

Potential applications of nanotechnology in major agriculture divisions - A Review

D. Kanjana

Central Institute for Cotton Research, Regional Station, Coimbatore – 641 003, Tamil Nadu, India.

Corresponding author: kanjana16@rediffmail.com

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Abstract

Nanotechnology, a promising interdisciplinary science has already been adopted by various sectors like medicine, pharmaceuticals, electronics and energy. But, recently, agriculture and food science door has been opened up for allowing nanoscience and technology to revolutionize them. Due to small size, large surface to volume ratio, chemical reactivity, enhanced solubility and unique magnetic and optical properties of nanoparticles, the long term positive effects on agriculture production including enhanced germination percentage, rapid and accurate gene delivery system, timely and controlled agrochemicals delivery system for better plant growth and effective monitoring of pest and disease occurrence by using nanosensor can be achieved. Additionally, this nanotechnology also helps to increase the span of life, freshness and quality of food by resisting the gas penetration, increasing the tensile strength and enhancing micronutrient and antioxidant absorption through food packaging and preserving nanomaterials. In this paper, recent research, development and potential applications of nanotechnology in major agricultural divisions like crop improvement, crop management, crop protection and food science have been reviewed.

Highlights

Nanotechnology is a new emerging technology because of having unique properties such as nanometer size of the particle, higher surface to volume ratio, greater surface reactivity with unique quantum size effects which offers great potential to renovate the science and technology.

Nowadays, nanotechnology has opened up a large scope to revolutionize the agriculture and food sectors with new concepts, ideas and tools by maximising the productivity and reduce the poverty in coming years.

Recent research, development and potential applications of nanotechnology in major agricultural divisions like crop improvement, crop management, crop protection and food science has been reviewed in this paper.

Keywords: Disciplinary, revolution, nanotechnology, antioxidant

Since time immemorial, Agriculture is the backbone of national economy particularly in developing countries, with more than 60% of the population reliant on it for their livelihood (Brock *et al.* 2011). Now days, it's facing numerous challenges such as

climate change, reduction of agricultural land due to urbanisation and low productivity of agricultural crops with higher resource cost that leads to poverty and malnutrition. Food security is the major concern for all developing countries of the world. Even

though we attained the highest food surplus for feeding every individual with the help of technology advancement like Green revolution, but in coming years, we could not feed the burgeoning population adequately due to stagnant crop productivity. This plateau level of food grain production should be increased around 1.5 % per annum (Robert *et al.* 1999). Moreover, by 2050, the world population is expected to be 9.1 billion people and hence, 50 - 70 % of more food needs to be produced to feed them enough (Naderi and Shahraki 2013). Therefore, to increase the productivity from stagnant level and to overcome the chronic hunger owing to food crisis, urgent need is required for alternate advanced technology to revolutionize the agriculture.

Recently, Nanotechnology has stepped into agriculture to revolutionize the field with new concepts, ideas and tools for maximising the productivity and reduce the poverty (Norman and Hongda 2013). Royal Society and Royal Academy of Engineering (2004) defined that "Nanotechnology is the Design, Fabrication and Utilization of materials, Structures, devices and systems through control of matter on the nanometer length scale and exploitation of novel phenomena and properties (physical, chemical, biological) at that length scale in At Least One Dimension". Nanotechnology employs nanoparticles (NPs) having one or more dimensions in the order of 100 nm or less (Auffan *et al.* 2009). Other authors refer to nanoparticles as colloidal particulate systems with size ranging between 10 and 1000 nm (Nakache *et al.* 1999). Nature and manmade macro and nano scale level things are depicted in Figure 1. Nanoparticles are having wonderful properties like smaller size *ie.*, nanometer scale, higher surface to volume ratio, greater surface reactivity with unique quantum size effects like mechanical, electrical, optical, magnetic, thermal stability and catalytic activity (Ghormade *et al.* 2011). The nanoparticles differ substantially from bulk materials, in fact, at this scale, matter behaves differently from the laws of applied quantum physics creating new objects with different properties (Maurice and Hochella 2008).

There are two approaches for nanoparticle synthesis, one is top down approach such as milling, high pressure homogenization and sonication, second is bottom up approach involves reactive precipitation and solvent displacement (Sasson *et al.* 2007). Different type of nanomaterials like metal, metal oxide, silicates and polymeric nanoparticles, quantum dots, nanobarcode, nanotube, nanoemulsions, nanofibres, nanoliposomes, nanosensor and others have been used as building blocks to create novel structures and introduce new properties in the nanoscale level for developing the agriculture and food market in the world. During the 21st century, nanotechnology will make a significant impact on World's economy, industry and people's lives (Dit a 2012).

Applications of nanotechnology in agriculture is in the nascent stage and theoretical, but it has the power to change the whole agriculture and food systems in coming years. This novel scientific approach has the potential to advance agricultural productivity through crop improvement, crop management, crop protection by involving genetic improvement of plants, delivery of genes and drug molecules to specific sites at cellular levels, nano-array based gene-technologies for gene expressions in plants and animals under stress conditions, protect the seed from diseases and pathogen, separate the unviable and infected seed and maintain the genetic purity during seed production, early and rapid disease and pest detection by using nanosensors, controlled and smart delivery systems for agrochemicals like fertilizers and pesticides (Cinnamuthu and Boopathi 2009). In food sector, fortification of nutrients, antioxidants, vitamins and food supplements in food, identification and detection of presence of any number and kind of bacteria and pathogens rapidly and accurately to keep the food fresh for long time can also be achieved by small particulate nanotechnology. So, this review has been prepared to focus on recent research, development and potential applications of nanotechnology in major agricultural divisions like crop improvement, crop management, crop protection and food science (Figure 2).



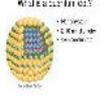
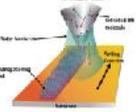
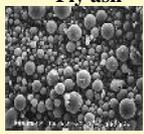
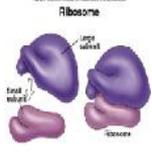
Macro level		Nano level	
Human  1 m	Plant and animal cell  100 μm	Hydrogen atom  0.1 nm	Quantum Dots (of CdSe)  8.0 nm
Mouse  10 cm	Human hair  60 -120 μm	Buckminster fullerene(C60)  1.0 nm	Dip pen nanolithography  10-15 nm
Fly  1 cm	Fly ash  10- 20 μm	DNA (width)  2.0 nm	Dendrimers  10 nm
Ant  5 mm	Red blood cell with white cell  2-5 μm	Nanotube  3-30 nm	Ribosome  25 nm
Head of a pin  1-2 mm		Proteins  5-50 nm	Quantum Dots  8.0 nm

Fig. 1. Scale of Things - Macro and nanometer level - Nature vs. Fabrication

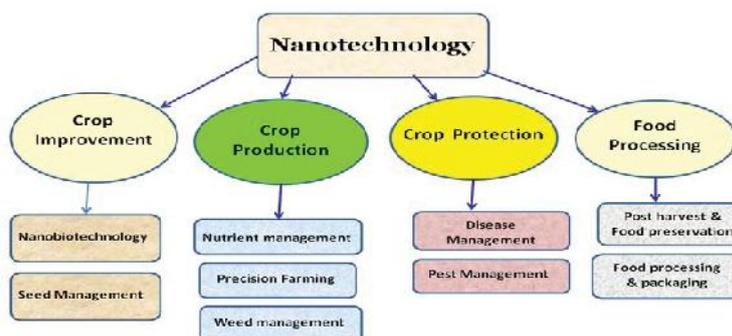


Fig. 2. Applications of Nanotechnology in Agriculture

Applications of Nanotechnology in Agriculture and Food Science

Crop Improvement

Nano biotechnology

Biotechnological research has been focusing on improving plant resilience against various environmental stresses such as drought, salinity, diseases, and others. Nanotechnology has the potential to advance agricultural productivity through genetic improvement of plants, modifying the genetic constitution of the crop plants, delivery of genes and drug molecules to the specific sites at cellular levels, and nano-array based gene technologies for gene expressions in plants and animals under stress conditions.

Recently, Nano biotechnology has been popularized as a new arena in cellular and molecular biology, the term was given by Lynn W. Jelinski, biophysicist at Cornell University which offers a new set of tools to manipulate the genes using nanoparticles, nanofibers and nano capsules. DNA (Deoxyribonucleic Acid) molecule *i.e.* genetic material which has been highly used in nanobiotechnology studies for development of pest, pathogen and stress resistant strains of crop plants through gene delivery system (Gelvin 2003; Price and Gatehouse 2008) and also used to build nanostructures and nanomachines.

Plant genetic transformation through viral gene delivery vector, microinjection, Agrobacterium mediated transformation and microprojectile bombardment (Gelvin 2003) face some obstacles like low use efficiency of transportation or can be applied only for dicotyledons (Sivamani *et al.* 2009). Hence, to overcome these obstacles, properly functionalized nanomaterial can be used as a vehicle and could carry a larger number of genes as well as substances able to trigger gene expression or to control the release of genetic material throughout time in plants (Nair *et al.* 2010 and Gutiérrez *et al.* 2011) particularly in both dicotyledonous and monocotyledonous. DNA coated nanoparticles can be able to enter easily into the plant cell due to smaller size and increased

transformation efficiency. Also cell damage will be minimum with increased plant regeneration in nanoparticle applied plants (Ghormade *et al.* 2011). For delivery of DNA genetic material into plant cell, gold nanoparticles (5–25 nm) embedded carbon matrices (Vijayakumar *et al.* 2010), honeycomb surface-functionalized mesoporous silica NP system with 3 nm pores capped with disulphide bond held gold NPs (10–15 nm) using gene gun (Torney *et al.* 2007) and starch NPs (50–100 nm) conjugated with fluorescent material Tris-(2,2'-bipyridine) ruthenium – (Ru (bpy)₃)²⁺ Liu *et al.* (2008) were employed.

Apart from these genetic transformations including cationic liposome gene transfer, polymer and biobeads based gene transfer are pursued as alternatives for DNA delivery due to formation of more stable polymer/ DNA complex, in which cationic polymer interact electrostatically with negatively charged DNA (Borchard 2001). Cationic polymers such as chitosan nanoparticles (100 – 250 nm) are used to condense and deliver DNA both in vitro and in vivo (Kim *et al.* 2007) due to its biocompatibility, low immunogenicity and minimal cytotoxicity nature. The discovery of RNA-based silencing has given new vision to crop improvement by allowing specific control of insect pests that feed upon the double stranded RNA(dsRNA) producing plants (Auer and Frederick 2009; Price and Gatehouse 2008). Chitosan NPs could prove to be efficient in dsRNA delivery due to their efficient binding with RNA, protection and the ability to penetrate through the cell membrane. NPs based siRNA formulations may contribute to insect pest control while avoiding the lengthy process of plant transformations. Micrometer-sized calcium alginate beads referred to as “bio-beads” that encapsulate plasmid DNA molecules carrying a reporter gene for efficient gene transformation in plants (Srilatha 2011).

Miller and Kinnear (2007) opined that nanotechnology is heading towards taking the genetic engineering of agriculture to the next level of atomic engineering, which can enable the DNA of seeds to be rearranged in order to obtain different plant properties including colour, growth and yield. They reported that



controlled biochemical manipulations in cells have been achieved through the integration of carbon nanofibers which are surface modified with plasmid DNA. Nowadays, gene gun or particle bombardment is being used for direct delivery of DNA into intact plant cells. Particles used for bombardment are typically made of gold since they readily adsorb DNA and are non-toxic to cells. Experiments showed that the plasmid DNA transferred by gene gun method using gold capped nanoparticles was successfully expressed in intact tobacco and maize tissues. The major advantage is the simultaneous delivery of both DNA and effector molecules to the specific sites that results in site targeted delivery and expression of chemicals and genes respectively (Nair *et al.* 2010).

Mutations both natural and induced have long since played an important role in crop improvement. Instead of using certain chemical compounds like EMS, MMS and physical mutagens like X-ray, gamma ray, *etc.* for conventionally induced mutation studies, nanotechnology has showed a new dimension in mutation research. In Thailand, Chiang Mai University's Nuclear Physics Laboratory has come up with a new white-grained rice variety from a traditional purple coloured rice variety called Khao Kam through nanotechnology. Using nanotechnology, the scientists changed the colour of the leaves and stems of Khao Kam from purple to green and the grain became whitish (ETC 2004). The research involves drilling a nano-sized hole through the wall and membrane of a rice cell in order to insert a nitrogen atom, using a particle beam and the nitrogen atom is shot through the hole to stimulate rearrangement of the rice's DNA. This newly derived organism through the change at the atomic level is designated as 'Atomically Modified Organism (AMO)' (Chinnamuthu and Boopathi 2009).

Seed management

In recent years, various researchers have studied the effects of different types of nanomaterials on seed germination and plant growth with the aim of better production of the crop. Metal and metal oxide nanoparticles like zinc, titanium, gold, copper,

aluminium and silver are highly influencing the seed germination and plant growth, that can be either positive or negative (Monica and Cremonini 2009). Positively, Khodakovskaya *et al.* (2009) reported that multiwalled carbon nanotubes (MWCNTs) can penetrate tomato seeds and increase the germination rate by increasing water uptake. The MWCNTs increased the seed germination (90 %) as compared to control (71%) and plant biomass (20 days old). Similarly, Zheng *et al.* (2005) reported that nano TiO₂ treated spinach seeds produced plants (30 days old) had 73 % more dry weight, three times higher photosynthetic rate and 45 % increased chlorophyll 'a' formation as compared to control. This spinach seed germination and growth rate was better in smaller size of the nanomaterials. The authors concurred that the nano size of TiO₂ might have increased the seed stress resistance and promote capsule penetration for intake of water and oxygen needed for fast germination. Likewise, Metal nanoparticles *viz.*, silica (Si), palladium (Pd), gold (Au) and copper (Cu) on lettuce seed germination by Shah and Belozerovala (2009) and they reported that nanoparticles of Pd and Au at lower concentrations, Si and Cu at higher concentrations and combinations of Au and Cu had a positive influence on seed germination and root shoot ratio of lettuce seedlings. But, Lin and Xing (2007) evaluated the phytotoxicity of nanomaterials, *ie.*, negative effect (Multiwalled carbon nanotubes, Al₂O₃, ZnO, Al and Zn) on germination of radish, rape, canola, ryegrass, lettuce, corn and cucumber. They revealed that higher concentrations of (2000 mg/L) of nano sized Zn (35 nm) and ZnO (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. Similarly, nano Al and Al₂O₃ affected root elongation of rye grass and corn respectively, whereas nano Al facilitated the radish and rape root growth.

Toxicity of nanomaterials could possibly be reduced by coating them with biocompatible products before their application to seeds, increasing their effectiveness for plant germination and growth while avoiding negative impacts on seedlings (Khot

et al. 2012). Lu *et al.* (2010) reported that citrate coated colloidal Ag nanoparticles were not genotoxic (genetic), cytotoxic (cell) and phototoxic (toxicity photo degradation) to humans however, powder form of citrate coated Ag nanoparticles through were toxic. But the author strongly recommended that powdered Ag nanoparticles toxicity can be reduced when coated with biocompatible polymers like polyvinylpyrrole. Hence, research is needed to investigate the effect of coating nano materials for controlled release of active ingredients like nutrients on seed germination and plant growth.

The other nanomaterials like nanobarcode, nanobiosensor and quantum dots are also used to protect the seeds from contamination, diseases and pests. Nanobarcodes, that are encodable, machine - readable, durable and sub-micron sized taggants are much useful for tracking of novel genes incorporated seeds in the market (Nicewarner Pena *et al.* 2001). Su and Li (2004) developed a technique known as quantum dots (QDs) as a fluorescence marker coupled with immuno-magnetic separation for *E coli* 0157:H7, which will be useful to separate unviable and infected seeds. Similarly, use of bionanosensors helps to alert the possible contamination of pollen and reduces the contamination to maintain the genetic purity of the crop.

Crop Production

Nutrient management

Fertilizer plays a pivotal role for enhancing the agricultural production but their nutrient use efficiency is still very low due to numerous pathway of losses such as leaching, denitrification, microbial immobilisation, fixation and runoff. Generally, about 40 -70 % of nitrogen, 80 – 90 % phosphorus and 50 -70 % potassium of the applied normal fertilizers is lost to the environment and cannot be absorbed by plants, which causes not only large economic and resource losses but also very serious environmental pollution (Wu and Liu 2008). Hence, nanotechnology has come to revolutionize the fertilizer industry by making the fertilizer as 'smart fertilizer' through smart delivery

systems, in which slow or controlled fertilizers can be developed by using nanoencapsulation technique. Earlier, literature on nanotechnology in soil science and plant nutrition was reported scantily but in recent times, various concepts like slow release fertilizers by using clay minerals, polymers and nanocomposites, insoluble fertilizer converted into soluble fertilizer through nanoscience, smart sensing techniques to assess the soil moisture, temperature and nutrient deficiency under precision farming can be collected.

Now a days, clay minerals particularly zeolite based nanofertilizer are very popular among researchers and fertilizer industries. Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations, with a three-dimensional lattice, furrowed by an inner network of pores and channels. Zeolites have a high cation exchange capacity and have often been used as inexpensive cation exchangers for various applications (Breck 1974). This natural super porous mineral (part of group of hydrated alumina silicates) carrying a negative charge can be used to trap positive cations such as ammonium and potassium for slow and steady releasing of nutrient during the crop nutrient requirement. Zeolite surface charge modification can be achieved by addition of surfactant hexadecyltrimethylammonium bromide (HDTMABr) to ensure the negatively charged elements like sulphate and phosphate entrapment (Preetha *et al.* 2014).

Slow release fertilizers are excellent alternative to soluble fertilizers which can reduce the application rate and frequency by releasing their nutrient gradually to coincide with the nutrient requirement of the plant. Recently, coating of polymers either through synthetic or natural have got an attraction in slow delivery technique of agrochemicals. Wu *et al.* (2008) prepared the double-coated slow-release NPK compound fertilizer with superabsorbent and water-retention by crosslinked poly(acrylic acid)/diatomite - containing urea (the outer coating), chitosan (the inner coating), and water-soluble granular fertilizer NPK (the core). This product with excellent slow release and water-retention capacity, being



nontoxic in soil and environmental friendly, could be especially useful in agricultural and horticultural applications. Corradini *et al.* (2010) studied the incorporation of NPK fertilizer sources such as urea, calcium phosphate and potassium chloride into chitosan with methacrylic acid (MAA) nanoparticles for controlled release of nitrogen, phosphorus and potassium nutrients. Encapsulation of urea and phosphorus fertilizers with sulfur nanocoating (≤ 100 nm layer) are useful slow release fertilizers, also the sulfur contents are beneficial especially for sulfur deficient soils (Brady and Weil 1999). The stability of the coating reduced the rate of dissolution of the fertilizer and allowed slow sustained release of sulfur coated fertilizer.

As per the definition of nanotechnology, nanoparticles are having 100 nm or less in size at least in any one of the dimension of the particle but in colloidal particulate system, the size is ranging between 10-1000 nm (Mukhopadhyay and Nirmal 2014). So, another potential area and concept of slow release fertilizer is polymer- clay nanocomposite, which is prepared by hybridization of inorganic clay minerals *viz.*, montmorillonite, bentonite, kaolinite with organic superabsorbent polymer that leads to changes in composition and structure of the product which impart higher water-holding capacity, swelling rate and slow-release property. Studies with pillared clay-modified phosphate fertilizers reported decreased fixation and increased bioavailability of soil phosphorus (Basak *et al.* 2012). Coating and cementing of nano and subnano-composites are capable of regulating the release of nutrients from the fertilizer capsule (Liu *et al.* 2006). A patented nano-composite consists of N, P, K, micronutrients, mannose and amino acids that increase the uptake and utilization of nutrients by grain crops has been reported (Jinghua 2004).

Apart from the various researches on sorption and release characteristics of the nutrients from slow or controlled release nano fertilizers in soil, penetration and transportation of nanoparticles has been discussed now a days by applying the nano nutrients through foliar spray which can also be

enabled as a promising nanofertilizer application method for increasing the crop productivity. Raliya and Tarafdar (2013) biologically synthesized zinc oxide nanoparticle with the average diameter of 3.8 nm in at least one dimension by using extracellular fungus *Aspergillus fumigatus* TFR-8 and they found that greater improvement in shoot-root growth, chlorophyll (photosynthetic pigment), total soluble leaf protein content, rhizospheric microbial population, and P nutrient-mobilizing enzymes (phytase, acid and alkaline phosphatase) by the application of biologically synthesized ZnO nanoparticle at 10 mg L^{-1} concentration on 2-week-old plants. The gum content and its viscosity in seeds of clusterbean at crop harvest were also significantly improved by application of nano ZnO. Application of titanium dioxide (TiO_2) on food crops has been reported to promote plant growth, increase the photosynthetic rate, reduce disease severity and enhanced yield by 30% (Agarwal and Rathore 2014).

The first nano-organic-iron chelated fertilizer in the world produced in Iran is reported to have unique features like ultra high absorption, increases production from 20 to 200 percent, results in rise of photosynthetic rate by 3.5 times and 70 percent expansion of the leaves. Commercially, Lithovit *ie.*, naturally occurring CO_2 foliar spray made from Limestone deposits is available to enhance the plant growth and productivity by increasing the natural photosynthesis on supplying carbon dioxide (CO_2) at optimum concentration. Likewise, NanoGro is a plant growth regulator and immunity enhancer, it is not a source of nutrients and hormones, but here the active ingredient is coded with sugar pellets (Kumar 2011).

Precision farming

Precision farming is one of the most important areas for increasing the productivity of crops by applying inputs in precisely required quantity and in required time (USDA 2002). Tiny sensors and monitoring systems enabled by nano technology will have a large impact on future precision farming methodologies. Precision farming has been a

long-felt goal to maximise output (*ie.* crop yields) while minimising input (*ie.* fertilizers, pesticides, herbicides, *etc.*) through monitoring environmental variables which helps to reduce the agricultural waste and keep environmental pollution to a minimum (Chinnamuthu and Boopathi 2009). The major role for Nanotechnology enabled devices is the use of autonomous nano sensors linked into the GPS system. Networks of wireless nanosensors positioned across cultivated fields provide essential data leading to best agronomic intelligence processes with aim to minimize resource inputs and maximizing output and yield (Scott and Chen 2003). Such information and signals include the optimal times for planting and harvesting crops and the time and level of water, fertilizers, pesticides, herbicides, and other treatments that need to be administered given specific plant physiology, pathology, and environmental conditions. For diagnosing the nutrient deficiency in plants, nano sensors are impregnated with nanoparticles that can be used to determine the nutrient status and deficiency of the plants, which assist in taking up appropriate and timely corrective measures to reduce the yield reduction.

USA and Australia have already exploited this technology. Certain vineyards in California have installed WiFi technology with the help of IT Company, Accenture. Although the initial cost of installing such a system is high but it is justified by the fact that it enables the best grapes to be grown which in turn produce finer wines, which command a premium price. With these nanosensors accurate information about crop growth and field conditions including moisture level, soil fertility, temperature, crop nutrient status, insects, plant diseases, weeds, *etc.*, farmer can able to enhance the crop productivity by making better decisions (Kumar 2011).

Weed management

In agriculture, weed management is a very big problem due to inefficacy of herbicides for multi weed species removal and emergence of herbicide resistance weeds due to continuous exposure of

single herbicide. This enables the crop loss of more than 40 % as compared to other environmental factors such as pests, diseases, soil related factors and crop related conditions *etc.*, Mostly, herbicides are applied through foliar spray, which does not kill them completely particularly perennial weeds such as *Cynodan dactylon*, *Cyperus sp.* and *Solanum elaeagnifolium*, but these herbicides destructs the structure and function of the plant-specific chloroplast, inhibits lipid biosynthesis, interference with cell-division by disrupting the mitotic sequence or inhibiting the plants (Wakabayashi and Peter Böger 2004). Hence, application of encapsulated herbicide molecule *via* root absorption is a simple process as compared to foliar absorption because roots do not have cuticles like leaves. Eventhough there is some barriers for herbicide absorption through roots, but liphophilic based herbicide molecules can be easily absorbed since it's having liphophilic structure. Chinnamuthu and Kokiladevei (2007) reported that target specific herbicide molecule encapsulated with nanoparticle aims for specific receptor in the roots of target weeds, which enter into system and translocated to parts that inhibit glycolysis of food reserve in the root system and it makes the specific weed plant to starve for food and gets killed. In rainfed farming, nano encapsulated herbicide will get the dispersement after it receives the sufficient moisture level. So that the weed seeds with the receipt of rain will get killed by the immediate release of new herbicides molecule. Gruere *et al.* 2011 claimed that nano surfactant based on soybean micelles make glyphosate resistant crops into susceptible.

Crop Protection

Pest management

In Today's agriculture, pest management is a challenging program due to poor diagnosis of pest occurrence, inefficacy of pesticides on plants, spray drift, resistance to the prevalent group of pesticide to control pests and emerging of new pests. For this, viable alternative technology *ie.*, Nanotechnology will be helpful to overcome these problems and to



enhance the efficacy of conventional agrochemicals due to higher surface area, higher solubility, induction of systemic activity, higher mobility and lower toxicity of nanoparticles (Sasson *et al.* 2007). In the normal spray of pesticides application, high volume and low value preparation of agrochemicals are involved but in nanotechnology based preparations, low volume and high value chemicals are involved (Ghormade *et al.* 2011). So, Controlled or smart delivery system is inevitable for targeted pesticide application which aims towards measure the release of necessary and sufficient amounts of agrochemicals over a period of time, to obtain the fullest biological efficacy and to minimize the harmful effects (Tsuji 2001). Potential nanomaterials like clay, polymeric particles and silica capsules possess good biocompatibility, biodegradability and low toxicity behaviour with controlled release properties (Bin Hussein *et al.* 2002; Choy *et al.* 2007). Kaolin a white, non-swelling, plate-shaped alumina silicate mineral is widely used in agriculture as a bio-pesticide and a repellent (Eigenbrode *et al.* 2006) by masking the visual cues. Similarly, Montmorillonite (MMT), hydrophilic and swelling type of clay having higher cation exchange capacity, which can be modified with cationic surfactant and render them hydrophobic (de Paiva *et al.* 2008), then encapsulate the various types of pesticides in both hydrophilic (Mishael *et al.* 2002) and hydrophobic MMT clays (Celis *et al.* 2005). By encapsulation, the efficiency of the insecticides diazinon and chlorpyrifos has been shown to improve from 4 weeks in the commercial formulation to as high as 20 weeks using the MMT clay (Choudary *et al.* 1989). Several polymeric nanoparticles are designed for efficient release of agrochemicals. Liu *et al.* (2008) studied on encapsulation of Bifenthrin by using polymers such as poly (acrylic acid)-b-poly (butyl acrylate), polyvinyl alcohol (PVOH). By following the health care industrial applications, mesoporous silica nanoparticles are being used in agriculture sector to encapsulate the agrochemicals and deliver the active ingredient in controlled manner. Surface functionalized hydrophobic silica can act as an insecticide by getting adsorbed into the cuticular lipids of insects and causing death of insects

by desiccation (Mewis and Ulrichs 2001). A similar effect was shown recently by Debnath *et al* against rice weevil *Sitophilus oryzae* (Debnath *et al.* 2011). Water soluble pesticide validamycin encapsulated in porous hollow silica nanoparticles (PHSN) with a loading capacity of 36% is shown to last for 800 min as opposed to instantaneous release of free validamycin (Liu *et al.*, 2006). Similarly, Li *et al.* (2007) reported that porous hollow silica nanoparticles with shell thickness of ~15 nm and a pore diameter of 4–5 nm encapsulated the avermectin with an encapsulation capacity of 625 g kg⁻¹ slowly released for 30 days by protecting them from UV radiation.

Other than pesticides coating technology (nanoencapsulates, nanocontainers and nanocages) for slow or controlled delivery of active ingredients, nanoemulsion delivery technique is potentially better pesticides delivery medium due to their better kinetic stability, smaller size, low viscosity and optical transparency (Xu *et al.* 2010). Nanoemulsion can be defined as non-equilibrium colloidal system comprising multiple phases, simplest being oil and water, which is visibly translucent and kinetically stable within the range of 20 – 200 nm in size (Solans *et al.* 2005). Nanoemulsion can improve the solubility and bioavailability of nanopesticides, also it enables uniform spreading on the plant leaves and improves internalization in insects (Ebert *et al.* 1999). Wang and coworkers demonstrated that the nanoemulsion of a water-insoluble model pesticide -cypermethrin was highly stable and did not form a precipitate when diluted from the concentrated solution (Wang *et al.* 2007). Similarly, a study on the neem oil nanoemulsions concluded that the larvicidal effect increased with decreasing droplet size (Anjali *et al.* 2012).

Many of the world's leading agrochemical firms are conducting research on development of new nano-scale formulations of pesticides. The world's fourth ranking agrochemical corporation, BASF of Germany has applied for a patent on pesticide formulation, in which active ingredient ideal particle size is 10-150 nm. Similarly, Bayer Crop Science of Germany company has also applied a patent for their

invention of nanoemulsion concentrate, in which the active ingredient is made up of nanoscale droplets in the range of 10-400 nm. Syngenta prepared two nanoemulsion product *ie.*, Banner MAXX (fungicide) and Primo MAXX (plant growth regulator) with the average particle size of 100 nm (Cinnamuthu and Boopathi 2009).

Timely detection of the pests through continuous monitoring of pest occurrence is considered as a time consuming process, but it helps to solve the problem of pest damage in crops by combining with effective diagnosis of insects, fungal, bacterial or viral pathogens, or nutritional stress problems. Diagnosis of pests and pesticide residues helps the farmers and the food manufacturers to ensure that the product meets the criteria for the quality and safety before despatch (Grunert 2005). Biosensors are such devices which can not only detect the pests and the pesticide residues, but are also capable of doing it more accurately and faster than the conventional devices with much smaller sample sizes.

Disease management

Diseases are one of the major factors in limiting crop productivity. Most of the times pesticides and fungicides are applied as a precautionary measure that results in residual toxicity and environmental hazards and on the other hand application of fungicides after the appearance of disease leads to some amount of crop yield losses (Cinnamuthu and Boopathi 2009). Currently, plant disease management by using nanotechnology has been considered as an alternative and effective method for control of plant pathogens. For controlling the plant diseases, some of the nanoparticles *viz.*, carbon, silver, silica and alumina silicates can be used because of having great potentiality as compared to systemic fungicides (Prasad *et al.* 2014). Normally, silver displays different modes of inhibitory action to microorganisms (Young 2009), it affects many biochemical processes in the microorganisms including the changes in routine functions and plasma membrane (Pal *et al.* 2007) and also prevent the expression of ATP production associated proteins (Yamanka *et al.* 2005).

Though, in an ionic state silver exhibits antimicrobial activity but it is unstable due to its high reactivity and thus gets easily oxidized or reduced into a metal depending on the surrounding media and it does not continuously exert antimicrobial activity (Agarwal and Rathore 2014). So, Nano silver has been considered as a strong bactericidal and broad spectrum antimicrobial agent to reduce various plant diseases caused by spore producing fungal pathogens. Silver nanoparticles, which have high surface area and high fraction of surface atoms, have high antimicrobial effect compared to the bulk (Suman *et al.* 2010). Mostly effectiveness of silver nanoparticles are depends upon the detection of penetration and colonization of fungal spores within the plant tissues and size of the nanoparticle. The smaller size of the Ag nanoparticles *ie.*, 1-5 nm effectively controlled the powdery mildew diseases. Nair *et al.* (2010) studied the harmful effects of Ag nanoparticles on conidial formation of unidentified fungal species of the genus *Raffaelea* causing mortality of oak trees and extending the vase life of gerbera flowers by inhibiting the microbial growth and reduced vascular blockage for increasing the water uptake and maintaining the turgidity of gerbera flowers.

Silicon (Si) is known to be absorbed by plants to increase disease resistance and stress resistance by promoting the physiological activity and growth of plants. Aqueous silicate solution is reported to exhibit exceptional preventive effects on pathogenic microorganisms causing powdery mildew or downy mildew in plants. Additionally, it promotes the physiological activity and growth of plants and induces disease and stress resistance in plants (Agarwal and Rathore 2014). Combination of nanosized silica and silver has the great potential to control the plant diseases (Sharon *et al.* 2010). Similarly, Zinc oxide (ZnO) and Magnesium oxide (MgO) nanoparticles are effective antibacterial and anti-dour agents (Shah and Towkeer, 2010). ZnO nanoparticles inhibited the fungal growth of *Botrytis cinerea* by influencing cellular functions, which caused deformation in mycelia mats. In addition,



Zinc oxide nanoparticles inhibited the growth of conidiophores and conidia of *Penicillium expansum*, which finally led to the death of fungal mats as reported by Abd-elsalam (2013). TiO_2 not only has the growth promoting effect but also has an excellent property of antibacterial and antifungal activity, which has been found to show their effectiveness on controlling of *Curvularia* leaf spot and bacterial leaf blight disease in maize, blast disease in rice and tomato spray mold with a correspondent 20% increase in grain weight due to the growth promoting effect of TiO_2 nanoparticles (Mahmoodzadeh *et al.* 2000). A combination of titanium dioxide, aluminium and silica was reported to be effective in controlling downy and powdery mildew of grapes by Bowen *et al.* (1992), possibly through direct action on the hyphae, interference with recognition of plant surface and stimulation of plant physiological defences.

Another alternative strategy in disease management program is invention of nanobased diagnostic kit to detect the molecular defects either at genomic or biochemical level, exact strain of virus and stage of application. Generally, Disease diagnosis is difficult mainly because of the exceptionally low concentrations of biochemical and also due to the presence of very low amount of detectable virus and many fungal or bacterial infections (Misra *et al.* 2013). Detection and utilization of biomarkers that accurately indicate disease stages with differential protein production in both healthy and diseased states lead to the identification of the development of several proteins during the infection cycle. These nano-based diagnostic kits not only increase the speed of detection but also increase the power of the detection (Cinnamuthu and Boopathi 2009). Biosystems are endowed with functional nanometric devices such as enzymes, proteins, and nucleic acids, which detect vital processes in plants.

Food Science Sector

Food packaging

In the food industry, novel applications of

nanotechnology have become apparent, including the use of metal and metal oxide nanoparticles, nanoemulsions, biopolymeric nanoparticles, nanocomposites and nanosensor, which are aimed at ensuring food safety. Most important problem in food packaging sector is oxygen entry into the food and spoils the fat in meat and cheese and turns them pale. Therefore, nowadays, nanocomposite materials are developed by thin film coating technology for food packaging not only protects the food by preventing the oxygen enters into food and increases its shelf life but can also be considered as a more environment friendly solution because it reduces the requirement to use plastics as packaging materials (Sozer and Kokini 2009). Researchers at Bayer Polymers developed the nanocomposite food packaging material by using polyamide 6 (the base polymer Bayer uses for Durethan®) plastic and layered silicates (clay) that reduces entry of oxygen and other gases and exit of moisture thus preventing food from spoilage. Similarly, Nanocor, a subsidiary of Amcol International Corporation, USA has developed a nanocomposite called Imperm that is used as a substitute for glass bot les to store beer and to minimize the loss of carbon dioxide and entry of oxygen into the bot les for increase the shelf life around 6 weeks (Sekhon 2010).

Polymeric nanoparticles are important component in food packaging industry to increase the gas barrier properties along with its biodegradable nature. Zein, a prolamine and the major component of corn protein has been considered as an important polymeric material in food industry owing to its unique properties and molecular structure which can be used as flavour compounds or for encapsulation of nutraceuticals as well as to improve the strength of plastic and bioactive food packages (Sozer and Kokini 2009). Likewise, chitosan based nanocomposites films especially silver-containing ones, showed a promising range of antimicrobial Activity. PEG (poly ethylene glycol) coating nanoparticles loaded with garlic essential oil could be used to control the store-product pests. Phytoglycogen octenyl succinate nanoparticles with ϵ -polylysine increased

the shelf life of the product significantly. Here, the nanoparticle created a stronger defense against oxygen, free radical and metal ions that cause lipid oxidation.

Recently, carbon nanotubes have been discovered as part of the food packaging material, it exhibits powerful antimicrobial effects on *E. coli* bacteria. Similarly, metal oxide nanoparticles like nanozinc oxide and nano magnesium oxide are also using in a food packaging due to its antimicrobial properties. Nano wheels, nanofibers and nanotubes are being investigated as a means to improve the properties of food packages. Nanoemulsions have been developed for decontamination of food packaging equipment and food. Nanoemulsions are effective against a variety of food pathogens, including Gram-negative bacteria. The growth of *Salmonella typhimurium* colonies has been eliminated by treatment with nanoemulsion (Sekhon 2010).

Recent studies have shown that nanoscale cellulosic nanomaterials obtained from crops and trees, opens up a whole new market for novel and value-added nano biomaterials and products of crops and forest. For example, cellulosic nano crystals can be used as light weight reinforcement in polymeric matrix as nanocomposite, which would be further used for (Laborie 2009; Chen and Yada 2011) food and other packaging, construction, and transportation vehicle body structures. The cellulosic nano whiskers (CNW) from wheat straw would be used to make biocomposites that could substitute for fiberglass and plastics in many applications, including automotive parts (Leistriz *et al.* 2007).

Post harvest and food preservation

In addition to food packaging, food preservation has also got importance in the food industry. Food spoilage leads to food poisoning that creates sensitivity for people lives and health care expenditures. Nanomaterials help to keep products fresh for a longer period of time by using nanosensors placed in food production and distribution facilities, food packaging or the food itself which can detect all kinds of food pathogens like *E.coli*,

Campylobacter and Salmonella by attaching themselves to the pathogens (Chinnamuthu and Boopathi 2009). Hence, nanosensor could be placed directly into the packaging material, where they would serve as electronic tongue or noses by detecting chemicals released during food spoilage. Nanosensors can work by different methods *ie.* nanosensors can be tailor-made to fluoresce into different colours or can be made out of magnetic materials. Different types of nanosensors such as electronic nose, array biosensors, microfluidic devices, nano electro mechanical systems (NEMS) and carbon nanotube biosensors are used in the food industry to detect compounds of interest rapidly and monitor any adulteration in food packaging and food preservation. Nanocantilevers biosensors have already had tremendous success in studies of molecular interactions and in the detection of contaminant chemicals, pathogens, toxins and antibiotic residues in food products. (Sozer and Kokini 2009).

In food and beverage industry, at empts have been made to add micronutrients and antioxidants into food substances. Nanoliposomes, archaosomes and nanococheleates are some of the most promising lipid based carriers for antioxidants, which help in preventing the degradation of food during manufacturing, processing and storage. Nanococheleates solve early oxidation by individually capturing and wrapping them in a phospholipids wrap and maintaining the internal nutrients secure from water and oxygen. Bio Delivery Sciences International have developed nanococheleates, which are 50 nm coiled nanoparticles and can be used to deliver nutrients such as vitamins, lycopene and omega 3 fat y acids more efficiently to cells, without affecting the colour or taste of food. The delivery vehicle is made of soy phosphatidyl serine which is 100% safe and provides a protective coat for range of nutrient additives (Narayanan *et al.* 2013). Microencapsulation is one of the potent methods to maintain the high viability and stability of probiotic bacteria during the food processing and storage time (Das *et al.* 2014). Apart from the polymeric coating materials such as gums, carbohydrates, cellulose and proteins for encapsulation of probiotics, nowadays,



agrowaste based nanofibre is considered as a novel encapsulant of probiotics (Fung *et al.* 2011).

Conclusion

This review has focused on applications of nanomaterials in agriculture divisions like crop improvement, crop management, crop protection and food sciences. Nanotechnology has the tremendous potential to change the agriculture scenario *ie.*, enhancement of crop production and productivity from confined land areas which could be achieved by managing the inputs through smart delivery system, nanoscale coatings, nanosensors and other nanomaterials. So, agricultural sector may be energized by introduction of second green revolution due to the acceleration of nanotechnology in the coming years and also this technology will become the fortune of every country. Though this interesting and promising technology has the power to shower the benefits not only to agriculture and food sciences but also for other sectors, but it has been apprehended with unforeseen risks. Therefore, creating the awareness about the advantages and challenges of nanotechnology for better acceptance of people and society along with extensive studies are required to understand the mechanism of nanoparticles, toxicity and their impact on environment.

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