography or binding assays, which can be time-consuming and costly (Ross et al. 2012).

In summary, molecular docking can be a valuable tool for predicting interactions between nanomaterials and plant receptors, but it should be used cautiously, considering its limitations and the need for experimental validation. It can help guide research efforts by providing a starting point for further investigation but should not be solely relied upon for drawing definitive conclusions about the biological activity or behavior of nanomaterials in complex systems.

10.13 Conclusions

Nanoparticles play a significant role in the agricultural domain due to their unique physicochemical features. They interact with plants, causing physiological, morphological, and genotoxic changes. The effects of nanoparticles on plant growth and development vary depending on the nanomaterial's characteristics, application technique, and plant type. They have been identified as beneficial agents for enhancing plant growth, facilitating developmental processes, and providing protective effects. However, there have been recorded cases of nanoparticle toxicity and bioaccumulation, leading to drawbacks. Nanoparticles can also positively impact several stages of plant development, including expansion, germination, biomass accumulation, and root and leaf development. The physiological effects of nanoparticles on plants led to increased seed germination rates and total biomass or grain yield. Within plant systems, nanoparticles can affect photosynthesis. Some nanoparticles may alter the ability of plants to take in solar energy, while others can have both negative and positive effects on photosynthesis. Nanoparticles have the potential to influence signaling molecules and pathways in photosynthetic organisms. However, they can also cause cell membrane leakage and membrane damage, leading to mutagenic DNA lesions and oxidative stress.

Pattern recognition receptors (PRRs) can recognize microbial infections and host cell-linked DAMPs. Membrane-bound or cytoplasm-bound PRRs generate cytokines and defend the host. By altering germline-encoded pathogen recognition receptors, nanoparticles may inhibit pathogen infection. These receptors detect pathogen-associated molecular patterns (PAMPs) and are the body's first defense against infections. PRR-targeted pathogen infection treatments are not authorized. The connections between nanoparticles, chloroplasts, signaling molecules, and pathways and the possible deleterious consequences of NPs on plant development and metabolism need more study.

Nanoparticles have been found to regulate gene expression for biotic stress in plants by modulating gene expression. PR genes, which encode antimicrobial proteins, are essential for preventing the proliferation of harmful microorganisms. Nanoparticles can stimulate the expression of PR genes, leading to increased defensive responses against pathogens in plants. Silver and titanium nanoparticles have been shown to stimulate the overexpression of PR genes in plants, enhancing the synthesis of PR proteins and reducing disease severity. The precise mechanisms by which nanoparticles regulate gene expression in plants are still being investigated, but it is believed that they interact with plant cell receptors and signaling molecules, triggering a cascade of molecular events that ultimately result in gene expression changes. Reactive oxygen species (ROS) produced by nanoparticles inside plant cells may serve as signaling molecules to turn on genes involved in defense.

Nanoparticles have become promising tools in plant science due to their ability to modulate gene expression and influence plant defense responses. Their interaction with plant cells at the molecular level, potentially involving specific genes and receptors, is crucial for harnessing their full potential in controlling and managing plant diseases. Receptor-mediated interactions between nanoparticles and plant hormones have been observed, with silver nanoparticles (AgNPs), titanium dioxide nanoparticles (TiO_2 NPs), and silicon nanoparticles (SiNPs) potentially influencing plant growth and defense responses. Bio-receptor-functionalized nanoparticles, such as antibody-functionalized gold nanoparticles, aptamer-functionalized magnetic nanoparticles, protein-functionalized silver nanoparticles, and enzyme-functionalized silica nanoparticles, have been shown to effectively detect and kill bacteria. However, further research is needed to fully understand the mechanisms underlying nanoparticle-mediated gene expression modulation and its impact on plant defense mechanisms. Nanocides are effective in controlling plant-fungal infections by selectively activating their pathogen-suppressing properties. These nanozymes, made from metal oxides, carbon-based nanomaterials, and metals like gold, silver, platinum, palladium, rhodium, ruthenium, and iridium, have shown a 99.99% elimination rate upon contact.

Molecular docking is a computer method that predicts the binding interactions between nanomaterials and pathogens, allowing researchers to develop and find new insecticides. This method helps estimate the binding energy, free energy, and stability of insecticide complexes, proving the viability of any insecticidal action. Molecular docking has transformed the study of interactions between tiny chemicals and protein targets, allowing entomologists to demonstrate the harmful impact mechanism of insecticides at the molecular level. Nanomaterials have emerged as a promising option for controlling plant pests due to their novel characteristics and potential therapeutic uses. Understanding the molecular connections between nanomaterials and diseases is crucial for developing effective treatment methods. Molecular docking is essential for studying nanomaterials' interactions with plant pests' essential enzymes and proteins, revealing unique binding locations, and revealing the therapeutic potential of nanomaterials. Docking studies help design nanomaterials with increased affinity and specificity by docking them onto pathogen biomolecular targets. The mode of action of nanomaterials can be deduced from their binding poses and interaction patterns inside pathogen biomolecular targets. This helps in determining the mechanisms through which nanomaterials interfere with pathogen activity, enzymes, and cellular functions. Experimental validation of molecular docking results is common practice to verify predicted interactions and assess therapeutic potential. Molecular docking is useful for learning about the mode of action of insecticides, such as synthetic chemical compounds, plant extracts, microbial insecticides, and nanoparticles.

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