

Chapter 12

Use of Metallic Nanoparticles and Nanoformulations as Nanofungicides for Sustainable Disease Management in Plants



Imran Ul Haq and Siddra Ijaz

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I. Ul Haq (✉)

Department of Plant Pathology, Faculty of Agriculture, University of Agriculture, Faisalabad, Pakistan

S. Ijaz

Centre of Agricultural Biochemistry and Biotechnology (CABB), Faculty of Agriculture, University of Agriculture, Faisalabad, Pakistan

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12.1 Introduction

Nanotechnology is gaining much popularity due to its broad applications in agriculture (Jha et al. 2011; Chowdappa and Gowda 2013). Nanobiotechnology has a key status among other disease management strategies for early disease detection, putative fungicides (nanofungicides), and efficient systems for delivery of fungicides to plants (Rai and Ingle 2012; Satalkar et al. 2016; Mishra and Singh 2015). This is a revolutionary science, which has turned the green revolution into a green nanobior-evolution (Khan and Rizvi 2014). This is based on two aspects: synthesis and application of nanosized materials.

Application of this technology provides real-time monitoring of crop plants for precision farming, which leads to maximum output while requiring minimum input (Scott and Chen 2003; Sharma et al. 2010). Extensive application of pesticides and fungicides results in ecotoxicity, as well as evolution of new phytopathogens that are resistant to them (Dzhavakhiya et al. 2012; Alghuthaymi et al. 2015; Chen et al. 2015). Hence, there is a great need to find alternative ways to manage plant pathogens and microbes (Vu et al. 2015).

There is an urgent global need for the use of eco-friendly approaches that generate less hazardous waste. This scenario has sensitized scientists to adopt and develop “green synthesis/biosynthesis” methods and strategies. Biosynthesis of nanoparticles (NPs) as a green synthesis approach helps to reduce the production of harmful waste by using nontoxic and environmentally safe resources. Therefore, in green chemistry, use of biological agents (plants and microbes) for synthesis of nanoparticles is a novel concept that opens up new avenues for exploring a broad array of biological species (Sharma et al. 2010; Chowdappa et al. 2013; Prasad et al. 2018a).

Plant extract-based bioreduction reactions for nanoparticle formation involve different biomolecules (phytochemicals) such as proteins, polysaccharides, tannins, organic compounds, plant resins, and pigments, as well as redox enzymes (Huang and Yang 2004; Nam et al. 2008; Wei and Qian 2008; Sanghi and Verma 2009; Prasad 2014). Microbe-assisted synthesis of nanoparticles is the branch of green chemistry that bridges microbial biotechnology and nanotechnology. For nanoparticle synthesis, microbes accumulate intracellular and extracellular inorganic compounds and execute bioreduction of different metals such as silver, platinum, copper, gold, and silica (Meyer 2008; Rai et al. 2009; Prasad et al. 2016).

Nanoparticles play pivotal roles in providing better food by promoting sustainable agriculture (Gruère 2012). A diverse range of microbes damage crop plants, ornamental plants, and trees, leading to major losses in the economy of a country (Tourmas 2005). Some of them exert hazardous effects even on the health of human beings. The world’s food demand is expected to double in the next half century, and that poses a big challenge for food production to feed the people (Tilman et al. 2002).

As has been documented, only a minute quantity of fungicides and pesticides (<0.1%) reaches the target site of action, because of depletion during application, photodegradation, and off-target deposition; these losses ultimately have effects on the ecosystem and increase the costs of production (Castro et al. 2013). When a

fungicide/pesticide/bactericide agrochemical is applied to target pathogens, they may change their population into a new species or strain by genome recombination; thereby, a new species evolves that has resistance against that particular fungicide or pesticide (Schaller et al. 2004; Hettiarachchi and Wickramarachchi 2011; Chowdappa et al. 2013).

In the current scenario, use of nanoparticles in disease management, disease detection, and precise and controlled distribution of functional molecules (Scott and Chen 2003; Johnston 2010) is the best way to tackle this problem. These nanosized particles target specific issues in agriculture regarding crop protection (disease management) and improvement (Ghormade et al. 2011). The characteristic of a high surface-to-volume ratio makes nanoparticles more reactive and biochemically active (Dubchak et al. 2010). They bind to the cell walls of pathogens, resulting in deformation of cell membranes due to high-energy transfer, which leads to the death of the pathogen (Schaller et al. 2004).

These nanoparticles and nanoparticle-based formulations mediate a strong nanoscale system, which provides entrapment and encapsulation of agrochemicals for slow and targeted delivery of their active compounds and to reduce agrochemical runoff into the environment (Chen and Yada 2011; Gruère 2012). Thereby, this emerging science may be the key player for sustainable agriculture globally. This chapter considers the prospects for this putative field and comprehensively discusses the importance, synthesis, and characteristics of nanoparticles (particularly metallic nanoparticles), as well as their role as nanofungicides for sustainable disease management in plants.

12.2 Nanoparticles and Their Synthesis

Nanoparticles are very tiny in size in comparison with bacterial and viral cells (Wang et al. 2011). These particles may be rod shaped, spherical, polyhedral, etc. (Dubchak et al. 2010; Wang et al. 2011), and possess a high surface area-to-volume ratio (Satalkar et al. 2016). Nanoparticles show differential actions based on their size and thereby exhibit new aspects that differ from the characteristics of their bulk form. For example, silver nanoparticles possess antimicrobial action, while their bulk form does not (Sofi et al. 2012). Nanoparticles are also known for controlling genotoxicity, oxidative stress, and apoptosis responses (Kuppusamy et al. 2014).

Different techniques have been established and employed for synthesis of nanomaterials. Thus, nanoparticle synthesis methods are categorized into two broad groups (Fig. 12.2):

1. Top-down approaches
2. Bottom-up approaches

In top-down approaches, nanoparticles are prepared from massive and bulk materials by cutting them into nanosized materials, whereas in the case of bottom-up approaches, atoms are built into nanoparticles (Mazhar et al. 2017), as shown in Fig. 12.1.

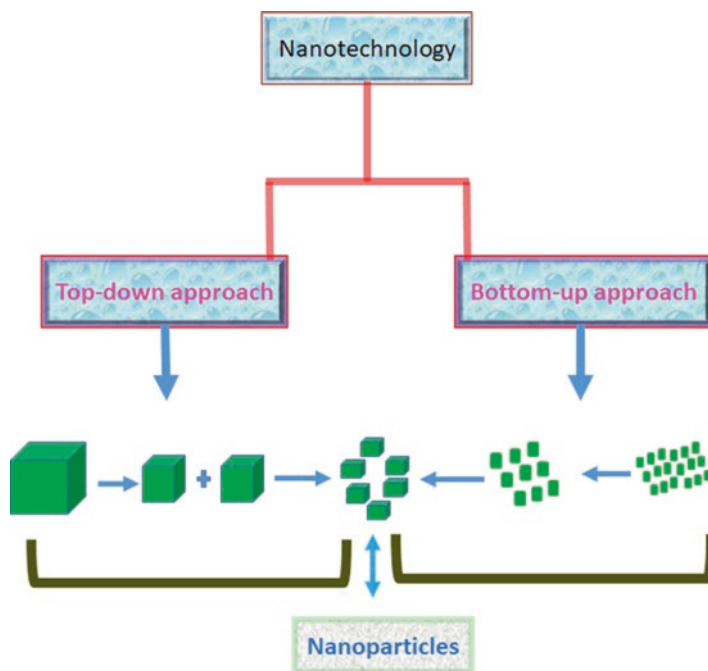


Fig. 12.1 Top-down and bottom-up approaches. Top-down approaches are based on reduction of the size of massive entities to nanosized materials, whereas bottom-up approaches are based on aggregation and build-up of atomic-state entities into nanomaterials

The different methods used for nanoparticles synthesis (such as biological, chemical, and physical methods, as listed in Table 12.1) affect their properties and efficiency (Narayanan and Sakthivel 2008; Rai and Yadav 2013). However, chemical and physical methods of nanoparticle synthesis are not cost effective and even require lethal and toxic compounds. It is a well-established fact that these methods have deleterious impacts on human or environment health through harmful radiation and the presence of synthetic reductants in concentrated forms and stabilizing agents (Pileni 1997; Joerger et al. 2000; Panigrahi et al. 2004; Oliveira et al. 2005; Gan et al. 2012). Conversely, biological methods based on plants and microbes have greater efficacy, are more cost effective and eco-friendly (Kumar et al. 2012; Bonde et al. 2012), and involve only a one-step bioreduction process (Sathishkumar et al. 2009; Iravani 2011), as shown in Fig. 12.2.

Plant secondary metabolites (phytochemicals) and microbial enzymes are utilized extensively in nanoparticle formulations because of their reducing actions (Bawaskar et al. 2010; Dar et al. 2013). The major loopholes of biogenic approaches are that it is hard to attain monodispersity and there is no control over the shape and size of the nanoparticles (Li et al. 2007; Nayak et al. 2011). However, with adjustment and optimization of the reaction medium and the metal concentration, the biosynthesis reaction may be controlled to influence the size and shape of the nanoparticles (Chandran et al. 2006; Shameli et al. 2012).

Table 12.1 Chemical, physical, and biogenic methods used for synthesis of nanoparticles

Chemical methods	Physical methods	Biological methods
Colloidal method	Electrochemical method	Plant extract-based synthesis
Chemical reduction method	Microwave method	Bacterial system-based synthesis
Sonochemical method	Solvothermal decomposition	Fungal system-based synthesis
Sol-gel method	Laser ablation	Microalgae system-based synthesis
Chemical solution deposition	Plasma arcing	
Chemical vapor deposition	Ball milling	
Catalytic route	Lithographic method	
Hydrolysis	Sputter deposition	
Langmuir-Blodgett method	Layer-by-layer growth	
Electrodeposition	Pulsed laser desorption	
Soft chemical method	Spray pyrolysis	
Wet chemical method	Molecular beam epitaxy	
Coprecipitation method	Ultra thin film	
	Diffusion flame-based synthesis	

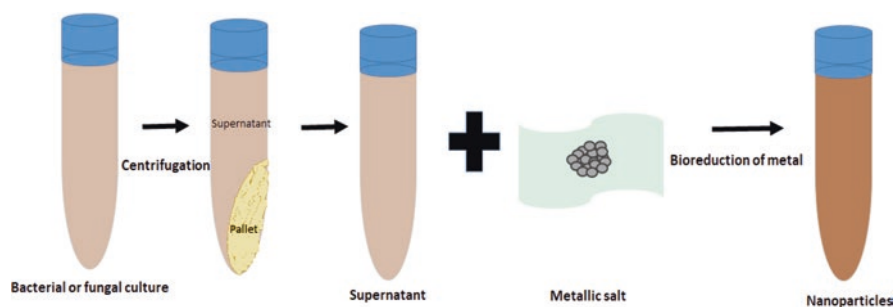


Fig. 12.2 Bioreduction process of metallic nanoparticle synthesis. This biogenic method of nanoparticle formation involves either a plant extract, a bacterial culture, or a fungal culture as a biological medium, which provides extracellular biological compounds for reduction of metals to metallic nanoparticles

In plant-assisted nanoparticle synthesis, plant extracts are used, comprising various biomolecules such as saponins, flavonoids, alkaloids, phenolic acids, and terpenoids. These secondary metabolites mediate the redox reaction and perform the reduction of the metals to nanoparticles (Aromal and Philip 2012; Prasad 2014; Prasad et al. 2018a).

In mycosynthesis of nanoparticles, the potential of fungi (especially filamentous fungi) is exploited because of their rapid growth on available substrates and metabolite production. Fungal-based extracellular synthesis of nanoparticles includes three mechanisms: (1) use of nitrate reductase action, (2) use of electron shuttle quinones, and (3) use of both of them (Sastry et al. 2010; Dhillon et al. 2012). Polysaccharides in the fungal cell wall are the main players in metal ion reduction (Sastry et al. 2003).

At the first step of the bioreduction process, metal ions are trapped and an interface is established between the metal ions and the cell surface of the fungus, which could be due to the electrostatic interaction among functional groups of enzymes (in the mycelial cell wall) that possess a positive charge. The next step involves enzyme-mediated reduction of metal ions, which leads to synthesis of nanoparticles (Meyer 2008; Dhillon et al. 2012; Prasad 2016, 2017; Prasad et al. 2018b).

12.3 Structure and Physicochemical Properties of Nanoparticles

Nanoparticles are particulate materials with dimensions measuring <100 nm (Laurent et al. 2010; Tiwari et al. 2012). They have attracted massive interest in multidisciplinary fields because of their exceptional attributes. The size of nanoparticles is the key factor that influences their chemical and physical attributes (Khan et al. 2017a, b). These nanomaterials exhibit sporadic biological, chemical, and physical properties that are entirely distinct and diverse from those of their bulk forms (Li et al. 2001). Variations in the physical characteristics of nanoparticles, such as their size and shape, lead to changes in their other physicochemical attributes (Dreaden et al. 2012; Barrak et al. 2016).

Physicochemical properties (e.g., chemical reactivity, mechanical strength, optical properties, and a large surface area) impart uniqueness to nanoparticles and make them suitable for wide applications (Wan et al. 2009; Gupta et al. 2013). On the basis of their physical and chemical nature, nanoparticles are categorized into different classes: (1) carbon-based nanoparticles, (2) metallic nanoparticles, (3) semiconductor nanoparticles, (4) ceramic nanoparticles, (5) polymer nanoparticles, and (6) lipid-based nanoparticles.

Nanoparticles are small particles but not simple ones. They comprise three discrete layers: a surface layer, a shell layer, and a core region (Shin et al. 2016); however, the core region is preferentially referred to as the nanoparticle itself (Khan et al. 2017a, b). The structural characterization of a substance is of prime importance in exploration of its composition and bonding nature (Ullah et al. 2017). Different techniques—such as x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), zeta sizing, infrared spectroscopy (IR), x-ray photoelectron spectroscopy (XPS), and energy-dispersive x-ray (EDX)—are employed to reveal the structural characteristics of nanoparticles (Ingham 2015).

Identification of single and multiphase nanoparticles, as well as their crystallinity, is achieved using an XRD approach (Ingham 2015; Ullah et al. 2017). SEM and TEM provide insights into and estimations of the size of nanoparticles. Estimation of the elemental composition of nanoparticles is done using EDX, because they are constituted from elements that emit characteristic energy x-rays. The intensity of a specific x-ray is in direct proportion to an explicit element concentration in a nanoparticle (Avasare et al. 2015). The XPS technique is widely considered the most sensitive approach to determine the elemental ratio and the nature of the bonds between elements in nanoparticles (Mansha et al. 2016).

12.4 Metallic Nanoparticles

Metals have been used to cure different diseases in plants, animals, and human beings since ancient times. Metallic nanoparticles with remarkable physicochemical attributes—such as nanoscale size, a high surface-to-volume ratio, structural stability, and target affinity—are used as antimicrobial agents and as the best alternative to synthetic fungicides (Kumar et al. 2010; Aziz et al. 2014, 2015, 2016). Bioreduction of metals to stable metallic nanoparticles through a green route is eco-friendly and safe (Kumar and Yadav 2009). As mentioned earlier, microbes and plants are attractive candidates for this green nanotechnology because of their nontoxic and cost-effective attributes (Prasad et al. 2016, 2018a). These metal-based nanoparticles have been shown to be effective weapons against phytopathogens; thus they will supersede synthetic fungicides, pesticides, and other agrochemicals, as a better option (Jo et al. 2009; Medici et al. 2015; Ismail et al. 2017; Gupta et al. 2018; Abd-Elsalam and Prasad 2018).

Several plant species have been designated as hyperaccumulators of metals. They accumulate metals in high concentrations and then assimilate them as nanoparticles (Dubey et al. 2009). Plant-based reduction of metals to nanoparticles involves phytochemicals (aldehydes, amides, carboxylic acids, flavonoids, ketones, terpenoids, quinones, etc.) (Bali et al. 2006; Ali et al. 2011). Besides plant-assisted synthesis, microbes (fungi and bacteria) have also emerged as suitable eco-friendly candidates for nanoparticle synthesis (Mandal et al. 2006; Ingle et al. 2009; Golinska et al. 2014; Tiwari et al. 2014; Prasad et al. 2016; Abdel-Aziz et al. 2018). Among the commonly used nanoparticles are silver-, gold-, silica-, copper-, and zinc-based nanoparticles.

12.4.1 Silver Nanoparticles

Silver nanoparticles possess antimicrobial properties in their ionic form, as well as in their nanosized form. Silver exhibits manifold inhibitory modes against microorganisms such as plant bacterial and fungal pathogens (Clement and Jarrett 1994; Kim et al. 2006; Wei et al. 2009). It has been shown in different *in vitro* and *in planta* assays that silver (in both its ionic and nanosized forms) inhibits colony formation by affecting spore and germ tube viability, and reduces disease progression (Kim et al. 2006; Gul et al. 2014). The reduction of silver nitrate to silver nanoparticles is due to the involvement of different metabolites and proteins in leaf tissues. A leaf extract provides a medium to synthesize and stabilize nanoparticles by acting as a reducing and capping agent (Singh et al. 2010; Jha and Prasad 2010). Silver nanoparticles have demonstrated highly significant inhibition of fungal phytopathogens in disease outbreaks under field conditions (Aguilar-Mendez et al. 2011; Gupta et al. 2018).

12.4.2 Silica Nanoparticles

Silica nanoparticles strengthen plants by enhancing their resistance against diseases and stimulating their physiological mechanisms (Carver et al. 1998; Brecht et al. 2004).

12.4.3 Copper Nanoparticles

Copper nanoparticles act as fungicides by generating highly reactive hydroxyl radicals, which may damage cellular materials (DNA, proteins, lipids, and other biomolecules) in fungal pathogens, leading to their death (EstebanTejeda et al. 2009; Brunel et al. 2013). Use of copper-based nanoparticles has been shown to be an effective control measure against bacterial blight in rice and leaf spot in mung bean (Gogoi et al. 2009).

12.4.4 Zinc Nanoparticles

Upon application as nanofungicides, zinc nanoparticles produce hydroxyl and superoxide radicals, which cause deformity of fungal cell walls and result in cellular death due to high-energy transfer (Patra et al. 2012). These nanoparticles interrupt the electron transfer chain and thereby disrupt related biological processes (Xia et al. 2008). Zinc nanoparticles deform fungal hyphae, impede conidiophores and conidial development, and eventually cause the death of fungal hyphae (Borkow and Gabbay 2005).

12.4.5 Gold Nanoparticles

The toxic effects of gold nanoparticles on *Salmonella* spp. were determined by Wang et al. (2011), who documented that they exhibited more toxic effects than gold in its bulk form.

12.4.6 Iron Nanoparticles

Iron nanoparticles establish a direct interface with fungal cell surfaces as a result of electrostatic interactions, and affect membrane permeability (Corredor et al. 2009; Parveen et al. 2018). When entering fungal cells, these nanoparticles generate oxidative stress by producing high levels of reactive oxygen species (ROS). Thereby, these nanoparticles inhibit growth, resulting in cell death (Yanping et al. 2011).

Because of their ability to rapidly permeate through the microbial cell membrane, metallic nanoparticles disorganize the cell's polymeric subunits, interrupt its protein synthesis mechanism, and thereby arrest the cell cycle (Sondi and Salopek-Sondi 2004; Kasthuri et al. 2009). Moreover, a pit appears on the cell wall, resulting in cell lysis. Coagulation of metallic nanoparticles on the microbial cell membrane results in increased permeability of the plasma membrane, which causes cellular content leakage (Sondi and Salopek-Sondi 2004; Panáček et al. 2006). The presence of nanoparticles inside microorganisms has been noted in different reports,

revealing their interactions with sulfur- and phosphorus-containing compounds (Panáček et al. 2006; Raffi et al. 2008; Kasthuri et al. 2009).

Biosynthesized metallic nanoparticles are considered to have a stronger fungicidal mechanism than synthetic fungicides. Metallic nanoparticles damage fungal membranes and intercellular modules, and destroy cell functioning. As a result of nanoparticle activity, both fungal spore formation and fungal growth are restricted (Gardea-Torresdey et al. 2002; Marambio-Jones and Hoek 2010). The consensus on the antifungal mechanism of nanoparticles is that when a fungal cell takes up these metallic nanoparticles, upon entry they interrupt the process of adenosine triphosphate (ATP) synthesis in the cell and halt its DNA replication mechanism. Because of this, excess ROS are generated, disorganizing the integrity of the cellular membrane and causing development of pits on the surface of the membrane, which leads to cellular death (Logeswari et al. 2012; Prabhu and Poulouse 2012; Reidy et al. 2013), as shown in Fig. 12.3.

As far as the effect of nanoparticles on bacterial cells is concerned, it is believed that a bacterial cell uses an enzyme for oxygen metabolism, which is required to sustain its life. Silver nanoparticles cripple this enzyme and inhibit oxygen metabolism, resulting in suffocation and ultimately leading to the death of the bacterium (Alvarez-Puebla et al. 2004; Raffi et al. 2008). The mechanism of the antibacterial

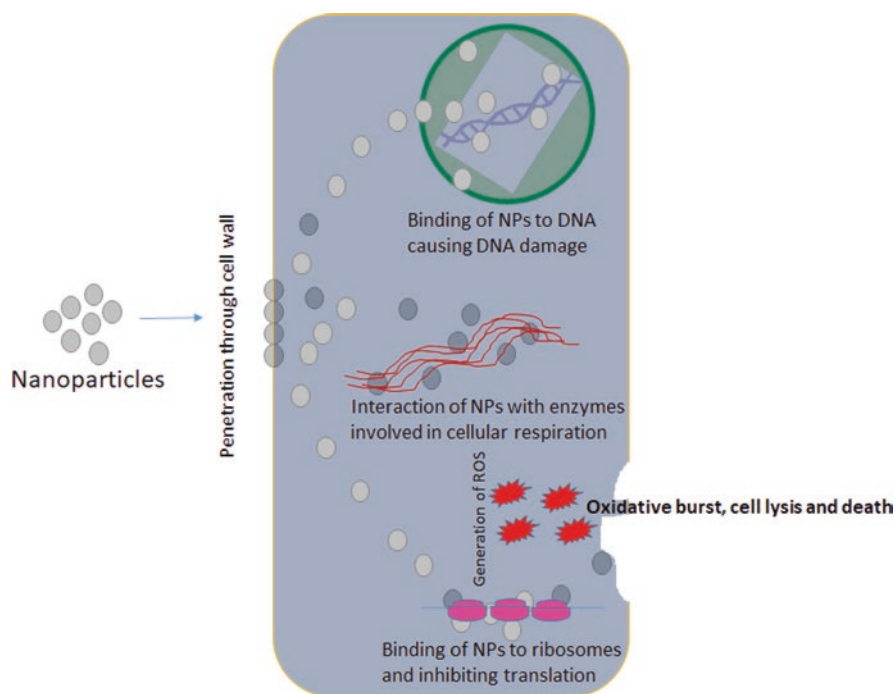


Fig. 12.3 Antifungal effects of nanoparticles (NPs) on a fungal cell and its functioning through interaction with the cellular machinery, resulting in cellular pathway arrest and generation of reactive oxygen species (ROS), which leads to an oxidative burst and fungal death

effect of metallic nanoparticles is believed to be their interaction with protein functional groups, particularly thiol groups of cysteine residues.

As a result of the oxidation reaction, a disulfide bond is established between thiol groups, which results in protein folding and structural alteration. Thus, a change in protein conformation results in inhibition of enzyme activity and, ultimately, inactivation of the bacterial cell (Liau et al. 1997; Schierholz et al. 1998). Each metal has different target sites in a cell; for example, Na⁺-translocating reduced nicotinamide adenine dinucleotide (NADH) ubiquinone oxidoreductase (an enzyme in the bacterial respiratory chain) is the target site of silver. Thus, interaction of this enzyme with silver results in inhibition of the enzyme NADH dehydrogenase (Gupta et al. 1998; Holt and Bard 2005; Prasad et al. 2016).

12.5 Use of Metallic Nanoparticles as Nanofungicides for Sustainable Disease Management in Plants

Fungi are responsible for about 70% of diseases in crop plants such as cereals, fiber crops, pulses, and fruits (Agrios 2005). Pre- and postharvest losses due to fungal diseases have been reported to exceed €200 billion, and more than US\$600 million is spent on fungicides annually in the USA (González-Fernández et al. 2010). Therefore, for sustainable disease management, effective and well-organized crop protection strategies are required because each stage of the fungus life cycle differs (Dhekney et al. 2007) depending upon the type of fungal pathogen.

For this purpose, different chemical controls (fungicides) and biological controls have been devised as plant disease management strategies. In general, chemical control is considered more effective for controlling fungal disease. Nevertheless, application of fungicides has some nonspecific impacts and causes ecological disturbance by destroying beneficial microbial communities that inhabit the rhizosphere of the crop plants afflicted with the fungal pathogen (Zaki et al. 1998; Manczinger et al. 2002). Injudicious use of fungicides results in fungicidal resistance in existing pathogens and creation of new physiological races and pathotypes, and even more virulent strains of fungal pathogens, which are resistant to fungicides.

In the case of agrochemical applications, control of fungal diseases is mostly influenced by fungicidal resistance in fungal pathogens. Fungicidal resistance develops by complex interactions of various factors such as the mode of action of the fungicide, the pattern of fungicide applications, the biology of the fungal pathogens, and the cropping system. Proper understanding of the biological philosophy of fungicide resistance (through unraveling of two major aspects—namely, how does fungicide resistance develop in pathogens, and how can it be managed?) is a prerequisite for sustainable disease management using fungicides. However, finding the exact answers to these questions is still difficult for scientists because of the multifactorial complexity of the mechanisms involved. Hence, they have begun to attempt alternative strategies and have now started to use nanomaterials to manage fungal diseases in plants (Kim et al. 2012).

After considering loopholes in chemical control, the scientific community has tried to open up new avenues in the form of nanoparticle synthesis and applications for plant disease management. Different protocols and practices have been implemented to evaluate and determine the efficacy of nanoparticles and to find the best alternatives to use of agrochemicals against different microbial pathogens, especially fungi (Jo et al. 2009; Rai et al. 2009).

Metallic nanoparticles are now becoming popular and accepted alternatives to agrochemicals. They have potential to eliminate unwanted and lethal microbes from soils, from plants, and even from hydroponic systems (Park et al. 2006; Sharma et al. 2012). Therefore, to determine the status and impact of metallic nanoparticles for disease management in plants, their effects can be addressed in two ways (Khan and Rizvi 2014): (1) direct application of nanoparticles to phytopathogens, and (2) use of nanoparticles in formulating fungicides. In both ways, nanoparticles are applied as nanofungicides.

These nanoparticles are applied as foliar sprays to kill pathogens that cause different plant diseases. In addition, the nanoparticles may even stimulate plant growth (Agrawal and Rathore 2014). Lower concentrations of these nanoparticles are recommended for effective control of plant diseases (Nel et al. 2003; Park et al. 2006). Nanoparticle administration is also effective for those microbes that possess less or even no sensitivity to antimicrobial agents because of poor penetration by the antimicrobial compounds through the cell membrane (Samuel and Guggenbichler 2004). Microscopic studies have revealed that metallic nanoparticles damage cell walls of fungal hyphae, resulting in hyphal plasmolysis (Min et al. 2009).

Different theories have been put forward by different scientists regarding the mechanism of action of nanoparticles. Those most widely accepted are the following (Zeng et al. 2008; Prabhu and Poulouse 2012; Lemire et al. 2013):

1. They bind to sulfur groups of proteins, prevent their functioning in the cellular membrane, and thereby affect membrane permeability.
2. They have a genotoxic effect and cause DNA damage.
3. They disrupt protein oxidation and the electron transport mechanism in the cell.
4. They generate ROS, which mediate cellular damage.
5. They hinder proper uptake of nutrients.

These mechanisms are interlinked, which illustrates the multitargeted action of nanoparticles in effectively combating phytopathogens (Alghuthaymi et al. 2015; Abd-Elsalam and Prasad 2018).

As discussed earlier in this chapter, bioreduction of different metals (such as silver, gold, zinc, copper, and iron) alone, or in combinations, has been evaluated in metallic nanoparticle synthesis. Moreover, different *in vitro* and *in vivo* assays have been documented in the literature regarding investigations into the antimicrobial effects of these metallic nanoparticles against various plant pathogens. Among them, silver nanoparticles have been shown to be more toxic to pathogens, and that is why they are generally known as nanoweapons (Alghuthaymi et al. 2015; Mishra and Singh 2015).

Different researchers around the globe have tested the toxicity of nanoparticles to pathogens and their safety for nontargeted organisms (such as plants, animals, human beings, and even other beneficial microbes present in the microflora of candidate plants) at low concentrations. They have suggested that application of nanoparticles for controlling and managing plant diseases is a relatively safer approach than use of synthetic agrochemicals (Thomas and McCubbin 2003; Zeng et al. 2008).

The fungicidal effect of metallic nanoparticles on *Raffaelea* species (a fungal pathogen causing oak wilt) was evaluated in vitro by Woo et al. (2009). They documented fungal growth inhibition, damaged hyphae, and restricted conidial germination. Likewise, their antifungal effect was tested against *Magnaporthe grisea* and *Bipolaris sorokiniana* (which cause cereal diseases) by Jo et al. (2009), who observed that the progress and severity of disease were inhibited in both cases.

Among metallic nanoparticles, silver nanoparticles are most commonly and widely used in biosystems. The antimicrobial effect of silver nanoparticles is due to their oligodynamic action, which inactivates enzymes that are key players in metabolic pathways in microorganisms (Thomas and McCubbin 2003). Silver nanoparticles are thus detrimental to microbial pathogens and cause cellular damage and dysfunction of the fungal ion efflux transport system (Morones et al. 2005). The disruption of ion efflux causes silver ion accumulation and thereby interrupts cellular processes such as respiration and metabolism. Upon entry into the cell, nanosilver rapidly produces ROS by reacting with oxygen molecules and damages biomolecules such as DNA, RNA, protein, lipids, and polysaccharides (Hwang et al. 2008; Aziz et al. 2016, 2019). Thus, DNA replication is halted, ribosomal protein is inactivated, other proteins and enzymes involved in ATP synthesis are degraded, and dysfunction of cell membrane-bounded enzymes takes place (Thomas and McCubbin 2003; Kim et al. 2012). Hence, silver nanoparticles are widely accepted as a nanofungicide and considered a potential agrochemical replacement. Moreover, numerous patents have been filed for use of silver nanoparticles in the treatment of plant diseases (Sharon et al. 2010).

The effectiveness of nanosilver depends on its physical characteristics (i.e., the size and shape of the particles). The efficacy decreases with an increase in the particle size (Cioffi et al. 2004; Duhan et al. 2017). The “-cidal” (i.e., lethal) effect of the nanoparticles is also influenced by their shape. Nanoparticles of a truncated triangular shaped exhibit more -cidal effects than rod-shaped and spherical ones (Cioffi et al. 2004; Kim et al. 2012).

The fungicidal properties of silver nanoparticles have also been evaluated against *Sclerotinia minor*, *Sclerotinia sclerotiorum*, and *Rhizoctonia solani*. Min et al. (2009) reported strong inhibition in germination of sclerotia, as well as inhibition of fungal growth. In the case of powdery mildew in cucurbits and cucumber, silver nanoparticles exhibited inhibitory and phytotoxic effects on conidial growth, as well as on fungal hyphae. Moreover, a good disease prognosis was observed upon application of nanoparticles in field conditions. Likewise, application of silver nanoparticles was shown to have a strong antifungal effect on the fungal pathogen of powdery mildew in roses (Sharon et al. 2010).

A nanocomposite constituted from pullulan and silver nanoparticles was tested by Pinto et al. (2013) against a phytopathogen, *Aspergillus niger*, and they reported

sporulation inhibition and disruption of spore cells of this fungus. Chowdappa et al. (2013) applied a chitosan–nanosilver composite against *Colletotrichum gloeosporioides* and observed inhibited germination of conidia and conidiophores.

Considering the strong antimicrobial action of nanosilver, Park et al. (2006) created a nanosilica–nanosilver composite for evaluation as a nanofungicide under both greenhouse and field conditions. When administered in a dose of 10 parts per million (ppm), it showed high efficacy and effectivity against powdery mildew in pumpkin and inhibited 100% of fungal growth; within 3 days after its application, the pathogen had disappeared from the infected plant parts and thereafter the treated plants were healthy. In other studies, silica–silver nanocomposites were found to achieve 100% control of powdery mildew in cucurbits under field conditions (Brecht et al. 2003; Banik and Sharma 2011; Patel et al. 2014).

Sulfur nanoparticles have shown efficacy in preventing early blight and wilt diseases in tomato (caused by *Fusarium solani*), as well as apple scab (caused by *Venturia inaequalis*) (Rao and Paria 2013; Boxi and Paria 2015). The fungicidal action of these nanoparticles is due to their deposition on the cell wall of the fungus and its subsequent lysis (Jampflek and Král'ová 2015). Silver nanoparticles of cylindrical and spherical shapes have been shown to significantly reduce the total lipid content of fungal cells upon their application to *Aspergillus niger* isolates. The expression of desaturase enzymes was downregulated, saturated fatty acid was accumulated in high levels, and lipid layer depletion was also observed with silver nanoparticle–mediated fungistasis. These nanoparticles have also been shown to significantly reduce the phospholipid content of *Fusarium oxysporum* cells (Choudhury et al. 2011, 2012; Chhipa 2017). Similarly, nanosized copper has been reported to exhibit a strong antifungal action against bacterial blight in pomegranate (Hezave and Esmaeilzadeh 2010).

12.6 Use of Nanoformulations as Nanofungicides for Sustainable Disease Management in Plants

Agricultural crops all over the world are affected by fungal diseases, which pose a considerable threat to their yield. A reduction in crop yield has a significant impact on the economy of a country. Different fungicides of narrow and broad spectra are prepared in order to combat fungal diseases in plants. However, this control measure is not widely and adequately effective. Therefore, there is a trend toward use of nanofungicides that consist of nanoparticles or contain an active nanoformulation compound (Jampflek and Král'ová 2015; Bhattacharyya et al. 2016). Broad application of fungicides causes environmental pollution, biodiversity loss, and evolution of new pathogens (Rai et al. 2015). To resolve these issues, nanoformulations are being applied, which more effectively facilitate site specificity for targeted and controlled delivery of fungicidal compounds, avoiding collateral damage (Nikhil and Bharat 2004).

Extremely small particle size and a large surface area are the features of core importance for permeation through cellular membranes and for carriage and trans-

port of compounds. Generally, nanosystems comprise two core components: an active material and a nanocarrier. Nanocarriers facilitate transportation and site-specific distribution of the active ingredients of fungicides/pesticides by stabilizing them. In nanoformulations, nanoparticles are combined with active chemical compounds and with other organic and inorganic compounds, all of which must be of a nanometric size (Jampflek and Kráľová 2015).

Nanoformulations are prepared in order to enhance stability and effectivity but with lesser amounts of fungicidal compounds (Zachariah et al. 1995; Parham and Saeed 2014; Kumar et al. 2014). Therefore, these nanobased fungicidal formulations are smart delivery systems for progressive farmers, and they assist growers to minimize their use of fungicides (Sarlak et al. 2014; Shyla et al. 2014). Moreover, high reactivity of materials at the nanoscale (in comparison with their bulk counterparts) support use of lesser quantities of nanoformulations, with improved impacts on crop protection (Badami 2008; Debnath et al. 2011). Thus, use of nanoparticle-based nanoformulations promotes safer administration of fungicides at low doses (Kuzma and VerHage 2006) by decreasing their toxicity while increasing their efficiency (Mousavi and Rezaei 2011).

The rate of release of nanoparticles loaded with fungicides is influenced by environmental factors (Lauterwasser 2005). Nanofungicide formulations improve the solubility of active compounds and facilitate their gradual release at the target sites. Thereby, the bioavailability of agrochemicals with poor solubility in water is increased (Kah and Hofmann 2014).

Combination of nanoparticles of diverse metal types with fungicides increases their activity (Zielińska-Jurek et al. 2012; Lopes et al. 2013). Combination of silica nanoparticles with chlorfenapyr has been reported to double its pesticidal activity. Likewise, combination of these nanoparticles with calcium carbonate have also shown controlled and effective release of the -cidal component for a longer time span (Sonawane and Dongare 2006; Türk and Bolten 2010).

Application of nanoformulations prior to pathogen attacks and disease outbreaks is also very helpful, because of their slow release pattern. Their presence in the plant root zone at the initial developmental stages of crop growth strengthen and protect the plants from invasive pathogens, as well as keeping pathogen populations below the threshold level (Bhattacharyya et al. 2010; Castro et al. 2013; Khan et al. 2014). The presence of nanofungicides prior to fungal pathogen invasion of host plants is effective because of the greater persistence and slow release (of active compounds) by the nanoformulations, which enhance their effectiveness against pathogens (Khan et al. 2011). These attributes reduce the net amounts of fungicides required to control diseases (Khan and Jairajpuri 2012), as well as decreasing their concomitant environmental menace.

As discussed earlier in this chapter, nanofungicides are small structures that provide fungicidal properties and/or formulations with active ingredients of fungicides in a nanoform. The stability and gradual release of the active -cidal ingredients for longer periods make them eco-friendly in comparison with agrochemicals. Scientists have experimented with preparation of a variety of nanofungicides in different forms such as nanocapsules (nanoencapsulated formulations), metallic nanoparticles, metal oxide-based nanoparticles, nanospheres, nanogels, and nanoemulsions (NEs) (Yan

et al. 2005). They are all nanofungicides and delivery systems with a large surface area and increased target affinity, and have been shown to be effective in plant protection strategies (Lyons and Scrinis 2009; Bordes et al. 2009; Bergeson 2010). Nanomaterials exhibit various favorable properties—such as solubility, crystallinity, enhanced permeation, stability, stiffness, and biodegradability—that are required to formulate nanofungicides and/or nanopesticides (Yan et al. 2005; Bouwmeester et al. 2009).

12.6.1 Nanoemulsions

Use of nanoemulsions is a better approach for nanofungicides or nanofungicide delivery systems because of their small size, optical transparency, low viscosity, and greater kinetic stability (Tice 2001; Senturk et al. 2013; Bernardes et al. 2014). Nanoemulsions improve the solubility of active agents of agrochemicals and thereby enhance the bioavailability of the active ingredients (Xu et al. 2010). According to the literature, nanoemulsion preparation by dispersion into liquid phases enhances the solubility and distribution ability of fungicides many times. The characteristics of nanoemulsions—such as wettability, spreadability, and better mechanical stability—make them helpful for low volatilization and lesser degradation of active compounds (Guillette and Iguchi 2012; Mason et al. 2006; Anton et al. 2008).

A surfactant-based nanoemulsion of β -cypermethrin was developed by Wang et al. (2007), and nanoemulsions of neem oil and permethrin were made by Anjali et al. (2010, 2012). According to their reports, the droplet size affected the activity and effectiveness of the nanoemulsions (Jiang et al. 2012; Díaz-Blancas et al. 2016). Droplets of a nanoemulsion can be used to encapsulate active compounds of agrochemicals in a formulation with less degradation of the functional ingredients (McClements and Decker 2000).

12.6.2 Metallic Nanoparticles

Use of metallic nanoparticles as nanofungicides has been discussed comprehensively in this chapter. These metallic nanoparticles are also used as part of nanoformulations. Because of their toxic effects on pathogens, silver nanoparticles are used in nanoformulations (Sondi and Salopek-Sondi 2004; Retchkiman-Schabes et al. 2006). A mixture comprising silver nanoparticles with macromolecules that have an amphiphilic hyperbranched conformation was shown to be an effective surface coating with antimicrobial effects on a diverse range of pathogens (Aymonier et al. 2002; Gu et al. 2003; Ahmad et al. 2005; Lead and Wilkinson 2006; Gong et al. 2007). Silver nanoparticles in association with fluconazole (a triazole fungicide) showed significant antifungal activity against *Trichoderma* spp., *Phoma glomerata*, and *Candida albicans* (Gajbhiye et al. 2009). Silver nanoemulsions showed strong growth inhibition of *Sclerotium rolfsii* in mung bean, and this nanoemulsion was also reported to have a strong inhibitory action against *Magnaporthe grisea* and *Bipolaris sorokiniana* (Agrawal and Rathore 2014).

12.6.3 Nanogels

Nanogels of chitosan with copper and pheromone were evaluated against *Fusarium graminearum* and fruit pests, respectively, and showed increased antifungal activity due to their synergistic effects (Brunel et al. 2013; Bhagat et al. 2013).

12.6.4 Nanocapsules

Nanocapsules are a nanosystem in which the active ingredient of a fungicide is placed within the core, surrounded by a membrane. Nanoencapsulation has potential scope for use in nanofungicide formulations. Polymeric and solid lipid nanocapsules loaded with tebuconazole and carbendazim have been created for use as nanofungicides (Campos et al. 2015).

12.6.5 Nanospheres

Nanospheres (in a monolithic system) comprise irregular spherical nanoscale particles in which -cidal compounds or active agents of fungicides are dispersed and/or dissolved in polymeric matrices (Sotthivirat et al. 2007). Various polymers such as natural polymers (proteins and polysaccharides), synthetic polymers (polyamide, polyacrylamide, polystyrene, polyesters, etc.) and inorganic compounds (zoolites, silica, ceramics, glass beads, inorganic oxides, etc.) have been tested to explore their potential in nanofungicide formulations for crop protection (Shukla et al. 1992; Chuan et al. 2013).

These nanofungicides can be formulated in easy and cost-effective ways. In this section, some examples are mentioned. Size reduction of the active ingredients or functional compounds of existing fungicides to the nanoscale and subsequent nanoencapsulation have been used to develop different nanofungicides. Syngenta have made nanofungicide formulations containing nanoparticles—for example, Banner MAXX™ (which contains the active chemical compound propiconazole), Apron MAXX™ (in which the active ingredient is fludioxonil), and Primo MAXX™ (containing cyclopropyl, a derivative of cyclohexanone) (Gogoi et al. 2009; Abd-Elsalam 2012).

Other nanoproducts have also been launched; for example, Nano-5 has been developed for use against different phytopathogens, and Nano-Gro—a nanoproduct from Agro Nanotechnology Corp. (Miami, FL, USA)—has been certified as organic nanomaterial with no harmful impact. This nanofungicide has reported to be effective against *Magnaporthe grisea*, for eliminating rice blast disease (Gogoi et al. 2009).

12.7 Effects of Nanoparticles on Ecosystems: Challenges and Prospects

The application of nanomaterials has been gaining importance and popularity; thus, assessment of toxic effects of nanoparticles in ecosystems is indispensable for their downstream applications. As their chemical and physical features determine the property of nanoparticles, accurate assessments of their physicochemical properties are required to investigate toxic manifestations of each aspect of nanoparticles. Hence, it could be said that the toxicity of nanoparticles depends upon their physicochemical characteristics. Different studies have been conducted over a long period to assess the ecotoxicological impacts of nanoparticles, but large knowledge gaps still exist, particularly regarding nanoparticle-related biological concerns (Antisari et al. 2011; Banik and Sharma 2011; Alghuthaymi et al. 2015).

A reactive interface develops between nanoparticles and their surrounding environment because of their high surface-to-volume ratio (Orts-Gil et al. 2011). Because materials of identical chemistry may vary to a significant extent on the basis of their size (Murdock et al. 2008), these materials need to be critically characterized in different physiological contexts to estimate the correlation of their biological impacts with their colloidal characteristics. A multitude of vital characteristics of nanoparticles should be investigated for their proper characterization, such as their size, shape, surface area, functional groups, size distribution, crystal structure, porosity, chemical composition, and charge (Oberdörster et al. 2005).

According to different reports published in the literature, metallic nanoparticles generate stress in plants, which disturbs the equilibrium between generation of ROS and their removal. Because of this, ROS start to accumulate in plant cells and affect photosynthesis and other metabolic and biosynthetic mechanisms (Barazzouk et al. 2005; Bujak et al. 2011; Keller et al. 2013). Nanoparticles have been found to be phytotoxic by altering photosynthesis processes, the quantum yield, and other processes in plant cells (Peralta-Videa et al. 2011; Olejnik et al. 2013).

As discussed earlier in this chapter, nanoparticles have enormous applicability for plant disease management. However, their broad applications may be the major cause of their accumulation in the environment, increasing their lethal and toxic effects in ecosystems. It has been shown in different studies that excessive amounts of nanoparticles beyond a certain limit lead to negative effects on the environment. For example, different metallic oxides (ZnO and TiO₂) have displayed negative effects on wheat biomass, as well as its growth, and repressed the biological activities of different enzymes such as catalases, proteases, and peroxidases (Du et al. 2011).

The first report on soil-based toxicity of nanoparticles (nanotoxicity) to plants was published by Yang and Watts (2005). They reported that aluminum oxide (Al₂O₃) in conjugation with phenanthrene, and even alone, showed adverse effects on root elongation and germination in different crop plants such as maize, soybean, carrot, cucumber, and different brassica species (Lin and Xing 2007). Likewise, application of titanium dioxide (TiO₂) caused a reduction in water use efficiency in maize and altered the apoplastic pathway (Asli and Neumann 2009). Palladium

nanoparticle accumulation has been observed in barley leaves (Battke et al. 2008), and iron oxide (Fe_2O_3) nanoparticles have been shown to accumulate in pumpkin tissues (Zhu et al. 2008; Lin et al. 2009).

All of these reports in the literature suggest that application of nanoparticles has environmental consequences because the presence of nanoparticles in the soil may affect and disturb the microflora, and even plants themselves, by absorption through the soil. From plants, they may be transferred to animals and human beings who consume and uptake food from them; thereby, they may affect the entire food chain. Hence, there is a dire need to explore strategies to set and standardize optimal criteria for nanoparticle synthesis and applications, and for their impacts on ecosystems. Thus, there is a need for determination of physicochemical properties of nanoparticles that affect plant diseases by targeting specific pathogens without having adverse impacts on ecosystems. Despite to standardize physicochemical attributes of nanoparticles, only doses of them that are known to be safe should be administered, in order to avoid detrimental effects of them on food chain.

In the field of agriculture, for sustainable disease management, most patents that have been filed for nanoparticle-based pesticides involve nanosilver. The increase in the popularity of nanopesticides and nanofungicides necessitates some regulations regarding their usage. Hence, in 2008, the International Center for Technology Assessment (ICTA) submitted a petition to the US Environmental Protection Agency (EPA) to regulate use of silver nanoparticles in the creation of nanoproducts (such as nanopesticides) under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (Baier-Anderson 2009).

12.8 Conclusions

Nanotechnology is merely alteration of the size and shape of particles to the nanoscale. Their small size imparts extraordinary and miraculous properties to these particles. The exploitation of their potential has moved on from basic research to their use in applied technologies. Nanotechnology, in juxtaposition with biotechnology, has extended the capability of nanomaterials in crop plant production and protection at a meaningful level. For plant disease management, use of nanoparticles for controlled delivery of agrochemicals holds great promise in the field of agriculture. Nanoparticles, nanoemulsions, nanoencapsulations, and other nanobiotechnology approaches light the path for targeted delivery of fungicides, pesticides, etc., in an efficient and environmentally friendly manner to tackle epidemic diseases in plants. Advancements in nanobiotechnology by application of green chemistry for synthesis of nanoparticles, using living cells and plant extracts, offers assurances of ecoprotection. The myriad potential of nanoparticles includes not only their utility as vehicles for targeted delivery of antimicrobial compounds but also their innate antimicrobial effects and characteristics, both of which demonstrate their value for use as nanopesticides or nanofungicides against plant pathogens. The epitome of the nanobiotechnology for the synthesis of nanoparticles and nanoemulsions and their use as nanofungicides or nanopesticides revolves around the prospects of its applications for plant disease management.

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