Applications of nanotechnology in agriculture

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1 Introduction

Agriculture is one of the building blocks of the national economy in developing countries. Rising food production rates play a significant role in the growth of a country's Gross Domestic Production (GDP). Food production rate is dependent on applied fertilizers and pesticides in the country. Various parameters like food security, climate change, soil-health and water availability directly impact food production and agriculture growth. Therefore, it is necessary to regulate the adverse conditions of agriculture to enhance food production for expanding world population in a sustainable manner.

Nanotechnology as an upcoming technology has shown its potentials in various fields like solar, electronics, optics, and pharmaceuticals (Chhipa & Joshi, 2016). To meet targets in food production and combat various rising issues in agriculture, scientists are working to deal with these issues using nanotechnology. Some of the rising issues are: (1) Food security for population increases, (2) reduced production on cultivable land, (3) low agriculture input efficiency, (4) large uncultivable land, (5) low shelf life of food products, (6) post-harvest losses of food products, and (7) increasing pest attacks and plant diseases (Bhagat, Gangadhara, Rabinal, Chaudhari, & Ugale, 2015). Subsequently, soil fertility is constantly decreasing by unjustifiable use of chemicals. Only a small portion of these chemical agri inputs are used by plants and the rest are unused chemicals that negatively impact on the ecosystem. The unused chemical fertilizers and pesticides are leached into the soil or runaway with water to water bodies and generate chemical pollution to untargeted organisms. The application of nanotechnology in agriculture minimizes the cost of fertilizers and pesticides by advancing these tools. Employment of nanotechnology based techniques improves the smart characteristics in the agri-inputs as targeted delivery, controlled release, increasing solubility and long shelf-life. These characteristics not only make them more efficient but also reduce the risk of environmental contamination (McKee & Filser, 2016; Mishra, Singh, Keswani, & Singh, 2014;

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Sodano & Verneau, 2014). Such smart nanomaterials increase agriculture production in a sustainable manner. Various metal, metal oxide, polymer based nanomaterials, carbon nanotubes, engineered nanomaterials, and nanoformulations with active ingredient based nanofertilizers and nanopesticides showed their potential in sustainable agriculture production (Al-Othman et al., 2014; Fraceto et al., 2016; Khadri, Alzohairy, Janardhan, Kumar, & Narasimha, 2013; Morsy, Khalaf, Sharoba, El-Tanahi, & Cutter, 2014; Parizi et al., 2014). Further, Green synthesis of nanomaterials increased the potential of metal and metal oxide nanomaterials in agriculture by reducing toxicity and increasing stability. On the other hand, the use of nanosensors in pest and soil condition detection also improved conventional agriculture to smart agriculture systems.

In contrast, negative impacts of nanotechnology in agriculture have also been reported for toxicity to plants and ecosystems (Prasad, Jauhari, & Tiwari, 2014; Rizwan et al., 2017) and the use of polymer based nanoparticles and green synthesis of nanomaterials extend the scope of nanotechnology in agriculture. Metal based nanoparticles also expressed positive results in seed germination, plant growth and pest control under limited concentration range (Lee, An, Yoon, & Kweon, 2008; Liu et al., 2005). Therefore in the current chapter, we summarized the application of various types of metal nanoparticles, metal oxide nanoparticles, polymer based nanomaterials, green synthesized nanomaterials, nanoformulation based fertilizers or pesticides in agriculture and their impact on plant growth and pathogen control. The application of nanomaterials as sensors for detection of soil nutrient, pest control and food safety was also discussed. The use of nanotechnology impacted agriculture in both positive and negative ways but more research is required for long term impact assessment.

2 Nanotechnology

Nanotechnology is the science of materials which have their size in the range of nanometre (<100 nm). In this size range, nanomaterials have specific and unique chemical and optical properties (Khan & Rizvi, 2014). In comparison to bulk material, nanomaterials have high surface to volume ratios and specific surface plasma resonance, which increases their potential for various applications. In agriculture, nanotechnology can also be used in various applications including nanofertilizers, nanopesticides, and nanosensors. The detailed description of nanotools in agriculture is given in the next section.

3 Nanotechnology in agriculture

Nanotechnology is an emerging technology in the area of medicine, electronics, electrical, solar, optical and agriculture. In agriculture, nanotechnology has provided different agri tools in the form of nanofertilizer, nanopesticide and nanosensor which have shown significant results for sustainable agriculture practice (Fig. 1). Such

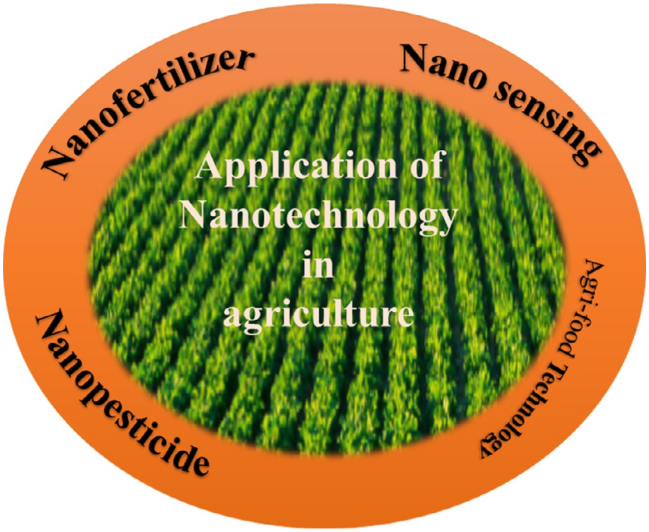

FIG. 1

Applications of nanotechnology in agriculture: Nanotechnology is used in the form of nanofertilizers, nanopesticides, nanosensors and agri food agents to increase food production in a sustainable manner.

nanoinputs not only reduced the amount of fertilizers or pesticides but also provided targeted delivery of active agents. Therefore, non-targeted organisms remain unaffected with these nanotools and environment safety can be retained. Nanosensors also provided quick and accurate information regarding soil conditions or pathogen detection so the control can be done on time and crop can be safe, which is helpful in reducing losses to farmers and improving their economic situation.

Different nanoparticles have been applied as nanofertilizers, nanopesticides and in nanosensing at lab and green house level. Some of these nanofertilizers have been developed as commercial products such as Nano-Gro™ for plant growth regulator and immunity inducer, developed by Agro Nanotechnology Corp, FL, United States, Nano green for plant nutrition developed by Nano Green Sciences, Inc., India, Nano-AgAnswer® developed by Urth Agriculture, CA, United States for plant nutrition, Biozar Nanofertilizer contains micro and macro nanonutrients synthesized by Fanavar Nano-Pazhoohesh Markazi Company, Iran, Nano Max NPK Fertilizer developed by JU Agri Sciences Pvt. Ltd., New Delhi, India, Master Nano Chitosan Organic Fertilizer developed by Pannaraj Intertrade, Thailand and TAG NANO which contains a mixture of micronutrients, vitamins, probiotics, seaweed extract and humic acid developed by Tropical Agrosystem India (P) Ltd., India (Prasad, Bhattacharyya, & Nguyen, 2017). The nanopesticides of known active compounds have also been developed as nanoformulations but more data is required on toxicity, durability, fate of nanopesticides in the ecosystem and regulatory agency approval for their commercial production (Kookana et al., 2014).

3.1 Smart nanofertilizers

Nanofertilizers are a recent advancement in the field of agriculture. The nanosize and high volume to surface area make them more efficient in comparison to normal fertilizers. Different types of nanofertilizers have been developed such as silver, iron, zinc, titanium, carbon nanotubes, molybdenum and silica and applied on various crop systems (Table 1). Researchers have found that nanomaterials showed efficient impact on root elongation, shoot elongation, plant biomass, chlorophyll content and seed germination at certain concentrations.

Mochizuki, Gautam, Sinha, and Kumar (2009) stated that fertilizers in nanoform move faster in comparison to conventional fertilizers. They explained that nanofertilizers follow the laws of thermodynamics and have more entropy due to colloid suspension state in comparison to ordinary fertilizers. The entropy is directly proportional to Gibbs energy which helps in faster movement of colloidal state nanofertilizers, facilitating their easy penetration into the cell membrane of plants. Kottegoda et al. (2017) worked on smart delivery of urea using hydroxyapatite and found that release of urea by urea-hydroxyapatite nanohybrid was controlled by up to 1 week. They developed these nanohybrids by mixing urea and hydroxyapatite in the ration of 6:1 (urea: HA NPs). Hydroxyapatite is known as a rich source of phosphorus and is bio-compatible in nature, making them a sustainable source of smart carrier of fertilizers. They inferred that urea bound weakly to hydroxyapatite nanoparticles (HA NPs) and was slowly released into the soil on demand, enhancing plant growth. Synthesis of nanochitosan-nitrogen, phosphorus and potassium (NPK) and their application in the growth of wheat has been reported by Abdel-Aziz, Hasaneen, and Omer (2016). These authors applied nanochitosan-NPK fertilizers using foliar spray on wheat plants and found that nanofertilizers entered into plants through stomata and were transported via phloem tissue. They observed that the use of nanofertilizers significantly increased wheat yield and reduced the life cycle of wheat plants by 23.5%. The nano-NPK improved photosynthesis via enhancing water absorption and worked as a biological pump for nutrient absorption (Ma, Liu, & Zhang, 2009; Wu, 2013). Further, it was also reported that plasma membrane permeability and cell mortality also increased with the nano-NPK exposure (Du et al., 2011; Wang, Tarafdar, & Biswas, 2013). The nanoparticles internalized in the cytoplasm during endocytosis or transport into the cytoplasm via embedded ion transporter carrier proteins. In the cytoplasm, nanoparticles bound with different cytoplasmic organelles and affected plant metabolic processes (Jia et al., 2005).

Zinc oxide nanoparticles (ZnO NPs) also exposed as nanofertilizers and showed both positive and negative impact on plant growth. The beneficial and detrimental impact of ZnO NPs on plants depend on the concentration of metal oxide. A concentration of 10 mg/kg ZnO NPs showed increased photosynthesis and biomass in lettuce (Xu, Luo, Wang, & Feng 2018). Zinc oxide nanoparticles supported the CO_2 supply at the carboxylation site in chloroplasts by improvement of carbonic anhydrase, which facilitated increasing photosynthesis (DiMario, Clayton, Mukherjee, Ludwig, & Moroney, 2017). Similarly, Raliya and Tarafdar (2013) also found growth

Table 1 Application of nanomaterials as nanofertilizer on various crop.

Nanoparticles	Crop	Positive impact on crop	References
Silver nanoparticles	*Crocus sativus*	Root elongation	Rezvani, Sorooshzadeh, and Farhadi (2012)
	Hordeum vulgare	Root elongation	Gruyer, Dorais, Bastien, Dassylva, and Triffault-Bouchet (2013)
	Boswellia ovalifoliolata	Improved growth	Savithramma, Ankanna, and Bhumi (2012)
	Brassica juncea	Improved growth	Sharma et al. (2012)
	Phaseolus vulgaris	Improved growth	Salama (2012)
Gold nanoparticles	*Brassica juncea*	Improved growth	Arora et al. (2012)
	Gloriosa superba	Improved growth	Gopinath, Gowri, Karthika, and Arumugam (2014)
Carbon-coated Fe-NPs	*Cucurbita pepo*	Chlorophyll increased	Delfani, Baradarn Firouzabadi, Farrokhi, and Makarian (2014)
Carbon nanotubes	*Solanum lycopersicum*	Germination increased	Khodakovskaya et al. (2009)
	Cicer arietinum	Growth increased	Tripathi, Sonkar, and Sarkar (2011)
Copper nanoparticles	*Phaseolus radiatus*	Growth increased	Lee et al. (2008)
	Triticum aestivum	Growth increased	Lee et al. (2008)
	Lactuca sativa	Growth increased	Shah and Belozerova (2009)
	Edodea densa	Photosynthesis increased	Nekrasova, Ushakova, Ermakov, Uimin, and Byzov (2011)
Iron nanoparticles	*Vigna unguiculata*	Chlorophyll increased	Liu et al. (2005)
	Glycine max	Chlorophyll increased	Malekian, Abedi-Koupai, and Eslamian (2011)
Manganese nanoparticles	*Vigna radiata*	Growth increased	Ghafariyan et al. (2013)
Molybdenum nanoparticles	*Cicer arietinum*	Increased nodule formation	Taran et al. (2014)
Multiwalled carbon nanotubes	*Lolium multiflorum,*	Root elongation	Lin and Xing (2007)
	Brassica napus,	Root elongation	Lin and Xing (2007)
	Zea mays	Root elongation	Lin and Xing (2007)
	Solanum lycopersicum	Improved plant growth	Khodakovskaya et al. (2013)
	Zea mays	Improved plant growth	Tiwari et al. (2014)
	Zea mays	Improved plant growth	Lahiani et al. (2013)
	Glycine max	Improved plant growth	Lahiani et al. (2013)
	Triticum aestivum	Improved plant growth	Wang et al. (2012)
	Brassica juncea	Germination increased	Ghodake, Seo, Park, and Lee (2010)
	Phaseolus mungo	Germination increased	Ghodake et al. (2010)
	Brassica juncea	Germination increased	Mondal, Basu, Das, and Nandy (2011)

Continued

Table 1 Application of nanomaterials as nanofertilizer on various crop.—cont'd

Nanoparticles	Crop	Positive impact on crop	References
Silicon nanoparticles	*Lycopersicum esculentum*	Improved growth	Siddiquee et al. (2014)
	Zea mays	Improved growth	Suriyaprabha et al. (2012)) and Suriyaprabha, Karunakaran, Yuvakkumar, Rajendran, and Kannan, 2012
	Larix olgensis	Improved growth	Bao-shan, Chun-hui, Li-jun, Shu-chun, and Min (2004)
	Cucurbita pepo	Improved growth	Siddiquee et al. (2014)
Single walled carbon nanotubes	*Allium cepa*	Root elongation increase	Cañas et al. (2008)
	Cucumis sativus	Root elongation increase	Cañas et al. (2008)
Titanium nanoparticles	*Spinacia oleracea*	Rubisco activity increased	Su et al. (2009)
	Lemna minuta	Growth increased	Song et al. (2012)
	Vigna radiata L.	Improved growth	Raliya, Biswas, and Tarafdar (2015) and Raliya, Nair, et al., 2015
Titanium nanoparticles and zinc nanoparticles	*Solanum lycopersicum L.*	Growth found	Raliya, Biswas, and Tarafdar (2015) and Raliya, Nair, et al. (2015)
Zinc complexed chitosan nanoparticles	*Triticum aestivum*	Improved zinc utilization	Dapkekar, Deshpande, Oak, Paknikar, and Rajwade (2018)
Zinc nanoparticles	*Vigna radiata* and *Cicer arientinum*	Growth increased	Mahajan, Dhoke, and Khanna (2011)
	Cucumis sativus	Growth found	Zhao, Liu, et al. (2014) and Zhao, Peralta-Videa, et al. (2014)
	Brassica napus	Root length	Lin and Xing (2007)
	Lolium perenne	Root elongation	Lin and Xing (2007)
	Arachis hypogaea	Increased seed germination and growth	Prasad et al. (2014)
	Glycine max	Increased seed germination	Sedghi, Hadi, and Toluie (2013)
	Triticum aestivum	Growth observed	Ramesh, Palanisamy, Babu, and Sharma (2014)
	Pennisetum americanum	Growth found	Tarafdar, Raliya, Mahawar, and Rathore (2014)
	Allium cepa	Seed germination	Raskar and Laware (2014)
	Cyamopsis tetragonoloba	Growth Increased	Raliya and Tarafdar (2013)
	Cucumis sativus	Growth Increased	de la Rosa et al. (2013)

in biomass, root, shoot and root area of *Cyamopsis tetragonoloba* at 10 mg/kg ZnO NP concentration. In the case of *Arachis hypogaea* seed germination and seedling vigour index improvement was achieved at 400–1000 ppm concentration. Prasad et al. (2012) found increased root length, chlorophyll content and biomass in *Arachis hypogaea* plant after seedlings were treated with 400–1000 ppm ZnO nanoparticles. Janmohammadi, Amanzadeh, Sabaghnia, and Dashti (2016) used micronutrient iron, zinc nanofertilizer and nanotitanium dioxide (TiO_2) on barley and grain in field experiments and found changes in chlorophyll, spike length, numbers of grain and grain mass. ZnO nanofertilizer showed various positive impacts on plant growth such as promoted germination, increased chlorophyll content, oxidative stress reduction, induced antioxidative compound production and promoted root growth in different crops such as *Arachis hypogaea*, *Vigna radiate*, *Cicer arietinum*, *Helianthus annuus*, *Lupinus termis*, *Solanum lycopersicum*, *Glycine* max and *Cyamopsis tetragonoloba* L. at different ZnO concentration (El-Kereti, El-feky, Khater, Osman, & El-sherbini, 2013; Latef, Alhmad, & Abdelfattah, 2017; Mahajan et al., 2011; Prasad et al., 2012; Singh et al., 2016; Subbaiah et al., 2016). Detailed information on Zn nanoparticles in plants has been reviewed by Sturikova, Krystofova, Huska, and Adam (2018).

To address the issue of toxicity of nanoparticles, researchers developed polymer based nanoparticles which reduced or decreased toxicity of metal nanoparticles to plants. Dapkekar et al. (2018) synthesized zinc complexed chitosan nanoparticles (Zn-CNP) and used them on wheat crops in field experiments. They reported that the efficiency of zinc was increased without affecting the grain yield, protein content, spikelets per spikes. They found that Zn-CNP were novel nanofertilizers which increased the fertilizers efficiency and reduced excess fertilizer runoff in soil. Similarly, iron oxide nanoparticles also showed a positive impact on plant growth and increased seed germination, chlorophyll and root growth in *Citrullus lanatus* (watermelon) and *Vigna radiata* L. (Li et al., 2013; Ren et al., 2011). Recently, Wang and Nguyen (2018) synthesized chitosan nanoparticles with zinc (Zn) and boron (B) and applied them to coffee plants at 0–40 ppm concentration. They found that micronutrient nanofertilizer increased chlorophyll content and photosynthesis. Therefore, leaf area and plant growth increased significantly. Nanosize of particles facilitated penetration into leaf stomata, cuticle and roots system of plants, and easy transportation to xylem and phloem and they reached the cell system to induce physiology and metabolic activity for plant growth (DeRosa, Monreal, Schnitzer, Walsh, & Sultan, 2010; Eichert, Kurtz, Steiner, & Goldbach, 2008).

Nanoparticles play a significant role in plant growth and affect different plant mechanisms. High surface to volume ratio and nanosize increased their catalytic activity in comparison to their bulk counterpart. Nanoparticles increased seed germination via enhancement of water absorption capacity of seeds, promoted antioxidant activity, reduced hydrogen peroxide, malonyldialdehyde content, superoxide radicals, increased enzymes like nitrate reductase, ascorbate peroxidase, catalase, guaiacol peroxidase, and superoxide dismutase (Feizi, Moghaddam, Shahtahmassebi, & Fotovat, 2012; Lei et al., 2008; Lu, Zhang, Wen, Wu, & Tao, 2002). ZnO NPs were found to be effective in seed germination and increased germination rate up to 20% in rice at exposure of 0–750 ppm concentration (Adhikari, Sarkar, Mashayekhi, & Xing, 2016).

In addition to nanoparticles alone, in combination with bio-fertilizers, nanofertilizers showed synergistic effects on plant growth. Rane, Bawskar, Rathod, Nagaonkar, and Rai (2015) developed a combination of calcium phosphate nanoparticles (CaPNPs) with mycorrhizal fungi *Piriformospora indica* and *Glomus mosseae* separately and applied them on *Zea maize*. These authors found an increased vitality of *Zea maize* plant in terms of increased chlorophyll content and root proliferation. Different micronutrient nanofertilizers like zinc oxide, iron oxide, titanium oxide showed improved uptake of nutrient and supported increased enzymatic activities in *Arachis hypogea*, *Cicer arietinum* L., *Spinacia oleracea*, *Glycin* max L. and *Pennisetum americanum* (Burman, Saini, & Kumar, 2013; Liu & Lal, 2014; Pradhan et al., 2014; Priester et al., 2012; Tarafdar et al., 2014).

3.2 Effective nanopesticide

Crop pests are also of serious concern in agriculture, which damage crop growth and production by inducing diseases and reduce the farmer's output. Worldwide, crops equivalent to $220 billion are lost annually due to crop diseases (Sharma, Kooner, & Arora, 2017). Plant diseases are caused by various pathogens such as bacteria, fungi, viruses, nematodes, parasites, insects, and protozoa. To control them, different chemical and biological pesticides have been applied but inappropriate use of chemical pesticides have destroyed the environmental balance and increased resistance in pests. To reduce the drastic impact on agriculture of increasing resistance in crop pathogens, there is a need for the innovation of new methods to control environmental imbalance and there is growing hope in the agriculture community that nanotechnology will fulfil this hope. Applications of nanotechnology in plant protection also influenced the agriculture field and increased crop production. Different types of metal nanoparticles including nanoformulations, nanoencapsulated active ingredients, and nanocomposites have been reported for protection of agriculture crops (Table 2).

Various nanomaterials have been shown to have high inhibitory activity against crop pathogens at lab as well as greenhouse levels (Fig. 2). Nanomaterials include silver nanoparticles (Ag NPs), nanocopper, nanosilica, and nanoformulations of chemical pesticides such as hexaconazole, sulphur showed good pesticide activity against different insect pests and fungal pathogens. Nanoformulations increased the solubility and shelf life of active ingredients and increased the activity with controlled release characteristic of nanocarriers. Different types of nanoformulations including essential oils (such as neem oil, garlic essential oil, *Artemisia arborescens* L essential oil and *Lippia sidoides* oil), plant extracts (capsaicin from chilli peppers and Lansiumamide B extract) have shown that nanoformulations increase shelf life by preventing premature degradation of active ingredients while not effecting non-targeted organisms under insecticidal application (Anjali, Sharma, Mukherjee, & Chandrasekaran, 2012; Bohua and Ziyong, 2011; Jerobin, Sureshkumar, Anjali, Mukherjee, & Chandrasekaran, 2012; Lai, Wissing, Müller, & Fadda, 2006; Xu et al., 2010; Yang, Li, Zhu, & Lei, 2009; Yin, Guo, Han, Wang, & Wan, 2012).

Table 2 Application of nanoparticles and nanoparticles based formulation in crop protectants.

S. No.	Nanoparticles/nanoformulation	Applications	References
1	Nanosilica (Si)	Anti-feedant	El-Bendary and El-Helaly (2013)
2	Silver (Ag)	Bactericidal	El-Rahman and Mohammad (2013)
3	Nanocopper (Cu)	Bactericidal	Mondal and Mani (2012)
4	Titanium oxide with Ag and Zn	Bactericidal	Paret, Palmateer, and Knox, (2013)
5	Silver nanoparticles on graphene oxide	Bactericidal	Ocsoy et al. (2013)
6	Titanium dioxide with zinc	Bactericidal	Paretet al. (2013) and Paret, Vallad, et al. (2013)
7	Zinc oxide (ZnO)	Bactericidal	Hafez, Hassan, Elkady, and Salama (2014)
8	Silver (Ag)	Fungicidal	Khadri et al. (2013)
9	Copper (Cu)	Fungicidal	Kanhed et al. (2014)
10	Thiamine dilauryl sulphate (TDS) nanoparticles	Fungicidal	Seo et al. (2011)
11	Validamycin loaded with nanosized calcium carbonate	Fungicidal	Qian et al. (2011)
12	Chitosan NPs (CSNPs)	Fungicidal	Chookhongkha, Sopondilok, and Photchanachai (2012)
13	Copper (Cu)	Fungicidal	Giannousi et al. (2013)
14	Chitosan-based nanoparticles (CSNPs)	Fungicidal	Saharan et al. (2013)
15	Copper and silver	Fungicidal	Ouda (2014)
16	Chitosan	Herbicidal	Grillo et al. (2014)
17	Carboxy methyl chitosan	Herbicidal	Yu et al. (2015)
18	Polyepsilon caprolactone	Herbicidal	Pereira, Grillo, Mello, Rosa, and Fraceto (2014)
19	Silver (Ag)	Pesticidal	Ali, Yousef, and Nafady (2015)
20	Silver (Ag)	Seed dressing	Anand and Kulothungan (2014)
21	Silver (Ag)	Surface sterilizer of seed crops	Morsy et al. (2014)

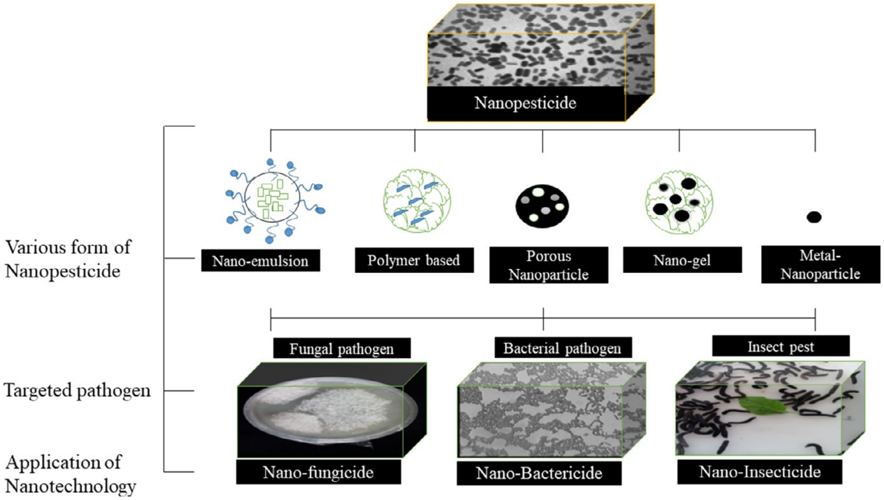

FIG. 2

Application of nanopesticides in agriculture: Nanopesticides have been used to control various fungal, bacterial and insect pathogens in the form of nanofungicide, nanobactericide and nanoinsecticide.

In addition to metal or polymer nanoparticles, currently, nanoemulsion is another interesting research topic in the field of nanopesticides. In nanoemulsion, surfactant amount has been decreased from 20% to 5%. Nanoemulsion increased the retention capacity of active ingredient to the plants due to nanosize and increased uptake. Anjali et al. (2010, 2012) reported that nanoemulsion of permethrin and neem oil showed higher efficacy in comparison to the active ingredient as larvicidal application. Nanoemulsion also provided efficient targeted delivery and decreased the impact on non-targeted organisms (Jiang et al., 2012; Lim et al., 2013).

3.2.1 Nanofungicide

Fungal pathogens are one of the major problems for the growth of crops, which are responsible for >70% of crop diseases and significantly reduce crop production by up to 100% loss (Baker, Volova, Prudnikova, Satish, & Prasad, 2017). Different types of metal nanoparticles and nanoformulations have been proposed to control fungal pathogens. Rabab and El-Shafey (2013) found that silver nanoparticles reduced the growth of *Magnaporthe grisea*, a fungal pathogen that causes rice blast disease. Previously, Gajbhiye, Kesharwani, Ingle, Gade, and Rai (2009) also used silver nanoparticles and fluconazole and found efficient antifungal activity against *Phoma glomerata*, *Phoma herbarium*, and *Fusarium semitectum*. Similarly, silver sulphide nanocrystals also showed antifungal activity against *Aspergillus niger*, and silver nanoparticles showed antifungal activity against *Bipolaris sorokiniana*, *Magnaporthe grisea, Fusarium culmorum, Fusarium oxysporum, Colletotrichum* *gloeosporioides* and sclerotia-forming phyto-pathogenic fungi (Aguilar-Méndez, San Martín-Martínez, Ortega-Arroyo, Cobián-Portillo, & Sánchez-Espíndola, 2011; Jo, Kim, & Jung, 2009; Kasprowicz, Kozioł, & Gorczyca, 2010; Min et al., 2009; Musarrat et al., 2010). Nanocomposites such as silver-silica nanoparticles also reported antifungal activity and prevented powdery mildew infection in pumpkin leaves within 3 days of spraying (Park, Kim, Kim, & Choi, 2006). Kim et al. (2007) also reported silver nanoparticles as anti-fungal agents against *Raffaelea* sp. a pathogenic fungus of oak trees in Korea.

Copper nanoparticles were also found to be suitable for the control of the fungal pathogens *Alternaria alternata* and *Botrytis cinerea* at 15 mg/L concentration (Ouda, 2014). Cioffi et al. (2005) synthesized a nanocomposite of copper with a polymer and found effective antifungal activity. Wani and Shah (2012) reported that zinc oxide and magnesium oxide can control the growth of *Rhizopus stolonifera, Mucor plumbeus, Fusarium oxysporum* and *A. alternate.* In fact, ZnO nanoparticles induced systemic defence and boosted immunity in plants. In eggplant and tomato, foliar spray of 1000 ppm ZnO nanoparticles decreased the *Fusarium* severity via induction of the plant defence system (Elmer & White, 2016). Similarly, ZnO nanoparticles were also found to be effective in growth reduction of *Penicillium expansum, Botrytis cinerea, Aspergillus flavus*, and *Aspergillus niger* (He, Liu, Mustapha, & Lin, 2011; Jayaseelan et al., 2012).

3.2.2 Nanobactericide

Nanomaterials have also been applied as antibacterial agents to control bacterial pathogens. Silver has been known to be an antibacterial agent for many years and is widely used to control pathogenic bacteria. Copper is another metal, reported as an antimicrobial agent. Copper nanoparticles have been reported in the effective control of rice blast and leaf spot disease pathogen *Xanthomonas oryzae* and *Xanthomonas campestris*. Mondal and Mani (2012) also found effectivity of copper nanoformulation on bacterial blight disease in pomegranate at 0.2 ppm concentration, which is 60,000 times less than copper oxychloride, the conventional treatment. The reduction in pesticide amount reduced the cost to farmers with better maintenance of environmental balance. Paulkumar et al. (2014) found that *Piper nigrum* extract based silver nanoparticle synthesis enhanced bactericidal activity. These green synthesized silver nanoparticles showed antibacterial activity against *Citrobacter freundii* and *Erwinia cacticida* phyto-pathogens. Similarly, sun root tuber extract based silver nanoparticles exhibited antibacterial activity against the bacterial pathogens *Ralstonia solanacearum* and *Xanthomonas axonopodis* (Aravinthan et al., 2015). However, there is still more scope for the development of new classes of nanomaterials to control phyto-pathogenic bacteria.

3.2.3 Nanoinsecticide

Nanotechnology has shown significant application for the production of nanoinsecticides. The use of polymers in the development of nanoformulations of active ingredients has produced new generation nanoinsecticides which showed controlled release and target specific activity. Nanoformulations of different ingredients with pesticide activity have been reported including imidacloprid, carbofuran, thiamethoxam, thiram, β-cyflthrin (Adak, Kumar, Shakil, & Walia, 2012; Kaushik et al., 2013; Loha et al., 2011; Pankaj, Shakil, Kumar, Singh, & Singh, 2012; Sarkar, Kumar, Shakil, & Walia, 2012). Nanogel formulations of pheromones have also been synthesized for the biological control of insect pests. The slow evaporation of pheromones from nanogels increased their long term effectiveness as crop protectants. Brunel, El Gueddari, and Moerschbacher (2013) reported synthesis of chitosan based nanogels improved the efficiency of impregnated copper as a nanopesticide. Except nanoformulations, metal nanoparticles such as nanosilica have been used to minimize feeding damage by *Spodoptera littoralis* on tomato plants and to be found effective in changing the feeding preference of pests. Researchers reported that nanosilica affected the fecundity of *Spodoptera littoralis,* so reduction in insect population decreased the crop yield loss (El-bendary and El-Helaly, 2013). Silica nanoparticles have also been found to be active against different insect pests such as white fly, coconut mite, mustard weevil, and rice weevil. The insecticidal activity of silica nanoparticles was found to be due to physio sorption in cuticle lipids of insects which stimulate insect killing (Barik, Kamaraju, & Gowswami, 2012).

3.3 Efficient nanosensor

Nanosensors have also proven their potential in agriculture. They can be facilitate real time monitoring of crop and field condition, crop growth, pest attack, plant disease and environmental stressors (Chen & Yada, 2011). The development of such nanosensors has and continue to play a significant role in the advancement of agriculture. Real-time monitoring has prevented the excess use of pesticides and fertilizer amounts, which is helpful in the reduction of environmental contamination and product cost. Applications of nanosensors convert the conventional agriculture practices into smart agriculture, which are more energy efficient and environmentally friendly approaches for sustainable agriculture practices. Fraceto et al. (2016) indicated that smart agriculture practices involved (a) nanoformulation based fertilizers or pesticidal delivery systems which increase dispersion and wettability of nutrients, (b) nanodetectors for pesticide or fertilizer residues and (c) remote-sensing based monitor systems for disease occurrence and crop growth. Nanosensors in agriculture are used to detect the humidity of soil, pesticide residue, nutrient requirement and crop pest identification. The low limit of detection and high sensitivity of nanosensors make them more useful for smart agriculture. Different metal nanomaterials have been used in nanosensor development for pesticide detection including gold nanoparticles (Au NP), carbon nanotubes (CNT), quantum dots (QD) and various nanocomposites with polymers (Table 3) (Cesarino, Moraes, Lanza, & Machado, 2012; Liu et al., 2012; Talarico et al., 2016; Zheng, Li, Dai, Liu, & Tang, 2011). The nanosensors showed many advantages over conventional sensors in terms of high sensitivity due to high surface to volume ratio, quick response within seconds, more stable and reliable results, smaller amounts of detection (up to nanogram or

Table 3 Application of nanotechnology in sensing.

Nanoparticle	Target compound/species	Detection limit	References
Titanium oxide (TiO_2)	Atrazine	0.1 ppt	Yu, Zhao, Liu, Lei, and Li (2010)
Carbon	Herbicide detection		Luo et al. (2014)
Gold (Au)	Acetamiprid	5 nM	Shi, Zhao, Liu, Fan, and Cao (2013)
Gold (Au)	Urea and urease activity	5 μM and 1.8 U/L	Deng et al. (2016)
Gold (Au)	Pantoea stewartii sbusp.	7.8×10^3 cfu/mL	Zhao, Liu, et al. (2014) and Zhao, Peralta-Videa, et al. (2014)
Gold (Au)	Herbicide detection		Boro et al. (2011)
Gold (Au)	Organophosphates detection		Kang, Wang, Lu, Zhang, and Liu (2010)
Gold nanorods	Cymbidium mosaic virus and Odontogloss um ringspot virus	48 pg/mL and 42 pg/mL	Lin, Huang, Lu, Kuo, and Chau (2014)
Graphene	Herbicide detection		Zhao, Song, Wang, Wu, and Wang (2011)
Graphene oxide	Nitrate	10^{-5} M	Pan et al. (2016)
Multi walled Carbon nanotubes (MWCNT)	Glyphosate and glufosinate	0.35 ng/mLand 0.19 ng/mL	Prasad et al. (2014)
MWC-chitosan nanocomposite	Methyl parathion	7.5×10^{-13} M	Dong, Fan, Qiao, Ai, and Xin (2013)
PEDOT nanofibers—graphene oxide nanosheets composite	Nitrate	0.68 mg/L	Ali et al. (2017)
Quantum dots	DNA	3.55×10^{-9} M	Bakhori, Yusof, Abdullah, and Hussein (2013)
Silver (Ag)	Herbicide detection		Dubas and Pimpan (2008)
ZnO-chitosan nanocomposite membrane	*Trichoderma harzianum*	1.0×10^{-19} mol/L	Siddiquee, Rovina, Yusof, Rodrigues, and Suryani (2014)

lesser), practicable in different matrixes, and support fast electron transfer kinetics (Scognamiglio, 2013). Yu et al. (2010) developed TiO_2 nanotubes based on nanosensors for detection of atrazine in soil at levels of parts per trillion (ppt). The detection of methyl parathion was also done with acetylcholinesterase enzyme immobilized on multi-walled carbon nanotubes (MWCNT) and chitosan nanocomposites modified with glassy carbon electrode at ultra-trace levels in soil and water by Dong et al. (2013). Detection of methyl parathion was based on the inhibitory effect of acetylcholinesterase enzyme. Similarly, detection of acetamiprid in soil was also measured by the development of a nanobiosensor based on gold nanoparticles functionalised with acetamiprid-binding aptamer. This nanobiosensor visibly detects acetamiprid in the concentration range of 75 nM and 7.5 μM (Shi et al., 2013). Further, Prasad et al. (2014) developed the nanobiosensor to detect phosphorus containing amino acid type herbicide in soil using nanofilm modified pencil graphite electrode and analysed glyphosate and glufosinate in the detection limit of 0.35 and 0.19 ng/mL, respectively. The electrode was used in pulse anodic stripping voltammetry to detect glyphosate and glufosinate.

Nutrient concentrations in soil are a major issue and their rapid estimation is necessary to analyse soil conditioning requirements. Quantification of soil nutrients would increase the productivity and reduce leaching of excess components. Development of nanobiosensor for fertilizer estimation is a growing field in the current decade. The nanotechnology based sensors can provide accurate information about fertilizer requirements, which can be helpful in reducing costs to farmers and save unutilized fertilizers. Detailed reviews on nanosensors in agriculture have been published by Antonacci, Arduini, Moscone, Palleschi, and Scognamiglio (2018) and Chhipa and Joshi (2016). Furthermore, Mura et al. (2015) developed a colorimetric assay using cysteamine modified gold nanoparticles to detect nitrate content in soil. Similarly, Pan et al. (2016) developed graphene oxide based nanosensors for nitrate detection, whereas Azahar Ali et al. (2017) developed a nitrate detection sensor with the use of graphite oxide nanosheet and poly (3,4-ethylenedioxythiophene) nanofibres. The detection of urea, urease activity and urease inhibition could be possible by the development of a biosensor based on Au NP-3,3′,5,5′-tetramethylbenzidine-H_2O_2 reaction (Deng et al., 2016). In this system Au NP works as a catalyst and produces a yellow colour in the reaction. The method has a detection limit of 1.8 U/L urease activity in soil.

The detection of crop pests is also an important aspect in agriculture production. Conventional detection methods are time consuming. The use of nanostructures for pest detection has provided rapid and accurate results, therefore, crops can be protected and damage can be controlled quickly. Safarpour et al. (2012) developed a quantum dot-FRET based nanobiosensor to detection of *Polymyxa betae*, a vector of beet necrotic yellow vein virus responsible for Rhizomania disease in sugar beet. Further, Bakhori et al. (2013) also used a FRET system to detect *Ganoderma boninense* using a synthetic oligonucleotide. The sensor was also developed with modified quantum dots and DNA probes. Gold nanoparticles (Au NPs) were also used in the detection of pathogens. The Au NPs tagged with horseradish peroxidase labelled antibodies were used in an electrochemical enzyme linked immunoassay for detection of the plant bacterial pathogen *Pantoea stewartii* (Zhao, Liu, et al., 2014; Zhao, Peralta-Videa, et al., 2014). The detection method for *Cymbidium mosaic virus* and *Odontoglossum ringspot virus* was developed using label free surface plasma resonance of Au nanorods and measured in 48 and 42 pg/mL LOD (limit of detection) for *Cymbidium mosaic virus* and *Odontoglossum ringspot virus*, respectively. Further, Siddiquee et al. (2014) developed a nanobiosensor to detect the soil born fungal pathogen *Trichoderma harzianum* using ZnO nanoparticles/chitosan nanocomposite modified gold electrode. Yao et al. (2009) used fluorescent silica nanoprobes conjugated with a secondary antibody of goat anti rabbit Ig and detected the bacterial plant pathogen, *Xanthomonas axonopodis* pv. vesicatoria in Solanaceous crops.

3.4 Smart food safety agent

Nanotechnology has also shown potential in food safety and in the food processing industry. Nanomaterials have been used as food packaging materials to preserve and enhance shelf life of packaged food materials. Nanocomposites have been found suitable in food packing as antimicrobial agents, increased mechanical and thermal resistance of packing materials, and reducing oxygen transmission rate. Nanoformulations of vitamins and taste enhancers in capsular form have shown controlled release profiles (Katouzian & Jafari, 2016). The nanoencapsulation of vitamins and taste enhancers increased shelf life and prevented rapid degradation. Nanoencapsulation of anthocyanin has been developed to enhance pigment stability by Zhang et al. (2014). Further, Yang et al. (2015) developed ferritin nanocages for the encapsulation of rutin (a dietary flavonoid) and found improved solubility in various applications in the food industry. Titanium and silicon oxide were also used as colour, fragrance and flavour enhancement agents in the food industry (Dekkers et al., 2011). The application of nanomaterials in food packing materials improved strength, barrier property, antimicrobial activity and food safety by sensing of food pathogens.

4 Can nanotechnology provide effective tools in sustainable agriculture?

Application of nanotechnology in the form of nanofertilizers, nanopesticides and nanosensors has transformed conventional agriculture practices into smart agriculture. It has been reported that the use of nanomaterials as agri input reduces excess amounts of chemicals, provides targeted delivery and does not affect non-targeted organisms (Chhipa & Joshi, 2016; Chhipa, 2017a, 2017b; Solanki, Bhargava, Chhipa, Jain, & Panwar, 2015). Nanotools showed improved solubility, increased shelf-life of active ingredients, controlled releasing capacity and were eco-friendly for lab to field applications. These characteristics make nanotools ideal for maintaining environmental balance by reducing the harmful impact of chemicals. Smart nanomaterials can provide nutrition on requirements and pest detection by smart sensing applications. Monitoring of filed conditions and pest attacks by nanosensors can reduce large scale crop loss due to their detection efficiency in minute amounts.

Various studies have also reported adverse impacts and toxicity of nanoparticles to plants and surrounding environments from the use of metals, metal oxides and synthetic polymers in the synthesis of nanofertilizers and nanopesticides. It has been found that metal, metal oxide, and synthetic polymers are not biocompatible and non-degradable and showed toxicity at certain concentrations, which is of serious concern for the use of nanotechnology in agriculture. Researchers reported that due to nanosize, nanomaterials accumulate in the environment and their concentration increases simultaneously. Excess amounts of nanomaterial accumulation are dangerous to humans, non-targeted organisms and the environment. But use of natural polymers such as chitin, chitosan and cellulose based nanomaterials can be advantageous for agricultural applications due to their biocompatibility and eco-friendly nature.

In limited concentrations metal nanoparticles also showed a positive impact on seed germination, seed treatment, plant growth and crop yield (Jain, Bhargava, Tarafdar, Singh, & Panwar, 2013; Raliya & Tarafdar, 2013). This suggests there is a need to do more research to determine the threshold for each metal nanoparticle-crop system, providing a guide for adequate concentration range to use metal nanoparticles for high crop yield and preventing toxicity to the environment. The green synthesis of nanoparticles is another route of biocompatible nanomaterial synthesis for agricultural applications. The coating of biological molecules on metal nanoparticles reduced the toxic nature and increased their potential for biological applications (Chhipa, 2018). Green synthesized and natural polymers based nanomaterials may be the next generation of nanoagro materials, which can provide eco-friendly nanotools to transform conventional agriculture in to precise agricultural practices. Such nanotools would be more capable of controlling the excess use of fertilizers and pesticides, understand the soil and plant requirement by sensing, and reduce the excess chemical burden on earth and environment.

5 Conclusion

Nanotechnology in agriculture as nanofertilizer, nanopesticide and nanosensor significantly proved their applications in plant growth and crop production in a sustainable manner. Nanosized controlled release and site targeted delivery made them efficient tools for smart agriculture systems. Different metal and metal oxide nanoparticles positively enhanced seed germination rates, root and shoot elongation, and plant biomass and plant growth within certain concentration levels. In contrast, some metal or metal oxide nanoparticles showed negative impact on plant growth. Such issues can be combated by use of polymer nanoparticles and nanomaterial synthesis using green approaches. Nanomaterial based sensors also showed potential in detection of residual pesticides or pathogens and ensured food safety to consumers. Nanoencapsulation and application of nanomaterials in food packaging improved the shelf life of food products and provided sustainable solutions for food degradation and deterioration during transport. Still more research is required to determine the threshold concentrations for each crop system for the prevention of toxicity. The long term assessment of each crop-nanoparticles system is required to understand the fate of nanomaterials in the environment.

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Further reading

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