Nanotechnology in the Life Sciences

Khalid Rehman Hakeem
Tanveer Bilal Pirzadah *Editors*

Nanobiotechnology in Agriculture

An Approach Towards Sustainability

Springer

Nanotechnology in the Life Sciences

Series Editor

Ram Prasad
Department of Botany
Mahatma Gandhi Central University, Motihari, Bihar, India

Nano and biotechnology are two of the 21st century's most promising technologies. Nanotechnology is demarcated as the design, development, and application of materials and devices whose least functional make up is on a nanometer scale (1 to 100 nm). Meanwhile, biotechnology deals with metabolic and other physiological developments of biological subjects including microorganisms. These microbial processes have opened up new opportunities to explore novel applications, for example, the biosynthesis of metal nanomaterials, with the implication that these two technologies (i.e., thus nanobiotechnology) can play a vital role in developing and executing many valuable tools in the study of life. Nanotechnology is very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale, to investigating whether we can directly control matters on/in the atomic scale level. This idea entails its application to diverse fields of science such as plant biology, organic chemistry, agriculture, the food industry, and more.

Nanobiotechnology offers a wide range of uses in medicine, agriculture, and the environment. Many diseases that do not have cures today may be cured by nanotechnology in the future. Use of nanotechnology in medical therapeutics needs adequate evaluation of its risk and safety factors. Scientists who are against the use of nanotechnology also agree that advancement in nanotechnology should continue because this field promises great benefits, but testing should be carried out to ensure its safety in people. It is possible that nanomedicine in the future will play a crucial role in the treatment of human and plant diseases, and also in the enhancement of normal human physiology and plant systems, respectively. If everything proceeds as expected, nanobiotechnology will, one day, become an inevitable part of our everyday life and will help save many lives.

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Khalid Rehman Hakeem • Tanveer Bilal Pirzadah
Editors

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Editors
Khalid Rehman Hakeem
Department of Biological Sciences
Faculty of Science
King Abdulaziz University
Jeddah, Saudi Arabia

Tanveer Bilal Pirzadah
Assistant Professor
University Centre for Research and Development (UCRD)
Chandigarh University
Mohali, Punjab, India

ISSN 2523-8027 ISSN 2523-8035 (electronic)
Nanotechnology in the Life Sciences
ISBN 978-3-030-39977-1 ISBN 978-3-030-39978-8 (eBook)
https://doi.org/10.1007/978-3-030-39978-8

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This book is dedicated to

***Fatima bint Muhammad Al-Fihriya Al-Qurashiya**,*
an Arab Muslim woman who is attributed with founding the oldest existing, continually operating and first degree-awarding educational institution for natural sciences in the world, the University of al-Qarawiyyin in Fez, Morocco in 859 CE. She is also known as "Umm al-Banayn"

(Source: wikipedia.org)

Foreword

Agriculture is the backbone of developing nations and provides employment to more than half of the workforce. The agricultural land is shrinking in respect of crop productivity due to land degradation, reduced soil fertility, and low water accessibility. The excessive use of chemical fertilizers and pesticides to increase the crop yield is not safe for environment and human health. In this regard, nanobiotechnology serves as a freelancer to tackle the problems related to agricultural sector. Nowadays, nano-agribusiness is an emerging field to enhance crop yield, rejuvenate soil health, provide precision farming, and stimulate plant growth. Thus, agri-nanobiotechnology plays a pivotal role in the agricultural sector, without possessing any pessimistic impact on the environment and biosafety issues.

This book *Nanobiotechnology in Agriculture: An Approach towards Sustainability* published by Springer includes 13 chapters. Chapter “Nanotechnology: An Overview” presents an overview on the methods of preparation of nano-engineered active ingredients of fertilizers, pesticides and their formulation of nanocarriers for their controlled release and targeted delivery. Chapter “Embodiment of Nanobiotechnology in Agriculture: An Overview” deals with the embodiment of nanobiotechnology in agriculture. Chapter “Nanotechnology: A Boost for the Urgently Needed Second Green Revolution in Indian Agriculture” focuses on the use of nanotechnology to boost the green revolution in Indian agriculture. Similarly, Chapter “Role of Nanotechnology in Crop Improvement” deals with the basis of crop improvement through nanotechnology. Chapter “Nanofertilizers: A Way Forward for Green Economy”, by the joint authorship of Indian and Saudi Arabian researchers, focuses on the various scopes and economic aspects of nano-formulations. In Chapter “Nano-enabled Agriculture Can Sustain “Farm to Fork” Chain”, the Indian author entails the vital role of nanotechnology to boost the agribusiness and food industry for their sustainable development. Chapter “Nano-Biosensors: NextGen Diagnostic Tools in Agriculture” by the Indian investigators discusses the importance and practices of nano-biosensors as a next-generation diagnostic tool to boost the agricultural practices, while Chapter “Development of Nano-formulations via Green Synthesis Approach” deals with the development of nano-formulations via green synthesis approach. However, Chapter “Nano-agrochemicals: Economic Potential and Future Trends” focuses on the economic potentials and future trends of nano-agrochemicals. Chapter “Pros and Cons of Nanotechnology” emphasizes on the pros and cons of nanotechnology. Chapter “Nanoparticles: The Magic Bullets in Mitigating Drought Stress in Plants” describes the role of nanoparticles in mitigation of drought stress in plants. However, Chapter “Nanotechnology: An Innovative Tool to Enhance Crop Production” deals with the potential of agro-nanotechnology to transform the agricultural and agro-business sector, while significances and potentiality of CRISPR/Cas 9 as a new revolutionary science in agricultural and horticultural sciences are summarized in Chapter “CRISPR/Cas9: A New Revolutionary Science in Agricultural and Horticulture”. This volume includes various aspects of agri-nanobiotechnology to resolve the issues related to global food security, sustainability and climate change, nano-formulation, etc. to boost up the agricultural and agribusiness sectors. I congratulate Prof. Khalid Rehman Hakeem and Dr. Tanveer Bilal for their decent academic effort in bringing out this book.

Dr. Mohd. Sayeed Akhtar
Department of Botany
Gandhi Faiz-e-Aam College
Shahjahanpur, Uttar Pradesh, India

Preface

Agriculture is regarded as the backbone of the national economy of the developing countries of the world as about two-fifth of their population depends upon agriculture for their livelihood. The progress in agriculture sector plays a critical role in population growth and economic forums as it produces raw materials for food and feed industry. Currently, due to the growing population and other anthropogenic activities, global agricultural production faces many challenges such as decreased crop yield, soil fertility, soil degradation, low efficiency and labour shortages due to expulsion from agriculture. In addition, losses of bioresources are occurring at an alarming rate, with dramatic effects on people's livelihood. The population is projected to reach 9 billion by 2050, and it will be mandatory to generate at least 50–70% more production to feed such a large population. The exorbitant use of conventional fertilizers and pesticides to increase production efficiency is of course not an appropriate choice for the long term, as these fertilizers are considered as double-edged sword, which increases crop yields but at the same time, they have a detrimental effect on the soil microflora and thus reduce fertility. In addition, it irreversibly damages soil texture and disrupts the balance of the food web in the ecosystem, which can lead to genetic mutations in future generations. The increased reliance on conventional fertilizers during and after the Green Revolution has caused serious problems of sustainability and health risks.

To overcome the disadvantages of conventional fertilizers, bioformulations have been created to revolutionize the agricultural sector because of their eco-friendly nature and their cost-effectiveness. Nevertheless, this approach has also been confronted with some problems, like short life span, stability, solubility, low absorption efficiency by plants and the high dosage requirement. To combat these problems, nano-formulations have received an overwhelming response due to superiority over bioformulations. Nano-biotechnologies have thus become a promising tool to tackle the above-mentioned problems, particularly in the agricultural sector, to combat global food production and boost the agricultural sector. Nano-agribusiness is a new field that improves crop yields, regenerates soil health, ensures precision agriculture and stimulates plant growth.

In this book, we have tried to integrate literature focusing the issue related to agricultural productivity, different practices to manage these issues and then the role of the nano-biotechnology in environmental and agricultural sustainability. The chapters in this book highlight importance of nano-biotechnology as an innovative tool to enhance production yield and environmental sustainability.

We are highly grateful to all our contributors for readily accepting our invitation for not only sharing their knowledge and research, but for venerably integrating their expertise in dispersed information from diverse fields in composing the chapters and enduring editorial suggestions to finally produce this venture. We greatly appreciate their commitment.

We thank Springer-International team for their generous cooperation at every stage of the book production.

Jeddah, Saudi Arabia Khalid Rehman Hakeem
Mohali, Punjab, India Tanveer Bilal Pirzadah

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About the Editors

Khalid Rehman Hakeem, PhD, is Professor at King Abdulaziz University, Jeddah, Saudi Arabia. After completing his doctorate (Botany; specialization in Plant Ecophysiology and Molecular Biology) from Jamia Hamdard, New Delhi, India, in 2011, he worked as a lecturer at the University of Kashmir, Srinagar, for a short period. Later, he joined Universiti Putra Malaysia, Selangor, Malaysia, and worked there as Postdoctoral Fellow in 2012 and Fellow Researcher (Associate Prof.) from 2013 to 2016. Dr. Hakeem has more than 10 years of teaching and research experience in plant ecophysiology, biotechnology and molecular biology, medicinal plant research, plant–microbe–soil interactions as well as in environmental studies. He is the recipient of several fellowships at both national and international levels; also, he has served as the visiting scientist at Jinan University, Guangzhou, China. Currently, he is involved with a number of international research projects with different government organizations.

So far, Dr. Hakeem has authored and edited more than 36 books with international publishers, including Springer Nature, Academic Press (Elsevier), and CRC Press. He also has to his credit more than 90 research publications in peer-reviewed international journals and 55 book chapters in edited volumes with international publishers.

At present, Dr. Hakeem serves as an editorial board member and reviewer of several high-impact international scientific journals from Elsevier, Springer Nature, Taylor and Francis, Cambridge and John Wiley Publishers. He is included in the advisory board of Cambridge Scholars Publishing, UK. He is also a fellow of Plantae group of the American Society of Plant Biologists, member of the World Academy of Sciences, member of the International Society for Development and Sustainability, Japan, and member of Asian Federation of Biotechnology, Korea. Dr. Hakeem has been listed in Marquis Who's Who in the World, since 2014–2019. Currently, Dr. Hakeem is engaged in studying the plant processes at ecophysiological as well as molecular levels.

Tanveer Bilal Pirzadah, PhD, is Assistant Professor at University Centre for Research and Development (UCRD), Chandigarh University, Mohali, Punjab, India. After completing his doctorate (Bioresources; specialization in Plant Stress Physiology and Biofuels) from the University of Kashmir, Srinagar, India, in 2017, he worked as a lecturer at the Cluster University Srinagar. Dr. Tanveer has about 8 years of research and teaching experience in bioresources management, biofuels, plant stress physiology, biotechnology and molecular biology, medicinal plant research, plant–metal interactions as well as in environmental studies.

He also has to his credit 20 research publications in peer-reviewed international journals and 22 book chapters in edited volumes with international publishers.

At present, Dr. Tanveer serves as an editorial board member and reviewer of several international scientific journals. He is also member of the World Academy of Sciences and Plantae group of the American Society of Plant Biologists. Currently, Dr. Tanveer is engaged in studying the plant processes at proteomic, metabolomic and molecular level to better understand the dynamic plant–metal interactions.

Nanotechnology: An Overview

Sheikh Tanveer Salam, Tanveer Bilal Pirzadah, and Pervaiz Ahmad Dar

1 Introduction

Nanotechnology was first used by Norio Taniguchi in 1974 and it is the art of manipulating matter at the nano-scale because at this scale materials behave differently because the rules that manage the behavior of the elements of our known world start to give way to the rules of quantum mechanics, and everything changes. The term "nano" is a Greek word meaning "dwarf" and it means 10^{-9} or one-billionth part of a meter (Thakkar et al. 2010). Due to small size nanoparticles have some unique properties like higher charge density and reactivity, more strength, increased heat resistance, decreased melting point, and different magnetic properties of nano-clusters. Differences in the exposed surfaces of different nanoparticles lead to variances in atomic distribution across the nanoparticles, which in turn affect the electron transfer rate kinetics between metal nanoparticles and corresponding adsorbed species. These unique properties give the following advantages to nanoparticles in agriculture such as higher solubility in suspension; higher penetration of seed coats and subsequently emerging roots; better bioavailability of molecules to the seed radicals; providing actual concentration and controlled release of fertilizers or pesticides in response to certain conditions; improved targeted activity and eco-friendly with safe and relaxed transport (Pirzadah et al. 2019). Here, we summarize the general overview and categorization of nano-formulations besides its applications in the agriculture sector.

S. T. Salam (✉) · P. A. Dar
Department of Zoology, Amar Singh College, Cluster University,
Srinagar, Jammu and Kashmir, India

T. B. Pirzadah
Assistant Professor, University Centre for Research and Development (UCRD),
Chandigarh University, Mohali, Punjab, India

K. R. Hakeem, T. B. Pirzadah (eds.), *Nanobiotechnology in Agriculture*,
Nanotechnology in the Life Sciences, https://doi.org/10.1007/978-3-030-39978-8_1

2 Categorization of Nano-agrochemicals

Nano-agrochemicals have been categorized into the following types:

2.1 Nano-fertilizers

Nano-enabled fertilizers can be applied in agriculture through various forms. Some of the potential approaches are explained as under:

Nano-composite Polymers

These are used to bind fertilizer nutrients into pellets to improve nutrient use efficiency. Brazilian Agricultural Research Corporation (EMBRAPA) claimed that they have observed in field experiment that by adding a nano-composite polymer to urea, nitrous oxide emissions were reduced by more than 50% (Pereira et al. 2015). Some of the nano-composite polymers that can be used in fertilizers are as under:

1. Polycaprolactone (PCL): It is easy and cheap to manufacture and has the technical advantage of being degraded slowly by micro-organisms like bacteria and fungi. PCL is a polymer of choice used in slow drug delivery for implanted medical devices and this property can be explored by researchers to use PCL to help in slow release of fertilizer nutrients.
2. Polyacrylamide hydrogel: It can be incorporated into pelletized fertilizers to improve montmorillonite's water retention performance, thereby reducing the water usage in landscape gardening. However, as the polymer breaks down, the resulting acrylamide is a lethal neurotoxin and carcinogen which can damage the microscopic soil engineers like bacteria, protozoa, and fungi. Besides this acrylamide can be absorbed through the skin or inhaled, thereby posing serious risks to fertilizer manufacturing workers and farmers.
3. Hydroxyapatite nanoparticle (HANP): Hydroxyapatite is a bioceramic compound used in medical applications to provide calcium, phosphate, and other minerals to bone and other hard tissues. Urea coated with HANPs slows the release of nitrogen due to chemical bonding properties between nitrogen and HA, increasing the plant's uptake of urea. In the farm field trials using urea-HA NP hybrids, about 50% reduction in urea use allows the yield to be maintained at about 7.9 tons/hectare, which is higher than the yields (7.3 tons/hectare) for urea only rice crop using the recommended levels of urea (Kottegoda et al. 2017).

2.2 Nano-biosensors

These are embedded into biopolymer coating of fertilizers to release nutrients just in time in response to the chemical signals from soil microbes like rhizobium in plants root system. Application of nanotechnology to increase the control of the plant over the release of nutrients was proposed in 2012 by a Canadian research team as “Intelligent Nano-Fertilizer.” The application is based on the discovery of root exudation of chemical signals in response to the decrease in the soil nitrogen. The Intelligent Nano-Fertilizer project has shifted its focus from incorporating a nano-biosensor in a polymer coating fertilizer to release urea, to a focus on increasing macro-nutrient uptake efficiency by putting nano-biosensors in a polymer that coats micro-nutrients like iron and zinc. This project has selected synthetic DNA aptamers as nano-biosensors that fold into unique three-dimensional structures capable of binding tightly to a target which here is chemical signals from the soil microbes in the rhizosphere of a plant (Qureshi et al. 2018). The polymer becomes more permeable delivering a payload of nutrients in response to the binding of aptamer with the target. Nano-biosensors face the challenge of accurate identification of specific signals by aptamer between the soil microbes and plant rhizosphere because misidentification can lead to no or sub-optimal release of nutrients (Neethirajan et al. 2018). Furthermore, if a polymer designed to be permeable in response to the rhizosphere, chemical signal becomes less permeable or even impermeable because of the effect of target binding on the properties of the polymer, the polymer would simply degrade, releasing the nutrient in an unintelligent fashion. The impurities in the nutrient payload can lead to aptamer misreading the chemical signal and binding incompletely with the target, leading to an inaccurate or partial delivery of the nutrients.

2.3 Nano-clays

These are added to the soil samples to create soil micro-structures and reduce nitrate loaded runoff and release of ammonia and nitrous oxide. One of the best examples of use of nano-clays is the loss control urea (LCU), which is a ternary system comprised of attapulgite (nano-clay), polyacrylamide, and urea which has highest content of nitrogen among all commonly used fertilizers (Cai et al. 2014). The addition of polyacrylamide, together with oxidation and hydrothermal processing of attapulgite increases the pore space in soils with clay and stops erosion and water runoff. Water soluble polyacrylamide is used as soil conditioner and without adding polyacrylamide; attapulgite rods (20–50 nm in diameter and 1 μ in length) would agglomerate and prevent creation of micro-structures to reduce nitrogen loss. It has been observed that under stimulated conditions, about 50% leaching, 36% volatilization losses, and 45% surface runoff of nitrogen can be reduced by this loss control technology (Cai et al. 2014).

2.4 Nano-pesticides

Nano-pesticides are in nanoparticle form so they can be easily taken up by plants and can also be programmed to be time released (Lauterwasser 2005). Nano-pesticide formulations are generally classified according to their intended purpose into the following categories:

Formulations Aiming to Increase the Solubility of Poorly Water-Soluble Compounds

The apparent solubility of poorly water-soluble active ingredients by making their nanoparticles with a simultaneous change in solid structure resulting in increase in the bioavailability of the active ingredients (Horn and Rieger 2001). Some of the common pesticide formulations for poor water soluble active ingredients are as follows:

1. Emulsifiable concentrates (ECs): These concentrates consist of active ingredients dissolved in an organic solvent and a blend of surfactant emulsifiers to ensure spontaneous emulsification into water in the spray tank. The main disadvantages of ECs relate to the relatively poor stability after dilution (droplets of about 10 μm) and the use of organic solvents, leading to increases in the cost and flammability as well as in dermal toxicity for the handlers (Knowles 2005).
2. Oil-in-water (O/W) emulsions: O/W emulsions have been proposed as an alternative to ECs. O/W emulsions generally consist of a mixture of a non-ionic surfactant, block polymers, and polymeric surfactants. The limitation to O/W emulsion is that emulsification requires a high-energy input, which is provided by high shear mixers (typically producing droplets of 2 μm diameter) or high pressure valve homogenizers (droplets down to 500 nm) (Knowles 2005).
3. Micro-emulsions: These are thermodynamically stable water-based formulations consisting of (a) dissolved active ingredients in oil, (b) surfactant solubilizers (blend), (c) a co-surfactant (often medium chain aliphatic alcohol), and (d) water (Knowles 2005; Lawrence and Warisnoicharoen 2006; Green and Beestman 2007). Once formulation design is established, micro-emulsions form spontaneously upon addition of water and gentle stirring unlike classical emulsions where preparation requires large energy input (Lawrence and Warisnoicharoen 2006; Pratap and Bhowmick 2008). The particle size in micro-emulsions may be about 250 times smaller than typical pesticide particles and several reports have suggested diameters of less than 100 nm (Knowles 2005; ObservatoryNano 2010). Scattering techniques (light, neutron, and X-ray) and pulsed field gradient nuclear magnetic resonance can be used to determine the microstructure of micro-emulsions (Lawrence and Warisnoicharoen 2006). Micro-emulsions are available in the market with different trade names like Primo MAXX (plant growth regulator), Banner MAXX (systemic fungicide for broad-spectrum disease control in turf and ornamentals), Subdue MAXX (systemic fungicide), and Apron MAXX

(disease protection for soybean; ObservatoryNano 2010). Micro-emulsions have the following advantages over other formulations like ECs such as improved tank mix compatibility; improved stability; reduced wear on equipment (e.g., preventing spray tank filters from clogging); low flammability (due to low solvent content in a continuous water phase (Knowles 2005; ObservatoryNano 2010); and enhanced herbicidal efficacy due to the improved penetration or uptake of the active ingredients that results from the high solubilizing power of surfactants (Knowles 2005; Green and Beestman 2007). Besides applications of micro-emulsions these also possess certain drawbacks like low active ingredient content (<30%); high concentration (20%) of surfactants (Lawrence and Warisnoicharoen 2006); limited number of suitable surfactant systems and phytotoxicity and handler toxicity issues (Knowles 2005).

4. Nano-emulsions: Nano-emulsions (also referred to as mini-emulsions, ultrafine emulsions, and submicron emulsions are emulsions with a droplet size that can overlap with those of micro-emulsions but micro-emulsions differ from nano-emulsions in equilibrium status. Micro-emulsions are thermodynamically stable but nano-emulsions have the tendency to separate into the constituent phases (mainly by Oswald ripening). Nano-emulsions may nevertheless possess a relatively high kinetic (meta-) stability (e.g., several years) (Gutierrez et al. 2008) and are often said to be metastable. Nano-emulsion production requires high-energy inputs but recent research has focused on developing a variety of reproducible low-energy emulsification methods, which can be divided into the following two main groups, viz., spontaneous emulsification methods and phase inversion temperature methods (Anton et al. 2008). Nano-emulsions contain lower concentration of surfactants than micro-emulsions (typically 5–10% of surfactant compared to about 20% in micro-emulsion) and many preparation methods include a step that consists of diluting a micro-emulsion. The range of droplet sizes typically quoted is 20–200 nm. Information collected by ObservatoryNano (2010) from industrial representatives suggested that the use of micro-emulsions is likely to dominate that of nano-emulsions (for which manufacturing opportunities have not yet been developed) due to the more challenging preparation and stabilization procedure required by the latter. However, it is possible that changes to the current regulations (i.e., more stringent restrictions on the amounts or types of surfactants employed) will improve the potential of nano-emulsions as viable alternatives.
5. Nano-dispersion: Dispersion of nano-crystals (crystalline or amorphous particles consisting of 100% active ingredients) in liquid media leads to the formation of nano-dispersions having similar properties to solutions (also called nano-suspensions; Muller and Junghanns 2006). The approach aims to maximize the surface area in order to increase the dissolution velocity and solubility saturation of poor water soluble active ingredients. The greatest increase in solubility is expected for crystals <50 nm (Muller and Junghanns 2006). A number of methods have been reported for preparing organic nanoparticles including dry/wet milling, extraction precipitation, and solvent evaporation from emulsions (Elek et al. 2010). Achieving stability over long periods is challenging and the addition

of surfactants or polymeric stabilizers is sometimes necessary (Muller and Junghanns 2006). Elek et al. (2010) described a method that rapidly converted a micro-emulsion of novaluron into powders consisting of active ingredients and surfactants. Electron and X-ray diffraction showed that the nanoparticles were amorphous. Amorphous particles are more soluble than crystalline particles (Hancock and Parks 2000) and could thus be indicative of improved bioactivity. However, an in vivo experiment on leaf worm larvae showed very similar insecticidal activity for the nano-formulation to that of a commercial EC formulation (Elek et al. 2010). In this context it is worth mentioning the nano-dispersion of the antimicrobial agent triclosan reported by Weatherly and Gosse (2017). A preparation method combining a processing technique of modified emulsion templating and freeze-drying resulted in the formation of stable dry powder composites that formed nano-dispersion upon addition of water. In contrast to the study using novaluron (Elek et al. 2010), a higher biocidal activity was observed for the nano-dispersion of triclosan than for an ethanol/water system (minimum inhibitory concentration was eightfold lower for the nano-dispersion; Weatherly and Gosse 2017).

3 Formulations Aimed for Controlled/Targeted Release and/or Protect Active Ingredients Against Premature Degradation

Slow/targeted release formulations are primarily aimed at active ingredients that tend to degrade or move away from the target. However, there are also a few examples for active ingredients with low aqueous solubility. Some of these formulations are described below:

3.1 Polymer-Based Formulations

The majority of polymer-based nano-formulations have the controlled release of active ingredients as a primary objective. Polymer-based nano-formulations can be used either as polymeric nano-spheres in which distribution of active ingredients is not specified or as nano-capsules which exhibit a core-shell structure that can act as a reservoir for active ingredients dissolved in a polar or nonpolar solvent (Anton et al. 2008). Nano-capsules may present advantages over larger capsules in stability of the spraying solution, increased uptake, increased spraying surface, and reduced phytotoxicity owing to a more homogeneous distribution. However, it is a great challenge to design capsules in the low nm size range while keeping the amount of active ingredients sufficiently high relative to the amount of polymer forming the core-shell structure. The distinction between nano-capsules and nano-spheres needs to be borne in mind when considering the product most commonly taken as an example to illustrate the potential (and related hazards) of sophisticated formulations based on nanotechnologies (Friends of the Earth 2008). Syngenta holds a patent on a gutbuster capsule that breaks open in alkaline environments such as the stomachs of certain insects (Syngenta 2000). Boehm et al. (2000) compared the properties of nano-spheres prepared with various amounts of poly (epsilon-caprolactone) to improve the delivery to plants. The release of the active ingredients was immediate and followed a release profile similar to that of a classical suspension. Boehm et al. (2003) later tested the efficacy of similar nano-spheres loaded with insecticide (average particle size of 135 nm and 3.5% loading rate) on cotton plants infested with aphids. The speed of action and sustained release showed no improvement over a classical suspension, but the small size of the nano-spheres was shown to enhance the penetration of active ingredients in the plants and consequently to improve the active ingredients. Liu et al. (2008) reported a method to produce polymer-stabilized bifenthrin nanoparticles using a multi-inlet vortex mixer to reach high super-saturation followed by rapid nucleation and growth of nanoparticles (named the flash nano-precipitation process). The authors claimed that this preparation method could be scaled up to produce formulations with the potential to provide higher efficiency, better uniformity of coverage for highly active compounds, and reduced exposure to workers (relative to compounds solubilized in organic solvents). Kumar et al. (2010) and Shakil et al. (2010) recently proposed a self-assembly preparation method using polyethylene glycol (PEG) and various copolymers for the controlled release of insecticides. The diffusion-controlled release rate of active ingredients could be adjusted by changing the proportions and molecular weights of the polymers. Several studies have also proposed the use of polymeric nano-spheres for the release of various fungicides for treating wood, using conventional pressure treatment methods (Liu et al. 2001, 2002a, b, c; Salma et al. 2010). Polymer nanoparticles can serve as a protective reservoir and diffusion-controlled release carrier. The biocide can thus be released at the minimum rate required to protect the wood, which results in longer protection and a reduction in losses due to leaching. Salma et al. (2010) recently reported the development of a novel approach aiming to tackle the weaknesses of the previously developed formulations (by providing lower-cost ingredients, a single preparation step, and optimization of delivery and release rates). Amphiphilic copolymers of gelatin grafted with methyl methacrylate were used to prepare nanoparticles of approximately 100 nm diameter loaded with tebuconazole. Leaching of active ingredients was significantly reduced and antifungal activity was preserved for longer periods. However, the novel formulation also exhibited significant aggregation that resulted in less efficient delivery. Regarding pesticide activity, most formulations tested provide effective protection against fungal attack at relatively low application rates. The surfactant-free formulations exhibited slightly greater biocidal efficacy, possibly due to slower release, reduced leaching (Salma et al. 2010), and/or more uniform distribution within the wood (Liu et al. 2002c).

3.2 Porous Hollow Silica Nanoparticles

Researchers from China have investigated the potential of hollow silica nanoparticles to be used as carriers for the controlled release and UV-shielding of avermectin and validamycin (Li et al. 2006, 2007; Liu et al. 2006). The rate of release was influenced by temperature, pH, and shell thickness. Although Li et al. (2007) mentioned the encapsulation of avermectin, the release profile exhibited a multistage pattern which was interpreted as being due to the release of active ingredients located in different parts of the particles (i.e., external, in pore channels, and in the internal core). Prado et al. (2011) recently reported a method to modify hexagonal mesoporous silica with carboxyl acid. The nano-spheres synthesized were <50 nm (determined by thermogravimetry) and had a mean pore diameter of 10 nm (derived from N2 sorption isotherms). The spheres were subsequently used as a support for the controlled release of 2, 4-D and picloram. Faster release was observed for 2, 4-D than for picloram (the release of 20% of active ingredients required about 7 and 20 days, respectively) but for both compounds, the delivery rate was maintained up to 30 days. Mesoporous silica nanoparticles have also been considered as carriers to transport DNA and chemicals into plant cells and leaves by bombardment (Torney et al. 2007). The nanoparticles were loaded with genetic material together with chemical inducer and the open ends were capped with gold nanoparticles to keep the molecules from leaching out. Uncapping the gold nanoparticles released the chemicals and triggered gene expression in the plants under controlled release conditions. Further development of similar technologies will open new perspectives in plant biotechnologies, with possible applications in the development of new plant protection strategies. Zinc-aluminium-layered double hydroxides and clays layered double hydroxides are good candidates to serve as a matrix for developing slow/targeted release formulations of agrochemicals. Even though the term nano-hybrids has often been used to describe layered double hydroxide formulations, size measurements have generally not been provided and some electronic microscopy images suggest that the resulting structures often belong to the µm range (Hussein et al. 2005). Although organo-clay formulations have also been classified as nano-formulations (ObservatoryNano 2010), size measurements again suggest sizes in the micrometer range (Maqueda et al. 2009). Park et al. (2010) evaluated the potential of a layered double hydroxide as a carrier for cinnamate, a natural antibiotic substance that has the potential to be used as a fungicide. Natural antibiotics are rarely used for pest control because they degrade rapidly in soil, need to be used at high doses, and are often not readily available in large quantities. The formulation tested by Park et al. (2010) resulted in a slow release of the antibiotic and a prolonged retention of cinnamate in soil. The formulation also showed promising fungicidal activity against root rot in red pepper. Research teams in Malaysia and Korea have investigated the influence of preparation parameters and the properties of nano-hybrids consisting of double-layered hydroxides loaded with various anionic herbicides, growth regulators, and fungicides. The addition of surfactants in a formulation based on layered double hydroxides (with the primary aim of intercalating the nano-ionic pesticide avermectin) resulted in the formation of structures with dimensions of about 400–600 nm (based on transmission electron microscopy (Qiu et al. 2009). The release of active ingredients was dependent on the pH, temperature, and presence of electrolyte (Qiu et al. 2009). Zhenlan et al. (2009) also reported the incorporation of two neutral active ingredients after prior formation of micelles with an anionic surfactant.

3.3 Nano-metals

Silver (Ag) has long been known for antimicrobial properties and several in vitro studies have demonstrated that nano-Ag can significantly inhibit the growth of plant pathogens in a dose-dependent manner (Chun et al. 2010; Jo et al. 2009; Jung et al. 2010; Kim et al. 2009; Min et al. 2009). Jo et al. (2009) showed that preventive application of both ionic and nano-Ag can significantly reduce the development of fungal diseases on rye grass (in vitro and growth chamber experiments at concentrations of 100–200 mg/L). Maximum efficacy was observed when application occurred 3 h before fungi inoculation. Efficacy was significantly reduced if application occurred later than 24 h after inoculation (Jo et al. 2009). Jung et al. (2010) carried out greenhouse experiments and showed that a weekly application of nano-Ag solutions to the roots of cultivated green onions efficiently inhibited the development of white rot. An increase in the rate of development of the treated plants was also observed (after 4–5 weeks, 1.4–2.5-fold increase in biomass). In addition, plate counting tests indicated that the application of nano-Ag did not appear to drastically reduce the number of soil bacteria and fungi (Jung et al. 2010). Other suggested applications of nano-Ag as a replacement for synthetic organic bactericides include the coating of fruit bags to efficiently control the development of black stain on fruit (Chun et al. 2010) and the treatment of cut flower stems to extend vase life (Liu et al. 2009; Solgi et al. 2009). Silicon (Si) has long been known to enhance plant tolerance of various abiotic and biotic stresses (metal toxicity, water stress, and fungal attack) (Fauteux et al. 2005; Zargar et al. 2010) and the application of nanoforms of Si (e.g., potassium silicate) is common practice. Surface modified hydrophobic nano-Si particles have been suggested as a potential candidate for the control of a range of agricultural insect pests but no supporting experimental data has been found in the literature (Nair et al. 2010). The efficacy of combined Si and Ag nanoparticles stabilized with polymers has been tested in greenhouse experiments on green squash plants infected with powdery mildew (Park et al. 2006). The antifungal effects of nano-Si-Ag were observed almost immediately after application at 3 mg/L, and symptoms of infection had completely disappeared after 3 weeks. The absence of phytotoxicity response was also demonstrated for several plants sprayed with solutions of nano-Si-Ag concentrations of up to 3200 mg/L (Park et al. 2006). Suggested benefits of nano-metals (and nano-Ag in particular) over synthetic fungicides are a possible reductions in human toxicity, development of resistance (due to the multiple modes of action of Ag), and plant protection related costs (Jo et al. 2009; Jung et al. 2010).

4 Nano-agrochemicals Versus Conventional Agrochemicals

Nano-fertilizer technology is very innovative technology intended to enhance the efficiency of fertilizers as nutrient use efficiencies of conventional fertilizers hardly exceed 30–35%, 18–20%, and 35–40% for N, P, and K, respectively. Nano-fertilizers are nutrient carriers that are being developed using substrates with nano-dimensions of 1–100 nm. Nanoparticles have extensive surface area and capable of holding abundance of nutrients and release it slowly and steadily such that it facilitates uptake of nutrients matching the crop requirement without any associated ill effects of customized fertilizer inputs (Pirzadah et al. 2019). Nano-enabled fertilizers can have the following advantages over conventional fertilizers such as:

4.1 Solubility and Dispersion of Mineral Micro-nutrients

Nano-sized formulation of mineral micro-nutrients may improve solubility and dispersion of insoluble nutrients in soil, reduce soil absorption and fixation, and increase the bioavailability unlike conventional fertilizers which have less bioavailability to plants due to large particle size and less solubility.

4.2 Nutrient Uptake Efficiency

Nano-structured formulation might increase fertilizer efficiency and uptake ratio of the soil nutrients in crop production and save fertilizer resource, whereas in conventional fertilizer applications bulk composite is not available for roots and decrease efficiency.

4.3 Controlled Release Modes

Both release rate and release pattern of nutrients for water soluble fertilizers might be precisely controlled through encapsulation in envelope forms of semipermeable membranes coated by resin-polymer, waxes, and sulfur, unlike conventional fertilizers where excess release of fertilizers may produce toxicity and destroy ecological balance of soil.

4.4 Effective Duration of Nutrient Release

Nano-structured formulation can extend effective duration of nutrient supply of fertilizers into soil, whereas conventional fertilizers are used by the plants at the time of delivery and the rest is converted into insoluble salts in the soil.

4.5 Loss Rate of Fertilizer Nutrients

Nano-structured formulation can reduce loss rate of fertilizer nutrients into soil by leaching and/or leaking. On the other hand, in case of conventional fertilizers there is high loss rate by leaching, rain-off, and drift.

5 Conclusion and Future Perspective

In conclusion, nanotechnology is an emerging field that plays a pivotal role in the agriculture sector to enhance yield production and thus could be utilized as a novel technology to reduce the food crises in near future. Many researchers foresee nanotechnology to develop high-tech agricultural fields, equipped with intelligent nanotools that allow limited inputs to get higher outputs. It helps to develop novel and effective agrochemicals in the form of nano-fertilizers and nano-pesticides for plant protection and nutrition and thus aids in sustainable smart agriculture. However, future research should be focused to unravel the dynamic interactions between plants and nano-agrochemicals and its impact on environment. Emphasis must be placed on future research to explore ways to circumvent the risk factors associated with the use of nanoparticles. The study of nanoparticle synthesis and the granting of some limited applications to laboratory conditions could not contribute to the full acceptance of nanotechnology in the agricultural sector. Therefore, the scientific community must work together to improve future research based on a more realistic approach.

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Nanotechnology: A Boost for the Urgently Needed Second Green Revolution in Indian Agriculture

**Kaizar Hossain, Syed Zaghum Abbas, Akil Ahmad, Mohd Rafatullah,
Norli Ismail, Gaurav Pant, and Maruthi Avasn**

1 Introduction

Agriculture is one of the major sectors that provide food for human, indirectly or directly in addition to feed, fibre, fire, and fuels. World agricultural industry is facing challenges such as climate change, urbanization, sustainable use of natural resources, and other environmental issues including urban runoff and accumulation of pesticides and fertilizers (Mukhopadhyay 2014). These problems are further intensified by an alarming population and food demand increment as an estimated population of 6–9 billion by 2050 is to be fed (Scott and Chen 2013; Chen and Yada 2011). India has targeted an average growth of 4% per annum for the agricultural sector by 2020 (Subramanian and Tarafdar 2011). However, India's agricultural growth has been experiencing decline during the last decade from about 3.6% (1985–1995) to less than 2% (1995–2005). Food grains production level is the major concern. The per capita annual production of cereals has shown declination from 200–205 kg in 1991/1995 to only 180–185 kg during 2004–2007, and it is still in decreasing trends which leads to great concerns towards food security. In order to achieve the 4% annual growth target, productivity and income per unit of these

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K. Hossain (✉)
Department of Environmental Science, Asutosh College (Estd.- 1916),
Kolkata, West Bengal, India

S. Z. Abbas · A. Ahmad · M. Rafatullah · N. Ismail
Environmental Technology Division, School of Industrial Technology, Universiti Sains
Malaysia, Gelugor, Pulau Pinang, Malaysia

G. Pant
Institute of Applied Sciences and Humanities, GLA University, Mathura, Uttar Pradesh, India

M. Avasn
Department of Biosciences and Biotechnology, Krishna University,
Machilipatnam, Andhra Pradesh, India

K. R. Hakeem, T. B. Pirzadah (eds.), *Nanobiotechnology in Agriculture*,
Nanotechnology in the Life Sciences, https://doi.org/10.1007/978-3-030-39978-8_2

scarce natural resources such as limited land and water resource have to be improved. The national agricultural research system has led the focus on the application of eco-friendly and green revolution technology model in short-duration high yielding cultivars, efficient irrigation, and intensive use of fertilizers and other agrochemicals (Subramanian and Tarafdar 2011). The ‘First Green Revolution’ observed during early 1970s ended in wonderful yield increase through four basic elements of production system, viz. semi-dwarf high yielding varieties of rice and wheat, extensive use of irrigation, fertilizers, and agrochemicals. Though, after wonderful growth, there has been a distinct slowdown in the agricultural growth rate since the mid-1990s. The agricultural production is facing a plateau, which has adversely affected the livelihood base of the farming community at large. The green revolution includes the implementation of micro-farm economics that directed the use of inputs such as land, cultivar, labour, machinery, and chemicals balanced against profits from crop yields and the macro-economic that ensured better access to inputs and markets (Khot et al. 2012). The green revolution model has increased the potential yields and farm incomes substantially, but less focus has been given on the efficient and sustainable use of soil nutrients and water. Macro policies that favoured Indian agriculture are affected by the globalization of agricultural trade. Local farmers are subjected to greater market risks. Hence, lead to decline in income of farmers as well as rural distress. Approximately about 60% of Indian work force is employed in the agricultural sector and therefore, it is very important to increase and stabilize agricultural income. However, there are many challenges faced by agriculture sector such as degradation of soil health, water resources, overexploitation of natural resources, excess use of fertilizers and pesticides that need to be addressed in near future (Chen and Yada 2011). The worrying situation in Indian agriculture has been described as ‘technology fatigue’. As the availability of arable land for agriculture would reduce in future due to urbanization, the only way out could be expected through productivity route. In fact, the country needs a ‘Second Green Revolution’ (Thakur 2009). In this background, the present paper attempts to investigate and review whether nanotechnology can be used as a catalyst to initiate ‘Second Green Revolution’ in India. Nanotechnology (NT) is said to possess high potential in bringing revolution to our current agriculture and food systems as well as to improve the conditions of the less privileged class (Roco 2003; Juma and Yee-Cheong 2005). Combining nanotechnology with other measures may be answer to the worldwide concerned sustainable issues in areas such as water, energy, health and environment, agriculture and biodiversity, and management of our threatened ecosystem. In 2002 United Nations Johannesburg Summit on Sustainable Development, these five areas have been identified and known as WEHAB (Report of the World Summit on Sustainable Development 2002). According to a survey conducted by UN, improvement in agricultural productivity especially in developing countries with the implementation of nanotechnology is considered as the second most vital area of efforts in achieving the millennium development goals. On the other hand, energy conversion and storage was identified as the top concern, while water treatment scored the third in areas of focus (Slamanca-Buentello et al. 2005). Evidences from various research conducted in many developed countries have inspired the study on applying nanotechnology into our current food and agriculture systems (Opara 2004; Ward and Dutta 2003). Research conducted in many developed countries have indicated the vast potential of nanotechnology in enhancing agricultural productivity through genetic improvement ((Kuzma 2007; Scott 2007), specific targeted site genes and drug delivery at cellular level (Maysinger 2007), nano-array based gene-technologies for gene expressions in plants and animals under stress conditions (Walker 2005). The potential is promising especially with incorporation of suitable technique and sensors for precision agriculture, natural resource management, early detection of contaminants in food products, smart delivery systems for agrochemicals, smart system in food processing and packaging as well as other areas such as agricultural and food system security monitoring (Day 2005; Moraru et al. 2003; Chau et al. 2007).

Continuous developments in nanotechnology are expected to play the vital role as main economic energetic forces for benefiting producers, farmers, ecosystem as well as our society. More than 100 research projects on synthesizing and assembly of ceramic particles, nanotubes, nanowires, nano-porous solids, nanostructured alloys, and DNA chips have been supported along with establishment of a number of shared facilities and infrastructure under this initiative. Some of the laboratories are actively engaged in the research on design and synthesis of inorganic nanomaterials, especially in utilizing high Tc superconductors, magnetic materials, catalysis, etc. (Hager 2011). If Indian agriculture is to achieve its broad national goal of sustainable agricultural growth of over 4–5%, it is important that the nanotechnology research is extended to the agricultural total production–consumption system, i.e., across the comprehensive agricultural value chain. This would require focusing on technologies that increase agricultural productivities, product quality, and efficacy of resource usage that reduces the farm costs, raises the production value, and increases farm incomes; as well as on conserving and enhancing the quality of the natural resources. It would also require a conscientious effort in providing a system to deliver these innovations based on nanotechnology to a product delivery stage and ensure that these reach the rural stakeholders at the end of the agri-value chain (Sekhon 2010).

The present study attempts to map out areas relevant to Indian agriculture, where nanotechnology can provide viable solutions towards the challenges faced by our agricultural industry. So we attempt in identifying areas where nanotechnology can bring immediate impacts especially in Indian rural areas. Possible areas of nanotechnology with potential applications in Indian agriculture are: nanofertilizers that possess slow release ability; nano-pesticides for controlled release; nano-emulsions for greater efficiency; nanoparticles for soil conservation; smart delivery of nutrients and drugs for livestock and fisheries; nanobrushes and membranes for soil and water purification, cleaning of fishponds; and nanosensors for monitoring soil quality, plant health, and for precision agriculture and controlled environment agriculture (National Planning Workshop 2003). Application of nanotechnology would be possible in food processing industry such as nanocomposites and nanobiocomposites for plastic film coatings used in food packaging, antimicrobial nanoemulsions for applications in decontamination of food equipment, packaging, or processing (Rai and Ingle 2012). We believe that the responsible development of nanotechnology and nanomaterials in Indian agriculture must be accentuated as application of nanotechnology and nanomaterials in agriculture and food systems in global scale has been showing promising results.

2 Applications of Nanotechnology and Nanomaterials in Agriculture and Food Sector

In the strategic Research Agenda 2007–2020 of the world technology platform on Food for Life, nanotechnology is highlighted as key technologies both for tailor-made food products and for intelligent packaging. Communities of all levels (national, international, and civil society organization) are closely monitoring the employment of nanotechnology especially in food and agriculture sectors. Nanotechnology in the food area is perceived to be much more negative compared with other applications such as surface treatments, medical applications, or energy saving (Athanassiou et al. 2007) (Table 1). However, it must be noted that the use of nanotechnology directly in the food industry is receiving higher level of awareness compared to their applications in agriculture industry. Applications in agricultural industry are rarely discussed and no longer in the priority interest of NGO-Groups since 2005 (Grobe and Rissanen 2012).

3 Nanotechnology and Agriculture Sector

In terms of agriculture, nanotech research and development are likely to facilitate and frame the next stage of development of genetically modified crops, animal production inputs, chemical pesticides, and precision farming techniques. The practice of nanotechnology in agriculture has been mostly theoretical but it has begun and will continue to have a substantial effect in major areas of the food industry, product development and design of methods and instrumentation for food safety and bio-security purposes (Joseph and Morrison 2006). Recent advances in material science and chemistry have produced mastery in nano particle technology, with implications in the field of agriculture. With the focus of nanotechnology in agricultural production, five major categories for nanotechnology applications are listed as below:

- Sensors and diagnostic devices for monitoring environmental conditions, plant and animal health
- Disease and pest control; including novel delivery systems for pesticides
- Water and nutrient control; including the use of novel delivery systems
- Genetic engineering of plants and livestock
- Agriculture as a means to produce nanomaterials.

Table 1 Application of nanotechnology in food science and its allied fields

Particle (nanoparticle)	Preparation/synthesis methods	Main applications	References
Organic nanoparticle (nanoscale vesicular system)	Nano-precipitation, emulsion–diffusion, double emulsification, emulsion–coacervation, polymer-coating, layer-by-layer	Enhanced nutritional value of food, drug delivery/controlled release of drug, food enhancement, encapsulation of active components	Anton et al. (2008) and Ezhilarasi et al. (2012)
		Recently a new class of water-soluble red fluorescent ONP have been prepared with an application of cell imaging which further can be used in the development of nanosensors	Xiqi et al. (2014)
		Dye removal (remediation) from soil as well as water fluorescent organic nanoparticles that combine the dye has been developed Can be used in water purification Nano-sensor development for water as well as agricultural products	Zhang et al. (2014)
Inorganic nanoparticles (INP) (inorganic ingredients manufactured at the nanoscale)	Gas phase INP synthesis method (flamed spray synthesis, synthesis by laser-induced gas evaporation, and plasma-based synthesis) and liquid phase INP synthesis method (co-precipitation method and sol–gel approach)	Antimicrobial agent, storage and packaging unit, catalyst, tooth repair, and sensors production of metal NPs	Athanassiou et al. (2007)
		Cellulose-based bactericidal nanocomposites containing silver nanoparticles have been developed bactericidal properties which may have future applications in active packaging of food and agricultural products	Márcia et al. (2012)
		Also, silver NPs incorporated into carboxymethylcellulose films have been studied for their *antimicrobial properties for food and agricultural products and* found suitable for the same	Siqueira et al. (2014)
		They are having a role in nanoreinforcement packaging, smart packaging, etc.	Ranjan et al. (2014)

(continued)

Table 1 (continued)

Particle (nanoparticle)	Preparation/synthesis methods	Main applications	References
Nano-clays (NCs): (fine-grained minerals having sheet-like geometry)	They are synthesized mainly by top-down approach from suitable materials	Geology, agriculture, construction, engineering, process industries, and environmental applications, in drug products as excipients and active agents, improve the mechanical strength of biopolymers	Garrido-Ramirez et al. (2010) and Carretero and Pozo (2009, 2010)
		Recently NCs have been found to have application in sensor development	Grasielli et al. (2012)
		Nanoremediation—mainly dyes, pesticides, etc.	Gholam et al. (2013) and Yan et al. (2014)
		Used in the manufacture of biodegradable nanocomposite materials	Jin and Zhong (2013)
		Used in nanoreinforcement packaging, nanocomposite active and nanocomposite smart packaging	Aníbal et al. (2014) and Ranjan et al. (2014)
Nano-emulsions (lipid phase dispersed in an aqueous continuous phase)	High-energy (high-pressure homogenization, ultrasound, high-speed devices) and low energy approaches (membrane emulsification, spontaneous emulsification, solvent displacement, emulsion inversion point, phase inversion point)	Encapsulate functional food components	Ranjan et al. (2014), Astete et al. (2009) and Finke et al. (2014)
		Increase bioavailability and bioactivity	Hira et al. (2014), Ranjan et al. (2014), Joseph and Heike (2014) and Ghosh et al. (2014)
		Antimicrobial, anthelmintic, insecticidal, pesticidal, weedicidal	Karthikeyan et al. (2011, 2012), Megha et al. (2014), Chaw et al. (2013) and Chaw Jiang et al. (2012)
		Nanoremediation	Alexey and Simon (2014) and Shams and Ahi (2013)

Sources: Modified from Dasgupta et al. (2014)

For this review, the first three sectors are discussed under the title 'precision farming'. Sensors and delivery systems are developed with the purpose of producing early, controlled, targeted, and more efficient interventions (irrigation, fertilization, pest control, harvest). In addition, as fewer pesticides are lost during delivery/application, adverse effects on the environment resulting from the accumulation of harmful pollutants contained can be constrained and costs can be spared (Grobe and Rissanen 2012). In accordance to Robinson and Morrison's analyses, FAO and WHO listed three main categories for the agricultural sector like nanosized agrochemicals; for smart delivery of agrochemicals in the field, better efficacy of pesticides, better control over dosing of veterinary products, second water decontamination; breakdown of organic pollutants, oxidation of heavy metals, elimination of pathogens through use of nano-iron or other photocatalysts and animal feed (use of nanosized additives, minerals, or vitamins) (Grobe and Rissanen 2012).

4 Smart Delivery Systems for Pests, Nutrients, and Plant Hormones

Plant parasitic nematodes are one of the world's major agricultural pests, causing a loss of about US$125 billion worldwide annually. Previously, nematode infestations were controlled by using nematicides which are toxic and are not eco-friendly. These chemicals are either heavily restricted or eliminated entirely for use in the United States due to their high toxicity. Therefore, research should be focused on novel chemicals and smart delivery systems that will not only enhance the production yield but are also eco-friendly in nature (Mousavi and Rezaei 2011). This nanotechnology based delivery system has the ideal attributes for agricultural application; it is robust and viable in a wide range of environments (Mousavi and Rezaei 2011). Nanosensors and nano-based smart delivery systems can be used to assist more efficient use of water, nutrients, and chemicals through precision farming. Through the use of nanomaterials together with global positioning systems with satellite imaging of fields, farm managers could remotely detect crop pests or evidence of stress easily such as drought (Fig. 1). Nanosensors dispersed in the field can also help to detect the presence of plant viruses and to monitor the level of nutrients in soil. Nano-encapsulated slow-release fertilizers are also receiving lots of attention as they help to reduce unnecessary fertilizer consumption and to minimize environmental pollution due to excessive use (Mousavi and Rezaei 2011). Some of the nanoparticles that have entered into the arena of controlling plant diseases are nanoforms of carbon, silver, silica, and alumina-silicates (Table 2). Nanoparticles of defined concentrations could be successfully used for the control of various plant diseases caused by several phytopathogens (Kuzma and Verhage 2006).

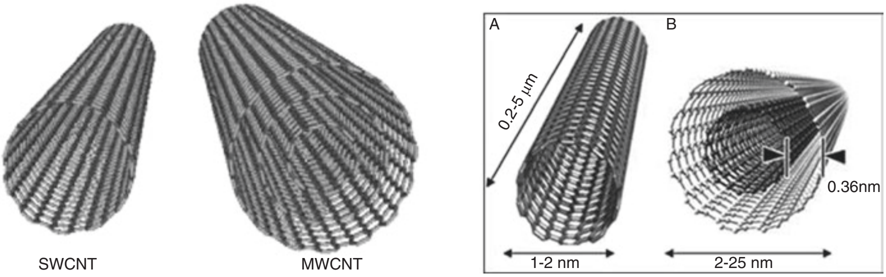

Fig. 1 Conceptual diagram of single-walled carbon nanotube (SWCNT) (**a**) and multi-walled carbon nanotube (MWCNT) (**b**) delivery systems showing typical dimensions of length, width, and separation distance between graphene layers in MWCNTs. (Source: Zheng et al. 2009)

Table 2 Nano particles which can use for controlling plant diseases

Nanoparticles	Uses/Application	References
Nano silver	Nano silver is the most studied and utilized nano particle for bio-system. It has long been known to have strong inhibitory and bactericidal effects as well as a broad spectrum of antimicrobial activities Silver nanoparticles, which have high surface area and high fraction of surface atoms, have high antimicrobial effect as compared to the bulk silver. Antifungal effectiveness of colloidal nano silver (1.5 nm average diameter) solution against rose powdery mildew caused by Sphaerotheca pannosa Var rosae It is being used as foliar spray to stop fungi, moulds, rot, and several other plant diseases	Márcia et al. (2012)
Nano alumino-silicate	Alumino-silicate nanotubes with active ingredients are popular. The benefit of alumino-silicate nanotubes are sprayed on plant surfaces are easily picked up in insect hairs Silica nanoparticles have shown that mesoporous silica nano particles can deliver DNA and chemicals into plants, thus creating a powerful new tool for targeted delivery into plant cells	Márcia et al. (2012)
Titanium dioxide (TiO_2) nanoparticles	TiO_2 is harmless and no toxic so it can use in food products up to 1% of product final weight TiO_2 photocatalyst technique has great potential in various agricultural applications including plant protection since it has non-toxic compounds and possesses great pathogen disinfection efficiency	Yao et al. (2009)
Carbon nanomaterials	Carbon-based nanomaterials (such as single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), buckyballs, graphene, etc.) occupy a prominent position in various nano-biotechnology applications (Fig. 1)	Jurgons et al. (2006)
Magnetic nanoparticles	Magnetic-based nanomaterials could be utilized for site-targeted delivery of systemic plant protection chemicals for the disease treatment which affect only specific regions of plants The carbon-based nanomaterials (such as SWCNTs and MWCNTs) are functionalized with magnetic nano particles can be used in internal space allows filling of suitable plant protecting chemicals and the functionalized magnetic nano particles allow external control of the movement of nano carriers inside the plant system	Mornet et al. (2004) and Jurgons et al. (2006)

5 Nano-formulations for the Control of Plant Diseases

Nanotechnology provides new ways for improving and modifying existing crop management techniques. Plant nutrients and plant protecting chemicals are used to crops by spraying. Due to the difficulty such as degradation by photolysis, hydrolysis and microbial degradation, leaching of chemicals, only a very low concentration of chemicals which is much below required minimal effective concentration, reach the target site of crops (Singh et al. 2015).

5.1 Nanotechnology for Detecting Plant Diseases

There is a need for detecting plant disease at an initial stage so that tons of food can be protected from the possible out-breaks. The Nanotechnologists have attempted to look for a nano-solution for protecting the food and agriculture from bacteria, fungus, and viral agents. It works as a detection method that can give results within a few hours. The technology is very simple, portable, and accurate and does not require any complicated technique for operation so that even a simple farmer can use the portable system. If an independent nanosensors linked into a GPS system for real-time monitoring can be distributed throughout the field to monitor soil conditions and crop yield, it would be of great help. As per Sharon et al. (2010) the union of biotechnology and nanotechnology in sensors will create equipment of increased sensitivity, allowing an earlier response to environmental changes and diseases.

6 Plant Pathogens in Biosynthesis of Nanoparticles

The research on nanoscience and nanotechnology essentially involves preparation and use of nanoparticles of various elements and compounds. Among the several uses, nanoparticles are also being used as antimicrobial agents for plant disease management. Formation of nanoparticles can be achieved via several processes which may be either chemical or biological.

6.1 Fungi

Fungi are relatively recent in their use in synthesis of nanoparticles. There has been a shift from bacteria to fungi to be used as natural ‘nano-factories’ owing to easy downstream processing, easy handling (Mandal et al. 2006; Pirzadah et al. 2019), and their ability to secrete a large amount of enzymes. However, fungi being eukaryotes are less amenable to genetic manipulation compared to prokaryotes. Therefore, any alteration of fungi at genetic level for synthesis of more nanoparticles would not be so easy. It is important to know the mechanism of synthesis of nanoparticles in microbial systems to get better control over shape, size, and other desired properties of the synthesized nanomaterials.

6.2 Bacteria

Among microbes, prokaryotes have received the most attention for biosynthesis of nanoparticles (Mandal et al. 2006). Bacteria have been used to biosynthesize mostly silver, gold, FeS, and magnetite nanoparticles and quantum dots (QDs) of cadmium sulphide (CdS), zinc sulphide (ZnS), and lead sulphide (PbS).

6.3 Plant Virus

Plant virus especially spherical/icosahedral viruses represent the examples of naturally occurring nanomaterials or nanoparticles. The smallest plant viruses known till date is satellite tobacco necrosis virus measuring only 18 nm in diameter (Hoglund 1968). Plant viruses are made up of single- or double-stranded RNA/DNA as genome which is encapsulated by a protein coat. The protein coat/shell structurally and functionally appears like a container carrying the nucleic acid molecule as cargo from one host to another. Their ability to infect, deliver nucleic acid genome to a specific site in host cell, replicate, package nucleic acid, and come out of host cell precisely in an orderly manner have necessitated them to be used in nanotechnology. A complete review on use of plant viruses as bio-templates for nanomaterials and their application has been recently reviewed by Young et al. (2008).

7 Amalgamation of Nanotechnology and Crop Biotechnology

Scholars have effectively created three-dimensional molecular structures, a breakthrough that unites biotechnology and nanotechnology. The scientists prepared DNA crystals by producing synthetic DNA sequences that can self-assemble into a series of three-dimensional triangle-like patterns. The DNA crystals have sticky ends or small cohesive sequences that can attach to another molecule in organized fashion. When multiple helices are attached through single-stranded sticky ends, there would be a lattice-like structure that extends in six different directions, forming a three-dimensional crystal as illustrated in Fig. 2. This method could be useful in improving important crops by organizing and linking carbohydrates, lipids, proteins, and nucleic acids to these crystals (Lok 2010). The nanoparticles can aid

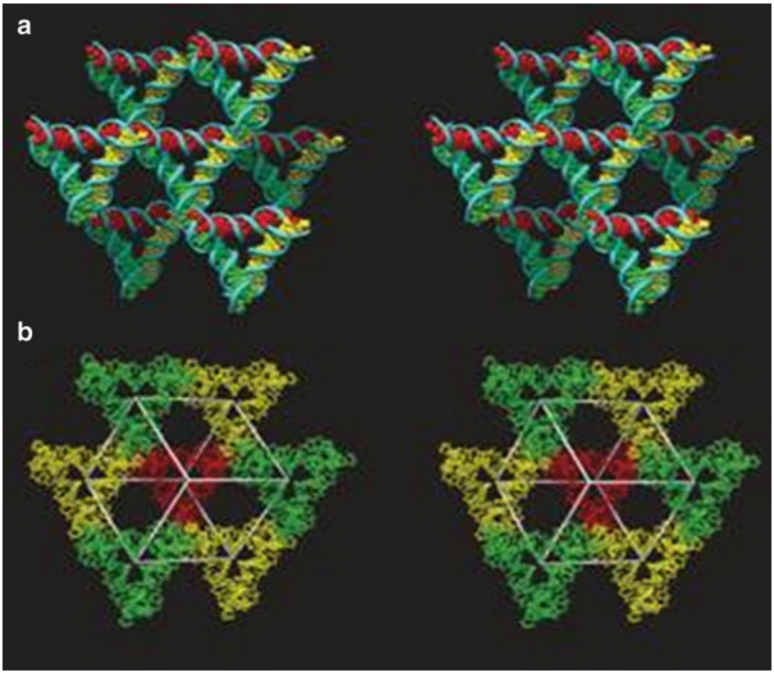

Fig. 2 (**a**) Stereographic image of the surrounding of a triangle; (**b**) Stereographic image of the rhombohedral cavity (white lines) formed by the triangles. (Source: F. Torney et al. 2007)

as magic bullets, containing chemicals, herbicides, or and genes, which target specific plant parts to release their content. Nano-capsules can empower effective penetration of herbicides through cuticles and tissues, allowing slow and constant release of the active substances (Perea-de-Lugue and Rubiales 2009). Scholars at the Iowa State University have employed a 3 nm mesoporous silica nanoparticle (MSN) in delivering DNA and chemicals into isolated plant cells. MSNs are chemically coated and help as containers for the genes delivered into the plants. The coating triggers the plant to take the particles through the cell walls, where the genes are introduced and triggered in a precise and controlled manner, without any toxic side and after effects. This technique has been applied to introduce DNA effectively to tobacco and corn plants (Torney et al. 2007).

8 Nanoparticles and Recycling Agricultural Waste

Nanotechnology can also help to prevent waste in agriculture, particularly in the cotton industry. Nanofibres can be produced using electrospinning technique to spin cellulose ($C_6H_{10}O_5$), a complex carbohydrate composed of glucose units that makes up 90% of the cotton material as nanofibres (Ranjan et al. 2014). When cotton is handled into fabric or garment, some of the cellulose or the fibres are discarded as waste or used for low-value products such as cotton balls, yarns, and cotton batting. The process of electrospinning usually uses an electrical charge to draw very fine fibres from a liquid. The application of current should be in high voltage with liquid droplet, the body of the liquid becomes charged, and electrostatic repulsion counteracts on the surface tension. At this juncture, the droplets are stretched at a critical point where a stream of liquid erupts through the surface as the Taylor cone and forms a charged liquid jet. The elongation and thinning of the fibre resulting from this bending instability leads to the formation of uniform fibres with nanometre-scale diameters (Fig. 3). These high-performance absorbents allow targeted application at desired time and location (Mousavi and Rezaei 2011; Bhattacharyya et al. 2014, 2015). In the past 2 years, the ethanol production from maize feedstock has augmented the global price of maize. Cellulosic feedstocks are now observed as a viable option for biofuels production and nanotechnology can also improve the performance of enzymes used in the conversion of cellulose to ethanol. Researchers are working on nano-engineered enzymes that will license simple and cost-effective alteration of cellulose from waste plant parts into ethanol (Ranjan et al. 2014). Rice husk, a rice-milling by-product can be used as a source of renewable energy. When rice husk is burned into thermal energy, a large amount of high-quality nanosilica is formed which can be further exploited in making other materials such as glass and concrete. Since there is an incessant source of rice husk, mass production of nanosilica through nanotechnology can alleviate the growing rice husk disposal concern (Mousavi and Rezaei 2011).

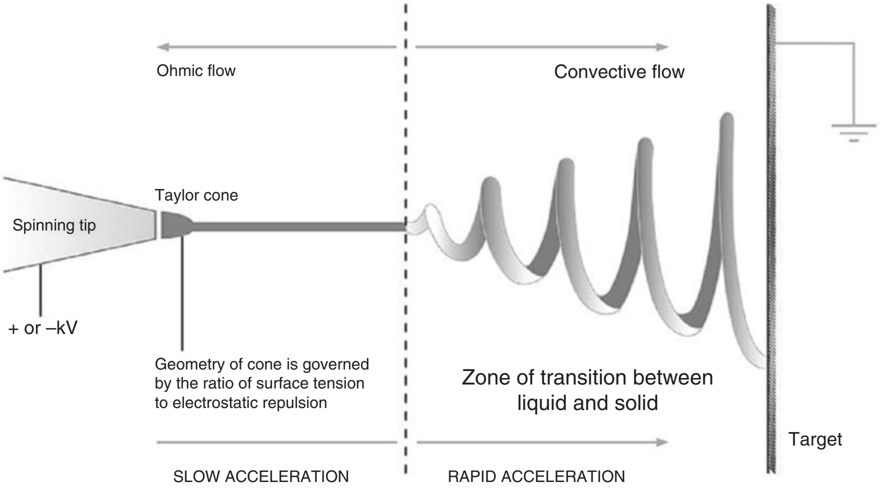

Fig. 3 Diagram showing fibre formation by electrospinning (Source- Joanna Gatford 2008 The New Zealand Institute for Plant and Food Research Ltd)

9 Nanotechnology in Food Sector

Two categories are often used to describe the broad field of nanotechnology applications in the food sector: First, ‘Nano inside’ for nutrients, food additives, or food supplements with nanostructured ingredients or structures modified through the use of nanotechnology; and second, ‘Nano outside’ for the use of nanotechnology in food contact materials, including food processing, packaging, and sensor technologies. The World Health Organization (WHO) discusses the development of nanotechnology in the food industry, their current and potential benefits, and compares them with conventional equivalents (FAO/WHO 2010). The applications of nanotechnology in the food sector are included in Table 3.

10 Risk Assessment of Nanomaterials in Agriculture and Food Sector

As the possible applications of nanotechnologies in agriculture and food industries are manifold and still emerging, generic statements on their risks are not possible. Risk assessment needs thus to be performed here—as in other fields of nanotechnology too—on a case-by-case basis (FAO/WHO 2010). Several authors have indicated that the knowledge base for common risk assessments is still too limited (SCENIHR 2009). The members of scholars are concluded in its scientific opinion on the potential risks arising from nanoscience and nanotechnology on food and feed safety that the traditional risk assessment paradigm (hazard identification, hazard characterization, exposure assessment, and risk characterization) can be applied to (engineered) nanomaterials in principle (Horie and Fujita 2011). The US Food and Drug Administration (FDA) published in 2012 a draft guidance document including factors manufacturers should consider in manufacturing processes involving nanotechnology or nanomaterials which create a significant change such as: affecting the identity of the food substance; affecting the safety of the use of the food substance; affecting the regulatory status of the use of the food substance; or warranting a regulatory submission to FDA (Krug and Wick 2011). Deficiencies were identified in characterization, detection, and measurement of (engineered) nanomaterials in food and feed and biological matrices, as well as in the availability of information to toxic kinetics and toxicology, including optimal methods for testing of (engineered) nanomaterials (Card et al. 2011). Overall, the scientific committee sees the available data on verbal exposure and on any consequent toxicity as extremely limited, as the majority of the available data comes from in vitro or in vivo studies using other exposure routes. In addition, the current knowledge on the exposure from applications and products in the food area was described as limited too, as well as the knowledge on their environmental impacts (Department of Health and Human Services 2012 U.S.).

Table 3 Categorical uses of nanotechnology in food sector (FAO-UN & WHO 2010)

Category	Area	Function as	Applications
Category-1	Nano-inside	Nanostructured food ingredients	Processed nanostructures in food or beverages for improved taste or texture
		Nanodelivery systems for nutrients and supplements	Nanomicelles, liposomes, or biopolymer-based carrier systems that are used for taste masking of ingredients and additives, for protection from degradation during processing, for improvement of the nutrients' or supplements' bioavailability, for antimicrobial activity, or for better optical appearance
		Organic nanosized additives for food, health food supplements, and animal feed applications	For better dispensability of water-insoluble additives in foodstuffs, enhanced taste or for enhanced absorption, and improved bioavailability in the body Example—vitamins, colourants, flavouring agents, and antioxidants
		Inorganic nanosized additives for food, health food supplements, and feed applications	Enhanced taste, enhanced absorption, and improved bioavailability in the body, including alkaline earth metals and non-metals, silver, iron, silica, titanium dioxide, selenium, calcium, magnesium
Category-2	Nano-outside	Food packaging applications	Plastic polymers containing or coated with engineered nanomaterials for improved mechanical or functional purposes
		Nanocoatings on food contact surfaces	Antimicrobial properties, for active or self-cleaning surfaces. Surface functionalized nanomaterials; adding functionalities such as antimicrobial activity or a preservative action (barrier properties)
		Nanofiltration	Filtrating of undesired components (tastes, flavours, toxins, etc.) in food or clarifying wines and beers, based on porous silica or regenerated cellulose membranes
		Nanosensors for food labelling	Incorporation of nanomaterials into intelligent inks, monitoring condition of the food during transportation and storage (improving food safety)

11 Socio-Economic Issues of Agricultural Nanotechnology

In consumer products, the appearance of the applications of nanotechnology has also raised the ethical and societal concerns in some countries, starting from safety, health, and environmental to consumer perception and intellectual property rights. The public are not concerned about many applications of nanotechnology with the exception of areas where societal concern already exists such as pesticides (Mousavi and Rezaei 2011). During the last two decades, number of patent applications in nanotechnology has increased more than tenfold in commercial sectors. Nanotechnology is inescapable in different fields of applications and nano-based developments could invade existing granted patents in those arenas. There are certainly already over 3000 patents internationally for potential agrochemical usage of nanotechnology but they are most possible patents with broad claims, filed with the scope of guarantee autonomy to function in the field in case of future commercial developments (Sozer and Kokini 2009). In developing countries like India, the nanotechnology can have significant applications in agricultural sector like rice production systems, food security, agri-biotechnology, input delivery, precision farming, healthcare of animals, food industry, and water use.

12 Current and Future Developments

The current regulatory and public debate as well as NGOs activities, ‘nano inside’—products where nanotechnology is directly applied to foodstuff will have a difficult starting position and it can be taken into doubt if the communicational patterns of the GMO-debate can be left behind without a quick and clear change of industries communication strategies. For intelligent packaging and other applications of ‘nano outside’ market acceptance could be easier if the key questions of risk assessment concerning abrasion or uptake of nanoparticles from the packaging or food contact materials are sufficiently answered. For applications in the agriculture sector the future development is difficult to predict if it is becoming a part of the NGOs agendas, and as the fronts are not yet hardened, the agriculture industry is in a better position to communicate transparently about the safety and sustainability of nanotechnological applications.

13 Conclusions

Nanotechnology is a potential technology to reduce pesticide use, improve plant and animal breeding, and create new nano-bioindustrial products in agriculture sector. The positive side of it is that the proposed technology will be boom and gloom to maintain the eco-factors of the agricultural field and the society in future however needs a design of actual governing body and strong governance system. India is basically an agrarian economy and has experience production boost during first green revolution. But the agricultural growth rate is experiencing a plateau and there is immediate need for enhancing agricultural productivity for maintaining self-sufficiency in agriculture. Forty-four countries of the world including India are pursuing R&D for nanotechnological application in agriculture for alleviating malnutrition and to achieve second green revolution. So far, it has been done mainly for developed countries only and now it is up to the Indian researchers and scientists to innovate and adapt them to suit the socio-economic milieu. The research in this sector in India is still at a preliminary stage and also at a conceptual level to understand realistic assessments. This critical evaluation and its potential assessment play a significant role before it could be used in any sectors.

Acknowledgement The authors acknowledge Asutosh College, Kolkata, GLA University and Krishna University, India, and Universiti Sains Malaysia, Malaysia, for providing world class infrastructure to continue the research work.

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Nano-enabled Agriculture Can Sustain "Farm to Fork" Chain

Deepu Pandita

1 Introduction

Agriculture is facing many challenges like climate change, urbanization, lack of new arable soil, reduction of the current agricultural land due to competing economic development activities, sustainable use of natural resources, malnutrition, and environmental issues like runoff and accumulation of pesticides and fertilizers. This dilemma is further intensified by an alarming increase in food demand, needed to feed an estimated population of 9.7 billion by 2050 (Pirzadah et al. 2019) so the overall agricultural production ought to increase by sustainable means by 60% compared to levels of 2005 (Alexandratos and Bruinsma 2012). Food and Agricultural Organization of the United Nations (FAO) states that if world population reaches 9.1 billion by 2050, then food production needs to augment by 70% universally and to double in the developing countries. The above-mentioned scenario of rapidly developing and sophisticated agriculture system is the greatest challenge that will be posed to the developing countries. Agriculture is regarded as the backbone of the national economy of the developing countries of the world as about 2/5th of their population depends on agriculture for livelihood (Brock et al. 2011). Profound structural changes within the agricultural sector have occurred due to the fast development within the technological innovations; however, these additionally pose challenges like sustainable production considering food security, ending hunger, improving nutrition, and promoting sustainable agriculture. Achieving food security will require a range of social and economic actions like reducing food waste, improving the efficiency of irrigation systems, supporting local rural communities, and tackling land degradation. Undoubtedly, scientific and technological innovation will also play an important role through increasing agricultural productivity. Nanotechnology, a novel emerging and fascinating scientific approach permits

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D. Pandita (✉)
Government Department of School Education, Jammu, Jammu and Kashmir, India

K. R. Hakeem, T. B. Pirzadah (eds.), *Nanobiotechnology in Agriculture*,
Nanotechnology in the Life Sciences, https://doi.org/10.1007/978-3-030-39978-8_3

advanced research in the field of biotechnology and agriculture that makes use of the manipulation of materials for their novel, physical as well as chemical properties at nanoscale. The application of nanotechnology to agriculture is getting attention nowadays (Shapira and Youtie 2015; Resham et al. 2015; Nath 2015; Prasad et al. 2014, 2017; Sekhon 2014; Jampílek and Kráľová 2015; Pirzadah et al. 2019). Nanotechnology could revolutionize the field of agriculture (Dimkpa and Bindraban 2016; Manjunatha et al. 2016) and the entire nanotechnology industry in 2015 was worth US$1 trillion (Harper 2015). The field of agri-nanotechnology is in its infancy, but it has the power to change the whole agriculture and food sector in coming years. Nanosciences and nanotechnology have been introduced into agricultural system during the last decade, with the primary goal of increasing the crop yield and improving food quality. This novel scientific approach has the potential to advance and enhance the agricultural productivity of the crop plants by the use of NPs through efficient nanofertilizers, nanopesticides, nanoherbicides (Tarafdar et al. 2013), nanosensors, nanotracers (Dimkpa et al. 2017) and disease management, nanoporous zeolites for slow release and efficient dosage of water and fertilizer, nanocapsules for chemical herbicide delivery, vector and pest control, and nanosensors for early and rapid disease and pest detection (Scrinis and Lyons 2007) coating with genetic and organic or inorganic nanomaterials (Fernández-Luqueño et al. 2016), genetic improvement of plants, delivery of genes and drug molecules to specific sites at cellular levels, by using nanosensors and controlled and smart delivery systems for agrochemicals like fertilizers and pesticides (Chinnamuthu and Boopathi 2009), detection of the presence of any kind of bacteria and pathogens rapidly and accurately to keep the food fresh for long time can also be achieved by small particulate nanotechnology (Fig. 1). Above 90% of Indian soils have low N and P content, while 50% of soil samples are low in K, zinc (49%), boron (33%), molybdenum (13%), iron (12%), manganese (5%), and copper (3%) (Singh et al. 2008) and these deficiencies cause stagnation in crop productivity. Chemical fertilizers improve crop productivity by 50% (Samra and Sharma 2009). But the nutrient use efficiency by crops is very low due to nutrient loss through fixation, leaching, volatilization, and microbial mineralization with losses averaging 10–75% presenting a prime target for improvement. Also the cost of production inputs like chemical fertilizers and pesticides is expected to increase at an alarming rate due to limited reserves of fuel like natural gas and petroleum (Prasad et al. 2012). Hence, it is necessary to minimize nutrient losses in fertilization, and to increase the crop yield through the exploitation of new applications with the help of nanotechnology and nanomaterials. Kah et al. (2018) reported that the median gain in efficiency with nanofertilizers was approximately 20–30%. Nanoparticles (NPs) can be utilized for delivery of pesticides, fertilizers, and other agrochemicals by the production of nanocapsules being highly stable and biodegradable (Jha et al. 2009). Nanofertilizers or nano-encapsulated nutrients might have properties that are effective to crops, release the nutrients on-demand, controlled release of chemicals fertilizers that regulate plant growth and enhanced target activity (De Rosa et al. 2010; Nair et al. 2010). Nanotechnology proponents (IFRI 2008) and academics keen to promote the Millennium Development Goals have suggested that agri-nanotechnology will

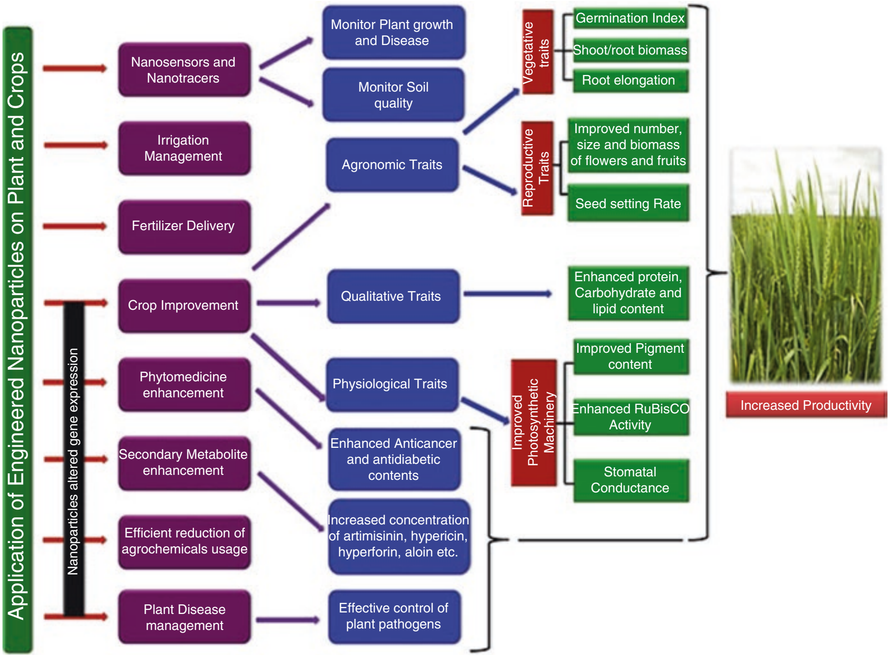

Fig. 1 Applications of engineered nanoparticles in the agriculture sector. Source: Misra P, Shukla PK, Pramanik K, Gautam S, Kole C (2016) Nanotechnology for Crop Improvement. In: Kole C, Kumar D, Khodakovskaya M. (eds) Plant Nanotechnology. Springer, Cham

deliver environmental sustainability and eradicate hunger (Salamanca-Buentello et al. 2005). The vision of many proponents of agricultural nanotechnologies is one of precise production, i.e., more uniform, more efficient, less labor intensive, more remotely managed atomically “improved” crops whose high productivity is made possible by entwined nano-surveillance and “smart” farm management systems, nano-modified seeds, and specialist interactive chemical treatments (USDA 2003). Nanotechnology permits disease prevention and treatment in plants using various nanocides (Carmen et al. 2003) and nutrient management of agriculture using nanofertilizers (Priester et al. 2012). According to the data of FAO, every year the damage done to crops by pests and diseases constitutes 20% of the potential world yield of food crops (FAO 2009). Among the total crop losses caused by different sources, 14.1% are lost due to plant diseases alone and the total annual worldwide crop loss from plant diseases is about US$220 billion. Commercial agriculture relies heavily upon inputs of pesticides and fungicides to protect crops against pests and pathogens (Agrios 2005) and their continuous and unchecked use has caused resistance in them (Patel et al. 2014) and environmental pollution. New physiological races and isolates of the existing pathogens will make them more virulent and destructive and many dreadful diseases will emerge fast due to climate change. Natural defense response of plants against pathogenesis depends upon early recognition of pathogens. Nanotechnology provides efficient tools for early detection of plant diseases by diagnostic tools in managing insects and pathogens by targeted controlled delivery of agri-based chemicals (Sharon et al. 2010; Sharma et al. 2012). NPs can be exploited directly or modified for pathogen detection or as a diagnostic tool to detect compounds indicating disease (Ghormade et al. 2011). The potential application of nanomaterials in crop protection helps in development of efficient and potential approaches for the management of plant pathogens (Gopal et al. 2011). Nanoparticles remain bound to the cell wall of pathogens and cause deformity due to high-energy transfer leading to its death. The discovery of nanosensors has led to a more precise and rapid disease diagnosis and pathogen detection (Khan and Rizvi 2014). Nanosensors can further play role in measuring crop nutrient status, moisture level, soil fertility, etc., which in turn helps in monitoring crop growth (Scott and Chen 2003). Use of nanodiagnostic methods (nanofluidics, nanomaterials, and bioanalytical nanosensors) in plant breeding (Abd-Elsalam 2015) or nanoparticle-mediated gene transfer to improve crop varieties for disease resistance (Rai et al. 2012) can minimize the expenditure on agrochemicals used in disease management. The use of NPs in plant pathology opens new avenues for plant protection, pathogen detection, and studying plant–pathogen interaction for effective plant disease management (Ismail et al. 2017). Nanotechnological application in plant pathology targets specific agricultural problems in host–pathogen interactions and could provide new avenues for crop protection. Studies focused on the use of nanoparticles for targeted delivery of pesticides and fertilizers demonstrated good potential in disease suppression and crop yield enhancement (Servin et al. 2015). The number of successful studies is still very limited, but nanosensors can be developed in the very near future. A great example is the recent building of single-walled carbon nanotubes (SWCNTs) radiometric sensors (for H_2O_2 and NO) performed by Giraldo et al. (2015) which proved the efficiency of radiometric nanosensing platform for detecting key compounds in plant tissues. Nanotechnology has massive potential to provide a chance for the researchers of plant science and alternative fields, to develop new tools for incorporation of nanoparticles into plants that would augment existing functions and add new ones (Cossins 2014). According to Galbraith (2007) and Torney et al. (2007) engineered nanoparticles are able to enter into plants cells and leaves, and also can transport DNA and chemicals into plant cells. This area of research analysis offers new prospects in plant biotechnology to target specific genes for manipulation and expression within specific plant cells. So far, the nanotechnology is at its nascent stage and many success stories have been documented especially from the crop production point of view. This chapter is focused on reporting the latest advancements in the field of agricultural production through nanotechnology-based agrochemicals, plant disease suppression via plant defense mechanism, crop protection, pest control, more efficient use of resources, enhanced food safety through sensors for the detection of pathogens or freshness, engineered water nanostructures to treat food, therapeutic nanoparticles deliver nutrients to agricultural crops against various deficiencies, plant stress tolerance in genetically modified organism (GMO) by genetic material delivery via nanoparticle-mediated chloroplast transgene delivery and overall impact on environmental and its future perspectives in sustainable agriculture.

2 Disease Management Through Nanotechnology

Nano-phytopathology deals with specific problems in plant protection, pathogen detection, deciphers plant–pathogen interactions, and offers new ways for disease management of plants (Mahendra et al. 2012). The nanoparticles like nanosilica can be used for the preparation of new formulations of pesticides, insecticides, and insect repellants (Gajbhiye et al. 2009). The poly-ethylene glycol-coated NPs loaded with garlic essential oil has been tested against *Tribolium castaneum* pest (Yang et al. 2009). Porous hollow silica nanoparticles (PHSNs) loaded with validamycin (pesticide) have been successfully employed as an efficient and controlled release formulation for water soluble pesticides (Liu et al. 2006). The insecticidal properties of nanosilica, silver, aluminum oxide, zinc oxide, and titanium dioxide NPs have been successfully utilized in the management of rice weevil and grasserie disease in silkworm (Goswami et al. 2010). Nanosilver (100 ppm) has been effectively used as an antifungal agent on potato dextrose agar (PDA) (Kim et al. 2012a). Teodoro et al. (2010) reported the insecticidal activity of nanoalumina against *S. oryzae* and *Rhyzopertha dominica* of stored food supplies. Zinc oxide (ZnO) and magnesium oxide (MgO) nanoparticles are verified effective as antibacterial and anti-odor agents (Shah and Towkeer 2010) and antimicrobial preservative for food products (Aruoja et al. 2009; Huang et al. 2005; Sharma et al. 2009). In nanoencapsulation of insecticides and herbicides, the nanochemicals using nanocarriers are released into the target plant body in a controlled way for improving their efficiency (Scrinis and Lyons 2007; Torney 2009). Silver NPs have strong antifungal potential against Botrytis *cinerea* (Oh et al. 2006), *Phoma glomerata*, *Phoma herbarium,* and *Fusarium semitectum* (Gajbhiye et al. 2009), *Aspergillus niger*, *Bipolaris sorokiniana,* and *Magnaporthe grisea* (Jo et al. 2009), *Fusarium culmorum* (Kasprowicz et al. 2010), *Fusarium oxysporum* (Musarrat et al. 2010), *Colletotrichum gloeosporioides* (Aguilar-Méndez et al. 2011), *Aspergillus niger*, *Aureobasidium pullulans*, and *Penicillium phoeniceum* (Khaydarov et al. 2011). Syngenta's Banner MAXX™ and "Nano-5" are two commercialized nanoformulation marketed products against plant pathogens and diseases (Gopal et al. 2011). Fluorescent silica nanoprobes have potential for speedy diagnosis of plant diseases. These nanoprobes conjugated with the secondary protein antibody of goat anti-rabbit IgG were used for the detection of plant pathogen, *Xanthomonas axonopodis* pv. *vesicatoria* in *Solanaceous* crops (Yao et al. 2009). NPs can act as biomarkers for quick detection of bacteria (Boonham et al. 2008), fungi (Chartuprayoon et al. 2010), and plant viruses (Yao et al. 2009) in plants. Nanochips containing fluorescent oligo capture probes are microarrays used for disease detection (Lopez et al. 2009). Nanochips are extremely specific and have high sensitivity to detect single nucleotide change in bacterial microorganisms and viruses. Yao et al. (2009) used a NP with fluorescence silica and antibodies to detect pathogen-causing bacterial spot disease caused by *Xanthomonas axonopodis* pv. *vesicatoria*. Singh et al. (2010) used nanogold-based immune sensors using surface plasmon resonance (SPR) for detecting the pathogen *Tilletia indica* causing Karnal bunt disease in wheat (*Triticum aestivum*). Nugaeva et al. (2005) devised the micromechanical cantilever arrays for detecting fungal spores of *Aspergillus niger* and *Saccharomyces cerevisiae*.

2.1 Nanobarcodes

In our daily life, identification tags have been applied in wholesale agriculture and livestock products. Due to small size, NPs have been applied in many fields ranging from advanced biotechnology to agricultural encoding. Nanobarcodes have been used as ID tags for multiplexed analysis of gene expression and intracellular histopathology (Branton et al. 2008). It has been proved economically proficient, rapid, and effortless technique in decoding and recognition of diseases as multiple pathogens in a farm could be tagged and detected at any time by fluorescent-based tools through this scientific technique (Li et al. 2005). The nanobarcodes serve as uniquely identifiable nanoscale tags and have also been applied for authentication or tracking in agricultural food and husbandry products (Han et al. 2001).

2.2 Nanosensors

Nanotechnology-enabled field sensing nanosensors help in real-time monitoring of the crop growth and field conditions like soil conditions (pH, moisture level, fertility), temperature, crop nutrients (Mousavi and Rezaei 2011), detection of phytopathogens and weeds (Prasad et al. 2017). With this vital information and signals, the best scenario for the planting and harvesting of crops along with the time, the level of water, agricultural fertilizers, pesticides, herbicides, nutritional status, deficiency of the plants and other treatments required for specific plant physiological, pathological and environmental conditions will facilitate to take up fitting and timely remedial measures to decrease the yield loss. Nanosensors have not solely been used as nanobiosensors however additionally for the control management of soil nutrients and these have helped in the decline of fertilizer consumption and environmental pollution (Ingale and Chaudhari 2013). Nanobiosensors have been developed to detect contaminants, such as crystal violet or malachite green concentrations in seafood and parathion residues or residues of organophosphorus pesticides on vegetables (Amine et al. 2006). Nanosensors can be employed as an identification tool for detecting bacterial, fungal, and viral pathogens in agriculture (Boonham et al. 2008; Prasad et al. 2014). Wang et al. (2016) have developed a nanosensor for monitoring the levels of by-products salicylic acid in oil seeds for detection of a pathogenic fungus *Sclerotinia sclerotiorum,* while CuO nanoparticles and nanostructural layer biosensors are used for detecting *Aspergillus niger* (Etefagh et al. 2013). The demand for onsite and real-time and sensor-based pathogen detection is expanding due to dynamic changes in plant-pathogen types. Methods based on direct-charge transfer conductometric biosensor (Pal et al. 2008), CNTs (Serag et al. 2013), and silver and gold NPs (Sadowski 2010) have been developed to detect DNA or protein-functionalized gold NPs to be used as target-specific probes. A CO_2 sensor was developed using polyaniline boronic acid conducting polymer for detecting real-time spoilage of stored grain (Neethirajan et al. 2010). The conjunction of NPs with enzymes has enhanced the sensitivity and stability of biosensors. Several NP-based enzymatic biosensors like nanofibers, nanocomposite, graphene, and nanotubes are available for detecting organophosphorus and non-organophosphorus pesticides (Zhang et al. 2015). Acetolactate synthase-inhibitor herbicides metsulfuron-methyl and imazaquin were detected by atomic force microscope tip functionalized with acetolactate synthase (da Silva et al. 2014). Another nanobiosensor type was made by entrapping acetylcholinesterase in the liposome setup which successfully detected organophosphorus pesticides paraoxon and dichlorvos (Vamvakaki and Chaniotakis 2007). Nanobiosensor based multi-walled carbon nanotubes (MWCNT)-immobilized acetylcholinesterase was introduced for pesticide detection (Du et al. 2007). The same setup was used to detect aflatoxin through MWCNT-immobilized aflatoxin oxidase (Li et al. 2017). Such ultrasensitive enzymatic nanobiosensors have a pesticide detection limit of 50 pg/liter (Verma 2017). DNA-based nanosensors can prove an important rapid solution for detection of plant diseases (Fang and Ramasamy 2015). By using smart nanosensors, the precise amount of plant-specific fertilizers and insecticides can be delivered. Designing diagnostic nanosensors that can be integrated with pesticide delivery system for automatically combating insect attack, fungal infection, or drought could revolutionize the agriculture field. Porous hollow silica NPs (PHSNs) complemented with a pesticide have been tested with success in agriculture for prolonged controlled delivery of a chemical agent (Liu et al. 2006). The graphene oxide biosensing enhances detection of aflatoxins in food materials (Zhang et al. 2016). Nanobased biosensors are available against *Cowpea mosaic virus*, *Tobacco mosaic virus,* and *Lettuce mosaic virus* (Lin et al. 2014).

3 Enhanced Food Safety Through Sensors for the Detection of Pathogens or Freshness

The global market value for food and food packaging products in 2006 which were developed through the use of nanotechnology was estimated by two market reports at US$4 million and US$7 billion, and predicted for growth to US$6 billion by 2012 and >US$20 billion by 2010 (www.cientifica.com, www.hkc22.com). The economic value of nanotechnology in the agri-food market in 2010 was expected to be US$20.4 billion (Farhang 2009), in form of product development (e.g., nano-delivery, nano-formulation, and packaging), food processing (e.g., nanocapsules, nano-powders, nano-ingredients), and food safety (e.g., nanosensors and nanotracers) (Chaudhry et al. 2008). Through nanomaterials, packaging materials with better mechanical strength, conductivity, and functionality will be produced (Brody et al. 2008; Azeredo et al. 2009). Nanotechnology can revolutionize the food sector to ensure security and safety using nanosensors to detect pathogens and food packaging systems by encapsulation of food products using nano-compounds (Prasad et al. 2014, 2017). Smart packaging (food packaging with antimicrobial or oxygen scavenging properties) embedded with nanosensors alerts consumers on the state of the food inside (e.g., freshness, storage temperature, microbial contamination) or when an eatable is no longer safe to eat. Sensors give warning signals prior to food spoilage or infer even the accurate nutritional status of the contents. Packaging equipped with nanosensors is additionally designed to trace either the interior or external conditions of foodstuffs, pellets, and containers, throughout the supply chain. Nanosensors can detect gases produced by food when it spoils and the packaging itself changes color to alert you. The nanosensors are able to respond to environmental changes (e.g., temperature or humidity in storage rooms, levels of oxygen exposure), degradation products, or microbial contamination (Bouwmeester et al. 2009). Usually, producers estimate the expiration date of food by considering distribution and storage conditions, especially temperature to which the food product is supposed to be exposed. However, such conditions are not always known, and foods are frequently exposed to temperature abuse; this is particularly worrying for products which require a cold chain. Furthermore, sealing defects in packaging systems can lead food products to an unexpected high exposure to oxygen, which can result in undesirable changes. Nanosensors, when integrated into food packaging, can detect certain chemical compounds, pathogens, and toxins in food, being then useful to eliminate the need for inaccurate expiration dates, providing real-time status of food freshness (Liao et al. 2005). Nanobiosensors have been developed and commercialized to detect pathogens, spoilage, chemical contaminants, or product tampering, or to track ingredients or products through the processing chain (Nachay 2007). Nanosensors based on carbon nanotubes have been noticed to possess many benefits over conventional/traditional detection methods like high performance liquid chromatography. Carbon nanotube based nanosensor is rapid and allows simple and cost effective high-throughput detection at reduced power requirements and easier recycling along with un-necessity of exogenous molecules or labels. Furthermore, a MWCNT-based biosensor has also been developed that can detect microorganisms, toxic proteins, and degraded products in food and beverages (Nachay 2007). The spherical selenium nanoparticles from *Bacillus subtilis* were used for building HRP (*horse radish peroxidase*) biosensor (Wang et al. 2010), while yeast cells were used for biosynthesis of Au-Ag alloy nanoparticles to make a sensitive electrochemical vanillin sensor (Zheng et al. 2010) and AuNP-based glucose oxidase (GOx) biosensors were synthesized for enhanced GOx enzyme activity (Zheng et al. 2010). Engineered nanosensors have conjointly been developed in packages to alter color to warn the buyer if a food is starting to spoil, or has been contaminated by pathogens using electronic "noses" and "tongues" to "taste" or "smell" scents and flavors

(Scrinis and Lyons 2007; Sozer and Kokini 2009). In real market applications, Nestlé, British Airways, Monoprix Supermarkets are utilizing chemical nanosensors that can detect color modification (Pehanich 2006).

3.1 Freshness and Spoilage Indicators

On-package indicator with polyaniline film, showing color change by a variety of basic volatile amines liberated during fish spoilage has been developed (Kuswandi et al. 2012). In this way the real-time fish spoilage monitoring either at various constant temperatures or with temperature fluctuations is done. Microorganisms cause food spoilage and their metabolism produces gases detectable by conducting polymer nanocomposites or metal oxides, through which quantification and/or identification of microorganisms as well as food freshness can be performed. The resistance changes of the sensors generate a pattern that matches to the gas under analysis (Kuswandi et al. 2012). The conducting polymer nanocomposite sensors having carbon black and polyaniline are designed for identification and detection of food borne pathogens by producing a specific response pattern for every microorganism, for example; *Bacillus cereus*, *Vibrio parahemolyticus,* and *Salmonella* spp. (Arshak et al. 2007). An “electronic tongue” in food packaging has also been developed (Joseph and Morrison 2006). Nanotechnology has the potential to change both the physical and functional properties of the food we consume. It is now possible that food scientists can develop “smart” foods which can respond to body’s nutrient deficiencies and distribute nutrients more efficiently without changing the taste or texture of the product. Some of the nanosciences advanced products available in the market (The project on emerging nanotechnologies 2009) are as follows:

1. *Tip Top UP® Omega-3 DHA* is fortified with nanocapsules containing Omega-3 DHA rich tuna fish oil.
2. *Canola Activa oil* is fortified with nonesterified phytosterols encapsulated via a new nanoencapsulation technology (NSSL: Nanosized Self-assembled Liquid structures), developed by Nutralease (Israel) for optimizing the absorption and bioavailability of target nutrients.
3. *Nanoceuticals*™ *Slim Shake Chocolate* is nanoscale ingredient that scavenges more free radicals, increases hydration, balances the body’s pH, reduces lactic acid during exercise, reduces the surface tension of foods and supplements to increase wetness and absorption of nutrients.
4. *Nanotea* is nano-fine powder produced using nanotechnologies.
5. *NovaSOL Sustain* is nanocarrier that introduces CoQ1O to address fat reduction and alpha-lipoic acid for satiety.

4 Nanotechnology in Enhancing Soil Security

Soil security aims at the long-term sustainable production of sufficient food quantity (Bouma et al. 2015). The security conception is more difficult once applied to soils. Rather than relate to a sustainable, daily need in terms of food intake, soil security relates to what might happen if soils degrade to the extent that sufficient food production is not feasible anymore. Soil degradation may be a long run process, very much related to varying socio-economic conditions. Except for erosion, its effects are often gradual and difficult to communicate and translate into environmental and economic values. However, once soils degrade to the extent that they cannot any longer offer certain ecosystem services, of which food production is only one provisioning service, the consequences for society are devastating. To mitigate degraded soils is very difficult and even impossible when soil has been removed by erosion. The challenge, therefore, is to create early awareness about the dangers of soil degradation that may, in the end, terminate many ecosystem services the soil can provide (Bouma et al. 2015). Nanomaterials (NMs) can work out soil restoration problems. These play an imperative part as clay minerals which control both the physical and chemical properties of the soil and governing cation exchange capacity (CEC) of the soil which in turn enhances fertility and productivity (De Boodt et al. 2013). Engineered nanomaterials (ENMs) improve plant growth, boost soil water and nutrient holding capacity of soil, enhance the amount of biosolids to agricultural fields, and clean up and restore soil after accidental spills (Gardea-Torresdey et al. 2014). Besides the soil security, the food security was and will remain a major global issue of the twenty-first century. Furthermore, principal determinants of food security include the availability and quality of soil resources, and their interactions with water resources as well as vegetation (crop species) through energy-based inputs using social control skills for optimizing the net primary productivity (Lal 2015). This net primary productivity is specifically affected by critical linkages that govern some specific functions of nexuses. These nexuses embody the primary one, soil and water for the plant, available water capacity by influencing water retention and transmission, conversion of blue and gray into green water, and elevate the consequences of pedologic and agronomic droughts (Lal 2015). The second one includes the soil and vegetation for biogeochemical cycling, which determines elemental budgets, nutrient use efficiency, root distribution and turnover, and soil/root respiration. The third is vegetation and energy for energy/mass transformation and influencing energy productivity, ecosystem carbon budget, and biomass feed stocks for biofuel production. Finally, the fourth one is energy and water affecting the hydrological cycle with specific impacts on water and energy balance on a landscape, energy use in irrigated systems, and moderation of the hydrological/meteorological droughts. These nexuses have an effect on and are influenced by climate changes and variability on the one hand and anthropogenic/manmade perturbations on the opposite (Lal 2015). Lal (2015) reported about the importance of nexuses and their inter-connectivity. There is a close relationship between soil security, water security, climate security, energy security, economic security, and political security (Lal 2015). Concerning the food security, it includes availability, access, nutritional quality, and retention, which strongly depends on soil security (quality, resilience), water security (quality, renewability, availability), energy security (dependability, supply, price), climate security (optimal temperature and moisture regimes, and low frequency of extreme events), economic security (income and access to resources), and political stability (peace and harmony). Therefore, the co-productivity generated by the anthropogenic use of primary resources (soil, water, climate) and secondary inputs (amendments, fertilizers, irrigation, tillage) should be optimized. Understanding and judiciously managing the water-soil-waste nexus for food security is important to enhancing human well-being, achieving the sustainable use of natural resources, improving the environment, and sustaining ecosystem functions and services (Lal 2015). The zero-valent iron NPs have high absorption affinity toward heavy metals and organic compounds because of which these help in remediation of pesticide-infested soil. Fe NPs possess great soil-binding qualities like $CaCO_3$. The nanosized sulfonated polyaniline (nSPANI) NM delays soil surface crust formation and has no impact on crop germination (Mohammadi and Khalafi-Nezhad 2012). Nanoclays stabilize sandy soil with soil application as grown media additive in small-scale cultivation (Boroghani et al. 2011) and cause thymol encapsulation with insecticide and bactericide activity (Guarda et al. 2011). Chitosan NPs lead to carvacrol encapsulation wherein bioactive compound found in thyme has bactericidal activity (Higueras et al. 2013). Zein NPs cause eugenol and curcumin encapsulation which have insecticide, nematicide, and bactericide activity (Zhang et al. 2014).

5 Important Nanoparticles in the Agro-Industry

5.1 Chitosan Nanoparticles (CNP)

It has been reported in the plant system that chitosan has the ability to induce multifaceted disease resistance (El-Hadrami et al. 2010) and antimicrobial activity (Prasad et al. 2017). Chitosan is an effective biotic elicitor that induces the systemic resistance in plants. CNP have antifungal properties in response to different plant pathogens (Saharan et al. 2013). The induction of natural defense mechanism involves overexpression of different defensive genes and enzymes, amplified deposition of phenolic compounds, cell wall synthesis, etc. Plants treated with different biological elicitor molecules have shown to provoke such innate immune response by mimicking variety of pathogens (McCann et al. 2012). As an exogenous elicitor, chitosan can stimulate resistance in plant host by increasing some defense-related enzyme activities, such as phenylalanine ammonia-lyase (PAL), peroxidase (POD), catalase (CAT), superoxide dismutase (SOD), and polyphenol oxidase (PPO) activities (Xing et al. 2015). Six plant defense responses to chitosan nanostructures including: reactive oxygen species (ROS), hypersensitive response (HR), pathogenesis-related proteins (PRP), defense-related enzymes (DRE), secondary metabolites accumulation (SMA), and complex signal transduction (CSR). Recently, Chandra et al. (2015) have reported that accumulation of CNP increases the plant defense by increasing the levels of SOD and CAT. CNP binds extracellular around the cell wall of the leaves. One of the most important signaling molecules is nitrogen oxide (NO), which is also coupled with many physiological processes involving initiation of defense system in plants. Plants treated with CNP showed increased levels of NO, as compared to control plants (Malerba et al. 2012). CNP-treated sets resulted in upregulation of PAL activity leading to the higher level of phenolic compound accumulation. Higher accumulation of flavonoids like gallic acid (GA), epicatechin (EC), epigallocatechin (EGC), and caffeine was seen when sets were treated with CNP. These accumulated phytochemicals assist in adaptation to various environmental circumstances and provide resistance against pathogen by performing as feeding deterrents. In CNP-treated plants higher expression of SOD and CAT was observed resulting in increased level of these enzymes.

5.2 TiO_2 Nanoparticles

TiO_2 increases the enzyme activities which decreases the accumulation of ROS. TiO_2 nanoparticle treatment defends chloroplasts aging for extended-time illumination by increasing the defense properties of POD, SOD, and CAT. Decrease deposition of ROS and the level of malondialdehyde (MDA) maintain steadiness of membrane structure of chloroplast treated with luminance (Hong et al. 2005). In *Phaseolus vulgaris*, nano-TiO_2 enhanced activities of SOD, CAT, POD, MDA, and 8-deoxy-2-hydroxyguanosine (8-OHDG) content (Ebrahimi et al. 2016).

5.3 Multi-Walled Carbon Nanotubes (MWCNTs) Nanoparticles

Tan et al. (2009) showed that when rice seedlings were exposed with MWCNTs, the ROS levels significantly increased and the cell viability decreased. This is because these nanotubes make contact with the cell walls and undergo ROS defense response cascade, which is ample to avoid microbial pathogens from finishing their life cycle (Smirnova et al. 2011). Moreover, Lin and Xing (2007) also observed apoptosis in cells of lettuce exposed to multiwall carbon nanotube. Multiwalled carbon nanotubes (MWCNTs) when coated with metallic nanomaterials like Ag NPs or Zn NPs control the growth of the phytopathogens, *Aspergillus fumigatus,* and *A. ochraceus* (Fosso-Kankeu et al. 2016).

5.4 Silicon Nanoparticles

Silicon nanoparticles are known to enhance the fungal resistance in maize by expressing higher level of phenolic compound and lower level of stress-responsive enzymes against fungi. A combination of *Pseudomonas fluorescens* and silica NPs in soil increases phenolic action and trims down the stress by the inhibition of responsive enzymes in maize. This elevated level of phenolics is established to induce silica accumulation in leaf epidermal layer, thereby conferring a defensive physical wall as well as induced disease resistance (Rangaraj et al. 2014). Suriyaprabha et al. (2014) reported the nanosilica acts as a potent antifungal agent against maize pathogens such as *Fusarium oxysporum* and *Aspergillus niger* and leads to higher expression level of phenolic compounds and lower expression level of stress-responsive enzymes. Tripathi et al. (2017) reported that silicon nanoparticles alleviate UV-B stress in wheat seedlings and detoxify arsenic and chromium stress in wheat and *Pisum sativum* seedlings, respectively (Tripathi et al. 2016).

5.5 Zinc Oxide Nanoparticles

Nano-Zn increased GSH levels and CAT activity in buckwheat leaves (Lee et al. 2013). Kim et al. (2012b) noticed high activity for SOD, POD, and CAT when treated by nano-ZnO in cucumber plants and higher SOD in *Spirodela polyrhiza* (Hu et al. 2013). The ZnO NPs increased the action of antioxidant defense enzymes and upregulated the production level of SOD and POX isoenzymes in *Gossypium hirsutum* plants (Priyanka and Venkatachalam 2016).

6 Plant Induced Resistance Through Nanoparticles

NPs are discovered to induce oxidative stress and alter gene expression in plants (Wang et al. 2013). ROS not only restrict pathogen entrance but also play an important role in activating local and systemic defense systems such as the stimulation of pathogenesis associated protein genes (Henry et al. 2013). The plant hormones salicylic acid, jasmonic acid, and ethylene play significant roles in defense reactions as signaling molecules (Robert-Seilaniantz et al. 2011). The speedy production of O_2 or phenoxyl radicals in tomato roots treated with MgO NPs may play a related role in the resistance response of tomatoes against *Ralstonia solanacearum* (Imada et al. 2016). Chitosan extensively elevates polyphenol oxidase activity in rice plantlets followed by inoculation of two rice pathogens (*Xanthomonas oryzae* pv. o*ryzae* and *X. oryzae* pv. *oryzicola*) (Li et al. 2013). Silver and ZnO NP treatment lead to increase in contents of free radicals, together with ROS, reactive nitrogen species, and hydrogen peroxide in duckweed (Thwala et al. 2013). Cu-chitosan NPs showed significant fungicidal activity against *Curvularia* leaf spot (CLS) in maize and induce the systemic acquired resistance as well as promote development of *Zea mays* (Choudhary et al. 2017). Cu-chitosan NPs adhere to fungal hyphae and obstruct the mycelial growth of *R. solani* and *S. rolfsii* and inhibit their sclerotia formation (Rubina et al. 2017).

7 Engineered Water Nanostructures to Treat Food Surfaces to Reduce Pathogen Presence

Food borne disease as a result of consuming microbiologically contaminated food is a major public health problem, with the annual worldwide toll reaching an alarming 600 million cases and 420,000 deaths (WHO 2015). During 2004–2012 the USA experienced 377 major food related outbreaks, wherein *norovirus*, *Salmonella* spp., and *E. coli* being the biggest culprits (Callejón et al. 2015). By 2014 USDA estimation, food borne illnesses cost the US$15.6 billion annually (USDA 2014). The food industry is challenged to find solutions to a fast-changing food production environment, dictated by new consumer preferences for "green" and organic foods, including consumption of more fresh fruits and vegetables (Van Boxstael et al. 2013). Currently, there are a number of antimicrobial strategies used by the food industry across the "farm to the fork" chain. These mainly include: chlorine-elemental or hypochlorite; chlorine dioxide (Pao et al., 2007); peracetic acid (Fraisse et al. 2011); hydrogen peroxide liquid or vapor (Rudnick et al. 2009); thermal approaches and ozone-gaseous and aqueous (Horvitz and Cantalejo 2014); irradiation (UV and gamma) (WHO 2008); electrolyzed water (Koseki et al. 2004). Some of these methods (chlorine-elemental, hypochlorite, chlorine dioxide) leave behind chemical residues are ineffective with a heavy organic load and are not approved for use with organic products (Karaca and Velioglu 2007). Moreover, some of the aforementioned methods can induce visible damage and negative sensory effects to products such as fresh produce (e.g., ozone) (Rico et al. 2007). Some interventions are also associated with high energy costs and significant environmental footprints (Ruder 2006). The food industry is, therefore, in need of novel, effective, green, and low cost intervention methods, in line with the new sustainable environmental approaches and emerging consumer preferences. Such methods should have the capability to be applied with ease at various stages from "farm to fork," and replace or supplement existing technologies and enhance food safety and quality (Newell et al. 2010). In the last two decades, nanotechnology has shown that it can enhance our arsenal of methods in the battle against pathogenic and spoilage microorganisms. Indeed, nanotechnology-based approaches, such as antimicrobial food surfaces, nano-enabled sensors, active/intelligent packaging, and novel disinfection platforms, are finding their way within the agri/food/feed sector, bringing great new opportunities to the food industry (Eleftheriadou et al. 2017). Recently, the authors have developed a completely unique, dry, organic chemical free, nanotechnology-based antimicrobial platform utilizing engineered water nanostructures (EWNS) synthesized as an aerosol employing a combined electrospray and ionization method. These EWNS have been shown to effectively inactivate a wide range of food related microorganisms on food surfaces, on food contact surfaces, and in air (Pyrgiotakis et al. 2015, 2016). These EWNS particles possess a unique set of physico-chemical properties that make them an effective antimicrobial agent. They have an average charge of 10–40 electrons per structure and an average nanoscale size of 25 nm (Pyrgiotakis et al. 2016). Earlier studies have shown that they contain a large number of reactive oxygen species (ROS), primarily hydroxyl ($OH^{\bullet}$) and superoxide (O^{2-}) radicals which are highly microbicidal (Pyrgiotakis et al. 2016). Recently Vaze et al. (2018) synthesized e-Engineered water nanostructures (eEWNS) utilizing integrating electrolysis, electrospray, and ionization of water, which are effective, green, dry, and chemical-free approach, antimicrobial platform for surface and air disinfection suitable for a variety of food safety applications and could be ideal for delicate fresh produce that cannot withstand the classical, wet disinfection treatments, where reactive oxygen species (ROS), generated and encapsulated within the particles during synthesis, were found to be the main inactivation mechanism and the ROS content is three times higher. The increase of the ROS content as a result of the addition of the electrolysis step before electrospray and ionization led to an increased antimicrobial ability. The results showed a 97% inactivation of the total natural microbiota viable count, a 99% reduction in the yeast and mold count, and a 2.5 times reduction of the inoculated *E.coli* after 45 min of exposure on the surface of fresh organic blackberries, without any visual changes to the fruit.

8 Therapeutic Nanoparticles Deliver Nutrients to Agricultural Crops Against Various Deficiencies

Agricultural ingredients are applied to crop plants either by irrigation or directly to their foliage. Foliar feeding circumvents problems associated with soil penetration and biodegradation. The efficiency of foliar applications strongly depends on absorption and mobility, where in many cases both requirements are deficient (Eichert et al. 2008). Nanocarriers hold big promise for bridging this gap, owing to their ability to carry complex payloads across biological barriers and target to specific tissues (Chhipa 2017). Liposomes, vesicles engineered nanoparticles with an inner aqueous core surrounded by a lipid bilayer, are widely used as carriers of medicinal small molecules, proteins, and nucleic acids (Abegglen et al. 2015). Liposomes specifically −100 nm PEGylated liposomes are stable in aqueous environments and subsequently fuse to the plasma membrane or internalized by cells through endocytic and signaling pathways and reduce hypersensitive responses in plants (Kabanov et al. 2015). Nanoparticles have proven to be effective carriers for a wide range of compounds, capable of enhancing biological targeting, delivery, and uptake (Meir et al. 2014). The nanoscale drug-delivery systems with agricultural nutrients (liposomes loaded with Mg or Fe), when sprayed to leaves of tomato plants with acute nutrient deficiency of Mg and Fe deficiencies, penetrate the leaf and translocate in a bi-directionally throughout the plant, taking advantage of the plant's natural transportation mechanisms and without exerting any toxicity. Liposomal formulations restored both chlorosis and epinasty, and activated plant-growth mechanisms. These research findings support developing the implementation of nanotechnology field for delivering micronutrients to agricultural crops for increasing yield (Karny et al. 2018). Intracellular (in the nucleus or cytoplasm) cargo release (dye from the liposomes) can be mediated by the disruption of the nanoparticle by lipases, or due to dye leakage caused by osmotic destabilization (Brodin et al. 2015). These results show that nanotechnology grants a new technological alternative for treating fully grown crops.

9 Genetic Material Delivery via Nanoparticle-Mediated Chloroplast Transgene Delivery

Zarei et al. (2018) reported that a great attention is recently given to the smart delivery systems of organic and inorganic agrochemical to deliver the nucleic acids into the plant cells. The nanosized materials are a promising tool for delivery of genetic material inside plant cells. Carbon nanomaterials can penetrate and enter into cells and thus can be employed for the purpose of DNA molecule delivery (Burlaka et al. 2015). The technology of nucleic acid and chemicals delivery to plant cells using mesoporous silica nanoparticle system (MSNPs) has become apparent (Galbraith 2007; Torney et al. 2007; Martin-Gullon et al. 2006; Martin-Ortigosa et al. 2014). Liu et al. (2009) proved the possibility of delivery of DNA by carbon nanotubes inside *Nicotiana tabacum* cell for the first time. Carbon nanotubes are the best example showing safe interaction with biomacromolecules and a remarkable potential nano-vector to transfect plant cells with genes of interest (Wang et al. 2014). The single-walled-CNTs (SWCNTs) act as nano-transporters for delivery of DNA and dye molecules into plant cells (Srinivasan and Saraswathi 2010). Khodakovskaya et al. (2012) reported MWCNTs induce cell division, proliferation, and activated expression of several genes of cell division (CycB), cell wall extension (NtLRX1), and water transport (NtPIP1) in tobacco callus after penetration. Martin-Ortigosa et al. (2012) reported improvement of delivery of DNA inside *Allium cepa* epidermal tissue with use of gold nanorods (NRs). Created MSNPs were effective for mediated co-delivery of protein and plasmid DNA into plant cells (Martin-Ortigosa et al. 2012). According to Nima et al. (2014), AuNR/Ag nanoparticles are excellent candidates for delivery of different molecules including nucleic acid into plant cells. Another promising type of nanomaterials for nucleic acid delivery is polymer nanoparticles. Thus, fluorescent conjugated polymer nanoparticles (CPNs) were used to deliver siRNAs and knockdown specific gene target in tobacco BY-2 protoplasts (da Silva et al. 2014). MSNPs can edit genome and generate precisely modified "nontransgenic" plants. Using MSNPs as carrier, cre-recombinase protein when delivered into *Zea mays* (Martin-Ortigosa et al. 2014) removed loxP-defined DNA fragment from maize genome. Different reports suggested that the MWCNTs have a more magic ability to influence the seed germination and plant growth and work as a delivery system of DNA and chemicals to plant cells (Lahiani et al. 2015). On the other hand, scientists indicated that both MWCNTs and SWCNTs were documented by using Raman spectroscopy and transmission electron microscopy (TEM) (Lahiani et al. 2015). The single-stranded DNA molecules wrapped around SWCNTs were able to target the cytoplasm of walled plant cells. So RNA pieces can be sent into the nucleus to activate or silence the genes and plasmids into protoplast for delivery into the plant cell genome (Serag et al. 2015). Plant genetic engineering can benefit from nanotechnology in the area of improvement of plant transformation. Plant transformation efficiency can be increased with nanovehicles by more precise delivery of genetic material, ability to control gene expression through release of incorporated chemical inducer and better detection of nano-delivered genetic material inside cell. Nanoparticle-mediated transformation signifies a promising approach for plant genetic engineering because of being simple, easy to perform, cost effective, applicable to adult plants across varied species, does not require specialized, expensive devices and thus is widely applicable. Based on the particle size and surface charge, SWCNTs can navigate the stiff plant cell walls, cell membranes, and chloroplast membrane by lipid exchange envelope penetration (LEEP), and finally get kinetically entrapped inside the chloroplasts (Giraldo et al. 2014; Wong et al. 2016; Lew et al. 2018). Recently Kwak et al. (2019) have demonstrated the possibility of chloroplast transformation (chloroplast-targeted gene delivery) using chitosan-complexed SWCNTs as nanocarriers designed using the LEEP model to maximize the trafficking efficiency and protect and deliver pDNA–SWNT 9pDNA encoding a YFP reporter gene) conjugates into the chloroplasts transiently transgene expression in mature *Eruca sativa, Nasturtium officinale*, *Nicotiana tabacum,* and *Spinacia oleracea* plants and in isolated *Arabidopsis thaliana* mesophyll protoplasts. This nanoparticle-mediated chloroplast transgene delivery tool provides practical advantages over current delivery techniques as a potential transformation method for mature plants to benefit plant bioengineering and biological studies. Recently, Demirer et al. (2019) reported efficient diffusion-based DNA delivery with nanomaterials and protein expression without transgene integration in *Nicotiana benthamiana* (*Nb*), *Eruca sativa* (arugula), *Triticum aestivum* (wheat), and *Gossypium hirsutum* (cotton) leaves and arugula protoplasts.

10 Conclusion and Perspective

Global economy reported that the agribusiness market estimation was in the range of US$ 20.7 billion to US$ 0.98 trillion in 2010 which was expected to go beyond US$ 3.4 trillion by 2020 (Hooley et al. 2014). Under National Nanotechnology

Initiative, USA invested US$ 3.7, while Japan and the European Union enhance nanotechnology area with annual funding of US$750 million and US$ 1.2 billion, respectively (Hirsh et al. 2014). The developing countries which face the stigma of population explosion, also need to take up research in this area and apply nanobiotechnology based concepts for the sustainable agriculture. The agri-nanotechnology may take many decades to maneuver from laboratory to land. To feed billions of people, agricultural practices like plant breeding and IPM are not sufficient and need smart alternatives that could match our current and future food demands. Nanotechnology, a novel high-tech for agriculture is most promising and attractive field which could potentially address global challenges in food and agriculture and will ensure food security, development of environment friendly and sustainable agriculture. By employing NPs we can reduce input on chemicals, minimize nutrient loss and environmental footprints, and enhance crop yield. Nanotechnology as a versatile platform is sufficient in alleviating problems of higher chemical input cost, poor efficiency of pesticides, herbicides, fungicides and fertilizers and their contamination in land and groundwater by providing cost-effective, reduced use of efficient high-targeting delivery and smart controlled releasing nano-agrochemicals. These nanochemicals release the nutrients during the demand-driven period in a precise manner. Nanotechnology also enables the environmentally acceptable solutions for reduced water pollution, food product residual contamination and the nanosensors and barcodes enable efficient and healthy useage of agricultural resources which increase the soil and environmental qualities. The mode of action of NPs is possibly more complex, linking to a long way of actions, which need to further investigate.

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Role of Nanotechnology in Crop Improvement

John Mohd War, Mohammad Afaan Fazili, Waseem Mushtaq,
Abdul Hamid Wani, and Mohd Yaqub Bhat

1 Introduction

Agriculture is considered as the backbone of most developing countries, having more than 60% of their population dependent on it for their livelihood (Raliya et al. 2017). In the twenty-first century, agriculture is facing diverse challenges for producing more food by addressing the problems of fast growing population, diminishing agricultural productivity, unpredictable climate change, variable labor force, and ever increasing urbanization. By 2050, these problems seem to intensify extremely, thus creates a major challenge to feed the population of over nine billion, and hence 50–70% of more food needs to be produced to feed them enough (Naderi and Shahraki 2013). As a source of food, feed, and fiber, agriculture has always been increasingly important in a world of declining resources with rapidly increasing global population (Brennan 2012). In order to come up with the solution of these emerging problems, agriculture-dependent countries need to adopt more advanced technologies, labor-saving practices, and innovative methods. In this scenario, the most recent technical improvement in the field of agriculture that holds a remarkable position in remodeling agriculture and food production and also fulfills the

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J. M. War · A. H. Wani · M. Y. Bhat
Section of Mycology and Plant Pathology, Department of Botany, University of Kashmir,
Jammu and Kashmir, India

M. A. Fazili (✉)
Section of Mycology and Plant Pathology, Department of Botany, University of Kashmir,
Jammu and Kashmir, India

Advanced Plant Physiology Section, Department of Botany, Aligarh Muslim University,
Aligarh, Uttar Pradesh, India

W. Mushtaq
Allelopathy Laboratory, Department of Botany, Aligarh Muslim University,
Aligarh, Uttar Pradesh, India

K. R. Hakeem, T. B. Pirzadah (eds.), *Nanobiotechnology in Agriculture*,
Nanotechnology in the Life Sciences, https://doi.org/10.1007/978-3-030-39978-8_4

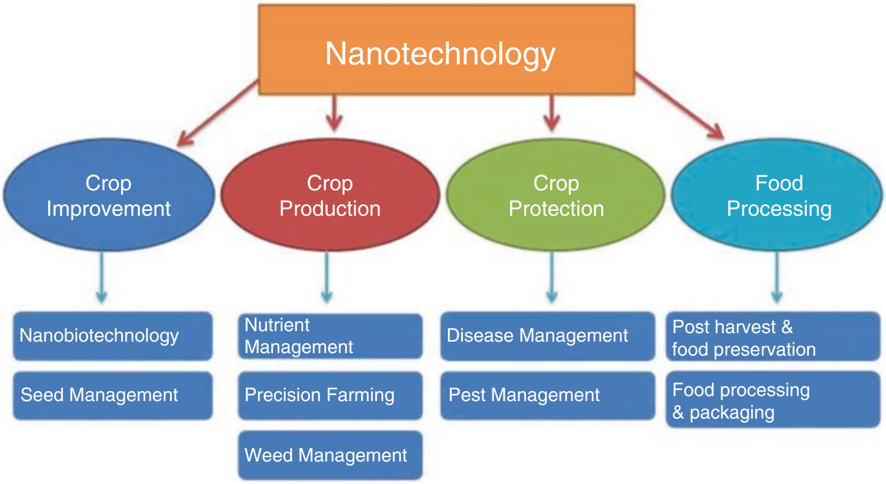

Fig. 1 Various applications of nanotechnology in agriculture sector

demands in an efficient and cost-effective way is nanotechnology. It is a promising tool that has the potential to foster a new era of precise farming techniques and hence may evolve as a possible solution for the current agricultural issues. There may be increase in agricultural potential so as to harvest higher yields in an eco-friendly way even in the challenging environments (Sugunan and Dutta 2008). Nanotechnology is expected as a potential complement to genetic engineering and molecular plant breeding besides traditional plant breeding in the near future.

Nanotechnology may work in multiple dimensions to benefit agriculture as it has the potential to play critical role in food production, food security, and food safety (Fig. 1). Its introduction in agriculture aims particularly to increase the yield based on nutrient management optimization, minimal nutrient loss in fertilization, and reduced application of plant protection chemicals (Chen et al. 2013) as well as to enhance the food quality by using strategies like monitoring plant growth, detection of diseases, increased plant protection, and reduced waste for strengthening agriculture sustainability (Frewer et al. 2011; Biswal et al. 2012; Ditta 2012; Prasad et al. 2012; Sonkaria et al. 2012; Pérez-de-Luque and Hermosín 2013; Pirzadah et al. 2019). Agro-nanotechnology currently focuses on target farming involving the use of nanoparticles (NPs) in order to boost crop and livestock productivity (Scott and Chen 2013; Batsmanova et al. 2013). Due to unique features of nanoparticles, they have been used in all stages of agricultural production in varied forms and procedures such as crop improvement (Tarafdar et al. 2014), plant protection ingredients (pesticides, fungicides, weedicides) (Park et al. 2006; Corradini 2010), nanofertilizer for balance crop nutrition (Janmohammadi et al. 2016; Abobatta 2017), monitoring the identity and quality of agricultural produce (Rameshaiah et al. 2015), nanosensors (Das et al. 2009), post-harvest technology (Meetoo 2011), bioprocessing of nanoparticles for agricultural use (Tarafdar et al. 2014), nanobiotechnology (Galbraith 2007), seed technology (Bharathi et al. 2016), plant growth regulators (Choy et al. 2007), soil management (Klingenfuss 2014), agricultural engineering aspects (González-Melendi et al. 2008), etc. Due to its rapid development, nanotechnology is expected to change greatly many areas of food science and industry with increasing investment and market share (He and Hwang 2016; Yata et al. 2018). In the field of crop improvement, scientists are trying to disclose the inherent potential of the nanotechnology through an array of experiments in different directions by taking the advantage of biotechnology (called as Nanobiotechnology). The use of nanoparticles in crop science is developing a great interest among the researchers because of their various beneficial effects (Zheng et al. 2005). A number of studies showed positive response towards plant growth and development on exposure to nanoparticles (Lu et al. 2002; Shah and Belozerova 2009; Sharon et al. 2010; Sheykhbaglou et al. 2010; Kole et al. 2013; Razzaq et al. 2016) and their role in relation to their uptake, internalization, translocation, and persistence has been well presented and documented in many research articles.

Nanotechnology is emerging as a paradigm shift and is evolving as an encouraging tool to initiate a new era of precise farming techniques and methods, hence may furnish with a possible solution for enhanced agricultural productivity and crop improvement (Misra et al. 2016). It will strengthen the mission towards evergreen revolution with limited inputs but maximum output. Although implementation of nanotechnology for agriculture sustainability is in its infancy stage, there are exceptional and unparalleled examples of nanoparticles where it has energized agriculture in many ways. In the present chapter, influences of different nanoparticles (carbon, metal-based, and metal oxide) on various growth parameters of different crop plants have been presented. Beneficial role of nanoparticles through plant biomass and yield, seed germination, increased root-shoot length as well as enhancement in secondary metabolite production of various crop plants including onion, cucumber, tomato, soybean, rice, maize, wheat, potato, chickpea, barley, mustard, mung bean, cluster bean cabbage, etc. has been discussed throughout the chapter.

2 Agro-Nanotechnology and Crop Improvement

Nanotechnology is an emerging field to revolutionize the agriculture and food sector. The properties of nanoparticles such as small size, large surface-to-volume ratio, enhanced solubility, chemical reactivity, optical and magnetic properties made them unique in the various fields especially in the agricultural sector. The introduction of nanotechnology in agriculture is getting importance due to reduced agricultural inputs, enhanced food values, improved nutrient contents and longer shelf life, freshness and quality of food by preventing gas penetration as well as by enhancing micronutrient and antioxidant absorption via preserving and packaging nanomaterials (Kanjana 2015). Its novelty has revolutionized and benefitted many of the agricultural aspects such as crop improvement, crop management, protection of crops via genetic improvements, target-specific delivery of genes, drugs, and other biomolecules (e.g., nucleotides, proteins, and activators), controlled release of agrochemicals (nutrients, fertilizers, pesticides, herbicides), gene expressions in plants and animals under stress conditions based on nano-array gene technologies, early detection of diseases and pests by nanosensors, seed management and their protection from pathogens and maintaining their genetic purity by separation of unviable and infected seeds (Chinnamuthu and Boopathi 2009). Due to its rapid progression and development towards possible solutions, nanotechnology is considered to play its important roles for the current problems in the field of agriculture (Abobatta 2018). A number of patents and products have been developed where nanomaterials have been incorporated into agricultural practices, for instance, nanopesticides, nanofertilizers, and nanosensors (Servin et al. 2015).

The advantageous role of nanoparticles in crop plants has been evidenced through effective demonstration of enhanced percentage in seed germination (Lu et al. 2002; Nair et al. 2010; Gopinath et al. 2014), increased shoot and root length (Liu et al. 2005; Hafeez et al. 2015), increased yield of fruits, enhancement in metabolite content (Kole et al. 2013), and a substantial increase in vegetative biomass of seedlings and plants in many crops. Likewise, the influence of nanoparticles in many biochemical parameters related to plant growth and development has also been reported, viz. enhanced photosynthetic rate and nitrogen use efficiency in many crop plants including soybean (Ngo et al. 2014), peanut (Prasad et al. 2012; Liu et al. 2005), spinach (Zheng et al. 2005; Hong et al. 2005; Yang et al. 2006; Gao et al. 2008; Klaine et al. 2008; Linglan et al. 2008). A much better understanding of the nature of dynamic interactions between nanoparticles (NPs) and plant responses, such as their uptake, localization, and activity, could significantly revolutionize crop production through increased resistance against diseases, nutrient utilization, and crop yield (Wang et al. 2016). Nanoscale materials can provide programmed, time-controlled, target-specific, self-regulated, and many more multifunctional capabilities (Nair et al. 2010). For example, engineered nanoparticles (ENPs) can deliver agrochemicals in an "on-demand" manner, which may serve either as nutritional demand or protection against pathogens and pests. Hence nanotechnology provides a way to avoid regular and repeated application of conventional agrochemicals and thus reduces adverse effects on plants as well as environment. In addition to this, nanoparticle-mediated targeted delivery of various phytoactive molecules including nucleotides and proteins has the capability to regulate plant metabolism and their genetic modification.

3 Role of Nanotechnology for Enhancement of Plant Biomass and Yield Production

3.1 Crop Growth on Exposure to Carbon Nanomaterials (CNMs)

In a long list of nanoparticles (NPs), the most significant group is formed by carbon nanomaterials (CNMs) due to their unique chemical, electrical, mechanical, and thermal properties. Carbon nanomaterials (CNMs) including single-/multi-walled carbon nanotubes (SWCNTs/MWCNTs), $C_{60/70}$ fullerenes, carbon NPs, and fullerols have attracted the interest of researchers because of their potential to enhance crop growth (Khot et al. 2012). However, there are many studies which show contradictory results based on size and concentration of NPs and also on plant species. For example, carbon nanotubes (CNTs) enhanced root elongation in cucumber and onion, but on the other hand it significantly reduced the root length in tomato plants (Canas et al. 2008). In a study, the effect of SWCNTs, MWCNTs, graphene, and bulk activated carbon (AC) was carried out using tomato plants that were grown in artificial medium wherein the results revealed that SWCNTs and MWCNTs helped in increased seed germination and plant biomass due to enhanced water uptake efficiency. It was shown that MWCNTs acts at the molecular level and significantly altered the gene expression such as the genes for water channel proteins called aquaporins (Mariya et al. 2011). Same research group in a separate study examined the potential control of MWCNTs on seed germination and growth of tobacco cell culture. Different concentrations (5–500 µg/ml) were used and it was found that growth of tobacco cell culture enhanced by 55–64% over the control; however, under the effect of activated carbon (AC), improved cell growth (16%) was observed at lower concentration (5 µg/ml), while at higher concentrations (100–500 µg/ml) intense inhibition was recorded in the cellular growth. A correlation was established between the stimulation of growth of cells exposed to MWCNTs, the upregulatory genes (responsible for cell division/cell wall formation) and water transport. It was shown that specific genes are involved in the regulation of cell division and extension by MWCNTs which is associated with the activation of aquaporins (Khodakovskaya et al. 2012). Soil-based life cycle study with tomato plants treated to MWCNTs and AC showed that water consumption, flower number, and plant height were all higher in soil exposed with MWCNTs as compared to AC exposed plants and control (Khodakovskaya et al. 2013). The effect of MWCNTs on other crop plants including barley, soybean, and corn grown in agar medium at concentrations of 50–200 mg/L in relation to their seed germination and growth for a period of 11 days was carried out and it was found that germination in all the species was enhanced by 50% besides increased shoot development in corn and soybean. The accumulation of MWCNTs was done by transmission electron microscopy (TEM) and Raman spectroscopy (Lahiani et al. 2013). In related work, chickpea was exposed to citric acid-coated CNTs at 6 g/L for 10 days which resulted in its intercellular uptake and stimulation of growth of the plant seedling. It was suggested from the experiments that an aligned network was formed inside the vascular tissue by these nanotubes that subsequently enhanced water efficiency uptake (Tripathi et al. 2011). Utilization of CNTs for enhanced water transport in dry and arid zone agriculture was supposed to be much effective and plausible for improving crop biomass and yield of plants like maize (Tiwari et al. 2014). Similarly, the exposure of water-soluble carbon nano-dot at a concentration of 150 mg/L was shown to help in enhanced growth of roots in case of wheat plant (Tiwari et al. 2014). As such, the influence of fullerol [C_{60} $(OH)_{20}$] or water-soluble fullerenes on bitter melon was studied and the results revealed that exposed plants had a 54–128% increase in biomass and fruit yield. There was also an increased level of antidiabetic (charantin, insulin) and anticancer (cucurbitacin-B, lycopene) compounds.

The accumulation and translocation of fullerols were demonstrated by Fourier transform infrared spectroscopy (FTIR) and bright-field imaging techniques (Kole et al. 2013). Lastly, it has been proposed that fullerene C_{60}, and CNTs possess the potential to improve biomass and yield in plants up to ~118% and also help in water retention capacity (Husen and Siddiqi 2014). All these findings suggest that CNMs may be considered as a promising nanoscale amendment for improving plant growth and promoting quality as well as yield which may be considered a remarkable achievement and progress of agro-nanotechnology in the field of crop improvement (Table 1).

3.2 Effect of Metal-Based Nanoparticles (MBNPs)

Different studies have been carried out to ascertain the effect of metal-based nanoparticles (MBNPs) such as silver (Ag), copper (Cu), gold (Au), iron (Fe), and molybdenum (Mo) on plants including wheat, maize, mung bean, mustard, spinach, etc. Application of MBNPs has a profound effect on various growth parameters of plants. They have been found to increase growth and physiological activities, water and fertilizer use efficiency, germination of seeds, stimulate nodule formation, and inhibit abscission of reproductive organs of plant. The use of silver nanoparticles (SNPs) for crop improvement has been a topic of interest for researchers. SNPs have variable responses in different plants and they affect plant growth by inducing changes at physiological and molecular levels (Yan and Chen 2019). In a study, the effect of soil applied SNPs at concentrations of 25–50 ppm on wheat plants showed increased plant height and fresh and dry weights as compared to control. The exposure of SNPs positively affected the number of seminal roots and at lower concentration (25 ppm), it enhanced yield by increasing grain number/spike (Razzaq et al. 2016). Thus, sensible use of SNPs to soil can improve the yield of wheat; however, further investigations need to be taken into consideration like concentration, mode and time of application so as to realize the potential of SNPs in crop growth and yield improvements for other plants in an ecofriendly manner. SNPs at 50 ppm concentration have been found to increase root fresh weight, total chlorophyll in mung bean plants (Najafi and Jamei 2014). Similar effects of these nanoparticles have been observed in case of Indian mustard seedlings wherein SNPs enhanced root and shoot length, fresh weight, vigor index, and chlorophyll contents (Sharma et al. 2012). SNPs delay senescence as reported in mung bean where application of 100 μL of SNPs effectively suppressed oxidative stress-induced senescence (Karuppanapandian et al. 2011). In another study, effects of different concentrations (20, 40, 60, 80, and 100 ppm) of SNPs on various growth parameters in common bean and maize was carried out and it was observed that at lower concentrations (20, 40, and 60 ppm), SNPs showed positive impact on the growth of both common bean and maize plantlets, viz. increasing shoot and root lengths, leaf area, chlorophyll, carbohydrate, and protein contents; however, at higher concentrations (80 and

Table 1 Application of ENPs of varying size at different concentrations on plants

NPs	Optimum concentration	Plant	Effects	Reference
CNTs, MWCNTs, fullerols Ag NPs	50 and 200 µg/mL	Tomato	Plant height and number of flowers	Khodakovskaya et al. (2013)
	47.2 nM	Bitter melon	Fruit yield	Kole et al. (2013)
	50 ppm	Potato	Weight and yield of potato mini-tubers	Tahmasbi et al. (2011)
	60 ppm	Common bean, maize	Dry weight of root and shoot	Salama (2012)
	60 ppm	Borage	Seed yield	Seif et al. (2011)
	–	Basil	Seed yield	Nejatzadeh-Barandozi et al. (2014)
	25–50 ppm	Wheat	Growth and yield	Razzaq et al. (2016)
Au NPs	10 ppm	Indian mustard	Growth and seed yield	Arora et al. (2012)
	10 µg/mL	Arabidopsis	Root and shoot length, early flowering	Kumar et al. (2013)
	1000 µM	Flame lily	Vegetative growth	Gopinath et al. (2014)
Ti NPs	0.25% w/v	Spinach	Fresh and dry weights	Yang et al. (2007)
	20 g/L	Wheat	Biomass and yield	Jaberzadeh et al. (2013)
Si, Pd, Au, and Cu NPs	0.013 and 0.066% w/w	Lettuce	Shoot–root ratio	Shah and Belozerova (2009)
Nanocrystalline powders (Fe, Co, and Cu) Iron oxide NPs		Soybean	Growth and crop yield	Ngo et al. (2014)
	0.5–75 g/L	Soybean	Yield and quality	Sheykhbaglou et al. (2010)
	50 ppm	Mung bean	Biomass yield	Dhoke et al. (2013)
	0.04% w/v	Wheat	Grain yield, spike weight, protein content	Bakhtiari et al. (2015)
	300 ppm and He, Xe irradiation 10 min	Pea	Growth and yield	Al Sherbini et al. (2015)
Nanoanatase-TiO_2 NPs Nano-TiO_2 Rutile (TiO_2)	0.25–4%	Spinach (naturally aged)	Plant dry weight	Zheng et al. (2005)
	0.01 and 0.03%	Maize	Content of carotenoids and anthocyanin	Morteza et al. (2013)

(continued)

Table 1 (continued)

NPs	Optimum concentration	Plant	Effects	Reference
ZnO NPs	20 ppm 1 ppm	Mung bean Gram	Root and shoot biomass	Mahajan et al. (2011)
	20 mg/L	Tomato	Growth and biomass production	Panwar et al. (2012)
	1000 ppm	Peanut	Stem and root growth, high yield	Prasad et al. (2012)
	500, 1000, 2000, 4000 ppm	Mung bean	Dry weight	Patra et al. (2013)
	1.5 ppm	Chick pea	Shoot and dry weights	Burman et al. (2013)
	10–40 µg/mL	Onion	Seed yield	Laware and Raskar (2014)
	50 mg	Mung bean	Biomass weight	Jayarambabu et al. (2015)
	10 mg/L	Cluster bean	Shoot length, root area, and plant biomass	Raliya and Tarafdar (2013)
Silicon dioxide NPs	15 kg/ha	Maize	Growth and growth parameters	Yuvakumar et al. (2011)
	–	Tomato	Antioxidant system	Haghighi et al. (2012)
	–	Squash	Antioxidant system under salt Stress condition	Siddiqui and Al-Whaibi (2014)
CuO NPs	500 mg/kg	Wheat	Biomass	Dimkpa et al. (2012)
	30 ppm	Wheat	Growth and yield	Hafeez et al. (2015)
CeO_2 NPs	2000 mg/L 4000 mg/L	Maize, alfalfa, soybean	Shoot growth and biomass	López-Moreno et al. (2010)
	125, 250, 500 mg/kg soil	Wheat	Yield and nutritional parameter	Rico et al. (2014)
$CaCO_3$ NPs	–	Mung bean	Seedling growth and biomass	Yugandhar and Savithramma (2013)

100 ppm), they show inhibitory effect (Salama 2012). Besides SNPs, gold (Au) nanoparticles are regarded as a promising tool in the field of crop improvement. Au nanoparticles have long ago been used for delivery of genetic material in plant cells. They have been reported to enhance seed yield by threefold over the control

in *Arabidopsis* at a concentration of 10 µg/ml (24 nm) (Kumar et al. 2013). In the same study, Au NP treatment at 10 and 80 µg/ml concentrations showed increased vegetative growth, seed germination, and free radical scavenging activity (Kumar et al. 2013). In another report, the influence of gold NPs on yield of Indian mustard was studied. Positive effect of Au NPs was visible on different growth parameters such as plant height, stem diameter, number of branches, number of pods, and seed yield. It was observed that average leaf area was not affected but there was an increase in total number of leaves per plant. The increase in the yield of seeds and reducing sugar and total sugar content was observed at concentrations of 10 ppm and 25 ppm, respectively (Arora et al. 2012). In an endangered medicinal plant, flame lily (*Gloriosa superba*), Au NPs showed positive impact on seed germination and vegetative growth. Seed germination rate was enhanced by 39.67% (at 1000 µM concentration) than control because of increased permeability for water and oxygen and uptake of gold ions that interacted with embryo cells and stimulate the activity of gibberellic acid (GA_3) to release α-amylase enzyme in the aleurone cell layer which then breaks down starch into simple sugar. A comprehensive effect on root initiation, node elongation, and number of leaves was observed in seeds exposed to 1000 µM Au NPs. Increase in biomass and fresh weight by 2.40- and 5.18-fold was observed, respectively, at 500 and 1000 µM concentrations of Au nanoparticles as compared to control (Gopinath et al. 2014).

Applications of other metal-based nanoparticles such as Fe, Cu, and Mo have been found to help in crop improvement by one way or the other. Iron (Fe) is one of the important elements for plant growth and plays a key role in the photosynthetic reactions. It helps in the activation of various enzymes that enhance photosystem performance and contribute in RNA synthesis (Malakouti and Tehrani 2005). As such, the effect of Fe NPs on spinach, grown in hydroponic solution, was investigated which revealed increased plant growth and biomass due to remarkable enhancement of Fe accumulation in leaves, stem, and root by 11- to 21-fold (Almeelbi and Bezbaruah 2012). Essential oil percentage and flower yield of pot marigold (*Calendula officinalis*) were reported to increase on application of Fe NPs (1 g/L) at the stem elongation stage (Amuamuha et al. 2012). Similarly, copper (Cu) nanoparticles were examined for their beneficial role in enhancing wheat growth and yield. Different concentrations (10, 20, 30, 40, and 50 ppm), respond well towards increase in growth and yield of wheat plant; however, at 30 ppm concentration of Cu NPs, there was significant increase in leaf area, chlorophyll content, number of spikes/pot, number of grains/spike, 100-grain weight, and grain yield (Hafeez et al. 2015). These results conclude concentration-dependent enhancement of growth and yield in wheat plants, hence further research is needed to optimize dose and mode of application to maximize yield production. Similarly, colloidal solution of molybdenum nanoparticles (Mo NPs) (8 mg/L) in the rhizosphere of chickpea (*Cicer arietinum*) has been reported to stimulate the development of agronomically valuable microflora that resulted in increase in number of nodules/plant by twofold as compared to control (Taran et al. 2014).

3.3 Effect of Metal Oxide Nanoparticles on Plants

Nanoparticles of metal oxides such as ZnO, TiO_2, Fe_2O_3, CeO_2, and SiO_2 have been used for crop improvement in various plants. They have a significant potential to improve seed germination, plant growth, and yield (Razzaq et al. 2016). However, their effect varies depending upon the dosage or concentration of the nanoparticle used. For example, ZnO NPs enhance root elongation in soybean at lower concentration (500 mg/L), but at the same time it shows inhibitory effect at higher concentrations (4000 mg/L) and hence reduces the root length (López-Moreno et al. 2010). Similarly, ZnO NPs showed concentration-dependent growth pattern in chickpea and mung bean seedlings. Maximum growth in case of mung bean was observed at 20 ppm, while for chickpea seedlings, the maximum growth occurred at 1 ppm concentration (Mahajan et al. 2011). ZnO nanoparticles have been proved much more beneficial for growth, flowering, and seed productivity in onion plants (Laware and Raskar 2014). Exposure of different concentrations (0, 10, 20, 30, and 40 μg/mL) of ZnO NPs was given to 6-month-aged onion bulbs and the treatment was given three times at the interval of 15 days and different growth parameters were assessed both at flowering as well as at the time of harvest. It was observed that plants treated with ZnO NPs at the concentrations of 20 and 30 μg/ml showed significant growth and flowered 12–14 days earlier in comparison with control. Moreover, a remarkable enhancement in yield was obtained due to production of high-quality and healthy seeds. ZnO nanoparticles have also been used to enhance nutritional quality and growth of leaves in spinach. Application of 500 and 1000 ppm ZnO nanoparticle has increased leaf length, width, surface area, and color of spinach leaves as compared to control. At the same concentration, elevated levels of protein and dietary fiber contents were observed (Kisan et al. 2015). In another study, chlorophyll formation, photosynthesis, and plant dry weight of spinach were enhanced by the application of TiO_2 nanoparticles (Hong et al. 2005). Thus, there is the possibility of using nanoparticles of ZnO and TiO_2 as biofortification agents so as to improve protein and dietary fiber contents of spinach leaves to reduce malnutrition. Feizi et al. (2013) reported that application of nano-sized TiO_2 at 60 ppm concentration increases seed germination in *Foeniculum* species. In *Zea mays*, nano-TiO_2 plays a significant role in increasing pigments when sprayed at reproductive stage which finally led to increase in yield (Morteza et al. 2013). Application of TiO_2 NPs exhibited positive response on regeneration efficiency in aromatic rice (cultivar KDML105) (Zahra et al. 2017).

The effects of iron oxide (Fe_2O_3) nanoparticles have been studied in peanut and it was demonstrated that application of nano-Fe_2O_3 significantly increased nutrient absorption that resulted in enhanced growth and photosynthesis (Liu et al. 2005). Similarly, exposure of nano-Fe_2O_3 (0.5 g/L) increased yield in soybean due to increase in leaf and pod dry weight (Sheykhbaglou et al. 2010). The application of Fe_2O_3 NPs on soybean via foliar and soil route had different effects. Enhancement in root elongation and photosynthetic potential were remarkably higher by foliar spray as compared to soil route probably due to accumulation of iron ions (Alidoust and Isoda 2013). However, nanoparticles vary in their effects depending upon mode of application, concentration as well as the type of plant species. Soil treatment of CuO NPs was given to mustard (*Brassica juncea*) to demonstrate their effect on photosynthetic rate and antioxidant levels. CuO NPs at different concentrations (2, 4, 8, 16 ppm) significantly increase the photosynthetic efficiency and antioxidant levels, but the optimum levels were achieved at 4 ppm NP concentration (Singh et al. 2018).

The impacts of cerium oxide nanoparticles (CeO_2 NPs) on *Coriandrum sativum* plants grown in organic soil were assessed. After the treatment with 0–500 mg/kg CeO_2 NPs, plants were analyzed for their growth and biochemical assays and the results revealed significant effects at 125 mg/kg concentration of CeO_2 NPs, including increased root and shoot length, enhanced biomass and activity of catalase in shoots, and ascorbate peroxidase in roots (Morales et al. 2013). Similarly, effect of CeO_2 NPs (0, 125, 250, and 500 mg/kg) on agronomic traits, yield, and nutritional parameters in wheat showed positive response and there was overall enhancement of growth, biomass and yield production. Besides, the composition of nutrients like amino acids was effectively changed and there was an increase in the amount of linolenic acids by 6.17% as compared to control (Rico et al. 2014). All these findings suggest the potential of CeO_2 NPs to modify crop physiology and food quality and hence demonstrate the fertilizing effects in wheat. Extended period for spike formation and physiological maturity has also been reported in wheat (Li et al. 2011; Marchiol et al. 2016).

The effect of SiO_2 nanoparticles on seed germination of tomato was investigated and it was observed that seed germination percentage, germination index, vigor index, seedling fresh weight and dry weight were significantly elevated on exposure to SiO_2 NPs. These findings offer a great scope to understand the mechanism of interaction between plants and nano-silica, since nano-SiO_2 may be used as a fertilizer for crop improvement (Siddiqui and Al-Whaibi 2014). Liu et al. (2016) reported that engineered NPs are not always more toxic than other chemicals comprising the same elements.

3.4 Role of Nanotechnology for Enhancement of Secondary Metabolites

Secondary metabolites are natural plant products (phytochemicals) responsible for medicinal properties of plants. A number of secondary metabolites are potential sources of nutraceuticals, pharmaceuticals, and agrochemicals. However, these secondary metabolites are produced in very low amounts by plants (Kabera et al. 2014). In order to enhance the production of important metabolites in plants, nanotechnological approach has been applied to a larger extent to achieve the same. Nanotechnology plays a vital role to enhance the secondary metabolite production due to their novel and unique properties as reported by Giraldo et al. (2014). Engineered nanoparticles have been used to deliver DNA and chemicals into plant cells (Galbraith 2007; Torney et al. 2007). Application of nanoparticles for enhancement of secondary metabolite production has been carried out under both in vivo and in vitro conditions. In the former, there is direct usage of nanoparticles in a precise concentration either by foliar spray or treatment with seeds or soil. Whereas in the latter case, nanoparticles have been used as elicitors for enhancing the expression level of genes related to the production of secondary metabolites (Isah 2019). Much of the work has been done to realize the effect of nanoparticles as elicitors for secondary metabolite production under in vitro conditions. However, there are many reports regarding the enhancement of secondary metabolites through in vivo nanotreatments. For example, foliar application of nano-iron (Fe NP) had significant effect on the production of essential oil content in pot marigold. Fe NPs (0, 1, 2, and 3 g/L) were sprayed at different stages and the effect on yield of essential oil was highly remarkable at first harvest. Highest percentage (1.573%) of essential oil was achieved when spraying at early stage (stem initialized) that led to the maximum yield of essential oil (2.397 kg/ha) in the flower (López-Moreno et al. 2010). Similarly, application of ZnO NPs improved gum content and its viscosity in cluster bean when 14-day-old plant was foliar-sprayed with NP concentration of 10 mg/L (Raliya and Tarafdar 2013). Likewise, the impact of fullerol [C60(OH)20] significantly increased phytomedicinal content in exposed bitter melon (*Momordica charantia*) fruits. There was an increase in the levels of both anticancer, including cucurbitacin-B and lycopene by 74 and 82%, and antidiabetic compounds, including charantin and insulin by 20 and 91%, respectively (Kole et al. 2013). Generally, plants produce secondary metabolites when exposed to different inducer molecules or elicitors (Zhao et al. 2005a, b). Nanoparticles are potentially effective and novel elicitors that have been used in plant biotechnology to enhance production of secondary metabolites (Fakruddin et al. 2012). Given below are the examples of secondary metabolites that have been significantly influenced by the application of nanoparticles under in vitro conditions.

Terpenoids

Artemisinin, a sesquiterpene lactone, is one of the important secondary metabolites produced by *Artemisia annua*. This secondary metabolite is used against malarial parasite (*Plasmodium falciparum* and *P. vivax*) (Snow et al. 2005) for treating various cancers including breast cancer, colon cancer, leukemia, and small carcinomas in lungs (Lei et al. 2011). However, production of artemisinin by *A. annua* is not sufficient to fulfill the demand. In this regard, application of nanoparticles has been reported as potential elicitors for the production of plant secondary metabolites. For example, nanosilver particles have been reported to act as potential elicitors and the exposure of Ag-SiO_2 core–shell nanoparticles (Ag NPs) in hairy root cultures of *A. annua* resulted in increased artemisinin content (Zhang et al. 2013). Similarly, nanocobalt particles were used in cell suspension cultures of *A. annua* for the elicitation of artemisinin. At the same time, the expression levels of SQS and DBR2 genes and artemisinin content were quantified using qRT-PCR and HPLC techniques, respectively. Different concentrations of nanocobalt (0.25, 2.5, and 5 mg/L) were used in the study and the cultures were regularly analyzed after 8, 24, 48, and 72 h and it was observed that artemisinin content was highest at 5 mg/L nanocobalt for 24 h at which expression levels of SQS and DBR2 genes were declined (Ghasemi et al. 2015). Similar type of study was carried out in hairy root culture of *A. vulgaris* to see the effect of nanocobalt and nanozinc (0, 0.25, 0.5, and 1 mg/L) on the expression levels of SQS, DBR2, ADS, and ALDH1 genes (Yarizade and Hosseini 2015). It was revealed that both nanocobalt and nanozinc maximized the expression levels of all the genes under investigation at 0.25 mg/L and 1.0 mg/L, respectively. However, it was suggested that nanocobalt is more effective elicitor than nanozinc because concurrent to the increase in the ADS upregulation, it also leads to downregulation of antagonist SQS gene.

Phenols

Aloin is one of the important secondary metabolites derived from *Aloe vera* that possesses antimicrobial and medicinal property, and is used to treat skin burns, cutaneous injuries, and ulcers. Cell suspension cultures of *Aloe vera* were treated with different elicitors (nano-Ag, nano-TiO_2, NH_4NO_3, and sucrose) to investigate their effects on aloin production after analyzing cultures at 6 h, 24 h, 48 h, 72 h, and 168 h. It was observed that elicitation by Ag NPs effectively enhanced aloin content at 48 h after which it declined and reached the control level. Same thing happened when nano-TiO_2 was used as elicitor and it was suggested that the decline in aloin production after 48 h might be due to feedback inhibition of increased aloin or NP on gene expression (Raei et al. 2014). Despite this fact, Ag NPs are still considered as potential elicitors for the production of some important secondary metabolites. Biologically synthesized Ag NPs had been shown to increase total phenol content in *Bacopa monnieri* when these plants are grown in hydroponic solution. This enhancement effect is due to slight stress on the growth and metabolism of *B. monnieri* by Ag NPs (Krishnaraj et al. 2012).

Flavonoids

Flavonoids and isoflavonoids are among the important groups of secondary metabolites in plants. Many legume plants are rich sources of these secondary metabolites (Heiras-Palazuelos et al. 2013). Impact of TiO_2 NPs (0.5, 1.5, 3, 4.5, and 6 mg/L) on the production of secondary metabolites (phenolic and flavonoid compounds) were studied in gram under in vitro conditions. Estimation of secondary metabolites from callus was done by HPLC and then compared with the mother plant. It was found that TiO_2 NPs significantly increased secondary metabolites in callus embryo of gram at the concentrations of 4.5 and 6.0 mg/L (Al-Oubaidi and Kasid 2015). Similarly, Au and Cu NPs have also been reported to enhance the production of phenolics and flavonoids in milk thistle plants (Khan et al. 2016).

Polyketides

Hypericum perforatum is a well-known medicinal plant and its extract is used against mild-to-moderate depression (Dias et al. 1998). The applications of Fe- and Zn-nano oxides have been used as elicitors to promote the production of two important polyketides, hypericin and hyperforin, present in *Hypericum perforatum* (Sharafi et al. 2013). Various concentrations of iron- and zinc-nano oxides (0, 50, 100, and 150 ppb) were used during the treatment, and cell suspension cultures were analyzed after 72 h. It was observed that both the nanoparticles significantly increased the production of hypericin and hyperforin at 100 ppb concentration. The contents of hypericin and hyperforin reached to the maximum (7.87 and 217.45 μg/g dry weight, respectively) by nano-zinc oxide, i.e., 3- and 13-fold higher than the control, while as it increased from 2.07 and 16.27 μg/g dry weight to 11.18 and 195.62 μg/g dry weight by nano-iron oxide.

Phenyl Propanoids and Terpenoids

Fennel is an annual or biennial aromatic plant which is used for the preparation of herbal drugs. Major components of fennel oil include phenyl propanoids and terpenoids. The amount of trans-anethole compound is the deciding factor for the quality of fennel volatile oil (Chaouche et al. 2011). Phytochemical analysis of normal and nanoelicited (TiO_2 and SiO_2) in vitro grown fennel plantlets was carried out and there was a significant difference between the two (Bahreini et al. 2015). Normal plants contain anethole, fenchone, limonene, and decane. However, it was observed that TiO_2-elicited plant extract contains phytol, octane, dodecane, and phenol 2, 4 bis (1, 1 dimethylethyl), while the constituents in SiO_2-elicited plants include benzoic acid, jasmonic acid, and hexadecanoic acid and pyrrolidinone as the major metabolites. All these differences in the chemical composition are due to the elicitation or induction by TiO_2 and SiO_2 nanoparticles. The metabolites like phytol and benzoic acid which appeared by elicitation process can be used as industrial and pharmaceutical precursors.

4 Crop Growth Enhancement Due to Nano-Enabled Disease Suppression

Diseases represent one of the major factors in limiting crop productivity. Annual agricultural crop losses due to plant diseases account for billions of dollars in the United States alone (USDA). In order to control fungal pathogens, cost over fungicide applications exceeds $600 million per year (González-Melendi et al. 2008). Disease causing organisms in plants include viruses, bacteria, fungi, and nematodes whose infection leads to economic loss by reducing yield, product quality, and/or shelf life. These economic losses may prove to be of secondary concern on agricultural productivity in addition to increasing global population and changing climate. Therefore, innovative and novel techniques are critically needed for crop disease management that will be a central component to any long-term strategy for sustaining agricultural production. Among the various strategies, the use of nanotechnology is currently considered as a promising and effective method for control of plant pathogens or phytopathogens. The active ingredients of traditional pesticides and fertilizers often have low water solubility due to which availability to targeted crops can be quite low and larger quantities of these formulations are required to control pathogens effectively to attain a good yield. In addition, fertilizers and metal-based pesticide formulations currently in practice are prone to leaching, precipitation, and volatilization. All this results in a highly expensive and inefficient approach towards pathogen control and plant fertilization (Servin et al. 2015). In comparison to this, nanofertilizers could offer more controlled release of nutrients and that too in a coordinated way so as to harmonize in regard to time with the uptake by the developing crop. This approach would both increase nutrient availability and minimize wasteful interactions with soil or air that result in loss of nutrients from the agricultural system. The application and production of nanoenabled pesticides and fertilizers is proceeding at a rapid pace because of their greater solubility, stabilized dispersal, decreased persistence, and greater target specificity (Rai et al. 2012; Pirzadah et al. 2019).

There are numerous reports showing positive impacts of metal and metal oxide nanoparticles on crop growth and/or pathogen inhibition. Nanoparticles such as Ag, Si, ZnO, Mg, and TiO_2 possess antimicrobial activity and likely suppress crop diseases directly (Prasad et al. 2014). Silver nanoparticles (Ag NPs) exhibit a strong inhibitory activity against various microorganisms due to which their application has gained a significant research for management of phytopathogens. For example, application of Ag NPs at 200 mg/L concentration reduces colony formation of pathogenic fungi that causes diseases in rye grass (*Lolium perenne*) to about 50% (Jo et al. 2009). These nanoparticles had been used in field trials where they inhibited the activity of *Colletotrichum* spp. (anthracnose pathogen) (Lamsal et al. 2011). Similarly, the combined effect of Ag NPs and fungicide fluconazole has been reported to exhibit greatest antifungal activity against several pathogenic fungi including *Candida albicans*, *Phoma glomerata*, and *Trichoderma* sp. (Gajbhiye et al. 2009). It has been shown that Ag ions bind to plasma membrane proteins containing cysteine amino acids, damaging its membrane integrity that causes change in physiological and biochemical processes of a cell. Subsequent penetration of Ag into cell cytoplasm causes inactivation of important enzymes and finally cell death (Ocsoy et al. 2013). ZnO NPs effectively reduce the growth of *Fusarium graminearum*, a pathogenic fungus in mung bean, by about 26% when compared to bulk oxide and controls (Dimkpa et al. 2013). These nanoparticles have also been reported to work against *Botrytis cinerea* and *Penicillium expansum*, reducing their growth by 63–80% and 61–91%, respectively. ZnO NPs function by cellular disruption in both the pathogens, leading to hyphal malformation and ultimately fungal death (He et al. 2011). A high inhibition rate in germination was found in the fungal spores of *Rhizopus stolonifer, Fusarium oxysporum, Alternaria alternata*, and *Mucor plumbeus* on exposure to ZnO and MgO NPs at concentrations as low as 100 mg/L (Wani and Shah 2012). The pathogenic bacteria, *Pseudomonas aeruginosa*, and fungi, *A. flavus*, were effectively suppressed when exposed to biosynthesized ZnO NPs (Jayaseelan et al. 2012).

Metal oxide nanoparticles such as TiO_2 have also shown a positive impact in various agricultural amendments due to their antimicrobial and photo-catalytic attributes. They could increase crop yield by 30% and also reduce pathogenic diseases effectively (Chao and Choi 2005). In a field study, application of TiO_2 NPs showed reduced infection of *P. syringae* pv. lachrymans and *P. cubensis* in cucumber by 69 and 91%, respectively (Cui et al. 2009). TiO_2 NPs could efficiently control bacterial spot disease, caused by *Xanthomonas* sp., in tomato and roses (Paret et al. 2013a, b). The use of TiO_2 NPs (up to 1% of the product mass) in food products has been approved by FDA because it is harmless and nontoxic (Ahmad and Rasool 2014).

Similarly, application of Cu nanoparticles was found to be more effective than non-nano Cu formulations against *Phytophthora infestans* in tomato plants. In a field study, nano- and non-nano Cu formulations controlled the growth of the pathogen by 73.5% and 57.8%, respectively (Giannousi et al. 2013). Conversely, chemically synthesized Cu nanoparticle showed highly effective and promising antifungal activity against other pathogens such as *Phoma destructiva*, *Fusarium oxysporum, Alternaria alternata*, and *Curvularia lunata* (Kanhed et al. 2014). Moreover, Cu NPs have been found to exhibit higher fungal inhibition potential than commercially available fungicide bavistin. Nanoparticle-mediated enhancement of crop growth and yield may simply be the result of reduced disease persistence which may be either due to anti-pathogenic activity of nanoparticle itself or by the induction of key defensive metabolites or pathways within the plant through nanoparticles. However, many of the nanoscale amendments discussed above entangle micronutrient elements, thus the combination of pathogen suppression and enhanced plant nutritional status may in fact be the reason for enhanced crop growth and yield (Servin et al. 2015).

5 Engineered Nanoparticles (ENPs) as Magic Bullets for Smart Delivery System

Engineered nanoparticles (nonmetal, metal, and metal oxide nanoparticles) possess unusual physicochemical attributes (e.g., small surface area, a typical surface structure, enhanced reactivity, etc.) that separate them from those of their molecular and bulk counterparts. These attributes are the consequences of small size, shape, surface structure, chemical composition, stability, and agglomeration of the nanoparticles (NPs) (Nel et al. 2006). Due to these unique features, ENPs have been applied in a range of consumer and commercial products such as catalysts, semiconductors, microelectronics, domestic products (e.g., sunscreens and cosmetics), and for drug delivery. Their immense uses in nanomedicine and nanopharmacology have made them as smart delivery systems. These systems have the ability to detect the effects of chemicals, pharmaceuticals, nutrients, food supplements, insecticides, fungicides, vaccinations, bioactive compounds, probiotics, etc., once after their delivery. In case of crop improvement, target-specific and controlled delivery of various chemicals, fertilizers, pesticides, and nutrients will certainly reduce applications of plant protection products, decrease nutrient losses from fertilizers, and increase yields through optimized nutrient management. Engineered NPs would reduce phytotoxicity and will allow controlled release of various agrochemicals “on demand” or “on command” basis.

5.1 Delivery of Pesticides

Pest management has become a challenging program in today’s agriculture because of weak diagnosis of pest occurrence, resistance against pesticides, inefficacy and spray drift of pesticides, and emergence of new pests. Thus, controlled or smart delivery system is necessary for targeted application of pesticides in order to release required agrochemicals in sufficient amounts over a period of time to achieve maximum biological efficacy and to minimize the harmful effects (Tsuji 2001). The approach of nanotechnology will be helpful to overcome these problems. It is because of the unique features of nanoparticles like increased surface area, greater solubility, higher mobility, induction of systemic activity, and lower toxicity. These features will help to enhance the efficacy of conventional pesticides and other agrochemicals (Sasson et al. 2007). The normal spray of pesticide application includes low value preparation and high volume agrochemicals, but in nanotechnology-based preparations, low volume and high value chemicals are used (Ghormade et al. 2011). Nanomaterials like clay, silica capsules, and polymeric particles are known for their controlled release properties as well as their biocompatibility, biodegradability, and reduced toxicity behaviors due to which they are being used as smart delivery systems for various agrochemicals (Choy et al. 2007; Hussein et al. 2002). Similarly, montmorillonite (MMT), a swelling type clay, hydrophilic, and having cationic exchange capacity, can be modified with cationic surfactant to make them hydrophobic (de Paiva et al. 2008) and then encapsulating different types of pesticides in both hydrophilic (Mishael et al. 2002) and hydrophobic MMT clays (Celis et al. 2005). It has been shown that the efficiency of the chlorpyrifos and diazinon insecticides improved from 4 weeks (commercial formulation) to as high as 20 weeks (using MMT clay) (Choudary et al. 1989). Several polymeric nanoparticles have been designed for effective release of agrochemicals, viz. encapsulation of bifenthrin by using polymers such as poly (acrylic acid)-b-poly (butyl acrylate) and polyvinyl alcohol (PVOH) (Liu et al. 2008a). Mesoporous silica NPs (MSNPs) have been used in agricultural sector in order to encapsulate and deliver agrochemicals in a controlled manner. MSNPs are designed to carry pesticide (e.g., avermectin) into its core, which beshield the pesticide from photodegradation and at the same time allowing for its sustained release (Li et al. 2007). MSNPs have also been applied against biotic stress of plants caused by insects mainly through physioabsorption of cuticular lipids, resulting damage to their waxy protective coat and subsequent death by dehydration (Barik et al. 2008) as in case of rice weevil *Sitophilus oryzae* (Debnath et al. 2011). The use of porous hollow silica nanoparticles (PHSNP) with a loading capacity of 36% proved much more effective and beneficial for controlled and sustained release of water-soluble pesticide called validamycin. After encapsulation in PHSNP, the release of validamycin lasts for 800 min as opposed to instantaneous release of free validamycin (Liu et al. 2006).

In addition to pesticide coating technology, nanoemulsion is another potential technique for slow and controlled delivery of pesticides or their active ingredients because of their efficient kinetic stability, smaller size, optical transparency, and lower viscosity (Xu et al. 2010). Nanoemulsion increases both solubility and bioavailability of nanopesticides, spreads it effectively on plant leaves, and enhances internalization in insects (Ebert et al. 1999). The neem oil nanoemulsions have been reported to have increased larvicidal effect with decreasing droplet size (Anjali et al. 2012). Nanoemulsions highly enhanced the stability of water-insoluble pesticide, cypermethrin, and resist its precipitation when diluted from concentrated solution (Wang et al. 2007). Development of new nanoscale formulations of pesticides has gained great attention nowadays and the research is being conducted by many agrochemical firms of the world. BASF—world's fourth ranking agrochemical Corporation (Germany) has applied for a patent on pesticide formulation, wherein the active ingredient ranges in size from 10 to 150 nm. Similarly, Bayer Crop Science of Germany has applied a patent for the development of nanoemulsion concentrate, containing nanoscale droplets in the range of 10–400 nm as the active ingredient. Two nanoemulsion products, i.e., Primo MAXX (plant growth regulator) and Banner MAXX (fungicide), had already been developed by Syngenta Company, with average particle size of 100 nm (Chinnamuthu and Boopathi 2009).

5.2 Delivery of Fertilizers

Agricultural production and crop quality largely depend upon plant nutrition. Nearly 40–60% of the total world food production is achieved by maintaining nutritional status via application of fertilizers (Roberts 2009). Fertilizers play a key role for the improvement of agricultural production; however, the nutrient use efficiency of normally used fertilizers is still very low and a large quantity goes waste due to runoff, leaching, denitrification, fixation, and microbial immobilization. There is a huge percentage of nutrient loss from the fertilizers to the environment and hence cannot be absorbed by plants. In general, nearly 40–70% nitrogen, 80–90% phosphorus, and 50–70% potassium are lost to the surroundings causing economy and resource losses as well as serious environmental pollution (Wu and Liu 2008). To overcome these problems, application of nano-based fertilizers is an advanced approach of nanotechnology that will revolutionize the fertilizer industries in near future. These fertilizers have been developed by using nanoencapsulation technique so as to allow slow and controlled release of nutrients to plants. This controlled release will reduce loss of nutrients to the surroundings and also enhance nutrient use efficiency (Abobatta 2018). Ideally, nanofertilizers release nutrients in accordance with the demand of plants. This timely release does not allow premature conversion of nutrients to chemical and/or gaseous forms which remain unavailable to plants (e.g., volatilization of NH_3 from urea) (DeRosa et al. 2010). Nanofertilizers are also called as smart fertilizers because of their smart delivery system. Slow-release fertilizers have advantage over soluble fertilizers as they can reduce the application rate and frequency by releasing their nutrients slowly and in accordance with the requirement of the plant. Due to large surface area to volume ratio, nanomaterials could effectively retain nutrients, thereby serving as a longer term and more stable nutrient reservoir to plants (Navarro et al. 2008). Wu and Liu (2008) reported a slow-release double-coated NPK fertilizer having high water retention and superabsorbent capacity by cross-linked poly(acrylic acid)/diatomite containing urea, chitosan, and water-soluble granular fertilizer NPK as outer coating, inner coating, and the core, respectively. This fertilizer with higher water retention capacity and controlled delivery system of nutrients is nontoxic and environment-friendly and hence could be immensely useful in agricultural and horticultural applications. Similarly, chitosan along with methacrylic acid (MAA) nanoparticles has been used for incorporation of NPK fertilizer sources such as urea, calcium phosphate, and potassium chloride for controlled release of nitrogen, phosphorus, and potassium nutrients (Corradini 2010). Nanocoating of sulfur ($\leq$100 nm layer) has been used for encapsulation of urea and phosphorus fertilizers for their slow and controlled release, with additional benefit of sulfur especially for sulfur deficient soils (Brady and Weil 1999). Increased stability on coating reduces the rate of dissolution of fertilizer and allows its slow and sustained release. Synthetic apatite nanoparticles have been used as a novel type of phosphorus (P) fertilizer for plants because of their slow and sustained release of phosphorus, thereby decreasing risk of water eutrophication (Liu and Lal 2014).

5.3 Delivery of Bioactive Molecules

Engineered nanoparticles (ENPs) are a source of new vector for the delivery of bioactive molecules including proteins, nucleotides, and activators. The employment of mesoporous silica NPs (MSNPs) has gained a special interest to deliver DNA and its activator into isolated cells of plants and even in intact leaves of tobacco (Torney et al. 2007). A honeycomb-like MSNP system (3 nm pore size) was armed with a gene (GFP gene) and its chemical inducer, with the ends of MSNPs covered with gold (Au) nanoparticles. An uncapping trigger was applied to break the bond interaction between Au NPs and MSNPs after their entry into the cells, resulting in the release of biomolecules followed by gene expression. MSNPs can also deliver proteins or enzymes into plant cells, thereby enabling their transient presence that may be used for genome modifications and biochemical analysis (Martin-Ortigosa et al. 2014). As such, lengthy process of DNA transgenics can be avoided and modified traits can be directly transferred into future generations. In addition to MSNPs, other nanoparticles are also used for the delivery of bioactive molecules into plant cells including single- or multi-walled carbon nanotubes (SWCNTs or MWCNTs) (Liu et al. 2009; Serag et al. 2011), quantum dots (QDs) (Etxeberria et al. 2006), magnetic virus-like NPs (VNPs) (Huang et al. 2011), Au NPs (Wu et al. 2011; Martin-Ortigosa et al. 2012), and starch NPs (Liu et al. 2008b). As compared to conventional methods of gene delivery, nanoparticle-mediated delivery systems have several benefits. They are highly efficient with ease of operation. For example, the amount of DNA required for detection of expression via nanoparticle methods is 1000 times lower than that required for conventional methods (Torney et al. 2007). Nano-based delivery system makes possible the transient DNA-free genome editing of plants via direct transfer of biomolecules in a controlled fashion (including gene silencing), leading to production of modified nontransgenic plants which differs from conventional genetic engineering methods. Nanoparticle-mediated delivery system has the potential to deliver more than one biomolecules simultaneously to the target cell, for example, DNA and proteins (Martin-Ortigosa et al. 2012), DNA and its activator (Torney et al. 2007), or even different genes. Moreover, ENPs can be easily armed with biological molecules through their surface functionalization for specific and targeted delivery.

5.4 *Nanoherbicides: Novel Chemicals to Suppress Weeds*

Weeds have always been one of the main reasons for reduction in crop productivity. Continuous exposure of plant community to different herbicides in different seasons has led to herbicide resistance in plants and becomes uncontrollable through chemicals. Target-specific herbicide molecules have been developed by virtue of nanoparticle encapsulation techniques and are aimed at specific receptors in the roots of target weeds which after translocation inhibit glycolysis and make the weed to starve for food and get killed (Chinnamuthu and Kokiladevi 2007). Application of herbicides in rainfed areas having insufficient soil moisture may lead to loss as vapor. Thus, herbicides cannot be applied in advance anticipating rainfall in these areas. However, nanoparticle-based herbicides may prove to be much more beneficial under all these circumstances. NP-based herbicides control parasitic weeds effectively at lower doses, thus reducing chances of adverse effects on the crops (Goldwasser et al. 2003). The release of active components from nano-based herbicides is pre-programmed as they have been encapsulated by using nanoparticles and hence can be trigged under certain conditions within the parasitic weed. Adjuvants for herbicide application are currently available that include nanomaterials. In one study, alginate/chitosan nanoparticles were prepared and used as a vector for paraquat herbicide (Silva et al. 2011). The release profiles of free paraquat and paraquat associated with alginate/chitosan nanoparticles showed significant differences during the observation. The herbicide in association with alginate/chitosan nanoparticles revealed changes in release profile as well as its interaction with the soil. It was suggested that this system may prove to be an effective means of reducing negative impacts caused by paraquat. Besides, it was also observed that soil sorption of paraquat in both free and associated case was dependent on the amount of organic matter.

5.5 Precision Farming

Precision farming is an innovative approach of nanotechnology that has potential to revolutionize agriculture, in particular, to increase the crop productivity by applying inputs on time and in preciously required quantity (Scott and Chen 2013). This approach has long been felt to minimize inputs (fertilizers, pesticides, herbicides, etc.) while maximizing the output (crop yields) by sensing environmental variables and reducing agricultural waste, thereby keeping environmental pollution to a minimum (Chinnamuthu and Boopathi 2009). Precision farming uses nanosensors and monitoring devices that are enabled by nanotechnology and will have a large impact on future farming methodologies. These sensors are autonomous and linked to the global positioning system (GPS) system. Networks of such wireless nanosensors are positioned across cultivated fields, providing essential data and leading to the best agronomic intelligence processes, the main objective of which is to minimize application of inputs and maximizing output (Scott and Chen 2013). The information and signals provided by nanosensors include ideal timing for planting and harvesting crops, their need for water, fertilizers, pesticides, herbicides, and other treatments on time and at appropriate level under given plant physiology, pathology, and environmental conditions. Nanosensors are impregnated with nanoparticles which determine the nutrient status and deficiency of the plants and provide timely corrective measures to reduce the both yield and quality loss. Valid information about the crop growth and field conditions including temperature, moisture, pH, soil fertility, nutrient status, insects, weeds, etc. can be determined on time and better decisions can be made regarding the enhancement of crop productivity (Kumar 2011). Timely detection of pests helps to solve the problem of pest damage in crops by combining with significant diagnosis of insects, fungal, bacterial, or viral pathogens. By diagnosing pests and pesticide residues, farmers and food manufacturers may assure product quality and safety before its dispatch (Grunert 2005) (Fig. 2).

6 Influence of Soil on Nanoparticle Activity

The activity of nanoparticles is highly influenced by the physical and chemical characteristics of the surrounding environment. The interaction of nanoparticles with biotic and abiotic soil components will certainly have an effect on their initial properties which will subsequently influence nanoparticle stability, transport,

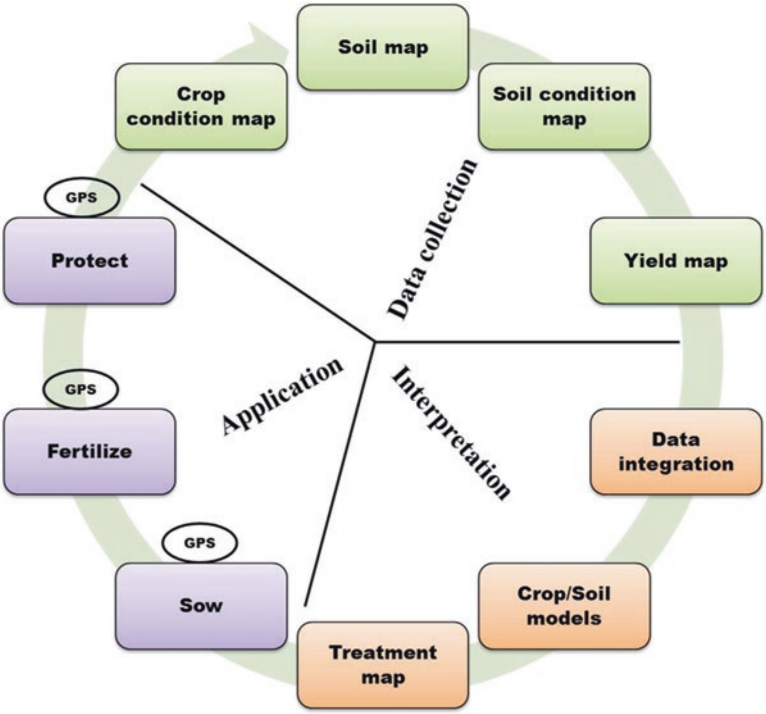

Fig. 2 Schematic representation of precision agriculture cycle

aggregation, and availability to biota. For example, Ag NPs shows greater mobility in negatively charged soils that will have a long-term impact on transport potential of NPs. The addition of stabilizing agents such as sodium citrate, sugars, polyvinyl pyrrolidone, amines, and amides significantly changed the interaction of NPs with soil and influenced its resulting mobility (Tolaymat et al. 2010). Sulfidation of Ag NPs occurs under both oxic and anoxic conditions and the transformed particles exhibit different mobility and activity (Thalmann et al. 2014). Interestingly, the effect of humic acid, a common soil component, has been reported to completely alleviate graphene phytotoxicity in wheat grown in hydroponic solution (Hu et al. 2014) and also increased the mobility of Ag nanoparticles (Tian et al. 2010). In the rhizosphere of cowpea, a rapid dissolution of ZnO NPs was found prior to uptake of ionic Zn into plant tissues (Wang et al. 2013). Soil pH is one of the important factors that determine the availability of nutrients to plants. For example, as soil pH approaches 7.0, nutrients like Cu, Fe, Mn, and Zn become progressively less available which results in low uptake by crop roots and hence compromised nutritional status (Sims 1986). Therefore, efficacious soil-based nanoscale supplements will need to consider physicochemical properties of soil such as pH. In a study, wheat was grown in acidic and alkaline soils amended with ZnO NPs and it was observed that there was a 200-fold higher soluble Zn content in the acidic soil as compared to the alkaline soil. Moreover, a tenfold higher concentration of soluble Zn content was found in wheat shoots when grown in acidic soil (Watson et al. 2015). High accumulation of Zn (344.07 mg/kg) was observed in case of soybean leaves when exposed to ZnO NPs. The aggregation and stability of ZnO NPs is highly affected by soil components such as organic matter (Priester et al. 2012).

7 Nanotoxicology and Regulatory Perspectives

Nanotechnology is a novel approach that has tremendous potential in the agricultural sector with its long lasting and beneficial influences. However, the increasing and unchecked use of nanoparticles resulted in a public discussion about their potential antagonistic effects in ecosystems. Over the past decade, many reports have shown opposite results regarding the effects of ENPs in plants (Miralles et al. 2012; Judy and Bertsch 2014). One of the reasons for this inconsistency is that different toxicity endpoints have been used which range from seed germination and seedling growth to cytotoxicity and genotoxicity. It is also evident that plants differ in their response to ENPs such as CNTs enhance seed germination by increasing water uptake efficiency in tomato (Wu et al. 2008) and rice (Nair et al. 2010), but exhibit inhibitory effect on root elongation in tomato and lettuce (Canas et al. 2008). Likewise, TiO_2 NPs increase rate of photosynthesis (Lei et al. 2007) and nitrogen metabolism (Linglan et al. 2008), but they also lead to the production of antioxidant stress (Lei et al. 2008). Leaves of lettuce had been reported to internalize the foliar-sprayed Ag NPs, thereby maximizing their chances of transfer to humans through food chain (Larue et al. 2014). Although toxicity due to Ag NPs in humans is an area of active research, the damage to cell membrane and DNA from the exposure has been reported (AshaRani et al. 2009; Gliga et al. 2014; Vrcek et al. 2014). Some methodological problems that are commonly encountered in plant nanotoxicology include: (1) the use of high concentrations of ENPs (e.g., up to 10 g/l), (2) the use of pristine form rather than realistic forms of NPs, and (3) neglecting appropriate requirements for control treatments.

ENPs can cause toxicity through the following ways: (1) release of toxic ions such as Zn^{2+}, Ag^{+}, and Cu^{2+} upon dissolution; (2) clogging due to mechanical damage (Asli and Neumann 2009); (3) excessive production of reactive oxygen species (ROS) (Shen et al. 2010; Zhao et al. 2012); (4) surface reconstruction of biomolecular structures due to release of surface free energy on binding interactions (Nel et al. 2009; Atha et al. 2012); and (5) biomolecular oxidation through catalytic reactions (Zhao et al. 2012). The nature of bonding between nanoparticles and plants is dependent upon the innate attributes of NPs such as their size, shape, chemical composition, surface roughness, hydrophilicity, and hydrophobicity (Nel et al. 2009; Sharifi et al. 2012). From a toxicological point of view, particle size is much more critical because as the particle size is reduced, there is increase in surface area which increases proportion of atoms or molecules of that particle on the surface layer. These size-dependent characteristics modify the interfacial reactivity and the capability to traverse physiological barriers. Many studies have revealed that the uptake and phytotoxicity of ENPs depends on particle size, the smaller particles generally get accumulated to higher levels and are more toxic than their bulk particles (Slomberg and Schoenfisch 2012; Judy et al. 2012). The shape and crystal structure of NPs also influence its uptake and toxicity, for example, anatase TiO_2 NPs being more toxic than rutile TiO_2; anatase NPs cause membrane leakage and cell necrosis, while rutile NPs lead to formation of ROS and cause apoptosis (Auffan et al. 2009). Similarly, ZnO nanopyramids showed significant inhibition of β-galactosidase enzyme as compared to ZnO nanoplates and spheres (Cha et al. 2015). The extrinsic properties of NPs such as surface charge (zeta potential), surface coating, stability characteristics, valence of the surface layer, and particle aggregation are also of great importance that influence their interactions with plants. Research-based evidences had shown that positively charged surfaces are absorbed through endocytosis (Navarro et al. 2008; Onelli et al. 2008), while negatively charged surfaces are more likely to be transported through vascular tissues (Zhu et al. 2012; Zhai et al. 2015). By modifying the surface coating, behavior of ENPs can be altered, e.g., coating MSNPs with triethyleneglycol to improve their penetration potential into plant cells (Torney et al. 2007). ENP coatings have also been successfully used as an effective means of reducing the dissolution properties and release of toxic ions (Yang et al. 2012). Extrinsic properties are however effectively influenced by the nature of suspending media (Auffan et al. 2009), its ionic strength, pH, and composition.

Although the risk of environmental exposure has increased due to global production and consumption of nanomaterials, there is a general agreement between the scientific communities that the information regarding the interactions of nanomaterials with plants and microbes is limited. A guideline was published by European Food Safety Authority (EFSA) in 2009 which emphasizes on potential toxicity of nanomaterials (Ganzleben et al. 2011). Nanoparticle-based antimicrobial pesticide called as HeiQ AGS-20 has already been approved by USEPA in 2010, but in case of other agrochemicals the regulations for use of nanomaterials remained elusive. Similarly, the use of nanomaterials (NMs) in food processing and packaging at the US FDA is lacking a specific regulatory guidance. However, in spite of lacking regulatory framework, it will not inhibit the application of NMs in agriculture. There is a need for extensive assessment of NPs in agri-food sector for public acceptance so that the challenges which were faced by genetically modified organisms (GMOs) worldwide could be prevented. Their application in agriculture (e.g., crop improvement) should be governed in a precise manner based on safety-by-design principle and guided by plant physiology, NP functionalization, and nanomedicine-inspired nano-delivery systems to effectively supply bioactive molecules, pesticides, and nutrients to crops with minimizing adverse effects on other organisms and environment.

8 Conclusions and Future Perspective

Nanotechnology holds an eminent position among most recent technical innovations in the field of agriculture. It has sufficient potential to remodel agricultural system and increases food production to fulfill demands in an efficient and cost-effective way. As per European Commission, nanotechnology is one of the "Key Enabling Technologies" that leads towards sustainable competitivity and growth in several industrial sectors. Its application in biotechnology (i.e., nanobiotechnology) led to the rapid development of marketable formulations with implementation of artificially designed nanoparticles (called engineered nanoparticles) for crop improvement. In order to avoid the indiscriminate and excess use of conventional pesticides and fertilizers in plants, nanoparticles turn out to be a gifted tool of this age. Nanotechnology has great potential to increase crop production and productivity from confined land areas by managing the application of inputs through smart delivery system, nanosensors, nanoscale coatings, and other nanomaterials. This technology is developing fast and its applications will highly energize the agricultural sector in the coming years that will lead to second green revolution. Although the approach of nanotechnology is interesting and promising and has the power to shower its advantages on agriculture and food sector, but it has been apprehended with unforeseen risks. Therefore, making awareness about the advantages and challenges of nanotechnology for its better acceptance by people and society is required and extensive studies need to be carried out to understand the mechanism of nanoparticle functions, toxicity, and their impact on environment.

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Nanofertilizers: A Way Forward for Green Economy

Bisma Pirzadah, Tanveer Bilal Pirzadah, Aarifa Jan, and Khalid Rehman Hakeem

1 Introduction

During 1970s first green revolution which was targeted to the four basic elements of production system viz., semi-dwarf high yielding varieties of wheat and rice, ample use of chemical fertilizers, irrigation which consequently resulted in an immeasurable increase in the agricultural production (Qureshi et al. 2018). However, extensive use of fertilizers, pesticides, and herbicides to achieve more production per unit area using high doses than optimum levels leads to major problems like environmental pollution, degradation in the quality of food material, development of resistance in different weeds, diseases, insects, soil degradation and deficiency in the essential nutrients in soil, toxicity to beneficial micro-organism present above and below the soil surfaces, etc. (Pirzadah et al. 2019). Nowadays because of these problems agricultural production is experiencing a sharp decline, which has untimely affected the livelihood base of the farming community at large besides, it leads to food crises in near future (Ghaly 2009; Quasem et al. 2009). Therefore there is need to produce nutritive agricultural produce rich in protein and other essential nutrient required to the human and animal consumption that is why emphasis should be laid on production of high quality food with the required level of nutrients and proteins (Pijls et al. 2009). The need of the hour is second green revolution in the world in which nano-scale science and

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B. Pirzadah (✉) · T. B. Pirzadah · A. Jan
Assistant Professor, University Centre for Research and Development (UCRD),
Chandigarh University, Mohali, Punjab, India

K. R. Hakeem
Department of Biological Sciences, Faculty of Science, King Abdulaziz University,
Jeddah, Saudi Arabia

Princess Dr Najla Bint Saud Al-Saud Center for Excellence Research in Biotechnology,
King Abdulaziz University, Jeddah, Saudi Arabia

K. R. Hakeem, T. B. Pirzadah (eds.), *Nanobiotechnology in Agriculture*,
Nanotechnology in the Life Sciences, https://doi.org/10.1007/978-3-030-39978-8_5

nanotechnology intend to have the capacity to revolutionize agriculture and food system. Nanotechnology has immense capacity to enhance crop production (Gruere et al. 2011), plant protection (Perez-de-Luque and Hermosin 2013), plant disease identification (Frewer et al. 2011), global expansion of food production (Biswal et al. 2012), improving quality of food materials (Sonkaria et al. 2012), and decrease misuse of resources for sustainable development (Prasad et al. 2014). The most important applications of nanotechnology were in the field of food and agriculture production (Coles and Frewer 2013; Chen et al. 2014). At the nanoscale, the matter presents altered properties which are novel and very different from those observed at macroscopic level. Due to the unique properties of nanoagrochemicals such as high surface-to-volume ratio, high reactivity, efficacy, and efficiency, these nano-formulations could be employed in the agricultural and food sector (Fig. 1) (Gutierrez et al. 2011). In addition to this, in agriculture there is need for the development of smart materials that can specifically deliver chemicals to particular target sites in plants which could be helpful in combating nutrient deficiency. This system is called "Smart delivery system" which means combination of particularly targeted, highly controlled, distantly regulated, and collective attributes to avoid biological barrier for target achievement (Nair et al. 2010). "Smart delivery system" involves the use of physiologically important metals for improving formulation of fertilizer or pesticide by decreasing loss of nutrient and increasing uptake in plant cell and technology advancement helps in the large scale production of these nanoparticles (Naderi and Danesh-Shahraki 2013). Therefore the development of these nanoparticles (nanofertilizers and nanopesticides) with unique properties for the improvement in crop production may act as an effective tool in agriculture for better pest and nutrient management (Scott and Chen 2012; Batsmanova et al. 2013). Hence, these agricultural useable nanoparticles developed with the help of nanotechnology can be exploited in the value

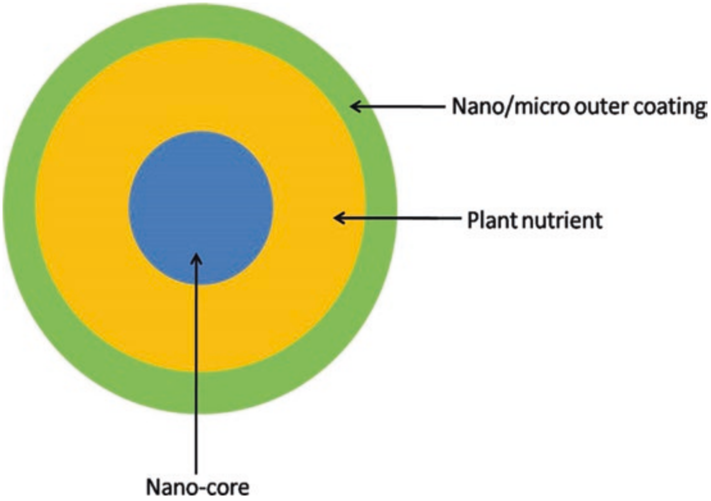

Fig. 1 Delivered as particles nano-scale dimensions, e.g., ZnO, CuO, TiO_2

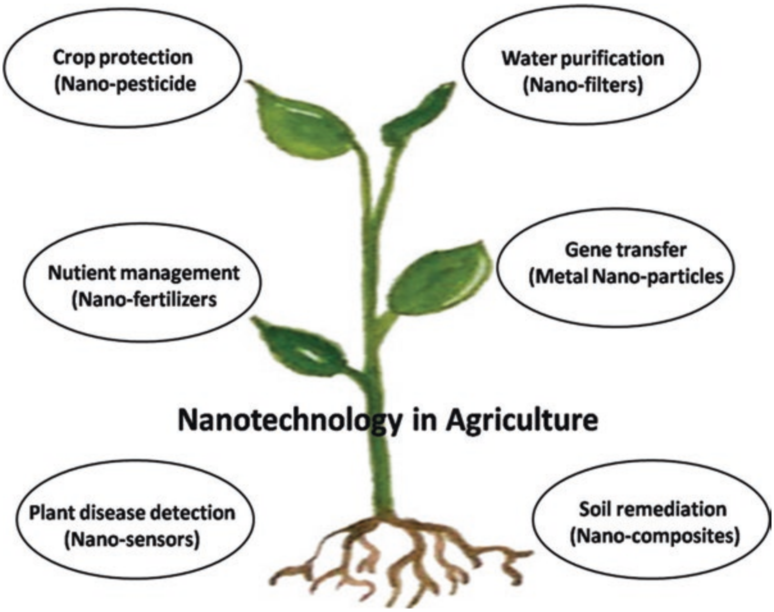

Fig. 2 Schematic representation of different nanotechnology applications in agriculture

chain of entire agriculture production system (Fig. 2) (Meena et al. 2017). The present chapter critically analyzes the pertinent information available on the scope and applications of nanofertilizer, nanofertilizer industry and its products. In this chapter, we also discussed the economic analysis as well as the current and future possibilities of nanofertilizer industry.

2 Nanofertilizer: As Smart Nano-Formulations

Conventional fertilizers are applied to the plants either through soil or by foliar application in order to improve plant growth and yield to a greater extent (Bahera and Panda 2009). Localized application of large amounts of fertilizer, in the form of ammonium salts, urea, and a nitrate or phosphate compound possesses deleterious effects to the soil and thus deteriorates the environment. Besides much of these fertilizers are unavailable to plants as they are lost as run-off and leaching (Wilson et al. 2008). Commonly available chemical fertilizers include nitrogen, phosphorous, and potassium that play an essential role in plant growth and development, viz., nitrogen enhances growth of leaf and synthesis of chlorophyll and protein; phosphorous enhances root, flower, and fruit growth; and potassium plays a role in the synthesis of protein and boosts root and stem growth (Mandal et al. 2009; Gu et al. 2009). In the applied dosage level of these fertilizers only 30–60% of nitrogen, 10–20% phosphorous, and 30–50% potassium were taken up by the plant and the remaining amount was left in the soil. This causes contamination to the soil and water resources as well as leads to the significant economic loss. These demerits of conventional fertilizers can be reduced with the help of nanotechnology in which major portion of these chemicals can be utilized by the plants and a minimum portion remains in the environment. This can be attained by utilizing nanomaterials which encapsulate the material with a thin coating of protective film or supplied as emulsions or nanoparticles (deRosa et al. 2010). Nanomaterials have potential contribution in slow release of fertilizers. Nano-coatings or surface coatings of nanomaterials on fertilizer particles hold the material more strongly from the plant due to higher surface tension than conventional surfaces. The comparison of nanotechnology-based formulations and conventional fertilizer applications is given in Table 1 (Cui et al. 2010). Moreover, nano-coatings provide surface protection for larger particles (Brady and Weil 1999; Santoso et al. 1995). Nanofertilizers are synthesized or modified form of traditional fertilizers which can be produced from different biological materials using various nanotechnological approaches in order to improve soil fertility, productivity, and quality of agricultural produces (Brunnert et al. 2006). At nano-scale physical and chemical properties are different than the properties of bulk material (Nel et al. 2006). Particles size of nanofertilizers is less than 100 nm which facilitates more penetration of nanoparticles into the plant from applied surface such as soil or leaves for efficient nutrient management which are more eco-friendly and reduce environmental pollution (Lin and Xing 2007).

Table 1 Comparison of nanotechnology-based formulations and conventional fertilizers applications (Cui et al. 2010)

Properties	Nanofertilizers	Conventional fertilizers
Solubility and dispersion of mineral micronutrients	Improve solubility and dispersion of insoluble nutrients in soil, reduce soil absorption and fixation, and increase the bioavailability	Less bioavailability to plants due to large particle size and less solubility
Nutrient uptake efficiency	Might increase fertilizer efficiency and uptake ratio of the soil nutrients in crop production and save fertilizer resource	Bulk composite is not available for roots and decrease efficiency
Controlled-release modes	Release rate and release pattern of nutrients for water-soluble fertilizers might be precisely controlled through encapsulation in envelope forms	Excess release of fertilizers may produce toxicity and destroy ecological balance of soil
Effective duration of nutrient release	Nanofertilizers can extend effective duration of nutrient supply of fertilizers into soil	Used by the plants at the time of delivery, the rest is converted into insoluble salts in the soil
Loss rate of fertilizer nutrients	Reduce loss rate of fertilizer nutrients into soil by leaching and/or leaking	High loss rate by leaching, rain off and drift

3 Scope of Nanofertilizers in the Agriculture Industry

In order to prevent loss of fertilizer in the environment, minimize the dosage level, and enhance efficiency, the fertilizers can be encapsulated or coated with some particular nanomaterials. The procedure of coating or binding nano- and subnano-composites helps to balance the delivery of nutrients from the fertilizer capsule (Liu et al. 2001). This process of coating or binding nano-composites (nitrogen, phosphorous, potassium, micronutrients, mannose, and amino acid) results in the increase of uptake and utilization of nutrients by several grain crops (Guo 2011). In addition to this, Zn-Al coated double-hydroxide nano-composites have been utilized for the slow delivery of chemical compounds that functions as regulators of plant growth. Besides, *Gliricidia sepium* nano-composite encapsulated by urea modified hydroxyapatite nanoparticle exhibited a moderate and controlled delivery of nitrogen at three divergent pH values over time (Kottegoda et al. 2011). In the crop productivity system, nitrogen fertilizer coated with nanoporous zeolite base can be utilized as a secondary approach to boost nitrogen efficiency (Manikanadan and Subramanian 2014). Carbon nanotubes are remarkable fertilizers which were found to perforate into tomato seeds and enhance their rate of development and growth. Carbon nanotubes actually perforated thick coat of seeds to help uptake of water in seeds which was proven by several analytical methods (Khodakovskaya et al. 2009). The process of fertilizer encapsulation within a nanoparticle is achieved by encapsulating or coated with thin protective film on the nutrients or may be released as emulsions or particles of nanoporous material (Rai et al. 2012). In recent years, the utilization of controlled delivery of fertilizers begin to be one of the most significant and novel technology to retain use of fertilizer and to reduce environmental pollution (Guo et al. 2005). This technology involves the encapsulation or coating of fertilizers with nanoparticle in order to protect the nanoparticles in the soil for longer period of time and allow its controlled or slow delivery into the soil for better management (Saigusa 2000; Teodorescu et al. 2009). The application of nanofertilizers results in the slow and controlled delivery of elements in the soil and halts eutrophication and restrains water pollution. Nanoparticles like chitosan have been widely explored as a carrier for drug delivery system and also described as an effective carrier for the slow/controlled delivery of nitrogen, phosphorous, and potassium fertilizers in the soil. Chitosan is a bactericidal polymer which is biodegradable (Coma et al. 2002; No et al. 2007) and shows a beneficial interaction due to the presence of polymeric cationic attributes which might be linked with negatively charged polymers and molecules. These chitosan nanoparticles produced by polymerization reaction with methacrylic acid were employed to absorb on to nitrogen, phosphorous, and potassium fertilizers for increasing efficiency and slow release in the soil resulting in the overall progress in plant growth and productivity (Corradini et al. 2010). Nanofertilizer technology is very innovative and scanty reported literatures are available in the scientific journals. The data remain constant for the past several decade and research efforts did not yield fruitful results. The current growing awareness of the phenomenon and availability of inexpensive natural zeolites in the world have aroused considerable commercial interest on developing zeolite based nanofertilizer (Ramesh et al. 2010). Chuprova et al. (2004) found the beneficial effects of zeolite fertilizers on mobile humus substances of chernozem and on biological productivity of maize. In another study, a patented nano-composite consists of nitrogen, phosphorous, potassium, and micronutrients and mannose and amino acids have been shown to increase the uptake and utilization of nutrients by grain crops (Jinghua 2004). Bhattacharya et al. (2004) reported that the balanced application of nitrogen, phosphorous, and potassium along with sulfur, zinc, boron, and molybdenum will be an effective solution for higher grain yield of pulses in red and lateritic soils. Liu et al. (2006) have shown that the organic material (polystyrene) intercalated in the layers of kaolinite clay forms a cementing of nano- and subnano-composites which are capable of regulating the release of nutrients from the fertilizer capsule. Thus nanoparticles could be used in the membrane control release of nutrients. Subramanian et al. (2008) reported that nanofertilizers and nano-composites can be used to control the release of nutrients from the fertilizer granules so as to improve the nutrient use efficiency while preventing the nutrient ions from either getting fixed or lost to the environment. Recently, Sharmila (2011) has monitored the nutrient release pattern of nanofertilizer carrying nitrogen and the data have shown that nano-clay based fertilizer formulations (zeolite and montmorillonite with a dimension of 30–40 nm) are capable of releasing the nitrogen for a longer period of time (>1000 h) than conventional fertilizers (<500 h).

4 Nanofertilizer Products-Novel Boon to the Farmers

In recent years research is being conducted to develop novel nano-products that help the farmers to enhance their production yield (Liu and Lal 2015; Servin et al. 2015). Remarkably most of the nanomaterials apparently evaluated on crops as “nano-fertilizers” either for commercial purposes produced and marketed by the chemical companies. In addition to this, probability for using nanofertilizers for large scale agriculture system is still problematic. However, many countries are moving forward with the plan of using nanofertilizers in their agriculture system for better crop production. For example, Myanmar government is currently working on a project in order to include nanofertilizers in their national administration (Qureshi et al. 2018). Table 2 shows list of expected nanofertilizers products which are believed to be imported into the country. It was evident from this table that the companies which were in the list are not among the key global fertilizer industry enterprises such as PotashCorp, Mosaic, Uralkali, Belaruskali, Yara International, OCP, CF Industries, ICL, Agricum, K+S, Safcoor Koch. Therefore until and unless such smaller companies are subservient to the larger ones, it was doubtful to what magnitude the current level of their perceptibility and generation scale would affect global developments in nanofertilizers production system. As for as the volume of the product was concerned, the products which were listed are below than 1 kg and as for their existence as nanofertilizers except for the tag “Nano” in their

Table 2 Nanofertilizer products approved for use in Myanmar (Dimkpa and Bindraban 2018)

Company name	Fertilizer name	Specification	Country of origin
SMTET Eco-technologies Co., Ltd.	Nano Ultra-Fertilizer (500) g	Organic matter, 5.5%; T-N, 10%; T-P_2O_5, 9%; T-K_2O, 14%; AC-P_2O_5, 8%; CA-K_2O, 14%; CA-MgO, 3%	Taiwan
Shan Maw Myae Trading Co., Ltd	Nano Micro Nutrient (Eco Star) (500) g	Zn, 6%; B, 2%; Cu, 1%; Fe, 6%+; EDTA Mo, 0.05%; Mn, 5%+; AMINOS, 5%	India
Green Organic World Co., Ltd.	Plant Nutrition Powder (Green Nano) (25) g	N, 0.5%; P_2O_5, 0.7%; K_2O, 3.9%; Ca, 2.0%; Mg, 0.2%; S, 0.8%; Fe, 1.0%; Mn, 49 ppm; Cu, 17 ppm; Zn, 12 ppm	Thailand
WAI International Development Co., Ltd.	PPC Nano (120) mL	M protein, 19.6%; Na_2O, 0.3%; K_2O, 2.1%; $(NH_4)_2SO_4$, 1.7%; diluent, 76%	Malaysia
PAC International Network Co., Ltd	Nano Calcium (Magic Green) (1) kg	$CaCO_3$, 77.9%; $MgCO_3$, 7.4%; SiO_2, 7.47%; K, 0.2%; Na, 0.03%; P, 0.02%; Fe, 7.4 ppm; Al_2O_3, 6.3 ppm; Sr, 804 ppm; sulfate, 278 ppm; Ba, 174 ppm; Mn, 172 ppm; Zn, 10 ppm	Germany
The Best International Network Co., Ltd.	Supplementary Powder (The Best Nano) (25) g	N, 0.5%; P_2O_5, 0.7%; K_2O, 3.9%; Ca, 2.0%; Mg, 0.2%; S, 0.75%; Fe, 0.03%; Mn, 0.004%; Cu, 0.007%; Zn, 0.004%	Thailand
Shan Maw Myae Trading Co., Ltd	Nano Fertilizer (Eco Star) (5) gm	N, 8.2%; K_2O, 2.3%; organic matter, 75.9%; C:N, 5.4	India
World Connect Plus Myanmar Co., Ltd.	Hero Super Nano (25) gm	N, 0.7%; P_2O_5, 2.3%; K_2O, 8.9%; Ca, 0.5%; Mg, 0.2%; S, 0.4%; pH 12.08	Thailand
The Best International Network Co., Ltd.	Nano Capsule (The Best) (60) capsule)	N, 0.5%; P_2O_5, 0.7%; K_2O, 3.9%; Ca, 2.0%; Mg, 0.2%; S, 0.8%; Fe, 2.0%; Mn, 0.004%; Cu, 0.007%; Zn, 0.004%	Thailand

names, it seems that the nanofertilizer products are just preparations of multiple traditional nutrients and other additive such as ethylenediaminetetraacetic acid (EDTA-chelating agent). Neither there was complete information regarding what makes a product Nano (i.e., size) nor the type of material which forms the nano-product (i.e., whether it is composite or nano-enabled bulk fertilizers, surface modified, or pristine nanofertilizers). There are many factors that could influence the quality of nano-products produced that is why the government of Myanmar in the year 2016 was trying to find out support with individual characterization and authentication of the products, possibly indicating doubts by them related to geniuses of the products as nanofertilizers (Dimkpa and Bindraban 2016). In order to assess the nature of nanomaterials, a particular set of criteria for the quality check has to be developed and utilized for ratification of nanofertilizers, besides it also requires chemical quality assessment check for all types of fertilizers (concentration and purity). Some of the basic and important perquisite examinations particularly related to the authentication of nanofertilizers include (1) size (100 nm or less), aggregates, or bulk (size>100 nm), (2) strength (to assess their finality as nano-product or the rate of transformation before and after interconnection with crop or soil, (3) shape, which affects the rate of termination and feasibly bioactivity (Misra et al. 2014; Prasad 2017), and (4) composition which determines the chemical nature of nano-products (surface modified or hybrid). Except for the volume/concentration ratio, the above-mentioned criteria require a number of analytical examinations with nanoscale responsiveness that do not generally applied to bulk materials.

5 Economic Aspect of Nanofertilizers

To invest in nanofertilizers production there are various factors such as efficiency of nanofertilizers, cost of production, awareness among farmer community, accessibility and affordability, and other related issues that should be taken into consideration in establishing the industry for mass production of nano-formulations (Pirzadah et al. 2019). Some of these issues related to economic potential of nanofertilizers have been highlighted by many nanotechnologists in order to enhance nanofertilizers and these are reported in both non-professional and professional news releases such as the Economist (2017) and the American Chemical Society's Chemical and Engineering News (2017). Nevertheless, despite the potential of nanofertilizers, one of the most important parameters which was still largely absent was the study of cost-effective technology and the resulting benefits. From the industry viewpoint, economic study of nanofertilizers industry was required that can differentiate which method for the synthesis of nanomaterial is cost-effective and sustainable with exorbitant turnover production rate. Besides, it was not clear at this point how the production cost of nanofertilizers in general differentiates the production cost of traditional fertilizer and whether at what intensity nanofertilizers would interrupt production system of conventional fertilizers and the cost related with such interruptions. So far, to attain grip on nanofertilizers for application in huge fields and worldwide acceptance, mass production of nanofertilizers is the need of hour besides its awareness among the farmers. Effectively all of the principal investigations describe agricultural benefits of nanofertilizers without enough information of the productive utilization of their application. Adhikari et al. (2014) reported that crop utilization of P from nano rock phosphate (RP) was at par with that of P from single superphosphate (SSP), while yield response to P from nano RP was marginally lower than to P from SSP but serve as a cheaper source. In addition to this, no definite confirmation of any residual outcome on consecutive crops was done to confirm the cost-effectiveness of the process. Delfani et al. (2014) similarly set the generating cost of 1 kg of nano-Fe at US$800; however, the application of nano-Fe at 0.25 and 0.5 g/kg enhanced yield of cowpea by 63% and 82%, respectively, compared to traditional Fe. Poorly the authors did not furnished any information on the similar cost production of the traditional Fe on the basis of which they have done a comparative cost-benefit analysis. In a study carried out by Dimkpa and Bindraban (2016) described an increase in yield by 24% and 52%, respectively, when egg plants are treated with nano-CuO fertilizer compared to traditional fertilizers, it was also important to note that a bottle of 25 g of the traditional CuO costs US$18.50 and the nano-CuO costs US$44. This difference in yield interpreted a profit of $4637 per acre from the CuO nanofertilizers application with an expense of $26 and it has been concluded from the above stated observations that the produced nanofertilizers yield better results than the traditional fertilizers. Therefore, to commercialize the nano-products economic analysis of nano-products is of paramount importance to boost the nano-agroindustry.

6 Conclusion and Future Recommendations

The above-mentioned statements revealed that the nanomaterials are not more toxic than their ionic or micro-scale counterparts and that they can improve crops when utilized sensibly. Hence completely utilizing the benefits of nanomaterials needed more attention to attract the industry that brings nanotechnology into the fertilizer management. In this regard, researchers of nanofertilizers require for accessing the needs what the fertilizer industry requires and how their present research viewpoint fulfilled those requirements. In carrying out such approaches, nanofertilizers should be treated as fertilizers; however, all assessments of their consequences on crops are performed in the same way to common fertilizers; there was also need to aware the farmers about the ratio of application of fertilizers associated with crops and soil; conclusion of results should be firm on investigations conducted in the growth pattern most suitable for the crops being investigated; introduction of conventional crops (relevant controls) in the experimental protocol; utilizing and investigating suitable strategies of nanofertilizers application; and experimenting mature crops. In addition to this, nanofertilizers evaluations should be done by utilizing combination of nanomaterials to imitate traditional fertilizer application managements commonly require applications of several nutrients (e.g., NPK) concomitantly. This was true for the concept of balanced nourishment for crops, which was applicable for the world's agricultural regions with impoverished soils, where crops did not respond to one nutrient use and where multiple nutrient inadequacy are ubiquitous. Principally Research and Development (R&D) on nanofertilizers should work more on macronutrient (NPK) which were the key nutrients for the nanofertilizers industry (Dimkpa and Bindraban 2018). In the meantime, scientist should not only generate representative of productive nanofertilizers but also expand plan and ideas that eventually help in the scale up process that could be sold to the industry. It has been realized from the past that there was a need to improve the application efficiency of current macronutrient fertilizers, efforts of R&D lead to the development of products with unique properties such as control release and targeted release of fertilizers and have scaled up all of these properties. With the advancements so far made to nanomaterials to produce modified nanofertilizer, it encompasses those which were already discussed in the previous sections including modification of surfaces with alginate and chitosan (Zhao et al. 2013; Saharan et al. 2016). The possibility of utilizing of other bio-based and non-biased materials like aminopropyltriethoxysilane, lignin, and clay was also noted in nanofertilizer model (Mukherjee et al. 2016; Pereira et al. 2015). Besides, the significant potential for producing nanofertilizer macronutrient like Nhap, nano-N, or urea-Nhap imparts a powerful statement for generating nanofertilizers (nano-enabled macronutrients) that should be proved to be attractive for the industry.

Several studies have demonstrated various nanotechnologies for producing nanofertilizer and one of the recent studies was carried out by Monreal et al. (2016) which described bio-nano-enabled technologies in progress that would enhance the nutrient use capacity on the basis of real-time molecular identification between root exudates and nano encapsulated nutrients. In addition, the production of NPK fertilizers treated with nanomaterial Zn, Cu, Fe, B, or other micronutrient might be visualized not only for enhancing the efficiency use of some macronutrients in the preparations but also to accelerate the essential micronutrient uptake into the plant, maintaining the nutritional quality of vegetables or grains for human consumption. Possibly nanomaterial (micronutrient-enabled) NPK can be developed in-line by utilizing aerosol or spray-coating colloidal technologies; however the bulk NPK fertilizer was either mixed with nanofertilizers or sprayed by aerosol and their surface were coated just before the end product evacuated from the development line, such an in-line methods taking place in downstream part of development that would be a supplementary technology that might not create any kind of disturbance in the upstream process of fertilizer development. This concept of fertilizer development was represented schematically in Fig. 3. The NPK nano-enabled micronutrient is ready to use and all in one product that might be more costly than its traditional components, but less costly than the different applications of micronutrients and NPK. Regardless, the increase in yield, quality enhancement of the production, and improvement of plant health calculated from the upgraded version must balance the extra input cost for the farmers. Besides, environmental risks are associated with the utilization of any agrochemicals whether traditional or nano. Remarkably nanotechnology nowadays established a similar insight as biotechnology in accordance with social unwillingness to believe the technology irrespective of risk sensitivity. A study carried out by Kah (2015) described the fact that how participants of agrochemical industry entirely separate themselves from the word “Nano” possibly describing clearly why not nano-agrochemicals have been raised so far from huge participants.

Besides, genuine evidences about positive criticism and concern and distinguish between nutrient nanomaterials and other nanoscale materials would help to manage nanofertilizer acceptance and development. In this context, nanotechnologist should proceed continuously to describe and distribute the nanofertilizer benefits in crops based on the sensible utilization and suitable growth matrices, differentiating existing fertilizers and sustainable utilization strategies.

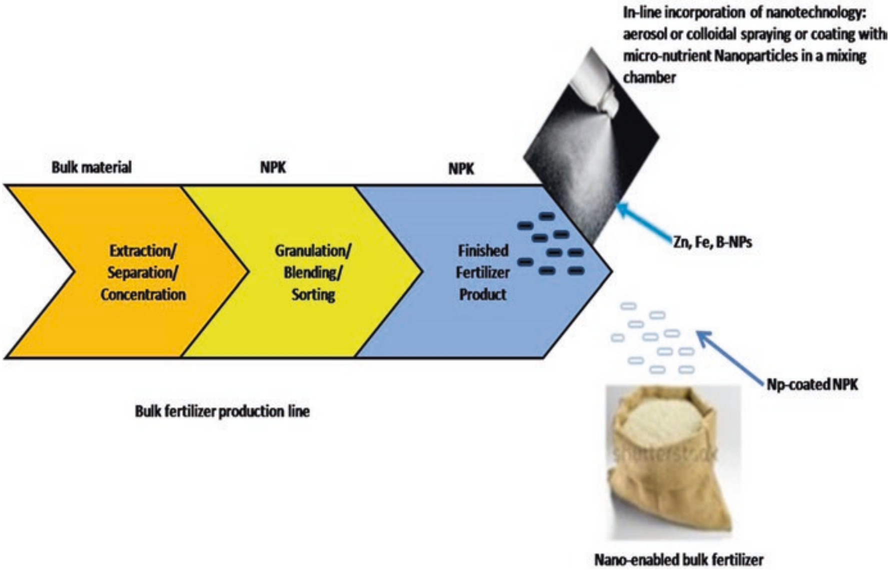

Fig. 3 Simplified illustration of the production of nano-enabled bulk fertilizer (in this case NPK). Production of NPK fertilizer occurs upstream and the finished fertilizers functionalized with separately produced nanoparticles (NPs) of micronutrient (e.g., Zn, B, Fe) by spraying or mixing the NPK with nanoparticles in-line, downstream

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Embodiment of Nanobiotechnology in Agriculture: An Overview

Tareq A. Wani, Gulzar A. Rather, Mudasar Ahmad, and Zahoor A. Kaloo

1 Introduction

Nanotechnology being an emerging field has gained a marvelous role in agriculture sector and has brought radical changes in agricultural production. The development of new and novel nanotech-based equipment may help to augment efficiency and overcome challenges faced by the modern agricultural industry. A*griculture practice makes widespread use of industrially generated chemicals to rouse growth and inhibit pests, insects, and disease* (Yunlong and Smit 1994). Recently, nanotechnology has proved to have the potential to improve the agri-food sector, minimizing adverse human health problems, agricultural practices on environment and improving food productivity and security required by the predicted rise in global population, while promoting social and economic equity. In this backdrop, we select and report on recent trends in nano-material based systems and nano-devices that could benefit the food supply chain specifically on sustainable intensification and management of soil and wastes. Agriculture is always highly important and most stable sector to boost nation's economy as it provides raw materials for feed and food industries and companies. Limited natural resources such as water, land, soil, etc., and the growing population in the world has forced scientific community to develop green approaches for the sustainable agriculture development (Mukhopadhyay 2014). Agricultural nutrient balance is differed perceptibly with economic growth, and especially from this surmise, the development of the soil fertility is very much significant in developing countries (Campbell et al. 2014). The growth of agriculture is necessary for the eradication of poverty and hunger in order to get a hold on

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T. A. Wani (✉) · M. Ahmad · Z. A. Kaloo
Department of Botany, University of Kashmir, Srinagar, India

G. A. Rather
Plant Biotechnology Division, CSIR-Indian Institute of Integrative Medicine, Jammu, India

K. R. Hakeem, T. B. Pirzadah (eds.), *Nanobiotechnology in Agriculture*,
Nanotechnology in the Life Sciences, https://doi.org/10.1007/978-3-030-39978-8_6

the present situation. Therefore, we should have to take one bold step for agriculture development. In present world, most of the population lies under below poverty levels, scattered across the rural areas where agriculture enlargement has not been so effective. Therefore, new technology should have to be adopted that decidedly focuses on getting better agricultural production (Yunlong and Smit 1994). The agriculture development also depends on the social inclusion, health, climate changes, energy, ecosystem processes, natural resources, good supremacy, etc., which must be documented in specific target oriented goals (Thornhill et al. 2016). No doubt that the sustainable growth of agriculture totally depends on the new and innovative techniques like nanotechnology. If we like to go in the year 1959 Feynman's lecture on "Plenty of room at the bottom," from this very day, the nano-process is in underway (Feynman 1996). Later on Professor Norio Tanaguchi proposed the actual term of nanotechnology (Bulovic et al. 2004; Gibney 2015). Subsequently, nanotechnology developed in more dramatic ways, as more recent appliances develop to isolate nanomaterials in more precise ways. Additionally, the number of publications related to the term of "nano" was also grown exponentially. About 14,000 documents with word nanotechnology in food or agriculture were listed until 2016 pointing towards the importance gained by this field. Also about 2707 patents matched this criteria are found in world patent database. The world market size of nanotechnology in 2002 was about US$ 110.6 billion and predicted to grow to US$ 891.1 billion in 2015 according to analysis of Helmut Kaiser Consultancy. In the present century, there is a big demand for fast, reliable, and low-cost systems for the detection, monitoring, and diagnosis for biological host molecules in agricultural sectors (Vidotti et al. 2011; Sagadevan and Periasamy 2014). The application of chemically synthesized nanomaterials nowadays is considered as toxic in the nature; however, biosynthesis of nanomaterials using microbial or phyto-engineering approach is safe and is considered as green nanotechnology (Prasad et al. 2014). Green nanotechnology is a safe process, energy efficient, reduces waste and reduces greenhouse gas emissions. Use of renewable materials in production of such products is beneficial, thus these processes have low influence on the environment (Prasad et al. 2014, 2016). Since the last decade, there is a paradigm shift toward the green synthesis of nano-particles and its implementation in agro-industry. Still it is not clear how the environmental sustainability of green nanotechnology will be achieved in future? These risks must be mitigated in advanced green nanotechnology solutions (Kandasamy and Prema 2015).

The development of the high-tech agricultural system with use of engineered smart nano-tools could be excellent strategy to make a revolution in agricultural practices, and thus reduce and/or eliminate the influence of modern agriculture on the environment as well as to enhance both the quality and quantity of yields (Sekhon 2014; Liu and Lal 2015). Further the development of biosensors in the smart agro-food sector is also a good field for exploitation of many strengths of nanotechnology (Sertova 2015; Fraceto et al. 2016). Additionally, use of nanomaterials let to miniaturize many biosensors to small and compact/smart devices such as nanosensors and other nano-systems that are very important in biochemical analysis (Viswanathan and Radecki 2008; Sertova 2015; Fraceto et al. 2016). Keeping in

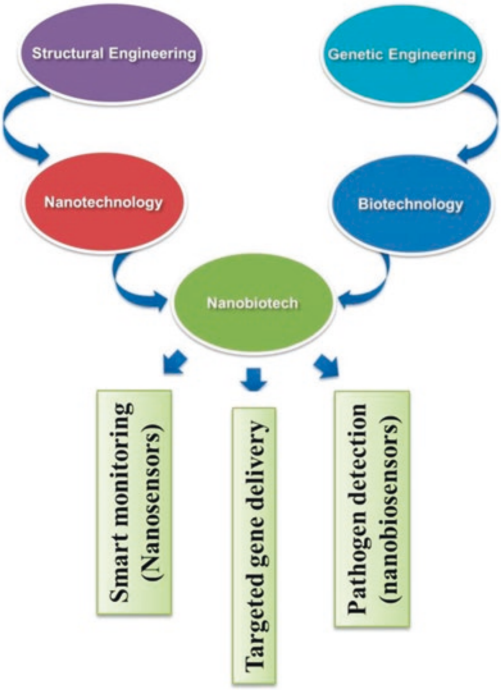

Fig. 1 Flowchart involving the convergence of nanotechnology and biotechnology results in nanobiotechnology, which entails knowledge of structural and genetic engineering

view of the above facts, here we summarize encapsulation of nanoparticles and how nanotechnology boosts the agriculture sector besides its negative impact on the environment (Fig. 1).

2 Micro- and Nano-encapsulation

Encapsulation is defined as the process in which the given object is surrounded by a coating or embedded in homogeneous or heterogeneous matrix, thus this process results in capsules with many useful properties (Rodríguez et al. 2016). The benefits of encapsulation methods are for protection of substances/objects from adverse environments, for controlled release, and for precision targeting (Ezhilarasi et al. 2012; Ozdemir and Kemerli 2016). Depending on size and shape of capsules different encapsulation technologies are mentioned, while the (macro) encapsulation/coating results in capsules in macro-scale, whereas the micro- and nano-encapsulation will give particles in micro- and nano-scale size (Ozdemir and Kemerli 2016). Nano-capsules are vesicular systems in which the substances are confined to a cavity consisting of an inner liquid core enclosed by a polymeric membrane (Couvreur et al. 1995). Recently, NPs are getting significant attention for delivery of drugs, for protection and increase in bioavailability of food components or nutraceuticals, for food fortification, and for the self-healing of several materials, and also it possesses big prospective phenomenon in plant science (Ozdemir and Kemerli 2016). Furthermore, the development of this technology will build more possibility to create new drugs with precise therapeutic action on embattled tissues. Nano-capsules can potentially be used as MRI-guided nanorobots or nanobots (Vartholomeos et al. 2011). Recently, a wide range of potential applications of nanotechnology have been envisaged also in agriculture, leading to intense research at both academic and industrial levels (Parisi et al. 2015). Indeed, the unique properties of materials at nano-scale make them suitable candidates for the design and development of novel tools in support of a sustainable agriculture. Some of the main applications of these nano-tools in agriculture are reported in the following paragraphs.

3 Precision Farming

The process of maximizing crop yields and minimizing the usage of pesticides, fertilizers, and herbicides through efficient monitoring procedures is referred to as precision farming. Precision farming utilizes remote sensing devices, computers, and global satellite positioning systems to analyze various environmental conditions in order to determine the growth of plants under these conditions and identify problems related to crops and their growing environments. Precision farming helps determine plant development, soil conditions, usage of water and chemicals, fertilizers and seeding and controls environmental pollution to a minimum extent by reducing agricultural waste (Prasad et al. 2017; Pirzadah et al. 2019). The implementation of nanotechnology in the form of small sensors and monitoring devices will create a positive impact on the future use of precision farming methodologies. Nanotech-enabled systems help in increasing the use of autonomous sensors that are linked into GPS systems to provide efficient monitoring services focused on crop growth and soil conditions. The usage of smart sensors in precision farming will result in increased agricultural productivity by providing farmers with accurate information that will enable them to make accurate decisions related to plant growth and soil suitability.

4 Nano Delivery Systems

There are many regulatory restrictions placed on pesticides in agriculture today. Pesticides such as DDT, which have caused extreme environmental hazards, have increased public and regulatory awareness of the use of chemicals in farming, shifting the industry's focus on to the use of integrated pest management systems, combining smarter and more targeted use of chemicals with granular monitoring of plant health. These agricultural systems can make excellent use of nanotech-enabled "smart" devices that can perform a dual role of being a preventive and early warning system (Singh et al. 2017). These devices can identify plant-related health issues even before they become visible to the farmers and simultaneously provide remedial measures. User-friendly and eco-friendly nano delivery systems for nutrients and pesticides have started to find their place in the market. These can allow the use of pesticides with the absolute minimum risk of environmental damage. Companies have implemented nano-emulsions in commercial pesticide products. Syngenta, a leading agrochemical corporation, produces a quick-release microencapsulated product, which is available under the name Karate® ZEON (Misra et al. 2016).

5 Systems for Sustainable Intensification in Agriculture

Sustainable intensification is a concept related to a production system aiming to increase the yield without adverse environmental impact while cultivating the same agricultural area (The Royal Society 2009). This paradigm provides a framework to evaluate the selection of the best combination of approaches to agricultural production considering the influence of the current biophysical, social, cultural, and economic situation (Garnett and Godfray 2012). In this context, novel nanomaterials based on the use of inorganic, polymeric, and lipid nanoparticles synthesized by exploiting different techniques (e.g., emulsification, ionic gelation, polymerization, oxidoreduction, etc.) have been developed to increase productivity. They can find application, as an example, for the development of intelligent nano-systems for the immobilization of nutrients and their release in soil. Such systems have the advantage to minimize leaching, while improving the uptake of nutrients by plants, and to mitigate eutrophication by reducing the transfer of nitrogen to groundwater (Liu and Lal 2015). Furthermore, it is noteworthy to mention that nanomaterials could also be exploited to improve structure and function of pesticides by increasing solubility, enhancing resistance against hydrolysis and photodecomposition, and/or by providing a more specific- and controlled-release toward target organisms (Mishra and Singh 2015; Grillo et al. 2016; Nuruzzaman et al. 2016).

6 Soil Quality Improvement Through Nanotechnology

Hydrogels, nanoclays, and nanozeolites have been reported to enhance the water-holding capacity of soil (Sekhon 2014), hence acting as a slow-release source of water, reducing the hydric shortage periods during crop season. Applications of such systems are favorable for both agricultural purposes and reforestation of degraded areas. For example; organic polymer and carbon nanotubes and inorganics like nano-metals and metal oxides nanomaterials have also been used to absorb environmental contaminants (Khin et al. 2012), increasing soil remediation capacity and reducing times and costs of the treatments.

7 Nanomaterials as Agents to Stimulate Plant Growth

Carbon nanotubes and nanoparticles of Au, SiO_2, ZnO, and TiO_2 can contribute to ameliorate development of plants by enhancing elemental uptake and use of nutrients (Khota et al. 2012). However, the real impact of nanomaterials on plants depends on their composition, concentration, size, surface charge, and physiochemical properties, besides the susceptibility of the plant species (Lambreva et al. 2015). The development of new protocols and the use of different analytical techniques (such as microscopy, magnetic resonance imaging, and fluorescence spectroscopy) could considerably contribute to understand the interactions between plants and nanomaterials.

8 Management of the Food Supply Chain Using Nano-tech Approach

Nanotechnology can find applications also in the development of analytical devices dedicated to the control of quality, bio/security, and safety not only in agriculture, but also along the food supply chain (Valdes et al. 2009). In this context, nanosensors represent a powerful tool with advanced and improved features, compared to existing analytical sensors and biosensors. Nanosensors are defined as analytical devices having at least one sensing dimension no greater than 100 nm, fabricated for monitoring physico-chemical properties in places otherwise difficult to reach. They have unique surface chemistry, distinct thermal, electrical, and optical properties, useful to enhance sensitivities, reduce response times, and improve detection limits, and can be used in multiplexed systems (Yao et al. 2014). Considering the huge amount of research in this area, real applications of nanosensors for field analysis are unexpectedly scarce, implying the potential for a new market. In this perspective, nanotechnologies could enhance biosensor performance to allow real applications in agri-food industry. Indeed, thanks to important progresses in nanofabrication, laboratory analytical techniques, such as surface plasmon resonance, mass spectrometry, chromatography, or electrophoresis chips, can support the development of viable sensor components. However, the real need of the market is the realization of automated embedded systems which integrate bio-sensing components with micro/nanofluidics, data management hardware, and remote control by wireless networks. This is a key issue for nanotechnology, which can provide the decisive approaches as well as novel nanomaterials for the realization of bio-sensing devices (Scognamiglio 2013). Indeed, as described by Mousavi and Rezaei (2011) “Nanosensors help farmers in maintaining farm with precise control and report timely needs of plants.” Thus, it will be mandatory to address research efforts to the development of nanosensors to aid decision-making in crop monitoring, accurate analysis of nutrients and pesticides in soil, or for maximizing the efficiency of water use for a smart agriculture. In this context, nanosensors could demonstrate their potential in managing all the phases of the food supply chain, from crop cultivation and harvesting to food processing, transportation, packaging, and distribution (Scognamiglio et al. 2014). Among them, nanosensors for dynamic measurement of soil parameters (pH and nutrients, residual pesticides in crop and soil, and soil humidity), detection of pathogens, and prediction of nitrogen uptake are only few examples to foster a sustainable farming (Bellingham 2011). Controlled-release mechanisms via nano-scale carriers monitored by nanosensors integrated in platforms employing wireless signals will avoid overdose of agricultural chemicals and minimize inputs of fertilizers and pesticides during the course of cultivations, improving productivity and reducing waste. Networks of nanosensors located throughout cultivated fields will assure a real time and comprehensive monitoring of the crop growth, furnishing effective high-quality data for best management practices (El Beyrouthya and El Azzi 2014).

Nanotechnologists are hoping that this technology will transform the entire food industry by bringing about changes in the production, processing, packaging, transportation, and consumption of food. Usage of nanotechnology in these processes ensures safety of food products, thus creates a healthy food culture and enhances the nutritional quality of foods. Smart food packaging systems can be developed using nanotechnology that in turn increases the shelf life of food products by developing active antifungal and antimicrobial surfaces, improving heat-resistance and mechanical properties, modifying the permeation behavior of foils, and detecting and signaling biochemical and microbiological changes. A number of companies have started to develop Smart Packaging systems—one such company is Bayer Polymers, who developed the Durethan KU2-2601 packaging film whose key purpose is to prevent drying of food content and protect the food content from oxygen and moisture. This packaging film is made from a number of silicate nanoparticles. Nanocapsules are added into food products in order to deliver nutrients, and nanoparticles when added to food increase the absorption of nutrients. An increasing number of companies are researching on additives that can be easily absorbed by the body and increase product shelf life. Bio-delivery Sciences International developed coiled nanoparticles called nano-cochleates that deliver nutrients and omega fatty acids to cells without causing any changes to the taste and color of food (Ravichandran 2010). The automation of irrigation systems is also a crucial requirement of smart agriculture, mainly in a scenario of water shortage. In this regard, sensor technology has the potential to maximize the efficiency of water use. Nanosensors estimating soil water tension in real time may be coupled with autonomous irrigation controllers. This feature allows a sustainable irrigation management based on drying soil, otherwise an approach too difficult for farmers because it involves evaluation of climate and crop growth aspects of high complexity (de Medeiros et al. 2001). Furthermore, nanosensors find also application in fast, sensitive, and cost-effective detection of different targets to ensure food quality, safety, freshness, authenticity, and traceability along the entire food supply chain. Surely, nanosensors represent one of the emerging technologies challenging the assessment of food quality and safety, being able to provide smart monitoring of food components (e.g., sugars, amino acid, alcohol, vitamins, and minerals) and contaminants (e.g., pesticides, heavy metals, toxins, and food additives). Food quality and food safety control represents a crucial effort not only to obtain a healthy food, but also to avoid huge waste of food products. The potential of nanosensor can also be demonstrated by the last trends on intelligent or smart packaging to monitor the freshness properties of food and check the integrity of the packages during transport, storage, and display in markets (Vanderroost et al. 2014). Many intelligent packaging involve nanosensors as monitoring systems to measure physical parameters (humidity, pH, temperature, light exposure), to reveal gas mixtures (e.g., oxygen and carbon dioxide), to detect pathogens and toxins, or to control freshness (e.g., ethanol, lactic acid, acetic acid) and decomposition (e.g., putrescine, cadaverine).

9 Nanotechnology and Agricultural Sustainable Development

The nanotechnology plays an important role in the productivity through control of nutrients (Mukhopadhyay 2014) as well as it can also participate in the monitoring of water quality and pesticides for sustainable development of agriculture (Prasad et al. 2014). Properties of NPs that include chemical composition, shape, surface structure, surface charge, behavior, extent of particle aggregation (clumping) or disaggregation, etc. have the influence on toxicity (Ion et al. 2010). For this reason even nanomaterials of the same chemical composition that have different sizes or shapes can exhibit their different toxicity. The implication of the nanotechnology research in the agricultural sector is becoming a necessary key factor for the sustainable developments as it leads to the production of nanofertilizers and nano-pesticides that helps to enhance production yield (Tables 1 and 2). In the agri-food areas pertinent applications of nanotubes, fullerenes, biosensors, controlled delivery systems, nano-filtration, etc. were observed (Ion et al. 2010; Sabir et al. 2014). This technology was proved to be as good in resources management of agricultural field, drug delivery mechanisms in plants, and helps to maintain the soil fertility. Moreover, it is being also evaluated steadily in the use of biomass and agricultural waste as well as in food processing and packaging system as well as risk assessment (Floros et al. 2010). Recently, nanosensors are widely applied in the precision agriculture for environmental monitoring of contamination in the soils and in the water (Ion et al. 2010). Nanomaterials not only directly catalyze degradation of waste and toxic materials but it also aids to improve the efficiency of microorganisms in degradation of waste and toxic materials. It is an interesting phenomena in considering the nano–nano interaction to remove the toxic component of the agricultural soil and make it sustainable (Ion et al. 2010; Dixit et al. 2015). The recent development of a nano-encapsulated pesticide formulation has slow-releasing properties with enhanced solubility, specificity, permeability, and stability (Bhattacharyya et al. 2016). These assets are mainly achieved through either protecting the encapsulated active ingredients from premature degradation or increasing their pest control efficacy for a longer period. Formulation of nano-encapsulated pesticides led to reduce

Table 1 List of some commercially available nanofertilizers

Commercial product	Content	Company
Nano-Gro™	Plant growth regulator and immunity enhancer	Agro Nanotechnology Corp., FL, United States
Nano Green	Extracts of corn, grain, soybeans, potatoes, coconut, and palm	Agro Nanotechnology Corp., FL, United States
Nano-Ag Answer®	Microorganism, sea kelp, and mineral electrolyte	Urth Agriculture, CA, United States
Biozar Nano-Fertilizer	Combination of organic materials, micronutrients, and macromolecules	Fanavar Nano-Pazhoohesh Markazi Company, Iran
Nano Max NPK Fertilizer	Multiple organic acids chelated with major nutrients, amino acids, organic carbon, organic micro nutrients/trace elements, vitamins, and probiotic	JU Agri Sciences Pvt. Ltd., Janakpuri, New Delhi, India
Master Nano Chitosan Organic Fertilizer	Water-soluble liquid chitosan, organic acid and salicylic acids, phenolic compounds	Pannaraj Intertrade, Thailand
TAG NANO (NPK, PhoS, Zinc, Cal, etc.) fertilizers	Proteino-lacto-gluconate chelated with micronutrients, vitamins, probiotics, seaweed extracts, humic acid	Tropical Agrosystem India (P) Ltd., India

the dosage of pesticides and human beings exposure to them which is environment-friendly for crop protection (Nuruzzaman et al. 2016), thus developing non-toxic and promising pesticide delivery systems for increasing global food production while reducing the negative environmental impacts to ecosystem (Bhattacharyya et al. 2016; Grillo et al. 2016).

10 Identification of Gaps and Obstacles

Despite considerable advances in identifying possible applications of nanotechnology in agriculture, many issues remain to be resolved in the near future before this technology may make significant contributions to the area of agriculture. Some of the main aspects that require further attention are: (1) development of specific hybrid carriers for delivering active agents including nutrients, pesticides, and fertilizers in order to maximize their efficiency following the principles of green chemistry and environmental sustainability (De Oliveira et al. 2014); (2) design of processes easily up-scalable at industrial level; (3) comparison of effects of nano-formulations/nano-systems with existing commercial products in order to demonstrate real practical advantages; (4) acquisition of knowledge and developments of methods for risk and life-cycle assessment of nanomaterials, nano-pesticides, nanofertilizers, as well as assessment of the impacts (e.g., phytotoxic effects) on non-target organisms such as plants, soil microbiota, and bees; (5) advances in the regulations about the use of nanomaterials (Amenta et al. 2015). In this context, the

Table 2 List of commercially available nano-pesticides/nanoherbicides

Carrier system	Agent	Purpose	Method
Chitosan	Imazapic and Imazapyr	Cytotoxicity assays	Encapsulation
Silica	Piracetam, pentoxifylline, and pyridoxine	Perfused brain tissue	Suspension
Alginate	Imidacloprid	Cytotoxicity, sucking pest (leafhoppers)	Emulsion
Polyacetic acid-polyethylene glycol-polyacetic acid	Imidacloprid	Decrease the lethal concentration	Encapsulation
Carboxymethyl chitosan	Methomyl	Control release for longer time period	Encapsulation
Chitosan/tripolyphosphate	Paraquat	Lower cyto- and genotoxicity	Encapsulation
Chitosan/tripolyphosphate chitosan-saponin chitosan-Cu	Chitosan, saponin, $CuSO_4$	Antifungal activity	Cross-linking
Xyloglucan/poloxamer	Tropicamide	Have significantly higher corneal permeation across excised goat cornea, less toxic, and non-irritant	Encapsulation
Wheat gluten	Ethofumesate	Reduce its diffusivity	Entrapment/extrusion
Alginate	Azadirachtin	Slower release	Encapsulation
Surfactants/oil/water	Glyphosate	Increase in bio-efficacy, alleviating the negative effect of pesticide formulations into environment	Emulsion
Alginate/chitosan	Paraquat	Increased period of action of the chemical on precise targets while reducing problems of ecological toxicity	Pre-gelation of alginate then complexation between alginate and chitosan
Polyhydroxybutyrate-co-hydroxyvalerate	Atrazine	Decreased genotoxicity and increased biodegradability	Encapsulation
Organic-inorganic nano-hybrid	2,4-Dichlorophenoxyacetate	Control release	Self-assembly

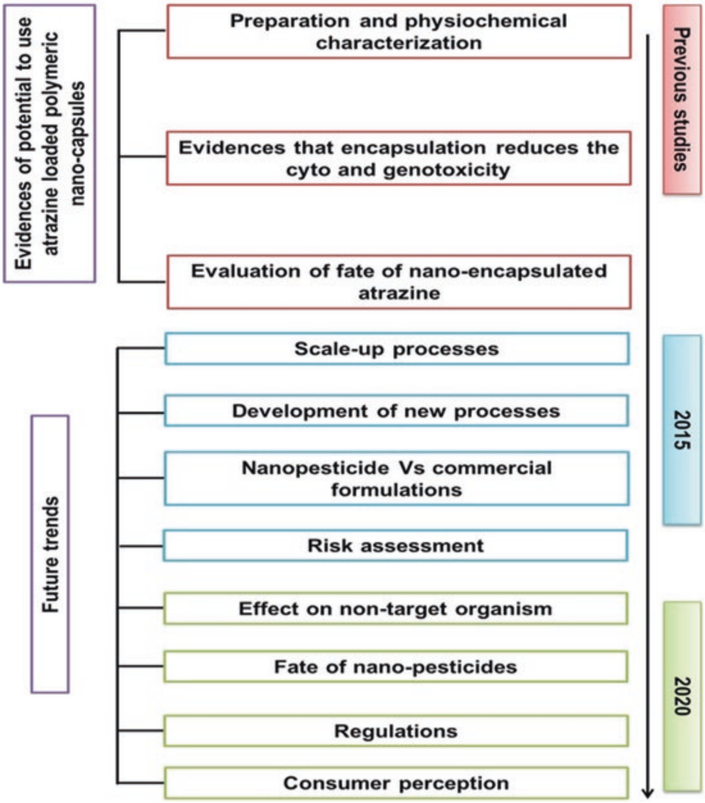

Fig. 2 Timescale for development of atrazine nano-pesticide

progress made in the exploitation of nano-pesticides (such as atrazine) represents a useful case study to identify the main parameters necessary to predict the behavior of nanomaterials in the environment (Grillo et al. 2012) (Fig. 2). In the study of the atrazine-nano-pesticide system, care was taken to understand the mechanisms of interaction with both target, mustard (Oliveira et al. 2015a), and non-target organisms, maize (Oliveira et al. 2015b), and risk assessment analyses were also considered (Kah et al. 2014). However, future case studies are necessary in order to address the safety of workers and consumers with respect to food produced using nanomaterials and nanoparticles. The implementation of nanotechnology in agriculture also requires the development of techniques capable of quantifying engineered nanoparticles at the concentrations present in different environmental compartments (Sadik et al. 2014). Currently available methods are not always adequate to understand the dynamics of nanomaterials in the environment, their interactions with target and non-target organisms, or the occurrence of synergistic effects. These methodological advances allow a life-cycle assessment of the new developed nanomaterials (Parisi et al. 2015). Moreover, studies on methodologies able to evaluate the arise of resistance mechanisms to nanomaterials by certain microorganisms should be undertaken. As a whole, the newly developed analytical methodologies would support predictive models to characterize, localize, and quantify engineered nanomaterials in the environments. In this context, knowledge exchange among scientists from different research fields would be essential (Malysheva et al. 2015). Besides, eco-toxicological research would increasingly focus attention on the environmental consequence of the materials and complexity of natural systems. Extensive research would be necessary to determine delayed impacts of environmental exposure to NPs and to help determine possible adaptive mechanisms (Cox et al. 2017; Singh et al. 2017). More research on bioaccumulation in the food chain and interaction of NPs with other pollutants in the environment should be focused. NPs in plants enter in cellular system; thereby they get translocated through the shoot and are accumulated in various aerial parts of the plant. Also, the possibility of their cycling in the ecosystem increases through various trophic levels. The accumulation of NPs in plants is problematic as it affects various physiological activities of the plant like rate of transpiration, respiration, altering the process of photosynthesis, and interferes with translocation of food materials (Du et al. 2017). The degree of toxicity is linked to this surface and to the surface properties of the NPs. The eco-toxicity of NPs is thus very important as it creates a direct link between the adverse effects of NPs and the organisms including microorganisms, plants, and other organisms including humans at various trophic levels (Tripathi et al. 2016).

11 Recent Developments in Agro-nanotechnology

With nanotechnology gaining recognition in the agricultural and food sectors, scientists have recently showcased their nanotechnology expertise to farmers in Africa. Three significant innovations were demonstrated: the scientists have planned to develop a plastic storage bag lined with nanoparticles that are capable of reacting with oxygen and preventing cassava from rotting. In this way, the African farmers can prolong the shelf life of cassava and prevent wastage of this vegetable. Secondly, milk container was designed with a nano-patterned, antimicrobial coating that helps the dairy farmers in Africa to preserve milk for a prolonged time period as they take almost a whole day to reach the cooling centers. These nanotechnology-based milk containers replace the currently used plain plastic bags. Besides, they have also planned to develop nano-patterned paper sensors to detect bovine pregnancy in order to enable the dairy farmers determine if their cows will run dry without milk due to udder infection or pregnancy (Fraceto et al. 2016; Prasad et al. 2017).

12 Conclusions and Future Perspective

Considering the great challenges we will be facing, in particular due to a growing global population and climate change, the application of nanotechnologies as well as the introduction of nanomaterials in agriculture potentially can greatly contribute to address the issue of sustainability. In fact, the efficient use of fertilizers and pesticides can be enhanced by the use of nano-scale carriers and compounds, reducing the amount to be applied without impairing productivity. Nanotechnologies can also have an impact on the reduction of waste, both contributing to a more efficient production as well as to the reuse of waste, while nanosensors technology can encourage the diffusion of precision agriculture, for an efficient management of resources, including energy (FAO and WHO 2013). However, with the application of all new technologies, there is the need to perform a reliable risk-benefit assessment, as well as a full cost accounting evaluation. In the case of nanotechnologies, this requires also the development of reliable methods for the characterization and quantification of nanomaterials in different matrices and for the evaluation of their impact on the environment (Servin and White 2016) as well as on human health (EFSA Scientific Committee 2011). Furthermore, it is very important to engage all stakeholders, including non-governmental and consumer associations, in an open dialogue to acquire consumer acceptance and public support for this technology.

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Nano-Biosensors: NextGen Diagnostic Tools in Agriculture

Fayaz Ahmad Dar, Gazala Qazi, and Tanveer Bilal Pirzadah

1 Introduction

Development of biosensors through nanotechnology has played an important role in enhancing the sensitivity and performance of biosensors, which has resulted in the formulation of nano-biosensors. These nano-biosensors are more refined and reliable as they are compact devices and offers rapid screening to the number of analytes at low cost. Nano-biosensors have a great potential in our day-to-day life as well as in agriculture. Nano-biosensors are a rapidly emerging technology that can be used effectively to improve our agricultural productivity in the form of nano-fertilizers, nano-herbicides, nano-pesticides, nano-insecticides, pathogenic control agents, moisture, and soil pH (Rai et al. 2012; Pirzadah et al. 2019). Besides, nano-biosensors have major implication in the area of agriculture like physical monitoring of temperature, humidity, soil quality and fertility, sensing microbiological microenvironment of the soil, indicator for seed viability and shelf life, response sensors for irrigation and safety in agronomy, precision agriculture, detection of residual pesticides, fertilizers and toxins, and plant pathological monitoring (Rai et al. 2012; Kaushal and Wani 2017). The physical and chemical properties of nanomaterials can be employed in the development of nano-biosensors. Moreover, the sensitivity and performance of nano-biosensors can be improved using nanomaterials through new signal transduction technologies (Sagadevan and Periasamy 2014).

F. A. Dar (✉)
Department of Bioresources, University of Kashmir, Srinagar, Jammu and Kashmir, India

T. B. Pirzadah
Assistant Professor, University Centre for Research and Development (UCRD),
Chandigarh University, Mohali, Punjab, India

G. Qazi
Department of Botany, Islamia College of Science and Commerce,
Srinagar, Jammu and Kashmir, India

K. R. Hakeem, T. B. Pirzadah (eds.), *Nanobiotechnology in Agriculture*,
Nanotechnology in the Life Sciences, https://doi.org/10.1007/978-3-030-39978-8_7

At present, nano-biosensors are in its infancy stage; however, development of rapid, sensitive, and cost-effective nano-biosensors is due to the technological advancements from the past few decades which have resulted in the production of nano-biosensor systems of vital importance in the fields such as health care, environment, agriculture, genome analysis, food and process industries, defense and security (Fogel and Limson 2016). For the development of nano-biosensors, various types of nanoparticles such as metallic (titanium, platinum, gold, silver, aluminum, iron, zinc, etc.), carbon nanotubes (CNT's), magnetic nanoparticles (MNP's), nanorods (NR's), and quantum dots (QD's) have been actively investigated (Prasad et al. 2017). In general, a biosensor is an amalgamation of two components, the biological one (receptors, antibodies, enzymes, nucleic acids, proteins, organelles, cell, tissue, and microorganisms) and the electronic component and their interaction yields a measurable signal intercepted by the transducer and finally detected by the detector. Thus, a biosensor is an analytical device that converts biological response into an electrical signal (Rai et al. 2012). Conversely, a nano-biosensor is an upgraded version of biosensor, which is compact, highly sensitive, and miniature structure compared to conventional biosensors. These nano-biosensors are known for their specificity, stability, specific interaction between analytes, independent of stirring, pH, and temperature. Besides reaction time with the analyte is quick with accurate, precise, reproducible, linear range and without any noise. These are tiny, biocompatible, non-toxic, non-antigenic, inexpensive, convenient, and easily operated. Nano-biosensor or nanomaterial based biosensor can play major role in agriculture and allied fields because of their improved detection sensitivity and high specificity. Nano-biosensors can also act as diagnostic tools to assess soil quality and various plant diseases and therefore can be used to treat diseases caused by bacteria, fungi, and viruses (Singh et al. 2011a, b, c; Singh and Choi 2010). Furthermore, nanodiagnostics is an integration of nanotechnology and molecular diagnostics that offers a promising tool for disease diagnosis in plants (Jain 2003).

2 Nano-biosensor Development-Brief Overview

Nanotechnology deals with the alteration or generation of materials that are extremely small in size (10^{-9} m). There has been a significant modification in the development of biosensors since the year 1962, and till now four generations of biosensors have been produced. The first generation of biosensors was based on electrical response only, the second generation of biosensors involved specific mediators between the reaction and transducer to create an improved measurable response, the third generation of biosensors involves that the reaction itself causes the response and no mediator diffusion is directly involved, and the fourth generation of biosensors involves the incorporation of micro, nano, and bionano electromechanical systems, nanotechnology, and biotechnology have introduced a lot of features (Rai et al. 2012; Dede and Altay 2018). The rapid evolution of nanobiosensors is basically dependent upon their progress in their analytical performance and bio-detection applications. Nano-biosensors involve the inclusion of nanotechnology in biosensor development that results in the development of more effective, reliable, fast, and economical biosensors. From the past few decades, there has been a rapid progress in the development of nano-biosensors especially in the agricultural and allied sectors, which has resulted in the production of fourth generation of nano-biosensors that are capable of detecting multiple signals and are highly sensitive, precise, and accurate (Dede and Altay 2018). A typical biosensor consists of three essential components, the biological element, the transducer, and a signal processing element (Sagadevan and Periasamy 2014). On the other hand, a nano-biosensor is a compact analytical device consisting of biologically sensitized element, a physicochemical transducer, and a signal processing device and all these components are constructed at a nano-scale level.

3 Categories of Nano-biosensors in Agriculture

There are various types of nano-biosensors that are used in agriculture, such as electrochemical nanosensors, optical nanosensors, nano-barcode technology, e-Nose and e-Tongue, wireless nanosensors, and wireless sensor network (Fig. 1). Some of the examples of various types of nano-biosensors and their mode of detection are given in Table 1.

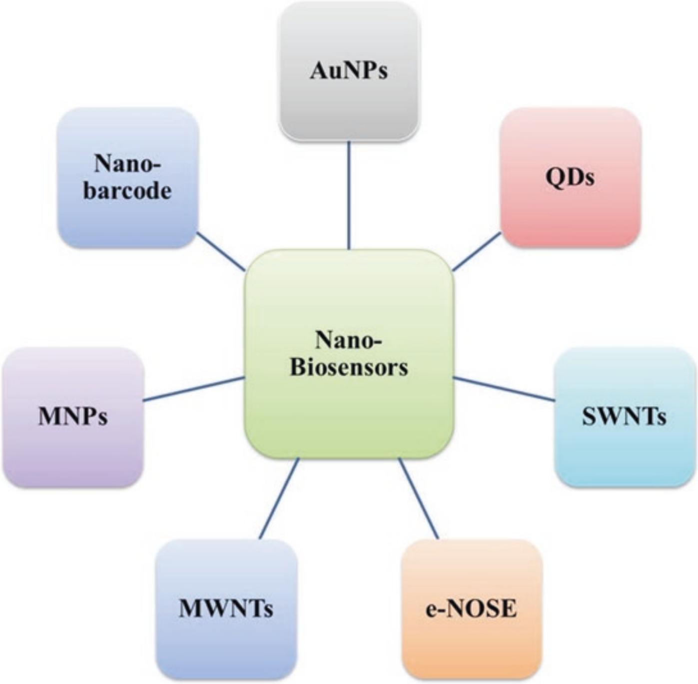

Fig. 1 Various types of nano-biosensors used in agricultural sector

Table 1 Application of various nanosensors/nano-biosensors and their mode of detection

Target element/pathogen/application	Mode of detection	Reference
Organophosphates	Amperometric nanosensor	Yan et al. (2013)
Sulfonamides	Amperometric nanosensor	Xu et al. (2013)
Ractopamine and salbutamol	Amperometric nanosensor	Lin et al. (2013)
Fructose	Amperometric nanosensor	Antiochia et al. (2013)
Hydrogen peroxide	Amperometric nanosensor	Nasirizadeh et al. (2015)
Carbosulfan	Voltammetric nanosensor	Nesakumar et al. (2016)
Heavy metal contamination	Voltammetric nanosensor	Yavuz et al. (2016)
Salmonella typhi	Voltammetric nanosensor	Singh et al. (2015)
Nitrite	Optical nanosensor	Chen et al. (2016)
Reactive oxygen species (ROS)	Optical nanosensor	Hu et al. (2014)
S. aureus, *V. parahemolyticus*, and *S. typhimurium, E. coli*	Optical nanosensor	Wu et al. (2014)
Concanavalin A, antibiotics, mycotoxins, and pathogen like *E. coli*	Optical nanosensor	Evtugyn et al. (2013); Huang et al. (2013); Zeng et al. (2014)
Malathion and sulfonamides	Optical nanosensor	Dasary et al. (2008), Guillén et al. (2011)
Salmonella enterica Serovar Enteritidis	Nanobarcode technology	Zhang et al. 2009
Aroma transfer from food plastics bags	e-Nose and e-Tongue	Torri and Piochi (2016)
Quality assessment of beef fillets	e-Nose and e-Tongue	Mohareb et al. (2016)
Alicyclobacillus acidoterrestris	e-Nose and e-Tongue	Huang et al. 2015
Edible oil	e-Nose and e-Tongue	Men et al. (2014)
Adulterated milk	e-Nose and e-Tongue	Yu et al. (2007)
Leaf wetness and leaf area index	Wireless nanosensors and WSN	El Maazouzi et al. (2014); Shimojo et al. (2013)
Green house management	Wireless nanosensors and WSN	ArunKumar and Alagumeenaakshi (2014)
Mango and black pepper farming	Wireless nanosensors and WSN	Kodali and Rawat (2013); Li and Shen (2013)

(continued)

Table 1 (continued)

Target element/pathogen/application	Mode of detection	Reference
Real-time traceability and food chain management system	Wireless nanosensors and WSN	Ko et al. (2014), Wang et al. (2015)
Marine fish farming and sustainability monitoring	Wireless nanosensors and WSN	Lloret et al. (2015)

3.1 Electrochemical Nanosensors

Electrochemical nanosensors are the most widely used sensors that are based on chemical reactions between nanofabricated biomolecule and the biological element and target analyte to produce or consume ions or electrons, which are measured as electrochemical signals (Asha Chaubey 2002). Quantitatively, the electrochemical signal generated is correlated with the amount of analyte present in a sample. These nanosensors are highly sensitive, compatible, robust, economical, rapid, low maintenance, energy efficient make them applicable for sensing in a wide range of applications. Based on their working principle, electrochemical nanosensors device could be categorized in amperometry (based on redox reaction), voltammetry (based on varying electric current), and potentiometry (based on variable potential difference of electrodes). Nanomaterials like electrochemically active carbon nanotubes, nanofibers, and fullerenes have been recently developed and applied for highly sensitive biochemical sensors. These nanosensors have also relevant implications for application in agriculture, in particular for soil analysis, easy biochemical sensing and control, water management and delivery, pesticide, and nutrient delivery. Nanomaterial is considered as one of the possible solutions to problems in food and agriculture, just like biotechnological issues of safety on health, biodiversity, and environment along with appropriate rules and regulation (Kuzma and verHage 2006).

3.2 Optical Nanosensors

Optical nanosensors depend on the detection of the change in the optical signal and consequently make it suitable for various spectroscopic measurements, such as absorption, fluorescence, phosphorescence, Raman effect, Raman scattering, and refraction by sensing changes in wavelength, phase, time, intensity, and polarity of the light. In general, the functioning of optical biosensors is based on fluorescence spectroscopy, surface plasmon resonance, interferometry, and spectroscopy (Srivastava et al. 2017). Recently, fluorescent nanoparticles (NPs) or quantum dots (QDs) have been developed for labeling the plant proteins (Pyrzynska 2011; Chahine et al. 2014). It has been observed that QDs at low concentration have no detectable cytotoxicity for seed germination and seedling growth. Therefore, based on such observation, QDs can be utilized for live imaging in plant root systems to verify known physiological processes (Hu et al. 2010; Das et al. 2015).

3.3 Nano-barcode Technology

Nano-barcoding and nano-processing are novel technologies that can change the way of keeping check on agricultural trade (Li et al. 2005). Although, barcoding is well known phenomenon and has been extensively used as a tool for the identification of plant, animal, and microbial species using a small stretch of gene sequence (Ferri et al. 2009). With the help of metallic and magnetic nanoparticles, significant development has been made in utilizing nanotechnology. For instance, the dual gold and iron oxide nanoparticle have been separately conjugated with two different DNA sequences for rapid and reliable detection of *Salmonella enteric, Serovar enteritidis* in the food sample (Zhang et al. 2009). Furthermore, grocery barcoding has been put into practice for the efficient analysis and identification of crop diseases. Nano-barcodes were created in such a manner, so that they can tag variable pathogens observed in the agricultural field and can be checked by utilizing tools reliant on fluorescence (Kaushal and Wani 2017). Nano-barcoding can be employed in labeling food products as well as in combination with nanoparticle based intelligent inks that may offer smart recognition of relevant food item. Printed labels on food items can provide reliable information about temperature, time, pathogens, freshness, humidity, etc. (Prasad et al. 2017).

3.4 e-Nose and e-Tongue

e-Nose and e-Tongue are nanomaterial based devices that are functionally similar to human sensory organs and are used to detect array of gases, odors, taste, and their variable concentration (Fig. 2). They have acquired critical importance to determine the quality and quantity of material such as food, beverages, agriculture, pharmacology, personal care product manufacturing and processing (Baldwin et al. 2011). For instance, e-Nose can be used to assess the release of volatile aldehydes by seeds during storage condition thereby preventing their degradation through timely intervention. Besides, there are nano-scale based smart delivery systems that can be used to prevent nutrient deficiencies and diagnose diseases in plants to provide complete protection (Shang et al. 2019). The main aim of these nano-scale based devices is to control, target, and regulate the plant systems to escape biological intervention (Kessler 2011). The nanosensor based e-Nose and e-Tongue are highly sensitive, selective, redundant, accurate, reliable devices that has wider application in agriculture, forestry, and food industry (Srivastava et al. 2017).

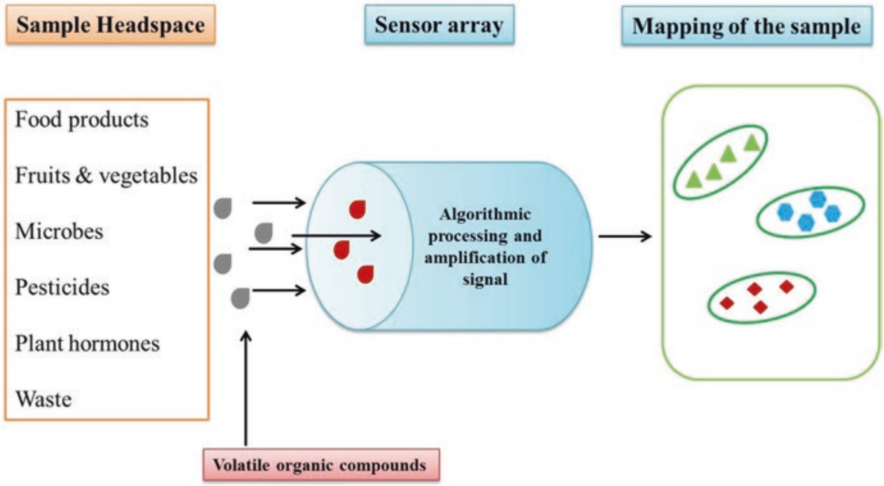

Fig. 2 Schematic representation of electronic nose with its component; sample head space, nanosensor array, unit for algorithmic processing, and classified data after the detection in form of a map

3.5 *Wireless Nanosensors/Wireless Sensor Network*

A wireless sensor network (WSN) is self-organizing with intelligent decision-making capability, self-dynamic, self-diagnostics, fault tolerance, and self-healing autonomous operating mode with information security system made up of several components of radio-frequency transceivers, sensors or nanosensors node, micro-controllers, and power sources (Srivastava et al. 2017). The wireless sensors gave a reliable measurement of small change in pressure, temperature, humidity along with the temporal observation. These features of wireless sensors make them suitable for their application in environment, defense, agriculture, and food industries (Srivastava et al. 2017). Wireless nanosensors can generate integrated information in precision farming and this information can be used to control precisely the application of fertilizers and irrigation in the field (Sahota et al. 2011). For instance, WiPAM is a wireless sensor network based irrigation management system that was used to check soil moisture and temperature related information. The design and deployment of the wireless sensors network are continuously expanding with multiple monitoring and control. In addition to irrigation management system, the wireless sensor technology is being deployed for many application, such as sensing leaf wetness and leaf area index in the agriculture field (El Maazouzi et al. 2014; Shimojo et al. 2013), precise greenhouse management (ArunKumar and Alagumeenaakshi 2014), in mango and black pepper farming (Kodali and Rawat 2013; Li and Shen 2013).

4 Role of Nano-biosensors in Precision Agriculture

The aim of precision agriculture/precision farming is to increase the crop yield with limited input of agrochemicals by employing high-tech information technological resources to monitor and control the environmental variables (Kaushal and Wani 2017). Remote sensing (RS), geographical information system (GIS), and geosynchronous positioning system (GPS) can play an important role in yield analysis, pest monitoring, natural catastrophes, and forecasting, thereby helping in addressing the problems due to pathogens and pests, fertilizer requirements, and other variables with accuracy and precision (Sekhon 2014). Variable rate technology (VRT) and yield monitors are the two main parts of precision agriculture which works in coordination of GIS and GPS along with the VRT field instruments. VRT is a device that manipulates and utilizes all the information based on variables like soil status, fertilizer, chemical and water requirement in order to increase yields and reduce input expenses, thus dropping waste and labor expenditure. Nanotech based sensors in combination with RS and GIS can provide efficient monitoring and information services in relation to crop growth and soil conditions (Kaushal and Wani 2017). Precision farming takes advantage of nanosensors and nano-based smart delivery systems to efficiently utilize the agricultural resources and precisely detect the crop pathogens in order to enhance the crop productivity in an economic way (Rai et al. 2012; Jones 2014; Prasad et al. 2014; Kaushal and Wani 2017). Therefore nanobiosensors can be major tool to distribute nutrients and fertilizers as per the requirement of the crop and to successfully achieve the goal of precision farming (Kaushal and Wani 2017).

5 Nano-biosensors as a Tool for Soil Health, Smart Delivery Systems and Disease Management

Nano-biosensors are very effective in promoting soil and environment health by making use of next generation technology thus enabling better control on environmental variables. Moreover, nano-biosensors have been found very useful in detecting pollutants and pathogens due to their molecular precision and sensitivity. Nanomaterial based biosensors have the ability to precisely monitor the temporal and seasonal changes occurring in the rhizosphere of the plant system (Choudhary et al. 2015: Rai et al. 2012; Sekhon 2014). It has been reported that 70% of conventional fertilizers and plant protection products (ppp's) do not reach their specific targets because they are unstable in the environment and difficult to be taken up (Solanki et al. 2015). Nano-based smart delivery systems have the ability to provide more efficient and targeted delivery to specific plant cells due to their size-related properties (Solanki et al. 2015; Chhipa and Joshi 2016; Gogos et al. 2012; Nair et al. 2010). Due to their greater stability in the environment, they are capable of improving nutrient availability and PPP's to crops (Rai and Ingle 2012;

Solanki et al. 2015; Liu and Lal 2015). Another important feature of smart delivery systems is to enhance the delivery of nutrients and ppp's as they enable their controlled release and extend their effectiveness from three to over 30 days (Adak et al. 2012; Solanki et al. 2015). Smart delivery of nutrients and ppp's improves the resistance of crops towards droughts, pests, and pollution and in the same way the effect of pesticides was found to be doubled (Song et al. 2012; Xiang et al. 2013; Kah and Hofmann 2014). Thus, there was a significant improvement in the quality and quantity of yields (Mukhopadhyay 2014; Solanki et al. 2015; Chhipa and Joshi 2016). Nano-biosensor based smart delivery systems can further enhance the process of releasing nutrients and ppp's in response to environmental stresses and biological needs and thus provides an opportunities for real time monitoring and control (Solanki et al. 2015; Liu and Lal 2015; Ramesiah 2015). Nano-biosensors and nano-based smart delivery systems could help in the efficient use of agricultural natural resources like water, nutrients, and chemicals through precision farming. Through the use of nanomaterials and global positioning systems with satellite imaging of fields, farm managers could remotely detect crop pests or evidence of stress such as drought. Once pest or drought is detected, there would be automatic adjustment of pesticide applications or irrigation levels. Nano-encapsulated slow release fertilizers have also become a trend to save fertilizer consumption and to minimize environmental pollution.

6 Nano-biosensors and Sustainable Agriculture

The concept of sustainable agriculture can be achieved by incorporating nanotechnology based biosensors due to their ability to provide new dimensions to utilize tools and techniques which can maximize agricultural productivity by addressing issues related to agro-technology, irrigation and fertilizer requirements, food production and processing, packaging and storage. Thus, nanotechnology based biosensors can offer wider applications in food and agriculture sector. For sustainable agriculture, optimum utilization of water resources is essential factor and to combat this problem, nano-biosensors like nano-hydrogel, which has the ability to absorb and release water molecules in a controlled manner thereby allowing efficient utilization of water resources is of paramount importance (Vundavalli et al. 2015; Pirzadah et al. 2019). Nano-hydrogels such as silver coated hydrogels and biodegradable hydrogels are utilized for this process and are very useful nano-biosensors especially in the areas which are under drought, one of the major environmental concerns in the near future (Magalhaes et al. 2013; Montesano et al. 2015). Moreover, recent studies on nano-encapsulated seeds have shown their ability to germinate faster and are more resilient to environmental stresses than non-encapsulated seeds (Adhikari et al. 2016). Nano-encapsulation increases seedling strength, growth, and longevity (Khodakovskaya et al. 2009; Dehkourdi and Mosavi 2013; Adak et al. 2016). Certain pollutants, pests, and diseases are also responsible for causing severe losses to crop plants. Biosensors based on organic detection mechanism have been developed having ability to detect these specific threats (Perumal and Hashim 2014; Otles and Yalcın 2015). Therefore, nano-biosensors provide a very precise tool that can be used to prevent pest out-breaks and monitor soil quality, which ultimately leads to improved yields. With the help of nanotechnological intervention, the sustainable agriculture intensification concept can be achieved. The application of nanotechnology approach to agricultural practices can play an important role in plant protection strategies, prevents nutrient losses, promotes rapid pest detection, and enhances yields through improved pest management (Ghormade et al. 2011; Shang et al. 2019). The applications of nanotechnology to agriculture can be broadly categorized as:

1. Nanoclays and nanozeolites have the ability to enhance water holding capacity of soil (Sekhon 2014).
2. Nanosensor based devices for the analysis of soil, water, nutrient, and pesticide management.
3. Nano-magnets for the expulsion of soil contaminants.
4. Nanoparticles (NPs) for the production of improved insecticides, pesticides, and insect repellents.
5. Nanomaterial based devices for the discharge of genetic material for crop enhancement (Kaushal and Wani 2017).

A variety of nano-biosensors have been developed by using inorganic, polymeric, and lipid NPs through different techniques which include emulsification, ionic gelation, polymerization to increase the plant protection and productivity (Fraceto et al. 2016). Such techniques can be used for the development of intelligent nano-systems which has the ability to minimize leaching and at the same time improving the uptake of nutrients by plants. Besides, such systems can mitigate eutrophication by reducing the transfer of nitrogen to groundwater (Liu and Lal 2015). Moreover, nanomaterials could also be exploited to improve the structure and function of pesticides by increasing solubility, enhancing resistance against hydrolysis and photodecomposition, and/or by providing a more specific and controlled release toward target organisms (Mishra and Singh 2015; Grillo et al. 2016; Nuruzzaman et al. 2016).

7 Nano-biosensors as a Tool for Crop Protection

Nanomaterial based products in agriculture are of greater importance for enhancing crop productivity and efficiency. The incorporation of advanced technologies for the development of nano-biosensors, quantum dots (QDs), nanostructured platforms, nano-imaging, and nano-pore DNA sequencing has increased the sensitivity and specificity of pathogen detection, facilitates high throughput analysis, and can be used for high quality monitoring and crop protection (Khiyami et al. 2014).

Furthermore, the availability of diagnostic kits has enabled fast and easy detection of harmful pathogens, made it possible through timely intervention the prevention of epidemic diseases (Savaliya et al. 2015; Khiyami et al. 2014). The application of nano-biosensors and nanomaterial based devices has made it possible to detect pathogens in a quicker, cost-effective and precisely for the treatment of diseases. Such accuracy in technology has enabled to devise effective integrated disease pest management systems in order to modify crop environments to stop the intrusion of plant pathogens (Kashyap et al. 2016). However, there is a need to assess the health hazards and toxicity caused by the use of nanomaterial based products in agriculture, environment, and human health. Nanomaterials such as fullerenes (C_{60}), CNTs, silver, iron, titanium dioxide, aluminum oxide, cerium oxide, zinc oxide, silicon dioxide, dendrimers, nanoclays, and gold nanoparticles are under investigation (Duhan et al. 2017). Although, nanomaterials have the ability to resolve the problems associated with agriculture like overdependence on irrigation, climatic instability, poor energy conversion to products like nanopesticides and nano-fertilizers, disease prevention in crops, use of agricultural wastes and nanosensors.

8 Conclusion and Future Recommendations

Nanomaterial based nano-biosensors have the ability to resolve the problems in agriculture like overdependence on irrigation, climate resilience, disease prevention, use of agricultural waste products, and high energy conversion to products like nano-fertilizers and nano-pesticides. Nanomaterial based nano-devices have a great potential in reshaping the agricultural setup. These devices are used in the form of variety of agricultural products, viz., nano-biosensors, nano-herbicides, nano-fertilizers, nano-pesticides, and so on. They have the ability to reduce the consumption of conventional agrochemicals employing smart delivery systems thereby minimizing the loss of nutrients, improves the overall crop yield through optimum resource management. However, the utilization of nanomaterial based products needs to be taken care off as they might show some adverse effects which needs to be properly assessed before their release to the agriculture and environment. Besides, nano-biosensors offer wider application in plant protection, seed germination, plant growth and development, pathogen/disease detection, pesticide/herbicide detection making them highly efficient and productive for the agriculture sector. Nano-biosensors are one of the great scientific, engineering, and technological innovations of the twenty-first century. Therefore, it is equally important to make improvements in these next generation biosensors so far as their sensitivity and specificity are concerned to become an important tool in plant diagnostics, disease detection, and crop improvement. In addition, there is a need for rapid, trustworthy, low cost, multiplexed screening to detect a wide range of plant based bio-products.

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Nanoparticles: The Magic Bullets in Mitigating Drought Stress in Plants

Javed Ahmad, Sadia Qamar, Nida Kausar, and M. Irfan Qureshi

1 Introduction

Plants being sedentary organisms are perpetually exposed to environmental variations and multiple stresses in single or in combination throughout their life. However, plants develop various mechanisms to respond against unfavorable conditions but their response varies even in same plant species (Ahmad et al. 2018a; Kollist et al. 2019). Therefore, elevation of stress tolerance in plants is always the main concern towards sustainable agriculture and crop production. In the last decades nanobiotechnology based applications attracted researcher's attention in this direction. It is a new emerging and fascinating field of science, permits advanced research in many areas, and nanotechnological discoveries could open up novel applications in the field of biotechnology and agriculture (Giraldo et al. 2019). Further, this is an area that involved technology of diverse fields at nanolevel. The term nanobiotechnology was coined by great biophysicist Lynn W. Jelinski and offers an opportunity to develop tools and technology for inspection and modification of agricultural sector. Nanobiotechnology creates the alternatives to make the nanomaterials that display some novel properties (Chhipa 2017). Such technology has large scope in agriculture sector during current food crises condition in the world. The number of applications is being utilized by scientific community; however, potential use of nanoparticles needs more exploration in agricultural sciences particularly their mechanism and role as stress mitigators in plants (Vishwakarma et al. 2018). Nanotechnology presents an interdisciplinary view of research in the area of life sciences, medicines, electronics, and energy, for example, transformation of agricultural and food waste to energy, and other many useful by-products via nanoenzymatic bioprocessing, technology with reproductive biology, biochemical sensors, cleaning of water, different nanocides used in agriculture and development

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J. Ahmad (✉) · S. Qamar · N. Kausar · M. I. Qureshi (✉)
Department of Biotechnology, Jamia Millia Islamia, New Delhi, India

K. R. Hakeem, T. B. Pirzadah (eds.), *Nanobiotechnology in Agriculture*,
Nanotechnology in the Life Sciences, https://doi.org/10.1007/978-3-030-39978-8_8

of stress mitigator for crops (Kim et al. 2018; Pandey 2018; Shojaei et al. 2019). For example, fertilizers play a vital role in crop growth and development but most of their part remains unutilized by plants due to many inherent factors, such as, leaching in soil, hydrolysis, decomposition, etc. Therefore, there is a constant need to develop novel applications with the help of nanotechnology and nanomaterials to increase the crop production and to minimize the nutrient loss of fertilizers (León-Silva et al. 2018; Saranya et al. 2019). Application of nano-fertilizers may provide alternative to increase resource's use efficiency and to reduce increased soil toxicity created due to accumulation of chemical fertilizers and pesticides in the soil (Pirzadah et al. 2019). Despite advances of nanotechnology in other sectors, development of nanobiotechnology and its applications in agriculture sector (Fig. 1) is still at native stage. However, there is an increasing interest of researchers in this field. In this chapter, we discuss the recent advances in nanobiotechnology research related to drought stress alleviation and modulation of crop yield.

2 Nanoparticles (Nano-powder/Nano-cluster/Nano-crystal)

Nanotechnology deals with various structures of matter having dimensions of the order of a billionth of a meter. Nanoparticles are small molecular aggregates having dimensions between 1 and 100 nm in size with a surrounding interfacial layer. This interfacial layer is an integral part of nanoscale matter, fundamentally affecting all of its properties (Jeevanandam et al. 2018; Baby et al. 2018). Due to extreme small size they acquire some queer properties compared to their bulk material. The term "nanoparticle" is not generally applied to individual molecules; it usually refers to

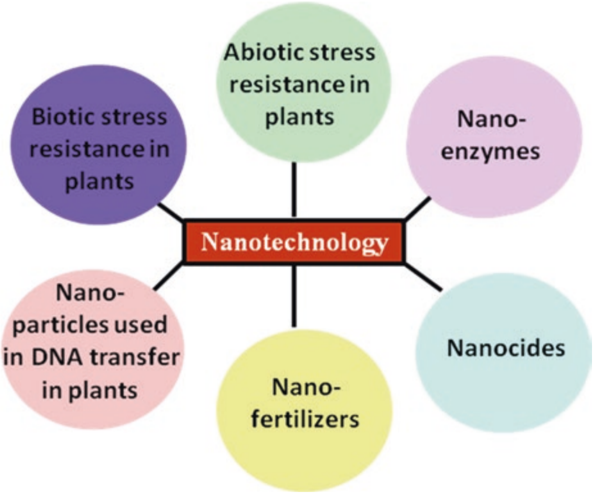

Fig. 1 Diagram showing various applications of nanotechnology in plant science

inorganic materials. Nanoparticles are of great scientific interest as they are, in effect, a bridge between bulk materials and atomic or molecular structures. Nanoparticles often possess remarkable optical properties as they are small enough to confine their electrons and produce quantum effects (Sudha et al. 2018). Nanomaterials have certain properties which make them different from that of the bulk materials, including large fraction of surface atoms, high surface energy, spatial confinement, and reduced imperfections. Nature knows nanoparticles very well in the form of clay, bacterial products, and minerals (Hong 2019). It has been utilized by ancient people as a colorant of metals. Various types of nanoparticles are used in agriculture sciences; however, recently the systematic designed and engineered/modified composite nanoparticles are also used in plant science research (Fig. 2). The engineered/modified nanoparticles may alter their properties and so their reactivity, dissemination, and translocation inside the plant are different as compared to non-engineered/modified same nanoparticles resulted different responses of plants (Khan et al. 2017). For example, Barrios et al. (2016) reported that exposure of capping of nanoparticles increases the plant responses as compared to treatment with naked nanoparticles. Such modified nanoparticles have specific properties which are not found in the same material. Engineered/modified nanoparticles are constructed with a range of materials and occur in diverse sizes and structure with the compatibility of extra addition of surface molecules which makes them unique from naturally occurring materials (Servin and White 2016; Tan et al. 2017). Engineered nanoparticles have great ability to enter the plants cells; therefore it can transport DNA and other useful molecules into plant cells efficiently. This area of nanotechnology opens new potential in the research of plant genetic engineering as transgenic plant development (Verma et al. 2018; Wang et al. 2016). Carbon nanotubes are other important form of nanoparticle and such nanoparticles (carbon

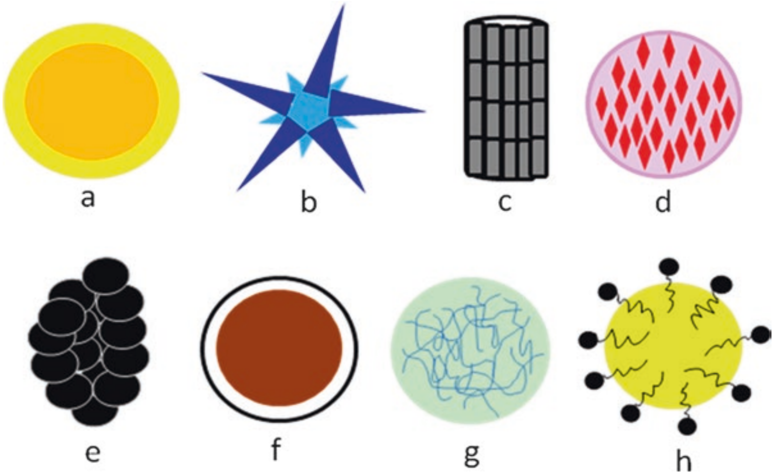

Fig. 2 Various types of nanomaterials: (**a**) polymer nanoparticle, (**b**) nano-crystal, (**c**) nanotubes, (**d**) nanogels, (**e**) nano-cluster, (**f**) nanoshell, (**g**) nanogels, (**h**) micelles

nanotubes) increased the plants' capability to collect the range of light energy after introducing the carbon nanotubes into chloroplast. These carbon nanotubes act as an artificial antenna which permits the chloroplast to collect the wavelengths of light besides the normal range, such as ultraviolet, green, and near-infrared (Khatri and Rathore 2018). The engineered/modified carbon nanotubes also improve the growth, physiology, metabolism, and tolerance level of plants which could be helpful under stress conditions (Vithanage et al. 2017). Though, the several studies on nanoparticles to date concern toxicity on plant system (Chichiriccò and Poma 2015; Tripathi et al. 2017). On the other hand, various studies have shown that nanoparticles have positive effects on the plant system (Table 1). Nanoparticles can be a potential tool to be used as nano-herbicides, nano-pesticides, nano-fertilizers, etc. which can effectively release their content in required quantity to target cellular organelles in plants (Cicek and Nadaroglu 2015). Different activities including the improper clearance of industrial waste and improper management of disposal of products by user can pollute the environment. Several mathematical models are being currently used to evaluate the discharge of nanoparticles in the environment (Nowack 2017). The NPs have high surface to volume ratio which improves their activity and properties. Environmental conditions also affect the properties of nanoparticles such as stability, oxidation state, precipitation, and aggregation. Hence, nanoparticles can act differently in different environmental conditions, and consequently their accessibility as well as reactivity in ecosystem is varied (Ealias and Saravanakumar 2017).

3 Abiotic Stress and Nanotechnology

Plants must cope with climate changes and environmental stresses such as drought, salinity, elevated temperatures, heavy metals, etc. for sustainability and maintenance of life on Earth. Such stresses might hardly occur in single but more commonly in combination. Climate change catastrophes impact all aspects of plant metabolism, growth, and development and thus posing a serious challenge for developing sustainable agriculture at a time of significant growth in the global population (Ahmad et al. 2018b; Roychoudhury and Tripathi 2019). To cope with environmental stresses plants have developed a wide spectrum of effective and integrative molecular programs to sense it rapidly and adapt accordingly (VanWallendael et al. 2019). Such responses can boost up by plant by the interaction of nanoparticles with plants. Nanotechnology holds the pledge of enhancing crop yield by improving plant tolerance mechanism under abiotic stress conditions (Khan and Upadhyaya 2019). Several studies demonstrated that nanoparticles play important role in protecting plants from abiotic stresses through modulation of various physiological, biochemical, and molecular processes (Fig. 3). In addition, nanoparticles are generally involved in enhancing the activities of enzymatic and non-enzymatic antioxidants under abiotic stress (Table 1). Many natural biological systems have native form of nanoparticles such as chemicals derived from soil organic content, nanoclay, magnetosomes, ferritin, viruses, exosomes, and lipoproteins which exhibit

Table 1 Impact of nanomaterials on plants under drought stress

Nanoparticles	Optimum concentration/ Treatment duration	Plant	Effect on drought stress	Reference
Cerium oxide nanoparticles (nanoceria)	50 or 100 mg/L 10 days	*Sorghum bicolor* (L.) *Moench*	Efficiently reduced free radicals and lipid peroxidation in drought stressed plants Increased leaf carbon assimilation rates, pollen germination, and seed yield per plant under drought then controls	Djanaguiraman et al. (2018)
Nano-titanium dioxide (nano anatase TiO2)	10 ppm 50 ml of TiO_2 NPs were sprayed on the plant shoots in each pot for three successive days	*Dracocephalum moldavica* L.	Drought stressed plants treated with 10 ppm TiO2 NPs showed high accumulation of proline and reduced H2O2 and malondialdehyde content as compared to controls	Mohammadi et al. (2016)
CuO and ZnO	CuO, 300 mg /kg and ZnO 500 mg /kg 7 days	*Triticum aestivum* L.	CuO and ZnO NPs interacted with root-colonizing microbes and altered plant growth and function under drought	Yang et al. (2017)
Fullerenol nanoparticles (FNPs, C60(OH)24)	0.01 and 0.001 nmol mm^{-2} per leaf area 13 days	*Beta vulgaris* L.	FNPs worked as intracellular binders of water Increased antioxidant enzyme activities (CAT, APx, and GPx), MDA and GSH content mitigating drought stress	Borišev et al. (2016)
Colloidal nanosilver	40 g/ha 1 week	*Carum copticum* L.	Showed no constructive effect on plant growth under drought	Seghatoleslami et al. (2015)

(continued)

Table 1 (continued)

Nanoparticles	Optimum concentration/ Treatment duration	Plant	Effect on drought stress	Reference
Composite NPs = SiO2 Nps (core) + chitosan (first semi-permeable coating) + sodium alginate and kaolin (outer most superabsorbent coating)	–	–	The SiO_2 Nps consisting of superabsorbent control release fertilizer was competent of releasing the nutrients slowly, withhold good quantities of water hence can facilitate plants control salinity and drought without disturbing the ecosystem	Mushtaq et al. (2018)
Nano TiO_2 and nano SiO_2	20 and 20 ppm	*Hordeum vulgare* L.	Present investigation showed beneficial effects of TiO_2 and SiO_2 on yield and biomass of barley genotypes	Ghorbanian et al. (2017)
Encapsulation of *S*-nitrosoglutathione into chitosan nanoparticles	100 µM 5, 8 days	*Saccharum* spp. cv. 99 IACSP94-2094	Such nanoparticles can be used for increasing NO-induced benefits for plants under stress, mitigating the negative impact of drought on plant physiology and metabolism	Silveira et al. (2019)
Nano ZnO	1, 3, and 5 mg Zn/kg 4 weeks	*Hordeum vulgare* L.	The ZnO-NPs promoted growth, yield, development, and fortify edible grains with crucial nutrients and also improved N acquisition under drought	Dimkpa et al. (2019)

(continued)

Table 1 (continued)

Nanoparticles	Optimum concentration/ Treatment duration	Plant	Effect on drought stress	Reference
Nano TiO_2	0, 10, 100, and 500 mg/L 3 days	*Linum usitatissimum* L.	Increased chlorophyll and carotenoids content, growth and yield, reduced H_2O_2 and malondialdehyde (MDA) content	Aghdam et al. (2016)
Nano TiO_2 and SiO_2	Nano TiO_2 (25, 50, 100, and 200 ppm) or nano SiO_2 (400, 800, 1600, and 3200 ppm) 24 days	*Gossypium barbadense* L.	Increased pigments content, total soluble sugars, total phenolics, total soluble proteins, total free amino acids, proline content, total reducing power, total antioxidant capacity, and antioxidant enzyme activities and yield	Shallan et al. (2016)
Yttrium doping-stabilized γ-Fe2O3 nanoparticles	0.5, 0.8, 1, or 2 mg ml^{-1} 5 days	*Brassica napus* L.	Reduced level of hydrogen peroxide and malondialdehyde and increased the chlorophyll and growth of plants under drought	Palmqvist et al. (2017)
Nano SiO_2	30, 60, and 90 ppm were applied three times at the stage of tillering, stem elongation and heading in the soil and through foliar application	*Triticum aestivum* cv. pishtaz	Increased leaf pigments and relative water content, plant height, and biomass	Behboudi et al. (2018a)
Nano TiO_2	0.1% 4 weeks	*Triticum aestivum* L. cvs	Improved leaf health and growth kinetic trait	Dawood et al. (2019)

(continued)

Table 1 (continued)

Nanoparticles	Optimum concentration/ Treatment duration	Plant	Effect on drought stress	Reference
Chitosan nanoparticles	30, 60, and 90 ppm were applied three times at the stage of tillering, stem elongation and heading in the soil and through foliar application	*Hordeum vulgare* L.	Increased the relative water content, grain protein, proline content, catalase, and superoxide dismutase	Behboudi et al. (2018b)
Nano SiO_2	100, 200, 300, and 400 mg/kg were applied from first day after transplantation of cucumber seedlings	*Cucumis sativus* L.	Increased nutrient uptake, fruit yield	Alsaeedi et al. (2019)

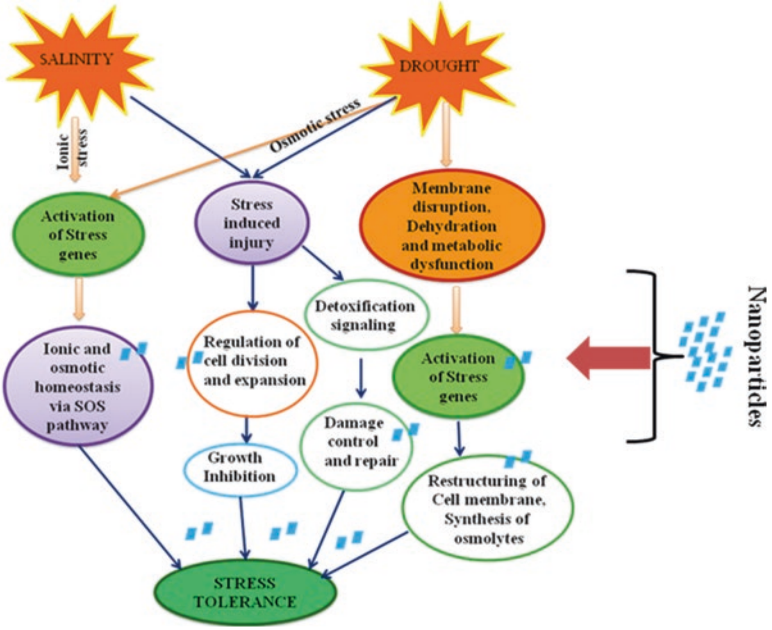

Fig. 3 Nanoparticles operate as signals that trigger the defense mechanism in plants to alleviate abiotic stresses

range of structures and biological functions (Elsakhawy et al. 2018). Nanotechnology alleviates the adverse effect of abiotic stress through the re-adjustment of physiological and metabolic re-adjustment of plant cell (Guerriero and Cai 2018). Such alleviation effect of NPs depends on size, shape, absorption, and dosage (Ahmad et al. 2019a). However, the molecular mechanisms related to NPs' protective role are still unclear. Therefore, understanding of plant defense mechanisms shows the benefit of using NPs in protecting plants from abiotic stress. Though, the queer properties of nanoparticles are gaining worldwide attention but the exact mechanism of their interaction with plants at various levels is still at infancy stage.

4 Dynamic Plant–Nanoparticle Interactions to Mitigate Drought Stress

Drought is a perennial and recurring feature in many parts of the world including India. Drought only affects 45% of the world's agricultural land (Dos Reis et al. 2016). Drought, as an abiotic stress, is multidimensional in nature, and it affects plants at various levels of their organization. In fact, under prolonged drought, many plants dehydrate and die off (Takahashi et al. 2018). Water stress in plants reduces the plant cell's water potential and turgor, which elevate the solutes' concentrations in the cytosol and extracellular matrices. As a result, cell enlargement decreases leading to growth inhibition and reproductive failure. This is followed by accumulation of abscisic acid (ABA) and compatible osmolytes like proline, which cause wilting (Ahmad et al. 2017; Hussain et al. 2019). At this stage, overproduction of reactive oxygen species (ROS) and formation of radical scavenging compounds such as ascorbate and glutathione further aggravate the adverse influence (Ahmad et al. 2019a; Hussain et al. 2019). Drought not only affects plant–water relations through the reduction of water content, turgor, and total water, it also affects stomatal closure, limits gaseous exchange, reduces transpiration, and arrests carbon assimilation (photosynthesis) rates (Schulze et al. 2019). Nanotechnology has the potential to improve function of photosynthetic machinery. Nanoparticles increase photosynthetic rate by changing the activity of enzymes involved in C_3 cycle and synthesis of photosynthetic pigments that could promote carboxylation, reflecting increase in plant growth (Lowry et al. 2019). Nanoparticles have a positive effect on germination and growth of plants. Effectiveness of NPs is determined by their concentration and it varies from plant to plant. Oxidative stress has largely been reported to be implicated in NP induced toxicity. It could activate a wide variety of cellular events such as cell cycle arrest, program cell death, modulation of proteins, and induction of antioxidant enzymes (Jalil and Ansari 2019).

As compared to the water sprayed control plants, the plants sprayed with the nanoceria show substantial reduction in the contents of malondialdehyde (such as MDA, a metric of lipid peroxidation) as well as in the level of free radicals (such as hydrogen peroxide and super oxides) when examined under drought condition. In sorghum plant, nanoceria foliar spray results in augmented seed yield per plant when compared to the water sprayed plants under drought conditions. The nanoparticles of TiO_2 have numerous intense effects on the morphological, biochemical, and the crop physiological characteristics (Djanaguiraman et al. 2018). However, during the growing period of the spinach plant exogenous application of nano TiO_2 promotes rubisco activase activity, formation of chlorophyll, and increased rate of photosynthesis which ultimately results in increase in the dry mass of the plant (Gao et al. 2008). It was further stated that the seed yield of cowpea (*Vigna unguiculata* L.) increases by foliar application of NPs and TiO_2 which may be possibly due to the augmented rate of photosynthesis (Owolade et al. 2008). Also the activity of various antioxidant enzymes like peroxidase and catalase has also been found to enhance in response to nano TiO_2 application. As a result of induction of the antioxidant systems of the plant the MDA accumulation is reduced (Ahmad et al. 2019a). Hence, TiO_2 has unlocked new and fascinating horizon for various plant physiologists or improves the performance of plants even under severe stress conditions. The effect of nano TiO_2 differs in all environmental conditions and may vary among different species of plant and varied applied conditions. In this context, under control and drought stress conditions, the influence of nano TiO_2 concentrations on biochemical and morpho-physiological characteristics of medicinal and aromatic plant dragon head was investigated by Mohammadi et al. (2016). Formulations of nano-sized ZnO and CuO act as a source of Zn and Cu and thus considered for agricultural applications and can be used as fertilizers. The effects of such nanoparticles (NPs) showed three way interactions of these NPs with the plants and its microbiome. At various doses that made shortening of root by both NPs, the NPs of Zn enlarge the formation of lateral roots whereas the NPs of Cu induce the proliferation and elongation of root hair which are closer to the tip of roots in wheat seedlings under drought stress (Yang et al. 2017). These responses usually occurred with roots colonized by a *Pseudomonas chlororaphis* O6 (PcO6) beneficial bacteria, which is isolated from the roots of the wheat grown in calcareous soils under dry land farming conditions. In seedling of wheat plant the drought stress tolerance induced by PcO6 was not reduced by the NPs. Rather PcO6-colonized plants growth with NPs thus resulted in general increased in the expression of those genes which are related with the water stress tolerance. The work elucidates that those plants which are grown under the ZnO or CuO exhibited cross protection for challenges of drought and metal stress. Emerging approaches for sustainable agriculture thus includes formulations using nanoparticles (NPs). NPs of ZnO and CuO are being reflected as fertilizers used to provide vital elements or as pesticides at higher doses. NPs of Zn and Cu also provide protection in different plants against drought stress (Yang et al. 2017). Although root hair formation is enhanced by CuNPs (CuO NPs) and ZnNPs (ZnO NPs) raises the production of lateral roots. The reduced length of root possibly lessens the access to water. Enhanced lignification of wall as described for mustard and *Arabidopsis* grown with the CuO possibly alter the flow of water and thus limit the extension of cell wall. The wall recognized response to the drought stress in plant is increased lignification. Impairment of the water flow may also be due to the association of Cu ions with pectins of cell wall (Nair and Chung 2015). Elevated level of anthocyanin for plants which are exposed to the NPs of CuO is continuous with the water stress, also it has been documented proline is increased during the strategy of drought tolerance. The roots of wheat grown with NPs of CuO show greater accumulation of the free radical in agreement with the fact that plants meet the challenges for NP results in ROS burst. The increased level of ROS, which further suggested the result of elevated ABA triggered by the drought stress, may cause transcriptional changes and thus leads to stress tolerance (Dimkpa et al. 2012).

Some remarkable results are found in certain studies such as seed germination and antioxidants increased in barley, soybean, and corn when treated with carbon nanotubes (CNTs) (Lahiani et al. 2013; Liu et al. 2016). CNTs induced root and shoot growth of wheat plants (Srivastava and Rao 2014). To reduce the effects of drought stress on quality and productivity of plants various significant efforts have been made over the past decades. We further recommend that the nanoparticles of fullerenol (FNPs), molecular formula $C_{60}(OH)_{24}$ may help to lessen the effect of drought stress by aiding as an extra water supply to intercellular cells of plants. Precisely, the nanoparticles of fullerenol (FNPs) able to enter the root and leaf tissue of plants, where they are able to bind molecules of water in different compartments of the cell. This hydroscopic FNPs activity further proposes that the FNPs could be useful in plants (Borišev et al. 2016; Verma et al. 2019). Such interesting study was done to investigate the effect of FNPs on sugar beet plants exposed to the drought stress (Borišev et al. 2016). Findings of this study further suggest that in those plants which are exposed to the drought stress, the foliar application of nanoparticles of fullerenol can modify the intracellular water metabolism. In roots and leaves of drought stressed plants made a significant elevation in the osmolyte proline in exposure of FNPs. These findings further suggest that the FNPs could also act as a binder of intracellular water, thus generating extra reserve for water and hence permitting the adaptation under the drought stress. Furthermore, amplification of various antioxidant enzymes in plants including (GR, SOD, GPX, APX, and CAT) indicates the foliar application of fullerenol may have some valuable effect on lessening the oxidative effects of the drought stress which further depends upon the concentration of applied nanoparticles (Liu et al. 2016). The exact mode of action, physiology, and mechanism of FNPs on plants further studies are needed. However, we can conclude that FNPs could directly be more effective on various agricultural practices, where supply of water is often a limiting factor. In addition, the insolubility of native fullerene in water is the main drawback for biological applications. To overcome this problem, derivatives of water-soluble fullerene have been synthesized and designed which maintain many of the exclusive properties of the native fullerene. These derivatives of fullerene due to their high solubility in the water represent attractive nanoparticles for different biological applications (Verma et al. 2019).

Silver (Ag) nanoparticle (AgNPs) is of the most frequently used nanoparticles in research experiments (Ahmad et al. 2019b). In some research the nanoparticles of silver have been validated for their inhibitory effects on the bacteria and other organisms (Beyene et al. 2017). Various researches have demonstrated the effects of silver nanoparticles on the hydraulic conductivity of plant stem, but on the other hand these nanoparticles may be able to penetrate the plant and could hinder the intracellular compartments and thus cause impairment to cell division (Tripathi et al. 2017). Hojjat and Ganjali (2016) reported positive interaction of AgNPs with lentil in drought stress. The germination rate, germination percentage, root length, root fresh and dry weight were increased under exposure of drought and AgNPs. The results of Mousavi et al. (2018) showed impact of nanosilver on *Tanacetum parthenium* plants under drought stress conditions has reduced the level of antioxidant enzymes may be less requirement of plant for antioxidant metabolism after exposure of nanosilver under drought. Nanoparticles may directly implicated in the removal of reactive oxygen species and, as result of purifying these free radicals, reduce the level of antioxidant enzymes. There is little knowledge on responses of medicinal plants, particularly in conditions like drought stress. The experiment was conducted to access the responses of *Carum copticum* under drought stress by various treatments testing the magnetic field and silver nanoparticles. Investigation indicated that exposure with magnetic field had more yield as compared to the control and nanosilver treatments (Seghatoleslami et al. 2015).

The nonporous material silica occupy analytical interest due to their great use in chromatography, biological images, delivery of drug, agriculture, cell markers, chemical sensors, and enzyme encapsulation (Asefa and Tao 2012). Due to wide application of the nanoparticles of silica in multidiscipline their production by different methods is receiving researcher’s greatest attention. The nanoparticles of silica can be used in the field of agriculture, as a silicon source to reduce the salinity stress in plants which are growing under saline and drought environments (Jeelani et al. 2019). The nanoparticles of silica have been successfully prepared by both organic and inorganic colloids. Ultrasonic synthesis of NPs of SiO_2 resulted in the synthesis of minute particles of about 13 nm (Jeelani et al. 2019). This research has been carried out by modified process of Stober (Sol-Gel) utilizing ultra-sonication based production of nanoparticle of SiO_2 (Noriega et al. 2019). The NPs of SiO_2 are further encapsulated in a compound-controlled release fertilizer used for improving the quality of agriculture in saline and drought areas (Mushtaq et al. 2018). Silicon has not been proven to be a vital element for the higher plants, but its useful effects on the plant growth have been reported in variety of crops including wheat, cucumber, and barley (Table 1). In plants, the deposition of silicon is in the form of amorphous silica (SiO_2-nH_2O) in the cell wall and improves the strength and rigidity of cell wall and interacts with the polyphenols and pectins (Bhatt and Sharma 2018). It was demonstrated by Marschner (2011) that in epidermal cell of the leaves Si^{4+} deposits and thus improving leaf exposure towards light by keeping leaves upright, whereas in roots it increases the elongation of cell and thus augmenting the elasticity of cell wall. Si acts as a mechanical–physical barrier that can inhibit the penetration of pathogens or pesticides into the plant cell. The deposition of silicon takes place on the epidermal walls, surface of leaves, and stem vascular tissues in most of the plants, particularly monocots and thus controls various physiological properties of plants.

5 Conclusion and Future Recommendations

The nanoparticles due to their unique physio-chemical properties are being used in the field of biotechnology and agriculture industry. Plenty of studies have concluded to explore mechanism by which nanoparticles influence on plant growth and development. Application of biosynthesized nanoparticles in agricultural field leads to sustainable development. They facilitate site targeted delivery of various nutrients needed for better growth and high productivity of plants. Nanoparticle increases the drought tolerance through enhancing antioxidant system, nutrient uptake, photosynthesis, reduction of reactive oxygen species, modulation of proteins, and signaling pathway. It is evident from compiled information that the effect of nanoparticles varies from plant to plant and depends on their mode of application, size, and concentration. Also more studies are required to explore the mode of action of nanoparticles, their interaction with biomolecules, and their impact on gene regulation and expression in plant under drought stress. Another application of nanoparticles in agriculture can be use as nano-biosensors in the crop protection and nano-devices for genetic manipulation of plants. However, some reports reflect the negative impact of nanoparticles on the environment. Therefore, the researchers should focus on dynamic interactions between plants and nanoparticles and its impact on the environment.

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Nanotechnology: An Innovative Tool to Enhance Crop Production

Aarifa Jan, Tanveer Bilal Pirzadah, and Bisma Malik

1 Introduction

Agriculture is backbone of many developing countries with more than 60% of population depending on it for their livelihood. Due to the rapid increasing population pressure, agriculture is facing many challenges for production of more food due to unpredictable climate change, shrinking of agricultural land, productivity, labor force, and increased urbanization. With the limited availability of land and water resources, the Indian policy makers ensure national food security by allocating 4% growth in agriculture annually. In order to feed the growing population the need of agriculture-dependent countries is to adopt more recent technologies which would be labor-saving and increase crop production. Among the various crop improvement technologies, nanotechnology holds an eminent position in crop improvement and food production to fulfill the demands in an efficient and cost effective way. Nanotechnology has the potential to revolutionize agricultural systems by precise farming techniques and therefore may emerge as a possible solution for increasing crop yields. It is the science of manipulating matter at nano-scale level and is developing as a revolutionary technology in current era. Agricultural production may be increased by nanotechnology in an eco-friendly way even in the challenging environment (Pirzadah et al. 2019). The full potential of nanotechnology in agriculture is not revealed and need to be explored to a large extent; this technique can benefit agriculture in multiple dimensions. Introduction of nanotechnology in agriculture aims at increase in yield, minimal loss of nutrients in fertilization, and reduction of chemicals for plant protection

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A. Jan (✉) · B. Malik
Department of Bioresources, University of Kashmir, Srinagar, Jammu and Kashmir, India

T. B. Pirzadah
Assistant Professor, University Centre for Research and Development (UCRD),
Chandigarh University, Mohali, Punjab, India

K. R. Hakeem, T. B. Pirzadah (eds.), *Nanobiotechnology in Agriculture*,
Nanotechnology in the Life Sciences, https://doi.org/10.1007/978-3-030-39978-8_9

(Chen et al. 2013). Nano-agrotechnology involves the use of nanoparticles (NPs) with unique properties to increase crop and livestock productivity (Scott and Chen 2002; Batsmanova et al. 2013). Various plant traits which contribute to growth, yield, and quality of produce can be altered by using engineered nanoparticles (ENMs) (Gardea-Torresdey et al. 2014).

Nanotechnology has the capability to ameliorate global food production and food quality through increased plant protection, detection of diseases, monitoring plant growth, and reduced waste for strengthening agriculture sustainability (Pirzadah et al. 2019). The use of nanotechnology in agriculture also involves fine delivery of fertilizers to increase plant growth and yield (Naderi and Danesh-Shahraki 2013), sensors for monitoring soil quality, and pesticides for pest and disease management (Liu et al. 2008). The potential of NPs, either metal-based (MBNPs) or carbon-based (CBNPs), has been documented in many research articles in relation to their uptake, internalization, translocation, persistence, and effect on growth and overall development in many plant species of different commercial importance. Some of these studies have shown beneficial role on plant growth and development upon exposure to NPs (Kole et al. 2013; Razzaq et al. 2016), while others show negative effects (Stampoulis et al. 2009; Yin et al. 2011). The beneficial role of NPs has been reported through the successful demonstration of enhanced percentage in seed germination (Gopinath et al. 2014), increased root and shoot length (Hafeez et al. 2015), increased fruit yield (Kole et al. 2013), enhanced secondary metabolite content (Kole et al. 2013), and a substantial increase in vegetative biomass of seedlings and plants in many crops. The use of NPs in crop improvement is still under investigation, its use must been seen on a regular basis in farmers' fields in the near future.

2 Nanoparticles as Magic Bullets to Modify Important Plant Traits

Seed germination rate is an important parameter for the initial assessment of the effects of various nanomaterials on the subsequent developmental stages of plants. The emergence of radicle and plumule is the initiation of seed germination and seedling growth. The effect of nanomaterials on plant germination and growth has been studied by various scientists with the aim to enhance its use in agriculture. For instance, TiO_2 nanoparticles (0.25–4%) promote photosynthesis and nitrogen metabolism in spinach and, therefore, improve the growth of the plants (Zheng et al. 2005; Klaine et al. 2008). Engineered nanoparticles (ENPs) may be classified into the metal (or non-metal) and metal oxide nanoparticles. Most widely used ENPs evaluated in the field of crop improvement include nano-ferrous/ferric oxides (Alidoust and Isoda 2013; Bakhtiari et al. 2015), nano-silver (Sharma et al. 2012; Razzaq et al. 2016), nano-gold (Arora et al. 2012; Kumar et al. 2013), nano-copper (Ngo et al. 2014), nano-zinc oxide (Burman et al. 2013), nano-titanium oxide (Feizi et al. 2013), nano-cerium oxide (Rico et al. 2014), carbon nanotubes, and fullerols (Villagarcia et al. 2012; Kole et al. 2013).

Carbon nanotubes enhanced elongation of roots in onion and cucumber and reduced root length in tomato as reported by (Cañas et al. 2008). It was reported that relatively low doses (10–40 μg/mL) of multiwalled carbon nanotubes (MWCNTs) were able to penetrate thick seed coats, increase germination, and stimulate growth in tomato plants which is due to enhanced water uptake efficiency (Khodakovskaya et al. 2013), surface chemistry of carbon nanotubes (Villagarcia et al. 2012), and activation of water channel proteins (aquaporins). Pristine MWCNTs enhanced growth and biomass of maize seedlings at low concentrations by increasing water absorption and concentrations of the essential nutrients Ca and Fe, but their effectiveness could be decreased by high concentrations of ions/polar species in the medium (Tiwari et al. 2014). They offered a credible utilization of CNTs for optimizing water transport in arid zone agriculture and for enhancing crop biomass yields. The diameter and length of single-walled CNTs (SWCNTs) are the major restraining attributes for their efficient penetration into the plant cell wall. Many researchers have shown the penetration of chemically shortened SWCNTs into both the cell wall and the cell membrane of tobacco (*Nicotiana tabacum*) and periwinkle (*Catharanthus roseus*) (Liu et al. 2009; Serag et al. 2011, 2012).

The effect of a carbon-based nanoparticle, fullerol, on agroeconomic traits in bitter melon was studied by Kole et al. (2013). The uptake, translocation, and accumulation of fullerol were confirmed through bright-field imaging and Fourier transform infrared spectroscopy. The seeds were treated with various concentrations (0.943, 4.72, 9.43, 9.88, and 47.2 nM) of fullerols; the positive and non-consequential effects on yield, plant biomass, fruit yield, and component characters were recorded. Increase in biomass yield 54% and water content 24% was recorded over control when treated with fullerol, whereas, fruit number, and fruit weight increased up to 20, 59, and 70%, respectively, that resulted in the improvement of up to 128% in fruit yield. The main factor responsible for increase in biomass and fruit yield is accumulation of fullerol in the different parts of plant at particular concentration. The potential of fullerene, C60, and CNTs to improve the water retention capacity, biomass, and fruit yield in plants up to 118% was proposed by Husen and Siddiqi (2014). These findings have a remarkable achievement of agri-nanotechnology in the field of crop improvement.

Different studies have been carried out to study the effect of metal-based nanoparticles (MBNP) such as silver (Ag), gold (Au), aluminum (Al), and copper (Cu) on plant growth and development (Barrena et al. 2009; Yuvakumar et al. 2011), promote growth and physiological activities (Salama 2012; Razzaq et al. 2016), enhance water and fertilizer use efficiency (Seif et al. 2011) and lead to nodule formation (Taran et al. 2014). SNPs have peculiar application in crop production. SNPs have a significant effect on plant growth by causing changes at physiological and molecular levels such as catalytic effects (Ma et al. 2010), decreasing the abscission of reproductive organs of plants (Seif et al. 2011), and are known to increase chlorophyll contents (Sharma et al. 2012). Silver nanoparticles are found to increase root length in maize and cabbage as compared to silver nitrate (Pokhrel and Dubey 2013). Razzaq et al. (2016) found that soil application of SNPs showed positive effect on wheat growth and yield. Application of SNPs at rate of 25–50 ppm resulted in increase in plant height, fresh and dry weight as compared to control. SNPs also affected the number of seminal roots in wheat. Soil applied SNPs showed favorable effects on plant growth which may be due to the more bioavailability and accumulation in plants, thereby stimulating plant growth. Razzaq et al. (2016) further reported that in order to explore precise concentration, suitable mode, and time of application to realize growth- and yield-enhancing potential of SNPs for wheat and other crops in an eco-friendly manner more investigations are required.

Indications of magnetic NPs were found in roots, stems, and leaves under hydroponic conditions, while the plants did not show any signs of magnetic NPs growing in soil or in sand confirming no particle uptake. Shah and Belozerova (2009) reported that nanoparticles (Pd, Au at low concentrations; Si, Cu at higher concentrations, and combination of Au and Cu) had a positive impact on seed germination and growth of the seedling of lettuce. The effect of colloidal solution of molybdenum nanoparticles (Mo NPs) on the microbial composition in the rhizosphere of chick pea (*Cicer arietinum*) was studied by Taran et al. (2014) and reported that seeds of chick pea when treated with combination of colloidal solution of Mo NPs (8 mg/L) and microbial preparation caused the development of "agronomically valuable" microflora and resulted in increase in number of nodules per plant by four times, while single treatment with colloidal solution of Mo NPs increased the number of nodules twofold as compared to control. Ma et al. (2010) reported the effects of four oxide nanoparticles (CeO_2, Lanthanum (III) oxide-La_2O_3, Gadolinium (III) oxide-Gd_2O_3, Ytterbium oxide-Yb_2O_3) on radish, rape, tomato, lettuce, wheat, cabbage, and cucumber plant species and reported that the nano-CeO_2 at 2000 mg/L concentration caused root elongation in lettuce and did not affect root elongation in other plant species. The other three types of nanoparticles (La_2O_3, Gd_2O_3, and Yb2O3) at same concentration greatly influenced root growth. The inhibitory effect of these nanoparticles was observed at various stages of root growth. The need is to understand the phytotoxic nature of the nanoparticles thoroughly before their application under field conditions. In order to avoid the phytotoxic effects of nanoparticles to other plant species the possible solution is to grow the plant seedlings in greenhouse and then transferring them to field.

3 Intervention of Nanoparticles in Metabolic Pathways

Secondary metabolites have medicinal properties and are also known as natural products or phytochemicals. It has been reported in various research papers that most of the secondary metabolites are beneficial for human body and are also considered as phyto-medicines. Secondary metabolites play a significant role in survival of plants, protection against pests, insect attack, mechanical injury, and other biotic and abiotic stresses (Misra et al. 2016). The various secondary metabolites include terpenoids, alkaloids, and phenolics (Kabera et al. 2014).

A great diversity of bioactive small molecular metabolites is present in plants that are highly important as pharmaceuticals, nutraceuticals, and agrochemicals. In some important medicinal plants the level of secondary metabolites is generally low. Nanotechnological approach especially ENPs are of great importance to enhance the production of essential medicinal compounds in plants. Although a number of studies have reported the effects of NPs on the growth and development of the plant, however only few reported the enhancement of secondary metabolite production in plants upon treatment with NPs (Nair et al. 2010; Krishnaraj et al. 2012). Raliya and Tarafdar (2013) reported that improved growth parameters and gum content might be due to adsorption of NPs on plant surface and taken up by the plants through natural nano or micro-scale openings.

Nanoparticles have the capacity to be used as novel effective elicitors in plant biotechnology for the elicitation of secondary metabolite production (Fakruddin et al. 2012). The role of NPs as elicitors is studied by many workers (Aditya et al. 2010; Asghari et al. 2012; Sharafi et al. 2013; Ghanati and Bakhtiarian 2014; Ghasemi et al. 2015). Ghasemi et al. (2015) and Yarizade and Hosseini (2015) studied the possible role of NPs as elicitors for improving the expression level of genes related to the production of secondary metabolites. The most popular groups of secondary metabolites in plants are flavonoids and isoflavonoids. Heiras-Palazuelos et al. (2013) reported that legumes are considered as rich sources of these secondary metabolites. Under in vitro conditions the increased production of secondary metabolites (phenols and flavonoids) in gram was recorded on exposure to TiO_2 NPs (AL-Oubaidi and Kasid 2015). It can be suggested that NPs can be appropriate candidates for elicitation studies of in vitro secondary metabolite production. An important stress hormone jasmonate (JA) enhances various plant defense responses, along with the biosynthesis of defensive secondary metabolites (Misra et al. 2016). Nanoparticles may play significant role in regulating the expression of genes for jasmonate production in treated cells. Induced jasmonate production may be responsible for enhanced production of hypericin and hyperforin. Misra et al. (2016) reported that secondary metabolites can be very important chemicals for the development of plants. The silver nanoparticles were used for elicitation of levels of capsaicin. Mediums with different hormonal combinations were prepared and growth was studied using qualitative analysis using iodine fumes. From this study it was concluded that the nanoparticles acted as an elicitor and brought about capsaicin increase effectively. The production of secondary metabolites through in vitro methods is widely being exploited. Various challenges are being faced for the synthetic production of the metabolites because of difficulty in decoding the biosynthetic pathway of the secondary metabolites. Therefore, in vitro methods like plant tissue culture and free cell suspensions in bioreactors are promising methods for obtaining the product in its natural form.

4 Conclusion and Future Perspective

Considering the major challenges faced by agricultural sector due to global climatic change, population explosion, and other geogenic activities nano-agrotechnology has a vast potential to enhance production yield by incorporating beneficial traits in the crops thus improves agricultural sustainability. Nanotechnology involves the efficient use of fertilizers and pesticides thus reduced the input cost. Moreover, this innovative technology involves the best approach of precision farming by employing the use of nano-biosensors which helps to monitor soil, temperature fluctuations for the effective management of bioresources. However, the nanotechnologists should focus on the cost–benefit analysis of nano-products and its impact on the environment besides unraveling the dynamic plant–nanoparticle interactions. Furthermore, there must be a collaborative approach and open dialog among government, non-government organizations (NGO), consumers, and other stakeholders regarding the acceptance and support of this novel technology.

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Development of Nano-formulations via Green Synthesis Approach

Tanveer Bilal Pirzadah, Bisma Pirzadah, Aarifa Jan, Fayaz Ahmad Dar, Khalid Rehman Hakeem, Seema Rashid, Sheikh Tanveer Salam, Pervaiz Ahmad Dar, and Mohammad Afaan Fazili

1 Introduction

Due to the growing population and other anthropogenic activities, global agricultural production faces many challenges such as decreased crop yield, soil fertility, soil degradation, low efficiency, and labor shortages due to expulsion from agriculture (Godfray et al. 2010; FAO 2017; Pirzadah et al. 2019). In addition, losses of biological resources are occurring at an alarming rate, with dramatic effects on people's livelihood. The population is projected to reach 8.5 billion by 2030, and it will be mandatory to generate at least 50% more production to feed such a large population (Wiens 2016). To combat future food crises, an effective protocol is

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T. B. Pirzadah (✉)
Assistant Professor, University Centre for Research and Development (UCRD),
Chandigarh University, Mohali, Punjab, India

B. Pirzadah · A. Jan · F. A. Dar
Department of Bioresources, University of Kashmir, Srinagar, Jammu and Kashmir, India

K. R. Hakeem
Department of Biological Sciences, Faculty of Science, King Abdulaziz University,
Jeddah, Saudi Arabia

Princess Dr Najla Bint Saud Al-Saud Center for Excellence Research in Biotechnology, King Abdulaziz University, Jeddah, Saudi Arabia

S. Rashid · S. T. Salam · P. A. Dar
Department of Zoology, Amar Singh College, Cluster University,
Srinagar, Jammu and Kashmir, India

M. A. Fazili
Section of Mycology and Plant Pathology, Department of Botany, University of Kashmir,
Jammu and Kashmir, India

Advanced Plant Physiology section, Department of Botany, Aligarh Muslim University,
Aligarh, Uttar Pradesh, India

K. R. Hakeem, T. B. Pirzadah (eds.), *Nanobiotechnology in Agriculture*,
Nanotechnology in the Life Sciences, https://doi.org/10.1007/978-3-030-39978-8_10

needed to manage and improve the agricultural sector. The exorbitant use of conventional fertilizers and pesticides to increase production efficiency is of course not an appropriate choice for the long term, as these fertilizers are considered a double-edged sword, which increases crop yields but at the same time, they have a detrimental effect on the soil microflora and thus reduce fertility (Pirzadah et al. 2019). In addition, it irreversibly damages soil texture and disrupts the balance of the food web in the ecosystem, which can lead to genetic mutations in future generations. The increased reliance on conventional fertilizers during and after the Green Revolution has caused serious problems of sustainability and health risks. To overcome the disadvantages of conventional fertilizers, bioformulations have been created to revolutionize the agricultural sector because of their eco-friendly nature and their cost-effectiveness (Mishra et al. 2015). Nevertheless, this approach has also been confronted with some problems, namely the short life span, stability, solubility, low absorption efficiency by plants, and the high doses required. To combat these problems, nano-formulations have received an overwhelming response due to superiority over bioformulations (Auffan et al. 2009). Nano-biotechnologies have thus become a promising tool to tackle the above-mentioned problems, particularly in the agricultural sector, to combat global food production and boost the agricultural sector (Shang et al. 2019). Nano-agribusiness is a new field that improves crop yields, regenerates soil health, ensures precision agriculture, and stimulates plant growth (Verma et al. 2018) (Fig. 1). Previously, these nano-formulations were pre-

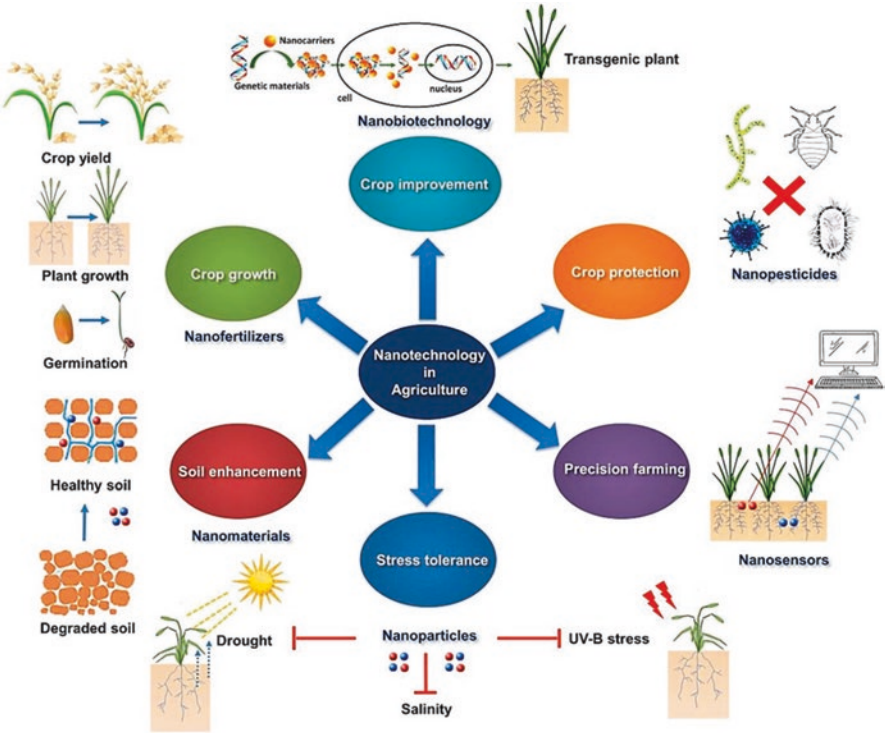

Fig. 1 Various applications of nanotechnology in the agricultural sector (Source: Shang et al. 2019)

pared by a conventional approach (chemo-synthesis) using different chemicals (ethylene glycol, hydrazine hydrate, sodium borohydride, etc.). However, this approach has not been considered environment friendly because of the adsorption of certain toxic chemicals besides, it was considered as costly approach (Huang et al. 2007). A green synthesis of nano-formulations has recently appeared in which biological entities (microbes and plants) play a leading role in the synthesis of different nano-formulations, leading to the evolution of a new field of nanobiotechnology. This sustainable path is gaining momentum because of its growing success and ease of formulation; it is also cost-effective and environment friendly. The exploitation of organisms for the production of nano-farming paved the way for a new and innovative approach for the development of these natural nano-agro-products (Iravani 2011; Pirzadah et al. 2019).

2 Microbes as Nano-factories for the Synthesis of Nano-formulations

Currently, synthesis of nano-formulations using microbes as nano-factories is an attractive and a promising alternative to conventional approach. The biological systems for synthesis of nano-formulations utilize mostly microbes since they naturally produce inorganic materials either intra-cellularly or extra-cellularly, for instance, magnetostatic bacteria used for magnetite, diatoms used for siliceous material, and S-layer bacteria used for gypsum and calcium carbonate (Sastry et al. 2003). Nano-biotechnological way for the synthesis of nano-formulations possesses many advantages, such as use of known microbial technologies and processes for scaling up of biomass. This is leading to economic viability, possibility of readily covering large surface areas by suitable growth of the microbes, which is of major advantage in the field of agriculture for easier production of bioformulations. The green synthesis of nano-formulations involves the use of microbial enzymes to break down the respective salts into nanoparticles (Duhan et al. 2017). Besides, these also act as templates in the biosynthesis process, assembly and organization of nanometer scale material to formulate precise micro and macro scale structures. Further the organic polymers can play important role in ecosystems by accumulating biologically important elements and also by retaining soil moisture after aggregating soil particles (Ding et al. 2015). Extracellular polymeric substances (EPS) play an important role in cell aggregation, cell adhesion, and biofilm formation that subsequently protect cells from a hostile environment (Ding et al. 2015). Furthermore, certain polysaccharides from microbial sources are surface active, and thus attempts have been made to use them as metal chelators (Sutherland 1998; Prasad et al. 2018), emulsifiers (Cirigliano and Carman 1984), and flocculants (Choi et al. 1998) in industrial and environmental fields/domain. Such use of microbial polysaccharides has infused renewed interest in its production and characteristics (Raliya et al. 2013). Worldwide efforts are being done in this direction to make the nano-formulation technology cost-effective. The formulation of any nano-formulations should be in such a way that they possess all desired properties such as high solubility, stability, effectiveness, time-controlled release, enhanced targeted activity with effective concentration, and less eco-toxicity with safe, easy mode of delivery and disposal (Torney et al. 2007). Recently, myconanotechnology has emerged as an attractive field where fungi can be used to synthesize the nanoproducts which possess great application in agriculture sector. Fungi play a lead role in the biosynthesis of nanoparticles because of the potent efficiency in extracellular as well as intracellular enzyme production compared to other microorganism like bacteria and actinomycetes (Rai et al. 2009; Narayanan and Sakthivel 2010; Prasad 2017; Pirzadah et al. 2019). Some microorganisms possess innate ability to survive in extremophilic conditions such as high metal concentrations and this is due to some important mechanisms like efflux systems, oozing out some organic acids that cause precipitation of metals through redox reactions or chelate formations. However, in case of microorganisms culturing protocol is an essential parameter, thus standardization of culturing parameters (pH, nutrients, temperature, light, etc.) is of paramount importance to enhance the activity of enzymes (Mukherjee et al. 2001a; Iravani 2011). The mode of nanomaterial fabrication using mycogenic approach is represented in Fig. 2. Several studies reported the

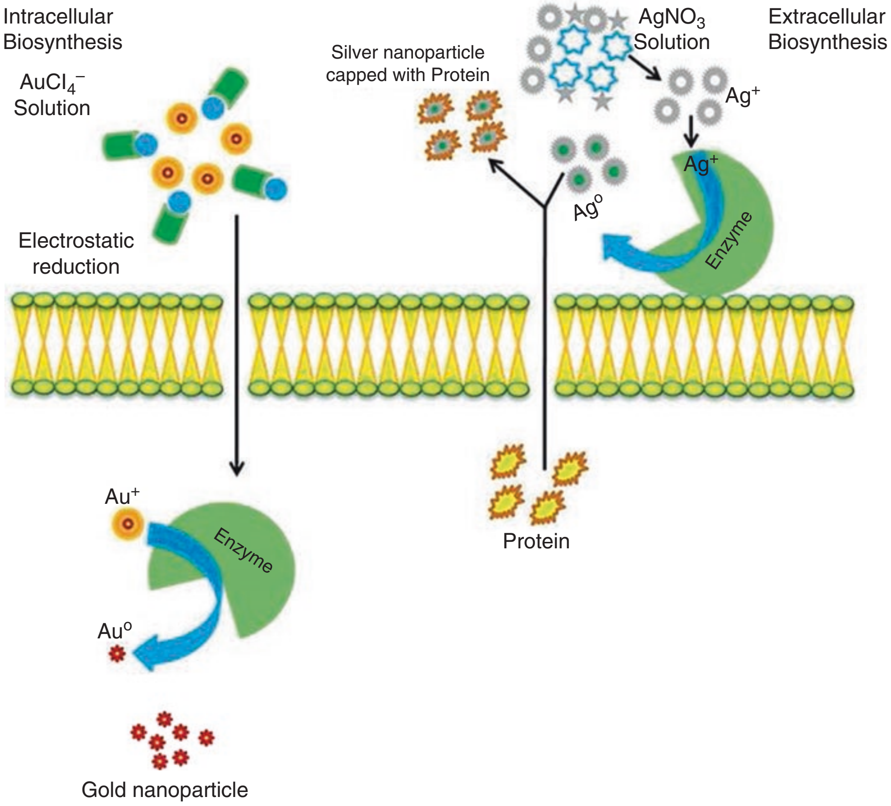

Fig. 2 Synthesis and fabrication of nanomaterials using mycogenic approach (Source: Pirzadah et al. 2019)

usage of distinct microorganism in the nano-formulation production and accordingly an appropriate framework for selecting a specific organism for a particular purpose has been developed (Fang et al. 2019) (Table 1). A number of microorganisms and algae have been reported for the biosynthesis of silver-nano-formulations (Ag-NP) viz., *Pseudomonas stutzeri*, *Verticillium* spp., *Lactobacillus* spp., *Fusarium oxysporum*, *Aspergillus* spp., *Trichoderma* spp., *Chaetomorpha linum, Oscillatoria limnetica* (Klaus et al. 1999; Mukherjee et al. 2001b; Nair and Pradeep 2002; Duran et al. 2007; Binupriya et al. 2010; Thakkar et al. 2010; Kannan et al. 2013; Hamouda et al. 2019). However, the main limitation of this approach involves costly media, maintenance, purification technique, and labor-intensive.

3 Synthesis of Nano-formulations Using Phyto-Nanotechnology Approach

Recently, phyto-nanotechnology gains a rapid momentum for the production of nano-formulations because of cost-effectiveness and eco-friendly nature. It is a promising alternative to conventional chemical approach and more complex culturing and isolation techniques needed for various microorganisms. Besides, the plant extract acts both as reducing and capping agent during synthesis of nano-formulations (Sathishkumar et al. 2009; Singh et al. 2010; Selvaraj et al. 2019). As plants are rich sources of secondary metabolites; however, the composition and

Table 1 Quality criteria of carriers for the development of smart fertilizers based on microbial inoculants (adapted from Sahu and Brahmaprakash 2016)

Quality criteria of model carriers of bioformulations	References
High water-holding and water-retention capacity and suitable for as many bacteria as possible/cost-effective	Mishra and Dahich (2010)
Free from lump-forming material/near sterile or easy to sterilize by autoclaving or by other methods like gamma irradiation/nearly neutral pH or easily adjustable and good pH buffering capacity	Keyser et al. (1993)
Available in adequate amounts/nontoxic in nature	Bazilah et al. (2011)
For carriers used for seed treatment, should assure the survival of the inoculants on the seed since normally seeds are not immediately sown after seed coating	Muresu et al. (2003)
For carriers that shall be used for seed coating, should have a good adhesion to seeds	Hegde and Brahmaprakash (1992)
No heat of wetting/easily biodegradable and non-polluting/supports growth and survival of bacteria/amenable to nutrient supplement/ manageable in mixing, curing, and packaging operations	Smith (1992)
Chemically and physically uniform	Bashan (1998)
The inoculant should be non-toxic, biodegradable, and non-polluting, and should minimize environmental risks such as the dispersal of cells to the atmosphere or to the ground water	Bashan (1998)

concentrations of these metabolites varies depend upon various parameters such as genotype, altitudinal variation, and edaphic factors. Some plants possess an innate ability to hyper-accumulate metal ions and reduce them into elemental form via redox reaction pathway and such a unique property of plants can be exploited for the production of nano-formulations or detoxify the toxic metals and thus rejuvenates the soil health (Kale et al. 2013; Kulkarni and Muddapur 2014). The commercial production of nano-formulations using plant extract is quite easy and less time-consuming as the isolation and purification technique of plant extract is efficient, feasible, and biocompatible in nature. Jinghua (2004) reported that patented nano-formulation (N, P, K, micronutrients, mannose, and amino acids) that significantly enhance the uptake and utilization of nutrients in grain crops. Deficiency of micronutrients such as zinc is a major problem especially in arid or Mediterranean soils which are rich in calcium carbonate and thus possess alkaline pH and such conditions cause precipitation of the zinc and thus makes it unavailable to the plants and therefore is considered as a main limiting factor that causes decline in the production yield (Takkar and Walker 1993). This problem can be overcome by the application of the zinc oxide nanoparticle due to high efficacy and available form to plants than using its conventional form (Gangloff et al. 2006; Duhan et al. 2017). Chaudhuri and Malodia (2017) carried out the synthesis of zinc oxide (ZnO) nano-formulation using the leaf extract of *Calotropis* which upon foliar application on various plants (*Azadirachta indica*, *Alstonia scholaris*, *Pongamia pinnata*) showed a significant growth. Copper nano-formulations prepared by using *Allium cepa* extract showed a positive impact in wheat plants by enhancing germination rate and growth of the seedlings (Bhanushali et al. 2017). In another study, iron oxide nano-formulations enhance the growth and carbohydrate concentration in *Catharanthus roseus* plants (Naderi and Shahraki 2013). Macronutrients such as nitrogen (N) have been recently reported to be used as nano-formulations (nano-urea) in China to enhance the production yield of some specific crops (rice, tomato, cabbage, celery, etc.). It has been reported that application of nano-urea in the rice field greatly enhances the grain yield and N uptake and prevents nitrogen loss (74%) with respect to conventional urea (Huang et al. 2015). Lahiana et al. (2013) reported that carbon nanotubes enhance germination rate and boosts growth of plants. Similarly, Benzon et al. (2015) reported that nano-formulation application in rice fields accelerates growth, metabolite concentration, and crop yield.

4 Chemistry Behind Green Synthesis of Nano-formulations

The nano-formulations synthesis via plants involves the mixing of the respective salts with the plant extract which undergo redox reactions and the production of nanoparticle is indicated by the change in color of the reaction mixture (Fig. 3). Usually, the synthesis of nanoparticles via plant extract involves the donation of electrons to the metal ions and resulting in the formation of nanoparticles. During the biosynthesis of nano-formulations, there is an initial activation period when

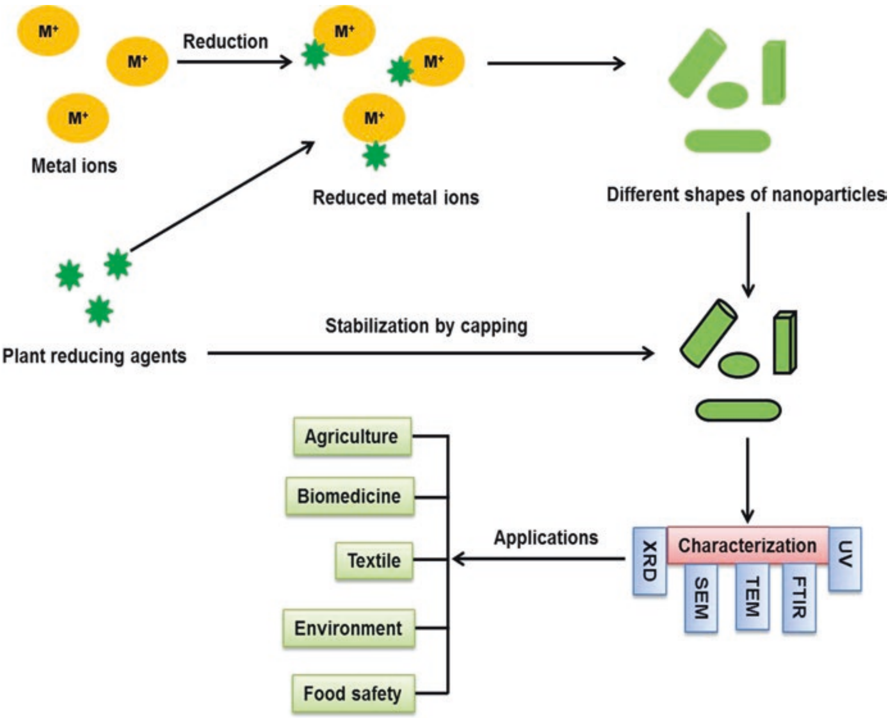

Fig. 3 Schematic diagram showing possible mechanism behind the biosynthesis of nanoparticles that involves mixing of the respective salts with the plant extract which undergo redox reactions and the production of nanoparticle is indicated by the change in color of the reaction mixture

processed metal ions are changed into their elemental form (zero valent) from mono or divalent oxidation states and later on nucleation of the reduced metal atoms takes place (Malik et al. 2014). This is rapidly followed by the amalgamation of smaller nanoparticles resulting in the formation of thermodynamically more stable larger nanoparticles while the process of reduction of metal ions continues and further growth processes lead to the production of nanoparticles in varied shape and size viz., hexagons, rods, wires, spheres, and cubes and the energy in the form of heat plays a key role in the reaction (Akhtar et al. 2013). This reaction continues until the capping agent from the biological entity (plant extracts), which will eventually inhibit the growth of the high-energy atomic growth planes which in turn leads to the formation of specific type of nanoparticles. In other words, these nanoparticles have the tendency to revert to their lower-surface energy state from high-energy state by agglomeration. Therefore, the presence of large concentration of reductants and stabilizing agents inhibits the agglomeration of nanoparticles and thus helps the formation of smaller nanoparticles. However, the morphology of the synthesized nanoparticle depends upon several factors like concentration of respective salt, pH, temperature, concentration and source of metabolites and reaction time (Mittal et al. 2013; Dwivedi and Gopal 2010; Malik et al. 2017).

5 Integration of Bio-fertilizers with Nanotechnology

An innovative approach to the use of green manure has been used as a promising alternative to fertilizers for sustainable agriculture (Mishra et al. 2015). However, the organic fertilizers possess certain limitations such as low stability, efficiency, and performance under changing weather conditions and the most important factor involves the application of high dosage for maximum coverage area. In recent years, nanotechnologies have become a tool in the agricultural industry to promote growth and productivity through the design and development of ultra-small particles possessing large surface to volume ratios and high efficacy compared to classical approaches. Nanotechnology is an emerging field that has revolutionized the world and it involves a multidisciplinary approach and is considered as the sixth most revolutionary technology of the present era (Knell 2010). The world's nanotechnology industry is predictable, with an estimated value of 75.8 billion US$ by 2020, thanks to remarkable global development (Research and Markets 2015). There is no doubt that nanotechnology has evolved into the development of solid applications in many of the aforementioned mechanical segments. At the same time, nanotechnology can potentially benefit society and change the agricultural sector. This technology has sponsored that agribusiness sector with yearly development rate of 25% (US$ 1.08 billion). Moreover, joining of cutting edge nanotechnology in agro-food business would increase global monetary development to US$ 3.4 trillion by 2020 (Sabourin and Ayande 2015). This makes it clear that the role of agro-nanobiotechnology in agriculture is essential, without negative impact on the environment and other problems of regulation of biosecurity. Agro-nanobiotechnology is an innovative green technology that offers global food security, sustainability, and climate change (Mishra et al. 2014).

6 Need of the Green Synthesis of Nano-formulations

The nano-fertilizers possess the efficiency to reduce nutrient loss via leaching and prevent brisk modifications in their chemical nature which in turn increases the nutrient use efficiency and thus addressing fertilizer related environmental concerns. Moreover, the application of nanotechnology in agriculture counteracts the problems such as crop yield, food security, climate change, and sustainability (Mishra et al. 2014). Nano-fertilizers are a nano-structured formulation that delivers nutrients to the plants, allowing dynamic uptake or gradual discharge of active ingredients. Nanoparticles are regarded as efficient vehicles to carry nutrients to the target site by encapsulation or in the form of emulsion of nanoscale dimension. However, the surface coating of nano-materials on fertilizer particles holds the material more firmly due to higher surface tension than the conventional surfaces and thus aids in controlled release (Brady and Weil 1999; DeRosa et al. 2010). Cui et al. (2010) reported that nano-fertilizers possess a great advantage over conventional fertilizers as they exhibit specificity, reduced toxicity, and gradual release of nutrients. Nanoparticles have great potential to deliver nutrients to specific target sites in living systems. The loading of nutrients on the nanoparticles is usually done by means of following approaches like absorption on nanoparticles, attachment on nanoparticles mediated by ligands, encapsulation in nano-particulate polymeric shell, entrapment of polymeric nanoparticles, and synthesis of nanoparticles composed of the nutrient itself. Corradini et al. (2010) evaluated the interaction and stability of chitosan nanoparticles suspensions containing N, P, and K fertilizers which can be useful for agricultural applications. Kottegoda et al. (2011) synthesized urea modified hydroxyapatite (HA) nanoparticles for gradual release of nitrogen with the crop growth. These nano-fertilizers showed initially burst and subsequently slow release of nitrogen up to 60 days of plant growth compared to commercial fertilizer which shows release only up to 30 days. The large surface area of HA facilitates the large amount of urea attachment on the HA surface. Strong interaction between HA nanoparticles and urea contributes to the slow and controlled release of urea. Similarly, polymer-based mesoporous nanoparticles can also provide efficient carrier system to agrochemical compounds which improves the efficiency and economical utilization. Mesoporous silica nanoparticles (150 nm) have been reported to entrap urea. It has been observed that 15.5% of urea was loaded inside the nanoparticle pores and demonstrated a controlled urea release profile in soil and water. The study revealed at least fivefold improvements in release period (Wanyika et al. 2012). Zinc solubility and dissolution kinetics of ZnO nanoparticles and bulk ZnO particles coated on macronutrient fertilizers (urea and monoammonium phosphate) have been compared by Milani et al. (2012). They reported that coated monoammonium phosphate granules show faster dissolution rate.

7 Conclusion and Future Perspective

In the present scenario, the exorbitant use of fertilizers in the agricultural sector to increase production not only affects the quality of the soil, but also has adverse effects on the environment. It is essential to improve agricultural production to meet the demand of the population, without negative impact on the environment, so eco-friendly synthesis approaches must be considered. Nanotechnology is a promising approach that has revolutionized the agribusiness sector. The use of microbial enzymes for nano-fertilizer biosynthesis is gaining momentum in nano-bioformulations because of its excellent efficiency and cost-effective nature. Due to the small size of nano-fertilizers (chemically synthesized), a risk assessment for our environment is needed, especially in terms of consumption in the form of food or feed. However, nano-biofertilizers appear to be more eco-friendly since they are synthesized from the biological form, but this does not mean that their risk assessment is not required. In addition, it is necessary to develop more technologies for the synthesis of nanoparticles containing microorganisms well adapted and adapted within the rhizosphere of a given plant. This could help to develop nano-biofertilizers specific to crops/plants (biomimetic approach) and thus help improve yield. This technology would not only help us today, but also future generations and play an active role in global food security.

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Nano-agrochemicals: Economic Potential and Future Trends

Gazala Qazi and Fayaz Ahmad Dar

1 Introduction

The human population is increasing at an alarming rate and the present status being 7.7 billion as per the recent United Nations reports; in contrast to this the agricultural land covering 38.4% as of 2011 of the world's land area (FAO/WHO 2013) is shrinking due to rapid urbanization, desertification, abandonment, and mal-agricultural practices thus, leading to the scarcity of food production. Further, the farmers find it challenging to generate the adequate money from the conventional agricultural practices, hence they are forced to use the fertilizers (especially the synthetic ones) and other chemicals like pesticides, herbicides, fungicides, etc. indiscriminately which leads to the increase in the yield but at the same time have the negative impact on the environment causing pollution, biodiversity loss, biomagnification, and ultimately degradation of soil quality. So, we are in dire need of a miraculous product which will eradicate this problem. Nanotechnology can rescue us in solving this problem because novel nano-agricultural products also known as nano-agrochemicals can be formulated through this emerging technology. The agricultural products thus formed are known as nano-agrochemicals which are an amalgamation of nanotechnology and agrochemicals and have resulted in the production of nano-fertilizers, nano-herbicides, nano-fungicides, nano-pesticides, nano-insecticides, and so on. Furthermore, agriculture is the backbone of developing nations, with more than 60% of the population depending on it for their livelihood (Brock et al. 2011). Currently, the major challenges faced by world agriculture

G. Qazi (✉)
Department of Botany, Islamia College of Science and Commerce, Srinagar,
Jammu and Kashmir, India

F. A. Dar
Department of Bioresources, University of Kashmir, Srinagar, Jammu and Kashmir, India

K. R. Hakeem, T. B. Pirzadah (eds.), *Nanobiotechnology in Agriculture*,
Nanotechnology in the Life Sciences, https://doi.org/10.1007/978-3-030-39978-8_11

include changing climate, urbanization, sustainable utilization of bioresources, and environmental issues like runoff and accumulation of pesticides and fertilizers. These problems are further intensified by an alarming increase in food demand that will be needed to feed an estimated population of 9.7 billion by 2050 (Chen and Yada 2011).

2 Advantages of Nano-agrochemicals Over Conventional Agrochemicals

Nanotechnology is the emerging science which involves integration of some basic science secrets and facts at nano-scale level (Rajemahadik et al. 2018). Nowadays, nano-agrochemicals have gained popularity due to their greater effectiveness compared to conventional agrochemicals thereby making them economically viable and eco-friendly. Nano-fertilizers are advantageous over conventional fertilizers as they increase soil fertility, yield, and quality parameters of the crop besides being non-toxic and eco-friendly in nature and therefore minimize the input cost and maximize profit. Further, nanotechnology provides many nano-devices as well as materials which have a remarkable role in agriculture, like nano-biosensors which can detect moisture content as well as nutrient status in the soil and thus finds its application in site specific water and nutrient management, nano-fertilizers for the efficient nutrient management, nano-herbicides for selective weed control in crop field, nano-nutrient particles to increase seed vigor, and nano-pesticides for efficient pest management (Qureshi et al. 2018). Hence, nanotechnology has greater role in crop production with environmental safety, ecological sustainability, and economic stability (Qureshi et al. 2018). The nanoparticles produced with the help of nanotechnology can be exploited in the value chain of entire agriculture production system (Hamid 2012). Nano-agrochemicals have the potential to revolutionize agriculture and some of the potential nano-agrochemicals which are expected to do wonders in agricultural sector are discussed as below:

2.1 *Nano-fertilizers*

Nano-fertilizers are considered as smart fertilizers that play a lead role in the agricultural sector to improve soil fertility, productivity, and quality of agricultural products (Meena et al. 2017). Nano-scale materials exhibit unique properties when compared at their bulk level (Klabunde 2002). These unique properties of nano-fertilizers include their penetration capacity, size, and more surface area than the identical material found in their bulk form. The reason for the higher surface area is the minute size of the particles making them very reactive and soluble in nature. Sometimes, the particle size of the nano-fertilizer is less than the pore size of roots and leaves, thus increasing their penetration power into the plant when applied even on the surface of the plant and subsequently increasing the nutrient use efficiency thus minimizes the input cost (Lin and Xing 2007; Nair et al. 2010). Fertilizers encapsulated in nanoparticles will increase availability and uptake of nutrient to the crop plants (Liscano et al. 2000). Nanoparticle size below 100 nm can be used as fertilizer for efficient nutrient management which are more eco-friendly and reduce environment pollution (Chinnamuttu and Kokiladevi 2007). Foliar application of nanoparticles as fertilizer significantly increases yield of the crop (Liu et al. 2005). Nanotech materials are being developed for slow release and efficient dosages of fertilizers for plant (Tarafdar et al. 2012). Slow-release fertilizers are excellent alternatives to soluble fertilizers as nutrients are released at a slower rate throughout the crop growth; plants are able to take up most of the nutrients without wastage by leaching.

2.2 Nano-herbicides

Nano-herbicides are promising alternative to conventional herbicides as they are effective to eradicate the weeds, thus plays a pivotal role in the weed management program (Berekaa 2015). These eradicate the weeds by either destroying their gene banks in the soil or prevent their germination. Owing to their minute size these nano-herbicides have the capacity to mingle with the soil and thus destroy the weeds in an eco-friendly manner without leaving any toxic residues besides these smart chemicals help to eradicate those weeds which have become resistant to conventional herbicides. For instance, alginate/chitosan based nanoparticles can be used as herbicide carrier material especially for herbicide such as paraquat (Ghaly 2009).

2.3 Nano-fungicides

Plant diseases have caused severe losses to humans ever since the beginning of agriculture (Dangl and Jones 2001) and these pathogens are able to contaminate any plant tissue at different stages of crop growth (Francisco et al. 2007). The main causative agents include fungi, bacteria, viruses, protozoa, and plant parasites; however, the fungi plays a dominant role and it has been reported that approximately 85% of all plant diseases are fungal in nature (Giraud et al. 2010; van Bruggen and Finckh 2016; Parul et al. 2017). Kamel and Mousa (2015) reported that phytopathogenic fungi comprise an important group of plant pathogens that cause approximately $45 billion losses in crop yield every year all over the world. To combat fungal diseases, farmers have been evolving their practices by using various types of chemical fungicides such as mancozeb (Pirozzi et al. 2016), kitazin (Bass et al. 1981), and copper hydroxide (Capinera and Dickens 2016) but the main limitation of using these conventional fungicides involves developing resistance by the microorganism against the particular fungicide thereby declines the crop yield

(Wiesner-Hanks and Nelson 2016). Moreover, the plants develop the resistance to fungicides either instantly or slowly. Thus, farmers either use single or a blend of fungicides or in bulk quantities to control various fungal diseases which can lead to either damaged crops or accumulation of residues in the plant which in turn enters food chain and causes detrimental effects to human health (Shukla and Arora 2001; Ragsdale and Sisler 1994; Lundqvist et al. 2016). Thus, with the escalating demand to control these fungal pathogens, there is a dire need to control the excessive usage of fungicides by discovering eco-friendly substitutes. Nanoparticle (NP) based materials have received increasing attention due to their unique physical and chemical properties, which differ significantly from their conventional macroscale counterparts (Phogat et al. 2016). Due to the antimicrobial properties of these nano-based materials, they find great applications in the agricultural sector by controlling various diseases (Panacek et al. 2009; Gutierrez et al. 2010; He et al. 2011; Wani and Shah 2012; Kanhed et al. 2014). However, Parul et al. (2017) reported the limited application of these smart chemicals in agriculture due to their cytotoxicity in plants.

2.4 Nano-pesticides

The nanotechnology has helped in making efficacious pesticides and prevention of their dangerous dissemination in the environment by placing these pesticides in nanometer capsules which can accurately control the rate of pesticide release from the capsule as per need of crops (Alfadul et al. 2017). Nano-encapsulated pesticide formulation is able to reduce the dosage of pesticides and human exposure to them, which is eco-friendly for crop protection (Nuruzzaman et al. 2016).

2.5 Nano-insecticides

Insecticides are the substances which are toxic in nature and are primarily used to kill insects that can cause various diseases in plants. It is estimated that insect causes an estimated loss of 14% which is approximately about US$ 2000 billion/annum in crop yield worldwide and thus affects the agricultural economics (Pimentel 2009; Kamel and Mousa 2015). To combat such a huge loses, insecticides are considered to be the main factor for increasing the agricultural productivity in the twentieth century. Further, nanoparticles as potential insecticides have been reported to play a lead role in insect pest management (Bhattacharyya et al. 2010). Nanotechnology in the management of polyphagous pest such as *Helicoverpa armigera* has been earlier reported (Vinutha et al. 2013). Synthesized silver nanoparticles possessed excellent anti-lice and mosquito larvicidal activity (Jayaseelan et al. 2011). Nano-encapsulation helps slow release of a chemical to the particular host for insect pest control through release mechanisms that include dissolution, biodegradation, diffusion, and osmotic pressure with specific pH (Vidyalakshmi et al. 2009). Nanoparticles loaded with garlic essential oil proved effective against *Tribolium castaneum* Herbst (Yang et al. 2009). Nanocopper particles suspended in water have been used since 1931, in a product commercially known as Bouisol as fungicide in the growing of grapes and fruit trees (Hatschek 1931).

3 Economic Importance of Nano-agrochemicals

Nano-agrochemicals owing to their enormous benefits in agriculture have helped the farmers economically by increasing the yield of crops both qualitatively and quantitatively thereby substituting synthetic fertilizers and pesticides in order to maximize the output and conserve the input which leads to economic prosperity. Reports of BCC (Business Communications Company) research released in 2016 indicated that the global nanotechnology market will reach $90.5 billion by 2021 from $39.2 billion in 2016 at an annual growth rate of 18.2%. The nanotechnology market is expected to grow by 30% annually and is expected to increase in near future due to its immense applications in the agro-industry (Shalini 2006). Nowadays, farmers are being exposed to the new innovations, formulations, and technologies which help them to increase the economic benefits from their farming practices. One such technology is the nanotechnology and as discussed earlier nano-agrochemicals have proved to be a boon for farmers as they tend to increase the production yield. Possible agri-food nanotechnology applications include nano-sensors/nano-biosensors for detecting pathogens and soil quality and plant health monitoring, nano-porous zeolites for slow release and efficient dosage of water and fertilizers for plants and of nutrients and drugs for livestock, nano-capsules for agro-chemical delivery, creating biofuels, nano-composites for plastic film coatings used in food packaging, antimicrobial nano-emulsions for applications in decontamination of food, nano-biosensors for identification of pathogen contamination, and improving plant and animal breeding (Bhupinder 2014). The development of high-tech nano-devices would certainly lead to a revolution in agricultural practices, and could possibly contribute in reducing the impact of modern agriculture on the environment (Scott and Chen 2002; Sekhon 2014; Liu and Lal 2015). The extent to which nano-agrochemicals develop will be strongly influenced by the regulatory system that controls their entry into the market and at present, great geographical discrepancies, which may eventually shape applications emerging in a given market (Watson et al. 2011). However, industry has a key role to play, for instance, by supplying the necessary data and product information, and sharing their technical, scientific, and policy expertise (Watson et al. 2011). The introduction of nanotechnology (nano-agrochemicals) in the agricultural sector has already paved a way to increase agricultural productivity and to protect the environment at the same time. The use of nano-materials has improved the quality of the environment and helped to detect and remediate polluted sites; however, only a small number of nano-materials demonstrated potential toxic effects (Mura et al. 2013).

4 Nano-agrochemicals and Environment

The use of nano-agrochemicals benefits the agriculture but at the same time it also has negative impact on the environment. The possible reasons being the size of these nanoparticles which can easily find their way into the living organisms, making them dangerous. The nano-agrochemicals are the novel products and the farmers are not aware about their benefits yet. Further, their use has the stigma attached to them due to the lack of awareness about them, thus these are not used extensively. Moreover, agro-nanotech innovative products are experiencing difficulties in reaching the market, making agriculture still a marginal sector for nanotechnology (Claudia et al. 2015). The reason being the high investments involved in manufacturing nano-agrochemicals, lack of knowledge about the benefits associated with their use, legislative unpredictability, and most importantly their acceptance by the common man. Agrochemicals are an integral part of agriculture, but till date nano-agrochemicals have received less attention in this sector. Due to their direct and intentional application in the environment, nano-agrochemicals may be regarded as critical in terms of possible environmental impact, as they represent the only intentional diffuse source of engineered nanoparticles in the environment (Kah et al. 2013).

5 Conclusion and Future Perspectives

It can be concluded that nanotechnology will have a bright future in agriculture because of the world’s unquenchable thirst for compact, efficient, and eco-friendly agrochemicals to meet the needs of growing human populations and shrinking agricultural land area. However, nano-agrochemicals are still in its infancy and are facing obstruction to reach the farmers. In near future, novel agro-formulations like organic based nano-materials with greater benefits are believed to transform and upgrade agriculture to a greater extent across the world. In contrast, it can also be predicted that nano-agrochemicals have the ability to become pollutants, because of their miniature size, that makes them toxic and therefore extensive research needs to be performed before they reach the farmers for application in the field. Further, market oriented inventions in the field of nanotechnology will create more economic opportunities. All scientific discoveries do not make it to the markets easily because a scientist can make an innovative product but he is not necessarily well equipped with skill of marketing the same. So, scientific discoveries should take the help of the marketing professionals in order to transform the scientific discovery into the commercially viable product.

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CRISPR/Cas9: A New Revolutionary Science in Agricultural and Horticulture

Quazi Mohammad Imranul Haq and Touseef Hussain

1 Introduction

For the past few decades, plant biotechnologists unravel our understanding of biology of the plants and have made crop plants with valuable novel agricultural and nutritional traits that are valuable to the farmers, consumers, and the environment to boost the sustainability (Ronald 2011). Biotechnology acts as an important tool to offer innovation and economic ways to produce a diverse range of new products. The plants with abiotic stress tolerance, disease, pest, herbicide resistance, and better nutritional profile have been produced through transgenic integration and RNA interference (RNAi)-gene silencing approaches (Sedeek et al. 2019). However, transgenic plants or genetically modified organisms (GMOs) are mostly produced with a single transgene inserted into the plant genome, and the transgenes are often from heterologous organisms. It is difficult to engineer plants that are resistant to more than one pest through the single transgene integration. Tolerant engineering plant is also a challenge because of a multiple environmental stresses, such as heat, drought, heavy metal, and salinity because there are complex responses from plants to stress (Pandey et al. 2017). Additionally, the integration of transgenes is random in the genome and difficult to control. Technologies other than transgene integration should be explored to better engineer stress tolerance and pest resistance in plants. Increasing public concern regarding genetically modified organisms (GMOs) should also be addressed (Bawa and Anilakumar 2012). Whole genome information and functional genomics have greatly enhanced our ability to engineer plant

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Q. M. I. Haq (✉)
Department of Biological Sciences and Chemistry, College of Arts and Sciences,
University of Nizwa, Nizwa, Oman

T. Hussain
Plant Pathology and Nematology Section, Department of Botany, Aligarh Muslim University,
Aligarh, U.P., India

K. R. Hakeem, T. B. Pirzadah (eds.), *Nanobiotechnology in Agriculture*,
Nanotechnology in the Life Sciences, https://doi.org/10.1007/978-3-030-39978-8_12

genomes in the past decade. As more information on the molecular mechanisms between plant and pest/stress interactions becomes available, it is feasible to manipulate plant genomes by disrupting the host factors that contribute to the pest and stress interactions. RNAi technology has been used to produce plants that are resistant to diseases because RNAi normally leads to downregulation rather than complete inhibition of target genes.

The new, exciting, and amazing gene editing technology known as Clustered Regularly Interspaced Short Palindromic Repeats/CRISPR-associated (CRISPR/Cas9) system that came into existence recently can potentially solve the problems encountered by conventional transgene and RNAi technologies. CRISPR/Cas9 system is usually used to refer to a revolutionary genome editing technique that enables efficient and accurate genomic modifications in a wide variety of organisms and tissues (Sedeek et al. 2019). CRISPR is the section of the genetic code, in which there is small duplication of the base sequence, followed by spacer DNA segments. It uses a synthetic guide RNA to introduce a double strand brake to a specific location within the strands of DNA. Cas9 had discovered several restrictions nucleases (or molecular scissors) that enable CRISPR genome editing. The CRISPR/*Cas9* system has been adapted as a powerful tool that brings the genome modifications to the mainstream. In the implementation of pathogen resistance in plants, genome editing technologies have rapidly progressed and become most important genetic tools (Borrelli et al. 2018). In this review, here we summarize how CRISPR/*Cas9* technology plays a pivotal role to generate abiotic stress tolerant crops to boost agricultural productivity.

2 CRISPR/Cas9: A Remarkable Genome Modification Tool in Plants

In recent years, genomic DNA had many independent studies reporting the repair applications of the CRISPR/Cas9 system, a DNA repair system prone to congenital errors that is ideal for mutation. Known for the remarkable adaptive immune system based on nucleic acid bacteria or archaea, the researchers re-initiated the CRISPR/Cas9 system into molecular technology to create double stranded breaks (DSBs) in specific genomic sites to facilitate site-specific genome editing (Schiml and Puchta 2016; Schwank et al. 2013). The creation of a unique RNA (sgRNA) guide, which is able to correctly address Cas9 at the predetermined site in the host genome, was the most innovative review. Therefore, the CRISPR/Cas9 system has been reduced not only by three or two component numbers, but has also been able to design modular or vector DNA expression for a possible simple and high-throughput selection of DNA sites in genomes in all organisms, including humans, animals, and plants.

In making such a modular DNA expression, the synthesis of oligonucleotides from targeting sites was necessary for a new orientation and, originally, they were required to be assembled in modular form for the cRNA spacer. This technical simplicity represents a significant reduction of the essential resources needed to create the previous genome modification tools, such as TALEN to indicate a new site because TALEN works in pairs and each TALEN compilation should synthesize the 2000 bp DNA fragment for mounting. This system has been tested on many plant species, including Arabidopsis, rice, sorghum, tobacco, and wheat. It is unique in terms of hardness and degree during the adoption of the CRISPR/Cas9 system in the plants because in August 2012 this system was demonstrated in bacteria (Shalem et al. 2014; Shan et al. 2014).

3 CRISPR/Cas9: An Innovative Genome Editing Tool to Enhance Production Yield

CRISPR/Cas9 technology was first reported in 2012 and since then thousands of research papers have been published (Adli 2018). Together with its applicability as a fundamental biological research tool in research laboratories, the CRISPR/Cas9 system has been prepared for its wide range of potential applications in the "real world." For example, many are interested in the possible applications of CRISPR/Cas9, in solving some of the challenges of genetic engineering such as the creation of bacteria that can break down hard plant material (e.g., lignin) in the production of biofuels (Roy et al. 2018). Increasingly, the potential applications of CRISPR/Cas9 for agricultural problems are presented in the context of crop improvement in particular, such as stress or disease tolerance and the most productive varieties, but in relation to livestock engineering (Yan and Fong 2017) (Fig. 1). The performance in the form of genome editing tool in Arabidopsis and Tobacco -CRISPR has been road-testing, in other crops including wheat, rice, soya bean, potato, sorbet, orange, and tomatoes has been done. By the end of 2014, scientists focus on the development of abiotic stress tolerant plants using CRISPR/Cas9 technology (Arora and Narula 2017). The potential application of CRISPR-Cas9 raises questions for the improvement of crops or animals: "does CRISPR-Cas9 have a role in food security?" The answer is far from simple, because it depends on a wide range of factors in the food system (Table 1). This innovative tool provides us the ways to achieve sustainability in the food sector to feed nine billion mouths by 2050 by incorporating value-added genes. The efficiency of CRISPR/Cas9 is due to its precise, fast, and specificity in nature. In some genes specific genomic sites were targeted with this system and the desired site-specific mutation rate was significantly higher. Transient expression of the CRISPR/Cas9 system in protoplasts (plant cells without cell wall) or tissue, recorded mutagenesis rate of 11.1% (*Arabidopsis* protoplast) up to 90.1% (rice immature embryo) (Lin et al. 2018). In cases of steady expression of systems in revived plants, the mutation rate was also higher, which was different from 4.0% to 91.6%. The highest mutation rate of 91.6% of the rejuvenated rice plants was observed in which the Lazy 1 gene was targeted (Viana et al. 2019). It has been demonstrated that the Lazy 1 gene of rice has an important

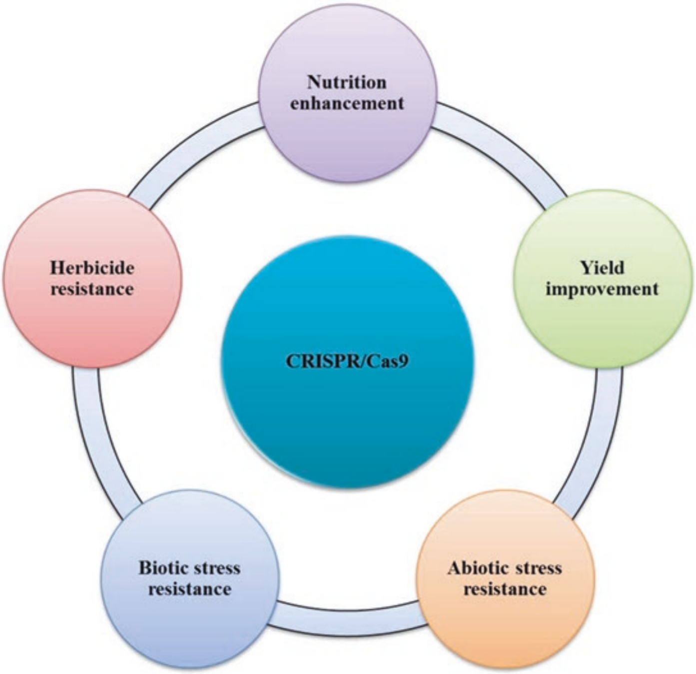

Fig. 1 Schematic representation of the application of CRISPR/Cas9 genome editing tool in agriculture

role in determining rice lazy angle and inhibit laziness, which results in plants spreading wide. Interestingly, in a recent report, it has been demonstrated that TAC1 gene that regulates the growth of pillow in peach is related to Lazy1. It is possible that by targeting the apple equivalent of TAC1 or Lazy1 gene, there can be a large angle of branches in the apple, which is an ideal and preferred tree form in the current orchard system (Smith et al. 2006).

4 CRISPR/Cas9 Achievements in Plants

The CRISPR/Cas system generates stable and inherited mutations, which can be easily separated from the Cas9/sgRNA construct to avoid further modifications by CRISPR/Cas. As a result, only one generation of homogenizing modified transgenic-free plants is developed. Transgenic rice has been successfully developed with the mutation of the desired gene by separating the transgenes with self-pollination in the T1 generation (Brooks et al. 2014; Fauser et al. 2014; Feng et al. 2014; Gao and Zhao 2014; Jiang et al. 2014; Schiml et al. 2014; Zhang et al. 2014; Zhou et al. 2014). Xu et al. (2015) reported that relative cleavage efficacy of Cas9 nucleases is better than before: TALEN and ZFN against the same target sites (Gaj et al. 2013;

Table 1 Application of genome editing tools in different plant species to improve yield, biotic and abiotic stress resistance, and nutritional quality (Sedeek et al. 2019)

Target trait	Plant species	Targeted sequence(s)	Result	Method	Reference
Yield	*Oryza sativa*	GS3, Gn 1a	Grain size and no. increases	CRISPR/Cas9	Shen et al. (2018)
	O. sativa	GW2, GW5, TGW6	Grain weight increases	CRISPR/Cas9	Xu et al. (2016)
	O. sativa	Gn1a, DEP1, GS3	Grain size and number increase and dense, erect panicles	CRISPR/Cas9	Li et al. (2016a, b)
Virus resistance	*Arabidopsis thaliana*	eIF (iso) 4E	Potyvirus resistance	CRISPR/Cas9	Pyott et al. (2016)
	A. thaliana	BSCTV genome	Beet severe curly top virus resistance	CRISPR/Cas9	Ji et al. (2015)
	Cucumis sativus	eIF4E1	Cucumber vein yellowing virus, zucchini yellow mosaic virus, and papaya ring spot mosaic virus-W	CRISPR/Cas9	Chandrasekaran et al. (2016)
	Nicotiana benthamiana	BSCTV genome	Beet severe curly top virus resistance	CRISPR/Cas9	Ji et al. (2015)
	N. benthamiana	TYLCV genome	Tomato yellow leaf curl virus resistance	CRISPR/Cas9	Ali et al. 2015
	N. benthamiana	AGO2	Virus resistance	CRISPR/Cas9	Ludman et al. (2017)
Fungus resistance	*Oryza sativa*	OsERF922	Rice blast resistance	CRISPR/Cas9	Wang et al. (2016)
	Solanum lycopersicum	SlMlo	Powdery mildew resistance	CRISPR/Cas9	Nekrasov et al. (2017)
	Triticum aestivum	TaMLO-A1	Powdery mildew resistance	CRISPR/Cas9 TALE	Wang et al. (2014)
Bacterial resistance	*Citrus sinensis*	CsLOB1	Canker resistance	CRISPR/Cas9	Peng et al. (2017)
	Oryza sativa	OsSWEET13	Bacterial blight resistance	CRISPR/Cas9	Zhou et al. (2015)
	O. sativa	Os11N3 (OsSWEET14)	Bacterial blight resistance	TALEN	Li et al. (2012)

(continued)

Table 1 (continued)

Target trait	Plant species	Targeted sequence(s)	Result	Method	Reference
Drought resistance	*Arabidopsis*	mir169a	Improved drought tolerance	CRISPR/Cas9	Zhao et al. (2016)
	Zea mays	ARGOS8	Improved grain yield under field drought stress conditions	CRISPR/Cas9	Shi et al. (2017)
Salt tolerance	*Oryza sativa*	OsRAV2	Salt stress tolerance	CRISPR/Cas9	Duan et al. (2016)
Herbicide tolerance	*Linum usitatissimum*	EPSPS	Glyphosate tolerance	CRISPR/Cas9	Sauer et al. (2016)
	Nicotiana tabacum	MEL1	Herbicide tolerance	ZFN	Cai et al. (2009)
	Nicotiana tabacum	ALS	Resistance to imidazolinone and sulfonylurea herbicide	TALEN	Zhang et al. (2013)
	Oryza sativa	ALS	Chlorsulfuron and bispyribac sodium tolerance	CRISPR/Cas9	
	Oryza sativa	EPSPS	Glyphosate tolerance	CRISPR/Cas9	Li et al. (2016a, b)
	Solanum tuberosum	ALS1	Chlorsulfuron and bispyribac sodium tolerance	CRISPR/Cas9	Butler et al. (2016)
	Zea mays	IPK1	Herbicide tolerance	ZFN	Shukla et al. (2009)
Nutritional improvement	*Camelina sativa*	FAD2	Increase seed oil content	CRISPR/Cas9	Jiang et al. (2017)
	Oryza sativa	SBEI, SBEIIb	High amylose content	CRISPR/Cas9	Sun et al. (2017)
	O. sativa	OsBADH22	Increase fragrance content	TALEN	Shan et al. (2015)
	Solanum tuberosum	GBSS	High amylopectin	CRISPR/Cas9	Andersson et al. (2017)
	Zea mays	ZmIPK	Reduce phytic acid content	CRISPR/Cas9 TALEN	Liang et al. (2014)

Johnson et al. 2015). Xing et al. (2014) developed a toolkit for modifying multiplex genomes in plants using the set of binary vectors based on CRISPR/Cas9 and a series of vectors of gRNA modules. This will facilitate the transient or constant expression of CRISPR/Cas9 in various types of plant systems and is particularly useful for the modification of high-efficiency multiplex plant genomes (Xing et al.

2014). Therefore, the only requirement for genetic modification methods is the provision of only two components of the host cell, i.e., the supply of Cas9 and sgRNA, the genomes of plants. Baltes et al. (2014) suggested that replication of the Gemini virus (GVR) can be used to administer plants with improved mutations to deliver Cas9/sgRNA when the replication protein gene co-formation has been transformed (REP) with the gene or the sgRNA. The rapid progress in the development of CRISPR/Cas9 in a series of tools for the study of cellular and molecular biology is remarkable, thanks to the simplicity of the system, its high efficiency, and versatility. In the nuclear design system, currently available for accurate genomic engineering, the CRISPR/Cas9 system is the easiest to use. It is now also clear that the probability that Cas9 reaches DNA beyond the rupture and its genome for the specific recruitment of proteins, its usefulness will be limited only by our imagination.

5 Future Prospects

Possible future crops for sustainable productive agriculture through genome editing are those that have better resistance to harmful insects, with greater nutritional value and which can survive in a changing climate. Climate-resistant agriculture to combat biotic and abiotic stress is the future of crop improvement by modifying the genome for manipulation mediated by direct mutagenesis and the study of transcriptional control by dissection of physiological and molecular interferences under combined stress (Kissoudis et al. 2014; Jain 2015). The genome assembly has played a very important role in the development of new bioenergy crops, which could give maximum performance in the different conditions and climate changes (Bosch and Hazen 2013). This technology could offer any new concept of genome modification for plants in order to improve crops for better nutrition and food safety. Furthermore, methods of direct administration of Cas9 and gRNA using *Agrobacterium* and viral replicons through the use of nanoparticles can be very useful for simplifying genome modification technology. (Hiei et al. 2014; Khatodia et al. 2014; Nonaka and Ezura 2014). The Cas9 inducible system for transcription modulation such as the Cas9 and chemically inducible system and the activated light Cas9 effector (LACE) could be used to improve culture in the future (Polstein and Gersbach 2015; Zetsche et al. 2015). The generation of large-scale, genome-wide sgRNA libraries for high-speed function loss detection applications based on the CRISPRi system such as the RNAi system is particularly feasible for model plants in the future (Heintze et al. 2013).

6 Conclusion

The CRISPR/Cas9 system was recently developed by reprogramming the immune system based on bacterial type II nucleic acids, a new site-specific genome modification tool. Given its remarkable technological simplicity, the CRISPR/Cas9 system is becoming the main choice technique that replaces the central role of TALEN-based biotechnology in site-specific genome editing. Crops produced through the Cas9-RNP genome/technology edition will certainly improve the precision farming approach to obtain useful traits and minimize the obstacle to deregulation for sustainable agriculture. The CRISPR/Cas9 system quickly adapted to both the model and the cultivated plants and was established with a desirable efficiency in the selection of genes for specific sites. It is likely that this system will become more efficient over time, allowing high-throughput applications that will direct the entire genome into plants. Ultimately, the wave of shock sent today to the community of genome engineers by the discoverers of this brainstorming genome modification technique will be perceived by agriculture in a positive way tomorrow.

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Pros and Cons of Nanotechnology

Waseem Mushtaq, Adnan Shakeel, Mohammad Afaan Fazili,
Ishani Chakrabartty, and Mustafa Sevindik

1 Introduction

Global food demand is rising at an alarming rate as the human population is increasing exponentially and may hit a record of nine billion by 2050. To combat this problem of food demand various strategies are being implemented to increase the productivity of crops and protect them from agricultural pests. The increased population rate forces agricultural society to find new ways of improved crop productivity. The problem of poverty and malnutrition has become a deep concern for countries across world. The progress in agriculture sector plays a critical role in population growth and economic forums as it produces raw materials for food and feed industry. With economic development, the soil nutrient balances are differed.

W. Mushtaq (✉)
Allelopathy Laboratory, Department of Botany, Aligarh Muslim University,
Aligarh, Uttar Pradesh, India

A. Shakeel
Environmental and Pathology Section, Department of Botany, Aligarh Muslim University,
Aligarh, U.P., India

M. A. Fazili
Section of Mycology and Plant Pathology, Department of Botany, University of Kashmir,
Jammu and Kashmir, India

Advanced Plant Physiology Section, Department of Botany, Aligarh Muslim University,
Aligarh, Uttar Pradesh, India

I. Chakrabartty
Department of Science, PAFGC, P.A. College of Engineering, Mangalore University,
Mangalore, India

M. Sevindik
Department of Food Processing, Bahçe Vocational School, Osmaniye Korkut Ata,
Osmaniye, Turkey

K. R. Hakeem, T. B. Pirzadah (eds.), *Nanobiotechnology in Agriculture*,
Nanotechnology in the Life Sciences, https://doi.org/10.1007/978-3-030-39978-8_13

In developing countries, the soil fertility plays a significant role to assist economy and agriculture (Campbell 2014). Present century holds a good demand for efficient, reliable, and cost-effective systems for detecting, monitoring, and diagnosis of biological host molecules (Sagadevan and Periasamy 2014). The traditional farming approaches are incapable of maintaining a pace at which food needs are required and consequently we have to depend and imply the nanotechnology in agriculture and its allied sectors. In modern agriculture, one cannot think of improving agricultural productivity without the use of chemical fertilizers and pesticides; however, most of the agrochemicals are not eco-friendly and are thus detrimental to human health (Kah 2015). Nanotechnology is a novel technique for improved and sustainable agricultural production and also harbors a good capacity to bring novel alterations in the agricultural systems. Nanotechnology introduces new technologies and materials for use in molecular biology for the identification of plant pathogenic microorganisms (Mousavi and Rezaei 2011). In agriculture, nanotechnology has the potential to revolutionize this sector by introducing new techniques for disease diagnosis, specific pathogen targeted treatment, and increasing the resistance of plants to fight pests. It can also improve nutrient uptake by plants and can boost plants to withstand ecological pressures. In developing countries, the soil fertility plays a significant role to assist economy and agriculture (Campbell 2014). The advantages of nanotechnology operated techniques for sustainable agriculture are discussed below under the following headings.

2 Nanofertilizers: An Alternate to Conventional Chemical Fertilizers

To enhance the crop yield production, fertilizers play a pivotal role in the agriculture sector; however, most of the fertilizers applied are unavailable to plant due to various factors. These include leaching, degradation of fertilizers by photolysis, hydrolysis, and decomposition. As a result of this, the soils and underground water become polluted or face nutrient imbalance. This problem can be solved through the use of nanofertilizers or nano-encapsulated nutrient. A nano-fertilizer can be defined as a substance having dimensions in nanometers and is capable of delivering nutrients to crops in an efficient manner. For instance, nanomaterial encapsulated in a thin protective polymer film or in the form of particles or emulsions of nanoscale dimensions (DeRosa et al. 2010). Nanofertilizers are expected to possess beneficial properties to crops which include sustained release of fertilizers to regulate plant growth and development with an enhanced target activity (Ghormade et al. 2011). For the effective release of nitrogen fertilizers, urea-fertilized zeolite chips were used (Millán et al. 2008). The solubilization of phosphate minerals has been reported to be improved through ammonium-charged zeolites. This results in enhanced phosphate uptake by plants which ultimately improve the yield of crops. Urea-modified hydroxyapatite nanoparticles encapsulated within softwood of *Gliricidia sepium* have been reported to regulate the sustained release of nitrogen fertilizers into soil (Kottegoda et al. 2011). The conventional fertilizers have nutrient use efficiencies of

Table 1 Comparison of nanofertilizers and conventional fertilizers (Cui et al. 2010)

S. No.	Properties	Nanotechnology fertilizers	Conventional fertilizers
1	Solubility and dispersion	Micronutrients formulated through nanotechnology may improve and increase bioavailability by reducing soil absorption and fixation	Less solubility due to macroscopic nature
2	Mode of nutrient release	Through encapsulation, nutrient release inclosing both rate and pattern can be controlled for water soluble fertilizers	The excess release of fertilizers result in toxicity and cause soil ecological imbalance
3	Duration of nutrient release	They might extend the effective period of nutrient supply of fertilizers into soil for plant use	At the time of delivery they are used by plants and rest remains as insoluble salts in soil
4	Uptake efficiency	Because of nano-dimensions, it might improve nutrient uptake and efficiency of fertilizers	It decreases efficiency and bulk amount is not available to plant roots
5	Rate of nutrient loss	They reduce the loss of fertilizer nutrients into soil	They show high nutrient losses due to leaching, rain off and drift

about 30–35%, 18–20%, and 35–40% for N, P, and K. However, nano-fertilizer has the ability to enhance nutrient use efficiency by using the properties of nanoparticles like increased surface area. Both physical and chemical approaches are used to fortify nutrients singly or in combination onto the absorbents with nano-dimensions. The nutrients are loaded on nanoparticles through different methods that includes (a) by encapsulating the nutrient in nanoparticulate polymeric shell, (b) by absorption on nanoparticles, (c) ligand mediated attachment to nanoparticle, and (d) through synthesis of nanoparticles by nutrient itself. The anionic nutrients (NO_3^-, PO_4^{2-}, SO_4^2) are surface modified before loading, while the cationic nutrients (NH_4^+, K^+, Ca^{2+}, Mg^2) are loaded as such. Corradini et al. (2010) studied the interaction of chitosan nanoparticles suspensions comprising of N, P, and K fertilizers and their stability and concluded their usefulness agricultural sectors. Mesoporous silica nanoparticles (150 nm) have been reported to entrap urea. This study reported five times improvement in release period of nitrogen than conventional fertilization (Wanyika et al. 2012). Milani et al. (2012) compared the ZnO nanoparticles coated on urea and monoammonium phosphate and found that the later showed faster dissolution rate. Table 1 presents a comparison between nanofertilizers and conventional fertilizers.

3 Nano-biotechnology and Plant Protection

The use of conventional methods for the control of pathogens and parasites adversely affects the environment and the farmer's economy, as 90% of applied pesticides are lost in the air or as runoff. Furthermore, the haphazard use of pesticides enhances resistance to pathogens and parasites, reduces soil biodiversity and the rate of nitrogen fixation, and facilitates bioaccumulation of pesticides (Ghormade et al. 2011; Tilman et al. 2002). To mitigate the loss of pesticide and its hazardous effects, nanoparticles or nano-capsules play a significant role due to their ability to control release of active compound. This also equips agricultural scientists to mitigate environmental pollution by production of eco-friendly pesticides. The nanoscale delivery system with active compound (pesticides and/or herbicides) can only be applied when necessary in the field (Gruere et al. 2011). It can also produce nanocrystals to augment the pesticide efficiency that decreases the dose of insecticides. In near future, the application of nanoparticles for the smart delivery of active components will be an attractive subject for treating all the pathological sufferings of plants (Mousavi and Rezaei 2011). Nano-biotechnology has produced innovative means to identify the pathogen and control the disease. Besides, nanosensors can be used to detect the plant pathogen and pesticide (Fig. 1). The formulation of biopesticides with nanomaterial and delivery of insecticides through encapsulation in nanomaterials for controlled release are the expected applications of nano-biotechnology in plant protection (Debnath et al. 2012). Generally large volume of enzymes is required in the biocontrol of plant diseases that becomes costly but application of nano-biosensors cuts down the cost by immobilizing the enzyme/inhibitor on a nanostructure which uses low volume of enzyme (Kim et al. 2006). Nowadays almost all the pathogens can be identified and typed through various methods. However, methods based on traditional culture are laborious and time consuming

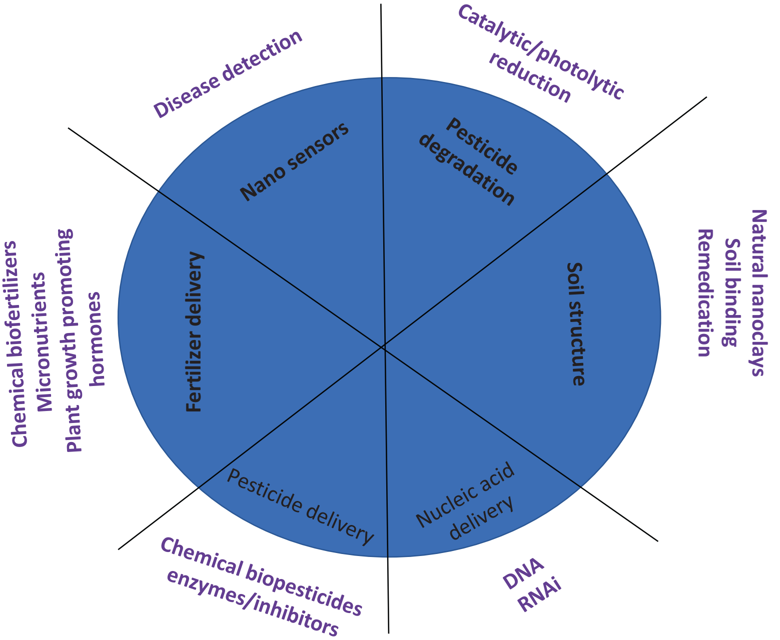

Fig. 1 Use of nano-biotechnology in plant protection and nutrition (Ghormade et al. 2011)

(Fletcher et al. 2006) and those based on population of strains characterized in the databases limit the identification using biochemical profiling. The antibody specificity is required in more sensitive serological specific techniques such as ELISA and indirect fluorescent antibody staining with immunofluorescence (Uddin et al. 2003). The modern polymerase chain reaction based methods, such as RFLP (restriction fragment length polymorphism), DNA fingerprinting, and amplification of rRNA gene's transcribed spacer region, increase the specificity of identification but all these methods are very costly (van Doorn et al. 2007). The nanotechnology based sensory systems for monitoring the environmental conditions and diagnostic system for protection may allow farmers to minimize the use of agrochemicals with an increased productivity (Ghormade et al. 2011). The development of silica-based nano-biosensors (60 nm) is a novel microbial technology and it is a very sensitive technique to detect a single bacterial cell (Zhao et al. 2004).

Recent literature supported the efficacy of metal nanoparticles against a wide range of plant pathogens and pests. Hence, nanoparticles could be employed in the new formulations of insect repellents and pesticides preparation (Owolade et al. 2008; Gajbhiye et al. 2009; Goswami et al. 2010). The pesticides which can be easily prepared and employed include polymeric nanoparticles such as iron oxide nanoparticles and gold nanoparticles (Sharon et al. 2010). Several insecticides, such as imidacloprid, carbofuran, and thiram, have been formulated through polyethylene glycol (PEG) to control the release of active compound (Adak et al. 2012; Pankaj et al. 2012; Kaushik et al. 2013) as PEG was noted to be required for the release of insecticide. The release of β-cyfluthrin improved through nanoformulation from 4 to 5 days under commercial formulation to 20 days under nanoformulation (Loha et al. 2011, 2012). In other study, a nanofiber network in which thiamethoxam (50%) was loaded over lactic acid and cellulose nanocrystals against white fly proved effective over a period of 9 days under greenhouse conditions (Xiang et al. 2013).

4 Nano-biotechnology in Plant Growth and Yield Production

The smart delivery and detection system developed through nano-biotechnology contribute to improved plant growth and agricultural productivity. The effect of nanoparticles on plant growth depends on its concentration, composition, size, chemical properties, and plant species (Ma et al. 2010). The use of nano-SiO_2 in low concentrations enhanced germination of tomato seeds (Siddiqui and Al-whaibi 2014). In maize the nano-SiO_2 enhanced seed germination by improving nutrient availability and correcting conductivity and pH of growth medium (Suriyaprabha et al. 2012). The germination of squash seeds was enhanced along with the activation of antioxidant system under salt stress through nano-SiO_2 (Siddiqui et al. 2015). Nanoparticles of silica, palladium, gold, and copper have a significant impact on seed germination of lettuce (Shah and Belozerova 2009). Not only germination but also other growth parameters are improved by nano-SiO_2. It enhances gas exchange and photosynthetic parameters, such as stomatal conductance, transpiration rate, potential activity of PSII, photochemical efficiency, photochemical quench, and electron transport (Siddiqui et al. 2015). The zinc nanoparticles (ZnONPs) have also been reported as beneficial for plant growth development. At lower concentrations, it enhances seed germination in wheat and onion (Ramesh et al. 2014; Raskar and Laware 2014). An enhancement in shoot and root growth, pigment and protein content, rhizospheric microbes, enzyme activity through ZnONPs was reported in *Cyamopsis tetragonoloba* (Raliya and Tarafdar 2013). The supplementation of MS-growth medium with ZnONPs enhanced the process of somatic embryogenesis, regeneration of explant, and shooting. It also stimulates the proline synthesis and antioxidant enzymes which result in improvement of plants to biotic stress (Helaly et al. 2014). Similarly gold nanoparticles (AuNPs) also have beneficial effects on plant growth and development (Kumari et al. 2009). Silver nanoparticles (AgNPs) have been reported to enhance plant growth in *Arabidopsis thaliana* (Syu et al. 2014), *Crocus sativus* (Rezvani et al. 2012), *Boswellia ovalifoliolata* (Savithramma et al. 2012), *Brassica juncea* (Salama 2012), beans and corn (Sharma et al. 2012, 2019).

5 Nano-biotechnology-Cost-Effective Approach for Ecological Remediation

Environmental pollution is one of the most serious concerns that need an immediate interest. Currently various organizations are working on the process of environmental remediation. Most of these programs are time consuming and costly. The use of nanotechnology based techniques could provide a cost-effective solution to environmental degradation. Nanoscale iron particles have some excellent properties for in situ applications. These properties include large surface area, high surface reactivity, and enormous flexibility. They are very effective in detoxification of various ecological pollutants, like organochlorine pesticides, polychlorinated biphenyls (PCBs), and chlorinated organic solvents. Recent studies have advocated that nanoscale iron particles play a critical role in the transformation and detoxification of a diversity of common ecological contaminants including chlorinated organic solvents, organochlorine pesticides, and PCBs. Additionally the pace and effectiveness of remediation can be improved by the use of catalyzed and supported iron nanoparticles which represent the modified iron nanoparticle that has been synthesized to improve the remediation process (Chinnamuthu and Boopathi 2009). The use of nanoscale iron particles in ecological remediation has several advantages. These are:

1. They can be used effectively for the transformation for a wide range of environmental contaminants.
2. They are less expensive.
3. They are nontoxic.

The heavy metal pollution of soil and water causes harm to both terrestrial and aquatic ecosystems. Use of "magnetic" bacteria could prove very effective for the removal of heavy metals from aquatic systems. The occurrence of magnetic ions like iron sulfide causes precipitation of heavy metal on bacterial cell wall. This results in magnetization of bacteria for removal by magnetic separation process. Chinnamuthu and Boopathi (2009) proposed a new way of synthesizing mesoporous magnetic nanocomposite particles for the remediation of environmental pollutants. This method employs molecular templates to coat nanoparticles of magnetite with mesoporous silica. The development of a biodegradable and quick-setting organic mulch technique based on soil binder by a US based company is a good example. This technique caused the silicates of soil and product to self-assemble into a layer that remained for longer durations. This layer was reported to retain soil water that enhanced the seeds blended in product to germinate. In Mexico it was claimed to prevent soil erosion that resulted from forest fires.

6 Pesticide Degradation and Detoxification of Herbicide Residues

The extreme use of pesticides and herbicides in crop protection causes harmful contamination to ecosystem. Various conventional methods for treatment of contaminated soil and water have been developed. These methods include incineration, phytoremediation, and photochemical methods. More innovative methods include advanced oxidation methods and ultrasound-promoted remediation (Farre et al. 2007). The use of nanoparticles in remediation provides an innovative and promising approach (Joo and Cheng 2006). Various common pesticides like atrazine, molinate, and chlorpyrifos can be degraded through nanoionized ZVI. The use of LbL (Layer-by-layer) nano-engineering for direct surface modification for colloidal substances is a novel approach. It involves the electrostatic interactions of oppositely charged electrolytes through a sequential adsorption process (Sasson et al. 2007). The excessive and continuous application of herbicide cause harm to succeeding crops. It can also lead to evolution of weed species with more resistance to herbicides and may cause a change in weed flora. The residual problem of atrazine, a globally used herbicide for broadleaved weeds, has limited its widespread use. Nanotechnology provides a reliable solution to the residual problem of atrazine through the application of modified silver NPs. AgNPs were modified through stabilization of magnetite nanoparticles with carboxymethyl cellulose (CMC). The residue atrazine was degraded by 88% through modified silver particles (Susha and Chinnamuthu 2012).

7 How Nanoparticles Interact with Plants?

As already mentioned, the shape, dimensions, molecular structure, stability, and functionalization of nanoparticles (NP) influence absorption, translocation, and accumulation; it has also been found that the properties are influenced in a variable way by the type of plant species and the site that facilitates the internalization of NP. The plant cell wall acts as the primary site of interaction with the external environment, which restricts entry to all foreign particles, including NPs. Functionalized active sites among components of the plant cell wall include the functional groups carboxylate, phosphate, hydroxyl, amine, sulfhydryl, and imidazole (Vinopal et al. 2007) which fit together to form complex biomolecules such as cellulose, carbohydrates, and proteins (Knox 1995) and facilitate selective absorption of NP. Absorption and differential or selective NP of cell wall translocation is due to its semipermeable property that allows small particles to move through them and shift the larger particles and limit their entry into the plant system. Thus, the pore size of the cell wall with a diameter varying in the range of 5–20 nm gives the plant a screening property and is based exclusively on NP uptake (Fleischer et al. 1999). Therefore, NPs with a comparable diameter as that of the pore size of the cell wall can penetrate through them and reach the plasma membrane. Navarro et al. (2008) also observed the formation of new pores in the cell wall during reproduction or expansion of existing pores under the influence of NP, which subsequently determines the most permeable cell wall and improves the absorption of nanoparticles (Ovečka et al. 2005). After penetration inside the cell wall, endocytosis mediated internalization of NPs occurs in which NPs are surrounded by the plasma membrane as a structure similar to a cavity. Another route of transport includes the complex formation of NP with root exudates or membrane transporters (Kurepa et al. 2010). Hall and Williams (2003) have identified a variety of ion transporters for various NP families. After their entry into the cells, the NPs follow an apoplastic or symplastic transport mode. In the cytoplasm, NPs interact and can bind a different organelle in different ways to interact more with the plant metabolism both in positive and negative (Jia et al. 2005). When NP is amnestied on leaf surfaces in various tissues filtered through openings or bases of static trichomes (Uzu et al. 2010), stomatal openings in the photosynthetic areas are obstructed because the accumulation of NP, the latter is heating leaf surface, cause alterations of gaseous exchanges and further modifies the cellular and physiological functions of plants (Da Silva et al. 2006). Ao et al. (2013) reported new conjugated nanospheres derived from 1-naphthylacético (NNA), 3-aminopropyltriethoxysilane (APTES), and tetraethyl orthosilicate as a controlled release nanodimensions (CRF) formulation for plant growth. However, the exact mechanisms of selective uptake of NP by different plant species are unknown and should be explored.

8 Phytotoxicity of Nanoparticles: An Agricultural Perspective

Yang and Watts (2005) studied the effect of nanoscale uncoated and phenanth rene-coated alumina on root growth in corn, cucumber, soybeans, cabbage, and carrot and advocated that the uncoated alumina particles in a concentration of 2 mg/L inhibited all the growth parameters. This was the first report on the phytotoxicity of nanoscale particles in relation to the coating and uncoating. Murashov (2006) is of view that the phytotoxic effect may not be nanospecific but could also be attributed to the dissolution of aluminum. With the rapid expansion of nanotechnology, there is apprehension about their possible entry into the food chain and subsequent bioaccumulation of manufactured nanomaterial (Priester et al. 2012). The use of nanomaterial is not inherently risky, for instance, traditional foods harbor numerous nanoscale materials including proteins in milk, fat globules in mayonnaise, carbohydrates, DNA, etc. However, the use of some nanoscale materials designed in agriculture, water, and food may prove detrimental for human health and environment (Gruere et al. 2011). Priester et al. (2012) documented that the exposure path for plants is the absorption of nanomaterial from the soil. Plants are considered as essential components of ecosystems and play a crucial role in the environment through the absorption and bioaccumulation (Xingmao et al. 2010). The underlying mechanism of bioaccumulation, bio-magnification, and biotransformation of nanoparticles designed in food crops is yet under study. Moreover few nanoparticles and plant species have been investigated to understand the accumulation phenomenon followed availability of nanoparticles in food crops. The engineered nanoparticles (ENP) are most common in the environment and are classified into one of the following five groups: carbon nanoparticles, metal oxides, quantum dots, zero valence metals, and nanopolymers. These ENPs interact closely with the surrounding environment and, consequently, the ENP will certainly interact with the plants and such interactions will lead to their absorption and accumulation in the biomass of the plant, which later on influence their fate and transport in the environment. For a successful ENP-plant interaction the penetration of ENPs in to the cell walls and plasma membranes of the epidermis of the roots and their subsequent entry in to the vascular tissues (xylem) is of paramount importance. It is assumed that the smaller ENP aggregates pass through porous network of polysaccharide fibrous network of cell wall. The smaller ENP induces the synthesis of newer and large pores that facilitate the internalization of large ENPs (Xingmao et al. 2010).

The phytotoxicity of five types of nanoparticles such as multi-wall carbon nanotubes, alumina, aluminum, zinc, and zinc oxide on germination percentage and growth rate of root has been reported in several plants including radish, canola, rye, lettuce, corn, and cucumber. The germination percentage of seed remain unaffected except for inhibition of zinc on nanoscale (nano-Zn) in ryegrass and zinc oxide (nano-ZnO) in maize at 2000 mg/L, a great variation was found in the inhibition of root growth depending on the type of nanoparticles used and plant in question (Lin and Xing 2007). The suspensions of 2000 mg/L of nano-Zn or nano-ZnO have practically completed the elongation of the root of the tested plant species (Lin and Xing 2007). It was estimated that the inhibitory concentrations (IC_{50}) of 50% of nano-Zn and nano-ZnO were close to 50 mg/L for the radish and about 20 mg/L for rapeseed and ryegrass (Lin and Xing 2007). Inhibition occurred during the seed incubation process instead of the seeds soaking phase. These results are significant in terms of the use and disposal of designed nanoparticles (Lin and Xing 2007). On the contrary, pods size and plant growth were reduced even at the low doses of nano-cerium oxide in soybean plants. Furthermore, it is apparent that nano-cerium oxides has entered into the root nodules and influence the process of nitrogen fixation. Priester et al. (2012) further reported that increase in the level of nano-cerium oxide in the soil, there was a progressive reduction in the nitrogen fixation process in soybeans. Furthermore, the nanomaterial produced may represent a greater risk for humans and livestock if it enters the food chain in an unregulated way. Nevertheless, it was also noticed that a very high concentration of nano-silica silver produced some chemical lesions in the analyzed plants. Several hydroponically cultivated plants are influenced by a large number of manufactured nano-materials (MNM), raising concern about the long-term effects of these materials on food supply (Rico et al. 2011). However, MNMs may not be bioavailable (i.e., accessible to organisms) in the soil (Tong et al. 2007). Multi-walled carbon nanotubes (MWCNTs) have been shown to be harmful to *Arabidopsis* T87 suspension cells when they differ as a function of dissolved agglomerates and fine agglomerates (obtained after ultrasound) (Lin et al. 2009). The cultured cells represented a decrease in dry weight, lower profitability, and lower chlorophyll content and superoxide dismutase activity. The effects were more pronounced in the fine agglomerates than in the loose ones. This was explained due to the characteristic of forming groups of plant cells with surrounding cells. Large but loose agglomerates could not penetrate such groups of cells, while small and thin agglomerates can easily be distributed into groups of plants because of their small size and their interactions with proteins and polysaccharides of the cell wall. These characteristics of NP could be responsible for the toxic behavior of NPs. Lin et al. (2009) also suggested that the presence of metallic impurities (residual metals used as catalysts for the synthesis of carbon nanotubes, CNT) could be the cause of the toxicity of MWCNT (Table 2). The CNT can be stabilized through the natural organic substance (NOM) according to its hydrophobic behavior (Navarro et al. 2008). Absorption, translocation, and accumulation of NOM-CNT were observed in rice plants (Lin et al. 2009), Fullerene C70-NOM-NOM or MWCNT with reduced hydrophobicity were studied in rice plants at different concentrations. This may have occurred through osmotic pressure and capillary action at the tip of the root of the plant, and the NP could penetrate through the pores of the cell wall and were transferred through the plasmodesmata. The presence of NP near the vascular bundle could interfere with the absorption of water and nutrients from plants, which has a secondary effect on plant growth. Epigenetic modifications through deacetylation of global histones were also induced by the treatment of single-walled carbon nanotubes (SWCNT) in the roots of *Zea mays* L., which translates into changes in gene expression and, consequently, influences growth and root development (Yan et al. 2013).

Table 2 Negative effects of NPs in routinely used food crops since 2009

Crop	Nanoparticles (NPs)	Size of NPs (nm)	Effects on growth	References
Oryza sativa	Single-walled carbon nanotubes	1.19 (major) 18, 722	722 Delayed flowering, decreased yield	Lin et al. (2009)
Cucurbita pepo	Multi-walled carbon nanotubes	Diameter range 10–30	Reduced biomass (38%)	Stampoulis et al. (2009)
Zea mays	TiO2/inorganic bentonite clay	30/1–60	Inhibited hydraulic conductivity, leaf growth, and transpiration	Asli and Neumann (2009)
Cucurbita pepo	Ag	100	Inhibited transpiration	Stampoulis et al. (2009)
Allium cepa	Ag	<100	Mitotic abnormalities	Kumari et al. (2009)
Cucurbita pepo	Cu	50	Biomass reduced to 90%	Stampoulis et al. (2009)
Zea mays, Solanum lycopersicum, Glycine max, Cucumis sativus	CeO_2	7	Germination reduced	Lopez-Moreno et al. (2010)
Glycine max	ZnO	8	Inhibited radicle growth	Lopez-Moreno et al. (2010)
Lycopersicum esculentum	NiO	~23	Induced oxidative stress and necrosis	Faisal et al. (2013)
Phaseolus vulgaris	CeO_2	~8	Induced oxidative stress	Majumdar et al. (2014)
Allium cepa	Al_2O_3	Not specified	Induced oxidative stress in root	Rajeshwari et al. (2015)
Cucurbita pepo	Nd_2O_3 and bulk	30–45	Induced oxidative stress and inhibition of uptake of minerals by roots.	Chen et al. (2016)
Lactuca sativa	CeO_2	16.5	Induced oxidative stress	Zhang et al. (2017)

9 Conclusion and Future Perspectives

Despite the progress of NP in the field of nanotechnological applications that reach the state of the art, its implications in agriculture and crop improvement are still in an elementary phase. In order to exploit the promised benefits of NPs, it has become essential to improve our understanding of plant-NP interactions through their characterization and related phytotoxic aspects. Another important problem that needs to be addressed is how to delineate the modes of absorption and translocation of NP from plants. However, several routes have been proposed and the results have been diverted based on growth conditions, plant species, and the size and concentration of NPs. Therefore, it is important to explore the absorption kinetics of NPs under the influence of particle size, agglomeration, and compositions. Its translocation, accumulation, and biotransformation in different parts of the plant are another approach to consider. Accumulated evidence suggests the toxic effects of NPs; however, the results were modulated to produce positive effects through the modification of the NP surface. It has been reported that NPs in different concentrations possess both positive as well as negative effects on different plant species. This function could be used simultaneously to promote the growth of edible crops and eliminate weeds or phyto-pathogens that affect crops. The size and concentrations of NP could be optimized to produce such desirable effects. Also the assimilation of NP and its subsequent accumulation in the food web represent an important concern. Therefore, one should try to design experimental models that describe the interaction between the plant and the animal and the effects studied at the individual atrophic level. The plant-NP interactions modifies the gene and the protein profiles of plant cells, which eventually lead to changes in biological pathways that produce changes in plant growth and development. Therefore, it is necessary to conduct an experimentation to generate information at the molecular level caused by the absorption and translocation of NP.

Acknowledgments The authors are thankful to the Aligarh Muslim University, India, for providing facilities and UGC for providing financial assistance.

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K. R. Hakeem, T. B. Pirzadah (eds.), *Nanobiotechnology in Agriculture*,
Nanotechnology in the Life Sciences, https://doi.org/10.1007/978-3-030-39978-8