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Nanoparticles for plant disease management

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Abstract
Engineered nanoparticles (NPs) (1–100 nm) that have demonstrated activity in suppressing plant diseases are metalloids, metallic oxides, nonmetals, and carbon nanomaterials. NPs have been integrated into disease management strategies as bactericides/fungicides and as nanofertilizers to enhance plant health. Although there are reports of over 18 different NPs of single element and carbon nanomaterials affecting disease and/or plant pathogens, only Ag, Cu, and Zn have received much attention thus far. Some NPs act directly as antimicrobial agents while others function more in altering the nutritional status of the host and thus activate defense mechanisms. For example, NPs of Ag and Cu can be directly toxic to microorganisms. Other NPs of B, Cu, Mn, Si, and Zn appear to function in host defense as fertilizers. As demand for food production increases against a warming climate, nanoparticles will play a role in mitigating the new challenges in disease management resulting in a reduction in active metals and other chemical inputs.

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Introduction

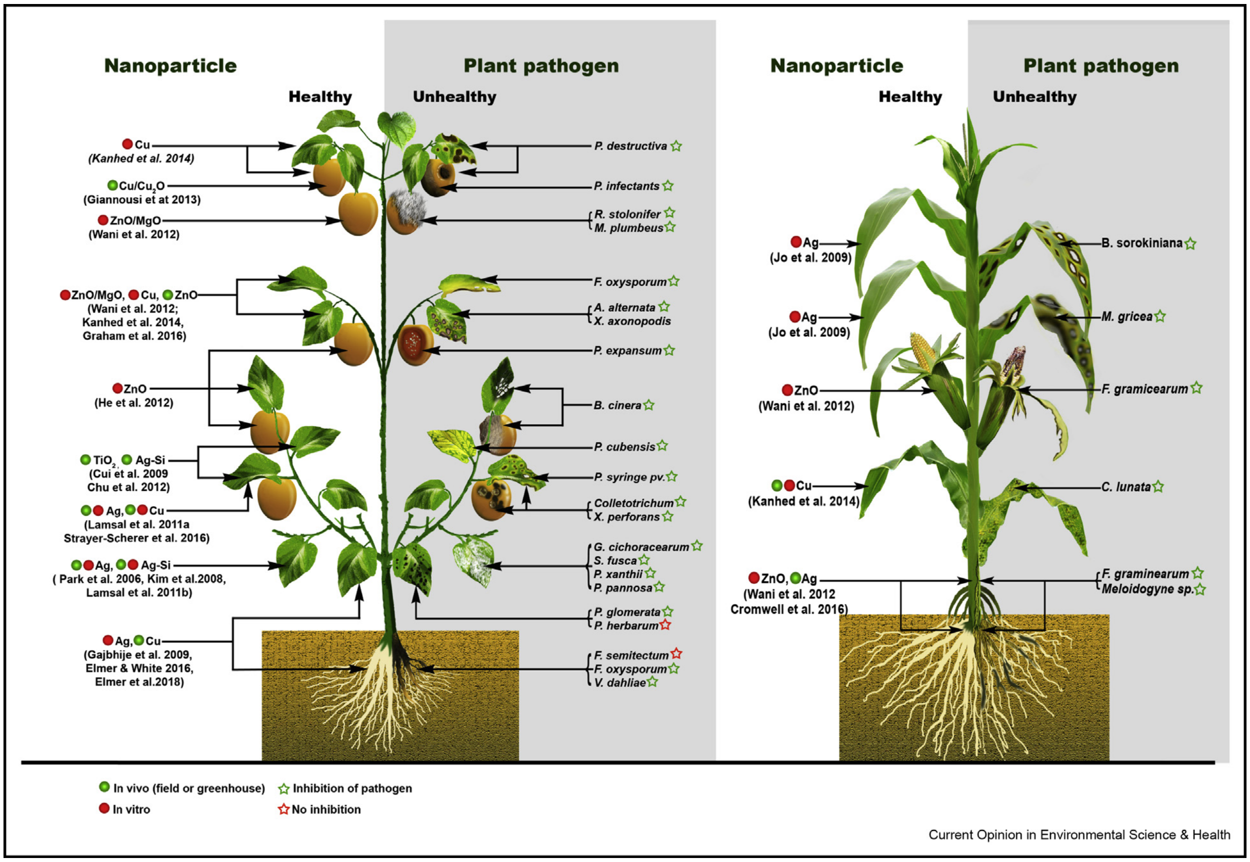
The demand for increased food production has forced many challenges on agriculturalists. Combined with climate changes that will likely extend drought events and elevate annual temperatures, crop yields in many agriculturally sensitive regions will become more vulnerable to disease and other stresses. Most agriculturalists assert that we can achieve the necessary increase in food and fiber, but only at unsustainable and ecologically damaging cost [50]. However, the advent of nanotechnology stands as a formidable weapon against many factors that threaten plant health. There are many advantages for using nanotechnology. One very attractive reason is the large reduction in active chemicals that actually enter the agroecosystem. Large proportions of applied bactericide/fungicide and fertilizers do not reach their target and ultimately enter ground water, contaminating vulnerable ecosystems. Given the large active surface area of nanoparticles, smaller amounts can deliver the same, if not more, active ingredient to the pest species or tissue site and minimize exposure to non-target areas when compared to the larger bulk or non-nano forms. Furthermore nanotechnology offers an array of additional unique properties that can be exploited in plant health management such as improved solubility, delivery, and more lasting residual activity of agrichemicals and longer residual activity.

Of the many nanoparticles (NPs) that exist, we acknowledge that most currently do not have application in plant pathology. However at the time of this writing, we report that the vast majority of nanotechnology studies in plant disease management have used NPs of metalloids, metallic oxides, nonmetals (single and composites), carbon nanomaterials (single- and multiwall carbon nanotubes, graphene oxides, and fullerenes). The following review summarizes the role of these NPs in plant health [Figure 1]. For more a detailed review that explores specific disease systems and the role of NPs in plant disease diagnostics see Ref. [19].

Metal, metalloid, and nonmetal NPs

The first NP to be investigated in plant disease management was Ag. Park et al. [44], Lamsal et al. [34] and Kim et al. [33] all explored the early use of NP Ag in the suppression of powdery mildew. Each discovered very good disease suppression. Lamsal et al. [34] found suppression at 100 μg/mL afforded a level of control comparable to conventional fungicide treatment and reported that curative response was observed. Other studies have confirmed the efficacy of Ag NPs against fungal pathogens [3,21,30,31,36–38], bacteria [40], and nematodes [1,4,12,39]. Other than direct antimicrobial action, it is not clear whether NP Ag also activates defense mechanisms, and additional research is clearly warranted. Another unanswered question in many of the studies was whether or not ionic Ag (salt) would have achieved the same level of disease suppression. Effort should be in made in all future studies to compared NPs of Ag to ionic or larger bulk form equivalents so the "nano" effect can be evaluated. If potential threats of applying Ag in the environmental can be adequately

Figure 1



Illustrative examples of nanoparticle studies with micronutrients and non-nutrients on diseases of citrus and maize. (Used with permission [19]).

addressed and minimized, nanoparticles of Ag might serve as a strong candidate for disease management when other conventional strategies are ineffective.

NP Cu was another logical choice in plant disease management given its long history in controlling plant diseases as a contact bactericide/fungicide [20,32]; however, serious investigation of NP Cu for disease management was not performed until 2013 [22] when foliar applications of NP CuO, Cu_2O, and Cu/Cu_2O composites were compared to conventional registered Cu fungicides to control late blight disease caused by *Phytophthora infestans*. Plants treated with NP CuO at 150–340 μg/mL performed better than the other treatments. Newer and more refined engineered composites of NP Cu have resulted in an array of new products. For example, Strayer-Scherer et al. [49] advanced a new strategy using engineered Cu NP composites possessing a core–shell Cu, multivalent Cu, and fixed quaternary ammonium copper in management of bacterial spot caused by the Cu-resistant *Xanthomonas perforans*. The nano-Cu products significantly reduced bacterial spot disease severity in the greenhouse and field when compared to Cu fungicides and water controls ($P < 0.05$). These composites were able to release higher amounts of active Cu^{2+} ions which were able to penetrate bacterial membranes more effectively. Importantly, the NP Cu products were equal or superior to the commercial Cu-based products, delivered less Cu per ha, and did not cause overt phytotoxicity.

In addition to the antibacterial activity of NP CuO towards many plant-pathogenic bacteria and fungi, NP Cu could operate by a nutritional mechanism. Copper is an essential plant micronutrient that plays a pivotal role in growth as well as defense against plant diseases. Three important proteins involved in host defense: plastocyanins, peroxidases, and multi-Cu oxidases, require Cu and are synthesized in response to pathogen attack [20]. Since these reactions to infection are non-specific, they have the potential to protect against a wide array of pathogens. Enhancing the availability and function of NP Cu to affect plant nutrition and defense from disease was first explored by Elmer and colleagues [7,17,18]. Utilizing NP Cu as a nanofertilizer to specifically boost disease resistance has been explored on a variety to plant/disease systems, including asparagus/Fusarium crown and root rot, chrysanthemum/Fusarium wilt, eggplant/Verticillium wilt [18], soybeans/sudden death syndrome [unpublished], tea/red root rot [45], tomato/Fusarium wilt, and watermelon/Fusarium wilt [17]. An analysis of gene expression (by RT-qPCR) in Fusarium infected watermelon revealed upregulation of polyphenol oxidase and pathogen-related genes in plants treated with NP CuO [17]. These findings suggest that NP CuO may serve as a highly effective delivery agent for Cu that can subsequently enhance disease suppression.

Many laboratories have demonstrated the antimicrobial activity of Zn NPs against bacteria [24,29], and a range of fungal pathogens [27,53], and viral infections [25]. However, field experiments showing definitive disease reduction are quite limited. NP Zn has been used to suppress bacterial leaf spot on rose [42]. Cercospora leaf blight of sugar beet [15], and *Fusarium graminearum* on sorghum [16]. One Zn-based nanoproduct (Zinkicide™) is currently in the registration process for use in controlling citrus canker caused by *Xanthomonas citri* subsp. *citri*. [24,54]. In field trials, disease incidence was reduced more than traditional cuprous oxide (Cu_2O) and cuprous oxide/zinc oxide (Cu_2O/ZnO) bactericides. It was also reported that Zinkicide™ treatments were effective in suppressing citrus scab (*Elsinoe fawcetti*) and melanose (*Diaporthe citri*) on grapefruit. In addition, the registering of new nano-Zn products for crop disease management is encouraging and highlights the recognition of nanoparticles as a viable alternative to conventional strategies.

There are numerous single reports of many less studied nano-metal oxides, metalloids, and nonmetals being used to suppress plant diseases. NPs of Al, Au, B, Ce, Fe, Mg, Mn, Mo, Ni, S, Si and Ti being used to manage a range of plant diseases [2,11,17,18,23,46,48,53]. Many of these reports arise from single studies so more information on their efficacy in other systems is needed, along with proper comparison to the salt and bulk equivalents. NP Si has received more attention in several systems given the known effect that Si has on plant health [13]. One unique feature of Si is that it is most effective when there is continuous supply, forcing grower to maintain constant availability of Si in the soil [13]. Single applications of NP Si would need to provide Si ions over a crucial period to maintain plant defense. Mesoporous NP Si may meet this criterion given the slow dissolution of Si from the product [5,51,55].

The use of NP Al_2O_3 [48], MgO [28,53], NP TiO_2 [8,14,18,41,43], NP S [10,23,46], and NP CeO_2 [2] have all show efficacy in suppressing diseases in different systems. Most studies have been able to correlate NP amendment with direct alteration of the host defense mechanisms. Furthermore, when the bulk or salt form of these elements/molecules was compared to the nano form, the latter was consistently more effective in promoting health, often with significantly less of the active metal being applied.

Carbon nanomaterials

The allotropic character of carbon allows for a wide array of nanomaterial morphologies and structures. Three types have demonstrated efficacy in plant disease suppression, but reports are still quite limited. To date, carbon nanotubes (single wall or multiwall), graphene oxide (oxidized and reduced forms), and fullerenes have demonstrated potential to affect plant health, which in turn suggests an important disease management tool could be exploited. *In vitro* studies have found that carbon nanotubes can restrict growth of many plant pathogens, including *Xanthomonas* [35], *Aspergillus* spp., *Botrytis cinerea* [26] and *Fusarium* spp. [52]. The mechanisms for inhibition may be physical, with the sharp nano-edges directly damaging cell walls of the pathogens [6,9,26,35,47,52]. Currently, there are no field studies with carbon nanomaterials and plant disease so much additional work is needed, but given the relatively low cost of producing carbon nanomaterials, serious investigation should be targeted at these materials as management tools.

Summary

Engineered nanoparticles are increasingly used in disease management strategies as bactericides/fungicides and as nanofertilizers to enhance plant health. To date, most reports have centered on NPs of Ag, Cu, and Zn for their antimicrobial activity and their ability to alter host defense. We predict that nanoparticles will ultimately may play a major role in suppressing disease in both the greenhouse and field. One major impact of using nanoparticles in disease management is the large reduction in active metals entering the environment when compared to the conventional metallic fungicides. One challenging obstacle facing researchers is that nanomaterials might behave differently in different plant/disease systems, requiring that each disease system may need separate evaluation. Chemists will need to continue to play a major role in developing novel nanocomposites and new formulations to overcome the tendency of many of these nanoparticles to hetero/homoaggregate or agglomerate over time into larger and less efficacious particles. Given the large challenges currently faced in agriculture, the development of nano-enabled disease suppression strategies will most certainly be an important tool in the effort to achieve and sustain global food security.

Conflict of interest statement

Nothing declared.

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