



Engineered nanomaterials in plant diseases: can we combat phytopathogens?

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Abstract

Engineered nanomaterials (ENM) have a high potential for use in several areas of agriculture including plant pathology. Nanoparticles (NPs) alone can be applied for disease management due to their antimicrobial properties. Moreover, nanobiosensors allow a rapid and sensitive diagnosis of pathogens because NPs can be conjugated with nucleic acids, proteins and other biomolecules. The use of ENM in diagnosis, delivery of fungicides and therapy is an eco-friendly and economically viable alternative. This review focuses on different promising studies concerning ENM used for plant disease management including viruses, fungi, oomycetes and bacteria; diagnosis and delivery of antimicrobials and factors affecting the efficacy of nanomaterials, entry, translocation and toxicity. Although much research is required on metallic NPs due to the possible risks to the final consumer, ENMs are undoubtedly very useful tools to achieve food security in the world.

Key points

- Increasing global population and fungicides have necessitated alternative technologies.
- Nanomaterials can be used for detection, delivery and therapy of plant diseases.
- The toxicity issues and safety should be considered before the use of nanomaterials.

Keywords Disease detection · Controlled release · Nanofungicides · Antimicrobials · Toxicity

Introduction

Pests and plant pathogens cause losses in the agricultural sector, limiting food production. The highest losses of cereals and legumes, generally corn and rice, are reported in sub-Saharan Africa and East and Southeast Asia, which can reach 18%. As far as the loss of fruits and vegetables is concerned, the highest losses are registered in sub-Saharan Africa where the percentages can be greater than 40% (FAO 2019), in addition to the costs of applying agrochemicals. Savary et al. (2019) reported that the yield losses associated

with pathogens and pests worldwide can reach on average 21.5% in wheat, 30.0% rice, 22.5% corn, 17.2% potato and 21.4% soybean. In addition, the greatest losses are associated with rapidly growing populations such as sub-Saharan Africa, mainland China and the Indo-Gangetic Plain. New diseases affect agricultural crops (García-González et al. 2018) and some of them must be quarantined due to the serious economic damage they cause (Avila-Quezada et al., 2018).

On the one hand, the global population is expected to grow 9.7 billion by 2050, while on the other hand, the tremendous use of chemicals is toxic to the environment and living beings. In addition, many phytopathogens have developed resistance to the chemical fungicides; consequently, the crop yield has decreased which necessitates the use of alternative technologies like nanotechnology for a higher yield to ensure supply for all. Based on this backdrop, FAO proclaimed 2020 as the international year of plant health, and 2021 as the international year of fruits and vegetables, with the aim of raising awareness worldwide about how the protection of plant health can help eradicate hunger, reduce poverty, protect the environment

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and promote economic development. Through nanotechnology, it is possible to streamline processes in food production due to the development of new tools. These tools allow minimizing the inputs used for production and maximizing agricultural production to achieve sustainability, food security and safety at a global level. The application of nanotechnology can reduce the toxicity of fungicides by decreasing the large volumes that are currently applied, improving the life of the active ingredient and increasing its solubility in water. These qualities of the NM will have a positive impact on the environment. Therefore, the development of high-performance nanofungicides will be more environmentally friendly and profitable. The NPs mostly used for the successful control of plant diseases are carbon, silver, silica and non-metallic oxides or aluminosilicates (Wang et al., 2014; Alghuthaymi et al., 2021). Metal NPs comprise pure metals and metal oxides, where the latter are produced by the addition of oxidizing agents (Vargas-Hernandez et al., 2020). For example, the nanoparticles such as Ag, Cu and Zn can be directly sprayed on infected parts of plants as antimicrobial agents (Elmer and White, 2018). While as carriers, NPs are effective to entrap, encapsulate, absorb or attach active molecules such as fungicides and act as a nanocarrier to deliver on the infected areas of the plants. For example, Machado et al. (2020) used lignin as a bio-based nanocarrier for fungicides including azoxystrobin, boscalid, tebuconazole and pyraclostrobin which demonstrated remarkable potential for inhibition of *Phaeoemoniella chlamydospora* and *Phaeoacremonium minimum*.

The most commonly investigated nanoparticle carriers have been mixtures of polymers, silica and chitosan against many fungi. NPs are used to improve the fungicide's low water solubility problems, decrease its volatilization and improve stability during slow and sustained release (Worrall et al., 2018). The slow and controlled release systems are used to reduce the loss of bioactive agents such as fungicides and insecticides. Such loss can be due to environmental conditions particularly soil pH, methods of application, etc. The main aim of slow and sustained release of fungicides is to maintain the concentration of fungicides, reduce dose and cost, prevent loss and toxicity. The slow and sustained release of fungicides reduces the chances of toxicity to humans and the environment and also the small amount of fungicides are used for an extended period. These systems are boon for low-input sustainable agriculture.

This review focuses on diverse nanomaterials used against plant pathogens, their use in the development of nanosensors, delivery of fungicides, slow release and therapy of plant pathogens that have developed resistance to different fungicides. It also addresses different factors concerning the efficacy of nanoparticles, entry of nanoparticles in plants,

their translocation studies and most important their toxicity to the plants, environment and human beings.

Diversity of ENM used in plant diseases

Nanomaterials have attracted the attention of consumers globally, and therefore, their applications have been increased in several fields. Concurring to their composition, nanomaterials can be classified into four categories: pure carbon nanostructures (Fullerenes, graphene and carbon nanotubes), inorganic nanomaterials (metal, metal oxide, zeolite, ceramic), organic nanomaterials (dendrimers, liposomes) and organic–inorganic hybrids (metallic–organic structures, covalent organic structures) (Ananikov, 2019).

In the case of organic NPs, such as liposomes, polymeric constructs and micelles, they have been used for drug and gene delivery. These techniques can also have application in the administration of agrochemicals. Protein-based nanostructures (albumin), poly (amino acids), polysaccharides (dextran, chitosan), surfactants, dendrimers, solid drug crystals (nanocrystals), synthetic polymers and other organic material have been used as drug delivery systems (Patra et al., 2018). Poly(amino acid)s (PAA) as biological molecules are composed of natural amino acids, and normally possess the active groups (e.g., hydroxyl, carboxyl, amino and thiol group) that are able to control drug loading or release. The use of organic materials to prepare organic nanostructures is beneficial because they are biodegradable and biocompatible and thus widely used for drug delivery, when a specific dosage is required. Similar to the inorganic NPs, the surface functional groups of organic nanosystems are easily designed (Lombardo et al., 2019). Depending on the chemical composition, they can encapsulate low molecular weight hydrophilic and/or hydrophobic ingredients, more complex agents, such as proteins, peptides, genes, oligonucleotides and siRNAs (Mundargi et al., 2008). Usually, based on the size of the final product needed, the properties of the drug or agrochemical to be encapsulated, the characteristics of the surface and functionality, biodegradability, the profile of the final product and the base polymer are selected (Mahapatro & Singh, 2011).

The action spectrum of nano-enabled fungicides can be designed using nanohybrid materials. The components of nanohybrids have a chemical origin that encompasses biological–inorganic, as well as natural/synthetic organic–inorganic materials. For example, aluminosilicate nanoplates are used to develop pesticide formulations with a dual purpose, better biological activity and greater environmental safety compared to the use of artificial NPs (Iavicoli et al., 2017). Antimicrobial nanohybrids

have been shown to be effective against diseases caused by pathogenic fungi. Combined organic/inorganic nanomaterials, also called surface-modified nanomaterials, provide some functionality to the matrix, such as antimicrobial activity. Hybrid nanomaterials such as polymer/metal/organic molecule with specific properties as selectivity and sensitivity can interact with each other and accelerate reaction kinetics to counteract mycotoxin detoxification. They can also be used for the detection and management of plant pathogenic fungi (Ananikov, 2019). In this context, Bhardwaj et al. (2019) developed a hybrid immunosensor with graphene quantum dots (GQD) and gold nanoparticles (AuNP), on an indium tin oxide (ITO) electrode modified with an antibody (anti-AFB1) (anti-AFB1/GQDs-AuNPs/ITO) to detect aflatoxin AFB1. Similar techniques are possible to develop methods to detoxify enzymes produced by pathogens. The hybrid nanomaterials used for the detection of mycotoxins and nullifying their effect include single-walled and multi-walled carbon nanotubes, metal and metal oxide NPs, silica-based and polymeric nanostructures such as dendrimers (Thipe et al., 2020).

Fighting with phytopathogens in nanoway

As mentioned before, the phytopathogens such as fungi, oomycetes, bacteria, viruses and phytoplasma affect crops and consequently cause serious losses in food production worldwide. Current control strategies include the use of foliar and soil-applied agrochemicals, the use of resistant varieties, crop rotation, among other management strategies.

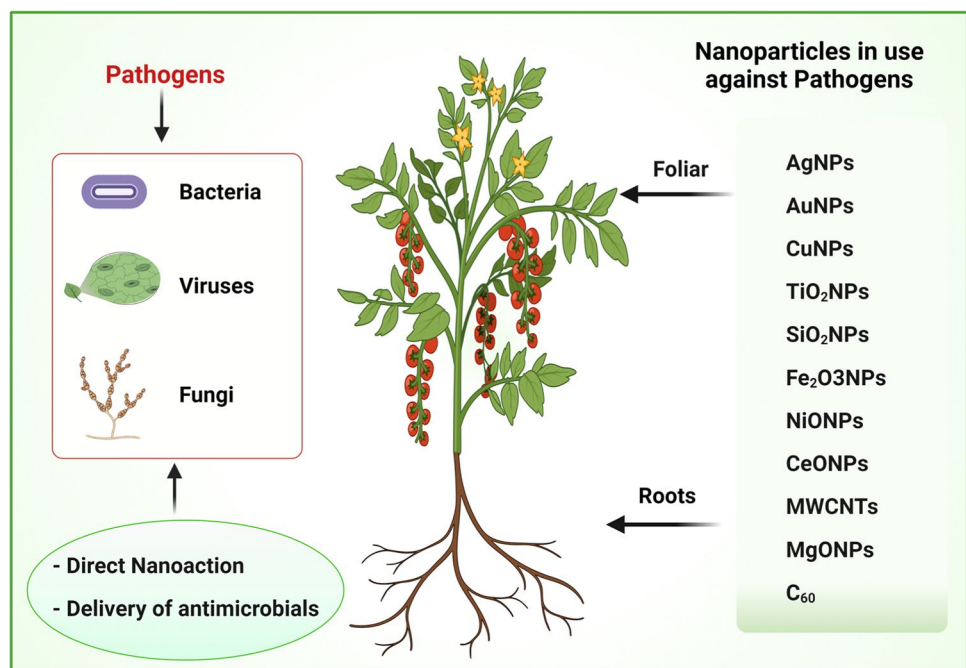
Since these strategies do not fully protect crops, other newer, low-cost and less toxic tools should be explored to combat plant pathogens, such as metallic NPs (Gogos et al., 2012; Athawale et al., 2018) as given in Fig. 1. Nanomaterials smaller than 100 nm have high reactivity with pathogens due to their size and large surface area.

Nanoparticles are the ideal candidates for reducing populations of phytopathogens because they adhere to the microbial cell membrane due to electrostatic attraction between the negatively charged cell membrane of microbes and NPs with positive charges. The morphological structures of the membrane are damaged by NPs, causing the membrane alteration, holes and finally the cell dies. According to some action mechanisms of metallic NPs against phytopathogens, there is loss of protein functions, production of reactive oxygen species (ROS) and antioxidant depletion, deterioration of membrane function, interference with nutrient absorption and breakdown of the double strand of DNA (Avila-Quezada & Espino-Solis, 2019).

Viruses

The viruses cause 50% of plant diseases (Vargas-Hernandez et al., 2020), and therefore, the accurate diagnosis of plant viruses is essential to prevent them. In this context, nanomaterials would be appropriate for the detection and control of viruses. The current studies provide evidence of the mechanisms involved in the mode of action of metallic NPs against viruses. For instance, silver nanoparticles (AgNPs) show a broad spectrum of antiviral activity against viruses of different families, by

Fig. 1 Application of different NPs against microbial pathogens



interacting with gp120, competing for cell binding of the virus, inactivating the virus prior to entry, interacting with double-stranded DNA and binding with viral (Galdiero et al. 2011). A study with norovirus showed that gold/copper sulfide core-layer NPs (Au/CuSNP) degrade the viral capsid protein (Broglie et al., 2015).

The antiviral activity of NPs has been demonstrated in vitro and in vivo with different plants. NPs are generally described as acting on the surface of the virus. For instance, Cai et al. (2019) reported antiviral activity of ZnONP and SiO₂NP against tobacco mosaic virus (TMV) in vitro; NPs appear to interact with envelope glycoproteins, causing direct damage to the virus capsid. Another way of controlling plant viruses is to control the vectors because 70% of the plant viruses are transmitted by insect vectors (Farooq et al. 2021). More studies are required on the mode of action of NPs to counteract the effect of viruses on the xylem and phloem of plants, and also, there is a need to unravel plant-virus-nanoparticle interaction.

Bacteria

The research on the antibacterial activity of nanoparticles has attracted the attention of the scientific community. The studies provide evidence that organic NPs are very promising for the protection of crops against bacteria. For example, a nanocarrier of biopolymeric NPs based on poly (DL-lactide-co-glycolide) copolymer PLGA and cellulose nanocrystals was useful to control *Pseudomonas syringae* pv. *tomato* in plants. The nanocarrier evenly covered the surface of the tomato plant leaves. It did not damage leaves of the plant, and the bacteria were not detected in tomato leaves with this treatment (Fortunati et al., 2016). In another study, hyaluronan/chitosan (HA/CHI) nanofilms assembled layer-by-layer proved to be useful against the quarantined bacterium *Xylella fastidiosa* (Hernández-Montelongo et al., 2016).

Moreover, there are many studies on the activity of metallic NPs against plant pathogenic bacteria. For example, AgNPs have demonstrated remarkable activity against bacteria. Ag⁺ ions interact with proteins and enzymes that contain cysteine in bacterial membranes, causing structural abnormalities and biochemical imbalances of the cell membrane. The silver ions penetrate into the damaged membrane and inactivate enzymes in the cytoplasm, inhibiting cell replication and causing cell death (Avila-Quezada & Espino-Solis, 2019). Another metal copper is also widely used in agriculture as it is required as a micronutrient (Ingle and Rai, 2017; Rai et al. 2018a, b); however, residual copper contaminates the soil and water and can develop resistance in bacteria. At present, it is possible to take advantage of the biological activity of copper

against phytopathogens, by means of copper nanoparticles (CuNPs), due to the use of its low quantity (Bramhanwade et al. 2016).

Fungi

Nanomaterials have been proved to be effective tools in the management of fungal pathogens (Jogee et al. 2017; Rai et al. 2018a, b). For example, carbendazim-conjugated silver nanoparticles (Cz-AgNP) are effective against *Colletotrichum gloeosporioides* in vitro (Nagaraju et al., 2020), the causal agent of anthracnose in many fruits and vegetables (Miranda-Gómez et al., 2014). The antifungal activity of nanomaterials can be achieved when they are directly internalized into the cell wall, through the adsorption mediated by specific receptors followed by internalization and through ion transport proteins (Kalia et al., 2020). After internalization, nanomaterials inhibit the enzyme β -glucan synthase, affecting the synthesis of β -1, 3-D-glucan and β -1,6-D-glucan in the fungal cell wall, producing deformation in the cell wall, membrane disintegration and damage to cytoplasmic organelles (Arciniegas-Grijalba et al., 2017).

As far as the interaction at the molecular level is concerned, nanomaterials interact with various biomolecules and cause structural deformations, inactivation of catalytic proteins and nucleic acid abnormalities. Metal ions trigger ROS and damage biomolecules leading to fungal cell death (Zhang et al., 2018).

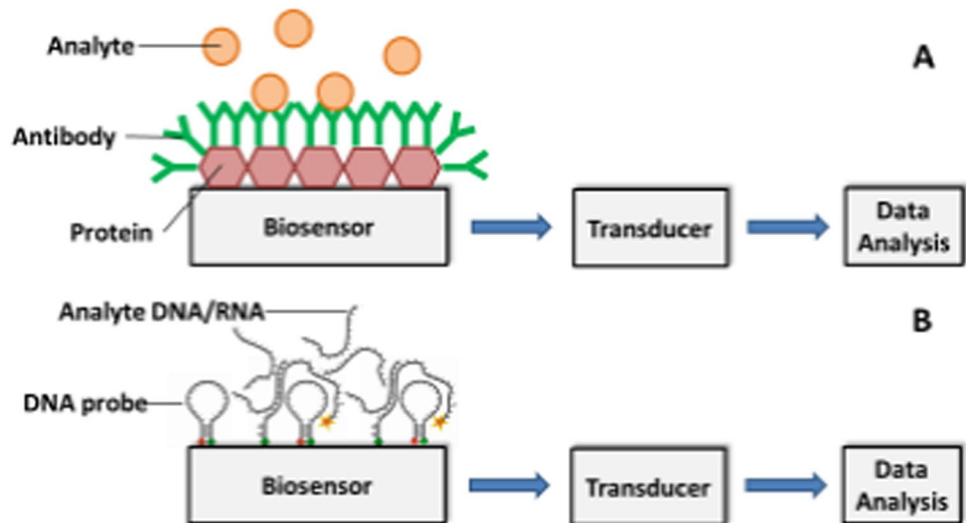
ENM in diagnosis and delivery of antimicrobials

Diagnosis

Early diagnosis of the pathogens is essential for timely management of the diseases. The most accurate technique for the detection of plant pathogens is the polymerase chain reaction (PCR). DNA-based detection has limitations because of false-positive results due to cross-contamination and the inability to use PCR at the field level (Khater et al., 2017).

In recent years, nanobiosensors are being used which can overcome the above-mentioned limitations. The biosensing of the microbial pathogen depends on the biological recognition of various receptors including DNA probe, antibodies, phage-DNA, etc. (Singh et al., 2013). However, in the case of antibody-based immunosensors, the coupling takes place between antibody and transducers, which converts the binding process with antigen (pathogen). Similarly, DNA/RNA-based biosensors/nanobiosensors can be used for analyte/pathogen detection (Fang & Ramasamy, 2015) (Fig. 2). It has been found that DNA-based biosensors are more important than antibody-based

Fig. 2 Schematic illustration of (A) antibody-based and (B) DNA/RNA-based biosensor for analyte (pathogen) detection. The specific combination of analyte and immobilized antibody (A) or DNA/RNA probe (B) produces a physicochemical change, such as mass, temperature, optical property or electrical potential. The change can be translated into a measurable signal for detection (reproduced from Fang and Ramasamy (2015) under Creative Common Rights Licence)



biosensors being more sensitive (Dyussebayev et al. 2021).

Nanobiosensor-based diagnosis is fast and sensitive because NPs can be conjugated with nucleic acids, proteins and other biomolecules (Kashyap et al. 2017). Nanoparticle-based sensors and kits have recently been developed for disease diagnosis and rapid tests. Quantum dots are size-dependent, tunable fluorescence nanocrystals, thus showing potential for diagnostics. In another study, Rad et al. (2012) developed a specific nanosensor based on quantum dots to diagnose *Candidatus Phytoplasma aurantifolia* in infected lime. In this context, Schwenkbier et al. (2015) also developed a chip-based hybridization technique that incorporates AgNPs for the detection of *Phytophthora* species.

Nanoantimicrobials delivery and release

The most commonly used method for the application of NPs is a direct application to the seeds or foliar spraying. The NPs can inhibit plant pathogens locally, in various parts of the plant, and can translocate through all conductive vessels of the plant, thus reducing the chances of incidence of disease (Ali et al., 2020). Nanomaterials are also used as carrier materials for active chemical ingredients for the controlled release of pesticides (Mujeebur & Tanveer, 2014).

Nanomaterials in general and mainly organic materials such as those based on polymers or biopolymers can be used as possible carriers of active organic ingredients (Patra et al. 2018). The functionalization of their surfaces and specific active ingredients encapsulation procedures represent a challenge for the controlled release.

Nanoformulations are important for the therapy of plant diseases and to achieve slow delivery of the active ingredient, protect it from degradation and improve the solubility to have an inhibitory effect against phytopathogens. The

controlled release of the active ingredients will depend on the system based on biodegradable polymers, and the diffusion will depend on the properties of the polymer. Therefore, the complete release of the active ingredients must coincide in time with the degradation of the polymer. It should also match the biology of the target pathogen cell (Kumar et al., 2019). The nanoformulations with controlled release based on polymers reduce the leaching of solutions, and hence, they are very efficient for use in agriculture. An example of this was discussed by Salma et al. (2010) in a trial of aqueous tebuconazole solution in wood. The release of the active ingredient can be adjusted by modifying the molecular weight of the polymers as per requirement.

In another study, Koli et al. (2015) synthesized controlled release nanoformulations of the systemic fungicide carbendazim (methyl 1H-benzimidazol-2-ylcarbamate), using functionalized amphiphilic copolymers based on poly (ethylene glycols) (PEG). It was evaluated against *Rhizoctonia solani* and found that the release of the amount of carbendazim from the formulation depended on the molecular weight of the PEGs, increased with increasing molecular weights. The range of carbendazim release was found to remain between day 10 and day 35 compared to the commercial formulation which remained only until day 7.

Factors affecting the efficacy of ENMs

The knowledge of the characteristics and properties of AgNPs, such as its size and shape, optical, electrical and magnetic properties and surface chemistry of the particles, provides us with data for the correct application as antibiotic, antifungal and antiviral activities. Besides these, the physical and chemical features of metallic NPs are related to their toxicity through the production of reactive oxygen

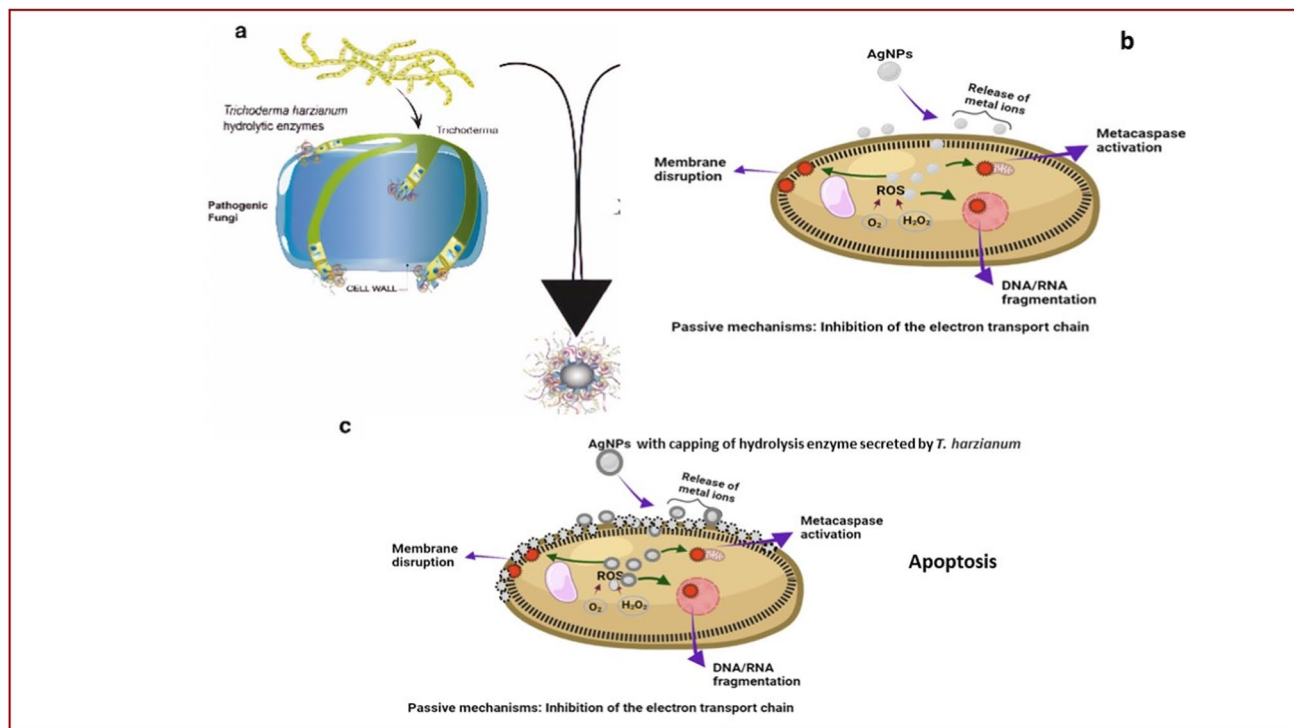


Fig. 3 Possible mechanism of action of the capped AgNPs against *S. sclerotiorum*. a Degradation of the cell wall by hydrolytic enzymes secreted by *T. harzianum*; b membrane disruption and oxidative stress

caused by AgNPs; c synergistic effect of the biogenic AgNPs and the capping hydrolytic enzymes against *S. sclerotiorum*

species (ROS) (Zhang et al., 2018). The antimicrobial effect of metal NPs also depends on the concentration and time of exposition (Ahmadi, 2020).

There are a large number of reports concerning the antimicrobial activity of AgNPs which depends on its size and shapes (Pal et al., 2007; Ivask et al., 2014). According to Hu et al. (2020), the zeta potential and the size of hydrophilic NPs influence the efficiency of delivery and translocation towards guard cells, extracellular spaces and specific organelles. In addition, nanoparticle formulations with surfactants reduce surface tension, which is crucial to allow rapid absorption of NPs through stomata and other cuticle pathways.

The antimicrobial activity of AgNPs depends on the concentrations used. Handoko et al. (2017) used AgNPs against Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria and reported a minimum concentration of 12.5 $\mu\text{g mL}^{-1}$ for *S. aureus* and 1 $\mu\text{g mL}^{-1}$ for *E. coli*. That is because the cell wall of Gram-positive bacteria is thicker and has a high concentration of peptidoglycans; thus, *S. aureus* is more resistant than *E. coli*. In addition to the concentration dependence, AgNPs release Ag⁺ ions, and as a result, ROS is generated causing mitochondrial dysfunction, affecting ATP synthesis, fragmenting DNA leading to apoptosis. Recently, Guilger-Casagrande et al. (2021) synthesised AgNPs by *Trichoderma harzianum* and proposed

a hypothetical mechanism of capped AgNPs. The authors reported that AgNPs and the agents responsible for their capping such as hydrolytic enzymes secreted by *T. harzianum* used for biosynthesis exert a synergistic effect against plant pathogen *Sclerotinia sclerotiorum* (Fig. 3).

Ivask et al. (2014) evaluated the toxicity of NPs of different sizes (10, 20, 40, 60 and 80 nm) on bacteria, algae, yeast, crustaceans and mammalian cells. The smallest size (10 nm) showed the highest toxicity. NPs of Ag < 10 nm create pores in the cell wall increasing permeability and causing cytoplasmic discharge and cell death (Sondi & Salopek-Sondi 2004). In the study of Morones et al. (2005), the size < 20 nm exhibited a higher binding of sulfur-containing membrane protein, which generated membrane permeability and cell death of bacteria.

Besides size, the shape of the NPs is another parameter to determine antimicrobial activity. There are different views concerning the role of the shape of NPs on their efficacy. For instance, truncated triangular silver nanoplates are more effective against *E. coli* compared to spherical and rod-shaped NPs according to a study by Pal et al. (2007). In another study by Talebian et al. (2013), the bactericidal effect of ZnONPs was found to be better when they were flower shaped for inhibition of *E. coli* than rod shaped. Also, the more exposed Zn-terminated polar facets have a better antibacterial effect (Sirelkhatim et al., 2015). Besides,

rod-shaped TeNPs had significant antibacterial activity against *P. aeruginosa* (Mohanty et al., 2014). More recently, Singh et al. (2020) reported that triangular and spherical NPs have remarkable antibacterial property, but the reason behind it is not yet well understood. Several NP shapes such as triangle, octahedral platelets, spherical, rodlike and size depend on temperature during their synthesis (Sneha et al., 2010). The surface charge also plays an important role in determining the efficacy of NPs. In a study, Abbaszadegan et al. (2015) reported the efficacy of different surface charges of AgNPs against Gram-positive (*Streptococcus mutans*, *Streptococcus pyogenes* and *Staphylococcus aureus*) and Gram-negative (*Proteus vulgaris* and *E. coli*) bacteria.

In fact, for each plant–microbe–nanoparticles interaction, models must be developed to predict translocation and distribution of nanomaterials in plants, and their interaction with plant pathogenic microbes. Understanding the interactions among NPs, plants and pathogens is crucial to advance the field of nanophytopathology.

The entry of ENM in plants

In foliar applications, only a small fraction of the NPs enter the plant, besides, a part of this fraction remains confined to the epidermis (Su et al., 2019). The fate of the NPs absorbed by cells depends on several nanoscale parameters such as size, surface/chemical charge or colloidal stability.

The absorption of NPs depends on their exposure routes. It is also related to the physiological and metabolic activities of the host-plant (Raliya et al., 2015). The leaves of the plants have stomata of various sizes depending on the crop, in which the penetration of NPs is possible. For example, the stomata of spinach leaves measure $5 \times 13 \mu\text{m}$ (Zhao et al., 2017), tomato leaves $5 \times 7 \mu\text{m}$ (Raliya et al., 2015), lettuce leaves $6 \times 16 \mu\text{m}$ (Larue et al., 2014), *Triticum durum* $6.31 \times 13.90 \mu\text{m}$ and *Triticum monococcum* $6.65 \times 52.84 \mu\text{m}$ (Khazaei et al., 2010). Based on the size of these natural openings, it is necessary to apply NPs of a smaller size for the successful uptake of NPs.

The abundance of stomata allows a fast and efficient entrance of NPs (Kurepa et al., 2010). Once NPs enter through the cuticle or stomata, they aggregate on the surface of a leaf. In a study, Keller et al. (2018) mentioned that CuONPs of 24–37 nm after 4 h of application on lettuce leaves, formed aggregates of 230–400 nm. Also, Hong et al. (2014) reported that less than 30% CuONPs of 24–37 nm entered the cucumber leaves, the majority remained in the epidermis. Similarly, $2.8 \pm 1.2 \text{ nm}$ TiO₂NPs accumulated primarily in some of the stomata of *Arabidopsis* leaf after 24 h of exposure (Kurepa et al., 2010). These findings indicate that the stomatal uptake pathway serves as a more efficient pathway for NPs entrance. The study of Cai et al.

(2019) confirmed that SiO₂NPs and ZnONPs maintained their nanoscale morphology even after interaction with biological tissues. After internalization, NPs are observed mainly in chloroplasts, without damaging the cell integrity (Cai et al., 2019).

However, the foliar application of NPs can lead to entry into plant cells through direct cell penetration mechanisms due to its small size (Wang et al., 2013). Indeed, NPs of 18–20 nm can be applied for site-directed delivery in plant tissues (Cai et al., 2018). Nonetheless, the trichomes of the leaves restrict the absorption and transport of NPs on the surface of the leaf (Cai et al., 2018). Even when only a small fraction of NPs enter the leaf in the foliar application, these can inhibit pathogens during the translocation. Furthermore, the injection of NPs into the trunk could enhance its effect. Plant roots are another organ that can allow NPs uptake, although less efficient than leaves (Su et al., 2019).

Translocation of NPs in plants

Once NPs enter the leaf stomata, they have relatively easy access to the descending vascular system particularly phloem (Wang et al., 2013). The mesophyll may have small intercellular spaces as in xerophytes or large as in some mesophytes and most hydrophytes. This size could affect the short-distance transport of NPs before entering the vascular system (Su et al., 2019).

The xylem carries the water from the roots to the leaves, while the phloem carries the sugar (produced during photosynthesis) from the leaves to the rest of the plant. In xylem, phloem and cell wall interstices, NPs can move together with water or sap (Pérez-de-Luque, 2017), although how sugars and proteins interact with the NPs surface is unknown. The hydrophobic NPs have superior penetration through the waxy leaf cuticle; however, it is not clear how these hydrophobic particles move through plant tissues (Yang et al., 2015) (Fig. 4).

NPs can inhibit plant pathogens internally since they can travel through vascular ducts, controlling pathogens. Various NPs have been evaluated to determine their possible plant toxicity due to their absorption, translocation and accumulation in plant cells (Kurepa et al., 2010). NPs absorption and translocation depend on their properties such as size, composition and surface area, application rate, manner of administration and the plant species. In the study of Cai et al. (2018) of foliar application of ZnONPs, Zn accumulated more in the stem and roots in the treated groups than in the control. ZnONPs easily penetrated the leaves, traverse the stem, reach the root, deposit on the lower leaves and spread throughout the plant tissue through the vascular system, while SiO₂NP had lower translocation to the roots. Raliya et al. (2015) concluded that translocation of metal oxides

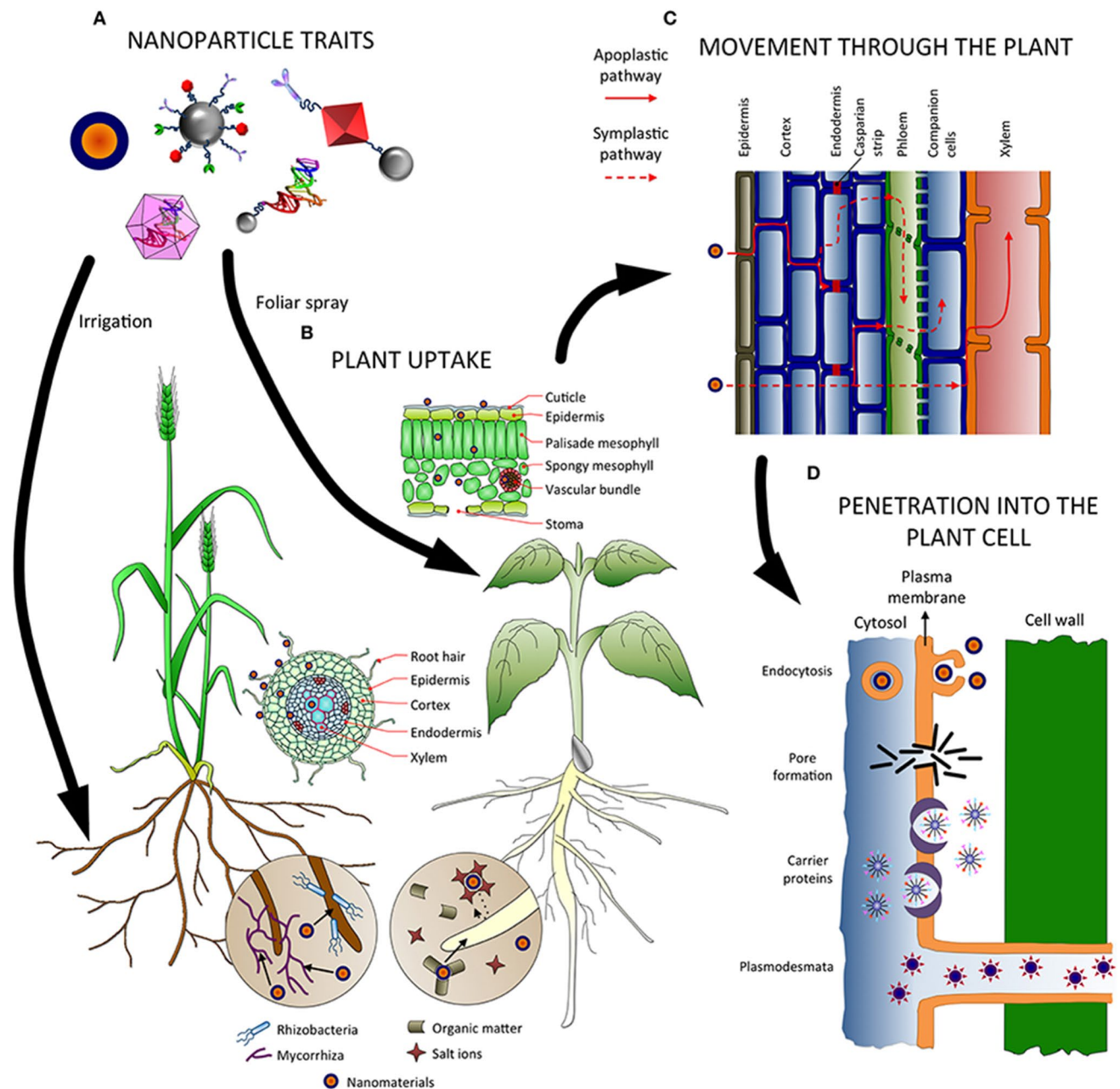


Fig. 4 Absorption, uptake, transport and penetration of NPs in plants: (A) NP traits affect how they are uptake and translocated in the plant, as well as the application method. (B) In the soil, NPs can interact with microorganisms and compounds, which might facilitate or hamper their absorption. Several tissues (epidermis, endodermis...) and barriers (Casparian strip, cuticle...) must be crossed before reaching the vascular tissues, depending on the entry point

(roots or leaves). (C) ENM can follow the apoplastic and/or the symplastic pathways for moving up and down the plant, and radial movement for changing from one pathway to the other. (D) Several mechanisms have been proposed for the internalization of NPs inside the cells, such as endocytosis, pore formation, mediated by carrier proteins and through plasmodesmata (reproduced from Pérez-de Luque (2017) under the Creative Commons Attribution Licence (CC BY))

and ions in plant stems is not easy; only a small amount is translocated from leaves to stems.

In a study, Cai et al. (2020) sprayed Fe_3O_4 NPs on *Nicotiana benthamiana* infected with *Tobacco mosaic virus* (TMV). The cells of the leaves absorbed Fe_3O_4 NPs which were observed in and around chloroplasts. NPs did not

damage the integrity of the cells. The cells of the tobacco leaf absorb Fe_3O_4 NPs and the vascular system biodistributes it from the leaves to the roots.

This shows that each plant–microbe–nanoparticle interaction is specific and the physiology of the plant, the characteristics of the nanoparticle and the biology of the pathogen

to be treated must be considered. Indeed, to reach roots from leaves, NPs cross barriers such as cell walls and internalize into plant cells through endocytosis. Then, for transportation through the vascular system by the sympathetic transport, NPs size must be up to 50 nm to pass through the plasmodesmata (Wang et al., 2016). Based on the findings of the above studies, it can be assumed that a pre-treatment of metallic NPs with the foliar application can stimulate the resistance of the plant to TMV because the NPs are distributed throughout the plant.

Toxicity of ENM

There are different nanoparticles including CuNPs, AgNPs, ZnONPs, TiO₂ and MgO which have been reported against various plant pathogenic microbes such as bacteria, fungi and viruses (Ali et al. 2020). The potential toxicity of NPs in humans or other living beings warrants new and more complex investigations that allow a risk/benefit assessment. There is controversy about the toxicity of NPs in humans, animals, plants and the environment (Sahu & Hayes, 2017). According to Wang et al. (2011), the accumulation of metallic NPs can alter plant physiology, affecting the growth and development of plants. Metallic NPs are toxic although they are rarely dispersed in the environment (Ali & Ali, 2019). As the production of secondary metabolites and phytohormones is affected, plant growth decreases (Sanzari et al. 2019). The toxicity that has been reported due to NPs in plants also includes reduced water transport in conductive systems, low production of growth hormone, metabolic disorder, oxidative stress, chromosomal abnormalities, deviation in the transcriptional profile of some genes and increased susceptibility to toxins (Morales-Díaz et al., 2017). There is a knowledge gap on the toxicity of metal NPs. For example, AgNPs are an efficient material that is used in different sectors including food. AgNPs show signs of some *in vivo* or *in vitro* toxicity due to their physicochemical properties, in addition to its possible discharge in water and absorption by aquatic species. Actually, the toxicity of silver is low; nevertheless, the toxicity derived from dissolved nanosilver or silver is a subject of debate (Deshmukh et al., 2019). While discussing the toxicity of AgNPs on plants, Yan and Chen (2019) argued that it is difficult to conclude the effects of AgNPs on plants because most studies reported detrimental effects of AgNPs but some studies also described the beneficial effects. The toxicity depends not only on the shape, size and surface charge but also on the pathogen/plant species and its behaviour.

The toxicity of nanoparticles can be reduced by using greener technologies for their synthesis. For example, the biogenic synthesis of nanoparticles by using plants and microbes (bacteria, fungi, algae) is eco-friendly and

economically viable and can be carried out at room temperature and pressure (Rai et al. 2021). These biogenic nanoparticles are more bioactive against the pathogenic microbes as compared to chemically synthesised nanoparticles (Bawskar et al. 2015). In this context, there are several reports of the application of biologically engineered CuNPs, ZnOPs and AgNPs against plant pathogens. Moreover, biologically engineered nanoparticles have demonstrated much lower toxicity compared to chemically synthesised nanoparticles (Rezvani Amin et al. 2019; Wen et al. 2021). The biogenically engineered nanomaterials can be considered eco-friendly ENM. However, deeper studies are required to arrive at the conclusion. The problem can be possibly minimized if biodegradable nanomaterials such as chitosan, pullulans, sulfur, β -D-glucan, etc. can be used for the management of plant diseases.

Conclusion and future perspectives

The new and alternative tools for the management of crop diseases are necessary to reduce the excessive use of pesticides, avoid the resistance of pathogens and maintain the balance of biodiversity. Thus, the effects of climate change will be minimized.

The application of NPs can inhibit various fungi, oomycetes, bacteria and viruses. Moreover, the NPs can be used for the delivery of fungicides/antimicrobial agents that can be directed at the target pathogen, in the part of the plant that could be affected by the pathogen. In this context, nanoencapsulation of antimicrobials can be used for the efficient management of phytopathogens. Another advantage of NPs is that the solubility and effectiveness of antimicrobials enhance that are used against microbial pathogens. The application of different kinds of NPs against pathogens of plants reduces the problems of diseases and the high economic and environmental costs related to fungicide/pesticide applications are one of the greatest challenges of the agricultural sector in the world. Finally, the application of NPs for tackling the problem of phytopathogens is an efficient, eco-friendly, economically viable and important solution for fighting with emerging resistance of pathogens to fungicides. However, more comprehensive research should be designed to develop safer nanotechnology-based strategies for managing plant pathogens, which will be a major step towards sustainable crop production.

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Author contribution M.R. conceived and designed the review. G.D.A. contributed substantially. P.G. co-wrote the manuscript. M.R. critically revised the mss. All authors read and approved the manuscript.

Declarations

Ethics approval This article does not contain any studies with human participants performed by any of the authors.

Conflict of interest The authors declare no competing interests.

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