Crop Protection 35 (2012) 64–70

Contents lists available at SciVerse ScienceDirect

Crop Protection

journal homepage: www.elsevier.com/locate/cropro

Review

Applications of nanomaterials in agricultural production and crop protection: A review

Lav R. Khot [a], Sindhuja Sankaran [a], Joe Mari Maja [a], Reza Ehsani [a,*], Edmund W. Schuster [b]

[a] Department of Agricultural and Biological Engineering, Citrus Research and Education Center, University of Florida, Lake Alfred, FL 33850, USA

[b] Laboratory for Manufacturing and Productivity, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

ARTICLE INFO

Article history:
Received 6 September 2011
Received in revised form
13 January 2012
Accepted 16 January 2012

Keywords:
Plant germination
Nanopesticides
Pesticide residue detection
Pathogen detection

ABSTRACT

Recent manufacturing advancements have led to the fabrication of nanomaterials of different sizes and shapes. These advancements are the base for further engineering to create unique properties targeted toward specific applications. Historically, various fields such as medicine, environmental science, and food processing have employed the successful and safe use of nanomaterials. However, use in agriculture, especially for plant protection and production, is an under-explored area in the research community. Preliminary studies show the potential of nanomaterials in improving seed germination and growth, plant protection, pathogen detection, and pesticide/herbicide residue detection. This review summarizes agricultural applications of nanomaterials and the role these can play in future agricultural production.

1. Introduction

Materials with a particle size less than 100 nm in at least one dimension are generally classified as nanomaterials. The development of nanotechnology in conjunction with biotechnology has significantly expanded the application domain of nanomaterials in various fields. A variety of carbon-based, metal and metal oxide-based dendrimers (nano-sized polymers) and biocomposites nanomaterials (EPA [Environment Protection Agency], 2007; Nair et al., 2010) are being developed. Types include single-walled and multi-walled carbon nanotubes (SWCNT/MWCNT), magnetized iron (Fe) nanoparticles, aluminum (Al), copper (Cu), gold (Au), silver (Ag), silica (Si), zinc (Zn) nanoparticles and zinc oxide (ZnO), titanium dioxide (TiO_2), and cerium oxide (Ce_2O_3), etc. General applications of these materials are found in water purification, wastewater treatment, environmental remediation, food processing and packaging, industrial and household purposes, medicine, and in smart sensor development (Jain, 2005; Wei et al., 2007; Chau et al., 2007; Byrappa et al., 2008; Zhang and Webster, 2009; Gao and Xu, 2009; Qureshi et al., 2009; Lee et al., 2010; Zambrano-Zaragoza et al., 2011; Bradley et al., 2011). The majority of applications in these areas have focused on the significance of the nanomaterials for improved efficiency and productivity. These materials are also used in agriculture production and crop protection (Bouwmeester et al., 2009; Nair et al., 2010; Sharon et al., 2010; Emamifar et al., 2010).

A precedent exists for conducting comprehensive literature reviews as a guide to the further development of nanomaterials applications. Reviews are available involving water disinfection (Li et al., 2008), the food industry (Sanguansri and Augustin, 2006), non-point source pollution control (Shan et al., 2009), treatment of environmental waste (Macaskie et al., 2010), and the design of trace concentration detection devices (Zhang and Fang, 2010). However in the field of agriculture, the use of nanomaterials is relatively new and needs further exploration. No previous literature reviews exist. As such, this article summarizes the developments and application of novel nanomaterials in agriculture. Topics include: plant germination and growth, plant protection and production, pathogen detection, and pesticide/herbicide residue detection.

2. Plant germination and growth

In recent years, various researchers have studied the effects of nanomaterials on plant germination and growth with the goal to promote its use for agricultural applications. Zheng et al. (2005) studied the effects of nano and non-nano TiO_2 on the growth of naturally-aged spinach seeds. It was reported that nano-TiO_2 treated seeds produced plants that had 73% more dry weight, three times higher photosynthetic rate, and 45% increase in chlorophyll-a formation compared to the control over germination period of 30

* Corresponding author. Tel.: +1 863 956 8770; fax: +1 863 956 4631.
E-mail address: ehsani@ufl.edu (R. Ehsani).

0261-2194/$ – see front matter
doi:10.1016/j.cropro.2012.01.007

days. The growth rate of spinach seeds was inversely proportional to the material size indicating that smaller the nanomaterials the better the germination. The key reason for the increased growth rate could have been the photo-sterilization and photo-generation of "active oxygen like superoxide and hydroxide anions" by nano-TiO_2 that can increase the seed stress resistance and promote capsule penetration for intake of water and oxygen needed for fast germination. The authors concurred that the nano size of TiO_2 might have increased the absorption of inorganic nutrients, accelerated the breakdown of organic substances, and also caused quenching of oxygen free radicals formed during the photosynthetic process, hence increasing the photosynthetic rate.

The key to increased seed germination rate is the penetration of nanomaterials into the seed. Khodakovskaya et al. (2009) reported that MWCNTs can penetrate tomato seeds and increase the germination rate by increasing the seed water uptake. The MWCNTs increased the seed germination, up to 90% (compared to 71% in control) in 20 days, and the plant biomass. However, authors insisted the importance of additional studies for evaluating the resistance of CNT germinated tomato plants to pests and also evaluating the toxic effects of CNT on other field plants prior to their direct field applications. Study on the influence of metal nanoparticles (Si, Palladium-Pd, Au, Cu) on germination of lettuce seeds (Shah and Belozerova, 2009) indicated that nanoparticles (Pd, Au at low concentrations; Si, Cu at higher concentrations, and combination of Au and Cu) had a positive influence on seed germination, measured in terms of shoot to root ratio and growth of the seedling. Authors also attempted to determine if the nanoparticles affected the soil microorganisms, but no definite effect could be found.

The effect of nanoparticles on plants can be positive or negative (Monica and Cremonini, 2009). One of the concerns for nanomaterials applications in seed germination is their phytotoxicity. The level of phytotoxicity may depend on the type of nanomaterial and its potential application. For example, the applicability of fluorescein isothiocyanate (FTIC)-labeled silica nanoparticles and photostable Cadmium-Selenide (CdSe) quantum dots were tested for their ability to be used as biolabels and for promoting seed germination. It was found that FTIC-labeled silica nanoparticles induced seed germination in rice, while quantum dots arrested the germination (Nair et al., 2011).

Lin and Xing (2007) evaluated phytotoxicity of nanomaterials (MWCNTs, Aluminum oxide-Al_2O_3, ZnO, Al and Zn) and its impact on germination rates in radish, rape canola, ryegrass, lettuce, corn, and cucumber. They conferred the hypothesis that the higher concentrations (2000 mg/L) of nano-sized Zn (35 nm) and ZnO ($\sim$20 nm) inhibited the germination in ryegrass and corn, respectively. Root length of studied species was also inhibited with use of 200 mg/L nano-Zn and ZnO. Phytotoxicity of nano-Al and Al_2O_3 significantly affected root elongation of ryegrass and corn, respectively; whereas, nano-Al facilitated the radish and rape root growth.

Ma et al. (2010) studied the effects of four oxide nanoparticles (CeO_2, Lanthanum (III) oxide-La_2O_3, Gadolinium (III) oxide-Gd_2O_3, Ytterbium oxide-Yb_2O_3) on the radish, rape, tomato, lettuce, wheat, cabbage, and cucumber plant species. Similar to Lin and Xing (2007), they found that the root growth depended on nanoparticles and its concentration. Ma et al. (2010) reported that the nano-CeO_2 did not affect root elongation in plant species except for lettuce at 2000 mg/L concentration. However, the other three types of nanoparticles (La_2O_3, Gd_2O_3, Yb_2O_3) greatly affected root growth at same concentration. Moreover, the inhibitory effect of these nanoparticles was observed during different stages of root growth.

Thus, the phytotoxic behavior of the nanomaterials needs to be thoroughly understood before utilizing nanomaterials under field conditions. A possible solution to avoid the phytotoxicity to other plant species would be to grow the plant seedlings in a greenhouse and later transferring them to field. This would be more suitable for ornamental and specialty crops.

Applicability and phytotoxicity of silver nanomaterials in agriculture is well debated by the EPA (Bergeson, 2010a,b). As reported by Bergeson (2010a), there are more than 100 pesticides that contain Ag due to its anti-microbial properties. However, toxicity of nanosilver to ecosystem and human is a major concern. Lu et al. (2010) have reported that the citrate-coated colloidal Ag nanoparticles were not genotoxic (genetic), cytotoxic (cell), and phototoxic (toxicity through photo-degradation) to humans, however; citrate-coated Ag nanoparticles in powder form were toxic. The authors argued that this could be because of the "chemical change of spherical silver nanoparticle in the powder to form silver oxides or ions." Interestingly, the photoxicity of the powdered Ag nanoparticles was repressed by coating them with biocompatible polyvinylpyrrole (Lu et al., 2010). Exploring such biocompatible coatings to reverse the toxicity of nanomaterials would increase the chances of applying nanomaterials in plant germination and growth. Research is also needed to investigate the adverse effect of such coatings on the desired seed/plant properties and the effectiveness of nanomaterials.

Oancea et al. (2009) hypothesized that controlled release of active plant growth stimulators and other chemicals encapsulated in nanocomposites made of layered double hydroxides (anionic clays) could be another feasible option for organic agriculture. However, leading food organic certifiers (e.g. UK soil association, Biological farmers of Australia) abstain from considering nanomaterial-based agri-foods as of organic standards (Scrinis and Lyons, 2010). Recently, German-based organizations such as Naturland and the International Federation of Organic Agriculture Movements (IFOAM) prohibited labeling food products grown with artificial nanomaterials as organic (Naturland, 2011; IFOAM, 2011).

Nonetheless, future research on nanomaterials for plant germination and growth should address some of the following challenges (as reported by Nair et al., 2010): 1) unpredictability in reaction of nanomaterials to different plants, 2) phytotoxicity due to higher concentrations, and 3) reduced intake and photosynthesis of plant due to larger nanomaterials.

3. Plant protection and production

Nanopesticides "involve either very small particles of pesticidal active ingredients or other small engineered structures with useful pesticidal properties" (Bergeson, 2010b). Nanopesticides can increase the dispersion and wettability of agricultural formulations (i.e., reduction in organic solvent runoff), and unwanted pesticide movement (Bergeson, 2010a). Nanomaterials and biocomposites exhibit useful properties such as stiffness, permeability, crystallinity, thermal stability, solubility, and biodegradability (Bouwmeester et al., 2009; Bordes et al., 2009) needed for formulating nanopesticides. Nanopesticides also offer large specific surface area and hence increased affinity to the target (Jianhui et al., 2005). Nanoemulsions, nanoencapsulates, nanocontainers, and nanocages are some of the nanopesticide delivery techniques that have been discussed recently (Lyons and Scrinis, 2009; Bouwmeester et al., 2009; Bergeson, 2010b) for plant protection. Table 1 reports some of the recent applications of nanomaterials in agricultural plant protection and production.

Basically, the nano-formulations should degrade faster in the soil and slowly in plants with residue levels below the regulatory criteria in foodstuffs. Jianhui et al. (2005) reported the development of such sodium dodecyl sulfate (SDS) modified photocatalytic TiO_2/Ag nanomaterial conjugated with dimethomorph