Understanding the Role of Nanomaterials in Agriculture

17

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Abstract

Nanotechnology offers immense opportunities for improvement in the quality of life through applications in agriculture and the food systems. Development of nanotechnology-based novel agro-products, viz., nanosensors, nano-fertilizers, nano-pesticides and nanoformulations of biocontrol agents, is currently a subject of intense investigation. A variety of nanomaterials has been recommended for use in agriculture, in order to help reduce the consumption of agrochemicals by use of smart delivery systems, minimize the nutrient losses and increase the yield through optimized water and nutrients management. Nanotechnology-derived devices have also been explored in the areas of plant breeding and genetics. Additionally, the agricultural products and/or by-products can be utilized as a source for developing bio-nanocomposites. Nevertheless, the potential advantages of nanotechnology applications in the agricultural sector are still marginal, and have not been commercialized to a significant extent, as compared to other industrial sectors. Researches in the area of agricultural nanotechnology are being extensively pursued in quest for the solutions to the agricultural and environmental challenges, such as sustainability, increased productivity, disease management and crop protection through innovative techniques for monitoring, assessing and controlling the agricultural practices. This chapter provides a basic knowledge about the role of nanotechnology in developing sustainable agriculture and environment, and eventually in the welfare of human society, at large, in the near future.

Keywords

Nanoparticles • Nano farming • Green synthesis • Nano-pesticides

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17.1 Introduction

Significant developments in the agricultural sector have been witnessed in recent years with the rapid technological advancements and innovations, to address the challenging issues of sustainable production and food security. Indeed, the demand for food will be increasing with the passage of time, while the natural resources such as water, fossil fuel, land and soil fertility are gradually being depleted. Furthermore, the cost of production inputs, viz., pesticides, chemical fertilizers and micronutrients, is enhancing at an alarming rate. Therefore, to address these pertinent issues, advanced researches in the area of nanotechnology are underway for development of precision farming practices. This will lead to reduction in the production costs and maximize the output with a precise control at a nanometer scale. In this context, nanotechnology offers enormous potential for improvement in the quality of life through its applications in agriculture and the food system (Ditta 2012). Nanotechnology-based devices are being explored in the field of plant breeding and genetic transformation (Torney et al. 2007). Smart delivery systems for agrochemicals, which were otherwise sprayed, have been developed using nanomaterials as carriers for the delivery of active ingredients, with minimum losses and increased yields through optimized water and nutrient management (Gogos et al. 2012). Further, the agricultural produce or its waste like wheat straw and soy hulls could be effectively utilized by converting into bio-nanocomposites, with enhanced physical and mechanical properties, for bio-industrial purposes (Alemdar and Sain 2008). Researches in the area of agricultural nanotechnology are being pursued for almost a decade, searching for solutions to various challenges, such as sustainability, improved varieties and increased productivity. Several studies have revealed the increasing trend of both the scientific publications and patents in agricultural nanotechnology, especially for disease management and crop protection (Sastry et al. 2010; Gogos et al. 2012). Most likely, the knowledge of nanotechnology gained in other emerging sectors, such as electronics energy and medical sciences, could be effectively transferred or adopted for agricultural applications. Also, the improved fuel additives and lubricants can improve the performance and the carbon footprint of agricultural machinery. Furthermore, the improved packaging measures could benefit farmers by reducing the post-harvest loses and degradation of products before consumption. Apart from the progress achieved in environmental monitoring and drug delivery techniques (Chen et al. 2013), nanotechnology can also benefit the poultry and livestock sectors. Nanotechnology is poised to provide better solutions to multiple problems in agriculture and food sciences by offering novel approaches in preservation of raw materials and their processing for development of better quality plant and other food products. Thus, agricultural nanotechnology has a potential for (i) reducing the amount of pesticide consumption through nanocarriers via effective targeted delivery to the pests; (ii) making nano-fertilizers/ nutrients more available to nanoscale plant pores, resulting in greater nutrient use efficiency; (iii) adding nano-silicon to increase water uptake efficiency in plants; and (iv) developing nanobiosensors for slow release of fertilizers and other agrochemicals, and providing many more benefits.

17.2 Nano Farming: A New Perspective

Precision farming or agriculture has emerged in recent years with the developments in the field of wireless networking and miniaturization of the sensors for monitoring, assessing and controlling agricultural practices (http://www.lofar.org/p/Agriculture.htm). It relates to site-specific crop management and covers a wide range of pre- and post-production aspects of agriculture from horticulture to field crop production (Burrell et al. 2004; Mayer et al. 2004; Zhang et al. 2004). Recently, precision farming based on tiny micro-electromechanical systems (MEMS) called 'smart dust' is regarded as a future nanotechnology for agricultural applications. Smart dust is comprised of sensors, robots and transponders that operate on a wireless computer network and sense light, temperature, vibration, magnetism or chemicals through radio-frequency identification. They can be sprinkled across a field and linked to existing farming equipment used in precision agriculture and to a personal computer. For instance, ASTRON, the Netherlands Institute for Radio Astronomy, has developed new radio telescope of the LOFAR (Low Frequency Array) based on tens of thousands of antennas that are connected to each other with a large ICT infrastructure. LOFAR_Agro has applied it for measurement of the microclimate in potato crops and to combat phytophtora infection in the crop. Phytophthora is a fungal disease in potatoes, which can enter a field through a variety of sources. The infestation in crop depends strongly on the climatological conditions within the field (Wallin and Waggoner 1950). The decision support system (DSS) gathers the information from the meteorological station and the wireless sensors from the Agro Server to help farmers to combat phytophtora in the crop. The DSS alerts the farmer of most susceptible patches within the fields based on the information maps of temperature distribution within the fields, along with the weather forecast, and help develops a strategy on how to prevent or control the disease *(*http://www.lofar.org/agriculture/fighting-phytophtora-using-micro-climate*)*. In the near future, smart dust will help in monitoring the soils, crops and livestock in a more efficient manner and may contribute significantly in increasing the agriculture productivity by providing accurate information for quick and useful decisions.

17.2.1 Green Synthesis of Nanoparticles

Plants have been used for the biosynthesis of a variety of nanoparticles by spontaneous, economical, eco-friendly process of one-pot synthesis, suitable for large scale production (Huang et al. 2007). Green synthesis of nanoparticles by plants material involves the phytochemicals such as flavonoids, terpenoids, carboxylic acids, quinones, aldehydes, ketones and amides, which cause the reduction of ions (Prabhu and Poulose 2012). Numerous plants have been investigated for their role in the synthesis of nanoparticles, such as *Cinnamomum camphora* leaf (Huang et al. 2007); *Pelargonium graueolens* leaf (Shankar et al. 2003); *Azadirachta indica* leaf (Shankar et al. 2004); *Emblica officinalis* leaf (Ankamwar et al. 2005); Aloe vera leaf (Chandran et al. 2006); Alfalfa sprouts (Gardea-Torresday et al. 2003); Helianthus annus, Basella alba and *Saccharum officinarum* (Leela and Vivekanandan 2008); *Carica papaya* callus (Mude et al. 2009); *Jatropha curcas* leaf (Bar et al. 2009); *Eclipta* leaf (Jha et al. 2009); *Glycine max* (soybean) leaf (Vivekanandan et al. 2009); *Coriandrum sativum* leaf (Sathyavathi et al. 2010); *Syzygium cumini* leaf (Kumar et al. 2010); *Cycas* leaf (Jha and Prasad 2010); *Allium cepa* (Saxena et al. 2010); *Stevia rebaudiana* leaves (Varshney et al. 2010); *Solanum torvum* (Govindaraju et al. 2010); *Zingiber officinale* (Singh et al. 2011); *Capsicum annuum* (Li et al. 2007); *Dillenia indica* fruit (Singh et al. 2013); *Alternanthera sessilis* (Niraimathi et al. 2013); *Morinda citrifolia* (Suman et al. 2013); *Phytolacca decandra, Gelsemium sempervirens, Hydrastis canadensis* and *Thuja occidentalis* (Das et al. 2013) (Pinus desiflora); *Diopyros kaki, Ginko biloba*, *Magnolia kobus* and *Platanus orientalis* (Song and Kim 2009); and *Ulva fasciata* (Rajesh et al. 2011). It has been reported that alfalfa plants grown in an $AuCI_4^-$ rich environment absorb gold metal and the gold nanoparticles produced by the plant can be recovered mechanically from the harvest by dissolving the plant tissue. Also, the geranium leaves immersed in a gold-rich solution for 3–4 h have been reported to produce 10 nm sized gold particles shaped as rods, spheres and pyramids. Similarly, the uptake of silver by the alfalfa plant in silver-rich solid medium transformed silver to silver nanoparticles (Gardea-Torresday et al. 2003).

17.2.2 Nano-Fertilizers: An Efficient Resource for Nrop Nutrition

Targeted delivery and slow or controlled release of nanoformulations in response to environmental stimuli and biological demand increase nutrients use efficiency, reduces soil toxicity, minimizes the potential negative effects of over dosage and reduces the frequency of the application (Naderi and Danesh-Shahraki 2013). The nutrients can be encapsulated inside nanoporous materials, coated with thin polymer film, or delivered as particles or emulsions of nanoscales dimensions (Rai et al. 2012). Increased food grain production depends upon proper irrigation, good quality seed and fertilizers. Imbalanced application of fertilizers, nutrient deficiencies and reduced level of soil organic matter are often very challenging and these issues can be addressed effectively by developing nano-fertilizer formulations with multiple functions. Nano-fertilizers, contrary to traditional methods of fertilizer application, make a gradual and controlled release of nutrient into soil, which may prevent autrification and contamination of water bodies and environment. Besides, significant increase in crop yields has been reported with the foliar application of nano fertilizers (Tarafdar 2012; Tarafdar et al. 2012a). Lately, the nanocomposites are being developed to supply the essential nutrients in suitable proportion through a smart delivery system. However, the supply of micronutrients as nano-formulations through soil-borne and foliar applications needs to be ascertained. Currently, the nitrogen use efficiency is low due to the loss of 50–70 % of the nitrogen being supplied in the form of conventional fertilizers. The novel nutrient delivery systems can exploit the porous nanoscale parts of plants and cause significant reduction in nitrogen loss by enhanced uptake. Tarafdar et al. (2012b) again suggested that the fertilizers encapsulated in nanoparticles can increase the uptake of nutrients.

Further, the nano clays and zeolites, a group of naturally occurring minerals with a honeycomb-like layered crystal structure, have also been used for increasing fertilizer efficiency (Chinnamuthu and Boopathi 2009). The main application of zeolites in agriculture is in nitrogen capture, storage and slow release (Leggo 2000). Millan et al. (2008) reported that urea-fertilized zeolite chips can be used as slow-release nitrogen fertilizers. Ammonium-charged zeolites have shown their capacity to raise the solubilization of phosphate minerals and thus exhibit improved phosphorus uptake and yield of crop plants. Similarly, the mixtures of zeolite and phosphate rock show the potential for slow-release fertilization of plants in synthetic soils by dissolution and ion-exchange reactions (Allen et al. 1993). Li (2003) demonstrated the possibility of using surfactant modified zeolite using hexa decyl trimethyl ammonium as fertilizer carrier to manage slow release of nitrate and other anions. Liu et al. (2006) suggested that coating and binding of nano and sub-nanocomposites are able to regulate the release of nutrients from the fertilizer capsules. Jinghua (2004) demonstrated that application of a nanocomposite consists of N, P, K, micronutrients, mannose and amino acids enhance the uptake and use of nutrients by grain crops. It has also been shown that fertilizer incorporation into cochleate nanotubes improves the crop yield (DeRosa et al. 2010).

17.2.3 Nano-Herbicides: An Efficient Weed Control Agent

Weeds are considered as a serious problem in agriculture as they significantly reduce the vigour and yield of crop. Nanotechnology provides a solution to the weed problem by application of nano-herbicides in an eco-friendly manner without causing any residual toxicity in soil and environment (Perez-de-Luque and Rubiales 2009). Owing to nanoscale dimensions, the nano-herbicide blends with soil particles and prevents the growth of weeds resistant to conventional herbicides (Prasad et al. 2014). Generally, the herbicides available in the market either control or kill the above-ground part of the weed plants, without affecting the underground parts like rhizomes or tubers, which results in regrowth of weeds. Therefore, herbicide molecules encapsulated with nanoparticles specifically for receptors on the weed roots could be developed for targeted interactions with root system (Joel et al. 2007).

17.2.4 Nano-Pesticides and Pest Control

Conventional pest controlling methods are based on large-scale application of over-the-counter pesticides, which not only make the crop production more expensive but also cause environmental and water pollution. Therefore, the need for minimizing the amount of pesticides to save the environment and to reduce the cost involved in crop production is strongly realized (Sharon et al. 2010). This could be achieved by increasing the retention time of pesticides without compromising efficiency. Persistence of pesticides in the initial stage of crop growth helps in bringing down the pest population below the threshold level, and consequently provides effective control for a longer period of time. In this context, nanotechnology proves to be a functional approach to improvise the insecticidal value. The USEPA (United States Environmental Protection Agency) is considered to be the first regulatory authority to have recognized the role and significance of nano-pesticides, and granted a conditional registration for the first nano silver pesticide (USEPA 2011). Indeed, the efficacious approach is 'controlled release of the active ingredient' that may greatly improve the efficacy with much lesser pesticide input and associated environmental hazards. For instance, 'Halloysites' (clay nanotubes) have been developed as cost-effective carriers of pesticides. These nanoparticles have been shown to greatly reduce the amount of conventional pesticide use and have extended the release time with better contact and minimum impact on the environment (Allen 1994). Further, the availability of nano-structured catalysts may increase the efficiency of pesticides and insecticides and also reduce the dose level required for plants (Joseph and Morrison 2006). Liu et al. (2006) have reported that the porous hollow silica nanoparticles (PHSNs) stacked with the pesticide validamycin can be effectively used for controlled release of pesticide. Also, the nanosilica has been studied to control agricultural insect pests (Ulrichs et al. 2005). By physio-sorption, the nano-silica gets strongly attached to insect cuticular lipids and eventually kills the insect (Ulrichs et al. 2005).

Lately, the nano-encapsulated broad-spectrum pesticides have been marketed under the trade name of Karate® ZEON to control the insect pests of soybeans rice and cotton *(*http://tirmsdev.com/Syngenta-Crop-Protection-Inc-Karate-with-Zeon-Technology*)*. It releases the active chemical lambda-cyhalothrin, when it comes in contact with the leaves. Similarly, another nano-insecticide with the trade name 'gutbuster' releases its contents under alkaline environment in the stomach of insects (Prasad et al. 2014). Several studies have suggested the development of new polymer-based nanoformulations with less harmful plant-protection products in combination with biodegradable polymers. Such polymers mainly consist of polysaccharides (e.g., chitosan, alginates and starch) and polyesters (e.g., poly-ε-caprolactone and polyethylene glycol). In recent years, there has been an increase in demand for biodegradable materials of biological origin such as beeswax, corn oil, ecithin (Nguyen et al. 2012) or cashew gum (Abreu et al. 2012). These eco-friendly matrices can be applied in organic crop production with no toxic effects. There are certain natural substances, which also exhibit pesticidal properties but are unstable and can easily undergo premature degradation (Macías et al. 2004). Therefore, polymer-based nanoformulations in the form of nanospheres, nanogels or nanofibers could serve as better alternatives and offer more advantages. In view of increasing use of nanoparticles, the USEPA is contemplating to release regulation for handling the issues pertaining to nano-pesticides. The Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) Scientific Advisory Panel, in consultation with EPA, embarked on the evaluation of nanometal pesticide products (FIFRA-SAP 2009).

17.2.5 Nano-Antimicrobials for Phytopathogens

Nanoscale materials are emerging as novel antimicrobial agents due to their high surface area to volume ratio, which increases their contact with microbes and their ability to permeate cells (Morones et al. 2005; Kim et al. 2007). Nano silver is one such example, which is known to attack a broad range of biological processes in microorganisms and disrupt the cell membrane structure and functions (McDonnell and Russell 1999; Sondi and Salopek-Sondi 2004). It also inhibits gene expression for the proteins associated with ATP production (Yamanaka et al. 2005). Also, the polymer-based copper nanoparticles have been investigated for their antifungal activity against plant pathogenic fungi (Cioffi et al. 2004). Silica-silver nanoparticles have also been reported to be effective antimicrobial agents against the plant pathogenic *Rhizoctonia solani, Pythium ultimum, Botrytis cinerea, Magnaporthe grisea* and *Colletotrichum gloeosporioides* (Park et al. 2006). Antifungal and antibacterial action of nanoparticles has been demonstrated against a variety of plant pathogenic fungi such as *Raffaelea* sp., *Bipolaris sorokiniana, Magnaporthe. Grisea, Fusarium, Phoma* and many other Gram-negative and Gram-positive bacteria (Kim et al. 2009; Gajbhiye et al. 2009; Esteban-Tejeda et al. 2010). Besides this, the nano-based products have been used for the control of pumpkin disease and powdery mildew (Lamsal et al. 2011). The infecting pathogens on the leaves disappear within 3 days after nanoformulation is sprayed. Growth of fungal hyphae and conidial germination could be significantly inhibited by nano-based products especially of silver and copper nanoparticles. Thus, the nano-herbicides, nano-fungicides and nano-pesticides have a tremendous scope in agriculture. There nanoformulations or nano-emulsions can be effectively used in preservation of pre- and post-harvest agricultural produce (Rickman et al. 1999; Zahir et al. 2012).

17.2.6 Nanotechnology and Integrated Pest Management (IPM)

Nanotechnology has a good scope in the IPM due to the insect pest controlling ability of nanomaterials. Nanoparticles have shown to be effective against a verity of plant pathogens and insect pests. Several different formulations of insecticides, pesticides and insect-repelling chemicals are reported (Esteban-Tejeda et al. 2010; Zahir et al. 2012). It is now possible to deliver any desired chemical into the plant tissues for eliciting the host plant defence against the pest insects (Torney 2009). For instance, the porous hollow silica nanoparticles loaded with validamycin work as effective transfer system for water soluble pesticides that can be released under controlled conditions (Liu et al. 2006). A wide range of agricultural insect pests can be controlled by the use of nano-silica (Ulrichs et al. 2005). Similarly, the nanoparticles coated with polyethylene glycol and garlic oil have been shown to exhibit biocidal activity against adult stage of *Tribolium castaneum*, a red flour beetle in stored grain pest (Yang et al. 2009). Thus, nano-emulsions are regarded as efficient pesticide formulations effective against several agricultural insect pests (Gao et al. 2007).

17.2.7 Categories of Nanoparticles

Nanoparticles can be categorized into two broad groups, i.e., organic and inorganic nanoparticles. Organic nanoparticles are mainly carbon nanoparticles (fullerenes, carbon nanotube, graphenes, etc.), whereas the inorganic nanoparticles may be magnetic nanoparticles, noble nanoparticles (gold and silver) or semiconductor nanoparticles (titanium oxide and zinc oxide). The inorganic nanoparticles have attracted more attention due to their superior material properties with versatile functions. The nano size, rich functionality and good biocompatibility of nanoparticles make them a suitable carrier for targeted drug delivery and controlled release (Xu et al. 2006). Synthesis of nanoparticles is of significance in nanotechnology due to variability in size, shapes, chemical composition, crop controlled dispersity and their potential applications in the agricultural sciences, for the better crop productivity and disease-free long-term post-harvest storage and preservation.

17.2.8 Inorganic Nanoparticles

17.2.8.1 Aluminium

Nanoalumina dust has been proposed to protect stored grains (Stadler et al. 2010). The insecticidal activity of nanoalumina dust comparable to the doses has been reported to be comparable to the recommended doses of commercially available insecticidal dusts. Stadler et al. (2010) suggested the insecticidal activity of nanoalumina on insect pests *Sarocladium oryzae and Rhyzopertha dominica*. Nanoalumina is regarded as a good alternative to products based on diatomaceous earth. However, the mode of action of nanoalumina has yet to be elucidated. Further studies are required to optimize the product in terms of the mineral composition of the dust and the type of formulations, in order to ensure efficacy for a range of insect species under varying environmental conditions.

17.2.8.2 Copper

Mondal and Mani (2012) reported that a nanoformulation of copper has been shown to suppress the growth of bacterial blight on pomegranate at concentrations of 0.2 mg/L, which is 4-fold lower than the recommended dose of copper oxychloride (2500–3000 mg/L). There is a need for testing nanoformulations under a range of conditions that are as realistic as possible.

17.2.8.3 Silver

Nano silver, being one of the most extensively used nanoparticles, exhibits the broad-spectrum inhibitory and bactericidal effects. The in vitro studies have demonstrated a dose-dependent growth inhibition of plant pathogens with nanosilver (Kim et al. 2012). Their possible use as coatings for fruit bags (Chun et al. 2010) and treatments to cut flowers (Liu et al. 2009a; Solgi et al. 2009) indicate their possible benefits over synthetic fungicides. Kim et al. (2008) have also demonstrated the antifungal activity of colloidal nanosilver against rose powdery mildew caused by *Sphaerotheca pannosa* Var *rosae*. Till date maximum numbers of patents have been filed for nano silver for preservation and treatment of diseases in the agriculture field. The International Center for Technology Assessment (ICTA) submitted a petition to EPA requesting for regulation of nano silver usage in products as a pesticide under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). Silver is now an accepted agrochemical replacement. It is being used as foliar spray to stop fungi, moulds, rot and several other plant diseases. Nano silver kills unicellular microorganisms by inactivating enzymes having metabolic functions in the microorganisms by oligodynamic action (Kim et al. 1998). It is also known to exhibit superb inhibitory effects on algal growth. Silver in ionic state is known to exhibit high antimicrobial activity (Kim et al. 1998; O'Neill et al. 2003; Thomas and McCubin 2003). However, ionic silver is unstable due to its high reactivity and thus gets easily oxidized or reduced into a metal with no antimicrobial activity. Silver as a metal or oxide is stable in the environment, but due to its low antimicrobial activity it is used in relatively large quantities, which is not economical. Therefore, Park et al. (2006) developed a new composition of nanosized silica silver for control of various plant diseases.

17.2.8.4 Nano Silica

Silicate is reported to exhibit preventive effects on pathogenic microorganisms causing powdery mildew or downy mildew in plants (Lamsal et al. 2011). Besides, it also promotes the physiological activity and growth of plants and induces disease and stress resistance in plants (Garver et al. 1998; Kanto et al. 2004). Since the effect of silica varies with the physiological environment, it has not been registered as an agrochemical.

17.2.8.5 Titanium Dioxide

The antimicrobial activity of titanium dioxide is well recognized. Several studies have suggested that titanium dioxide exposure to crops can suppress the bacterial and fungal pathogens (Norman and Chen 2011). Nanoscale titanium dioxide either alone or doped with silver or zinc is effective against the bacterial spot disease in tomatoes (Paret et al. 2013a) and roses (Paret et al. 2013b). Greenhouse and field trials (Paret et al. 2013a, b) demonstrated that titanium dioxide/zinc can significantly reduce the bacterial spot severity compared to untreated controls. Some phytotoxicity may occur upon repeated applications, which could be avoided by using electrostatic sprayers instead of conventional sprayers (Paret et al. 2013a). In general, the titanium dioxide/zinc formulation exhibits relatively lower ecological and toxicological risks, compared to currently used copper-based treatments.

17.2.9 Biodegradable Polymers

Polymers such as cellulose, chitin, starch, polyhydroxyalkanoates, polylactide, polycaprolactone, collagen and other polypeptides are naturally synthesized by the organisms. Based on the nature of their synthesis, they are classified as (i) agro-polymers, such as starch or cellulose; (ii) microbial polymers, such as polyhydroxyalkanoates (PHAs); (iii) chemical polymers, such as polylactic acid (PLA) obtained from agro-resources; and (iv) polymers obtained from fossil resources. All these polymers are easily degradable by the microorganisms and cellular enzymes (Kaplan et al. 1993; Chandra and Rustgi 1998).

17.3 Smart Delivery System

One of the important applications of nanoparticles is their use as 'smart' delivery systems. Particularly, the use of nanocapsules has a huge scope in agriculture (Liu et al. 2002; Cotae and Creanga 2005; Pavel and Creanga 2005; Joseph and Morrison 2006). A typical example is the gene transfer by bombardment of DNA-absorbed gold particles to generate transgenic plants in a species-independent manner (Christou et al. 1988). Torney et al. (2007) have reported the efficient delivery of DNA and chemicals through silica nanoparticles in plant cells. Adak et al. (2012) recorded that amphiphilic copolymers, synthesized from poly (ethylene glycols) and various aliphatic diacids as nano-micellar aggregates, can be used to develop controlled release formulations of imidacloprid (1-(6 chloro-3-pyridinyl methyl)-N-nitro imidazolidin-2-ylideneamine) through encapsulation technique. Thus, high solubilization power and low critical micelle concentration of these amphiphilic polymers may increase the efficacy of formulations. Some common polymers, both synthetic and natural, that have been studied for smart delivery of insecticides are listed in Table 17.1.

Table 17.1 Nano products developed for agriculture use

Nano products	Active ingredients	Polymer matrix	Reference
Capsule	Neen Seed Oil	Alginate-glutaraldehyde	Kulkarni et al. (1999)
Capsule	Bifenthrin	Polyvinylpyrrolidone	Liu et al. (2008)
Capsule	B-Cyfluthrin	Polyethylene glycol	Loha et al. (2012)
Capsule	Deltamethrin	Polyethylene	Frandsen et al. (2010)
Capsule	Carbaryl	Carboxymethylcellulose	Isiklan (2004)
Capsule	Itraconazole	Acrylic acid-Bu acrylate	Goldshtein et al (2005)
Capsule	Etofenprox	Chitosan	Hwang et al. (2011)
Spheres	Carbaryl	Glyceryl ester of fatty acids	Quaglia et al. (2001)
Fiber	Pheromones	Polyamide	Hellmann et al. (2011)
Particle	Azadirachtin	Carboxymethyl chitosan	Feng and Peng (2012)
Particle	Imidacloprid	Chitosan-poly(lactide)	Li et al. (2011)
Particle	Chlorpyrifos	polyvinylchloride	Liu et al. (2002)
Film	Endosulfan	Starch-based polyethylene	Jana et al. (2001)
Granules	Imidacloprid	Lignin	Fernandez-Perez et al. (2011)
Micelle	Carbofuran	Polyethyleneglycol	Shakil et al. (2010)
Gel	Cypermethrin	Methyl methacrylate	Rudzinski et al. (2003)
Gel	Aldicarb	Lignin	Kok et al. (1999)
Powder	Novaluron	Anionic surfactants	Elek et al. (2010)
Resin	Pheromones	Vinylethylene	Wright (1997)
Clay	Imidacloprid	Alginate-bentonite	Fernandez-Perez et al. (2011)

17.3.1 Controlled Release of Agrochemicals from Nanocarriers

The nanomaterials that have been used for controlled release of agrochemical include nanosphere, nanogel, nanotubes and micelle formulations, as specified below.

17.3.1.1 Nanospheres

Nanospheres are aggregates in which the active compound is homogeneously distributed into the polymeric matrix. They are spherical particles of size between 10–200 nm in diameter and exhibit some novel size-dependent properties in comparison to larger spheres of the same material. They can be formed by dissolution, entrapment, encapsulation or attachment of chemicals and drugs with the matrix of polymers. Nanospheres can be amorphous or crystalline in nature and possess the ability to protect the chemicals from enzymatic and/or chemical degradation (Singh et al. 2010).

17.3.1.2 Nanogels

Nanogels are considered as better carrier than nanospheres for the reason that they are insoluble in water and thus less prone to swelling or shrinking with changes in humidity (Bhagat et al. 2013). They can significantly improve the loading and release profiles and avoid the occurrence of bursts or potential leaks (Paula et al. 2011). Owing to these advantages, the nanogels have been recommended, as per the organic farming standards (Kok et al. 1999), for delivery of pheromones and essential oils. Pheromones are considered to be highly specific and eco-friendly biological control agents, but their deployment requires slow release and protection from decomposition under ambient conditions. Bhagat et al. (2013) proposed the immobilization of pheromones within a nanogel without using any toxic cross-linkers or antioxidants. Evaporation of the pheromones in the nanogel gets significantly reduced, and the efficacy could be increased up to 33 weeks compared to only 3 weeks in case of pure active ingredients (Bhagat et al. 2013). The efficacy of a nanogel formulation of the essential oil of *Lippia sidoides* has also been reported to be better than free oil. Brunel et al. (2013) suggested the use of pure chitosan nanogels to improve the performance of antifungal treatments based on copper. The advantages of using a nanogel over a solution include easier handling, improved distribution on the leaves and the long-term release of copper on to leaves or into the soil without comparing its antifungal properties. Formation of the copper (II)–chitosan complex is pH dependent. Since most fungi tend to reduce the pH of their surrounding environment, therefore the release of copper (II) can be easily triggered by the growth of the pathogen. A strong synergistic effect between chitosan and copper in inhibiting the growth of *Fusarium graminearum* has been reported (Brunel et al. 2013).

17.3.1.3 Nanotubes

Nanotube devices served as excellent candidates for electrical sensing of individual biomolecules when integrated with other chemical, mechanical or biological systems (Chopra et al. 2007). Nanotube electronic devices have been shown to function very well under extreme biological conditions such as saline water (Liu et al. 2009a, b). Indeed, there are practical difficulties in reliable, rapid and reproducible nanofabrication of complex arrays of nanotubes; however, such devices have the potential to revolutionize exact diagnosis, drug delivery and livestock disease and health management, as well as in the identification and site-specific control of plant pests and diseases (Perez-de-Luque and Rubiales 2009).

17.4 Nanobiosensors

Nanobiosensors are analytical devices, where immobilized layer of a biological material is in contact with a sensor that analyses the biological signal and converts it into electrical signal (Gronow 1984). Biosensor offers a new analytical tool with major applications in environmental, clinical diagnostics and agriculture. In agriculture, the nanobiosensors can be effectively used for sensing a wide variety of fertilizers, herbicides, pesticides, insecticides, pathogens, moisture and soil pH, and their controlled use can support sustainable agriculture for enhancing crop productivity (Rai et al. 2012).

17.4.1 Role of Biosensors in Agriculture

Excessive use of agrochemicals has lead to the elevated levels of herbicides, pesticides and heavy metals in agricultural soil. In order to monitor their status in soil and also to forecast the possible occurrence of soil disease, regular monitoring through the specific biosensors needs to be done. Biological diagnosis of soil using a biosensor means to study the reliable prevention and decontamination of soil. The basic principle of soil diagnosis with the biosensor is to estimate the relative activity of good and bad microbes in the soil based on quantitative measurement of differential oxygen consumption by soil microorganisms. Accurate sensors need to be developed as miniaturized portable devices and remote sensors, for the real-time monitoring of large areas. Field use of biosensor can reduce the time required for microbial testing and immunoassays, and also for detection of contaminants in water supplies, raw food materials and food products. Electronic nose (E-nose) is one such example for identification of different types of odours based on the pattern of response across an array of gas sensors. E-nose consists of gas sensors, composed of nanoparticles such as ZnO nanowires (Xu et al. 2008). Biosensors provide high specificity and sensitivity, rapid response, user-friendly operation and compact size at a low cost (Amine et al. 2006). Mendes et al. (2009) have reported the biosensor for the detection of the fungus *Phakopsora pachyrhizi* that causes Asian rust or Soybean rust, using the SPR (Surface Plasmon Resonance) technique. Amine et al. (2006) have also reported a biosensor for the detection of aflatoxin in olive oil.

In recent years, significant advances have been made towards the synthesis of colloidal semiconductor quantum dots (QDs), particularly II–VI compounds such as CdSe, CdS and CdTe (Park et al. 2007; Reiss et al. 2009). These highly visible luminescent nanomaterials are very promising for various applications in optoelectronics and biological labelling (Kaufmann et al. 2007; Walker et al. 2010). The optical properties of QDs per se and in conjugation with other entities have been extensively studied for their role in agricultural production. Pesticides/herbicides and growth promoting hormones have been widely used in agricultural production and their residues accumulate in various agricultural products and soils. Therefore, efficient and reliable methods for detecting residual pesticides and other agrochemicals were developed exploiting QDs for highly sensitive and selective detection.

17.5 Nanoparticle–Soil Interactions

Interaction of nanoparticles with the environmental components such as plants, microorganisms and soil have been extensively studied (Abhilash et al. 2012; Bakshi et al. 2014; Mohanty et al. 2014). Once the nanoparticles find their way into the soil environment, their fate, transport, bioavailability and consequent toxicity are largely affected by the soil physico-chemical properties (Shoults-Wilson et al. 2011; Cornelis et al. 2012; Benoit et al. 2013). Comprehensive information on the occurrence, activities and effects of nanoparticles on the agro-ecosystem is depicted in Fig. 17.1. The factors such as soil texture, pH, cation exchange capacity and soil organic matter govern the transport, mobility and sorption of nanoparticles in the soil (Oromieh 2011; Benoit et al. 2013). Oromieh (2011) and Benoit et al. (2013) have demonstrated that the soil pH and cation exchange capacity significantly affect the bioavailability of silver nanoparticles and silver metal in soil. At higher pH, the soil exhibits a greater cation exchange capacity due to which Ag ions are absorbed onto the soil surface, which reduces their bioavailability. Also, the soil organic matter affects the sorption and mobility of nanoparticles. High organic contents of soil promote the strong binding of nanoparticles to the soil, and thereby retard their mobility, availability for biological uptake and subsequent toxicity (Shoults-Wilson et al. 2011). Furthermore, physico-chemical properties of soil and nanoparticles such as size, shape and surface charge are believed to exert important control on dissolution, agglomeration and aggregation of nanoparticles. Interestingly, enhanced ionic strength and divalent cations are reported to promote silver nanoparticle aggregation and retention in soil (Lin et al. 2011; Thio et al. 2012). Cornelis et al. (2013) have suggested that hetero-aggregation of silver nanoparticles with natural soil colloids significantly reduce their mobility. However, agglomeration of polyvinylpyrrolidone (PVP)-silver nanoparticles has not found to be influenced by increasing ionic strength, which reflects the importance of stabilizing agents.

17.5.1 Nanoparticles Interaction with Soil Bacteria

The broad-spectrum antimicrobial properties of nanoparticles, particularly the nano silver, against human and plant pathogens have been extensively reported (Shahverdi et al. 2007; Kim et al. 2009; Musarrat et al. 2010). The interaction of nanoparticles with soil microbiota and the plausible mechanism of cyto and genetic toxicity are represented in Fig. 17.1. However, their impact on soil biota is still not well understood. Certain studies have suggested the adverse effect of silver nanoparticles on denitrifying bacteria, which disrupts the process of denitrification in soil (VandeVoort and Arai 2012). Also, the effect of nanoparticles on *Pseudomonas stutzeri* (denitrifier), *Azotobacter vinelandii* (nitrogen fixer) and

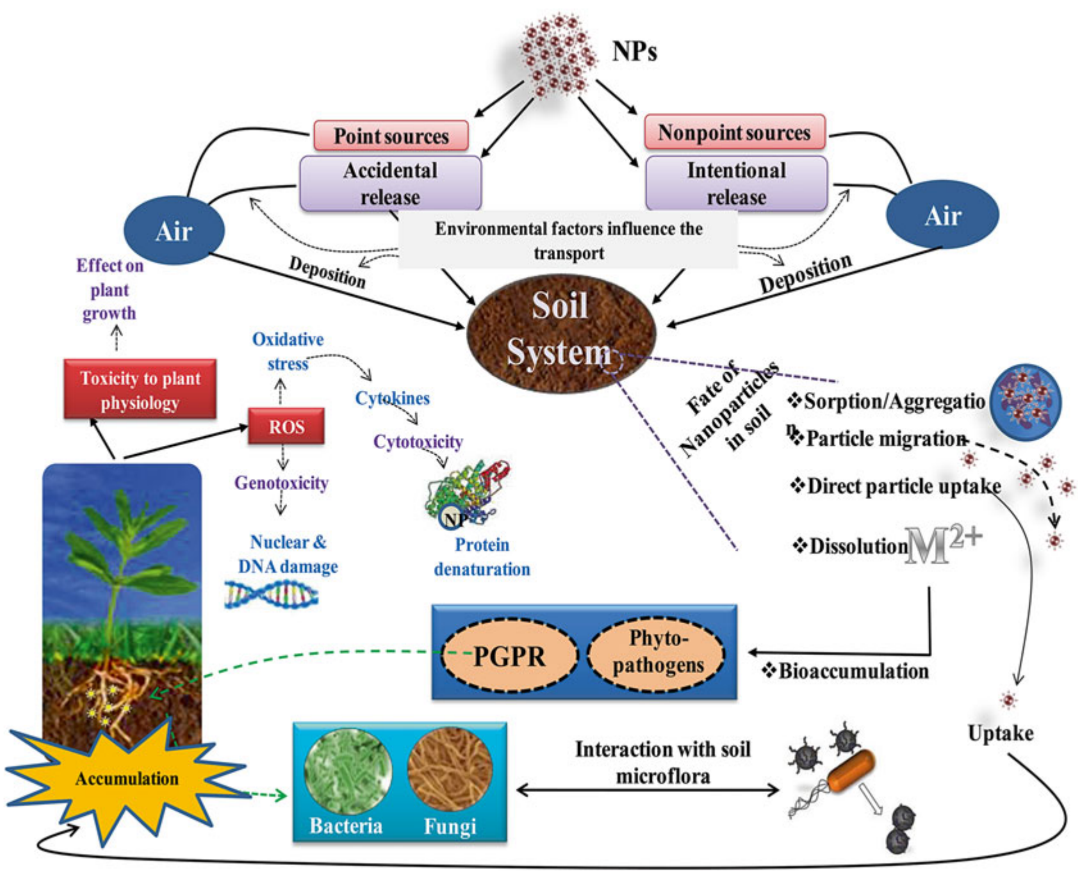

Fig. 17.1 Occurrence, activities and effects of nanoparticles in the agro-ecosystem

Nitrosomonas europaea (nitrifier) have been reported (Yang et al. 2013). Shahrokh et al. (2014) have demonstrated that nano silver at low doses exerts no adverse effect on nitrate reductase activity of *Rhizobium* and *Azotobacter*. However, size-dependent toxicity of nanoparticles has been demonstrated by Choi and Hu (2008), who have suggested that nanoparticles of size < 5 nm exhibit more toxicity to nitrification bacteria. On the contrary, Zhang et al. (2014) reported no significant impact of the long-term exposure of nano silver at concentrations of 0.10 μg/mL on microbial community structure and nitrifying bacterial community in an activated sludge. Studies have reported an increase in the copy number of the silver-resistant gene silE, which may change the population dynamics (Silver 2003). Also, an increase in diversity of nirK denitrifiers (nirK encodes the copper nitrite reductase) has been reported with increasing concentration of nano silver in soil, whereas the gene copy number and denitrification activity have been found to be decreased (Throbäck et al. 2007). Besides microbial diversity, the microbial community functions also get influenced, simultaneously, by nano silver exposure (Silver 2003). Hansch and Emmerling (2010) suggested a dose-dependent effect of silver nanoparticles on soil microbial biomass and enzyme activities. However, no significant effect on microbial biomass nitrogen and enzymatic activities is reported on C, N and P cycling in soil. Similarly, exposure to zinc oxide nanoparticles (ZnO-NPs) also has shown to exert adverse effect on plant development (Lin and Xing 2007). For instance, the growth of garlic raised under hydroponic conditions gets retarded at a ZnO-NP concentration as low as 15 μg/ mL, with dose-dependent effects found up to 50 μg/mL (Child et al. 2007). ZnO-NPs are also reported to reduce cucumber biomass in hydroponic cultures (Dimkpa et al. 2012), whereas the growth of wheat, bean, corn and rye grass has been attenuated in sand or liquid growth systems (Parker et al. 2005; Wang et al. 2009). In addition to reduction in root elongation, stimulation of lateral roots occurs in wheat, which causes a change in root architecture upon ZnO-NPs treatment (Jackson and Taylor 1996). Similarly, the exposure to CuO-NPs has also demonstrated negative impact on growth and DNA integrity in case of raddish, rye grass and buckwheat (Lok et al. 2006; McQuillan et al. 2012). A study in tomato suggested the role of CuO-NPs as fungicides against plant pathogens with little or no deleterious effect on plant performance (Nel et al. 2006). Toxic effect of CeO_2-NPs has been reported in wheat and pumpkin (Kloepper et al. 1980). These nanoparticles were also found to induce significant antioxidative enzyme activity and prevented membrane peroxidation and leakage of cytoplasmic membrane in maize (Lodewyckx et al. 2002). Also, the TiO_2-NPs have been shown to inhibit maize leaf growth and transpiration (Xiu et al. 2012) and result in impaired growth of wheat (Kahru et al. 2008). Tomato root and stem elongation, as well as biomass production, has also been shown to be inhibited by TiO_2-NPs and mitigate the growth of root-knot nematodes infesting the plants (Lewinson et al. 2009). However, in spinach plant, the TiO_2-NPs caused improved physiological and growth responses due to increase in ribulose-1,5-bis-phosphate carboxylase/oxygenase activity and chlorophyll production, responsible for enhanced photosynthesis (Miller et al. 2009; Loper et al. 2012). The effects of TiO_2-NPs on *Lepidium sativum* (cress) varied with soil type and have exhibited both positive and negative growth outcomes at varying concentrations (Li et al. 2008).

17.5.2 Conclusion and Future Perspective

Nanotechnology is a promising technology with the potential to engender colossal changes in food and agricultural sectors. Extensive research on the application of nanomaterials in agriculture is expected but with a caveat for environmental security and food safety. Indeed the risk assessment of the nanomaterials and nanoformulations developed for use in agriculture is still not well defined. Undoubtedly, nanotechnology-based applications can increase production and allow better management and conservation of inputs. However, the extensive use of nanomaterials has raised critical issues regarding their disposal and other associated risks. Extensive studies are warranted to understand the mechanism for nanomaterials toxicity and their impacts on environment and human health. Furthermore, the innovative agro-nanotech products are facing difficulties in market outreach, making agriculture still a marginal sector for nanotechnology. Perhaps this is due to relatively high production costs of nanotech products, indistinct technical benefits and legislative uncertainties. Therefore, it is important to create awareness about the potential advantages of nanotechnology in agriculture for general public interest and acceptance.

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