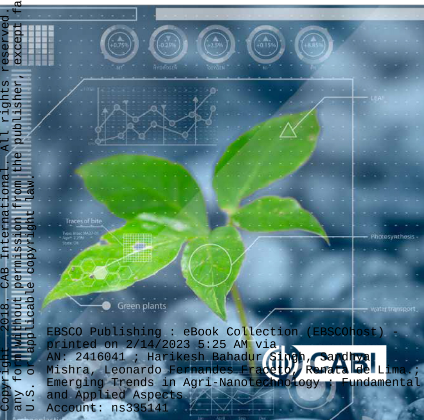
# Emerging Trends in Agri-nanotechnology

## Fundamental and Applied Aspects

Edited by Harikesh B Singh, Sandhya Mishra,
Leonardo Fernandes Fraceto and Renata de Lima



# EMERGING TRENDS IN AGRI-NANOTECHNOLOGY: FUNDAMENTAL AND APPLIED ASPECTS

**Harikesh B. Singh**
This book is dedicated to my beloved wife, Mrs Suman Singh, for her love, support and care.

**Sandhya Mishra**
This book is dedicated to my beloved son, Mr Divyank Chaturvedi, who has been a source of tremendous strength. I used to be late home because of my busy schedule during editing of this book but in spite of this fact he always welcomed me home with his smiling face, which gave me huge inspiration and support.

**Leonardo Fernandes Fraceto**
This book is dedicated to my Family, in special to Renata and Camila, all dogs (Toninho – *in memoriam*, Celeste, Flora – *in memoriam*, Marrom, Helena, Frida and Mandela) and the bird (Sansão) for all everyday love and making my life happy.

**Renata de Lima**
For those who stay behind the scenes of our scientific life showing us in every moment why it's worth continuing. You are above all! To Leonardo, Camila, Toninho (*in memoriam*), Flora (*in memoriam*), Celeste, Marrom, Helena, Frida, Mandela and Sansão.

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# Foreword

Since the discovery in the 1950s that material properties may potentially be altered or controlled by changing the particle size to the nanoscale this has opened up a door for numerous novel applications in almost all industrial sectors. The agricultural sector, being the largest and the oldest in the history of mankind, has also started to see the use of the new processes, materials and products derived from nanotechnology. The multifaceted nature of the agricultural sector means that research on the development of nanosubstances is already targeting every key area, including seed treatment, fertilizers and plant growth regulators, pesticides, biocides, veterinary medicines, aquaculture, fisheries, as well as nanosensors for monitoring environmental conditions and pests, diseases and contaminants on the farm. In this context, this book is very timely as it provides an up-to-date account of the various developments relating to the use of nanotechnology in various segments of the agriculture sector.

The book comprises 18 chapters that have been written by leading world experts, which not only provide a comprehensive account of the potential benefits of the technology, but also present the current state of knowledge and the gaps that require further research. This balanced approach has made the book very informative because it highlights both the benefits and the potential risks. In addition, the experts in their respective fields have also looked into the future prospects and trends of the new technological developments and have provided their valuable suggestions for the possible ways forward.

In this context, Chapter 1 looks at the emergence of nanotechnology in terms of the history of agriculture. It regards nanotechnology as an important revolutionary technology that is likely to have a considerable impact on the whole of the agricultural sector, including plant breeding, waste remediation, nanobioprocessing, plant disease management, crop productivity etc. The potential of nanotechnology to enable a reduction in the use of agrochemicals during food production is also a theme of this and the other chapters that follow. For example, this chapter highlights that the use of smart delivery systems for nanofertilizers could potentially reduce the losses and runoffs that are known to be damaging to the (aquatic) eco-environment. Similarly, the use of nanopesticides could lead to a decrease in the overall quantities of the toxic chemicals used on the farm.

Chapter 2 discusses the potential benefits and challenges in the application of nanotechnology in agriculture. It discusses the possibilities for various benefits of the use of nanofertilizers and nanopesticides, especially when developed in the form of nanoencapsulated active ingredients. It also discusses the key areas where there are still challenges ahead – e.g. in relation to dosimetry, safety assessment, and determining the impacts of nanosubstances on human health and the environment, regulatory aspects, and potential harmful effects during applications, and/or persistence in the environment. It proposes a full life-cycle study of such applications to ensure that food production using nanotechnology is safe for the consumer and the environment.

Chapter 3 describes the potential different effects that nanomaterials may have on plant growth and crop yield compared to larger-sized counterparts. It discusses the prominence of green nanotechnology in relation to meeting the global challenge of feeding the projected population of the mid-21st century. It proposes a cautious approach to such developments and highlights the need for more detailed research into the potential harmful effects of nanomaterials.

Chapter 4 presents an interesting example of an innovation that nanotechnology could offer in the form of synthesis of nanonutrients by certain fungal species. Although more work is needed to optimize the process in relation to the control of particle characteristics (such as size, dispersity and stability), the use of nanonutrients – such as Zn and Fe – has been shown to enable plants to better cope with stress, and minimize membrane damage, etc. This could lead to substantial improvements in crop yields and also in the production of polysaccharides by certain microorganisms.

Chapter 5 discusses the multitude of nanotechnology applications that could lead to increased productivity in agriculture. It touches upon the use of the technology for early detection of pests, diseases, nutrient deficiencies, delivery of nanoagricultural inputs, seed treatments, as well as nanofoods and smart packaging. It highlights the potential for improvement of agricultural productivity using smart delivery systems that may enhance the efficiency and thus minimize the use of soil nutrients and other agrochemicals.

Chapter 6 discusses the various ways by which nanoparticles can be synthesized and used in agricultural applications. It discusses the synthesis of nanosubstances by biological means as an alternative to chemical synthesis, through the utilization of natural agents such as microbes and plants (as such, or extracts) and other macromolecules such as proteins, carbohydrates, etc. It also discusses alternative ways of nanomaterial synthesis that do not involve the use of chemical reducing agents – such as the use of light, electric current, or certain additives to enhance the reducing potential of biomolecules.

Chapter 7 discusses the potential impacts of nanomaterials on the agroecosystem. It highlights how the potential widespread use of nanomaterials in agriculture could have negative impacts on the agroecosystem – e.g. through alterations in the soil constituents and the microflora. It also highlights that the available information so far on this subject is limited and that extensive studies would be needed to fully understand the biochemical, physiological and molecular mechanisms for the interaction of nanoparticles with plants.

Chapter 8 identifies the current knowledge gaps in relation to the potential toxicity of engineered nanomaterials to plants and highlights that a systematic approach is needed to assess the likely level of human and environmental exposure of nanomaterials from use in agriculture. Chapter 9 highlights the crucial need for models that can predict nanomaterial exposure while considering their potential transport, transformation and toxic effects in the natural flora and fauna. It rightly highlights that the potential benefits of the use of nanomaterials in agri-food production, fisheries and aquaculture should be balanced against concerns over the any negative impacts on human health and the environment.

Chapter 10 provides an overview of the main nanomaterials and colloidal formulations related to the agricultural sector that are either available on the global market, or are currently undergoing patenting process. The overview concludes that there is a substantial growth in the use of nanomaterials and colloidal formulations for agricultural applications in recent years. While many nanomaterials are currently under R&D, various commercial products are also getting to the market for use in some countries. It highlights the potential benefits, safety concerns and future perspectives of such products.

Chapter 11 looks through the past technological developments and concludes that, to be a successful future technology, nanotechnology needs to be developed in an eco-friendly manner so that any negative impacts on human health and the environment are minimized. It stresses stringent quality control, regulation and monitoring of the products derived from nanotechnology, as well as the need for mechanisms to prevent misuse of the technology that could be lead to harmful products and applications getting to the market.

Chapter 12 highlights the potential benefits and gaps in knowledge in relation to safety of the use of nanotechnology applications in agriculture. Chapter 13 discusses both the positive and negative effects of nanotechnology. It identifies the potential for increased productivity to benefit agri-economics, and decrease the use of certain agrochemicals (e.g. chemical fertilizers), which may also minimize pollution. It stresses the need for more studies to establish ways of minimizing any negative impact of the technology on health and the environment.

Chapter 14 provides an interesting overview of the nano(bio)sensors as a means of fast, accurate, cost-effective and in-field detection of soil humidity, soil nutrients, pesticides, and pests and pathogens, and thus could support precision agriculture. It regards such capabilities important because they could lead to increased productivity without negatively impacting human health and the environment.

Chapter 15 discusses the role that nanotechnology derived fertilizers (especially encapsulated nanosystems) could play in enhancing the efficiency of transport, delivery, and plant uptake of the nutrients, which would enable their optimal use. It also proposes a new model of compartmentalized nanosystems based on the way natural systems work.

Chapter 16 looks into biosafety and regulatory issues relating to the use of nanotechnology in agriculture and food. It highlights the importance of understanding biosafety issues that might emanate from the use of nanotechnologies in the agri-food chain and the need for pragmatic regulatory controls. In this context, it stresses the need for reliable methods for characterization of nanomaterials, and sharing the knowledge and information with all key stakeholders, including the general public.

Chapter 17 explores the potential uses of nanotechnology for water purification and wastewater treatment, and detection of a variety of contaminants and pathogens in food and the environment. In doing so, it not only identifies opportunities but also recognizes the likely challenges ahead and attempts to clarify some over-expectations and misconceptions about nanotechnology. Chapter 18 discusses the new and emerging field of nanopesticides. It also considers the possible use of nanotechnology in nanoparticle-mediated gene transfer for the development of insect resistant plant varieties. It proposes the use of green and ecological substitutes for pest management that do not damage the natural environment.

In summary, the book is the most comprehensive single source of information on the current and projected applications of nanotechnology in agriculture sector. It provides a critical yet balanced view of the nanotechnology-inspired innovations for the wider agriculture sector. It is therefore commended as essential reading for anyone who has an interest in this area from academic, research, industrial or regulatory perspective.

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# Preface

Nanotechnology is recognized as the sixth most revolutionary technology in the modern era. Among the preceding revolutions introduced at different timescales, the Green revolution of the 1960s and currently nanotechnology have vastly affected the agricultural field. After witnessing the unsustainable approach of the Green revolution and certain performance-based limitations of biofertilizers/ biopesticides, modern agriculture is using the innovative approach of nanotechnology to combat a wide spectrum of challenges such as crop production, food security, sustainability and climate change.

In this context, the present book, *Emerging Trends in Agri-nanotechnology: Fundamental and Applied Aspects*, provides a timely update on the recent progress in all aspects of agri-nanotechnology with special emphasis on nanofertilizers, nanopesticides, nanoherbicides, nanosensors and smart delivery systems for controlled release of agrochemicals, as well as the biosafety concerns and regulatory issues of this innovative technology and its relevance into the market.

The book is organized into 18 chapters covering the following subjects: history (Chapter 1); use of nanomaterials in agriculture (Chapter 2); green nanotechnology (Chapter 3); nanonutrients (Chapter 4); enhanced productivity (Chapter 5); synthesis and applications of nanoparticles in agriculture (Chapter 6); toxicity, fate and transport of nanomaterials (Chapters 7, 8 and 9); global market (Chapter 10); nanoproducts (Chapter 11); applications and emergence in agriculture (Chapter 12); effects of nanotechnology in agriculture (Chapter 13); nanosensors (Chapter 14); nanofertilizers (Chapter 15); biosafety and regulatory aspects (Chapter 16); water treatment (Chapter 17); and nanopesticides (Chapter 18).

This book provides a thorough analysis of the progressive journey in agriculture from Green revolution to Nano revolution, with recommendations of certain key points to be addressed in current and future agri-nanotechnology research, on the basis of recognized knowledge gaps. We hope that the current volume will serve as a reference book for students, scientists, professors, teachers and researchers who are involved in the study and research on the various aspects of agri-nanotechnology.

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**Editors**

# 1

# Rewinding the History of Agriculture and Emergence of Nanotechnology in Agriculture

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## 1.1 Introduction

Agriculture has been the key factor for development and rise of human civilization by nurturing the ever-growing human population. Agricultural history dates back thousands of years when people started to harvest their food from the surroundings about 10,000 years BC (Wieczorek and Wright, 2012). The field of agriculture has witnessed groundbreaking revolutions with the main aim of enhancing food production in order to feed the constantly growing human population. The major concern for agriculturists is to enhance crop production in a sustainable manner with the aim of fulfilling food demand for the ever-growing human population, which is expected to grow to around 9.3 billion in 2050. In this regard, researchers are attempting to bring substantial changes in agricultural technology to shape the infrastructure of modern agriculture (Mba *et al.*, 2012; Mishra *et al.*, 2014b).

The Green revolution (GR) is credited with the development of high-yielding varieties, and enhanced crop yield has led to transformation of management techniques through uncontrolled use of synthetic fertilizers and pesticides. However, despite the largely excellent outcome from GR, there are adverse effects from synthetic pesticides and fertilizers on ecosystems, including diminished soil fertility and groundwater pollution. The major concerns and issues associated with GR raised important question about the sustainability and efficiency to cope with the

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emerging challenges of the 21st century (Thompson *et al.*, 2007). Consequently, efforts were channelled to address biosafety issues and sustainability in agriculture and this led to the development of organic farming through biofertilizers and biopesticides. Enhanced crop productivity and plant disease management without any adverse impacts on soil microflora are the major advantages of using these bioinoculant-based fertilizers and pesticides (Adesemoye and Kloepper, 2009; Bhardwaj *et al.*, 2014). In spite of this, the major concerns of shelf life and unpredictable performance under stressed environment limit its complete effectiveness in agricultural practices. Therefore, changes in agricultural technology are urgently needed by modern agriculture in order to face the major constraints in a sustainable manner. Hence, nanotechnology has emerged as a cutting-edge solution, as this revolutionary technology provides the opportunity for precision farming (Mishra and Singh, 2015; Mishra *et al.*, 2017a).

## 1.2 A Brief Outline of Nanotechnology-based Researches in Agriculture

In recent times, nanotechnology has emerged as the sixth revolutionary technology after the Industrial Revolution in the mid-1700s and the Green revolution of the 1960s (NAAS, 2013) (Fig. 1.1). In actual fact, the multidisciplinary approach of nanotechnology has been exploited in a broad range of sectors, including cosmetics, pharmaceuticals, electronics and agriculture (Mishra *et al.*, 2016). The agricultural sector has witnessed tremendous advancements due to the integration of nanotechnology providing new avenues in the field of agri-nanotechnology (Mishra *et al.*, 2017a). The innovative field of agri-nanotechnology has contributed successfully in various areas such as genetics and plant breeding,

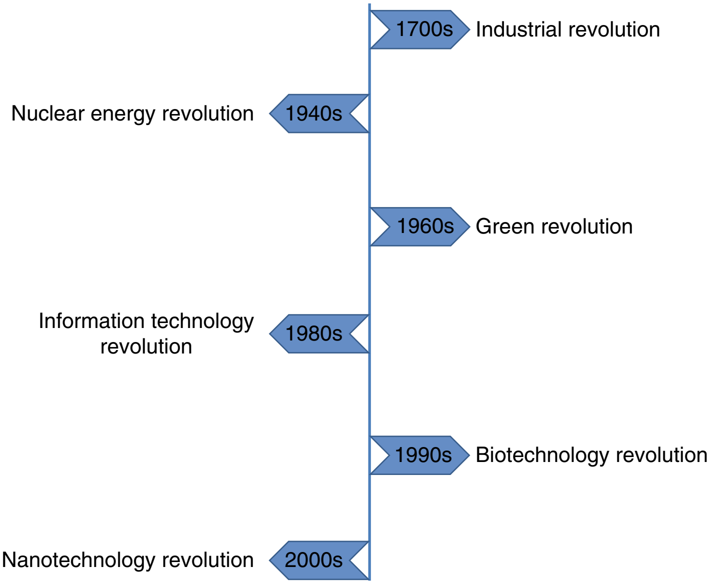

**Fig. 1.1.** Evolution of the technology in agriculture section.

waste remediation, nanobioprocessing, plant disease management and crop productivity (Moraru *et al.*, 2003; Nair *et al.*, 2010; Mishra *et al.*, 2014a; Mishra *et al.*, 2017b).

The concept of nanotechnology in the agriculture sector originated approximately half a century ago (Mukhopadhyay, 2014). The remarkable popularity of nanotechnology-based researches in the agriculture sector is demonstrated by the fact that Google Scholar Search on the phrase '*nanotechnology in agriculture*' shows about 464,000 results while Google patents search displays 2283 patents (at time of writing).

This progressive increase in scientific publications and patents reveals the potential benefits of nanotechnological applications in agriculture. It is worth mentioning here that the scientific fraternity is seeking nanotechnology solutions to various agricultural and environmental challenges due to its robust application. Agriculture benefits from nanotechnology in a number of ways, such as reduced use of agrochemicals due to smart delivery system, nanofertilizer for reducing the loss and runoff of synthetic fertilizers, killing of phytopathogens by nanopesticides, bionanocomposites, nanosensors as a smart detecting tool (Nair *et al.*, 2010; Parisi *et al.*, 2015; Mishra *et al.*, 2017a,b) (Fig. 1.2).

The growing trends of publications in different areas of agri-nanotechnology depict the ongoing researches and their excellent outcome. As evident

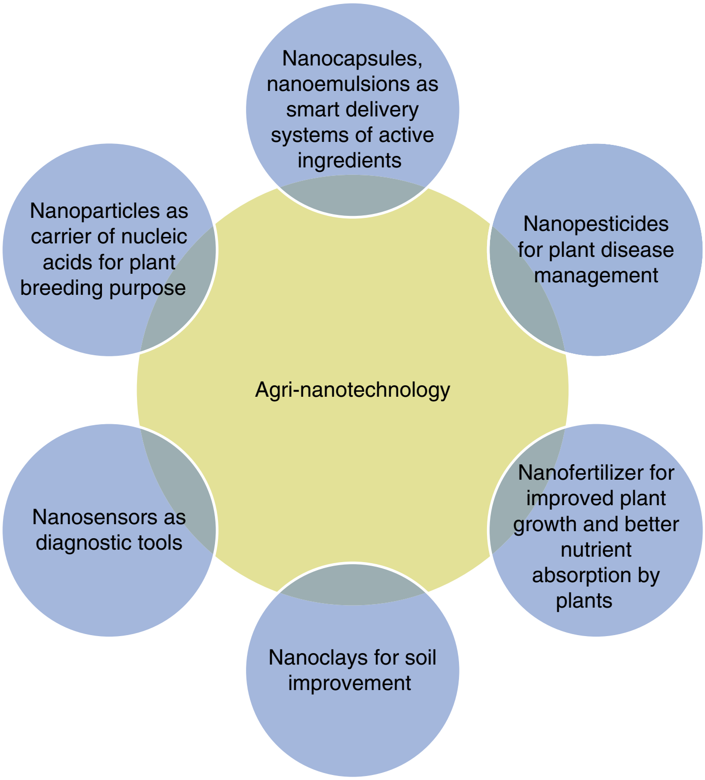

**Fig. 1.2.** Potential applications of nanotechnology in agriculture.

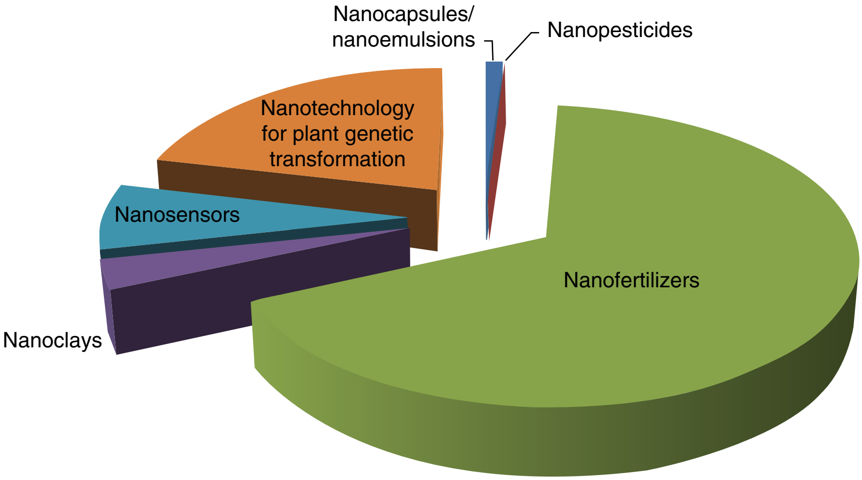

**Fig. 1.3.** Figure generated based on Google search results of published articles in the representative areas.

from Fig. 1.3, the majority of research has been carried out in the area of nanofertilizers, while a limited number of studies has been attempted in the area of nanopesticides. The global scenario of research trends in agri-nanotechnology is expected to benefit both society and the agricultural sector enormously.

## 1.3 Achieving Sustainability in Agriculture Through Nanotechnology: What Are the Possibilities?

Sustainability has been the main goal in agricultural researches and is being given priority in order to protect the environment. Integrating the concept of sustainability into any technology and research design is necessary to deal with the global challenges of environment security and societal benefits. However, coping with sustainability issues is proving to be difficult due to the complicated interaction between the ecosystem and society (Rao, 2002; Wennersten *et al*., 2008). In 2000, when nanotechnology research began, the main goal was the discovery, synthesis, characterization and modelling of nanoscale materials, which are popularly known as nanoparticles. With continuous advancements in nanotechnology-based studies, the research agenda has become more focused towards addressing the major issue of sustainability. The sustainability of any technology is based mainly on three components: ecosystem health, societal benefits and economic profitability (Diallo and Brinker, 2011) (Fig. 1.4). Achieving sustainability in agriculture is necessary to meet the current and future needs of society and the environment without having any detrimental effects on the ecosystem.

There are certain millennium development goals (MDG) established by the United Nations with which one can identify the sustainability of the technology (Brutland, 1987). Keeping these goals in mind, we can predict the sustainable approach of nanotechnology in the following ways.

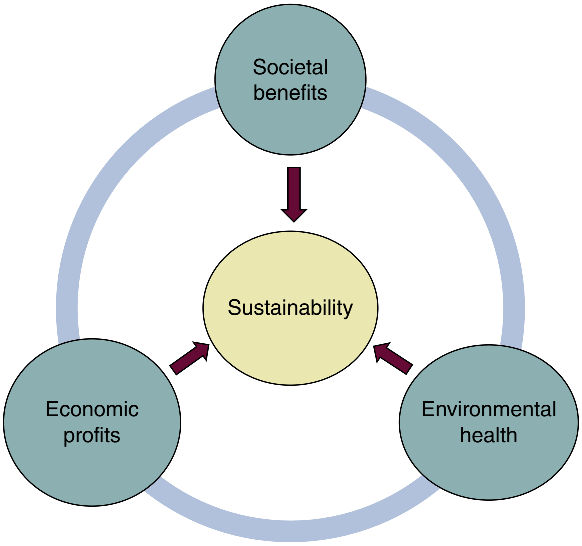

**Fig. 1.4.** The key components of sustainability in agriculture.

**1.** Nanotechnology has the potential to advance modern agricultural systems with huge positive impacts on society. Moreover, the food safety sector also benefits through the integration of nanotechnology.
**2.** Taking into account the hygiene and sanitation issues of society, nanotechnology has offered promising applications in the field of water treatment technologies, eradicating the occurrence of water-borne diseases. Moreover, groundwater contamination has been another serious issue that can easily be addressed with the help of nanotechnology.
**3.** Nanotechnology-based advanced methodologies for detecting, monitoring and prevention of plant diseases.
**4.** Restoring and maintaining soil fertility through application of nanofertilizers.

Subsequently, these optimistic disclosures of the potential of nanotechnology indicate an environmentally sustainable approach for agricultural uses. Furthermore, modernization of the agricultural sector through involvement of nanotechnology has contributed greatly to the food sector by improved methods for food supply (Srinivas *et al.*, 2009).

## 1.4 Challenges in Forthcoming Years

The potential applications of nanotechnology in agriculture are high; however, some topics need to be addressed (Fraceto *et al.*, 2016). In coming years, nanotechnology has the potential to become a reality in the agriculture sector (Fig. 1.5); however, some key points should be improved.

**1.** *Nanomaterials to be used on the field* – at the moment, agrochemical companies need to work together with the universities and research institutes in order to

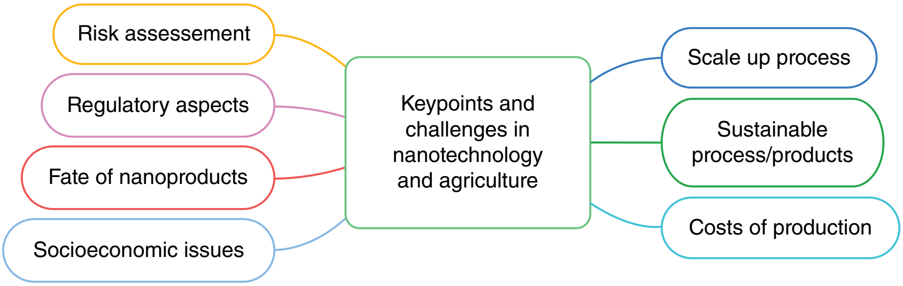

**Fig. 1.5.** Keypoints and some challenges in the coming years in nanotechnology applications in agriculture.

make feasible the technology transfer aiming to produce new and more efficient crop protection products to increase agricultural production.

**2.** *Development of process and products using sustainability principles* – researchers involved in the development of new nanotech-based products need to seek ways to develop clean technology; for example, based on green chemistry, as well as the use of naturally occurring compounds for pest control, such as botanical insecticides and repellents. Another aspect concerns the development of systems that can contribute to preserving the soil microbiota, thus bringing great benefits to soil fertility over the years.

**3.** *Reduction in costs of process and nanoproducts to be used in the field* – because many of the processes involving nanotechnology are still expensive, the scaling process, as well as the raw materials to be used to produce nanoproducts should be low cost, with preference given to biodegradable materials with a biological origin.

**4.** *Understanding of the fate of nanoproducts* – an understanding of the fate of nanoproducts in the environment is of the utmost importance for guaranteeing the use of these in agriculture. In this regard, researchers need to make efforts to understand the mechanisms of their interaction with soil, water and air, as well as, in some cases, the development of new models that can predict the fate of these new nanoproducts.

**5.** *Investigation of risk assessments of nanoproducts* – the entire scientific community involved in the development of nanoproducts must be clear about the potential risks to the environment and human health from the use of nanoproducts in agriculture. Transport studies along the food chain should be performed, as well as determination of the limits allowed for each of these nanoproducts in order to ensure that they do not carry risks.

**6.** *Regulation aspects of the use of nanoproducts into the field* – regulatory agencies, researchers and companies should ensure regulatory frameworks for the use of nanotechnology in agriculture, as well as what limits are important to ensure food security.

**7.** *Discussion about socioeconomic aspects of the use of nanotechnology in agriculture* – researchers, companies and governments should work towards demonstrating the possible advances of nanotechnology in order to guarantee food security through the people. Another aspect concerns the impacts of the use of these technologies related to the job positions due to the use of the technology, as well as the needs of qualifications for the employees in the field of nanotechnology applied to agriculture.

Therefore, such aspects need to be discussed in a very short space of time in order to ensure that nanotechnology can really be a revolution for the agricultural sector, in particular with increased productivity, coupled with a decrease in environmental impacts caused by the use of agrochemicals in the field.

## 1.5 Future Approach

Regarding the future for nanotechnology in agriculture, we believe that it can be used in conjunction with other actions, such as smart grid technology. In this context, crop problems could be solved through the use of effective nanopesticides in order to meet local, regional and global demands. In this context, the association of effective methods of applications of nanopesticides, nanofertilizers and systems for maintenance of water in the soil could be carried out by drones to correct locally the deficiencies in the crops. It is also worth noting that in the future, all these actions could be controlled by intelligent decision-making systems connected with very sensitive and specific nanosensors (Fig. 1.6).

Such actions could provide a better control against pests in crops, thus minimizing problems of resistance of organisms to nanopesticides. Moreover, there is a wide scope for nanotechnology to be part of an efficient management system in agriculture in order to provide increased productivity associated with reduced impacts on environment and human health.

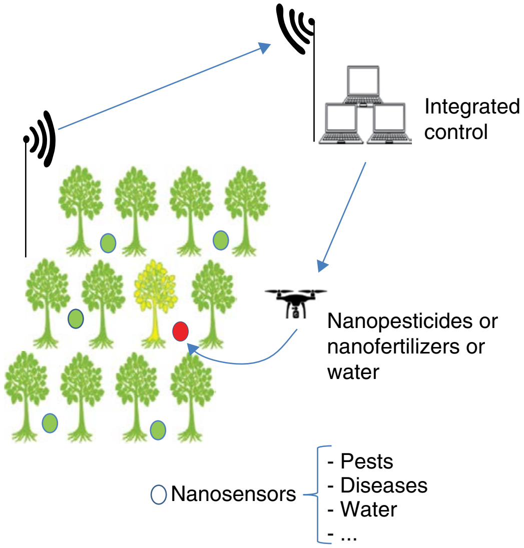

**Fig. 1.6.** Integrated system for crop protection.

## Acknowledgements

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# 2

# Use of Nanomaterials in Agriculture: Potential Benefits and Challenges

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## 2.1 Introduction

Agrochemicals are essential to increase the quantity of food; additionally, they are an important way to decrease or eradicate pests. On the other hand, with the development and adoption of transgenic crop plants, more agrochemicals, especially pesticides, are being utilized. Because of increased pesticide residues, there is more contamination of food and water. Novel technologies are becoming available for example, nanotechnology, including agrochemicals, is currently an emerging technology, and may soon be in everyday use. In the last decade, the area of nanotechnology has grown enormously from patents to scientific publications, in a variety of areas, such as energy production, electronics, medicine and agriculture (Chen *et al.*, 2013; Cozzens *et al.*, 2013; Kah, 2015). In the area of agriculture, scientific production is evident, concentrating on nanoagrochemicals, from nanopesticides to nanofertilizers (Kah, 2015; Mishra *et al.*, 2016; Mishra *et al.*, 2017) (see Fig. 2.1). By the end of 2011, the agrochemical sector accounted for more than 3000 lodged patents and 60 published peer-reviewed papers (Kah *et al.*, 2013). But is this technology safe? Will we have the legal and scientific means to assess the risks of its development and application? Or will this be another stigmatized breakthrough like GMO (genetically modified organisms)? These issues are essential in assessing the safety of nanoagrochemicals related to human and environmental health, as emerging contaminants (Kah, 2015). With

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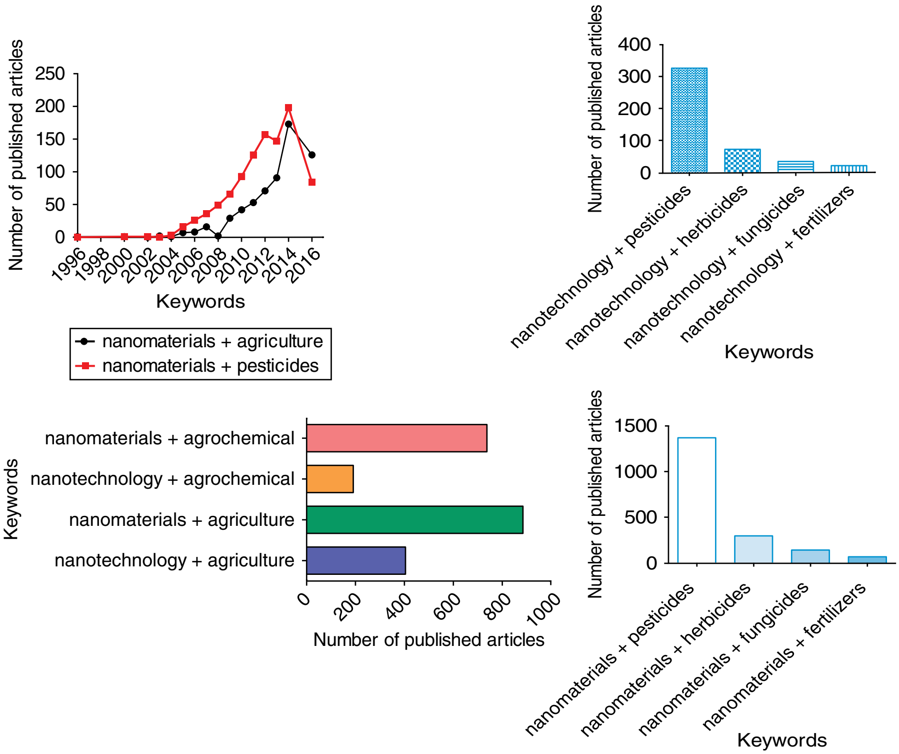

**Fig. 2.1.** Scientific activity related to nanoagrochemicals in numbers. Different types of promising products presented in the literature have been increasing in the last decade.

this in mind, this chapter will explore interesting aspects related to use, benefits and potential challenges; additionally, toxicological evaluation and regulation are also discussed.

## 2.2 Nanobiotechnology in the Context of Agriculture

Global warming and increasing population with reduction of land area for plantations are of great concern. Hence, more efficient and productive methods for all food production processes are necessary and the application of nanoscience to agriculture can provide these benefits. Increasing crop yields without causing a significant environmental impact while cultivating the same agricultural area is the goal of a production system called sustainable intensification (Royal Society, 2009). In this context, nanomaterials based on the use of organic, inorganic, polymeric or lipid nanoparticles have been developed for different phases of food production, as described below.

**1.** Systems that improve soil quality, such as hydrogels, nanoclays, and nanozeolites that have been reported to enhance the water-holding capacity of soil

(Sekhon, 2014) or metal oxide nanomaterials that absorb environmental contaminants and improve soil remediation (Khin *et al.*, 2012).

**2.** Nanomaterials that stimulate plant growth, such as $SiO_2$ and ZnO nanoparticles, which enhance elemental uptake of nutrients by the plants (Khot *et al.*, 2012).

**3.** Nanofertilizers such as NPK NPs (nitrogen, phosphorus and potassium nanoparticles) or hydroxyapatite ($Ca_5(PO_4)_3OH$) NPs that can supply one or more nutrients to the plants and enhance their growth and yields (Liu and Lal, 2015).

**4.** Nanomaterials that enhance seed germination and seedling growth, such as iron nanocomposites and carbon-based nanomaterials (Ratnikova *et al.*, 2015; Lahiani *et al.*, 2016; Raju *et al.*, 2016). Under abiotic conditions such as drought, salinity and cold, nanoparticles containing $SiO_2$, ZnO and analcite depict this property (Khan *et al.*, 2016).

**5.** Nanopesticides, nanoformulations containing herbicides or insecticides that can slow the degradation of the compound and its release to the plant, then reducing the amount of pesticides applied.

Many of these nanoagrochemicals and other nanomaterials related to agriculture described in the literature do not fit into the current marked guidelines. Some have low agronomic relevance, others describe more disadvantages than benefits, and others are not economically competitive. Because of that, critical investigations assessing the impacts, the competitiveness and safety of these nanomaterials must be addressed. Thus, it is possible to point out the facts of the advantages and disadvantages using conventional chemicals and nanoagrochemicals (Fig. 2.2).

## 2.3 Evaluation of Nanoagrochemical Toxicity: Studies in Laboratory Models and Environmental Impact

Nanopesticides are one of the new strategies used to address the problems of regular pesticides. Regarding their safety, they cannot be considered as a single entity due to the combination of several surfactants, polymers, and metal nanoparticles in the nanometer size range. Besides, nanopesticides cover a wide variety of products, and so nanomaterials serve equally as additives (mostly for controlled release) and active constituents. Specific nanoencapsulated pesticides have the ability to kill target insects only, thereby reducing the effective dose when compared to traditional pesticides. On the other hand, these nanoagrochemicals are absorbed on the surface of the plant, prolonging their release that lasts for a longer time compared to conventional pesticides that are washed away by precipitation (Sekhon, 2014). Although this might be an advantage, elevated cerium content was detected in plant tissues exposed to cerium oxide nanoparticles, suggesting that these nanoparticles were taken up by the roots and translocated to shoots and edible tissues (Wang *et al.*, 2012). Nanopesticides can increase the dispersion and wettability of agricultural formulations and unwanted pesticide movement.

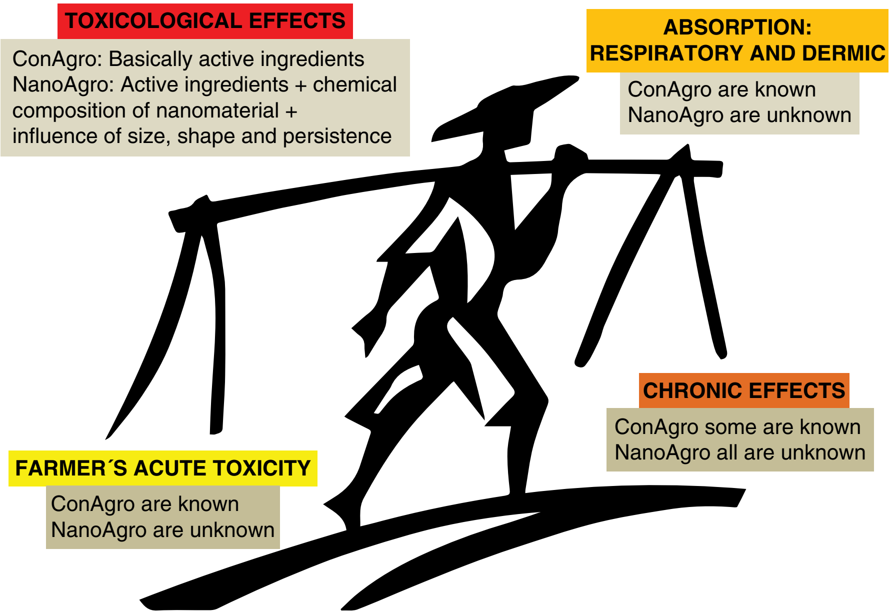

**Fig. 2.2.** Comparison on advantages and disadvantages between conventional and nanotechnology-based agrochemicals.

This observation sheds light on the long-term impacts of nanopesticides on plant health and its implications for food safety and security (Khot *et al.*, 2012).

The major concerns associated with application of nanomaterials in agriculture include toxicity of the ecosystem, potential residue carry-over in foodstuff, and nanomaterial phytotoxicity. At least three distinct mechanisms have been implicated in nanoparticles toxicity: (i) release of toxic substances, ions such as $Fe^{2+}$, $Ag^{+}$, $Cu^{+}$, $Mn^{2+}$, $Cr^{5+}$ and $Ni^{2+}$ released from soluble nanoparticles; (ii) generation of reactive species through surface interactions between the nanoparticle and the biological system; and (iii) direct physical interaction of nanoparticles with biological targets such as membranes, DNA, mitochondria and other cell components (Mehrian and De Lima, 2016).

One of the concerns around nanoagrochemicals is their phytotoxicity. The phytotoxicity may depend on the type of nanomaterial and its potential application. Fluorescein isothiocyanate (FITC)-labelled silica nanoparticles and photostable cadmium-selenide quantum dots were tested as biolabels and for seed germination promotion. It was observed that FITC-labelled silica nanoparticles induced seed germination in rice, while quantum dots arrested the germination (Nair *et al.*, 2011). The phytotoxicity of several nanomaterials, including multi-walled carbon nanotubes (MWCNTs), aluminium oxide-$Al_2O_3$, ZnO, Al and Zn, and its impact on germination rates in radish, oilseed rape, ryegrass, lettuce, maize, and cucumber was evaluated. It was hypothesized that the higher concentrations (2000 mg/l) of nanosized Zn (35 nm) and ZnO (20 nm) inhibited the germination in ryegrass and maize, respectively. The root length of the studied species was also inhibited by 200 mg/l nano-Zn and ZnO. Besides, nano-Al and $Al_2O_3$ significantly affected root elongation of ryegrass and maize, whereas nano-Al facilitated the radish and rape root growth (Lin and Xing, 2007). Similarly, Ma *et al.* (2010) verified the effects of $CeO_2$, lanthanum (III) oxide-$La_2O_3$, gadolinium (III) oxide-$Gd_2O_3$ and ytterbium oxide-$Yb_2O_3$ on the radish, rape, tomato, lettuce, wheat, cabbage and cucumber plant species. It was observed that root growth depends on the concentration of nanoparticles. In this study, nano-$CeO_2$ did not affect root elongation except for lettuce at 2000 mg/l concentration, but the other three types of nanoparticles greatly affected root growth at the same concentration (Ma *et al.*, 2010). In the same way, it was verified that CuO nanoparticles inhibited the growth and development of transgenic and conventional cotton, especially due to a reduction of the uptake of nutrients, such as B, Mo, Mn, Mg, Zn and Fe, and an inhibition of the Na and Mn transport (Van *et al.*, 2016). Furthermore, both ZnO and CuO nanoparticles could inhibit root elongation both in maize or rice, mainly because metal ions ($Cu^{2+}$ and $Zn^{2+}$) can interfere in the uptake of nutrients by roots (Yang *et al.*, 2015). Such alterations were accompanied by interference with the plant antioxidant defence system and destruction of chloroplasts. This was observed with $CeO_2$ nanoparticles, which aggregated on the external surface of the chloroplasts, causing its swelling and rupture (Nhan Le *et al.*, 2015). Interestingly, in lettuce $CeO_2$ nanoparticles seem to have a dual effect: at 100 mg/kg potting soil they increase the nitrate content, promoting vegetative development, while at 1000 mg/kg potting soil, an inhibition of plant growth was noted. Moreover, a down-regulation of superoxide dismutase (SOD) and peroxidase (POD) activities and an increase in lipid peroxidation were observed at 1000 mg $CeO_2$ nanoparticles/kg potting soil, probably due to the release of $Ce^{3+}$ ions (Gui *et al.*, 2015).

The antimicrobial property of silver nanomaterials is well known and hence more than 100 commercially available pesticides contain Ag. It was reported that citrate-coated colloidal Ag nanoparticles were not genotoxic, cytotoxic or phototoxic to humans; however, citrate-coated Ag nanoparticles in powder form were toxic. This effect might be due to the chemical change of spherical silver nanoparticle in the powder to form silver oxides or ions. Interestingly, the phototoxicity of the powdered form was repressed by coating the nanoparticles with biocompatible polyvinylpyrrole, indicating that exploring biocompatible coatings would increase the chances of applying nanomaterials in plant germination and growth (Lu *et al.*, 2010). Two important points on toxicity of nanofertilizers are: (i) there are many types of naturally occurring nanoparticles in ecosystems, therefore plants should have specific mechanisms in moderating these small particles; (ii) crops need only trivial amounts of micronutrients to maintain normal physiological activities while extremely high concentrations of any micronutrient would cause phytotoxicity (Liu and Lal, 2015).

Recently, the *in vitro* or in culture assessments have speculated beneficial and stimulatory effects of carbon nanotube exposure on plants. Additionally, the suppression of organic contaminant uptake by plants has been reported in the presence of select carbon nanotubes. These findings have increased the attention to the potential applications in agriculture, although the findings are somewhat inconsistent. MWCNTs can be internalized in plant roots. Single-walled carbon nanotubes (SWCNTs) have been reported to efficiently cross the cell wall and membranes of tobacco cells upon *in vitro* exposure, with subsequent transport to specific cellular organelles. Toxicity of carbon nanotubes was found to be largely dependent on concentrations, growth/exposure conditions, and plant species. Another mechanism of toxicity is the induction of reactive oxygen species, which may directly interact with cellular organelles to induce DNA damage or protein inactivation, resulting in apoptosis and cell death. Besides, it has been suggested that carbon nanotubes may have a significant negative effect on the soil microbial community. It is noteworthy that carbon nanotubes can co-transport other contaminants, such as toxic metals (Ni, Co, and Fe), or mediate alteration in pesticide uptake/toxicity in terrestrial plants, which could alter its overall toxicological profile (Mukherjee *et al.*, 2014).

Two nanoagrochemicals including Nano-Gro (a water-soluble granule measuring 4 mm, weighing 0.05 g, containing sulfates of iron, cobalt, aluminium, manganese, nickel and silver) and Avatar-1 (a colloidal solution of ultrapure carboxylates of natural food acids and pure nanosized biogenic metals in deionized water) were evaluated regarding ecotoxicity (Makarenko *et al.*, 2016). The agrochemicals, at recommended doses for agricultural production, led to a decrease in mitotic activity and to changes in the duration of the separate phases of the mitotic cycle in *Allium cepa* L. The formulations increased the duration of prophase and metaphase, and reduced the duration of meta- and anaphase. Preparations induced, thereby, a mutagenic response. Furthermore, Nano-Gro reduced cell size after treatment with 2 times the recommended dose, while Avatar-1, even at the recommended dose, resulted in cell size decrease. Nanoagrochemicals, at seed germination stages, have a stimulating effect; however, this effect can be inhibitory even at the first stages of plant growth and development, especially of the root system. The authors concluded that the toxicity depends on the size and structure of the nanoparticles, with a stronger effect the smaller the nanoparticles; in addition, nanocomposites of crystal structure are more toxic compared to amorphous ones (Makarenko *et al.*, 2016).

The literature depicts a clear motivation for insecticide-related formulations. This is partly because the active ingredients of many conventional insecticides have limited water solubility, requiring a delivery system for their application in the field. Another area of interest is the use of alternative insecticides that are less harmful to non-target organisms and might reduce the development of resistance (Kah and Hofmann, 2014). In mice, it was observed that chlorfenapyr nanoformulation was less toxic than the common formulation (Shi *et al.*, 2010). Similarly, the herbicides ametryn, atrazine and simazine presented a decrease in genotoxicity after encapsulation with poly epsilon-caprolactone (PCL) (Grillo *et al.*, 2012). Besides, it was demonstrated that the atrazine nanoencapsulation with PCL effectively increased its pre- and post-emergence herbicidal activity against mustard plants, a target species. On the other hand, some acute and transient effects were observed on photosynthetic and oxidative stress parameters in maize leaves, a non-target species, after post-emergence treatment with atrazine-loaded nanocapsules. Interestingly, these effects were not persistent and did not affect shoot growth (Oliveira *et al.*, 2015).

Similar effects were observed evaluating the pre-emergence herbicide activity of PCL containing atrazine in *Z. mays*, a non-target species, and *Brassica* sp., a target species. The herbicide presented no effect in the non-target species and the effect was greater in the nanoformulation, compared to the free herbicide, in the target species. Also, the atrazine nanocapsules produced fewer chromosomal aberrations in *A. cepa* cells compared to free atrazine (Pereira *et al.*, 2014). In another study, it was demonstrated that atrazine-loaded nanocapsules presented lower toxicity to green alga *P. subcapitata* when compared to free atrazine, showing the potential of nanotechnology in decreasing adverse environmental and human effects compared to normal pesticide application (Clemente *et al.*, 2014).

The trophic transfer of some nanoparticles has also been studied. In a simulated terrestrial food chain, gold nanoparticles were transferred from tobacco and tomato to a primary consumer, tobacco hornworm (*Manduca sexta*). Although a biomagnification of the nanoparticles was not shown, the trophic transfer was clear (Wang *et al.*, 2016). These findings raise concerns about human exposure via food dietary uptake or food chain contamination. Considering the toxicity of nanoagrochemicals, intrinsic properties such as size, chemical composition, shape and angle of curvature, crystal structure, surface roughness, and hydrophobicity or hydrophilicity should be taken into account. Moreover, extrinsic properties are also of importance in the expression of toxicity, including surface charge (zeta potential) and coating, stability characteristics, particle aggregation, and valence of the surface layer.

## 2.4 *In Vitro* and *In Vivo* Safety Evaluation of Nanoagrochemicals

The direct or indirect impact of NPs exposure in general is a growing public debate; however, these are very early studies. It has been hypothesized that there are three putative mechanisms for NPs entry into the cells: (i) direct diffusion by the cellular lipid bilayer, depending on their size, charge, hydrophobicity, composition and shape; (ii) by endocytosis; and (iii) by channels or membrane protein transporters that can mediate NPs translocation. Once in the cells, NPs can cause a wide range of cellular effects.

The encapsulation of paraquat in chitosan/tripolyphosphate nanoparticles also led to a decrease of cytotoxicity in CHO cells and the chromosome aberration in *A. cepa* compared to free paraquat (Grillo *et al.*, 2014). The environmental effects of the herbicide clomazone, free and associated with chitosan-alginate nanoparticles, was evaluated in bullfrog tadpoles. Amphibians are considered the most vulnerable targets for environmental changes because of their biphasic lifecycle. In this species, a lipidosis, characterized by lipid accumulation in the vacuoles of different sizes in the cytoplasm of the hepatocytes, was verified. Furthermore, the abundance of melanomacrophage centres in the liver in groups exposed to nanoparticles associated, or not, with the herbicide, suggested that the tadpole organism might recognize the chitosan-alginate nanoparticle as a toxin. However, the exact mechanism for this immunomodulation is still unknown (de Oliveira *et al.*, 2016). The fungicides carbendazim and terbuconazole also presented lower toxicity in 3T3 and MC3T3 cells after nanoencapsulation, but the cytotoxicity of the nanoformulation was higher in HeLa cells. This was attributed to the difference in uptake of these nanoparticles by the cells and the ability of carbendazim to inhibit the proliferation of human cancer cells, such as HeLa cells. In *Phaseolus* *vulgaris*, fungicide nanoformulations presented smaller effects in terms of fresh plant mass, probably due to the more gradual release of the fungicides from the interior of the nanocapsules (Campos *et al.*, 2015).

The available literature reports that many nanoagrochemicals are out of the conventional nano-range (1–100 nm) (European Food Safety Authority, 2009; Kookana *et al.*, 2014). A published review reported that, of all the studies analysed, only 37% of the patents and 54% of the published formulations were below 100 nm (Gogos *et al.*, 2012). Usually smaller particles are absorbed faster than larger particles (European Food Safety Authority, 2009).

For instance, when gold nanoparticles (with a diameter of 10, 50, 100 and 250 nm) were injected intravenously into rats, after 24 hours, the gold was present in the liver and spleen, of all particle sizes. However, smaller particles (10 nm) were present in the blood, liver, spleen, kidneys, thymus, heart, lungs and brain, whereas larger particles were found only in blood, liver and spleen (De Jong *et al.*, 2008). This size-dependent distribution pattern was also found in another study with gold nanoparticles (Hillyer and Albrecht, 2001). Colloidal gold nanoparticles (with a diameter of 4, 10, 28 and 58 nm) were orally administered to mice. It was found that smaller particles crossed the gastrointestinal tract faster than larger ones (Hillyer and Albrecht, 2001). Similarly, in rats exposed by gavage to polystyrene microspheres (50 nm to 3 μm), the smaller particles (50 nm and 100 nm) were found in the liver, spleen, blood and bone marrow, whereas particles larger than 100 nm were not found in the marrow bone, or blood (for particles larger than 300 nm) (Jani *et al.*, 1990). Different materials, such as titanium dioxide particles, were also found in the liver, spleen, kidneys and lung tissues of mice after oral administration (Wang *et al.*, 2007). It is important to emphasize that these studies did not use nanoparticles originated for the purpose of nanopesticides. However, many of these materials are constituents of the elemental composition of nanoformulations used in plant protection and fertilizers (Gogos *et al.*, 2012; Al-Samarrai, 2012). Studies such as Wan-Jun *et al.*, that reported DNA damage in peripheral blood lymphocytes, along with chromosome damage in bone marrow cells in rats exposed to nanopesticide chlorfenapyr and their common formulation, are rare (Wan-Jun *et al.*, 2010). In fact, there are few published studies analysing the toxicological effects of nanopesticides in animal models, which increases the risk of using these products.

Depending on the stage of development of nanoformulations, alternative models may be more financially viable, also decreasing the irrational use of animals in science. *Caenorhabditis elegans* is often used in studies with nanoparticles, nanotoxicity endpoints such as survival, life span, brood size and body length are possible, besides the fact that C. *elegans* allows *in vivo* imaging of fluorescent labelled nanoparticles, because of its transparent body (Pluskota *et al.*, 2009; Mohan *et al.*, 2010; Li *et al.*, 2012; Scharf *et al.*, 2013; Gonzalez-Moragas *et al.*, 2015). This feature allowed studies to describe properties of nanoparticles such as the accumulation in the pharynx, vulva and spermatheca in *C. elegans* (Scharf *et al.*, 2013; Gonzalez-Moragas *et al.*, 2015; Charão *et al.*, 2015). Other models such as *Drosophila melanogaster*, *Eisenia fetida* and *Danio rerio* (zebrafish) are described for toxicological studies with nanoparticles. Acute and chronic toxicity was observed in a study with *Drosophila melanogaster*, where flies exposed acutely to silver nanoparticles were unable to finish their developmental cycle, whereas in a chronic exposure the fertility of these flies was affected (Panacek *et al.*, 2011). The toxicity of oxide nanoparticles like $TiO_2$ and ZnO was evaluated in the earthworm *Eisenia fetida* and showed damage to DNA and mitochondria (Hu *et al.*, 2010). Finally, a study reported the acute toxicity of 31 different nanoparticles in zebrafish. Of the analysed particles, six types (calcium oxide, copper, copper in the form of oxide and $CuZnFe_4O_4$, magnesium oxide, and nickel) caused cumulative mortality, whereas copper and silver nanoparticles presented $LC_{50}$ values as high as 3 mg/l (Kovrižnych *et al.*, 2013). Nanoagrochemicals could be environmentally friendly, not harming the soil and organisms living in it, from bacteria to plants. However, some studies reveal the toxicological implications of the application of nanomaterials in the environment.

Johansen *et al.* reported reduced growth of soil bacteria and protozoans by 20–30% upon exposure to fullerene $C_{60}$ nanoparticles (Johansen *et al.*, 2008; Dubey and Mailapalli, 2016). In the same sense, microbial stress was observed in exposures to metal oxide nanoparticles ($CeO_2$, $Fe_3O_4$, $SnO_2$) (Vittori Antisari *et al.*, 2013; Dubey and Mailapalli, 2016). Kim *et al.* reported that soil enzymes (dehydrogenase, phosphatase, and β-glucosidase) were reduced by 17–80% upon exposure to Zn and ZnO nanoparticles (Kim *et al.*, 2011; Dubey and Mailapalli, 2016). The specificity of a pesticide with its target is extremely important, because not obeying this specification means that there will be damage to non-target organisms. However, studies demonstrate the toxic potential of nanoparticles to soil organisms. Growth, survival and fertility were affected in *C. elegans* exposed to silver nanoparticles (Roh *et al.*, 2009; Dubey and Mailapalli, 2016). Traces of $TiO_2$ and ZnO nanoparticles were found inside the *Eisenia fetida* earthworm, resulting in mitochondrial damage (Hu *et al.*, 2010). Temsah and Joiner found 100% mortality in *Eisenia fetida* exposed to 750 mg/kg of nanosized zero-valent iron (El-Temsah and Joner, 2012; Dubey and Mailapalli, 2016) .

In studies related to plant health, Du *et al.* reported the reduction of wheat biomass due to exposure of $TiO_2$ nanoparticles (Du *et al.*, 2011; Dubey and Mailapalli, 2016). Green pea (*Pisum sativum L.*) exposed to nanoparticles of ZnO and Fe-ZnO showed Zn bioaccumulation in roots (200%) and stems (31–48%) as the nanoparticles concentration increased (Mukherjee *et al.*, 2014). Finally, tobacco exposed to aluminium oxide nanoparticles had reduction, in a dependent-concentration manner, of the root length, biomass per seedling and germination rate (Burklew *et al.*, 2012; Dubey and Mailapalli, 2016). These studies demonstrate that there should be harmonization in the laws regulating application of nanomaterials.

Safety assessment of nanoagrochemicals is needed and must be evaluated. High amounts of known pesticides have been used, affecting the farmers' health. Nanoagrochemicals are a promising option due partly to reduction of pesticide application. However, the increased soil absorption and potential increased persistence of these nanoformulations and/or persistence of the nanomaterial itself may cause even more toxicity to farmers and animals that live in the environment, especially chronically. Additionally, toxicity could be more acute and more frequently lethal in farmers. It will be necessary to educate farmers on the application of nanoagrochemicals. Moreover, there are

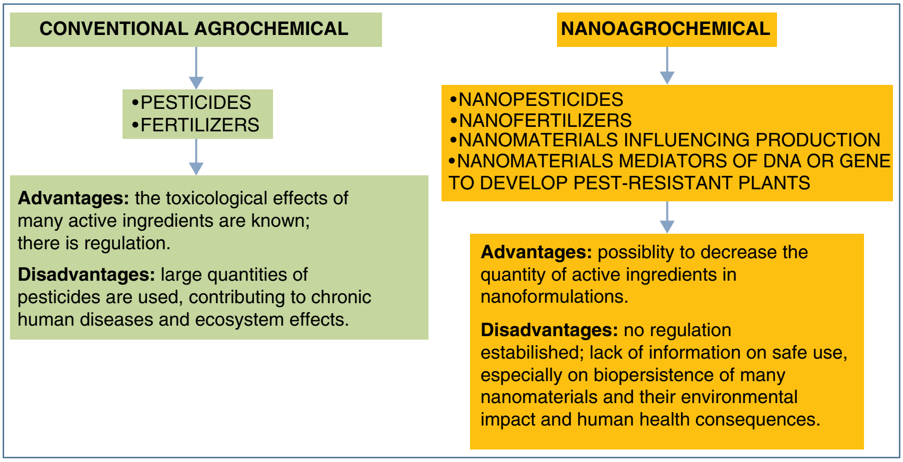

**Fig. 2.3.** Comparative assessment of conventional agrochemical (ConAgro) and nanoagrochemical (NanoAgro).

many gaps about toxicological effects of nanoagrochemicals, especially considering that toxic pesticides and/or fungicides will be nanoencapsulated (Fig. 2.3). Thus, only *in vivo* studies may, in fact, potentially demonstrate the toxicological effects to environment and human health of nanopesticides and nanofungicides, especially.

Conventional agrochemicals, especially pesticides and fungicides, possess toxic effects, including to human health. There are many studies about these and the studies are specific to active ingredient. On the other hand, e.g. nanopesticides will have the active ingredient added to nanomaterials (nanoformulations). Thus, the composition of nanomaterials, their size, shape and persistence will also contribute to their toxic effects. Conventional agrochemicals are not safe; however, information on their risk and care are available. On the other hand, there has been little research on the toxicological effects of nanoagrochemicals, or on routes of absorption, acute or chronic effects.

## 2.5 Regulation: Is it the Greater Challenge for Use of Nanoagrochemicals?

The world population has been increasing considerably throughout the years. According to the Food and Agriculture Organization of the United Nations (FAO, 2009), one of the challenges in agriculture in the 21st century is to produce enough food for this growing population. The adoption of sustainable and efficient methods is of great importance in this scenario, and the use of nanoagrochemicals has arisen as an alternative to improve food production. However, some questions regarding these products remain unanswered and the regulation concerning these products is still incipient and lacks specificity.

Current approaches used in the risk assessment of conventional agrochemicals (non-nanopesticides and -fertilizers) are not considered appropriate on the evaluation of nanoagrochemicals, because parameters relevant in nanoproducts, like particle number and particle size distribution, are not taken into account. Some studies have already demonstrated that novel methods are needed to evaluate these formulations properly (Kah and Hofmann, 2014; Kah, 2015). Thus, modifications in current assessment guidelines are required to make them appropriate to evaluate all the risks related to these substances (Coles and Frewer, 2013; Kookana *et al.*, 2014).

The environmental risks of nanoagrochemicals are of great concern for regulatory purposes. Since nanoformulations present different properties when compared to conventional ones, there is a concern that these particular properties could increase environmental risks. On available regulations, the predicted environmental concentration is calculated for soil, groundwater and surface water. The patterns involved in the substance use and the persistence and phase partitioning of the substance in the environment determine these concentrations. Models are used to evaluate the movement of the substance through soil and groundwater. In this case, the toxicity is related to the concentration of the active ingredient in the formulation. However, in nanoagrochemicals in general, there are other parameters involved in the toxicity of the formulation. The composition, particle concentration, particle size distribution, particle agglomeration and the level of free and bound active ingredient particles are essential for the environmental risk assessment (Kookana *et al.*, 2014). Considering this, a detailed evaluation of the nanoformulation is necessary during the study. Detailed characterization is necessary, including during different stages of the study, since numerous factors (such as pH, soil characteristics, ionic strength) may interfere in the formulation. A clear understanding of the product composition is crucial in order to design an appropriate and relevant test protocol. The current protocols also need improvement to evaluate the bioaccumulation of the nanoagrochemicals, since the uptake into biota differs from conventional formulations and the release of the active ingredient varies according to the matrices used. In the same way, evaluation on aquatic conditions must be improved as well, to adapt to nanoformulation characteristics (Handy *et al.*, 2012; Kookana *et al.*, 2014).

Another important point to be taken into account regarding nanoagrochemicals is their safety for humans. The classical risk assessment framework needs to be adapted to allow an appropriate evaluation of the toxicity of these materials to human health. Adequate characterization of the formulation is also required to evaluate its biological toxicity, and all the changes that may occur during the life cycle of the product must be known. The characteristics involved in the toxicity of the formulations vary according to their nature and intended uses, but in general, they are: (i) particle size and shape; (ii) surface area and charge; (iii) size distribution; (iv) aggregation and agglomeration; (v) zeta potential; (vi) dissociation constant; (vii) structure (crystal or amorphous particles); (viii) interfacial tension and porosity (OECD, 2012; APVMA, 2015).

Inhalation, oral exposure and dermal absorption need careful attention, since they are the most prevalent routes of exposure for these products. The toxicokinetic profile of nanoformulations containing pesticides need to be evaluated according to each case, due to the great variety of formulations produced using nanotechnology (Kookana *et al.*, 2014). Special attention must be given to the toxicity of nanoagrochemicals, especially considering the agricultural workers, due to their close contact with these substances. Regulation regarding their safe manipulation and development of adequate personal protective equipment to prevent the exposure of the workers to these products are also required.

To date, the Australian Pesticides and Veterinary Medicines Authority has released a report on the evaluation of regulatory aspects concerning pesticides and animal husbandry (APVMA, 2015). The document was released in July 2015, and did not aim to provide formal guidelines in the field. The purpose of the report was to inform and stimulate the discussion on these emerging technologies and their use in agriculture and animal husbandry. It also discusses regulatory considerations on these products, based on the current available knowledge.

Considering all of these aspects on nanoagrochemicals, the fast advances in this field and the necessity of improving food production through sustainable and safe methods, their regulation on environmental and human safety is clearly a great challenge and requires mutual efforts from the existent regulatory agencies.

## 2.6 Conclusions

Nanotechnology can have different applications in agriculture, e.g. as nanopesticides, especially through nanoencapsulation of active ingredients already used (insecticides, herbicides and fungicides). In the development of nanofertilizers, bioencapsulation of nutrients is another possibility. The use of the nanomaterial itself, e.g. carbon, might increase the crop production or the contents of phytomedicine compounds. In this case, the use of nanoformulations in agriculture is very interesting because it is possible to decrease the quantity of active ingredients applied and increase its efficiency, besides other positive effects. On the other hand, there are many gaps to elucidate: dosimetry; safety assessment; impact on environmental and human health; regulation; potential increase of acute toxification during application, lethality and biopersistence. In fact, the use of nanomaterials in agriculture, on a greater scale, requires a complete study on toxicity in different sectors: soil, water, residues in food and impact on acute and chronic effects on human health. The proposal is good, but investments in studies are essential to ensure safe food production using nanotechnology before its use becomes reality.

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# 3

# Green Nanotechnology for Enhanced Productivity in Agriculture

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## 3.1 Introduction

Green nanotechnology refers to producing environmentally friendly nanomaterials and nanoproducts without harming the environment or human health. It uses existing principles of green chemistry and green engineering to make nanomaterials and nanoproducts without toxic ingredients at low temperatures using less energy and renewable inputs wherever possible, and using life-cycle thinking in all design and engineering stages. Moreover, green technology offers manufacturing processes for production of nanomaterials and environmentally friendly products with no adverse impacts to the environment. The main aim of green nanotechnology is to develop nano-based products that benefit the environment either directly or indirectly (Green Nanotechnology, n.d.).

It is well known that the small size of nanomaterials gives them unique properties which differ from their larger counterparts. For example, zinc oxide is more soluble, cerium oxide displays enhanced antioxidant property, silicon exhibits electrical conductivity, and gold becomes chemically reactive at nanoscale. Such peculiar properties are being exploited and tailored for different applications; for instance, spurring scientific discoveries, promoting economic growth, creating jobs, improving human health; preventing/curing diseases, and safeguarding the environment.

Today, one route in which nanomaterials enter the environment and humans is through agriculture. Nano-enabled agriculture is particularly attractive because it offers highly beneficial improvements exceeding those of farm mechanization and the green revolution (Gruère, 2012; Khot *et al.*, 2012; Handford *et al.*, 2014; Mishra *et al.*, 2017). Nanotechnology is claimed to alter plant growth,

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phenological development, grain formation and crop yield, which may have serious implications in agricultural productivity. In fact, nanoagricultural inputs like nanofertilizers and nanopesticides have been commercially available for several years, and new products are expected to inundate the market as thousands of patent applications are currently in the pipeline.

Up to now, tropical forests cannot be maintained unless agricultural productivity is greatly improved. However, to feed the ever-growing population of the mid-21st century even at present levels, not to mention the level approached by the developed countries, agricultural efficiencies would have to be far greater than is currently the case in most countries.

Consequently, the very real need to address agricultural sustainability is a key priority for many nations along with nanotechnology as a powerful enabler to combat the threat of resource scarcity and climate change.

One of the striking discrepancies of public perception over nanotechnology and its future application is the inordinate bias placed on the consumer goods market and the benefits in particular across consumer electronics, especially on smart phones. The potential uses of nanomaterials should be highlighted, which have the capability for much further reaching positive change in addressing some of the more pressing issues that humanity faces in terms of resource scarcity and climate change.

As for resource scarcity, one of the most important issues of this era is the global food crisis, currently eighth in the WEF (World Economic Forum) top ten risks of highest concern in 2014. Mineral diminution in soil system has been considered as a growing problem linked to poor crop yields and lower nutritional value of the food produced. High-intensity farming has put a strain on the topsoil while nitrogen and potassium are often replaced with standard fertilizers; many other important micronutrients are often overlooked such as iron, zinc and manganese.

## 3.2 Nanotechnologies for Enhanced Productivity in Agriculture

The use of nanotechnology therefore has the potential to significantly change the landscape of the resource economy, but it is vital that nanomaterial supply chains are organized to be capable of delivering the high volumes required in order to meet the world's critical needs in the markets for energy generation and storage, bulk materials and agricultural production.

### 3.2.1 Nanofertilizers

Nanofertilizers can be utilized to reduce nitrogen loss due to leaching, emissions and long-term incorporation by soil microorganisms. They could be selectively released according to time or environmental conditions. The best way to improve soil by decreasing toxic effects associated with fertilizer over-application is use of slow-release system of fertilizers. The introduction of nanofertilizer products can radically enhance uptake and enrichment of minerals through soil. In wheat varieties, as much as 99% increase of grain yield and 32.4% increase of grain iron levels have been observed as compared to control samples (Liu and Lai, 2015).

### 3.2.2 Nanofibres

With the use of newly developed solvents and a technique called electro spinning (Li and Xia, 2004), scientists produce 100 nm-diameter fibres (from the cotton wastes such as cotton balls, yarns and cotton batting) that can be used as a fertilizer or pesticide absorbent. These high-performance absorbents allow targeted application at a desired time and location (Paul *et al.*, 2012). Nanofibres are also used for encapsulating chemical pesticides, so as to prevent scattering of chemical pesticides in the environment, thereby leading to water and soil pollution. As a result, it increases durability and security applications of chemical pesticides. When the fibres are degraded through biological means, chemical materials are released slowly in the soil (Oliveira *et al.*, 2012; Xu *et al.*, 2014; Saud *et al.*, 2015).

When hydrophobic organic pollutants enter the soil through water, they get readily absorbed by the water-insoluble solids. Porous nanopolymers have a very similar affinity to the pollutant molecules, and are considered the most suitable means for separating organic pollutants of soil and water. Similarly, nanofibre-based fabrics are being used as a detection technology platform to capture and isolate pathogens. The nanofibres in this fabric are embedded with antibodies against specific pathogens. The fabric can be wiped across a surface and tested to determine whether the pathogens are present, perhaps indicating their presence by a change in colour (Feng *et al.*, 2013; Patil *et al.*, 2014; Zhang *et al.*, 2016).

### 3.2.3 Nanopesticides and nanoherbicides

Pesticides inside nanoparticles can be released to an environmental trigger or time schedule. Combined with a smart delivery system, herbicide could be applied only when it is necessary, resulting in greater production of crops and less injury to agricultural workers. Agrochemicals are conventionally applied to crops by spraying and/or broadcasting. In order to avoid the problems such as leaching of chemicals, degradation by photolysis, hydrolysis, and microbial degradation, a concentration of chemicals lower than minimum effective concentration to reach the target site of crops is required. The nanoencapsulated agrochemicals are designed in such a manner that they hold all the essential properties such as effective concentration, time-controlled release in response to certain stimuli, enhanced targeted activity, and less ecotoxicity with safe and easy mode of delivery, thus avoiding repeated application. The best example is the reduction of phytotoxicity of herbicides on crops by controlling the parasitic weeds with nanoencapsulated herbicides (Pérez-de-Luque and Rubiales, 2009; de Oliveira *et al.*, 2014; Fathi *et al.*, 2014; Mishra and Singh, 2015; Grillo *et al.*, 2016; Nuruzzaman *et al.*, 2016).

### 3.2.4 Smart drug-delivery systems

As mentioned above, smart delivery systems can detect and treat an animal infection or nutrient deficiency and provide timed-release drugs or micronutrients

(Kashyap *et al.*, 2015). It shows that the major advantages of encapsulating agrochemicals and genetic material in a chitosan matrix include its ability to function as a protective reservoir for the active ingredients, thereby protecting the ingredients from the surrounding environment while they are in the chitosan domain, and then controlling their release, allowing them to serve as efficient gene-delivery systems for plant transformation or controlled release of pesticides. While research interest into chitosan nanoparticle-based delivery systems is increasing, the current level of knowledge does not allow a fair assessment of the pros and cons that will arise from the use of chitosan-based nanopesticides in agriculture.

### 3.2.5 Nanosensors

Nanosensors can be used to detect contaminants, pests, nutrient content and plant stress due to drought, temperature or pressure. They may also potentially help farmers increase efficiency by adjusting inputs only when it is necessary, according to variations between standards and detected data. Nanosensors fabricated with carbon nanotubes (CNTs) for detecting contaminants are shown in Fig. 3.1.

One of the major problems associated with plant disease management is the detection of correct stage of disease. Mostly, plant protection chemicals (such as fungicides and pesticides) are applied only after the appearance of symptoms thereby resulting in significant crop losses. Therefore, it is essential to detect and diagnose plant diseases at their early stage itself, so that plant protecting chemicals could be applied at the correct dose at the right time, thus avoiding residual toxicity and environmental hazards. Most of the molecular systems for the detection of microorganisms are primarily based on specific nucleotide probe detection or on specific antibodies and such systems are highly sensitive and selective and hence mostly suited for laboratory uses only. Proper sensing systems that could detect and quantify pathogens in defined positions of the field would help the growers in site-targeted and optimized application of agrochemicals with minimal environmental hazards. In this scenario, nanobiosensors, once installed in the field, could detect pathogens with high sensitivity and specificity. Such nanosensors are highly portable systems with real-time monitoring of results. They do not need extensive sample preparations and detection is also label-free (Liu *et al.*, 2008; Sadanandom and Napier, 2010; Chen and Yada, 2011; Peters *et al.*, 2016).

### 3.2.6 Carbon nanotubes (CNTs)

Cañas *et al.* (2008) reported the effects of functionalized single-walled carbon nanotubes (SWCNTs) and non-functionalized SWCNTs on root elongation of six different crop species, such as cabbage (*Brassica oleracea*), cucumber (*Cucumis sativus*), carrot (*Daucus carota*), onion (*Allium cepa*), lettuce (*Lactuca sativa*), and tomato (*Solanum lycopersicum*). They showed that the root elongation in onion and cucumber was enhanced by non-functionalized SWCNTs, and the interaction of both functionalized SWCNTs and non-functionalized SWCNTs with root surface, resulted in the formation of nanotube sheets on cucumber root

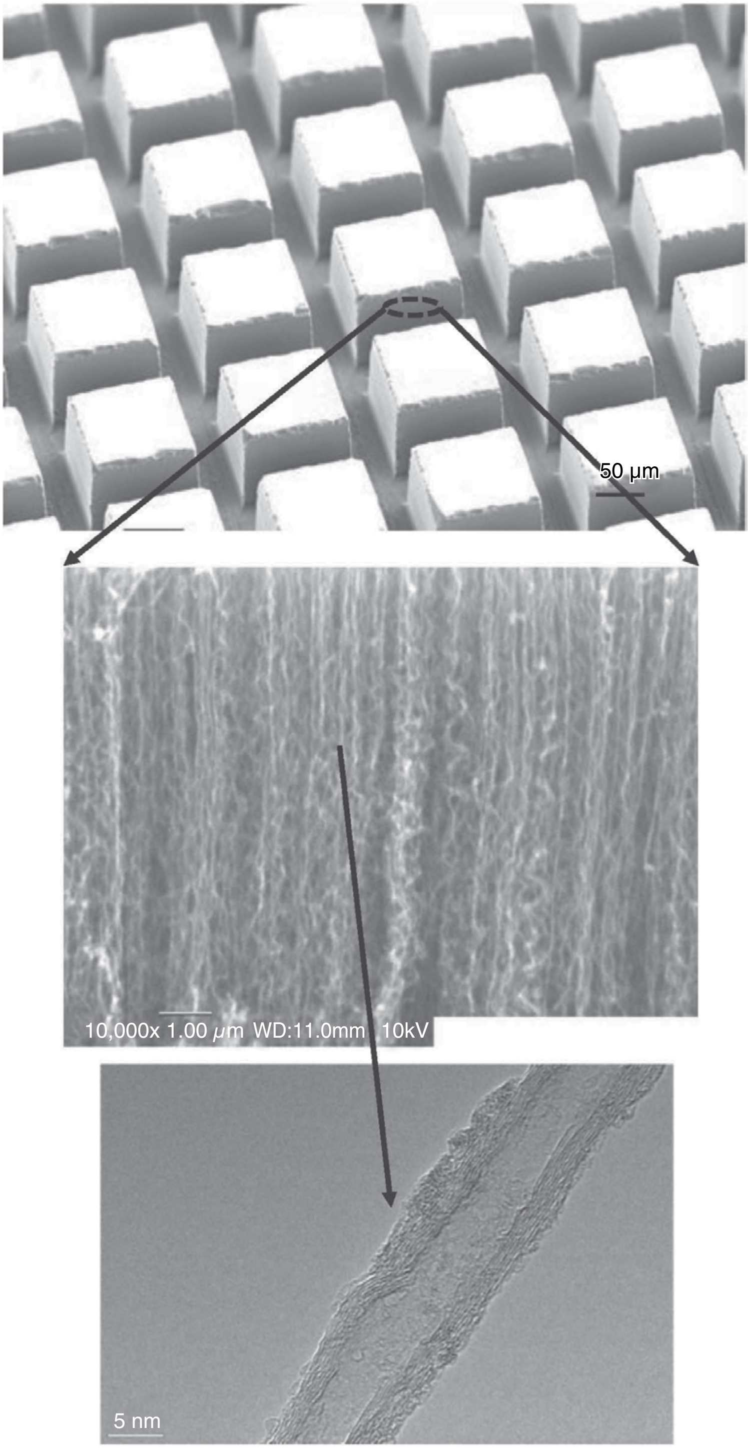

**Fig. 3.1.** Nanosensor fabricated by carbon nanotubes (CNTs).

surface, without entering into the roots. However, cabbage and carrot remained unaffected by either form of nanotubes. Furthermore, functionalized SWCNTs inhibited the root elongation of lettuce, while tomato was found to be most sensitive to non-functionalized SWCNTs with significant root length reduction, whereas a positive response has been shown on the seed germination and growth of tomato plants upon interaction with multi-walled carbon nanotubes (MWCNTs) (Khodakovskaya *et al.*, 2011). They showed that the presence of MWCNTs increased water uptake by seeds which in turn enhanced the germination process. Similar positive effects of MWCNTs on seed germination and root growth of six different crop species – radish (*Raphanus sativus*), rye grass (*Lolium perenne*), rape (*Brassica napus*), lettuce (*Lactuca sativa*), corn (*Zea mays*), and cucumber (*Cucumis sativus*) – was also reported (Lin and Xing, 2007). Nair *et al.* (Nair *et al.*, 2010) also reported the positive effects of both SWCNTs and MWCNTs on the germination of rice seeds and observed an enhanced germination for seeds germinated in the presence of nanotubes.

## 3.3 Nanoparticles

One of the processes using nanoparticles is photocatalysis. It is a combination of two words: photo (light) and catalysis (reaction caused by a catalyst). It means that a chemical reaction is promoted by light and enhanced by the presence of a catalyst, in this case a nanocatalyst. So, it involves reaction of catalyst (nanoparticles) with chemical compounds in the presence of light. A proposed mechanism of this reaction is that when nanoparticles of specific compounds are subjected to UV light, the electrons in the outermost shell (valence electrons) are excited resulting in the formation of electron hole pairs, i.e. negative electrons and positive holes. These are excellent oxidizing agents and include metal oxides like $Al_2O_3$ (Mustafa *et al.*, 2015), $CsO_2$ (Peralta-Videa *et al.*, 2014; Dahle *et al.*, 2015), $Fe_3O_4$ (Antisari *et al.*, 2013), $SnO_2$ (Kusior *et al.*, 2013; Abdelkader *et al.*, 2016; Ali *et al.*, 2016; Othmen *et al.*, 2016), $TiO_2$ (Pan *et al.*, 2015; Ramesh *et al.*, 2016; Hassan *et al.*, 2016), ZnO (Chen *et al.*, 2015; Di Mauro *et al.*, 2016; Dong *et al.*, 2016; Moussa *et al.*, 2016) and sulfides like ZnS (Chauhan *et al.*, 2011; Shamsipur and Rajabi, 2014). Due to their large surface-to-volume ratio, these have highly efficient rates of degradation reaction and disinfection process in agriculture. As the size of particles decrease, surface atoms are increased, resulting in tremendous increase in chemical reactivity and other physico-chemical properties related to some specific conditions such as photocatalysis, photoluminescence, *etc*. Hence, this process can be used for the decomposition of many toxic compounds such as pesticides, which take a long time to degrade under normal conditions (Hossaini *et al.*, 2014; Sood *et al.*, 2015; Štengl *et al.*, 2015).

## 3.4 Knowledge Gap

Understanding nanoagriculture is a critical issue of gaining public acceptance. Unfortunately, it is an area where a huge knowledge gap exists. The fate of nanomaterials and the resulting implications for organisms that consume nanomaterial-contaminated food crops are not well understood. The wider use of these materials has increased their release into the environment through soil, water and air, which may lead to unintended contamination of terrestrial and aquatic ecosystems.

The present state of knowledge in nanoagriculture is still in a foundational stage. Not only are the data limited and inconclusive regarding nanomaterial impacts in agricultural productivity and food safety, but more information is needed on properties that control nanomaterial effects in plants. Moreover, the interplay of these factors gives confounding results making it almost impossible to predict nanomaterials impacts in plants.

Unlike herbicides and pesticides wherein mechanisms of action can be established based on the functionality of the active ingredients, chemical characteristics that can predict environmental behaviour and impacts of nanomaterials are unknown.

Current knowledge highlights the contradictory effects of nanomaterials in plants, which is not surprising given the complex processes involved in plant–nanomaterial interactions. López-Moreno *et al.* (2010) reported that exposures of wheat and barley to nanoceria (cerium oxide nanoparticles) under similar soil conditions stimulated shoot biomass in barley, while on other hand there was not any noticeable change in wheat. They also found that nanoceria were detrimental to grain production in barley, but improved grain yield despite the delay in grain formation and maturity in wheat. A similar trend of toxicity behaviour has been noticed in other related studies, revealing that nanomaterials impose unknown risks to plant-associated microorganisms, enzyme activity, and microbial compositions/processes in soil, all of which may elicit critical changes in soil health, nutrient cycling, and bacteria–plant symbiotic function. In spite of the fact that nanomaterials can benefit agriculture, available evidence is inconclusive to support widespread nanomaterial application in agricultural practices (López-Moreno *et al.*, 2010).

Hence, plant responses to nanomaterial treatments have been reported, but the mechanisms of action are not yet understood. The accumulation of nanomaterial in plants depends on crop species and type of nanomaterial; however, there is overwhelming evidence showing the storage of nanomaterials and/or component metals (e.g. zinc from zinc oxide nanoparticles) in the edible portions of food crops such as tomato, coriander, cucumber, rice, barley, maize, beans, green peas, and groundnut.

Other shortcomings in current nanophytotoxicity studies are the lack of assessments of materials developed for agricultural applications and use of dosages that reach up to several orders of magnitude higher than predicted environmental concentration. Once nanomaterials are absorbed by plants, they can move through trophic levels and compromise the food web. In fact, there are studies demonstrating the trophic transfer and biomagnification of nanomaterials in aquatic and terrestrial organisms. Also, the possible compromise of nutritional quality since nutrient uptake can be altered in crops exposed to nanomaterials and also increased accumulation of already existing soil contaminants in plants (Sadik *et al.*, 2014; Malysheva *et al.*, 2015; Parisi *et al.*, 2015; Servin and White, 2016).

Therefore, the difference between the potential benefits and harm from nano-enabled products is quite subtle and a large knowledge gap exists on the long-term impacts of nanomaterials to the environment, crop production and human health. If nanotechnology is to bring about the next industrial revolution, as is often cited, it will surely be driven by changes to the world's resource economy rather than household gadgets and sports equipment.

## 3.5 Conclusion

Nanotechnology holds the promise of controlled delivery of agrochemicals to improve disease resistance, plant growth enhancement and nutrient utilization. Research and development in green nanotechnology should be investigated for the benefit of more efficient and targeted use of pesticides, herbicides and insecticides in an environmentally friendly greener way to enhance the productivity in a relatively safer way. With the advancement of nanotechnology, application of green chemistry in synthesis of nanomaterials by using plant extracts and living cells would be promising to reduce the use of toxic solvents and guarantees eco-protection. Even though the toxicity of nanomaterials has not yet been clearly understood, it definitely plays a significant role in agriculture due to its unique physical and chemical properties. The application of nanomaterials is relatively new in the field of agriculture and it needs further research investigations along with environmentally friendly effects.

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# 4

# Nanonutrient from Fungal Protein: Future Prospects on Crop Production

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## 4.1 Introduction

There is enormous interest in the synthesis of nanomaterials due to their unusual optical (Krolikowska *et al.*, 2003), chemical (Kumar *et al.*, 2003), photoelectrochemical (Chandrasekharan and Kamat, 2000), and electronic (Peto *et al.*, 2002) properties. There are various physical, chemical and aerosol (physicochemical) methods employed for the synthesis of nanoparticles (Panacek *et al.*, 2006; Tarafdar and Adhikari, 2015). However, these methods have certain disadvantages due to the involvement of toxic chemicals and radiation. Therefore, research is shifting towards biological methods of synthesis of nanoparticles, as these are cost-effective and eco-friendly. Thus, microorganisms have been applied in nanoparticle production (Gade *et al.*, 2010; Tarafdar, 2013a). The importance of biological synthesis is being emphasized globally at present because chemical methods are capital intensive, toxic, non-eco-friendly and have low productivity. For biosynthesis of nanoparticles, potential biological systems such as microbes or plants are commonly being used. The synthesis of inorganic materials may occur either extracellulary or intracellularly. Exposure to varying temperature, pH, substrate concentration, protein level, and shaking speed influences directly or indirectly, the rate of nanoparticle fabrication. It is important to understand the biosynthetic mechanism involved in the fabrication of nanoparticles mediated by a biological system in order to gain better control of the process and products.

Important plant nutrients such as N, P, K, Ca, Mg, S, B, Cu, Fe, Mn, Mo and Zn can be prepared in nano-form from the respective salts by the action of microbial enzymes/proteins. It is a need of today's nanotechnology to develop reliable, non-toxic, clean and eco-friendly experimental protocols for the synthesis of nanonutrient of controlled size, shape and monodispersed, which is possible

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through ambient biological resources. It is necessary to collaborate this technology in a consolidated way with an approach that provides an overview of the current trend of research on the biosynthesis of nanoparticles for their further applications (Punjabi *et al.*, 2015; Tarafdar and Rathore, 2016). The biomineralization of nanoparticles in protein cages is one of such approaches used in the generation of nanoparticles.

## 4.2 Synthesis of Nanonutrients by Microorganism

Most microorganisms like fungi, bacteria, yeast and algae are capable of synthesizing nanonutrients. The fundamental principle of synthesis is breakdown/reduction of salts/ions to nanoparticles (Tarafdar and Raliya, 2013). Figure 4.1 represents how nanoparticles have been produced from the respective salt solution by fungal protein. Various microbes have been reported as synthesizing different nanonutrients (see Table 4.1).

Synthesizing nanoparticles through biological entities acting as biological factories offers a clean, non-toxic and environmentally friendly method of synthesizing nanoparticles with a wide range of sizes, shapes, compositions and physicochemical properties (Mohanpuria *et al.*, 2008). Another interesting feature of many biological entities is their ability to act as templates in the synthesis, assembly and organization of nanometre scale materials to fabricate well-defined micro- and macroscale structures. For example, viruses have been used to assemble iron oxide nanoparticles to form microstructures (Khan *et al.*, 2013), bacteriophages have also been used to form intricate nanometre- and micrometre-scale

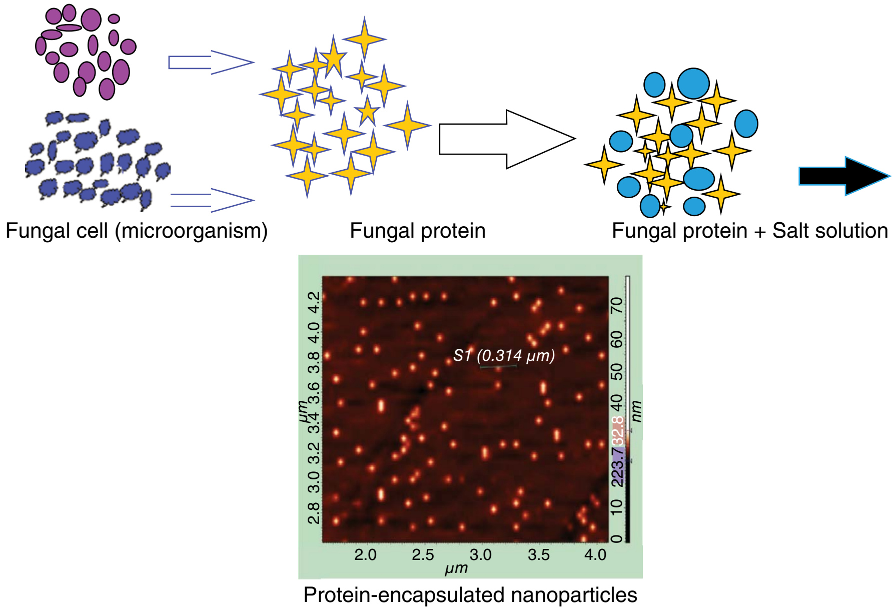

**Fig. 4.1.** A process of biosynthesis of nanonutrients by fungal protein.

**Table 4.1.** Nanonutrients produced by different isolated fungi.

| Name of the organisms | Type of nanoparticle | Average size of nanoparticle | References |
|---|---|---|---|
| *Aspergillus terrus* CZR1 | Ag | 2.5 nm | Raliya and Tarafdar (2012) |
| | Zn | 6.8 nm | |
| | Mg | 3.9 nm | |
| *Aspergillus tubingenesis TFR5* | P | 28.2 nm | Tarafdar *et al*. (2012a) |
| | Ti | 44.8 nm | |
| *Rhizoctonia bataticola TFR6* | Zn | 18.5 nm | Raliya and Tarafdar (2013) |
| | Au | 6.2 nm | |
| *Aspergillus fumigatus TFR8* | ZnO | 3.8 nm | Tarafdar and Rathore (2016) |
| *Aspergillus tubingensis TFR3* | ZnO | 2.8 nm | Tarafdar and Rathore (2016) |
| *Aspergillus oryzae TFR9* | Fe | 17.3 nm | Tarafdar and Raliya (2013) |
| *Aspergillus brasiliensis TFR23* | Mg | 5.9 nm | Rathore and Tarafdar (2015) |
| *Aspergillus tubingenesis TFR29* | N | 1.4 nm | Thomas *et al*. (2016) |
| *Aspergillus ochraceus TFR23* | K | 2.2 nm | Tarafdar and Rathore (2016) |
| *Pseudomonas stutzeri* | Cu | 50–150 nm | Ratnika *et al*., (2011) |
| *Aspergillus tubingenesis* TFR-29 | Mo | 7.9 nm | Tarafdar *et al*. (unpublished) |
| *Bacteriophage* | Ca | Fibrils | Wang *et al*. (2010); Xu *et al*. (2011) |

structures (Cao *et al.*, 2011; Kale *et al.*, 2013; Courchesne *et al.*, 2014). Comparing the abovementioned biological identities and their potential to become efficient biological factories, synthesizing nanoparticles via plants is a relatively straightforward and advantageous approach (Thakkar *et al.*, 2010; Iravani, 2011). The advantage of the plant approach is that it does not need any special, complex and multi-step procedures such as isolation, culture preparation and culture maintenance. Furthermore, synthesis in plants tends to be faster than microorganisms, is more cost-effective and is relatively easy to scale up for the production of large quantities of nanoparticles (Bar *et al.*, 2009; Jha *et al.*, 2009; Swami *et al.*, 2004).

The mechanism for synthesis of nanoparticles in principle remains the same for microorganisms and plants. Salts comprised of ions are first reduced to atoms by means of a reducing agent. Thereafter the obtained atoms then nucleate in small clusters that grow into particles. Although lots of reports for synthesis of nanoparticles using the biological route are available, very few have data for understanding the exact mechanism for the same. A generalized interpretation is involvement of proteins like enzymes and cofactors that have redox potential as well as act as electron shuttles play key role in the reductions. The study (Hosseini-Abari *et al.*, 2014) proposed the dipicolonic acid moiety as the main mechanism for production of silver nanoparticles by *Bacillus stratophericus*. Jain *et al.* (2011) studied the protein profile of cell-free filtrate. The SDS-Page profile revealed presence of two extracellular proteins 32 and 35 KDa found to be responsible for synthesis and stability of silver nanoparticles. The similar results with P nanoparticles were also reported by Tarafdar *et al.* (2012b). The prospective mechanisms of P nanoparticle synthesis are shown (Tarafdar *et al.*, 2012a).

Plant extracts are comprised of various reducing and stabilizing agents that play key roles in nanoparticle synthesis. The nature of plant extract affects the type of nanoparticles synthesized to a great extent. The source of plant extracts being the most vital factor affecting the morphology of the synthesized nanoparticles. This is so because different plant extracts contain different concentrations of biochemical reducing agents. The change in concentrations of biochemical reducing agents differs regionally as well as seasonally in most plant extracts. This variation will lead to differences in nanoparticles synthesized in every batch (Malik *et al.*, 2014).

The phytosynthesis approach for bulk production of nanoparticles remains less popular because plant cell culture is relatively difficult as compared to microbial cultures and complicates the process (Malik *et al.*, 2014). Thus scaling-up of nanoparticle synthesis for bulk production definitely requires employment of such methods, wherein stock culture of reducing-agent plant or microbe is available persistently. And, to avoid batch variation in nanoparticle morphology, development of such *in vivo* methods are prerequisite.

## 4.3 Factors Affecting Synthesis of Nanoparticles

The important factors that affect the biosynthesis of nanonutrients are pH, temperature, reaction mixture, reaction period, salt concentration, precursor compound, etc. In general, pH plays a bigger role in the nanoparticle synthesis. The average nanoparticle size of Zn, Mg and Ti was reduced with increase in pH from 4.0 to 5.5, which was further enhanced up to pH 8.0 (Raliya, 2012). In general, the pH 5.5 was found the most suitable not only for accelerating the rate of reaction but also to substantially reduce nanonutrient size as compared to other pH levels. Although, alkaline pH 8.2 proved more suitable for synthesis of silver nanoparticles (Oza *et al.*, 2012).

Temperature is one of the important physical parameters for synthesis of nanoparticles. The maximum production of nanonutrients was recorded between temperatures of 28 and 30°C. The broad peak displayed at low temperature shows formation of large-sized nanoparticles while the narrow peak obtained at high temperature indicates that nanoparticles synthesized are smaller in size.

The biosynthesis of nanonutrients was timed at between 24 to 72 hours. It was also observed that further incubation beyond 72 h and up to 120 h neither reduced the size of nanoparticles nor was economical to harvest appreciable yields. In a few cases, 100% nanoparticle yield was also noticed between 2 and 24 hours.

The optimization of salt concentration for biosynthesis of nanonutrients showed more nanoparticle production with the salt concentration between 0.1 and 0.5 mM. In general, 1:1 microbial protein:salt ratio was found to be optimum for nanonutrient production and encapsulation.

## 4.4 Characterization of Biosynthesized Nanoparticles

Nanoparticles may be identified using a particle size analyser/DLS, transmission electron microscopy, scanning electron microscopy, atomic force microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, US-VIS adsorption spectroscopy, energy dispersive X-ray spectroscopy, lithography, inductively coupled plasma mass spectrometry and inductively coupled plasma optical emission spectrometry. The properties of nanoparticles depend upon a variety of parameters such as particle size, dispersity, surface area, porosity, solubility, aggregation, zeta potential, etc. The relevant instruments to characterize the nanoparticles are as follows.

### 4.4.1 Scanning electron microscopy (SEM)

This is an electron microscopy technique which uses a high-energy beam of electrons in a raster scan pattern imaging the sample's surface. This produces signals which reconstruct the sample using information provided like topography, composition, conductivity, etc. The SEM gives information on surface structure of the particle (Fig. 4.2).

Advantages of SEM are its two-dimensional imaging, easy sample preparation and provision of digital data forms. One limitation is that improper sample preparation can lead to confusion between artefacts and actual data. Moreover, size, cost and maintenance are obvious limitations.

### 4.4.2 Transmission electron microscopy (TEM)

This is a microscopy technique that transmits a beam of electrons through an ultra-thin specimen, which interacts with the beam. An image is formed of the particle (Fig. 4.3) with the help of electrons, which is then magnified and focused on a fluorescent screen that is then detected. It measures all three dimensions of the nanoparticles along with their composition. Advantages of TEM include high quantity, detailed and powerful magnification of element and compound structures. Its limitations are laborious sample preparation, covering a limited area of the sample.

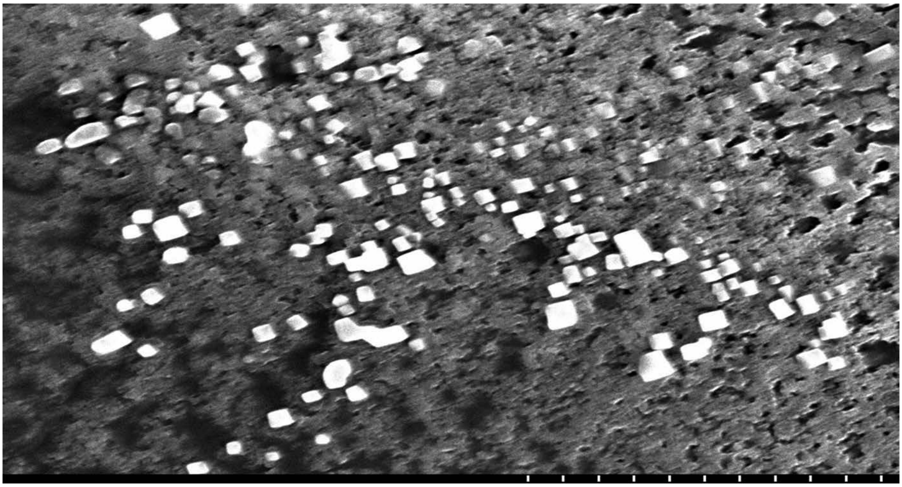

**Fig. 4.2.** SEM image of biosynthesized K nanonutrients.

### 4.4.3 Atomic force microscopy (AFM)

It is a very high resolution type of scanning probe microscopy. The AFM is one of the most accurate tools for nanoparticle analysis with precise imaging, measurement and manipulation of nanoparticles. The forces inside the nanoparticles like mechanical contact force, van der Waals force, magnetic, electrostatic and chemical bonds are measured by this technique. Due to their high resolution, the three-dimensional picture of the particle is very beautiful as well as detailed with structural information (Fig. 4.4).

Advantages are that AFM provides a higher resolution image than SEM. It gives true atomic resolution comparable to scanning tunnelling microscopy and transmission electron microscopy. Limitations include single scan image size, AFM cannot scan images as fast as SEM and image artefacts.

### 4.4.4 X-ray diffraction (XRD)

This instrument is determining the arrangement of atoms within a nanoparticle. The X-ray beam strikes the crystal and diffracts into different directions. From the

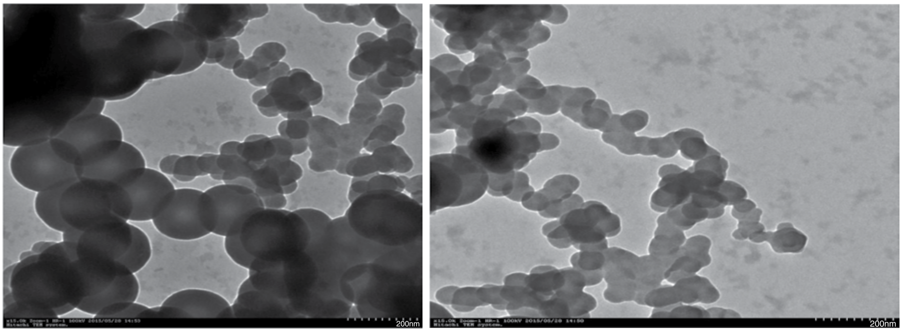

**Fig. 4.3.** TEM images of K nanonutrients synthesized by fungal protein.

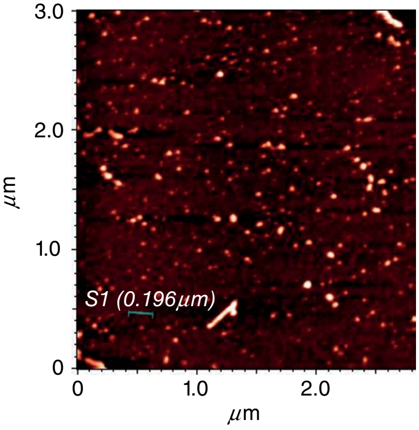

**Fig. 4.4.** AFM image of K nanonutrients synthesized by fungal protein.

diffraction angles and intensities of these beams, we can get a three-dimensional picture of the atoms inside the nanoparticles. There are many methods through which crystals of nanoparticles can be created, such as the hanging drop method, sitting drop method, microdialysis, etc. When the X-ray pattern is recorded, the relative peaks are formed by the mathematical interpretation of the data and the peak provides us with the three-dimensional structure. From the peaks one can identify the particles (Fig. 4.5).

Advantages of XRD are simplicity of sample preparation, rapidity of measurement, analysis of mixed phases and determining sample purity. Its limitations are the requirement of homogeneous and powdered material, and peak overlaps leading to unclear data.

### 4.4.5 Fourier-transform infrared (FTIR) spectroscopy

Here, the target is analysed by placing it in front of an infrared beam. The main aim in this method is to determine the chemical functional groups present in the sample. Different functional group absorbs different IR frequencies. The radiation is then mathematically converted to the nanoparticle structure using Fourier transforms. This is usually better than other methods as it is a non-destructive, environmentally friendly technique that has good speed and more reliable outputs. It gives an indication of which functional group is involved in the breakdown or absorption of particles. Sometimes energy dispersive X-ray (EDX) spectroscopy is associated with SEM, TEM or AFM, which provides information on purity of the particle.

Advantages of FTIR are identifying and detecting changes in protein secondary structures, which can resolve between similar components. Its limitations are that overlapping peaks make it difficult to distinguish and difficult to quantify; there are better results with solid components.

### 4.4.6 EDX

This technique is used normally in configuration with SEM. The energy dispersive X-ray (EDX) technique is used to identify the key composition of nanomaterials using the characteristic X-rays.

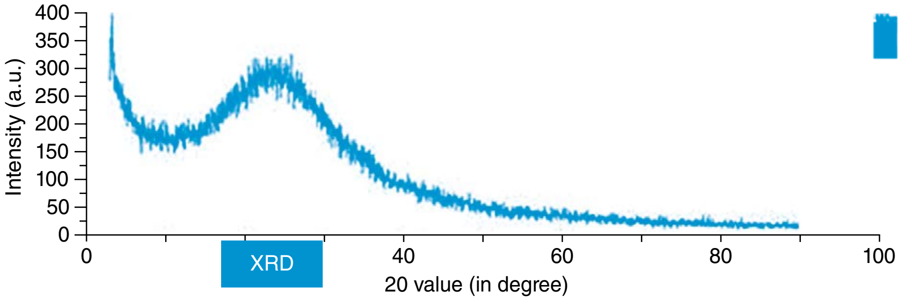

**Fig. 4.5.** XRD image of biosynthesized Fe nanonutrients.

Advantages of EDX (Fig. 4.6) are that it improves quality control and helps in process optimization, identification of contaminant, and gives higher production yield. Its limitation is that quantitative analysis requires standards of known composition and that fluorescence of emitted X-rays limits the precision.

### 4.4.7 Particle size analyser (PSA)

This instrument measures the particle size distribution, polydispersity index (PDI) and zeta potential. In this method, light hits the nanoparticles and is scattered in all directions. Larger particles scatter more light than smaller particles, as the area of contact for the larger particle is greater.

Dynamic light scattering (DLS) measures the time-dependent fluctuations in the scattering intensity to determine the translational diffusion coefficient and subsequently the hydrodynamic diameter from the Stokes–Einstein equation. The concentration of the particles determines how hard it is to scatter the given solution (Fig. 4.7). This technique also measures the polydispersity index (PDI) of the particle and zeta potential of the solution. If the PDI value is less than 1,

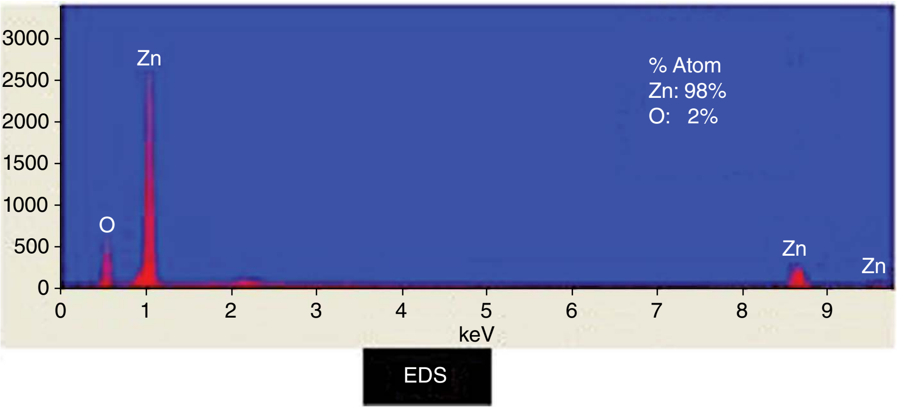

**Fig. 4.6.** EDX peaks showing purity of biosynthesized Zn nanonutrients.

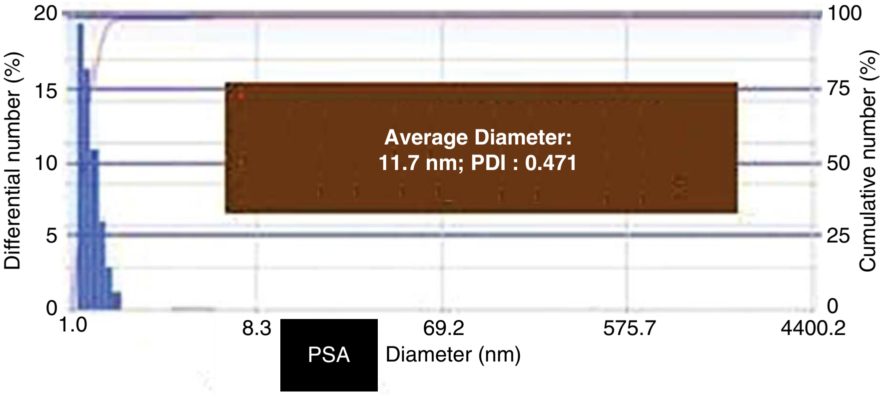

**Fig. 4.7.** Particle sized distribution of biosynthesized Fe nanonutrients.

then the particle is considered as monodispersed. The zeta potential of the solution determines the degree of aggregation of nanoparticles. The higher the zeta potential, the lesser is the aggregation.

Advantages include measurement of particle sizes of less than 1 nm, precision of ± 1%, repeatable analysis, no sample preparation for liquid sample. Its limitations are low resolution of polydispersed samples and multiple light scattering.

## 4.5 Application of Nanonutrients

Nanonutrients can best be applied on 2-week-old plants to foliage wih an aerosol sprayer. In general, nanoparticles under 20 nm and cube-shaped moved faster inside the plants (Tarafdar *et al.*, 2012b). The nanonutrients can enter mainly through cuticle, stomata, hydathodes, stigma, cortex, lateral root junctions and wounds. The optimum concentration of different nanonutrients standardized so far are presented in Table 4.2.

In general, a wide variation of doses of different nanonutrients for plant application was observed (Table 4.2). The dose varies between 2 and 80 ppm of different nanonutrients. The required concentrations of most of the nutrients showed similar results for cereals and legumes. However, requirement of nano-B was higher in legumes while requirement of nano-Mo and nano-K was higher in cereal crops as compared to legumes.

After entering inside the plants, the nanoparticles move though cell sap and trigger the different co-enzyme systems (Tarafdar and Adhikari, 2015) making plants more active to release the enzymes. With time, most of the particles may agglomerate to form megaparticles on the pathway. They are mostly absorbed as nutrients by the plants or are deposited at the vacuoles (Tarafdar and Rathore, 2016).

## 4.6 Effect of Biosynthesized Nanonutrients

In general, 18 to 283% improvement of soil beneficial enzyme activities was noticed, with the foliage application of nanonutrients, in the rhizosphere. The improvement of various beneficial enzymes under different crops is summarized in Table 4.3.

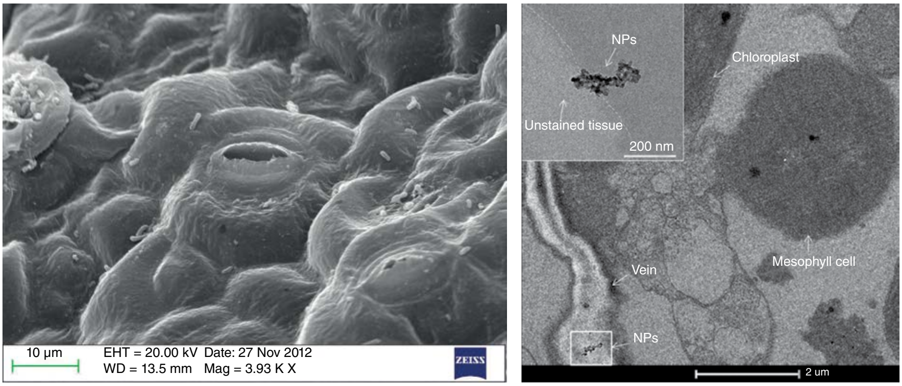

**Fig. 4.8.** TEM picture of entrance and transportation of Zn nanonutrients through stomata of mung bean.

Application of P in nano-form (40 ppm concentration) to the crop plants resulted in improvement of the organic acid concentration in the rhizosphere of arid plants, and ultimately the effect on P uptake (Table 4.4).

It has been found that there was 2–10% reduction in carbon release due to the application of nanonutrient on pearl millet and clusterbean (Tarafdar and Rathore, 2016), which resulted in more accumulation of biomass C. Nano-Zn and -Fe application was associated with high protein content and low super oxide dismutase activities, resulting in more stress tolerance by the

**Table 4.2.** Optimum concentration of nanonutrients to be applied to plants.

| | Optimum concentration (ppm) | |
|---|---|---|
| Nanonutrient | Cereals | Legumes |
| N | 80 | 80 |
| P | 40 | 40 |
| K | 40 | 20 |
| Mg | 20 | 20 |
| Zn | 10 | 10 |
| Fe | 30 | 30 |
| B | 4 | 10 |
| Mo | 6 | 2 |

**Table 4.3.** Improvement in beneficial enzyme activities in the rhizosphere of crops with the application of recommended doses of nanonutrients (average of five crops).

| Serial no. | Name of the enzyme | % increase in activity |
|---|---|---|
| 1 | Dehydrogenase | 25–68 |
| 2 | Esterase | 23–90 |
| 3 | Acid phosphatase | 21–72 |
| 4 | Alkaline phosphatase | 18–136 |
| 5 | Phytase | 23–83 |
| 6 | Nitrate reductase | 12–47 |
| 7 | Aryl sulphatase | 19–68 |
| 8 | Cellulase | 39–182 |
| 9 | Hemicellulase | 42–283 |
| 10 | Lignase | 33–105 |

**Table 4.4.** Per cent improvement over control in organic acid concentration in the rhizosphere and P uptake by the plants.

| Crops | Organic acid concentration | P uptake |
|---|---|---|
| Cluster bean | 23.2 | 27.2 |
| Moth bean | 19.5 | 23.5 |
| Mung bean | 20.7 | 22.7 |
| Pearl millet | 15.5 | 17.3 |

**Table 4.5.** Effect of Zn and Fe nanoparticles on chlorophyll and malondialdehyde content on mung bean.

| Treatments | Chlorophyll (mg/g FW) | Malondialdehyde (mM/g FW) |
|---|---|---|
| 10 ppm ZnO (bulk) | +31.6 | –4.3 |
| 10 ppm ZnO (nano) | +68.1 | –5.7 |
| 1.5 ppm $Fe_2O_3$ (bulk) | +20.7 | –1.2 |
| 1.5 ppm $Fe_2O_3$ (nano) | +41.5 | –4.0 |

plants. It has been reported (Tarafdar, 2015) that nano-Zn and -Fe application on the plant leaf increases chlorophyll content and decreases malondialdehyde content, resulting in increased prevention of membrane damage (Table 4.5).

The results showed that with the application of ZnO in nano-form, the chlorophyll content was enhanced from 31.6 to 68.1 mg/g FW. A similar result was also observed with the application of nano-$Fe_2O_3$ where chlorophyll content was doubled as compared to bulk particle application. Similarly, almost 33% reduction of MDA (malondialdehyde) activities was noticed with the application of nano-ZnO as compared to bulk at the similar concentration; while more than twofold reduction was noticed in MDA activities with the application of nano-Fe, resulting in increased prevention of membrane damage (Table 4.5). The nano-form of nutrients also showed 21–22% more light absorption and 16–17% more improvement in chlorophyll content, as compared with the bulk particle of similar concentration (Rathore and Tarafdar, 2015).

The effect of nanoparticles on root growth and development was studied for different crops (clusterbean, moth bean, mung bean and pearl millet). The results showed nanonutrients like P application improved root length between 28–33%, root area between 20 and 23%, root biomass between 10 and 13% and root nodulation by legumes between 65 and 80%. Similar results were also observed with the application of nano-Zn, -Fe and -Mg with improvement in root length (2–7%), root area (4–18%), dry biomass (1–55%), while nodulation increased between 5 and 47%. The effect of nanoparticles after 4 weeks of application on clusterbean under arid conditions compared to the similar concentration of megaparticle application is shown in Fig. 4.9.

A tremendous improvement in nutrient use efficiency (NUE) was observed for different crops with the application of different nanonutrients (Tarafdar *et al.*, 2015) as compared to bulk fertilizer. In general, four times more nutrient use efficiency by plants was observed with the application of nano-P as compared to bulk and 17–22 times more use efficiency was noticed with different micronutrients (Fig. 4.10).

## 4.7 Nanonutrient for Enhancement of Gum Production

Fifteen gum-producing organisms were found to be responsive to induce gum production due to activation of nanoparticles. In general, Zn and Fe nanoparticles

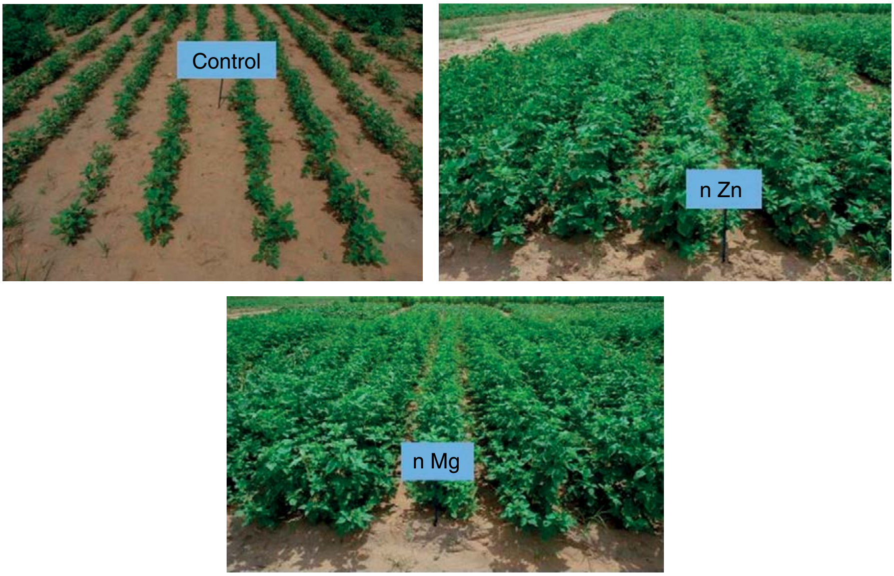

**Fig. 4.9.** Effect of nano-Zn (10 ppm concentration) and nano-Mg (20 ppm concentration) on clusterbean.

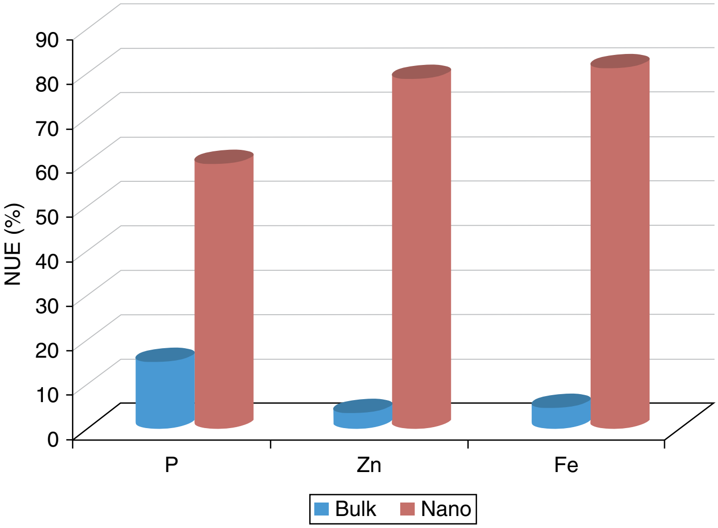

**Fig. 4.10.** A comparison of nutrient use efficiency (NUE) of biosynthesized nanonutrients as compared to bulk.

were found to be more responsive to enhancing gum production in both fungi and bacteria. There was much increase in polysaccharide production between 8 and 15 times due to application of nanonutrients. The microbial gum was identified as polluan, xanthan and curdlan. Nano-induced polysaccharide powder was used to improve soil aggregation, carbon build-up and moisture retention, and it was found that in an arid environment, the soil aggregation was improved by 33–83% within a month (Table 4.6). The aggregate percentage was further improved in 1 mm aggregate size as compared to 0.5 mm or 0.18 mm size with the application of bacterial polysaccharide of 1% concentration.

The improvement of moisture retention was studied at different concentrations of polysaccharide ranging from 1 to 6%. The retention capacity was measured after 4 weeks of application. It was found (Table 4.7) that the moisture retention improved from 10.7 to 14.2% at different levels of polysaccharide concentrations. The results clearly indicate that 1% polysaccharide application gives economically higher moisture retention, although maximum moisture retention was observed at 6% polysaccharide application.

The carbon build-up with the application of microbial polysaccharide was also studied at weekly intervals up to 28 days and at crop harvest with three nano-induced polysaccharide concentrations (1%, 4% and 5%). The results suggested that initial carbon build-up was enormous, but with time there was gradual decline in carbon concentration due to corresponding microbial build-up. The carbon build-up at crop harvest was noted between 3 and 5% (Tarafdar, 2013b).

## 4.8 Nanonutrient on Crop Yields

Multiple field trials (both research and farmer field) were conducted with different biosynthesized nanonutrients of P, Zn, Fe and Mg on 11 different crops (pearl

**Table 4.6.** Improvement of arid soil aggregation using nano-induced polysaccharide powders.

| | Per cent improvement of aggregate size over control after 30 days (1% w/v) | | |
|---|---|---|---|
| Treatment | 1.0 mm | 0.5 mm | 0.18 mm |
| Polysaccharide from *Bacillus coagulans* | 80.7 | No change | No change |
| Polysaccharide from *Alcaligenes faecalis* | 33.4 | 82.9 | 56.4 |

**Table 4.7.** Improvement of moisture retention[a] due to polysaccharide application.

| Polysaccharide percentage | Improvement in moisture retention (%) |
|---|---|
| 1 | 10.7 |
| 2 | 12.2 |
| 3 | 12.5 |
| 4 | 12.8 |
| 5 | 13.6 |
| 6 | 14.2 |
| LSD ($p = 0.05$) | 2.3 |

[a] After 4 weeks of application.
LSD, least significant difference

millet, clusterbean, moth bean, mung bean, maize, castor, cauliflower, tomato, rice, capsicum and wheat) with the recommended doses/concentration of application (P-40ppm, Fe-30ppm, Mg-20ppm, Zn-10ppm). The result shows 12–54% more crop yield with the application of different nanonutrients, as well as an advancement of crop maturity up to 21 days. The results in farmed fields were found marginally better than in research fields. The effect of four nanonutrients on nine different crops (Table 4.8) showed that nano-P was more effective for different crops tested where yield increase ranges between 20.7 and 47.9% over control followed by nano-Zn (18.0–35.1%). The effect of nano-Fe was found between 12 and 22% and nano-Mg was between 13 and 17.1%. Pearl millet was most responsive to nano-P and nano-Zn whereas clusterbean was most responsive to nano-Fe and mung bean was most responsive to nano-Mg.

A similar result was also observed under farmed fields, where the yield increase with the application of nano-P varied between 24.1 and 53.9%, followed by nano-Zn with increase in crop yield ranges from 20.8 to 48.6% (Table 4.9). The yield increase due to nano-Fe applied to different crops ranges between 18.1 and 25.5% while the effect of nano-Mg ranges from 18.4 to 24.0% over control. In general, the cauliflower was found to be most responsive to nano-P and nano-Zn. Nano-Mg was found to be better on clusterbean, while mung bean shows most

**Table 4.8.** Effect of biosynthesized nanonutrients (% increase over control) on research fields of nine crops.

| Crops | Fe | Mg | P | Zn |
|---|---|---|---|---|
| Capsicum | – | – | 24.1 | 19.0 |
| Clusterbean | 22.0 | 14.1 | 35.9 | 27.9–29.0 |
| Maize | – | – | 23.0–32.1 | – |
| Moth bean | 12.0 | – | 30.9 | 22.3–23.0 |
| Mung bean | 20.9 | 17.1 | 404–42.0 | 25.5 |
| Pearl millet | 14.5 | 13.0 | 47.9 | 35.1 |
| Rice | – | – | 22.0–28.0 | – |
| Tomato | – | – | 23.0 | 18.0 |
| Wheat | – | – | 20.7–32.2 | – |

**Table 4.9.** Effect of biosynthesized nanonutrients (% increase over control) on farmers' fields of seven crops.

| Crops | Fe | Mg | P | Zn |
|---|---|---|---|---|
| Castor | – | – | 28.4–37.0 | 23.9–26.9 |
| Clusterbean | 21.0–23.0 | 21.0–27.0 | 31.0–37.1 | 25.9–28.9 |
| Cauliflower | – | – | 49.0–53.9 | 47.0–48.6 |
| Moth bean | 18.3–20.2 | – | 24.1–27.0 | 20.8–23.5 |
| Mung bean | 23.8–25.5 | 23.0–24.3 | 24.8–37.9 | 25.6–27.4 |
| Pearl millet | 18.1–20.4 | 18.4–19.2 | 36.8–43.0 | 23.8–29.6 |
| Tomato | – | – | 29.0 | 25.4 |

response to nano-Fe among the seven crops tested in the farmed field. The overall results clearly indicate that nanofertilizer from fungal protein plays an important role in increasing the agricultural production and definitely has the potential to replace chemical fertilizer in future.

## 4.9 Safety Assessment of Nanonutrients

Many experiments were conducted in different research stations in India to find out the effect on foods with the application of critical doses of P, Fe, Zn and Mg nanonutrients. The results showed that nanonutrients have no adverse effect on seed germination percentage or soluble seed protein content in important arid crops of clusterbean, moth bean, mung bean and pearl millet. In general, microbial population increased significantly with the application of nano-Zn; up to a concentration of 10 ppm there was no adverse effect on body weight, grain consumption rate and blood pH of mice with nanoparticle-sprayed plant grains as compared to control.

Pre-clinical safety evaluation of pearl millet and mung bean grown with biosynthetic nanofertilizers by NIN Hyderabad reported:

- No pre-terminal deaths were recorded in any groups investigated.
- No abnormal clinical signs, behavioural activity, etc. were observed in animals which received test materials.
- No significant effect on feed intake or body weight gain was observed between the individual groups.
- There were no changes in gross necropsy and any organ weights.

The results clearly indicate that pearl millet and mung bean grown with biosynthesized nanonutrients did not induce any adverse effect in rats, even after feeding more than 2.5 times the limit dose.

Histopathology analysis was performed at the National Institute of Pathology (NIOP), New Delhi, India, with the feed of pearl millet and mung bean grown with biosynthesized nanonutrients. The liver, kidneys and spleen of control (group A) and test groups (group B, C, D, E) were fixed in 10% neutral buffered formalin for 120 h and then transferred finally to 70% ethanol through 30% and 50% ethanol gradients. The tissues were processed using routine histological techniques. After paraffin embedding, 3 μm sections were cut and stained with haematoxylin and eosin (H&E) for histopathologic evaluation. The H&E staining provides a comprehensive picture of the microanatomy of organs and tissues. Haematoxylin precisely stains nuclear components, including heterochromatin and nucleoli while eosin stains cytoplasmic components including cytoplasmic granules, extracellular components including collagen and elastic fibres, muscle fibres and red blood cells. Histopathology analysis of liver, kidney and spleen tissues revealed that oral exposure of test substances produced no significant adverse effects, as evidenced by the normal tissue architecture observed in the exposed animals at post-instillation time period of 90 days, in comparison to the normal diet exposed controls. Mild inflammation resultant of acute biological response was observed at many sites within liver and kidney, shown by the noticeable abundance of lymphocytes; however, these histological alterations cannot be pronounced as an indication of cell injury due to test substance, as similar results were witnessed in control groups. Overall analysis of all the samples leads to the conclusion that the gross architecture was intact with no noticeable necrosis or fibrosis within the analysed tissue (Table 4.10).

A complete bio-informatics study was conducted with the application of different nanonutrients to pearl millet and mung bean. Gene ontology (GO) sequence distribution helps in specifying all the annotated nodes comprising GO functional groups. The GO sequence distributions were analysed for all the three GO domains, i.e. biological process, molecular functions and cellular component. Under pearl millet, an enzyme known as endo-β-mannanase was found in the nano-P sample, but it was absent in the control sample. This enzyme plays a key role in plant growth and development, including embryogenesis, seed germination, shoot growth, leaf formation, flower development and fruit ripening. The GO distribution for unigenes of 6-week-old pearl millet was shown as Table 4.11. In general, 26% more unigenes were noticed in the nano-P sample than in control samples of pearl millet.

The study on mung bean with nano-Mg showed more unigenes under biological processes, molecular functions and cellular components (Table 4.12). The results showed 2488 unigenes were exclusively present in mung bean nanoproduct, helping in metabolic activities like carbohydrate metabolism (605), lipid metabolism (237), nucleotide metabolism (323), amino acid metabolism (110), etc.

**Table 4.10.** Summary of histopathological analysis for estimating toxicological effect of test substance (-ve indicates no toxicity observed).

| Tissue/Groups | Group A | Group B | Group C | Group D | Group E |
|---|---|---|---|---|---|
| Liver | - ve | - ve | - ve | - ve | - ve |
| Kidney | - ve | - ve | - ve | - ve | - ve |
| Spleen | - ve | - ve | - ve | - ve | - ve |

**Table 4.11.** Gene ontology distribution for unigenes in pearl millet (6-week-old plant).

| Treatment | Biological processes | Molecular functions | Cellular component |
|---|---|---|---|
| Control | 9,222 | 12,044 | 6,223 |
| Nano-P | 10,902 | 14,435 | 9,415 |

**Table 4.12.** Gene ontology distribution of mung bean (6-week-old plants).

| Treatment | Biological processes | Molecular functions | Cellular component |
|---|---|---|---|
| Control | 3926 | 4660 | 2277 |
| Nano-Mg | 8395 | 9862 | 4481 |

## 4.10 Conclusion and Future Prospects

Nanonutrients are in their infancy stage but have tremendous potential, especially in agriculture. Fungal synthesis of nanonutrients has emerged as a rapidly developing research area of nanotechnology across the globe. Much work is needed to improve the synthesis efficiency and control of particle size and morphology. The synthesis process is quite slow; reduction of synthesis time will make this biosynthesis process much more attractive. Effective control of particle size, monodispersity and stability must be extensively investigated. The major advantage of using fungi for biofabrication of nanoparticles includes enhanced solubility and stability of synthesized nanoparticles (which is crucial for agriculture and biomedical application) because of coating with more protein. The nanonutrients were characterized using DLS, TEM, SEM, FTIR, AFM, Zeta potential, XRD, EDS, etc. and standardized to optimum concentration, size, shape of nanoparticles to be sprayed onto plants and microorganisms for maximum benefits. Nano-Zn and -Fe help in increased stress tolerance and prevention of membrane damage. In general, a 12–54% improvement in grain yields was observed under 11 different crops with the application of recommended doses of nanonutrients of P, Zn, Fe and Mg. The nutrient use efficiency (NUE) under nanonutrient-treated plants increased several times over, compared to conventional fertilizers. The beneficial enzyme activities in the rhizosphere increased between 18 and 283%, resulting in 30% more native nutrient mobilization compared to bulk. The polysaccharide production, by polysaccharide-producing microorganisms, has been increased more than 10 times by applying Zn and Fe nanonutrients. The microbial polysaccharide was found to be very efficient in soil aggregation (33–83%), moisture retention (10–14%) and carbon build-up (3–5%) under arid soils. No adverse effect was observed on seed germination, soluble protein content, soil microbial population, total RNA in plant tissue, body weight and consumption rate of mice and nanoparticle concentration in the seeds at crop harvest with the application of recommended doses of nanonutrients. No abnormal clinical signs, behavioural activity, etc. were observed and reported in animals which received nano-treated test materials. Histopathological analysis for estimating toxicological effects showed no adverse effect on liver, kidney and spleen tissues due to intake of nanofoods.

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## 5

# Multifarious Applications of Nanotechnology for Enhanced Productivity in Agriculture

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## 5.1 Introduction

Global agriculture underwent a series of metamorphoses that has led to the paradigm shift from traditional farming to precision agriculture. Such a shift is phenomenal in tropical agricultural production systems, particularly in India, where farming has faced a wide array of challenges. In the past decade, agriculture is being threatened by a burgeoning population, shrinking farmland, restricted water availability, imbalanced crop nutrition, multinutrient deficiencies in crops, yield stagnation and decline in organic matter. In order to overcome challenges ahead, people think of an alternate technology such as ‘nanotechnology’ to precisely detect and deliver the correct quantity of agri-inputs required by crops that promote productivity with environmental safety. Nanotechnology is highly exploited in energy, environment, electronics, medicine and health sciences while its application in agricultural sciences is yet to scratch the surface. However, nanotechnology can be applied to any spheres in agricultural sciences from plough to plate. Several reviews and research papers unequivocally demonstrated that inclusion nanotechnology may revolutionize agricultural productivity through smart delivery systems (Nair *et al.*, 2010; Subramanian and Tarafdar, 2011; Rai *et al.*, 2015; Subramanian *et al.*, 2015; Mishra *et al.*, 2017a).

Nanotechnology is a fascinating field of science which manipulates atom by atom, and thus processes and products evolved are so precise that they are impossible to achieve by the conventional systems. Nanoparticles measure a dimension of $10^{-9}$ m, i.e. one-billionth of a metre or one-millionth of a millimetre. For instance, a virus particle may be sliced into 100 nanoparticles or 80,000 nanoparticles can be arranged across a human hair. If the entire Indian population

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of 1.27 billion people were small enough to be assembled in 1 m length, each Indian would be the dimension of a nanoparticle. Since the nanoparticles are extremely small, their surface–mass ratio is huge, which facilitates manipulation at the atomic scale to evolve novel properties. Nanoparticles exhibit different physical strength, chemical reactivity, electrical conductance and magnetic properties (Nykypanchuk *et al.*, 2008). Approximately, 1 $m^3$ of material undergoes 24 divisions to attain nanosized particles.

Nanoscience infuses intelligence to the truck-load of chemical constituents that are to be delivered at appropriate locations and cleaves from the site after the task is complete. Such a process is likely to reduce the cost besides ensuring environmental safety. Nanoscale devices with their unique properties make the agricultural system smarter and effective; such devices are capable of responding to different situations by themselves, thus taking appropriate remedial action without the need of external directions from humans. In short, these devices act as detectors and, if the need arises, serve as a solution/remedy for the particular issue. These smart delivery systems of chemicals in a controlled and targeted manner are considered synonymous to the proposed nano-drug delivery system in human (Patolsky *et al.*, 2006). Nanotechnology application in agriculture is quite diverse, encompassing diagnostic kits for early detection of plant diseases (Chen and Hu, 2013), nanoagricultural inputs such as nanofertilizer (Subramanian *et al.*, 2015), nanoherbicides (Chinnamuthu and Kokiladevi, 2007) and nanoinsecticides (Gunasekaran, 2011b), nanoseed science (Natarajan and Raja, 2015), plant health management (Mishra *et al.*, 2014; Subramanian *et al.*, 2016), nanofood systems (Anusuya *et al.*, 2016), besides environmental remediation (Subramanian and Tarafdar, 2011).

## 5.2 Early Detection of Diseases, Pests and Nutrient Deficiencies Using Nano-Based Diagnostic Kits

Pests, diseases and nutrient deficiencies constitute a major loss to the tune of 40–65% of any agricultural or horticultural crops. Early detection is essential to protect the crops from infection and prevent yield and quality losses. Conventionally, pesticides are sprayed only after the expression of symptoms are obvious, based on visual diagnosis. When spraying is performed, it may be too late to protect the crops. Biosensors can be developed in order to accurately measure the moisture, nutrients, pathogenicity and pest incidence so as to take up timely corrective measures. Biosensors for major insect pests (e.g. Eriophyid mite, mealy bugs, cotton weevil, etc.), diseases (e.g. red rot in sugarcane, downy mildew in grapes) and abiotic stresses (drought, salinity, Zn deficiency) are being developed across the globe to protect the crop from devastation.

Nanotechnological approaches are widely used for early detection of diseases, particularly cancer in humans. Similar diagnostic approaches and devices can be exploited in agricultural production systems. In the past two decades, viral diseases in several crops can be detected using ELISA (enzyme linked immunosorbent assay) tests. This method is based on antigen–antibody reaction that is very specific and accurately detects the diseases. In spite of this technique being highly useful, it takes a couple of weeks to get the ELISA tests done in nearby plant pathological laboratories; by which time extensive damage could have been done and it becomes too late to undertake control measures. The dip-stick method is being employed, wherein proteins or nucleic acids serve as reference molecules. The plant extract is allowed to react with the stick and the detection of an event is done within a couple of minutes in the field itself. This technique has been proved effective in detecting viral diseases in potato and banana. The precision and validity of the method can be further improved using nanoparticles.

Biosensors are also be used to detect pest incidence in crops. Magnetic nanoparticles are known to be omnipresent and their distribution patterns are used for the detection of pest incidence in crops. The magnetic material is present in the head, thorax and abdomen of insects like *Solenopsis substitute* (Fabricius), an ant. These magnetic nanoparticles in social insects act as geomagnetic sensors (Esquivel *et al.*, 2007). The observation, which was made through electron microscope technique, clearly demonstrated that several species of ants recognize magnetic signals with the help of magnetic nanoparticles (Abracado *et al.*, 2005). Magnetic nanoparticles in *Apis mellifera* (the honey bee) abdomens are well accepted as involved in their magnetoreception mechanism (Jaccoud El-Jaick *et al.*, 2001). Fire ant (*S. invicta)* workers, queens and alates were analysed by magnetic resonance imaging (MRI) for the detection of natural magnetism. All ferromagnetic materials are magnetic nanoparticles, which are solely responsible for localization of specific direction for food and host of insects. Recently, cicada wings have been investigated by atomic force microscopy (AFM) for observing nanoparticles. Similarly, the navigation ability of the pigeon is due to the presence of iron oxide nanoparticles in the beak. In plants, volatile phytochemicals and nanoparticles of insects are solely responsible for plant–insect interaction (Gorb and Gorb, 2009). Nanoscience strongly suggests that nanoparticles can be exploited to assess the occurrence of insect pests rapidly, which facilitates fast reaction to sense and prevent the pest damage.

In nanomechanical biosensors, receptor molecules are immobilized on the surface of a microcantilever such as those used in atomic force microscopy but without scanning probes. The most common method is measuring the deflection of a cantilever, in which only a single side is coated with receptor molecules. Molecular recognition on the sensitized cantilever side gives a change of the surface stress due to the electrostatic, van der Waals, configurational and stearic interactions between the adsorbed molecules. This technique can be exploited to detect pests and diseases (Franca *et al.*, 2011). The development of diagnostic kits for detection of diseases, pests and nutrient deficiencies are quite appropriate in the context of Indian agriculture for identifying the causes in quick reaction time to take corrective measures.

## 5.3 Nanoagricultural Inputs

### 5.3.1 Nanofertilizers

Fertilizers are indispensable in agriculture, deciding one-third of crop productivity. Despite the fact that the importance of fertilizers has been unequivocally demonstrated in the last few decades, imbalanced fertilization, multinutrient deficiencies, low soil organic status, lower fertilizer response ratio, and nutrient mining are the emerging issues and scientists are looking for nanotechnology interventions. Nanofertilizers intended to improve the nutrient use efficiencies by exploiting unique properties of nanoparticles. The nanofertilizers are synthesized by fortifying nutrients singly or in combinations with adsorbents in nanodimension. The nutrients are loaded as they are for cationic nutrients ($NH_4^+$, $K^+$, $Ca^{++}$, $Mg^{++}$) and after surface modification for anionic nutrients ($NO_3^-$, $PO_4^{--}$, $SO_4^{--}$) in the case of using clay minerals as carriers. Nanofertilizers are known to release nutrients slowly and steadily for more than 30 days, which may assist in improving nutrient use efficiency without any associated ill-effects (Subramanian and Sharmila Rahale, 2012b; Selva Preetha *et al.*, 2014). Since the nanofertilizers are designed for a sustained release of nutrients for a longer period of time this reduces the environmental hazards significantly.

Nanofertilizers are designed to deliver nutrients slowly and steadily matching with the crop requirement. This can be achieved by preventing nutrients from interacting with soil, water and microorganisms, and releasing nutrients only when the crops are able to internalize the nutrients directly (De Rosa *et al.*, 2010). Liu *et al.* (2006) have shown that coating and cementing of nano- and sub-nanocomposites are capable of regulating the release of nutrients from the fertilizer capsule. Further, the effectiveness of nanoparticles was closely monitored and confirmed using transmission electron microscope (TEM) and scanning electron microscope (SEM). A planted nanocomposite that consists of N, P, K and micronutrients, along with mannose and amino acids, has been shown to increase the uptake and utilization of nutrients by grain crops (Guo, 2004). In order to regulate the release of nutrients from the fertilizers, nanozeolites are known to be used and found effective in enhancing nutrient use efficiencies by crops. Reduction of size through top-down approaches (ball milling) appears to regulate the release of nutrients with or without surface modifications with suitable surfactants. Nutrient use efficiencies of nitrogen (Manikandan and Subramanian, 2013, 2014), phosphorus (Bansiwal *et al.*, 2006), potassium (Subramanian and Sharmila Rahale, 2012c), sulfur (Thirunavukkarasu and Subramanian, 2014b) and Zn (Subramanian and Sharmila Rahale, 2012a) are reported to be enhanced by such manipulations. These reports tended to indicate that a nanocomposite can be developed in order to supply all required essential elements by fortifying into nanozeolites that can facilitate balanced crop nutrition and sustained farm productivity. The nanofertilizer research done across the globe has been recently reviewed (Subramanian *et al.*, 2015). The research accomplishment is briefly summarized in Table 5.1.

There is a dearth of literature on nanofertilizers across the globe; however, the data clearly indicated that these customized nanofertilizers have a potential role to play in sustaining farm productivity.

## 5.4 Nanotechnology for Rainfed Agriculture

### 5.4.1 Moisture conservation

More than 60% of agriculture is rainfall-dependent and soil moisture decides the fate of productivity of crops. Several drought management strategies, such as mulching, organic manuring, soil hybridization, use of super-absorbents and anti-transpirants, as well as inclusion of tolerant varieties, are being recommended.

**Table 5.1.** Crop and soil responses to applied nanofertilizers.

| Nutrients | Nutrient carrier | Approach | Crop/soil | Responses | References |
|---|---|---|---|---|---|
| N | Zeolite | Physical | Maize | Higher N use efficiency by 30% over control | Subramanian and Sharmila Rahale (2013) |
| | Zeolite | Chemical | Rice | 10–15% higher biomass | Mohanraj (2013) |
| | Zeolite | Physical | Maize | | Manikandan and Subramanian (2014) |
| P | Zeolite | Physical | Clay loam | Sustained release of phosphates up to 1176 h (conventional fertilizer – 384 h) | Subramanian and Sharmila Rahale (2013) |
| | Zeolite | Chemical | Sandy loam | Surface-modified zeolites retained phosphates up to 1080 h (conventional – 264 h) | Bansiwal *et al*. (2006) |
| K | Zeolite | Physical | Clay loam | Sustained release of K up to 1200 h (conventional fertilizer – 216 h) | Subramanian and Sharmila Rahale (2013) |
| NPK | Nano-coating of sulfur layer | Chemical | – | Controlled release of nutrients | Wilson *et al*. (2008) |
| | Chitosan | | | | |
| | Zeolite | Physical | Greengram | Nanocomposite with multinutrients enhances growth attributes by 25–40% | Selva Preetha (2011) |
| S | Zeolite | Physical | Red sandy loam | Surface-modified nanozeolites facilitates higher retention (29%) and release (77%) of added sulfates | Thirunavukkarasu and Subramanian (2014b) |
| | | | | Enhanced growth and nodulation in nanofertilizer applied plants | Thirunavukkarasu and Subramanian (2014a) |
| Zn | ZnO | Physical & chemical | Maize | Higher Zn use efficiency of 22% with 50% of the recommended dose of Zn | Chaitra (2014) |
| | Core shell Zn | Chemical | Rice | 27–30% higher grain yield in encapsulated-Zn fertilized plants | Yuvaraj and Subramanian (2014) |
| B | Zeolite | Physical | Greengram | Higher B uptake with nanocomposite | Selva Preetha (2011) |
| Ca | Nanolime | Physical | Radish | Effective remediation of acid soil with nanolime | Bhargava Rami Reddy and Subramanian (2015b) |
| | | | Greengram | Effective remediation of acid soil with nanolime | |
| Ca & Mg | Nanodolomite | Physical | Radish | Effective remediation of acid soil with nanodolomite | Bhargava Rami Reddy and Subramanian (2015a) |
| | | | Greengram | Effective remediation of acid soil with nanodolomite | |

These practices have been tested over the past several decades but found futile, as the intensity and occurrence of drought varies with location and the coincidence of the critical stage of crop water requirement. This situation warrants infusion of innovative technologies such as nanotechnology, wherein the design and fabrication of moisture conservation inputs is possible by atom-by-atom manipulation and demand-driven smart delivery.

Soil breeding is a well-known practice in which heavy textured clay soil is blended with light (sandy) soils in order to improve the physical fertility thereby moisture conservation is achieved. Despite the practice being very effective, farmers could not afford to adopt it, due to heavy investments on transport of bulky materials. With a view to reduce the bulkiness while taking advantage of clays, nanoclays have been widely studied as a measure to mitigate drought. Olesen (2010) reported that application of nanoclay improved the water-holding capacity of sandy soils in Egypt. Further, intercalation of Zn-coated nanoclays with polyacrylamide polymer can improve moisture conservation in rainfed rice (Jatav *et al*., 2013). Nanoclay polymer composite (NCPC) increased the water-holding capacity besides serving as a slow-release formulation for nutrients (Sarkar *et al*., 2014). Recently, scientists have attempted to spray the montmorillionite nanoclays on the soil that facilitates aggregate stability which eventually resulted in improving the moisture-retention capacity of the soil (Padidar *et al*., 2016).

Organic polymers possess the unique property of the ability to hold several times their own weight of moisture. One such acrylamide-based super-absorbent polymer was introduced in the late 1980s and tested in rainfed agriculture. Nandhagopal *et al*. (1990) have shown that super-absorbent polymer (Jalshakthi) was found to increase the gravimetric moisture content in sandy loam soil (Alfisol), but the moisture release in the rainfed sunflower was achieved due to the retention of soil moisture at high atmospheric pressure. Recently, nanotechnology approaches are being employed to enhance the moisture retention and regulated release which coincides with crop water demand. Further, hydrophobic nanopolymeric materials can be used as a cover to conserve moisture while preventing drainage loss (Davidson and Gu, 2012). Super-absorbent polymers with a complex of carboxy methyl cellulose and starch cross-linked with aluminum are reported to retain 73% higher moisture (Nnadi and Brave, 2011; Wang *et al*., 2014). In addition to organic polymers, inorganic complex such as iron-oxalate-capped iron oxide (OCIO) nanomaterials can improve water retention in soils by reducing bulk density and improving soil aggregation (Das *et al*., 2016). Organic (polyacrylic acid and carboxy methyl cellulose) and inorganic (montmorillonite) compounds have been blended to develop nanocomposites to enhance moisture retention and release characteristics of soil (Shahid *et al*., 2012; Zhang *et al*., 2014; Rashidzadeh *et al*., 2015).

## 5.5 Weed Management

Weeds are a menace in agricultural production systems. Agriculture under rainfed conditions is critical due to limited use of herbicides, so weeds have the potential to jeopardize the total harvest in the delicate agroecosystems. Among the weed species, nut grass (*Cyperus rotundus*) is one of the most notorious weeds that is very difficult to eradicate due to the fact that this weed species produces tubers that carry

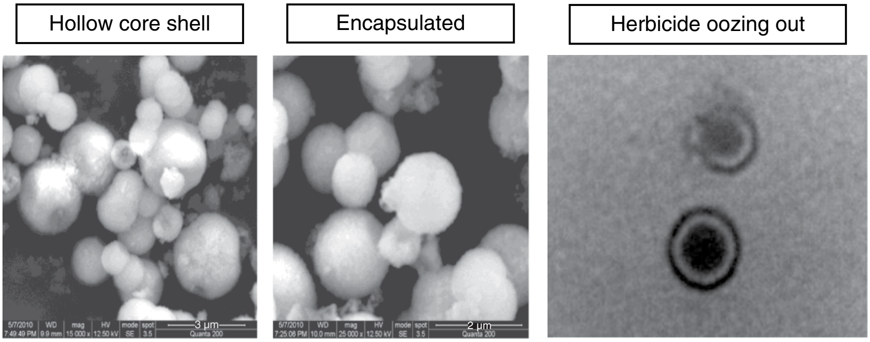

**Fig. 5.1.** Sequential steps involved in encapsulation of herbicides.

large amounts of starch. The herbicides available in the market mostly target above-ground parts, particularly the foliage. As a result, tubers in the ground rejuvenate and emerge in the successive days, reducing the efficacy of herbicides.

Under rainfed conditions, there is no guarantee for moisture availability and thus herbicides are to be designed and fabricated to release the active ingredient only when the soil receives a short spell of rainfall. Nanotechnology can be employed to synthesize smart herbicides that release active herbicide molecules only when moisture is available in rainfed systems, besides targeting both leaves and tubers. The existing herbicide molecules can be encapsulated with suitable hydrophilic polymers, such as polystyrene sulfonate (PSS) and polyallylamine hydrochloride (PAH), that facilitate the release of herbicide molecules synchronized with soil moisture which prevents weed seeds from germinating (Fig. 5.1). Nanoherbicides are ideal for rainfed farming, where the weed menace is harder to overcome (Kanimozhi and Chinnamuthu, 2012).

Nanoencapsulated herbicides are known to control the notorious parasitic weeds while reducing the phytotoxicity of herbicides on crops, demonstrating the benefits of smart delivery systems in agriculture. Properly functionalized nanocapsules provide better penetration through cuticle and allow slow and controlled release of active ingredients on reaching the target weed. Nanoencapsulation of chemicals with biodegradable materials makes them safer and easy to handle by the growers. Efforts are underway to kill the notorious weeds like *Cyprus rotundus* through a smart delivery system. This weed produces tubers rich in starch that has to be exhausted through a suitable smart delivery system (Perez-de-Luque and Diego, 2009; Kanimozhi and Chinnamuthu, 2012). Nanoencapsulated agrochemicals should be designed in such a way that they possess all necessary properties (effective concentration, stability and solubility) for time-controlled release in response to certain stimuli, enhanced targeted activity and less ecotoxicity, with a safe and easy mode of delivery, thus avoiding repeated applications.

## 5.6 Nanotechnology for Plant Protection

The persistence of insecticides in the initial stage of crop growth helps in bringing down the pest population below the economic threshold level and to have an effective control for a longer period. Hence, the persistence of pesticides is one of the most cost-effective and versatile means of controlling insect pests. In order to protect the active ingredient from the environmental conditions and to promote persistence, nanoencapsulation can be used to improve the insecticidal value. Microencapsulation comprises nanosized particles of the active ingredients being sealed by a thin-walled sac or shell (protective coating). In Tamil Nadu Agricultural University, neem-based nano-emulsion (~200 nm) has been developed and found effective in controlling sucking pests such as thrips, aphids and mites in chillies (Gunasekaran, 2011a). Recently, several research papers have been published on the encapsulation of insecticides. Nanoencapsulation of pesticides offers proper absorption of the chemical into the plants unlike the case of conventional formulations (Scrinis and Lyons, 2007). Nanoencapsuation of insecticides, fungicides or nematicides will help in producing nanoformulations, which offer effective control of pests while preventing residues in soil.

In addition to the encapsulated forms of insecticides, some of the nanoparticles are being used as an effective strategy to protect the crops from the damage by pests and diseases. Surface-modified hydrophobic nanosilica has been successfully used to control a range of agricultural pests (Barik *et al.*, 2008). This functionalized lipophilic nanosilica is absorbed into the circular lipids of insects by physiosorption and damages the protective wax layer and induces death by desiccation. The use of such nanobiopesticide is more acceptable since they are safer for plants and cause less environmental pollution in comparison to conventional chemical pesticides (Rahman *et al.*, 2009).

The successful use of silver nanoparticles (AgNPs) in diverse medical streams such as antifungal and antibacterial agents has led to their applications in controlling phytopathogens. AgNPs with a broad spectrum of antimicrobial activity reduce various plant diseases caused by spore-producing fungal pathogens (Mishra *et al.*, 2014; Mishra *et al.*, 2017b). The effectiveness of AgNPs can be improved by applying them well before the penetration and colonization of fungi within the plant tissues (Singh *et al.*, 2008). The small size of the active ingredient effectively controls fungal diseases like powdery mildew. However, it was also observed that a very high concentration of nanosilica-silver produced chemical injuries on the cucumber. The use of AgNPs as an alternative to fungicides for the control of sclerotium-forming phytopathogenic fungi was also investigated. Exposure of AgNPs causes potential damage to fungal hyphae by the separation of layers of hyphal wall and collapse of hyphae. The efficacy of AgNPs in extending the vase life of gerbera flowers was also studied and the results show inhibited microbial growth and reduced vascular blockage which increased the water uptake and maintained the turgidity of gerbera flowers (Solgi *et al.*, 2009). Apparently, the use of biocide-containing polymeric nanoparticles for introducing organic wood preservatives and fungicides into wood products, thereby reducing the wood decay, was also studied (Liu *et al.*, 2001). Among the nanoparticles, AgNPs are widely used accounting for more than 30% of the nano-based commercial products in the world. The use of nanoparticles in plant protection and production is summarized in Table 5.2.

**Table 5.2.** Use of nanoparticles in agro-ecosystems.

| Nanomaterials | Applications | References |
|---|---|---|
| Metal nanoparticles/nanoproducts | | |
| Gold (10–15 nm) | Genetic material delivery (DNA) | Torney *et al*., 2007 |
| Gold (5–25 nm) | | Vijayakumar *et al*., 2010 |
| Gold (40 nm) | As pesticide sensor for carbofuran/triazophos | Guo *et al*., 2009 |
| Gold (30 nm) | As pesticide sensor for DDT | Lisa *et al*., 2009 |
| Iron oxide (30 nm) | Sensor for dimethoate | Gan *et al*., 2010 |
| Zirconium oxide (50 nm) | Sensor for organophosphate | Wang *et al*., 2009 |
| Iron sulfide (200 nm) | Lindane degradation | Paknikar *et al*., 2005 |
| Nanosilica (3–5 nm) | Plant origin: nanosilica for insect control<br>*Artemisia arborescens* | Barik *et al*., 2008 |
| Silica (7–14 nm) | Microorganisms: *Lagenidium giganteum* cells in emulsion | Vandergheynst *et al*., 2007 |
| Titanium oxide (30 nm) | Imidacloprid degradation | Guan *et al*., 2008 |
| Porous hollow silica (15 nm) | Avermectin delivery | Li *et al*., 2007 |
| Zirconium oxide (50 nm) | Sensor for detecting organophosphate residues | Wang *et al*., 2009 |
| Polymeric and other nanoparticles/nanoproducts | | |
| Nano-coating of sulfur (100 nm layer) | NPK controlled delivery | Wilson *et al*., 2008 |
| Chitosan (100–200 nm) | Double-stranded RNA | Zhang *et al*., 2010 |
| Starch (50–100 nm) | Genetic material delivery (DNA) | Liu *et al*., 2008 |
| Solid lipid (200–294 nm) | Essential oil encapsulation | Lai *et al*., 2006 |
| Polyvinylpyridine and polyvinylpyridine-co-styrene (100 nm) | Tebucanazole/ chlorothalonil | Liu *et al*., 2001 |
| Solid lipid (300 nm) | Gamma cyhalothrin delivery | Frederiksen *et al*., 2003 |
| Poly-caprolacetone (135 nm) | Ethiprole or phenylpyrazole delivery | Boehm *et al*., 2003 |

## 5.7 Nanoparticles for Seed Invigoration

Seed is a basic input deciding the fate of productivity of any crop. Conventionally, seeds are analysed for their germination and distributed to farmers for sowing. Despite the fact that the germination percentage registered in the seed-testing laboratory is about 80–90%, it rarely happens in the field due to the inadequacy or non-availability of sufficient moisture under rainfed system. In India, more than 70% of the net area sown is under rainfed system, it is quite appropriate to develop technologies for rainfed agriculture. Seed coating or hardening techniques have been optimized and extensively studied for a wide array of crops and evolved strategies to ensure germination. This process will make the seed hardened and emerge faster besides withstanding early drought. It is a useful strategy but rarely adopted by farmers due to practical difficulties. This necessitates evolving an alternate and innovative method to tackle the issue of poor germination in rainfed system. Recently, some preliminary works have been done in order to improve the emergence of seed utilizing a wide array of nanoparticles and metal oxides.

Carbon nanotubes (CNTs) are nanomaterials widely used in biological and material sciences. Single- and multi-walled carbon nanotubes are commercially available to carry out smart delivery of water, nutrients and medicines, etc. Since CNTs carry extensive surface area, they have the potential to regulate the moisture under constraints of irrigation or drought conditions. Khodakovskaya and her team in 2009 at the University of Arkansas, USA, have used carbon nanotubes for improving the germination of tomato seeds. In this elegant experimental system, the substrate was impregnated with differential quantities of carbon nanotubes. The data have vividly shown that there is a direct relationship between the quantities of CNT and rate of germination. The authors suggest that CNT serves as new pores for water permeation by penetration of seed coat. Further, the CNT can act as a gate to channel the water from the substrate into the seeds. Indeed, CNTs have been shown to improve the germination and seedling vigour of several crop species tested (Table 5.2).

The metal oxide NPs, such as ZnO, are known to improve the germination and seedling vigour of a wide spectrum of crops such as tomato, onion, chilli, groundnut and blackgram (Table 5.3). In all the cases, the improved germination resulted from the quenching of reactive oxygen species that emanated during storage. On entry of the ZnO into the seeds, the ZnO undergoes dissociation which eventually resulted in quenching reactive oxygen species that closely coincided with cell membrane integrity. Further, Zn as a nutrient can assist in promoting growth hormones in germinating. In *Cicer arietinum*, Pandey *et al.* (2010) found that ZnONPs increased the level of IAA (indole-3-acetic acid) in the roots (sprouts) and thereby an increase in the growth rate of plants was observed. Consequently, ZnONPs have improved the germination, seedling growth and vigour index in blackgram (Senthilkumar, 2011). Pulse seeds dressed with ZnONPs at 1000 mg/kg were found to increase the germination under *in vitro* conditions.

Silver (Ag) nanoparticles are widely used in agri-food systems. These NPs are well known for their antimicrobial properties. As a result of antimicrobial and antipathogenic effects, seed-borne pathogens are effectively controlled that eventually has resulted in improved germination of many crop species (Table 5.3). Almutairi and Alharbi (2015) observed the significant enhancement of the germination percentage in watermelon and zucchini plants with AgNPs as compared to untreated seeds. Despite the fact that AgNPs are beneficial, excessive use is reported to have deleterious effects on crops. AgNPs showed a toxic effect on corn root elongation. This study showed that exposure to AgNPs caused both positive and negative effects on plant growth and germination.

**Table 5.3.** Nanoparticle(s) on plant growth and development.

| Nanoparticle(s) | Plant | Concentration(s) | Impact observed on | Reference(s) |
|---|---|---|---|---|
| 1. Carbon nanotubes (CNTs) | | | | |
| Graphene oxide | *Vicia faba* L. | 400 and 800 mg/l | Improved germination | Anjum *et al*. (2014) |
| Carbon nanotubes (CNTs) | *Lycopersicon esculentum* Mill. | 40 μg/ml | Enhanced germination and seedling growth | Morla *et al*. (2011) |
| | *Medicago sativa* L.<br>*Triticum aestivum* | 75 wt% CNTs | Improved root elongation and growth | Miralles *et al*. (2012) |
| | *Medicago sativa* L.<br>*Triticum aestivum* | 75 wt% CNTs Impurities | Improved root elongation and growth | |
| Single-walled carbon nanotubes (SWCNTs) | *Allium cepa* L.<br>*Cucumis sativus* L. | 315 and 1750 mg/l | Improved root elongation and growth | Cañas *et al*. (2008) |
| Multi-walled carbon nanotubes (MWCNTs) | *Hordeum vulgare* L.<br>*Glycine max* L.<br>*Zea mays* L. | 25–100 μg/ml | Improved germination | Lahiani *et al*. (2013) |
| | *Lycopersicon esculentum* Mill. | 50 and 200 μg/ml | Increased plant height and no. of flowers | Khodakovskaya *et al*. (2013) |
| | *Nicotiana tabacum* L. | 5 up to 500 μg/ml | Improved growth of plants | Khodakovskaya *et al*. (2012) |
| o-MWCNTs | *Triticum aestivum* L. | 10–160 μg/ml | Enhanced root growth and vegetative biomass | Wang *et al*. (2012) |
| wsCNTs | *Cicer arietinum* L. | 6.0 μg/ml | Improved growth rate | Tripathi *et al*. (2011) |
| MWCNTs, dMWCNT | *Lycopersicon esculentum* Mill. | 40 μg/ml | Increased the nutrient uptake efficiency (K, Ca, Fe, Mn and Zn) | Tiwari *et al*. (2013) |
| Pristine MWCNTs | *Zea mays* L. | 20 mg/l | Improved the nutrient transport and biomass | Tiwari *et al*. (2014) |
| 2. Zinc oxide NPs | | | | |
| ZnONPs | *Cucumis sativus* L. | 400 mg/kg | Increased the micronutrients (Cu, Mn and Zn) content and growth | Zhao *et al*. (2014) |

| | | | | |
|---|---|---|---|---|
| | *Arachis hypogea* L. | 1000 ppm | Improved germination, stem, root growth and yield | Prasad *et al*. (2012) |
| | *Vigna radiata*<br>Tomato (*L. esculentum* Mill.)<br>Onion (*Allium sp*.)<br>Groundnut (*Arachis hypogeal*)<br>Chilli (*Capsicum annum*) | 1000 mg/kg | Improved germination, seedling growth and vigour index in naturally aged seeds. Increased the lipid peroxidase activity | Sridhar (2012)<br>Shyla *et al*. (2014)<br>Senthilkumar (2011) |
| | *Vigna radiata* L. Wilczek | 1000 ppm | Increased dry weight of plant | Patra *et al*. (2013) |
| 3. Silver NPs | | | | |
| AgNPs | *Boswellia ovaliofoliolata* | 10–30 µg/ml | Improved germination and seedling growth | Savithramma *et al*. (2012) |
| | *Phaseolus vulgaris* L.<br>*Zea mays* L. | 60 ppm | Increased root & shoot length, and dry weight of seedling | Salama (2012) |
| | *Vigna radiata* L. | 100 µM | Antagonistic inhibition by 2,4-dichlorophenoxyacetic acid<br>(2,4-D) at 500 µM of plant growth | Karuppanapandian *et al*. (2011) |
| $SiO_2$NPs | *Zea mays* L. | 15 kg/ha | Improved all the growth parameters of plant | Suriyaprabha *et al*. (2012) |
| 4. Titanium oxide NPs | | | | |
| $TiO_2$NPs | *Arabidopsis thaliana* | 400 mg/l | Enhanced root length | Lee *et al*. (2010) |
| | *Foenicutum vulgare* | 60 ppm | Improved germination and seedling growth | Feizi *et al*. (2013) |
| | *Lemna minor* L. | Lower than 200 mg/l | Improved plant growth | Song *et al*. (2012) |
| | *Triticum aestivum* L. | 1000 mg/l | Increased chlorophyll content | Mahmoodzadeh *et al*. (2013) |
| | *Spinacia oleracea* L. | 0.25% | Protected chloroplasts from ageing | Hong *et al*. (2005a, b) |

*Continued*

**Table 5.3.** Continued.

| Nanoparticle(s) | Plant | Concentration(s) | Impact observed on | Reference(s) |
|---|---|---|---|---|
| | *Lycopersicon esculentum* Mill. | 50–200 mg/l | Net photosynthetic rate, conductance of $H_2O_2$ and transpiration rate, regulation of photosystem II (PSII) | Qi *et al*. (2013) |
| 5. Zero-valent iron NPs | | | | |
| ZVI | *Arabidopsis thaliana* | 500 mg/l | Improved root elongation | Kim *et al*. (2014) |
| | *Vigna radiata* | 1000 mg/kg of seed | Improved germination, seedling growth and vigour index in naturally aged seeds | Senthilkumar (2011) |
| 6. Other NPs | | | | |
| $CeO_2$NPs | *Arabidopsis thaliana* | 250 ppm | Increased the biomass content | Ma *et al*. (2013) |
| | *Raphanus sativus* L. | 5000 mg/l | Improved root elongation and growth | Wu *et al*. (2012) |
| CuONPs | *Triticum aestivum* L. | 500 mg/kg (sand culture) | Increased the biomass content | Dimkpa *et al*. (2012) |
| Hydroxyapatite suspension | *Lactuca sativa* L. | 100–2000 mg/l | Improved root length and growth | Wang *et al*. (2012) |
| Sulfur NPs | *Vigna radiata* L. | 2000 and 4000 ppm | Increased dry weight of seedling and plant | Patra *et al*. (2013) |
| AuNPs | *Arabidopsis thaliana* | 10 and 80 μg/ml | Improved germination , root and shoot length , early flowering and yield | Kumar *et al*. (2013) |
| Aluminum oxide NPs | *Arabidopsis thaliana* | 400–4000 mg/l | Improved root length | Lee *et al*. (2010) |
| | *Lemna minor* L. | 10 mg/l | Enhanced root elongation and length | Juhel *et al*. (2011) |

In addition to ZnO, $TiO_2$NPs are found to have favourable effects on seed invigoration. On entry to the seeds, $TiO_2$NPs quench the reactive oxygen species (ROS) and break the dormancy caused by the phenolics in the seeds. Several reports have clearly indicated the beneficial role of $TiO_2$ in enhancing germination (Table 5.3). Feizi *et al.* (2013) reported that $TiO_2$NPs treatment @ 60 ppm improved the germination in *Foeniculum vulgare*. $TiO_2$NPs enhanced the seed germination and promoted radicle and plumule growth of canola seedlings (Mahmoodzadeh *et al.*, 2013). Zero-valent iron (ZVI) NPs also exhibited similar effects in several crops.

Other NPs such as copper, silica, alumina and cerium have been reported to improve germination of a wide array of crops (Table 5.3). In most cases, the entry of NPs led to the donation of electrons and pairing of unpaired electrons which ultimately caused the repair of damage caused by lipid peroxidation. In addition, these NPs have antimicrobial properties which facilitate protection against seed-borne pathogens.

Overall, the NPs have potential beneficial effects in enhancing the seed quality by circumventing oxidative damages caused by seed deterioration. The mechanisms underlying NP-induced enhancement of seed germination are furnished in Table 5.4. Optimal use of NPs can help to improve the germination and seedling vigour without associated ill-effects. On the other hand, excessive use has deleterious impacts especially for ZnO- and AgNPs. Care should be taken to gain the benefits of nanoparticles while impeding the ill-effects of excess use. More research is required to commercialize NP use in seed invigoration.

**Table 5.4.** Mechanisms of generating scavenging ROS by nanoparticles.

| NPs | Chemistry/mechanism involved | References |
|---|---|---|
| $TiO_2$ | Produces free radicals in light or dark ($O_2^{\bullet-}$, $HO^{\bullet}$ and $CO_2^{\bullet-}$) conditions; $Ti^{4+}$ / $Ti^{3+}$ oxidize/reduce $O_2^{\bullet-}$/ $^{\bullet}O_2$ to $O_2$/$H_2O_2$ | Fenoglio *et al*. (2009) |
| ZnO | Traps electron from $^{-}OH$ and produces $HO^{\bullet}$ | Lei *et al*. (2008); McLaren *et al*. (2009) |
| $CeO_2$ | Alternates between $Ce^{4+}$ and $Ce^{3+}$ to scavenge $O_2^{\bullet-}$ and $^{\bullet}OH$ and mimics the superoxide dimustase activity | Heckert *et al*. (2008); Horie *et al*. (2011) |
| NiO | Probably produces $HO^{\bullet}$ via Haber–Weiss reaction similar to Ni ions. However, the reaction is not confirmed | Faisal *et al*. (2013) |
| CuO | Produces $HO^{\bullet}$ via Fenton reaction | Fubini *et al*. (2007) |
| $Fe_3O_4$, C | Block aquaporins and disturb respiration | Wang *et al*. (2012); Ghodake *et al*. (2011) |

### 5.7.1 Emerging nanotechnologies in seed quality enhancement

Several decades of seed research provided insights into the mechanisms relating to the seed quality that closely coincided with the development of invigoration techniques. Indeed, none other than seed as an input has a direct relevance in sustaining the farm productivity and profitability. In India, traditionally, seeds of the previous season will serve as an input for the succeeding cropping season. Currently, there is a paradigm shift from the use of owned seed source to procurement from the market. The span between the cropping decision and procurement of seeds from authentic source is very narrow and it is hardly possible for the Indian farmers to check the seed quality prior to sowing. This situation necessitates infusing innovative technologies and techniques for quick detection of seed quality and invigoration of seed lots using customized materials. These innovative technologies are often referred to as the third-generation seed treatments for quality enhancement and assurance that encompass seed quality detection using electronic nose (e-nose), nano-barcoding, high resolution imaging, seed quality enhancement using customized nanoparticles, seed coating and smart delivery of agri-inputs through seeds. Since, seed is a ‘nano-input’ and a miniaturized laboratory it can serve as a single solution to address complex and multidimensional field problems.

## 5.8 Conclusion

Nanotechnology is a fascinating field of science that is widely exploited in various disciplines and this chapter highlights how best the tools and techniques can be employed in agricultural sciences to promote productivity without associated impacts on the environment. Nanoscience and technology is being visualized to revolutionize the agricultural sector in years to come. Future agriculture should focus on the development of processes and products intended to deliver inputs precisely, besides offering a solution to unresolved issues at the farm gate. The use efficiency of agricultural inputs hardly exceeds 25–30% and the major portion is wasted and the research efforts taken to tide over the problems in the past few decades have not exhibited any fruitful results. This necessitates an alternate strategy of infusing nanotechnology in the agricultural sector to enhance input use efficiency within the complex environmental conditions. Despite the fact that nanotechnology applications in agriculture are just beginning to surface, the reported literature review has clearly indicated that there is a vast range of nanotechnology in developing the smart delivery of agricultural inputs such as fertilizers, seed invigoration chemicals, pesticides, soil moisture conservation amendments, as well as developing diagnostic kits and tools for early detection of diseases, pests, moisture status and quality of crop produce. In order to augment the research efforts in nanotechnology, agricultural scientists should take a cue from medical sciences which serve as a guiding force that can be exploited in agricultural production systems. In this chapter, the literature review has clearly suggested that there is an abundance of scope to exploit the smart delivery of agricultural inputs which facilitate enhanced use efficiency and ensure environmental protection.

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# 6

# Different Methods of Nanoparticle Synthesis and Their Comparative Agricultural Applications

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## 6.1 Introduction

Agriculture is one of the most fundamental practices implemented by mankind ranging from kitchen gardening for a family to large-scale production for mass survival. In earlier days, agriculture was the only source of household wages, food, and had significant monetary value as well as contributing to the status of the family. However, in the history of mankind, there have been several instances where natural calamities such as drought, flood and climatic disturbances have caused mass deaths due to famine (Smil, 1999; Meena, 2015). Apart from the natural calamities, there have been many other challenges such as uncontrollable pest growth, low production yield, low crop quality, which have accounted for the death of millions from starvation and malnutrition.

In response, a leader of a Mexican research team, US agronomist Norman Borlaug, introduced a new variety of wheat called draft wheat in Mexico in 1961. This new variety of wheat could be grown well in various climatic conditions, giving double the yield when compared with normal wheat and benefitting from a high dose of chemical fertilizers. Around the same time (1960s), with the disastrous circumstances in many developing countries such as India, Pakistan, China and the Philippines many more also started importing high-yield varieties of crops (Pingali, 2012).

Within four to five years of using these high-yield varieties of cereals, many of these countries became self-sufficient in cereal production, with additional newer technological advancements in irrigation methodologies. Along with these amendments in agricultural developments, several other challenges were also addressed; most importantly, the crop disease management and its protection

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using pesticides. After the successful implementation of using high-yield varieties of cereals, high-tech irrigation methodologies, fertilizers and pesticides with resultant higher yields the development of agriculture has grown profoundly. Furthermore, research and development have also started focusing on different aspects of agricultural practices for further improvement, most importantly improving nutritional contents of the crops (Mann, 1997; Zhu *et al.*, 2000; Knight, 2003; Cakmak *et al.*, 2004).

With the complete transformation of agricultural status in many countries due to the action of the green revolution, which was mainly based on scientific studies, it further intrigued scientific researchers to explore more possibilities of improvements (Pinstrup-Andersen and Hazell, 1985; Pingali, 2012). With more years of research, many of the long-term drawbacks of the green revolution also came into the picture which were neglected at the time of execution. Towards the beginning of the 1990s, it was evident that some of the chemicals used in chemical fertilizers and pesticides posed a potential risk to humans and animals, as well as the environment (Jeyaratnam, 1985; Igbedioh, 1991; Forget, 1993; Aktar *et al.*, 2009; Savci, 2012). Most importantly, it has recently been observed that long-term excessive usage of chemical fertilizers has led to contamination of groundwater with several chemicals and this has resulted in the increase in many life-threatening diseases. One of the cases that can be discussed is the nitrate contamination of groundwater due to excessive use of nitrogenous fertilizers. These nitrogenous fertilizers consist of nitrosamines (carcinogenic molecules), which may lead to several deadly diseases at certain concentrations when consumed as edible plants (Majumdar and Gupta, 2000). Further, there are also instances where excessive use of phosphate fertilizer also influences the arsenic (As) contamination in soil, as phosphate is known to enhance the mobility of As in soils by competing for adsorption sites. This may lead to accumulation of As in soil resulting in deadly diseases such as cancer (Campos, 2002).

Utilization of chemical fertilizers and pesticides has led to the manifold increase in production of all the agricultural products. However, the recent environmental risk assessments of water pollution due to toxic chemical ingredients and the consequent health risks signify the urgent need for an alternative to the present practices in agriculture. This improved alternative methodology is expected to increase the efficiency of fertilizers or pesticides for direct supply to the site of action, making it effective at a lower dose. In the literature, there are various examples where the efficiency of enzymes or molecules interacting with other molecules has been resolved using only one technology. Currently, the most promising alternative method for addressing improvement of crop production is the technology known as ‘nanotechnology’.

Nanotechnology is a promising tool for electronic sensors, catalysis and in biomedical applications (Ansari *et al.*, 2010; Choi and Frangioni, 2010; Pavlovic *et al.*, 2013). With the recent awareness of health and environmental risks due to excessive and continued usage of chemical fertilizers in agriculture, newer ways of executing nanotechnological platforms are being practised. At present, nanotechnology is emerging as a potential component to revolutionize the agricultural field (Sanguansri and Augustin, 2006; Ghormade *et al.*, 2011; Khot *et al.*, 2012; Liu and Lal, 2015; Solanki *et al.*, 2015; Mishra *et al.*, 2016). Applications of the nanotechnology can range from directed supply of nutrients, fertilizers and pesticides that not only improve quality of plant growth and development, but also improve seed quality and soil texture, as well as conserving essential microbial fauna (Solanki *et al.*, 2015).

With the understanding of several promising applications of nanomaterials, it is important to consider methods available for their synthesis that may also contribute to additional cost and environmental concerns. Broadly, the methods of nanoparticles (NPs) formation have been categorized as chemical, physical, bioconjugates and biological methods (Iravani *et al.*, 2014). However, with the recent emergence of nanotechnological applications in agriculture, currently the studies are usually performed using the chemical and physical methods based on synthesized NPs. However, with the environmental concern of nanomaterials-based toxicity due to the subsidiary byproducts or toxic chemicals used in the physicochemical synthesis process, nanomaterials synthesized using biological methods should be preferred in the field of agriculture also. Several studies have revealed that compared to the chemical and physical methods of NP synthesis, biological methods are non-toxic, eco-friendly, low cost, have a low energy consumption (low temperature-based reactions) and, more importantly, no health and environmental risks are involved (Iravani *et al.*, 2014). All these salient features of biologically based nanomaterials can avoid short-term as well as long-term detrimental effects of the toxic materials sourced from nanomaterials (Makarov *et al.*, 2014).

## 6.2 Significance and Applications of Nanotechnology in Agriculture

The green revolution has solved the major problems related to agriculture using the high yield varieties of cereals, chemical fertilizers, pesticides and improved irrigation practices. However, due to the non-directed supply of chemical fertilizer or pesticide dosage, excessive chemicals are supplied to the soil to overcome its unavailability to the plant roots by any means. Most of the applied chemicals run off during irrigation, get adsorbed into the soil particles or most of these chemicals leach down to the groundwater level. Thus, all these problems result not only in the high cost of production, but are also detrimental to human health and the environment. Emergence of newer applications of nanotechnology in several other aspects of day-to-day life and understanding the constraints and the present status of agricultural practice, on the other hand, has come to one point where nanotechnology has shown a new direction.

In general, in nanotechnology, very small materials of nanometer ($10^{-9}$m) dimensions are used, possessing characteristic physical, chemical and electronic properties (Kelly *et al.*, 2003). Because of their unusual characteristics, nanomaterials have been found in a variety of fields ranging from miniaturization of electronics to therapeutic and diagnostic biomedical applications (Azzazy and Mansour, 2009; Chen and Chatterjee, 2013). However, very recently, its applications have also been observed in the agricultural field. In agriculture, nanomaterials have been applied in many different ways, from use as a nanocarrier in the form of nanofertilizers and nanopesticides or the size-based effect that can be specific in each type of nanomaterial towards each type of crop or plants (Bhagat *et al.*, 2015).

### 6.2.1 Role of nanotechnology in fertilizers

Generally, nanomaterials applied in the form of nanofertilizers perform one main function, i.e. smart delivery. This delivery can take many forms: micronutrients that have to be absorbed by the roots to supply it to the whole plant, nutrition supply directed to the fruit only, or any other directed supply of any molecules with a particular function. For the normal growth and development of plants, they essentially require sunlight, water, $CO_2$ and many chemical elements. Among these components, the chemical components are acquired by the plants from soil through roots or aerial parts (Schachtman *et al.*, 1998; Kuzyakov *et al.*, 2016). Out of 16 essential elements for the growth of plants, those required in low concentrations are known as micronutrients (iron, copper, zinc, manganese, boron, molybdenum, nickel, sodium, chlorine), and those required in high concentrations are called macronutrients (nitrogen, phosphorus, potassium, magnesium, calcium, sulfur, silicon). Generally, due to the deficiency of these elements in soil or incapability of plant roots to absorb them from the soil, the production and quality of crops decreases very drastically. However, this has been solved by the excessive administration of chemical fertilizers in the fields but without the investigation of risks to human beings and the environment. In this context, the risks posed by the green revolution open recently the development of nanotechnology applied to agriculture in order to solve problems relating to the inefficient administration of fertilizers, as well as the losses during the irrigation process via leaching resulting in ground water contamination (Solanki *et al.*, 2015).

Currently, administration of nanofertilizers has solved most of the problems associated with loss of fertilizers to soil or water bodies. By definition, a nanofertilizer is a combination of nanomaterial and fertilizer. However, there are different ways to make nanomaterials that can be used to formulate nanofertilizers. Most often this is achieved by the nanoencapsulation method, followed by nanoconjugation and by nanoparticles. Nanoencapsulation methodology is mainly based on polymer, lipid, porous inorganic and clay, where the fertilizers are converted to their nanoparticulate state by mixing them with nanoporous materials of different types (Nuruzzaman *et al.*, 2016). Nanoconjugation consists of directly or indirectly conjugating active molecules of fertilizers or pesticides or nutrient molecules to the nanoparticle surface chemically or physically. In nanoconjugation preparations, chemical conjugation involves specific chemistry that might be specific to the targeted site, but further adds to the cost of nanofertilizers (Ghormade *et al.*, 2011). Finally, there are several instances where the nanoparticulate forms of inorganic nanoparticles are directly used as a source of essential micro- and macronutrients by mixing them with seeds or soil during administration. The use of nanofertilizers with chemical fertilizers in the soil can increase the permeability of nanoparticles to roots, as well as the translocation processes through the cells. Nanofertilizer usage also accounts for the smart, slow and controlled release of the fertilizers. Among the nutrients, the nitrogen, phosphorus and potassium are supplied in the form of N-fertilizer, P-fertilizer, K-fertilizer or NPK-fertilizer and other nutrients such as calcium, boron and sulfur are supplied by embedding in zeolite for slow and controlled release (Bansiwal *et al.*, 2006). A large number of elements such as iron, copper, zinc, manganese, nickel, magnesium, calcium and silicon are supplied in the form of oxide nanoparticulate form designated mostly as $Fe_2O_3$NPs, CuONPs, ZnONPs, MnONPs, NiNPs, MgONPs, $CaPO_4$- or $CaCO_3$NPs and $SiO_2$NPs. The studies carried out to date provide several instances where these nanoparticles have been actively transported to different parts of plants. These oxide forms of nanoparticles control the slow release of metal ions, but also play a role in water retention of the plants (Janmohammadi *et al.*, 2016).

Applications of these nanomaterials range from biofortification, germination, growth and even in to improve the yield of a wide range of edible plants. Recently, iron oxides or EDTA-coated iron oxide nanoparticles have been used as nanofertilizers for biofortification and growth of many edible plants such as ginger, soybean, groundnut and sunflower (Sheykhbaglou *et al.*, 2010; Shahrekizad *et al.*, 2015; Rui *et al.*, 2016; Siva and Benita, 2016). Soybean and sunflower are a major source of edible oil and this application can improve the nutritional value. Similarly, ZnO nanoparticles have been also applied in agriculture for biofortification, improving growth, flowering and seed productivity of maize, *Sesamum indicum*, onion, pearl millet and groundnut (Prasad *et al.*, 2012; Laware and Raskar, 2014; Sabir *et al.*, 2014; Tarafdar *et al.*, 2014; Narendhran *et al.*, 2016; Subbaiah *et al.*, 2016). $TiO_2$ nanoparticles are another form of NPs applied in agriculture in many ways. It has been reported to improve germination of aged spinach seeds as well as increasing the rate of germination and growth of roots and shoots of *Mentha piperita*. Most interestingly, it has been also reported to aid in clustering and adherence of beneficial bacteria to plant roots, resulting in crop growth and stress management, in addition to its role in improving seed germination, development and mitosis of root tip cells of *Vicia narbonensis* L. *Zea mays* L. and seed germination of wheat (Zheng *et al.*, 2005; Castiglione *et al.*, 2011; Feizi *et al.*, 2012; Palmqvist *et al.*, 2015). Very recently, $SiO_2$NPs have been reported to play an important role in root elongation and seed germination of *Zea mays* L., enhancing seedling growth and photosynthesis in wheat and lupin, and specifically seed germination of rice, tomato and maize (Adhikari *et al.*, 2013; Karunakaran *et al.*, 2013; Azimi *et al.*, 2014; Siddiqui and Al-Whaibi, 2014; Sun *et al.*, 2016). Another very important metal is magnesium. Chemically, it is an alkaline earth metal that plays an essential role in all living cells, in the formation of important biological compounds such as ATP, DNA and RNA. Additionally, there are a number of enzymes which require $Mg^{2+}$ ions to perform their catalytic function. Most importantly in the case of plants, $Mg^{2+}$ ions are at the centre of the photosynthetic pigment, chlorophyll, and thus a crucial additive to fertilizers. Very recently, MgONPs have been also reported to play a beneficial role in seed germination and improved growth of shoots and roots in maize (Jayarambabu *et al.*, 2016). MgONPs also act as plant nutrition, particularly in the clusterbean (*Cyamopsis tetragonoloba*) (Raliya *et al.*, 2014). Among the rare earth elements (REE), cerium elements have been applied in agriculture since the 1980s, as fertilizers for crop production (Hu *et al.*, 2004; Diatloff *et al.*, 2008; Yin *et al.*, 2009). To understand the role of cerium in the growth of plants, the role of $CeO_2$NPs was investigated and found to be important in plant growth; however, understanding of its exact role is still incomplete (Hernandez-Viezcas *et al.*, 2013; Zhao *et al.*, 2013; Pulido-Reyes *et al.*, 2015). Furthermore, new types of nanoparticles are being investigated to understand their role in the plant. One of the best examples is the use of carbon nanotubes. Applications of carbon nanotubes are immense in electronics and biomedical applications (Li *et al.*, 1999; Yang *et al.*, 2007). However, currently they have also been reported to play an important role in seed germination, nutrient uptake and growth of many plants such as mustard, tobacco, maize, cabbage, carrot, cucumber, lettuce, onion and tomato (Cañas *et al.*, 2008; Mondal *et al.*, 2011; Khodakovskaya *et al.*, 2012; Tiwari *et al.*, 2014). Nanoparticles have also been used in smart delivery systems, as nanoemulsions, as nanosensors, nanocatalyst for pesticides and fertilizers (Joseph and Morrison, 2006; Nuruzzaman *et al.*, 2016).

### 6.2.2 Nanopesticides

Nanomaterials in the form of nanopesticides have been mainly used for their smart delivery system to control pests for efficient disease management. Similar to nanofertilizers, nanopesticides have been prepared using different strategic methodologies such as nanoencapsulation, nanoconjugation or nanoparticulates (Nuruzzaman *et al.*, 2016).

There are several examples of nanoencapsulation and nanoconjugation, one of which uses multi-wall carbon nanotubes (MWCNTs). This confirms that carbon nanotubes are being used as nanofertilizers as well as nanopesticides (Sarlak *et al.*, 2014). In this study, the carbon nanotubes were primarily coated with citric acid using a long incubation period and a high temperature (24 h and 120°C) and later the pesticides (Mancozeb or Zineb) were used to coat nanoparticles by uniform mixing. The results obtained confirmed that pesticides coating nanoparticles were more effectively toxic to *Alternaria alternata* fungi than the pesticides supplied as solution (Sarlak *et al.*, 2014). Another interesting study reported $TiO_2$ functionalization with copolymer (poly citric acid-PEG-poly citric acid) and then coating it further with a pesticide-indoxacarb was found to be effective against lepidopteran pests (Memarizadeh *et al.*, 2014). Another study also reported imidacloprid pesticide coating on mesoporous silica nanoparticles for improved action on pests (Popat *et al.*, 2012). Further, nanoparticles themselves have been reported to have insecticidal properties, of which the most frequently reported are AgNPs, $SiO_2$NPs and ZnONPs. Silica and silver nanoparticles showed insecticidal properties on the larval stage and adults of *Callosobruchus maculatus* on cowpea seed (Rouhani *et al.*, 2012a). AgNPs, ZnONPs and MgONPs are most commonly known to have antibacterial properties and they also inhibit microorganism growth, making them effective fungicides (Seven *et al.*, 2004; Jo *et al.*, 2009; Mishra *et al.*, 2014; Salem *et al.*, 2015; Mishra *et al.*, 2017). The role of AgNPs and ZnONPs as insecticides against *Aphis nerii* compared to the conventional insecticide imidacloprid has also been reported (Rouhani *et al.*, 2012b). In addition to the role in disease control, nanoparticles are also being used as nanosensors to detect the level of active molecules causing disease in plants, plant pathogens, level of soil nutrition, fertilizers, pesticides, insecticides and soil temperature or moisture (Sharon *et al.*, 2010; Rai *et al.*, 2012; Rameshaiah and Pallavi, 2015; Inbaraj and Chen, 2016). Thus, at this stage, it is very significant to understand the process by which nanoparticles are generated and how these methodologies contribute to toxicity concerns for health and environment and the different functionality of the nanoparticles.

## 6.3 Development of Different Methodologies for Nanoparticle Formation

With understanding of the role of nanomaterials in agriculture, it is very important to understand the different processes of nanomaterials synthesis and their consequent applications. The fascinating properties of nanoparticles and promising applications in a wide array of fields have attracted more and more researchers to develop new design, synthesis protocols and manipulation for a specific size or shape. Since then, different methods for forming nanoparticles have been developed, such as chemical, physical, nanobioconjugate and very recently developed biological-based methods (Fig. 6.1). Of the main three methods of nanoparticle formation, chemical-based methods are the oldest and have been studied extensively to understand the concept and mechanism of nanoparticle formation.

### 6.3.1 Chemical method of nanoparticle synthesis

The chemical method of nanoparticle synthesis includes two major components: a reducing agent and a stabilizing agent. The reducing agent is involved

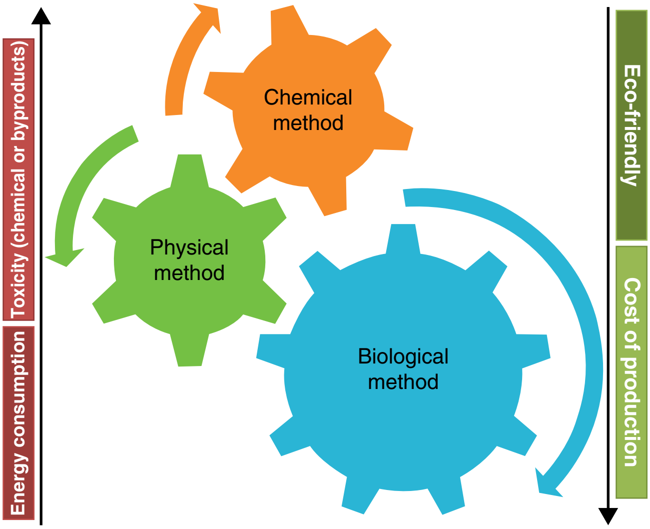

**Fig. 6.1.** Different methods of nanoparticle synthesis. This is the schematic representation of the different methods of nanoparticle synthesis and their comparative limitations and merits.

in the conversion of ionic to atomic form of metal, which will induce the nucleation state and the stabilizing agent, providing a capping shield to keep the particles stably suspended in the liquid medium under nanodimensions. The most commonly used reducing agents are trisodium citrate (Turkevich *et al.*, 1951), sodium borohydrates (Brust *et al.*, 1994) and ascorbic acid (Tyagi *et al.*, 2011); whereas the stabilizing agents include sodium dodecyl sulfate (SDS) (Song *et al.*, 2009), polyvinylpyrrolidone (PVP) (Zhang *et al.*, 1996; Carotenuto, 2001; Wang *et al.*, 2005), polyvinyl alcohol (PVA) (Jun *et al.*, 2010) and trisodium citrate (Turkevich *et al.*, 1951). The first and most popular chemical method was described by Turkevich, which consists of reduction of $Au^{3+}$ ions to $Au^0$ with citric acid, resulting in stable nanoparticles that can be exchanged with other ligand (Turkevich *et al.*, 1951). The Brust–Schiffrin method involves sodium borohydride used as a reducing agent and the acid is immediately replaced by selected mercaptan (Brust *et al.*, 1994). In the first method, water can be used as a solvent, whereas in the second method, the choice of a solvent is dependent on the hydrophobicity of the mercaptan, which acts as stabilizer. The chemical method of nanoparticle synthesis also includes the photochemical method (X-ray or microwave or gamma or UV irradiation) (Sotiriou and Pratsinis, 2010), electrochemical method (electrolysis) (Roldan *et al.*, 2013) and pyrolysis (Ghorbani *et al.*, 2011). In the case of metal oxide nanoparticle synthesis, the most commonly used method is the co-precipitation method, where a chemical precipitant is used and the filtered precipitate is dried at a high temperature for many hours and then calcinated at a temperature of around 500–600°C in a furnace for 5–8 hours (Petcharoen and Sirivat, 2012). ZnONPs use oxalate deposition methods, where the zinc oxalate is precipitated and, further, the oxalate is ground and decomposed at a high temperature for 45–60 minutes to form stabilized ZnONPs (Ghorbani *et al.*, 2015). Most $TiO_2$NPs are synthesized using a chemical method called the sol-gel method (Seisenbaeva *et al.*, 2013). In this method, alkoxides are the precursor molecules and the reaction is performed at room temperature. $SiO_2$NPs have been known to be synthesized using the sol-gel and wet chemical methods (Gorji *et al.*, 2012). Carbon nanotubes in most of the agricultural applications are sourced from the chemical deposition method, involving a high temperature (720°C) and chemicals (Che *et al.*, 1998; Dervishi *et al.*, 2007). Although nanoparticle fabrication using chemicals is a controlled method resulting in a definite size or shape of nanoparticles, it is not an energetically efficient method. Next, we look at the physical method for nanoparticle synthesis.

### 6.3.2 Physical method of nanoparticle synthesis

Different physical approaches such as evaporation, condensation and laser ablation are most importantly applied in the physical method of metal nanoparticle synthesis. Some of the very successful physical methods include photo-irradiation (Ershov and Henglein, 1993; Chen *et al.*, 2002), radiolysis (Henglein, 2000), ultrasonication (Grieser and Ashokkumar, 2006), spray pyrolysis, solvated metal atom dispersion (Wegner *et al.*, 2002), chemical vaporization (Swihart, 2003), and electrochemical methods (Rodríguez-Sánchez *et al.*, 2005).

Chemical and physical methods are both commonly used. However, the advantage of the chemical method is that monodispersed nanoparticles are formed, with size depending on ratio of the reducing agent to the substrate. Unfortunately, this method has limitations when it comes to the translational stage for biomedical usage due to toxicity concerns. For example, in the most popular Brust–Schiffrin method, toxic mercaptans and organic solvents are frequently used. When the nanoparticles produced by these methods are utilized for functionalization and applications, the chemicals and their byproduct(s) may contribute manyfold due to the high surface-to-volume ratio of the nanoparticles. While in the case of the physical method, the absence of solvent contamination in the prepared thin films and the uniformity of nanoparticle distribution is advantageous in comparison with chemical processes. However, it consumes a great amount of energy (high temperature) and requires a lot of time to achieve thermal stability. Moreover, it requires a dedicated system for synthesis, power consumption of several kilowatts or more, and a preheating time of several dozen minutes to reach a stable operating temperature (Magnusson *et al.*, 1999; Kruis *et al.*, 2000).

To date, chemical and physical methods are well established and standard protocols are available to form definite sizes of nanoparticles in a reproducible and controlled manner. Nanoparticles are often assumed to be non-toxic but there are reports that they can cause DNA damage (Kang *et al.*, 2010), induce ROS (reactive oxygen species) in cells (Nel *et al.*, 2006; Li *et al.*, 2008), autophagy (Li *et al.*, 2010), mitochondrial damage (AshaRani *et al.*, 2008; Chairuangkitti *et al.*, 2013), apoptosis (Hsin *et al.*, 2008) and toxicity towards bacteria (Chatterjee *et al.*, 2011; Zhou *et al.*, 2012).

Looking at the long-term consequences of these nanoparticles, such as adverse environment effects due to nanotoxicity and high energy consumption, there emerges a need for a new method with non-toxic, eco-friendly and energy conserving properties. This has resulted in studies on minimizing the use of toxic substances and replacing them with natural molecules, creating the trend known as ’green chemistry’ (Quaresma *et al.*, 2009). The main priorities of green chemistry include lower energy consumption, and hence costs, by lowering the temperature of the reactions, use of catalysts, elimination of toxic solvents and organic substrates, replacing them with natural molecules or exchanging for less toxic ones (e.g. replacement of benzene with toluene) and finally reduction or elimination of byproducts requiring disposal. Although this new direction of study seemed promising, it led to the addition of a few more steps in nanoparticle formation, where the nanoparticles formed were modified to function with biological materials. Further, when the wide range of applications of these bioconjugated nanoparticles were evident, it led to a whole new method of nanoparticle formation, i.e. conjugating biomolecules to chemically synthesized nanoparticles which not only reduce toxicity but also help in customizing specific applications (Wang *et al.*, 2008; Arruebo *et al.*, 2009; Thanh and Green, 2010; Oliveira *et al.*, 2015).

After several years of witnessing the immense possibilities of nanoparticles applications, researchers in nanotechnology are turning towards nature to provide inspiration to develop novel innovative methods for nanoparticle synthesis. Currently used chemical and physical methods of nanoparticle synthesis use toxic chemicals in their synthesis protocols. The toxic residues from these nanoparticles make them unsafe for agricultural, environmental and food-related applications. There is a need to develop nanoparticles using greener alternatives.

### 6.3.3 Biological methods of nanoparticle synthesis

Biological methods of nanoparticle synthesis have been developed very recently. Synthesis of metal nanoparticles using chemical and physical methods has been employed in nanotechnology due to their availability and ease of modulation in the functional behaviour of nanostructures. However, reports illustrate toxic effects of various chemicals and organic solvents used in physical and chemical methods, which are critical for nanoparticle usage in biomedical, agricultural and food-related applications. This has led to increased interest in the utilization of natural products as the biosynthetic machinery of metal nanoparticles (Quaresma *et al.*, 2009).

#### *Nanoparticles synthesis using microorganisms*

Gold and silver are the most studied metal nanoparticles in terms of synthesis protocols or their application. The first report of gold nanoparticle biosynthesis was published by Beveridge and Murray (1980) by utilizing *Bacillus subtilis*. Similarly, biosynthesis of silver nanoparticles was first carried out by exploiting *Pseudomonas stutzeri* AG259 (Klaus *et al.*, 1999). Later, several reports appeared where gold and silver nanoparticles were synthesized by using various other microbes (bacteria, fungi and actinomycetes), but were primarily isolated from terrestrial sources (Thakkar *et al.*, 2010). Similarly, inspired by the first discovery of magnetotactic bacteria in 1961, iron oxide nanoparticles were synthesized using magnetotactic bacteria (Blakemore, 1975; Bazylinski *et al.*, 1994; Donaghay and Hanson, 1995). $SiO_2$ and $TiO_2$ nanoparticles have also been synthesized using microbes (Bansal *et al.*, 2005; Jha *et al.*, 2009). In the case of AgNPs and AuNPs, most of these earlier reports have focused on soil microflora being a potential candidate for their production. However, Sharma *et al.* (2012) have reported that marine habitats can also be exploited to identify the organisms responsible for the biosynthesis of gold nanoparticles (Sharma *et al.*, 2012). This work also emphasizes that, as marine flora and fauna can easily adapt themselves to extreme environmental conditions, it is important to explore marine resources for the biosynthesis of various types of metal nanoparticles. Further, in order to understand the mechanism of how microbes are capable of forming nanoparticles, reported by Malhotra *et al.* (2013), strains from marine-sourced microbes were screened for nanoparticle synthesis. Among the 50 strains, GSG-2 and M-7 were capable of forming nanoparticles. GSG-2 was capable of forming both Ag- and AuNPs from its extracellular secretion; however, M-7 was capable of forming only copper nanoparticles (Malhotra *et al.*, 2013; Kaur *et al.*, 2015). Interestingly, the SDS–PAGE analysis of secretory material of the bacterium in two different growth media provided an indication of a possible role for certain low molecular mass proteins (~36.9, ~17.6 and ~14.9 kDa) in bioconversion of AgNPs and AuNPs. Here, our previous study has hypothesized that these proteins might be involved in the biosynthetic mechanism and/or in the capping of gold and silver nanoparticles.

However, as the expression concentration of the speculated proteins were very low, purifying each protein from the extracellular extract was nearly impossible with large culture cultivation, followed by concentrating the extracellular content with many other proteins and then finally purifying using size-exclusion chromatography (SEC), where the protein is again diluted around 25 times. So, the present method to decipher the protein component responsible for NP formation was multi-step and a very cumbersome process to carry out (Malhotra *et al.*, 2013). MgO nanoparticles have been also reported to be synthesized using microbes and to increase the growth of maize (Raliya *et al.*, 2014; Jayarambabu *et al.*, 2016). For application of the microbial-based nanoparticles, here the nanoparticles can be applied in agricultural applications with no toxicity concerns at a low cost of production. On the verge of screening biological systems, along with microbes, plant systems have been also screened for nanoparticle formation.

### *Nanoparticles synthesis using plant extract(s)*

Microbial-based nanoparticle synthesis is eco-friendly and includes very simple processes. However, requirements of highly aseptic conditions and their maintenance, along with the primary cost of microbial isolation and their culture media, adds to the cost, thereby requiring an alternative method. Procedures for developing nanoparticles from plant sources are more economical and easily scalable in contrast to the processes involving microorganisms (Mittal *et al.*, 2013). Plants can be a good alternative to microbial-based nanoparticle synthesis due to the ease of processing. It is the best platform for synthesis of nanoparticles, free from toxic chemicals as well as providing natural capping agents for the stabilization of nanoparticles. Similar to the microbial system, there are a number of reports of whole plant as well as plant extract-based nanoparticle synthesis (Shankar *et al.*, 2003; Panigrahi *et al.*, 2004; Kasthuri *et al.*, 2009; Ahmad *et al.*, 2010; Singh *et al.*, 2010; Ahmad *et al.*, 2012; Mittal *et al.*, 2013). The number of different microbes and plant extracts with the capability to form nanoparticles keeps increasing, but an understanding of how and which component of these microbes or plant extracts makes them capable of this function is limited to date (Habeeb, 2013; Prasad, 2014; Shah *et al.*, 2015). There are several instances where biosynthesized nanoparticles have been shown to perform better in agricultural applications (Tarafdar *et al.*, 2014; Narendhran *et al.*, 2016).

In addition to the plant extracts, agricultural waste products, such as rice bran, have also been reported to form nanoparticles (Malhotra *et al.*, 2014). In addition to the green chemistry, this finding can also resolve the problem of agricultural waste management. Materials such as grape seeds, skin, stalk and organic waste are the cheapest source and need no additional maintainance; rather, nanoparticles are synthesized from agricultural waste and then used in agricultural applications. There is no further chemical contamination, completely avoiding the risk of health and environmental concerns.

### *Nanoparticle synthesis using biological molecules*

Biomolecules, by definition, are any molecule including large macromolecules such as proteins, carbohydrates, lipids and nucleic acids, as well as small molecules such as primary metabolites, secondary metabolites and natural products.

These are the basic functional components of cell machineries, with a diverse range of functions, and at present there is understanding of these molecules, due to decades of exhaustive research in protein biochemistry and crystallography. So, combining the well-studied biomolecules such as BSA (bovine serum albumin), lysozyme, peptides, aptamers and antibodies with the nanoparticles having great properties may lead to promising and customized applications in biomedical applications (Wu *et al.*, 2008; Tiwari *et al.*, 2011).

## 6.4 Emergence of Biological Methods and Comparative Advantages of Biosynthesized NPs Over Chemically Synthesized NPs

The need for an alternative method of nanoparticle synthesis, with inspiration from the natural process of biomineralization of metals in soil, led to development of the biological method. Biological methods have been very recently developed, so their application has been rarely implemented. As in the case of all the currently existing application of metal nanoparticles, the chemically synthesized nanoparticles are studied due to the ease of synthesis. For example, iron nanoparticles were synthesized using the co-precipitation method, using a chemical precipitant and high temperature (>400°C), involving a long synthesis period (Petcharoen and Sirivat, 2012). In comparison to the chemical methods of NP synthesis, very recently the biological method of nanoparticles has shown potential in many other applications in addition to agriculture (Hussain *et al.*, 2016; Siddiqi *et al.*, 2016). Most importantly, the advantage of biological methods over the chemical methods is the freedom from chemicals, since nanoparticles are synthesized using plants and microbes which are already part of the ecosystem (Table 6.1). Further, the conditions of nanoparticle synthesis using the biological method involves low temperatures, resulting in low-cost production (Hoag *et al.*, 2009). There are many nanoparticle types that have been used in agricultural applications, including ZnO, $TiO_{2,}$ and $SiO_{2.}$

ZnO nanoparticles were synthesized using oxalate deposition methods. Using this method, the zinc oxalate is precipitated and the oxalate was ground and decomposed using a high temperature for 45–60 minutes to form stabilized ZnO nanoparticles (Ghorbani *et al.*, 2015). ZnONPs synthesized using the biological method are utilized in different fields including agriculture, and are not only produced at low cost, but are non-toxic (Gunalan *et al.*, 2012; Sivaraj *et al.*, 2014; Narendhran *et al.*, 2016; Ravindran *et al.*, 2016). Additionally, $TiO_2$NPs applied in agriculture have been synthesized using a chemical method known as the sol-gel method (Seisenbaeva *et al.*, 2013). This method of metal oxide nanoparticle synthesis is performed at ambient temperatures, but with alkoxides as precursor molecules. Similar to the other metal oxide nanoparticles, $TiO_2$NPs have been reported to form using plant, microbes and biological molecules (Malarkodi *et al.*, 2013; Jalill *et al.*, 2016). $TiO_2$NPs are also considered safe for human consumption and are used in the EU as food colouring E171, so biological-based nanoparticles can be safely implemented in any field from medicine to agriculture and food. In most applications, $SiO_2$NPs used the chemical or physical methods;

**Table 6.1.** Various methods for nanoparticle synthesis.

| Source | NMs | Merits and demerits | Applications | References |
|---|---|---|---|---|
| **Synthesis method:** chemical and physical methods | | | | |
| Sodium citrate | AgNPs | *Merit:* Easy process *Demerit:* Chemical, high temperature | Nanofertilizer, nanopesticides | (Henglein and Giersig, 1999) |
| $NaBH_4$ | AgNPs | *Merit:* Easy process *Demerit:* Toxic | Nanofertilizer, nanopesticides | (Métraux and Mirkin, 2005) |
| Sodium citrate | CNTs | *Merit:* Easy process *Demerit:* Chemical, high temperature | Nanofertilizer, nanopesticides | (Sarlak *et al*., 2014) |
| Sodium citrate and oxalates | AgNPs, ZnONPs, MgONPs | *Merit:* Easy process *Demerit:* Chemical, high temperature | Nanopesticides and antibacterial and fungicidal properties | (Seven *et al*., 2004; Jo *et al*., 2009; Salem *et al*., 2015) |
| Sodium citrate | $Fe_2O_3$ | *Merit:* Easy process *Demerit:* Chemical, high temperature | Biofortification and growth of many edible plants | (Petcharoen and Sirivat, 2012; Siva and Benita, 2016) |
| Oxalate deposition method | ZnO | *Merit:* Easy process *Demerit:* Chemical, high temperature | Biofortification, improving growth, flowering and seed | (Narendhran *et al*., 2016; Subbaiah *et al*., 2016) |
| Sol-gel and chemical methods | $SiO_2$ | *Merit:* Easy process *Demerit:* Chemical, high temperature | Root elongation, seed germination and photosynthesis | (Gorji *et al*., 2012) |
| Sol-gel method | $TiO_2$ | *Merit:* Low temperature is used *Demerit:* Alkoxides | Seed germination, development and mitosis of root tip cells | (Seisenbaeva *et al*., 2013) |
| Chemical deposition method | Carbon NTs | *Merit:* Easy process *Demerit:* Chemical, high temperature | Seed germination, nutrient uptake and growth of many plants | (Che *et al*., 1998; Dervishi *et al*., 2007) |
| **Synthesis method:** biological methods | | | | |
| **Microbes or microbial extracts** | | | | |
| *B. subtilis* | AuNPs | *Merit:* Non-toxic *Demerit:* Polydisperse | Can be applied for directed delivery of nutrition or molecules | (Beveridge and Murray, 1980) |
| *P. stutzeri AG259* | AgNPs | *Merit:* Non-toxic *Demerit:* Polydisperse | Directed delivery of molecules | (Klaus *et al*., 1999) |

| | | | | |
|---|---|---|---|---|
| *Magnetotactic bacteria* | $Fe_2O_3$NPs | *Merit:* Non-toxic *Demerit:* Polydisperse | Directed delivery of molecules | (Revati and Pandey, 2011) |
| *Actinobacter* sp. | $SiO_2$ | *Merit:* Non-toxic *Demerit:* Polydisperse | Germination of tomato | (Singh *et al*., 2008; Siddiqui and Al-Whaibi, 2014) |
| *Lactobacillus* sp. and *Sachharomyces cerevisae* | $TiO_2$ | *Merit:* Low-cost, green and reproducible<br>*Demerit:* Polydisperse | Help in adherence of beneficial soil bacteria to the plant roots | (Jha *et al*., 2009; Palmqvist *et al*., 2015) |
| **Whole plants or plant extracts** | | | | |
| *Brassica juncea* | AgNPs | *Merit:* Clean and eco-friendly method<br>*Demerit:* Polydisperse | Simple, cost-effective, non-toxic, and eco-friendly methods | (Prasad, 2014) |
| Plants and its extracts | $Fe_2O_3$NPs | *Merit:* Clean and eco-friendly method<br>*Demerit:* Polydisperse | Delivery of iron ions to plant roots | (Herlekar *et al*., 2014) |
| Tea (*Camellia sinensis*) | FeNPs | *Merit:* Clean and eco-friendly method<br>*Demerit:* Polydisperse | Effective method for treatment of toxic organic contamination in the environment | (Hoag *et al*., 2009) |
| Rice straw waste extracts | $SiO_2$ | *Merit:* Clean and eco-friendly method<br>*Demerit:* Polydisperse | Delivery of Si ions to plant roots | (Nandiyanto *et al*., 2016) |
| *Curcuma longa* extract | $TiO_2$ | *Merit:* Clean and eco-friendly method<br>*Demerit:* Polydisperse | Help in adherence of beneficial soil bacteria to the plant roots | (Jalill *et al*., 2016) |
| **Pure biological molecules** | | | | |
| Proteins | Metal NPs | *Merit:* Clean and eco-friendly method | Directed delivery to site of actions | (Au *et al*., 2010; Merlino *et al*., 2015) |
| Oligonucleotides | AgNPs | *Merit:* Clean and eco-friendly method | Directed delivery to site of actions | (Berti *et al*., 2005) |
| Carbohydrates | AgNPs | *Merit:* Clean and eco-friendly method | Directed delivery to site of actions | (Filippo *et al*., 2009) |

however, one study reports on rice husk-based $SiO_2$ nanoparticles and their role in plant growth, promoting rhizobacteria, increasing soil nutrition and producing 100% seed germination in maize. This process of $SiO_2$ is naturally sourced and inexpensive as compared to the chemical method (Karunakaran *et al.*, 2013). Similar to the nanoparticulate forms of the metal oxides, silver nanoparticles have been used in many agricultural applications. AgNPs have been synthesized using classical methods such as citrate and sodium borohydrate, requiring high temperature or boiling water, and another involves the addition of a toxic chemical (Henglein and Giersig, 1999; Métraux and Mirkin, 2005). Since the first report of microbial-based silver nanoparticles, they have been reported to be synthesized using ambient conditions and different biological sources, with the complete absence of toxic chemicals (Klaus *et al.*, 1999). Very recently, carbon nanotubes have found an application in agriculture, but the literature reports their synthesis using the chemical deposition method, involving a temperature of 720°C and chemicals (Che *et al.*, 1998; Dervishi *et al.*, 2007). They can also be formed using the biological method, so adding extra benefits and closer to green chemistry (Yan *et al.*, 2008).

All these studies are evidence that in the near future, all the biomedical, agricultural and food applications of nanoparticles can be produced from biological source materials or molecules. Apart from the lower dose application of chemical fertilizers and pesticides, the biomediated nanoparticles will replace chemical substances in agriculture. Thus, two very significant challenges can be managed: the toxicity imparted by the chemicals used in the process of nanoparticle formation; and making use of agricultural waste.

## 6.5 Conclusions

There are numerous kinds of nanoparticle synthesis, from the most primitive chemical methods to the most advanced biological methods. The chemical method of nanoparticle synthesis is well established; however, the risk of toxicity in agricultural products as well as groundwater has been addressed very recently. With the urgency of replacing the chemical method, new processes such as biological methods are being studied. Biological methods use any naturally found products, ranging from whole microbes or microbial extracts, whole plants or plant extracts, pure macromolecules (biomolecules such as proteins, peptides, oligonucleotides and carbohydrates) or small molecules, to form nanoparticles. In the past, researchers used chemical reducing agents and biological molecules as stabilizers. However, recent research suggests that factors such as light, electric current or additives can enhance the reducing potential of biological molecules to reduce and stabilize the nanoparticulate formation. Nowadays, agricultural applications of nanoparticles synthesized using biological methods are used as nanofertilizers, nanopesticides, nanoherbicides, nanocarriers and many more. Thus, using biologically sourced materials to form nanoparticles can address and solve the current state of toxicity caused by the byproducts and toxic chemical residues in chemically synthesized nanoparticles.

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# 7 Nanotoxicity to Agroecosystem: Impact on Soil and Agriculture

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## 7.1 Introduction

Nanotechnology has emerged as a way of developing new compounds and innovative technologies in different areas of knowledge. The manufacturing and production of nanotechnological products is gaining much attention from scientists and entrepreneurs because of its multiple applications in pharmaceuticals, engineering, electronics, agriculture, and so on. Nanomaterials correspond to materials with one or more external dimensions in a size range of 1–100 nm, with characteristics and properties distinct from their analogues (Umair *et al.*, 2016). These properties and intrinsic characteristics of nanomaterials are not the only features responsible for their success and versatility. Other properties are high surface area and high reactivity; consequently, the market of nanomaterials is growing to billions of dollar globally (Reddy *et al.*, 2016; Tripathi *et al.*, 2016). The toxicity, safety and impact of nanomaterials on the environment are still incompletely known. What is known is that the smaller particles have a greater penetration capability in biological systems and thereby cause an increased risk of toxicity or side effects (Li *et al.*, 2016).

Nanomaterials readily diffuse into air, water and soil directly and have an impact on toxicity and permeation of biological barriers (Hu *et al.*, 2016; Tripathi *et al.*, 2016). The impact on the environment reinforces the need for greater control and more selective laws about use and final destination. Toxicology emerges as an ally in the study of the security of these materials and as a way to understand

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the parameters and properties that regulate their activity. The nature and composition of these materials change their impact on the human body and govern their toxicity.

These biological responses include growth inhibition, structural damage, oxidative stress, genotoxicity, protein modification and metabolic disturbance. Nanotoxicology focuses on the physiology, pathology and biomolecular mechanisms of nanomaterials. Nanosafety addresses the evaluation of nanomaterial risks in natural environments and biology (Hu *et al.*, 2016). For further interpretation of the adverse effects from nanoparticles (NPs), there are two distinct mechanisms that should be considered: (i) chemical toxicity by the release of possible ions and/or formation of reactive oxygen species (ROS); and (ii) physical stress or stimuli caused by NPs size, shape and surface properties (Vale *et al.*, 2016).

By understanding the mechanism of nanotoxicity, safe nanomaterials can be designed, and the adverse effects of the nanomaterials can be predicted beforehand (Jain *et al.*, 2016).

Although nanomaterials are being applied to different products, analytical methods that enable the characterization and detection of these compounds in conjunction with other matrix materials and products are still under development (Wacker *et al.*, 2016). The effects of engineered nanomaterials in soil seem to be influenced by the microbial composition of the soil. The presence of bacteria in soil depends on the nature of nanomaterials (Tong *et al.*, 2012; Frenk *et al.*, 2013). Exposure to nanomaterials resulting in adverse effects on plants shows that the nature of the material, shape, size and coating can act positively or negatively on the growth of plants. The type of plant also has an impact on the positive and negative effects (Cox *et al.*, 2016; Hatami *et al.*, 2016). Nanotechnology promises to solve many challenges that still need elucidation, but its use needs to be better understood, safe and rational. The aim of the present chapter is to discuss different toxicity-related issues in soil and agriculture.

## 7.2 Impact of Nanoparticles on Soil Environment

The impact of NPs on the physicochemical properties of soil, such as pH, humic and organic carbon content, is not well known, but researchers are studying the effect of NPs on soil (Schlich *et al.*, 2013; Mishra and Singh, 2015). Schlich and Hund-Rinke (2015) demonstrated the effect of silver nanoparticles (AgNPs) on pH and organic content of five different types of soil. They reported that the toxicity of AgNPs decreases with increase in pH of soil. It was proved that AgNPs release silver ions, which are more toxic. Generally, the toxicity of AgNPs is more in acidic soil, whereas in an alkaline environment they are less toxic. In another study, Heggelund *et al.* (2014) reported that the toxicity of zinc oxide NPs (ZnONPs) depends on the type of soil and its pH. Similar to AgNPs, ZnONPs were also found to be less toxic in alkaline conditions; however, in acidic, zinc oxide NPs release $Zn^{2+}$ ions, which has a negative impact on the soil microorganisms. At neutral soil pH, ZnONPs are also very toxic (Read *et al.*, 2016). Moreover, there are some contradictory reports regarding the effect of NPs on organic content of the soil. Aiken *et al.* (2011) demonstrated that NPs can affect the organic content of the soil.

On the contrary, Schlich and Hund-Rinke (2015) found that there was no effect of AgNPs on organic carbon content of the soil. Coutris *et al.* (2012) and Ben-Moshe *et al.* (2013) reported that when humic and organic content of soil is greater, AgNPs are less mobile in soil, and therefore, the toxicity is also much lower. The organic content present in soil decreases the surface coating and charge present on the surface of NPs. The humic and organic content of the soil balances the mobility and transportation of NPs. Organic content prevents the oxidation of NPs and inhibits the formation of ions, which are toxic to the beneficial soil microorganisms (Sagee *et al.*, 2012). In addition, toxicity and grain size of NPs are interdependent. Grain size means the sand and clay content of soil: when the sand content is higher, the toxicity of NPs is at its maximum. On the contrary, higher clay content prevents the aggregation of NPs, which can inhibit their negative impact on the soil microorganisms (Sagee *et al.*, 2012; Schlich and Hund-Rinke, 2015).

## 7.3 Toxicity of Nanoparticles to Soil Microflora

It is very important to know about the size, shape, surface capping and composition of NPs because these properties play an important role in the toxicity of NPs. The ever-increasing production and application of NPs in fields such as medicine, pharmaceuticals, cosmetics, textiles and agriculture results in the release of NPs in the environment (Tassi *et al.*, 2012). Usually, it is not possible to measure the concentration of NPs released or present in the environment due to the unavailability of a proper method and several technical errors. As compared to the air and water ecosystems, the soil ecosystem is a major reservoir where NPs are present in more concentration (Keller *et al.*, 2013; Sun *et al.*, 2014). For example, copper NPs (CuNPs) and ZnONPs are used in the agricultural sector, but on the other hand, these NPs are highly reactive with components of the soil and the flora and fauna of the soil environment. Previous reports have suggested that the harmful effect of NPs is mainly due to the accumulation or deposition of NPs (Shah and Belozerova, 2009; Ben-Moshe *et al.*, 2013). If NPs accumulate within a biological system like soil microflora, they interact with the biomolecules present and aggregate in the plasma membrane, which leads to disturbance in the integrity of the membrane. In addition, the metabolism of organisms is hampered, which decreases the activity of microbial enzymes. NPs interfere in the metabolism of cell, tissue and organs, and thereby ultimately lead to the malfunctioning of soil microorganisms (Gupta *et al.*, 2015).

NPs can be introduced in soil through various routes such as sewage treatment, accidental industrial spills, landfill sites, and sewage sludge used as fertilizer. Research has demonstrated that soil treated with sewage waste may consist of a high percentage of titanium dioxide NPs ($TiO_2$NPs), as well as AgNPs and fullerenes. It was reported that zero-valent iron NPs can be used in the remediation of soil contaminated with chlorinated organic or inorganic compounds (Simonin and Richaume, 2015). Soil microflora are a very sensitive indicator of soil perturbations, as microorganisms play a crucial role in the biodegradation of pollutants, biogeochemical cycling of nitrogen, carbon, sulfur and phosphorus, crop production, etc. Soil microorganisms are the most significant agent of soil and help in the transformation of organic matter and nutrients of soil (Holden *et al.*, 2014).

Toxicity of NPs also depends on type of NPs released into soil. Reports are available on toxicity studies of three types of NPs: metal and metal oxide NPs, carbon-based NPs and zero-valent iron NPs. Inorganic and organic NPs differ in their core material. Inorganic NPs are divided into two classes, metal and metal oxide NPs (Simonin and Richaume, 2015). Generally, carbon- based NPs are considered organic in nature. Hänsch and Emmerling (2010) studied the effect of AgNPs on sandy, loamy soil and reported that the biomass of microorganisms decreases with an increase in the concentration of AgNPs. Peyrot *et al.* (2014) found that AgNPs at lower concentration decrease the activity of microbial enzymes such as phosphomonoesterase, β-D-glucosidase, arylsulfatase and leucine-aminopeptidase. Rousk *et al.* (2012) investigated that copper oxide NPs (CuONPs) decreases the growth of bacteria in mineral soil. ZnONPs decrease the growth and biomass of microorganisms. Ge *et al.* (2013) reported the toxic effect of $TiO_2$NPs, which is supposed to decrease the bacterial diversity. It was also demonstrated that metal and metal oxide NPs have potential to modify the activity of soil microorganisms, which affect the biogeochemical cycles. AgNPs at low concentration show more toxic effect as compared to other metal NPs.

It was found that carbon NPs such as carbon nanotubes and fullerene do not have any toxic effect on the enzymatic activity of microorganisms; they are toxic only at a much higher concentration. Single-walled carbon nanotubes are toxic and reduce the enzymatic activity of microorganisms, when concentration ranges between 300 and 1000 mg $kg^{-1}$ (Jin *et al.*, 2013). Moll *et al.* (2016) studied the effect of different NPs such as $TiO_2$NPs, multi-walled carbon nanotubes and cerium dioxide NPs (CeONPs) on agricultural soil individually and found that the toxicity of NPs is dependent on dose and type of soil.

## 7.4 Nanoparticle-induced Phytotoxicity

Nanotechnology-based products having direct use for humans are currently in great demand (Feizi *et al.*, 2013). Potential applications of NPs in the agricultural sector have attracted many biotechnologists and agricultural scientists to use them, so as to provide enough food for the increasing human population. At the same time, it is also important to keep in mind that this technology is in its early stage of development and very few studies have been carried out on its implications, and hence there are diverse opinions in scientific community about its safety. It is well known that NPs can interact with the surroundings and, similarly, NPs used for agricultural purposes can interact with the crop plants. In this regard, NP-induced phytotoxicity can have a great impact on plant growth, and subsequently the contamination will be propagated in the food chain.

## 7.5 Translocation of Nanoparticles via Root Uptake

For successful establishment of plants in the soil, rapid seed emergence and development of a deep root system is required (Chen and Arora, 2013). During the NP–plant root interaction, there is a high chance of adherence of NPs to them, thereby exposing the plant to physical and/or chemical toxicity. Lin and Xing (2008) studied the probable mechanism of phytotoxicity on ryegrass (*Lolium perenne*) induced by ZnONPs. They reported that there was no profound translocation of NPs from root to shoot, suggesting the non-involvement of NP dissolution. In fact, the toxicity was the result of the NPs adhering to the plant root surface as it was demonstrated in their previous study about the exposure of multi-walled carbon nanotubes, aluminum, alumina, zinc and ZnONPs in six higher plants: cabbage, carrot, cucumber, lettuce, onion and tomato (Lin and Xing, 2007). In field conditions, ZnONPs are found to reduce the wheat biomass thus affecting the yield. Release of Zn ion from ZnONPs, followed by its uptake by wheat, was claimed to be the factor governing its toxicity (Du *et al.*, 2011).

A few minutes' exposure of industrially synthesized $TiO_2$NPs to seedlings of *Zea mays* L. interfere with the water transport in the root, transpiration, and also inhibited leaf growth. Here, $TiO_2$NPs were found to inhibit apoplastic flow through nanosized root cell wall pores (Asli and Neumann, 2009). As mentioned earlier, soil microflora is very important for plant growth. Aluminium oxide NPs ($Al_2O_3$NPs) reduced the growth of the plant root by disturbing the soil microflora (Yang and Watts, 2005); however, these NPs do not cause any defect in plant roots. $CeO_2$NPs are reported to have the ability to translocate to shoots via absorption by the root, showing the low impact in the plant parts present above ground. Nevertheless, they inhibit water transpiration in exposed plant leaves (Asli and Neumann, 2009; Zhao *et al.*, 2012). This clearly indicates that, although the NPs are accumulated near the root, adverse effects can be revealed on the upper part of the plant.

The adsorption of NPs by the root may involve the functional groups, physical adsorption, chemical reactions with surface site, ion exchange and surface precipitations (Mazumdar and Ahmed, 2011). After interaction with carbon NPs, the roots of *Oryza sativa* absorb and translocate to the shoots. The roots can also uptake fullerene C70 and move it to the plant shoot. Conversely, C70 NPs entering through leaves were found to translocate downwards through phloem (Lin *et al.*, 2009). All of these studies imply that NPs enter plants through the root absorption process and, later on, exert an adverse effect. Apart from the root (particularly root hairs), other plant parts, such as pollen exine, cuticle and stomata, also have the ability to absorb nanomaterials. Chichiricco and Poma (2015) reviewed various possible pathways by which nanomaterials are absorbed by plants, which are schematically presented in Fig. 7.1.

## 7.6 Mechanism of Phytotoxicity

As compared to the existing data on the mechanism of nanotoxicity to mammalian systems, understanding about the mechanism of NP-induced phytotoxicity is sparse. The development of cancer in plants is negligible, but accumulation of mutagen or cytotoxic materials can lead to the destabilization of the plant genome, resulting in decreased plant growth.

AgNPs have been shown to inhibit plant growth through their interference in various stages of cell division and collapsing root cortical cells, epidermis and

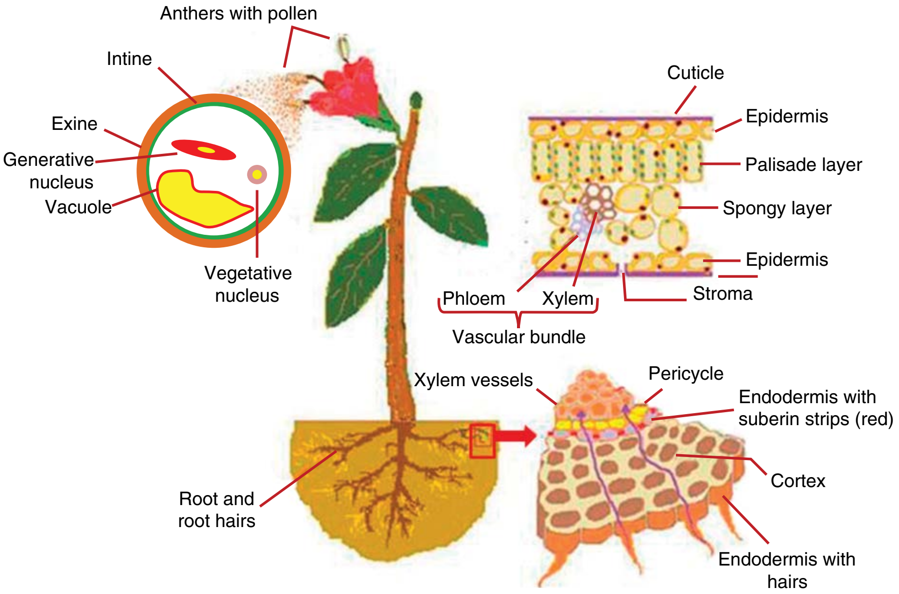

**Fig. 7.1.** Schematic representations of pathways by which nanomaterials are absorbed in a plant, i.e. pollen exine, cuticle, stomata and root hairs. (Adapted from Chichiricco and Poma, 2015.)

root cap (Kumari *et al.*, 2009; Stampoulis *et al.*, 2009; Yin *et al.*, 2011). At the concentration of 3 mg/l AgNPs and $Ag^+$ ions reduce the plant cell size. Moreover, AgNPs: (i) flattened the chloroplast wherein the grana lamellae became thinner and ambiguous; (ii) widened the distance between two thylakoid membranes; (iii) increased the number of osmiophilic globules (OG) in the chloroplast; (iv) were absorbed by roots and transferred to leaves, leading to the appearance of electron-dense deposits in the intracellular space (Qian *et al.*, 2013). For plants, the photosynthetic system is much more important in order to produce chemical energy. If it is altered by NPs, then it will affect the plant efficiency. In other research, gold NPs (AuNPs) were thought to penetrate the seeds and translocated to the leaf. They were also found to accumulate in the cotyledon, unifoliate, and trifoliate leaves, causing harmful effects (Falco *et al.*, 2011).

CuONPs have applications in the manufacturing industry and as a potent antimicrobial agent. Therefore, there is always a risk of them being released into the environment and reaching plants. In this respect, Atha *et al.* (2012) have tested the oxidative stress induced by CuONPs on three different terrestrial plants: perennial ryegrass (*Lolium perenne*), annual ryegrass (*Lolium rigidum*) and radish (*Raphanus sativus*). The study concluded that they have significant activity against radish seedling, with special reference to DNA damage. On the other hand, they were found to be less harmful to both the grassland plants.

Due to their small size, NPs can diffuse through the cell membrane, ion channels and transporter proteins permit them to travel across the plasma membrane (Chang *et al.*, 2012). In some cases, the cell membrane becomes wrapped around the NPs, and thus enters the cell via endocytosis. Later, they can induce reactive oxygen species (ROS), causing DNA strand breaks (Chang *et al.*, 2012). Thus, at cellular and molecular level, almost all important processes are affected by NPs, resulting in the disturbance of cellular homeostasis.

## 7.7 Are Ions or Nanoparticles Responsible for Toxicity?

Among the scientific community across the globe, there is constant debate over whether NP toxicity is mediated by the particle itself or the ions generated by its dissolution in the medium in which it is suspended. The easy release of ions from metal-based NPs such as silver, copper, zinc oxide, nickel etc. is suspected to play an important role in toxicity (Griffitt *et al.*, 2008; Limbach *et al.*, 2007; Miao *et al.*, 2009; Yin *et al.*, 2011). In the case of AgNPs used for wastewater treatment, NPs are suspended in water. After the treatment of wastewater, sludge is produced, which is applied as a soil amendment, subsequently carrying the AgNPs or ion released by its dissolution to the environment, including plants. Possibly, they can affect the plant growth and productivity (Navarro *et al.*, 2008; Lee *et al.*, 2012; Dimkpa *et al.*, 2013). Through a comparative experiment performed on exposing *Arabidopsis thaliana* to AgNPs and silver ions, it has been demonstrated that both NPs and the ions generated by their dissolution have a deleterious effect on the plant. Both the NPs affected the root elongation. More specifically, the AgNPs were reported to be more harmful to the plant compared to the silver ion (Qian *et al.*, 2013). At the cellular level, ionic silver prevents the function of respiratory enzymes. They induce the accumulation of reactive oxygen species (ROS), thereby resulting in the development of oxidative stress (Kim *et al.*, 2009; Yin *et al.*, 2011). The ROS generation can further damage DNA, mitochondria and cell membrane, finally making an impact on plant growth and viability (Apel and Hirt, 2004). After applying AgNPs to *Thalassiosira weissflogii*, a marine diatom, Miao *et al.* (2009) claimed that it decreased the cell growth, the process of photosynthesis and production of chlorophyll. Silver ions released from the AgNPs were reported to affect the photosystem II quantum of *Chlamydomonas reinhardtii*, thus supporting involvement of ions in toxicity (Navarro *et al.*, 2008). Additionally, silver ions inhibit (i) activation of plant hormone ethylene and (ii) mitochondrial function, causing adverse effects in plants (Knee, 1992; Stampoulis *et al.*, 2009). Whereas in the case of AgNPs, DNA damage leads to disturbances in the metaphase with multiple breaks in the chromosome (Kumari *et al.*, 2009; Panda *et al.*, 2011; Patlolla *et al.*, 2012). Conversely, zinc ions generated by the dissolution of ZnONPs were found to be safe compared to the ZnONPs. ZnONPs caused inhibition of mitosis in the root apical meristem in garlic, whereas Zn ions at the concentration of 0.5, 1, 1.5 and 2 mg/l were reported to be safe (Shaymurat *et al.*, 2012).

The hazard associated with the NPs used in the agricultural sector is not yet fully understood. Due to their high reactivity, there is a need to address the safety issue. To date there is insufficient scientific evidence available providing a clear understanding about the risk factors associated with NP toxicity. There is also a need to work on the safe disposal of NPs after their use. In addition, it is also expected to focus on finding differential effects of particles and their ions on crops in given environmental conditions. All of the studies suggest that NPs applied above threshold concentrations may exert toxic effects on the biological system. Therefore, there is a need for increased focus on such an important issue.

## 7.8 Minimizing the Negative Impact on Agroecosystem: A Challenge

It is well known that nanotechnology involves material and processes on an ultrasmall scale and it is currently an intensely studied area of scientific research due to the wide range of potential applications in various fields including agriculture. From the above mentioned evidence, it is clear that on the one hand, use of different nanomaterials can provide solutions for certain problems, while on the other hand, there are potential impacts on the environment, agroecosystem and ultimately on soil health and its microflora. It has been proved that chemical composition, shape and size of nanomaterials contribute to the toxicological effects in many cases (Sohaebuddin *et al.*, 2010). Apart from these, in some NPs, their nature and aggregation may play an important role in toxicity (Dominguez-Medina *et al.*, 2013; Tripathy *et al.*, 2014; Niska *et al.*, 2016).

Rickerby and Morrison (2007) recommended some aspects related to the use of nanomaterials in different applications, which are very important and need to be taken into consideration.

1. An important concern regarding nanomaterial is that there should not be uncontrolled and unethical release into the environment. Detectable level of nanomaterials in the environment can create difficulties, if remediation is needed.
2. Efficient and accurate methods should be developed to detect the level of nanomaterials in the environment and also their shape, size and surface area (i.e. factors that play a role in their toxicity).
3. Detailed information about composition, chemistry, structure–function relationships and surface area of nanomaterials is needed to study their functionality and toxicity.
4. Complete risk assessment studies should be performed on new nanomaterials that present a real risk of exposure during manufacture or use.
5. The life cycle of nanomaterials must be studied, which will be a useful tool for assessment of their real impacts on the environment.
6. When the use of toxic or hazardous material is mandatory for the application of nanomaterials, an effective strategy for recycling and recovery is necessary.

As discussed earlier, size, shape, surface area, nature and aggregation of nanomaterials are mainly responsible for their toxicity. Moreover, control of some of these parameters can help to reduce toxicity. Unfortunately, very few studies have been carried out particularly on toxicity of nanomaterials to the agroecosystem, and hence it is a great challenge and environmental issue. Generally, it is believed that the smaller the size of NPs, the more adverse will be the consequences. Therefore, it is necessary to use NPs of specific size, depending on their application. In fact, it is very difficult to control the size of NPs in their reproducible preparations because of differences in chemical properties of NPs and their bulk counterparts.

However, some strategies have been proposed, which include the use of citrate as a reducing agent in the chemical synthesis of AgNPs (Pillai and Kamat, 2004). Nguyen *et al.* (2013) demonstrated that size-controlled synthesis of AgNPs was possible by autoclaving a mixture of aqueous silver ions containing glass powder and glucose at 121$^0$C and 200 kPa for 20 min. They have reported that size of NPs can be regulated by using different concentrations of glucose. Higher concentration of glucose leads to the synthesis of larger NPs. Treatment of UV radiation in the presence of air also helps to synthesize the NPs in a specific size range. Sau *et al.* (2001) successfully synthesized AuNPs having a size range of 25–110 nm by treatment with UV irradiation and ascorbic acid as reducing agent. Recently, Piella *et al.* (2016) demonstrated that the use of traces of tannic acid together with an excess of sodium citrate and the precursor of gold helps to synthesize AuNPs of controlled size in the range of 3.5–10 nm. In addition, they also proposed that reaction parameters such as pH, temperature, concentration of sodium citrate and gold precursor also play an important role in size control. Similarly, in another study, a seed-mediated growth method was proposed for the synthesis of nanomaterial of controlled size and shape. In this study, newly formed gold atoms were added onto gold-seeded iron oxide octahedrons to form iron oxide-gold core-shell NPs of three different shapes (sphere, popcorn, and star) with controlled size range of 70–250 nm were prepared (Kwizera *et al.*, 2016). All these studies suggested that there is scope to control the size and shape of NPs, provided that certain reaction parameters and precursors are optimized.

Another most important factor responsible for the toxicity is the nature of nanomaterial/NPs used. Actually, the capping molecules present on the surface of nanomaterials also decide their bioactivities as well as toxicity. Therefore, synthesis of NPs with reduced toxicity is a great challenge. But functionalization of NPs with certain polymers (non-toxic materials) like poly (vinyl pyrrolidone) (PVP), poly (vinyl alcohol) (PVA), gum arabic (GA), etc. can be possible, which help to reduce the toxicity of NPs (Cheng *et al.*, 2011). Cheng *et al.* (2011) further reported that capping of AgNPs with PVP and GA under sunlight irradiation significantly decreases the toxicity of AgNPs. The discharge of waste material into sewage water bodies from industries using AgNPs hazardously affects the flora and fauna of water bodies. However, the use of sulfate anions with AgNPs can reduce their toxic effects, thereby preventing the loss of important flora and fauna of water bodies (Hou *et al.*, 2013). Some other studies also proved that use of capping agents such as polyethylene glycol (PEG) with gold nanorods (Niidome *et al.*, 2006) and N-acetyl cysteine with quantum dot (Choi *et al.*, 2010) reduces their toxicity. Recently, Niska *et al.* (2016) demonstrated that capping of AgNPs with various materials such as lipoic acid, polyethylene glycol and tannic acid significantly reduce the toxicity of AgNPs when tested against human gingival fibroblast cells. Overall, the use of different capping agents is a most promising and convenient approach for the significant reduction in toxicity of various NPs.

Similarly, the aggregation of NPs plays a crucial role in toxicity and greatly affects their bioactivities. It is well known that the higher the surface area of NPs, the more will be their activity and *vice versa*. Unfortunately, the aggregation of NPs has resulted in the decrease in their surface area, which negatively influences their activity and may cause toxicity. Dominguez-Medina *et al.* (2013) demonstrated that citrate-stabilized AuNPs form aggregation due to the interaction of citrate anion with $Na^+$ ions from saline solution. However, adsorption of bovine serum albumin on its surface prevents their aggregation completely. In another study, Newton *et al.* (2012) also investigated that use of tetradecyltrimethyl ammonium bromide (C14TAB), acetyltrimethyl ammonium bromide (C16TAB) and nonylphenolethoxylate (NP9) with platinum NPs (PtNPs) helped to reduce the aggregation to a certain extent. Overall, control of size, shape and surface area, capping of NPs with various non-toxic polymers, and prevention of aggregation of NPs can collectively reduce the toxicity of nanomaterials, and hence only these approaches can overcome the problem of nanomaterial toxicity.

## 7.9 Future Perspectives

The emergence of nanotechnology has opened up new possibilities in the field of agriculture, promising significantly enhanced productivity, better management of plant pathogens, efficient use of plant nutrients, early detection of pathogens, increased shelf life, and efficient storage and transport of food grains. The use of nanomaterials in several agricultural products, due to their novel properties as compared to the bulk, will increasingly enter into the environment, enter agricultural soils through land applications or nanopesticides and fertilizers, and thus may affect the agriculture ecosystem. As nanomaterials enter into the soil environment, they may alter the soil function and crop plants. For this reason, concern is increasing about toxicity to the environment in general and humans in particular.

The applications of nanotechnology in agricultural products are developing at a much faster rate than our understanding of their nanotoxicological impacts (Mishra *et al.*, 2017). A major question that scientists are trying to solve is whether nanomaterials formed due to the reduction of precursor or ions will significantly increase their toxicity as well, as compared to ions. There are several reports demonstrating stronger effects of nanoparticles on plants than their bulk counterparts or ions (Li *et al.*, 2016). Questions are being raised about the fate of nanomaterials used in agriculture, such as: Do the soil constituents react with the nanomaterials? Is toxicity of the nanomaterials influenced by their chemical composition, structure, particle size, shape and surface area? Substantial research is needed on the physicochemical properties of nanoparticles and their interaction with soil components.

Servin and White (2016) have recommended several research areas: chronic, low-dose exposure with sensitive endpoints; trophic transfer studies; transgenerational studies; evaluating impact on nutritional quality; co-contaminant accumulation within or toxicity to food crops and effects on rhizosphere biota and endosymbionts; better understanding of the risks and benefits of nanotechnology in the agriculture system. One of the greatest challenges to the field of nanotechnology is the societal acceptance of new types of technology. It will be important for scientists and engineers in this field to work with the public to ensure long-term investments and commercial acceptance of the new technologies.

Developing more effective policies for nanotoxicology in the agroecosystem requires in-depth understanding of both the direct toxicological and indirect toxicological effects on biological systems and environment. Therefore, more research is needed on the nanotoxicological aspects of using nanomaterials in agriculture and assessing their impact on the soil.

## 7.10 Conclusions

Nanotechnology can be used as an enabling technology to revolutionize the world. Moreover, there is no doubt that nanomaterials have numerous applications in various sectors including agriculture. There are a few studies which claim the positive effect of NPs in plant growth, and most focus on the negative effects and toxicity of various NPs. On the one hand, NPs promote the growth of the plants; on the other hand, they exert a negative impact on the agroecosystem, such as soil constituents and microflora. It is evident from various studies that the effect of NPs varies from plant to plant, and depends on their size, shape, composition, concentrations and mode of application. The toxicity of nanomaterials to the agroecosystem has become a great challenge; the development of effective strategies for the control of size, shape and surface area, capping of NPs using different non-toxic materials, and prevention of aggregation will help in the reduction of adverse consequences. Some available reports focus on the interaction of NPs with plants and their mode of toxicity; however, extensive studies are needed to understand biochemical, physiological and molecular mechanisms for the interaction of plants and NPs and their toxicity.

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# 8

# Factors Affecting the Fate, Transport, Bioavailability and Toxicity of Nanoparticles in the Agroecosystem

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## 8.1 Introduction

The basic need for the current scenario is to face the global problem of production, food security and sustainability in constantly changing climatic conditions. The exhaustive use of agrochemicals to increase production has polluted the groundwater and topsoil. A significant increase in food production is compulsory, but we have to ensure minimal damage to the environment by using new approaches. One of the new approaches, the use of nanotechnology in the agricultural sector, is very important. The synthesis of nanomaterials through nanotechnology helps slow the release of pesticides and fertilizers, to reduce dosage and waste (Ghormade *et al.*, 2011). Hence, the integration of nanotechnology in agriculture is extending the opportunity for better yield and quality food and this new and exciting beginning is getting increasing attention for sustainable agriculture (Mishra *et al.*, 2014a). However, although there is literature regarding the application of nanotechnology in agriculture, this does not extend to translational research in normal field conditions. The facts about bioavailability, transport, toxicity and unregulated use prevent the complete acceptance of nanotechnologies in agriculture (Mishra *et al.*, 2017a; Mishra *et al.*, 2017b). The current scenario of research trends is not adequate to get an overview of risk factors and toxicity of nanoparticles in the context of agroecosystem components such as plants, soil

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and microbes beyond their application into the environment. Soil is the most crucial part of agriculture because no one can grow plants and food for humans and their livestock without soil. The biotic and abiotic factors: sorption/desorption, chemical reactions of organic and inorganic ligands in soil has great capability to control the bioavailability, toxicity and leaching of nanoparticles. These processes are also affected by several factors, namely pH, chemical nature of sorbents, root exudates, presence and quantity of organic and inorganic ligands, fulvic acid and humic acid, microbial metabolites and nutrient contents.

The emerging field of nanotechnology opens a new approach in agriculture by enhancing food production significantly with the great efficacy of lower cost and waste (Scott and Chen, 2013; Kah, 2015). However, the application of nanotechnology in agriculture and other food sectors has also created safety concerns towards human health and environment. The term nanotoxicology is one of the major challenges of nanotechnology application which may cause severe hazards during the exposure (Servin and White, 2016). Nanoparticles can be synthesized through chemical, biological and physical methods (Chen *et al.*, 2008). In both physical and chemical processes, the cost of nanoparticle production is very high (Li *et al.*, 1999). During chemical synthesis, the use of chemicals such as sodium borate is very hazardous for the environment (Honary *et al.*, 2011). The other parts, such as vapour condensation and grinding of materials, are very expensive and produce hazardous byproducts. In contrast to chemicals, the biological methods remove all processing costs. Hence the biological methods of nanoparticle production are cost-effective and sustainable due to the absence of toxic byproducts (Shankar *et al.*, 2004; Vigneshwaran *et al.*, 2007; Mishra *et al.*, 2014b; Mishra and Singh, 2015). Crop plants can be regarded as one of the cheapest renewable resources for nanoparticle synthesis through biological methods and the process is known as phytosynthesis. In phytosynthesis, the plant biomass extracts are also used for nanoparticle production. The new way of nanoparticle synthesis uses the different plant parts, namely, flowers, seeds, stem, leaves and fruits. This green chemistry of biological methods is very cost-effective and environmentally friendly in comparison with physical and chemical methods (Shekhawat *et al.*, 2012). Thus, the use of biological methods for nanoparticle synthesis is a good alternative for safety reasons (Mukherjee *et al.*, 2001; Shankar *et al.*, 2004).

Nanoparticles are also helpful for early detection of pests and plant disease management (Li *et al.*, 2005). Conventional methods, which are used to manage pests and pathogens, affect farmers, environment and the economy of agriculture. So that 90% of the synthetics or biopesticides that are accumulated in air and water are lost. In addition to the unregulated use of chemical pesticides, pathogens and pest resistance increases and reduces the soil biodiversity, affecting nitrogen fixation and damaging the habitat of various organisms. By the use of nanotechnology, scientists proved the regulation of plant hormones, such as auxin, which are responsible for the growth of roots and shoots. Through nanotechnology, nanosensors have been developed to respond with auxin. Carbon nanotubes are used as a vector to deliver the desired molecule during seed germination and are in various forms of carbon in a cylindrical shape (McLamore *et al.*, 2010). The use of chemical pesticides, fungicides and herbicides can increase environmental problems and exerts adverse effects on human and animal health. Nanobiotechnology offers many new set of tools for manipulating genes, using nanoparticles, nanofibres and nanocapsules. Nanomaterials can be used to carry a large number of genes and are also able to control the release of genetic material and gene expression in plants (McLamore *et al.*, 2010). Several studies in the field of nanotechnology show they have long-term major effects in the agricultural sector. The positive effects of nanoparticles include increasing growth rate, root and shoot germination biomass, and increased physiological parameters such as increased photosynthetic activities and nitrogen metabolism in many crop seedlings. Nanotechnology improves the controlled liberalization of agricultural chemicals *in situ*, to transfer molecules to increase plant disease resistance (Agrawal and Rathore, 2014). Phytosynthesis of nanoparticles and their potential use in agriculture has attracted attention globally and there is a possibility that such technology can play a major role in providing food for the growing population in the future. Many countries with the potential to utilize nanotechnology in agriculture are investing in the field. Commercialization and applications that can have an important role in improving agricultural production are on the rise. Nanoparticles are used for sensor-based precision in agriculture, natural resource management, early detection of food disease factors and pollutants, prevention of the leaching of nutrients, drought-stress detection, and intelligent delivery systems for chemicals. Nanotechnology is in the early stages of its development and expansion, and biosafety concerns are still under debate (Moghadam *et al.*, 2015). The effect of CNM (carbon nanomaterials) in the environment is a subject requiring more and clearer knowledge and understanding. There are a few studies suggesting that nanomaterials have both good and bad effects on different groups of soil microbes. The reasons for these mixed effects are numerous (different exposure scenarios, growth conditions, particle type/concentration, and species, among others). As such, reliable risk assessment is necessary for widespread application of CNMs in agriculture, which is not possible with the present knowledge base. Hence, future research should also focus on the molecular and genetics level under the relevant environmental conditions to get a greater insight (Mukherjee *et al.*, 2016).

## 8.2 Phytotoxicity of Nanoparticles

The effects of plant nanotoxicology can be categorized under three groups: (i) mechanical effects based on size; (ii) interactions based on affinity; and (iii) catalytic and surface effects (Fig. 8.1). Treatment of *Cucurbita pepo* with copper and silver nanoparticles shows reduced growth (Musante and White, 2012). The silver NPs have a negative effect on the growth of phytoplankton. It is also important to mention that the process of bioaccumulation, biomagnification and biotransformation of genetically engineered NPs in food crops are still unexplored (Rico *et al.*, 2011). Few nanoparticles and plant species have been studied with respect to the consumption and subsequent availability of NPs in food crops (Yin *et al.*, 2011).

One study reported phytotoxicity of five types of nanoparticles. Research shows that Zn and ZnO have a significant role in inhibition of seed germination

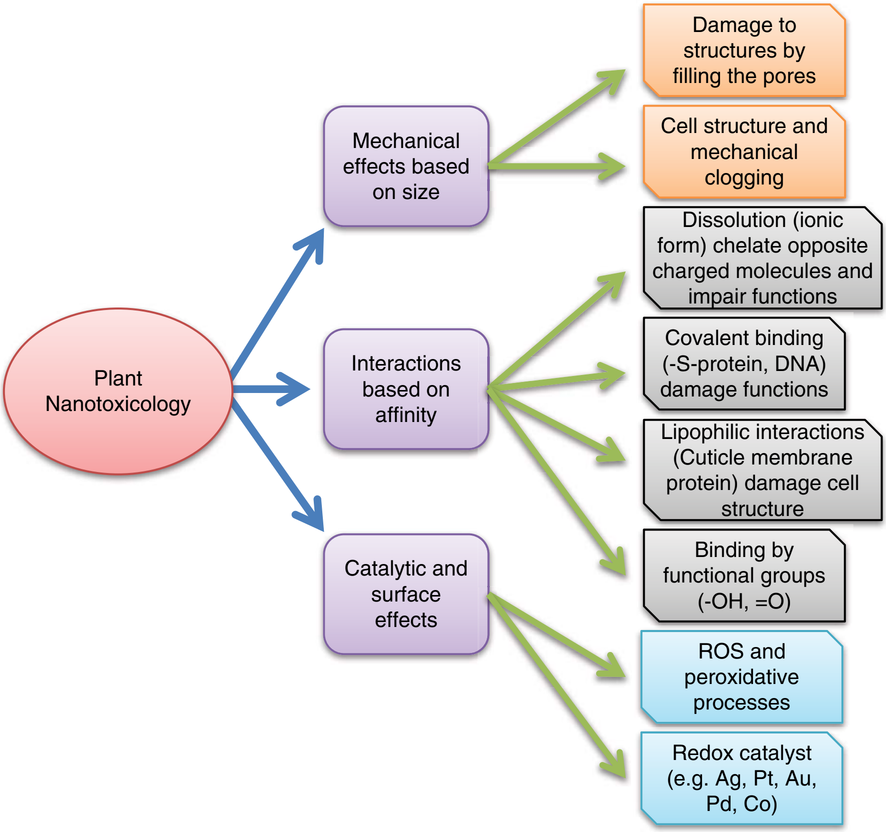

**Fig. 8.1.** Categorization of nanoparticle-dependent various toxicity mechanisms.

and root growth of six different plant species (Lin and Xing, 2007). In the same experiment, it was observed that the harmful effect of both ZnO and $TiO_2$ NPs was detected in rice seed germination. Nano-ZnO was found to reduce both root length and number of roots, whereas $TiO_2$NPs showed no effect on root length (Boonyanitipong *et al.*, 2011). The effect of alumina nanoparticles mixed with and without phenanthrene was studied for the detection of root elongation in the hydroponic method. The NPs mixed with phenanthrene particles showed decreased inhibition of root elongations (Yang and Watts, 2005). In a similar way, Ma *et al.* (2013) also studied the various concentrations (0–1000 mg/l) of nano-zero-valent iron (nZVI) in an hydroponic experiment with two plant species namely cattail (*Typhalati folia*) and hybrid poplars (*Populous deltoids*). They found that more than 200mg/l showed a high toxic effect but a lower concentration supports plant growth (Ma *et al.*, 2013). They have also pointed out that nZVI reduced the rate of transpiration as well as growth of hybrid poplar plants at higher concentration. Moreover, the presence of an irregular coating of nZVI on plant roots and some amount of nZVI penetration into epidermal cells for several layers was also observed.

Several studies of nanoparticles focus on how the toxic potential of nanoparticles to plants could be harnessed for both positive and negative purposes (Menard *et al.*, 2011). Positive effects, including promotion of plant growth, increase in rate of photosynthesis, and increase in nitrogen fixation, were reported for $TiO_2$NPs in spinach (Hong *et al.*, 2005; Yang *et al.*, 2006). The study used seeds of alfalfa (*Medicago sativa*), tomato (*Lycopersicon esculentum*) cucumber (*Cucumis sativus*) and corn (*Zea mays*) treated with nanoceria of 0–4000 mg/l concentration. The report suggested that there is a reduction in the germination of corn seeds by 30% at 2000 mg/l and by 30% and 20%, respectively in tomato and cucumber seeds. In the second aspect, a significant increase was found in the root growth of cucumber and corn, but a reduction in alfalfa and tomato; however, a concentration of nanoceria promoted shoot length in all four plants. There are several reports about the cytotoxic and genotoxic effect of nanoparticles in the plant system. A report by Kumari *et al.* (2009) used various concentrations of silver nanoparticles on *Allium cepa* cells to check their effect on chromosomal aberrations such as chromosomal breaks, stickiness, disturbed metaphase, cell wall disintegration and gaps. In the same study, DNA damage was observed at low concentration of $TiO_2$ in *Alium cepa* and damage decreases with a 10mM concentration. The decrease in damage at higher concentration was correlated with precipitation of nanoparticles at higher concentration; however, genotoxicity and cytotoxicity of nanoparticles correlated with generation of superoxide radicals in plants by lipid peroxidation (Ghosh *et al.*, 2010). Similarly, DNA damage due to ROS production was reported in bacterial system (Cabiscol *et al.*, 2000). Some reports suggest that nanoparticles are transmitted to the next tropic level in algae and tobacco (Navarro *et al.*, 2008; Landsiedel *et al.*, 2009) (Table 8.1).

## 8.3 Effect of Nanoparticles on Soil Microbial Populations

It is important to check the effect of nanoparticles on the bacterial system as the terrestrial and aquatic ecosystems are mainly affected by bacteria in various food webs. Bacterial agents have the ability to absorb and accumulate different forms of nanoparticle, which causes the movement of nanomaterials into the food chain and enters different populations such as plants, fish and bacteria in the food web (Holden *et al.*, 2012). Most plants are dependent on soil bacteria and fungi for the mobilization and absorbance of nutrients from the soil. Thus, nanoparticles such as AgNPs could have a holistic effect on the ecosystem. A recent study suggested the negative role of microbicidal Ag nanoparticles on plant growth, as well as being a killing agent of soil microbes (Zeliadt, 2010). A number of soil enzymes are found to have significantly reduced activity from ZnO and $TiO_2$ nanoparticles (Du *et al.*, 2011).

Nanoparticles not only affect the activity of soil enzymes but also the soil microbial population (Fig. 8.1). Soil microbes, which have the ability to act as a catalyst to different processes, are found abundantly in soil (Horst *et al.*, 2010). A few studies focused on the role of nitrifying bacteria, cultivated in shaking incubators with silver nanomaterials, in which an electron micrograph showed nanomaterials adhering on the microbial cell and causing a detrimental effect by pitting

**Table 8.1.** Nanophytotoxicity on some food and agricultural crops.

| Serial no. | Nanoparticles | Crop | Toxicity | References |
|---|---|---|---|---|
| 1 | Ag | Onion | Cell wall breaks, deformed chromosomes, indistinct disturbed metaphase and mitosis | Kumari *et al*., 2009 |
| 2 | Ag | Flax, ryegrass, barley | Reduced germination and shoot length | El-Temsah and Joner, 2012 |
| 3 | Al | Corn, lettuce | Decline in root length | Lin and Xing, 2007 |
| 4 | Al | Ryegrass | Reduced germination and decreased root length | Lin and Xing, 2007 |
| 5 | $Al_2O_3$ | Corn | Reduced root length | Lin and Xing, 2007 |
| 6 | $Al_2O_3$ | Carrots, cabbage, cucumber, maize | Decline in root growth | Yang and Watts, 2005 |
| 7 | $CeO_2$ | Alfalfa, cucumber, maize, soybean, tomato | Reduced germination, biomass, shoot and root growth | López-Moreno *et al*., 2010 |
| 8 | Cu | Mungbean, wheat | Reduced seedling and shoot growth | Lee *et al*., 2008 |
| 9 | $TiO_2$ | Onion | DNA damage, lipid peroxidation | Ghosh *et al*., 2010 |
| 10 | Zn, ZnO | Ryegrass, radish, rape, lettuce, cucumber, corn | Decline in root growth | Lin and Xing, 2007 |
| 11 | ZnO | Ryegrass | Seedlings failed to develop root hairs, reduced biomass, had highly vacuolated and collapsed cortical cells, broken epidermis and root cap | Yin *et al*., 2011 |
| 12 | ZnO | Soybean | Decline in root growth | López-Moreno *et al*., 2010 |
| 13 | nZVI | *Typha latifolia*, hybrid poplars (*Populous deltoids* × *Populous nigra*) | Strong toxic effect, reduced the transpiration and growth, penetrated into several layers of epidermal cells | Ma *et al*., 2013 |
| 14 | ZnO | *Zea mays* | Decrease in antioxidant enzymes | Zhao *et al*., 2013 |
| 15 | Si | Zucchini | Inhibit seed germination | Stampoulis *et al*., 2009 |
| 16 | Iron | Barley | Reduced germination | El-Temsah and Joner, 2012 |
| 17 | Ag | Wheat | Reduced shoot and root length | Dimkpa *et al*., 2013 |

*Continued*

**Table 8.1.** Continued.

| Serial no. | Nanoparticles | Crop | Toxicity | References |
|---|---|---|---|---|
| 18 | FeO | Clover | Reduced above-ground and below-ground biomass | Feng *et al*., 2013 |
| 19 | $TiO_2$ | Wheat | Reduced germination, reduced shoot and seedling lengths | Feizi *et al*., 2012 |
| 20 | $TiO_2$/inorganic bentonite clay | Maize | Inhibited hydraulic conductivity, leaf growth and transpiration | Asli and Neumann, 2009 |

the cell wall (Choi *et al*., 2008). Treatment of contaminated and uncontaminated Aroclor-1242 soil with nZVI up to 28 days causes no effect on the congener profile of Aroclor, but changes the physicochemical conditions such as pH, redox potential (Eh) and other factors. Observations showed that addition of nZVI affected the soil microbial community and reduced the activity of microorganisms with chloroaromatic mineralizing property (Tilston *et al*., 2013). Nanoparticles have the ability to cause production of reactive oxygen species (ROS) by damaging the membrane, which further leads to oxidation of double bonds on fatty acids of the membrane by lipid peroxidation. The process of lipid peroxidation may be responsible for fluidity of the membrane, which makes the cells more susceptible to osmotic stress and nutrient uptake failure (Cabiscol *et al*., 2000). After peroxidation, fatty acids acquire the ability to trigger reactions, which generates other free radicals, leading to more cell membrane damage. Some inorganic nanomaterials such as $SiO_2$, ZnO and $TiO_2$ were found to have a toxic effect on the bacterial cell; however, its toxicity increased significantly in the presence of light (Adams *et al*., 2006). Several reports have been reviewed to establish the physicochemical properties of engineered metal and metal oxide nanoparticles and their response to biological organisms during nanoparticle–microbial interactions. It has been found that nanoparticles have species-specific toxicity according to size and shape. The surface coating of the material is able to ameliorate or promote microbial toxicity greatly, depending on environmental conditions (Suresh *et al*., 2013).

Engineered nanoparticles have both positive as well as negative impacts on bacterial population diversity, depending on the dose of nanoparticles. In some taxa, it increases the proportion of the community, while in others it is decreased, but mostly the effect is to reduce diversity (Ge *et al*., 2012). Soybean growth is found to be impaired via $N_2$-fixation elimination as a result of uptake of the manufactured $CeO_2$ nanomaterials into roots and root nodules (Priester *et al*., 2012).

Several studies have been conducted on the toxicity of NPs on growth and cell viability of the ecologically relevant bacterial species such as *E. coli, Bacillus subtilis, Pseudomonas putida* and others. All of these indicated the uptake of the NPs by the microbes but further study is needed related to beneficial soil microbes such as $N_2$ fixing, phosphate solubilizers, arbuscular mycorrhizal (AM) fungi to elucidate the mechanism insight to NPs uptake as well as their accumulation in soil and microbes.

Iron oxide nanoparticles (FeNPs) are most commonly used for crop protection, fertilization and remediation of soil organic pollutants on agricultural land during the last few years (Fajardo *et al.*, 2012; Wang *et al.*, 2011; Khot *et al.*, 2012; Arruda *et al.*, 2015; Liu and Lal, 2015). He *et al.* (2016) reported the positive role of IONPs on soil microbial activity and their nitrification potential. In *Lactuca sativa*, higher phosphorus uptake in root and shoot was found under the influence of IONPs (Zahra *et al.*, 2015). Increases in root and shoot biomass were reported in pumpkin and ryegrass (Wang *et al.*, 2011), as well as growth promotion in tomato (Antisari *et al.*, 2015). Although there is a very significant positive impact on plant growth and development, we cannot ignore the toxicity of nanoparticles on soil microflora during plant–microbe interaction. Iron oxide nanoparticles impose negative effects on fungi by decreasing their activity in soil, and nutrient acquisition from soil (Antisari *et al.*, 2013; Feng *et al.*, 2013; Frenk *et al.*, 2013). An increased metabolic quotient (a measure of soil pollution) was also found in IONP-treated soil as compared to control soil, indicating the stress exerted by nanoparticles on soil microbial activity. These nanoparticles are taken up by soil microbes during their life cycles (Antisari *et al.*, 2013), and are transferred to the next level of the soil food web in biotic predators, leading to altered biological and ecological functioning of the soil (Rashid *et al.*, 2016).

Recently, it was reported that zero-valent iron nanoparticles have a role in decreased root and shoot length, as well as chlorophyll and carotenoid content in rice (Wang *et al.*, 2016). The cortical tissues of the plants are damaged under the influence of the nanoparticles, which are responsible for blockage of iron active transport in the root and shoot of rice. In the same way, the biomass of clover was also decreased by the application of IONPs associated with AM fungi. All these studies demonstrate the role of nanoparticles in reducing glomalin production capacity and nutrients acquisition by fungi (Feng *et al.*, 2013).

Nanoparticles also affect bacterial activity and diversity in soil having low organic matter and clay content compared to a clay soil rich in organic matter (Frenk *et al.*, 2013). Parameters like pH, soil salinity and ionic strength also influence the toxicity or bioavailability of nanoparticles in the soil (Fang *et al.*, 2009; Tourinho *et al.*, 2012). Soil parameters are a potential determinant of dissolution, agglomeration or aggregation of nanoparticles in soil solution and their stability in soil (Tourinho *et al.*, 2012). Higher mobility of electrons within their structure and diffusion of $Fe^{2+}$ ions are also important for the weak stability of IONPs (He *et al.*, 2011). This affects the bioavailability of nanoparticles in the soil, and also their toxicity. Consequently, studies regarding the nanoparticles' behaviour in soil are required over various incubation times on a scale of months to years (Tourinho *et al.*, 2012; Antisari *et al.*, 2013).

In bacterial and fungal counts, the carbon and nitrogen content and mineralization in microbial biomass as well as grass litter in a litter-amended sandy soil significantly decreased under IONPs. Nitrogen mineralization efficiency affected by IONPs in a time-dependent manner clearly indicates that the toxicity of IONPs significantly reduces the soil function of nutrient mineralization. Such an effect was not found in the case of grass-litter carbon mineralization. Reduced soil mineralization was the result of the higher metabolic quotient in sandy soil amended with nanoparticle and litter. It was concluded that IONPs have a toxic impact on grass-litter decomposition, nitrogen mineralization, and may also affect other soil ecosystem properties. So their use in agricultural system for fertilization or remediation purposes requires reconsideration (Rashid *et al.*, 2017).

## 8.4 Particle Size-dependent Toxicity

The use of nanomaterials (NMs) helps to improve the working properties of nanoparticles and also affects the surface area, enhancing the surface reactivity compared to the other large components. It was reported that the application of silver nanoparticles inhibits the seedling growth and the root hair development at the concentration of 40 mg/l GA-coated silver nanoparticles. It also produced a broken root cap and epidermis layer, and a collapsed and highly vacuolated cortical cell (Yin *et al.* 2011). The application of the same concentration of supernatants by ultracentrifuged AgNP or silver nitrate to seedlings showed no defect in their growth. The toxicity of AgNP that affect growth is dependent on the net surface area of NPs, and smaller AgNPs (6 nm) are much stronger than the same concentration of large-surface-area NPs (25 nm). The possible environmental toxicity of zero-valent nanoparticles of iron (nZVI) and three other types of silver nanoparticle (average size from 1 to 20 nm) was evaluated for seed germination with flax, barley and ryegrass (El-Temsah and Joner, 2012). During this experiment, it was observed that a high concentration of nZVI (1000–2000 mg/l) inhibited seed germination, but low concentration of these components did not show any effect on the plant. A lower concentration of silver nanoparticle inhibited seed germination, but the size of silver nanoparticle that inhibits the germination is not clearly reported.

The application of copper nanosized particle increased the toxicity 15–65-fold (Manceau *et al.*, 2008). The *in vitro* experiment shows that the copper nanoparticle has the ability to damage both the DNA (Midander *et al.*, 2009) and mitochondria (Karlsson *et al.*, 2009). The copper nanoparticle toxicity has not been well studied, but the data generated through the experiment suggested that ionic copper and nanoparticle of copper are both able to produce toxicity. Recent studies demonstrated that nano-CuO is toxic to soil bacteria, but the bulk macro particulate of CuO was not toxic (Rousk *et al.*, 2012). Further studies show that the toxicity of copper is size-dependent. Toxicity and size are inversely proportional, i.e. the smaller the particle size, the higher the toxicity (Murashov, 2006). Yang and Watts (2005) show that the surface property of alumina has an important role in determining the phytotoxicity of alumina nanoparticles during a hydroponic study of root elongation. The nanoparticle easily crosses the cell barrier due to its high surface reactivity and small size. These nanoparticles interact with intracellular compounds and produce cellular and genetic toxicity through the elicitation of oxidative stress (Landsiedel *et al.*, 2009; Kovacic and Somanathan, 2010). The mechanism of toxicity of the nanoparticle is not well understood, but experimental studies show that genetic and cellular toxicity is dependent on the size of nanoparticles.

## 8.5 Sources and Status

AgNPs ultimately come into contact with soil through various routes such as production source, organic waste in agriculture, recycling of sewage sludge into fertilizers, incineration of waste plant product, and landfill (Mueller and Nowack 2008; Navarro *et al.*, 2008; Benn *et al.*, 2010; Bernhardt *et al.*, 2010; Glover *et al.*, 2011; Coutris *et al.*, 2012). However, the waste management system, improper application, disposal, and accidental spillage also significantly contaminate various soils (Blaser *et al.*, 2008; Calder *et al.*, 2012). In spite of this, knowledge regarding the proper release of AgNPs into the environment is scarce. Apart from this, AgNPs are produced according to an eco-friendly and cost-effective routine (Poliakoff *et al.*, 2002; Sharma *et al.*, 2009; Ahmed *et al.*, 2013; Bhaduri *et al.*, 2013; Khan *et al.*, 2013; Rao and Paria, 2013), but still a huge quantity of AgNPs are accumulating in the soil from various environmental sources all over the world. The current scenario of AgNP production worldwide is approximately 500 ton per annum (Mueller and Nowack, 2008), and a constant increase in manufacturing has been estimated for forthcoming years (Boxall *et al.*, 2007). Therefore, their proper disposal will strongly affect the sector of the environment that receives this huge concentration of AgNPs (Fabrega *et al.*, 2011). Although the soil is ultimately the major receiver of these manufactured NPs, there is insufficient information on methodology to assess their retention in soils and their influence on bioavailability and mobility (Cornelis *et al.*, 2010). From soil, plants provide potential passage for the NPs into the wider environment, acting as the main pathway for their accumulation in the food chain. Several research teams are investigating the effect of various NPs on plant growth, development and metabolic functions (Nair *et al.*, 2010). On the basis of the studies evaluated here, an integrated approach will be the best way for future research activities in order to reduce AgNP accumulation, bioavailability, transformation and toxicity to soil and plant systems that subsequently affect the environment and human health (Anjum *et al.*, 2013).

## 8.6 Fate of Nanoparticles After Use and Generation of Nanowaste

Quantitative data analysis shows that the concentration of nanoparticles has not been reported so far, but in the natural environment, NPs occur in a concentration of approximately 1 to 100μl/l (Boxall *et al.*, 2007). The colloidal organic component concentration in environmental freshwater is 1 to 10 mg/l (Klaine *et al.*, 2008). The consumption of nanoparticles increases day by day in soil and water because of consumer products that use NPs; it is reported that nanoparticles have been observed in wastewater (Biswas and Wu, 2005; Bystrzejewska-Piotrowska *et al.*, 2009). Cornelis *et al.* (2012) observed that the retention of nanoparticles in the soil is directly correlated with the negative charge of AgNP, which is adsorbed on positively charged clay-sized minerals. The availability of organic carbon content in the soil also acts as an organic surface coating and provides the NP mobility from the soil to microbes.

The surface properties of NPs are the most important, because they supply mobility and stability as colloidal state, and also the aggregation or adsorption and deposition of the nanoparticles. Zhao *et al.* (2013) noticed that ZnO nanoparticles coexist with the dissolved Zn species and spontaneously release to the soil in order to refill the zinc and Zn nanoparticle clean-up by the plant root system in a similar way to the alginate-treated soil that enhanced the bioconservation of Zn in the tissues of the maize plant (Zhao *et al.*, 2013). Other studies show that the effect of ZnO- and CuNPs takes place over 162 days. These two different types of nanoparticle move through the soil matrix at different rates, but the retention time of Cu nanoparticles is more than the ZnONPs. The leaching processes were also observed as a function of time for Cu and Zn ions from their ancestor NPs (Collins *et al.*, 2012). The physical and chemical properties of both soil (pH, organic matter, clay content, ionic property, etc.) and NPs (size, shape and charge) will affect the physicochemical process and the result is aggregation, dissolution and agglomeration of NPs. The nature of the nanoparticle manages their bioavailability and mobility to the soil microbes. A number of studies suggest that the metallic ion Cu nanoparticles are the least mobile nanoparticle in comparison to ZnO, $TiO_2$, CuO and $Fe_3O_4$ (Ben-Moshe *et al.*, 2010). The excess leachates and after-use of the nanoparticle gather for a long time in aggregate and colloid form that make an extra nano-waste (anthropogenic waste) in the agricultural ecosystem. This nano-waste makes a negative impact on the life of beneficial microbes in the soil with their toxic effect (Table 8.1). Thul *et al.* (2013) show a simple but very important pathway for continuous monitoring of the fate of nanoproducts in anthropogenic waste and soil microbial life. ZnO nanoparticle release through alginate in soil enhances the bioaccumulation of Zn in maize plants. For the first time it was demonstrated that alginate, a natural component, may affect the fate of ZnO nanoparticles in plants and soil. Further research is required to explore the effect of alginate on ZnO nanoparticles in plants and their maturity (Zhao *et al.*, 2013).

## 8.7 Conclusion

The application of nanotechnology in agriculture is a globally emerging field. A range of nanotechnology applications are being developed to enhance plant growth, development, yield and disease reduction. Nanocapsules and nanoparticles are the best and most efficient way for nanotechnology to release fertilizers and pesticides with high specificity and reduce the collateral damage in a controlled manner. The application of nanoparticles and their transportation in the form of systemic chemicals to a particular site opens up a novel solution for plant treatments in the context of plant pathogen interaction. Nanoparticles can replace agrochemicals, such as fungicides and insecticides, or other substances, such as plant growth regulators and elicitors, into localized sites in plant tissues. The release of nanoparticles is properly capitalized throughout the plant vascular system, targeting certain tissues, and it is helpful to assess studies on the biochemical, physiological and genetic impacts on plants. The nanoparticle interaction with the plant cell makes an alteration in gene expression and subsequent biological pathways, which consequently affects plant growth, development and yield. Thus, further research should continue to explore nanotoxicity in plants, including the possibility of uptake and translocation in plants, and the physical and chemical effects of nanoparticles on root surfaces in the rhizosphere.

In future, the improvement in use of nanotechnology in agriculture is to promote the optimum use with the perfect precision by applying the natural resources. The availability of various sensors and controlled release technologies will change the scenario of farming practices. The network sensors in whole agricultural areas will be able to report variability in environmental conditions for the crops and pests. These reports will be very helpful for farmers during the irrigation, time for fertilization, use of pesticides and even harvesting. In spite of this, the measurement should be proper because it requires skilled, laborious and hardworking persons to collect records of every time. With these huge data, remote monitoring and sensing through *in situ* nanotechnology, backup of data analysed through software, the farmers will be able to create their own information in field conditions and use agrochemicals as per the requirements.

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# 9

# Nanotechnology: Comprehensive Understanding of Interaction, Toxicity and the Fate of Biosynthesized Nanoparticles in the Agroecosystem

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## 9.1 Introduction

The concept of nanotechnology was first given by American theoretical physicist Richard Feynman, 1959 in his classic talk 'There's Plenty of Room at the Bottom' (Feynman, 1960). The term 'nanotechnology' was first coined by Norio Taniguchi (Taniguchi, 1974). It is the science of manipulation of matter on an atomic, molecular and supermolecular level. The Royal Society defines nanotechnology as 'the design, characterization, production, application of structures, devices, and systems by controlling shape and size at nanometer scale' (RSRAE, 2004). The National Nanotechnology Initiative (NAI) defines nanotechnology as the art and science of transformation of matter sized 1–100 nm (Roco, 2011). The upsurge of nanotechnology in the field of research and development has increased due to the quality and properties of nanoparticles (NPs). Through this technology, a material can acquire new physiochemical properties which increase the surface area, reactivity and absorption (Khodakovskaya *et al.*, 2012; Siddiqui *et al.*, 2015). These novel properties of nanoparticles open new avenues for this technology, which previously was not achievable by the same bulk material.

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## 9.2 Classification and Source of Nanoparticles (NPs)

Nanotechnology is an emerging and fast-growing field of science which is being exploited in a number of disciplines (Mishra *et al.*, 2016), dealing with matter at nanoscale (1–100 nm) and its implementation for the welfare of mankind (Fraceto *et al.*, 2016). The nanosized materials exhibit some typical properties which are totally different from the macroscale of the particles. These nanotechnological applications possess the potential to enhance agricultural production by better management and regulating the inputs of plant production. The technologies are used in the form of: (i) nanosensors and nanopesticides (Mukal *et al.*, 2009; Mishra and Singh, 2015b); (ii) smart delivery systems for nanoscale pesticides and fertilizers (Mukal *et al.*, 2009); (iii) biosynthesized nanoparticles for agricultural use (Mahajan *et al.*, 2011; Tarafdar *et al.*, 2012a,b,c; Mishra *et al.*, 2014a,b; Mishra *et al.*, 2017a,b); (iv) plant growth regulators (Choy *et al.*, 2006); (v) feed additives (Shi *et al.*, 2006; Spriull, 2006); (vi) aquaculture (Kumar *et al.*, 2008) as biosensors (FSA, 2008); (vii) nanoscale adjuvants for pesticides (BioBased, 2010); and (ix) veterinary medicines (Ochoa *et al.*, 2007).

There are various approaches for synthesizing nanoparticles (Fig. 9.1) and accordingly, the synthesis methods can be classified into the various groups listed below.

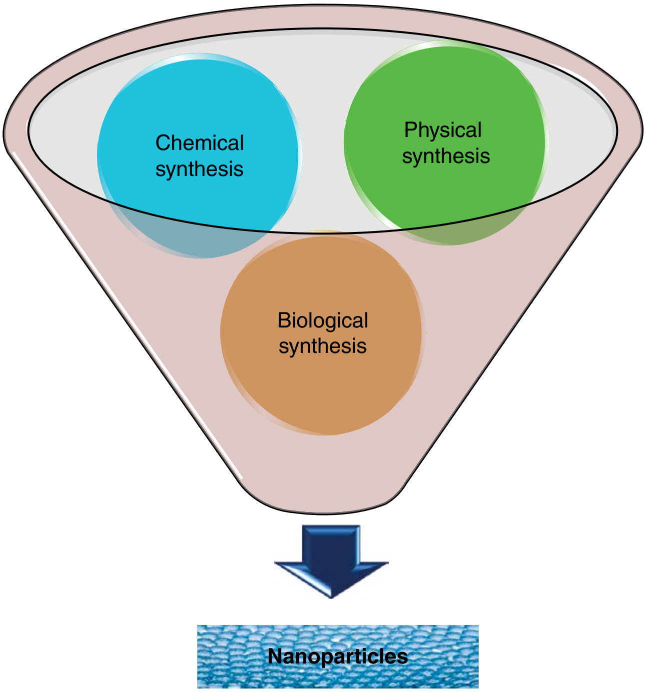

**Fig. 9.1.** Approaches for synthesizing nanoparticles.

1. Conventional method
    a) Chemical synthesis
    b) Physical synthesis
2. Biological method
    a) Plant extract
    b) Bacteria
    c) Fungi
    d) Yeast
    e) Algae

While most of the nanoparticles are manufactured physically and chemically, nowadays biologically produced nanoparticles are gaining more attention due to their eco-friendly nature. Many microbes are used for biosynthesis of NPs, such as *Bacillus megatherium* JCT 13 (Rathore *et al.*, 2015) produces phosphorus (P), *Staphylococcus aureus* (Nanda and Saravanan, 2009), *Geobactor sulfurreducens* (Law *et al.*, 2008), *Pseudomonas stutzeri* produces silver nanoparticles (Haefeli *et al.*, 1984), a fungus *Aspergillus oryzae* TFR-9 (Raliya and Tarafdar, 2014), which produces Zn, P, Ag, Au, Fe and Ti, and *Trichoderma asperellum* (Mukherjee *et al.*, 2008) produces AgNPs. The high surface area of nanoparticles makes them highly reactive, increases strength, confers heat resistance, decreases the melting point, while the low surface energy of NPs gives stability (Fig. 9.2).

## 9.3 Need

Given the unprecedented pressure on food and water resources, particularly due to crop yield stagnation, low nutrient use efficiency, declining organic matter, multinutrient deficiencies, climatic changes, shrivelling arable land, decreasing

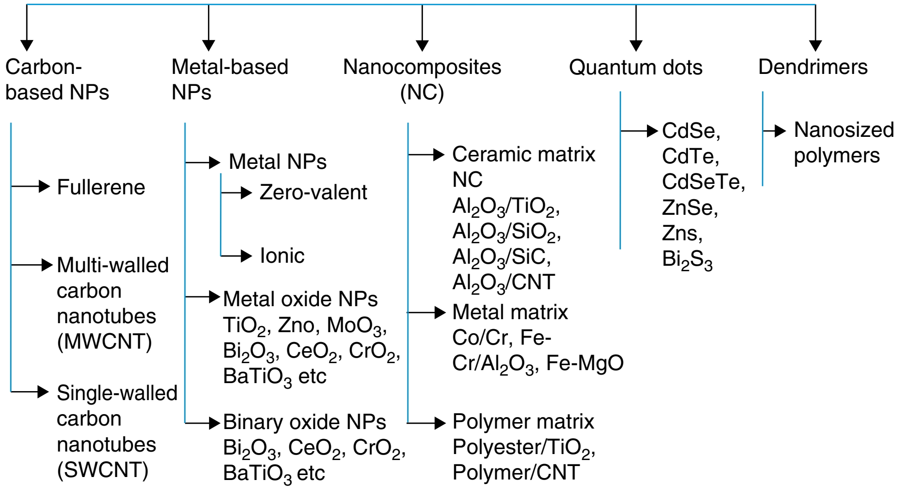

**Fig. 9.2.** Classification of engineered nanoparticles on the basis of their chemical composition.

water availability, resistance to GMOs and shortage of labour from farming, nanotechnology as a technical innovation is playing an extremely important role. It provides remarkable potential to revolutionize the agriculture and other allied sectors, including aquaculture and fisheries. Nanomaterials, such as nanocapsules and nanoparticles, are basically aimed at minimizing the use of plant protection products and nutrient losses to increase the yield through precise detection and delivering the appropriate amount of nutrients and pesticides that enhance productivity with environmental safety and efficiency (Subramanian and Tarafdar, 2011).

Nanotechnology has the ability to enhance agricultural production through various applications which include: (i) nanoformulations of agrochemicals for crop improvement; (ii) nanosensors for monitoring and detection of diseases, residues of agrochemicals and storage conditions; (iii) nanodevices for the delivery of genetic material into plants and animals to develop resistant strains and varieties; and (iv) usage in food processing and storage to increase the shelf life of product (Sekhon 2014; Mishra *et al*., 2016).

## 9.4 Production

The recent statistics suggest that the USA, China, Germany, France, Japan, Switzerland and South Korea are the production centre of about 90% of the nano-based patents and products while India's investments and progress is lacking far behind (Subramanian and Tarafdar, 2011). Considering the immense power of nanoscience technology and to further excel this sector, the Indian government has invested about Rs 1000 crores (US$150 million) through the Nano mission project (Subramanian and Tarafdar, 2011). Even, the Indian Council of Agricultural Research (ICAR) has provided a unique platform to utilize the nanotechnology applications in agriculture. The ICAR – Nanotechnology Platform encompasses five major areas: (i) nanoparticles synthesis for agricultural purpose; (ii) quick detection kits for pest control; (iii) nano-agri inputs for enhanced utilization efficiencies; (iv) nanofood systems; and (v) biosafety (Spriull, 2006; Mukal *et al*., 2009). At present, the main focus is on biosynthesis of nanoparticles, developing smart delivery system for nutrients and active ingredients from nanofertilizers and nanoencapsulated herbicides respectively, etc.

## 9.5 Interaction of Nanoparticles with Agroecosystem Components

### 9.5.1 Soil and soil biota

The soil arrangement consists of particles of different sizes, namely, colloidal, clay, silt, sand and gravel. The 'ultrafine' fraction of the soil has special properties and it is the smallest fraction of the soil, which governs the soil physical and chemical properties like cation–anion exchange, water-holding capacity, tortuosity, particle aggregation, etc. (Kheyrodin, 2014). Natural nanoparticles in the soil occur as nanominerals and mineral nanoparticles (NPs). The nanominerals are based on size range, e.g. certain clays and Fe and Mn oxides, and mineral NPs consist of the larger sizes. The upper surface of the soil is considered as an abundant source of soil microbiota such as actinomycetes, bacteria, fungi, nematodes, etc., which are known as good decomposers converting complex molecules to simple ones. It also plays a significant contribution in recycling all of the major elements (e.g. C, N, P), thus maintaining the physical condition of the soil. A fertile soil consists of a greater amount of beneficial soil microbes, which regulate the soil microbial process such as $N_2$-fixation, nutrient availability and gaseous exchange.

Investigations regarding the behaviour and effects of nanomaterials should be made for soil under different environmental conditions, as it is the most important component of agricultural production (Mishra and Singh, 2015a). Soil health and fertility depends on three important parameters: (i) pH; (ii) cation exchange capacity (CEC); and (iii) organic matter (OM) content. These factors govern the transport, mobility and aggregation of NPs in the soil (Oromieh, 2011; Benoit *et al*., 2013). Sometimes pH of the soil and CEC both considerably interrupt the bioavailability of NPs and Ag in soil (Oromieh, 2011; Benoit *et al*., 2013). The bioavailability of nanoparticles is inversely related to high pH, as some researchers have reported that a high pH of the soil directly raises CEC, due to which some nanoparticles aggregate onto the soil surface, resulting in lower availability. Moreover, there is some evidence that soil OM content also affects aggregation and mobility of NP ions, because a higher OM content in soil enables strong binding of NPs to the soil particles. This reduces the availability and mobility of nanoparticles, further reducing their biological uptake, leading to their continuous sedimentation, resulting in soil toxicity (Shoults-Wilson *et al*., 2011) (Fig. 9.3).

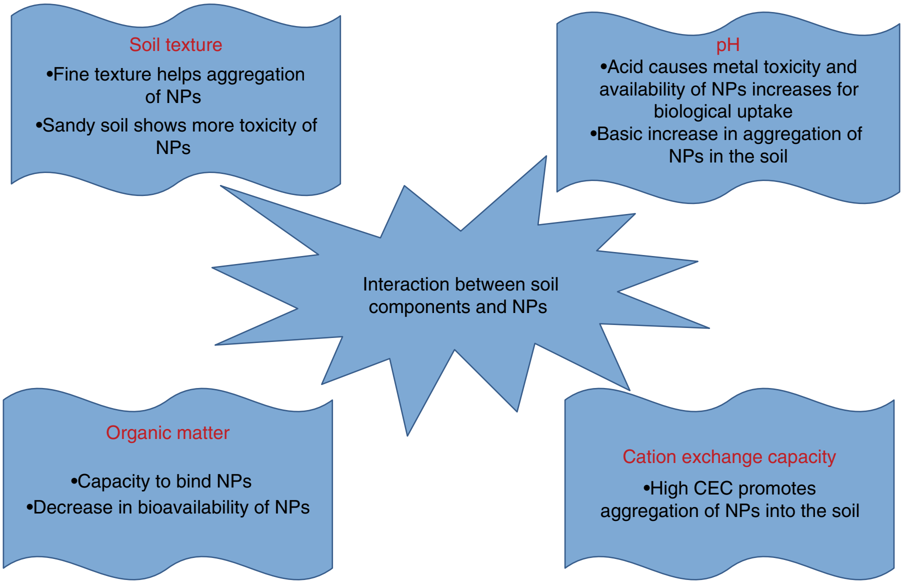

**Fig. 9.3.** Interaction between soil physicochemical components and nanoparticles.

### 9.5.2 Plant system

NPs can easily interact with plants in different ways, exerting positive, negative and inconsequential impacts on plants (Chichiriccò and Poma, 2015). Usually, the commercially available NPs contain stabilizers, in whose absence, the life of NPs in solution is always very short. Interaction of engineered nanoparticles (ENPs) and plants can be categorized under phytotoxicity, uptake, translocation, and accumulation. Current literature revealed that all of the abovementioned interactions depend on the species of the plant, its type, size, chemical composition, stability and functionalization of ENPs. They can interact with plants chemically by adsorption on the roots as well as through physical interactions, and induce phytotoxicity. During the phytotoxic effects, other factors such as solvent factor, threshold level of toxicity, as well as interaction of plants with growth substrate in the soil, can have an effect on phytotoxicity by ENPs (Crane *et al.*, 2008; Ma *et al.*, 2010).

Carbon- and metal-based nanomaterials have been used to enhance morphological features such as germination rate and percentage, seedling vigour, shoot and root length, and their ratio in wheat, maize, soybean, alfalfa, tomato, rapeseed, spinach, radish, lettuce, onion and pumpkin (Begum *et al.*, 2011). Metal-based nanoparticles have also been observed to enhance photosynthetic process and nitrogen metabolism in spinach, soybean and groundnut (Zheng *et al.*, 2005; Liu *et al.*, 2005; Giraldo *et al.*, 2014).

## 9.6 Nanoformulations of Agrochemicals for Crop Improvement

Nanofertilizers and nanopesticides have gained popularity due to their low rate of application and greater effectiveness over a short period, compared to classical formulations with reduced efficacy due to lower stability under field conditions, which has led to residue accumulation of chemicals (Xu *et al.*, 2010; Mishra *et al.*, 2014b). Nanoformulations with control release of the agrochemicals, either regulated by time, location, or triggered under certain circumstances, decreases the loss of active ingredients through infiltration, volatilization, runoff, leaching, photochemical- and biodegradation and makes it a compelling approach for subsequent progress (Pérez-de-Luque and Hermosín, 2013). Nanopesticide formulations with a large specific surface area increase the affinity to the target and hence efficiency for controlling the pathogens (Bergeson, 2010). Nano-cages, nanocontainers, nanotubes, nanoemulsions and nanoencapsulates can efficiently carry higher concentration of active ingredients of pesticides, and would regulate the release of chemicals from the nanocarriers as per requirement (Bouwmeester *et al.*, 2009; Lyons and Scrinis, 2009; Bergeson, 2010). Corradini *et al.* (2010) reported the controlled release of NPK fertilizer by chitosan nanoparticles, which are highly biodegradable, bioabsorbable and bactericidal in nature.

Double-layered hydroxides have been deployed for controlled release of agrochemicals as fertilizers, plant growth promoters and pesticides. Nanoclays possess good compatibility, low toxicity, controlled release and the ability to protect agrochemicals from UV degradation (El-Nahhal *et al.*, 1999; Choy *et al.*, 2007;

Ghormade *et al.*, 2011). Ultra size reduction in micronutrient particles increases their uptake by the crop when applied as foliar spray, and produces better plant growth and soil health by slow release of nanomaterials (Ghormade *et al.*, 2011).

Nanofungicides have been used for management of plant disease by biosynthesis of AgNPs, AuNPs and ZnONPs. Mishra *et al.* (2014a) reported that silver nanoparticles synthesized using plant growth-promoting rhizobacterium (*Serratia* sp.) were used for the management of spot blotch in wheat, *Bipolaris sorokiniana*. Silver nanoparticles have an insecticidal property and have been used against larvae of *Anopheles subpictus* and *Culex quinquefasciatus* (Jayaseelan *et al.*, 2011). Nanoformulations of agrochemicals are prepared by combining several surfactants polymers (organic), and metal nanoparticles (inorganic) in the nanometer size range and hence should not be considered as a single entity (Sekhon, 2014).

## 9.7 Role of Nanosensors in Monitoring and Detection of Plant Diseases

Nanobiosensors, a modified version of a biosensor, can identify the soil pH, humidity and microbial load, and can be used in combination with precision farming to enhance agricultural productivity by better management of inputs (Rai and Ingle, 2012) Nanobiosensors are ultra-sensitive and can detect and quantify even an ultra-low-volume plant virus, bacteria and the level of soil nutrients. Nanosensors are linked to global positioning system for tracking soil health and crop growth (Mukhopadhyay, 2014). Nanobarcodes are used in the multiplexed detection of pathogen DNA by developing a multiplexed diagnostic kit in order to detect the exact strain of pathogen and stage of application (Li *et al.*, 2005). Nanoparticles have also been utilized as biomarkers for identification of distinctive compounds produced in different stages of diseased plants as compared to the healthy ones (Chartuprayoon *et al.*, 2010). Thus, nano-based diagnostic kits and sensors increase speed, power and limit of detection (Chinnamuthu and Boopathi, 2009; Yao *et al.*, 2009). Nanosensors confer a highly sensitive, selective and fast response to pesticide residue detection, even at low concentration (Liu *et al.*, 2008).

Nanoparticle-based sensors might offer improved detection limits in detecting viral pathogens in plants (Baac *et al.*, 2006). Enzyme-based biosensors coated with nanoparticles of Au, Ag, Co, Ti, etc., may greatly help in the precise and quick diagnosis of plant infection and also residue detection of pesticides (Khan and Rizvi, 2014). A nanosensor based on atomic force microscopy has successfully detected the herbicide metsulfuron-methyl, which inhibits the enzyme acetolactate synthase (da Silva *et al.*, 2013).

## 9.8 Nanodevices for the Delivery of Genetic Material in Plants and Animals to Develop Resistant Strains and Varieties

Due to the lower response of crops to *Agrobacterium*-mediated gene transfer, biolistics and microinjection, there is a need for efficient new methods (Christou *et al.*, 1988; Gelvin, 2003). First, DNA-coated vertically aligned carbon nanofibres

(VACNFs) penetrate the cells and then deliver the DNA into target cell (McKnight *et al.*, 2003). The first nanomachine to be used as a vector for transformation was a virus (Choi *et al.*, 2000). In 2010, Vijayakumar and co-workers used a gene gun to deliver DNA-coated gold nanoparticles to carry out genetic transformation. Recently nanovesicles, especially cationic vesicles prepared from vernonia oil, were reported to deliver DNA through the plant cuticle, bringing about *in vivo* transformation (Wiesman *et al.*, 2007). Starch nanoparticles induce pores in membranes and the cell wall, permitting the injection of foreign genetic material (Liu *et al.*, 2008). Mesoporous silica nanoparticles have been used to deliver DNA and their activators through thick plant cell walls with specially designed nanotubes (Galbraith, 2007; Torney *et al.*, 2007).

## 9.9 Nanotechnology in Water Treatment and Reuse

Water contamination with pesticides, industrial residues and harmful microorganisms is a burning problem of the current era. Nanomaterials are eminent catalysts, adsorbents and sensors due to more surface area, high reactivity, better retention and separation of nanoparticles from water surface permits the recycling and reuse of contaminated water. Engineered nanomaterials such as nano-magnetite with superparamagnetic property and high irreversible adsorption capacity allows the separation of arsenic and other heavy metals under low magnetic field (Mayo *et al.*, 2007). Nanomaterials like activated carbon or alumina with additives like zeolite and iron containing compounds have been used to hold aerobic and anaerobic biofilms for removing ammonia, nitrites and nitrate contaminants (Gillman, 2006). ENMs enhanced water treatment is used for (i) Household water treatment for removal of pollutants to meet specific water quality standards, (ii) catalytic degradation of metallic contaminants and (iii) disinfection and microbial control by production of reactive oxygen species, interruption of energy transduction, inhibition of enzyme activity and DNA synthesis (Li *et al.*, 2008; Brame *et al.*, 2011).

Many nanomaterials have catalytic and photocatalytic properties, utilized for oxidative or reductive deterioration of agricultural chemical pollutants (e.g. pesticides and antibiotics) and for disinfection. An antimicrobial and viral inactivation property has been demonstrated for functionalized fullerenes (Lyon *et al.*, 2006), and $TiO_2$-based nanocomposites in the presence of visible and UV light (Agrios and Gray, 2005). This scheme shows a remarkable improvement over current chemical disinfection methods that produce harmful disinfection byproducts and are ineffective on resistant pathogens such as *Cryptosporidium* and *Giardia*. The same process can be used to treat recalcitrant pollutants such as pesticides, residual antibiotics, pharmaceutical compounds and other endocrine disruptors. Several natural and engineered nanomaterials have also been shown to have strong and broad-spectrum antimicrobial activities, including nano-chitosan, silver nanoparticles (AgNPs), photocatalytic $TiO_2$, fullerol ($nC_{60}$, $C_{70}$), and carbon nanotubes (CNT) (Wei *et al.*, 1994; Qi *et al.*, 2004; Morones *et al.*, 2005; Cho *et al.*, 2005; Badireddy *et al.*, 2007; Kang *et al.*, 2007).

## 9.10 The Transport and Fate of Nanoparticles in the Agroecosystem

These days, none of the areas such as plant protection, food processing industry, plant nutrition, water treatment and plant breeding remains untouched by nanotechnology (Thul *et al.*, 2013). Therefore, our concern is to understand the effect of nanomaterials or nanoparticles on agroecosystem as well as the fate of NPs on the different agrocomponents and requires an understanding of their mobility, reactivity, ecotoxicity and persistence. Studies on the impact of nano-waste in the agroecosystem and the phytotoxic effect of NPs on the plant system are also necessary.

The recent studies for hazard assessment of ENPs on different food-chain-level organisms, such as bacteria, algae, fish, crustaceans and nematodes, indicated that metal ENPs (such as Ag, $TiO_2$, ZnO and Cu) are toxic at environmentally relevant concentrations (Holden *et al.*, 2014; Cupi *et al.*, 2015).

The toxic action of metal and metal oxide nanoparticles involves three distinct mechanisms: (i) release of toxic substances, e.g. free Ag ions from silver particles; (ii) surface interactions with media and production of chemical radicals or reactive oxygen species (ROS); (iii) interaction (direct or indirect) of particles or their surfaces, such as carbon nanotube interaction with membranes or intercalation with DNA (Ma *et al.*, 2013).

## 9.11 Uptake Mechanism of Plant for ENPs

Uptake, accumulation and build-up of nanoparticles vary depending on the type, size and the composition of the plant (Miralles *et al.*, 2012). Most information revealed that ENPs could adhere to plant roots and cause chemical or physical uptakes in plants. Indeed, the verification of the uptake mechanism of ENPs is limited and is focused on stock solutions rather than the actual concentration (Ma *et al.*, 2013). The stock solution is prepared either from a series of dilutions or media renewable periods. As such, most method being reported might not produce similar results for different shapes, sizes and forms of nanomaterials. Most of the data correspond to the germination stage and cell culture, which are normally focused on metal-based nanomaterials, such as $TiO_2$, $CeO_2$, $Fe_3O_4$, ZnO, Au, Ag, Cu and Fe. In this case, only fullerene and fullerols showed a ready uptake in plants (De Volder *et al.*, 2013).

Several avenues for the uptake of nanomaterials by plant cells are proposed. Some of the data suggested that the nanomaterials could enter plant cells by being bound to a carrier protein, through aquaporin, ion channels, or endocytosis via the creation of new pores, ending up being bound to organic chemicals (Rico *et al.*, 2011; Solanki *et al.*, 2015). This phenomenon is preferred in carbon nanotubes rather than other types of nanomaterials. Meanwhile, the greater surface area to mass ratio of the nanoparticles compared to the bulk metals induces higher activity compared to the surroundings (Khot *et al.*, 2012). As a result, the nanomaterials may interact with membrane transporters or root exudates, leading to the formation of complex forms before being transported into the plants. Most metal-based nanomaterials that have been reported as being taken up by plants include elements for which ion transporters have been identified (Aubert *et al.*, 2012). Once the nanomaterials enter the plant cells, they may be transported either apoplastically or symplastically from one cell to another via plasmodesmata (Antisari *et al.*, 2015)

However, the relations between the selectivity of the uptake of nanomaterials and the type of plant remain unknown and are open to exploration. Some studies suggested that the gradual increase in ENP uptake was observed with reducing granule size, and only the powder from produced plants with ENP concentrations remains in the sufficient range (Gogos *et al.*, 2012; Sajid *et al.*, 2015). Different particle sizes (1.5 mm, 2.0 mm and 2.5 mm in diameter) of ZnO granules with the same quantity or weight produce better results than 1.5mm particle size, due to the surface contact area; it also increases the uptake of Zn fertilizers (Lin *et al.*, 2008).

## 9.12 Translocation Mechanism of ENPs

Some studies have suggested that the translocation of ENPs depends on the amount being supplied and the nature of the plant as a species (Rico *et al.*, 2011). The higher translocation of other nutrients is recorded by the increment on its demand. The translocation mechanism is initiated by the penetration of ENPs through cell walls and plasma membrane of root cells. One of the main passages of uptake and transportation to the shoot and leaves of plant is the xylem (Yang and Watts, 2005; Siddiqui *et al.*, 2015). In this case, the pore size of the cell wall must be in the range of 3–8 nm, which is smaller than ENPs (Carpita and Gibeaut, 1993; Kurepa *et al.*, 2010; Sabo-Attwood *et al.*, 2012). The penetration rate was studied for leek (*Allium porrum*), and it was found that the ENPs route through the leaf followed the stomatal pathway. Engineered nanomaterials move from leaves to roots, stem and developing grain, and from one root to another (Corredor *et al.*, 2009; Deng *et al.*, 2014).

## 9.13 Transmission Mechanism

The first step to understanding the possible benefits of applying nanotechnology to agriculture should be to analyse the transmission mechanism of ENPs in plants. Transmission of ENPs was detected at different levels: chains of nanomaterial aggregate-carrying cells apparently close to the application point, when such application was made by the ‘injection’ of the ENPs suspension into the pith cavity of the stem, suggesting the flow of nanoparticles from one cell to another (Luttge, 1971; Fellows *et al.*, 2003). The nanomaterials are capable of penetrating through the leaf cuticle and into the cell cytoplasm (Zhai *et al.*, 2014). Plants act as a potential pathway for nanomaterial transportation to the environment and also for bioaccumulation into the food chain (Holbrook *et al.*, 2008; Chen *et al.*, 2010). The wall of the plant cell acts as a barrier for easy entry of any external agents, including ENPs into plant cells. The sieving properties are regulated by the diameter of pore in the cell wall, ranging from 5 to 20 nm, and ENPs having a smaller diameter could easily pass through and reach the plasma membrane (Hischemöller *et al.*, 2009).

There is also a chance for the enlargement of pores or induction of new cell wall pores upon interaction with ENPs, which will, in turn, enhance nanoparticle transmissions (Lin *et al.*, 2009). They may also cross the membrane using embedded transport carrier proteins, or through ion channels, and may interact with various cytoplasmic organelles and hinder the metabolic processes occurring at that site (Lee *et al.*, 2010)

When ENPs are applied on the surface of leaves, they will enter through the stomatal openings or through the bases of trichomes and are then translocated to various tissues (Dietz and Herth, 2011). However, the accumulation of ENPs on the photosynthetic surface causes foliar heating, which results in alterations to gas exchange, due to stomata obstruction, which produces changes in various physiological and cellular functions of plants (Navarro *et al.*, 2008). The application of microscopy techniques visualizes and tracks the transport and deposition of ENPs inside the cell (Bandyopadhyay *et al.*, 2012). One of the pathways also showed that AgNPs with a particle size of 20 nm may be transported inside the cells through plasmodesmata (Larue *et al.*, 2014; Sun *et al.*, 2014). Particles must enter through the cell wall and the plasma membrane of root cells. Xylem is one of the main passages of uptake and transportation to the shoot and the leaves of plant. The pore size of the cell wall was in the range of 3–8 nm, which is smaller than ENPs. The penetration rates of foliar application of polar solutes are highly variable and the mechanism is not fully understood. Investigation in leek (*Allium porrum*) and broad bean (*Vicia faba*) on size-exclusion limits and lateral heterogeneity of the stomata foliar uptake pathway for aqueous solutes and water-suspended nanoparticles were performed (Eichert *et al.*, 2008). Thus, the nanomaterial pathway through the leaf follows the stomata pathway, which differs fundamentally from the cuticular foliar uptake pathway. This consequently proved the limitation of transmission and the distribution of AgNPs in *Medicago sativa* and *Brassica juncea*. In contrast to *Brassica juncea*, *Medicago sativa* showed an increase in metal uptakes with a corresponding increase in the substrate of metal concentration and exposure time (Masarovicova *et al.*, 2014; Dauthal and Mukhopadhya, 2016). The AgNPs were located in the nucleus which suggested that both *Brassica juncea* and *Medicago sativa* are hyperaccumulators of AgNPs (Prasad, 2014).

## 9.14 Fate of NPs

ENPs show unique properties as they lie in the intermediate zone between individual molecules and corresponding bulk materials, and possess high surface area and surface energy. These unusual properties may result in substantially different environmental fate and behaviours than their bulk counterparts (Taylor and Walton, 1993). An emerging area of research is now focused on short- and medium-term studies of the environmental and ecological impact of released ENPs.

Plants have a critical role in the fate and transport of ENPs in the environment through bioaccumulation in tissue and plant uptake (Monica and Cremonini, 2009). ENPs can also become attached to plant roots and exert physical or chemical toxicity on plants. Recent publications have noted the interactions of ENPs with plants (Lin and Xing, 2007; Battke *et al.*, 2008; Lin *et al.*, 2009). Most of these studies are aimed at the potential toxicity of ENPs to plants and mentioned positive, negative or inconsequential effects (Rico *et al.*, 2011). Several recent research papers have also indicated that particle size and specific surface area are better scales for measuring phytotoxicity (Barrena *et al.*, 2009).

## 9.15 Toxicity

Everything in this world has its pros and cons. The increasing number of applications of nanotechnology represents a remarkable rise in the number of engineered nanomaterials (ENPs) inevitably entering our living system. It is worth mentioning here that an excess dose of engineered nanomaterials could adversely affect seed germination by influencing the shoot-to-root ratio and the growth of seedlings (Lee *et al.*, 2010; Khodakovskaya *et al.*, 2013). Studies have reported that certain types of engineered nanomaterials can be toxic once they are not bound to a substrate or freely circulating in living systems as different engineered nanomaterials affect the different routes, behaviour and capability of the plants (Mattiello *et al.*, 2015). Some opposing conclusions have also been drawn regarding the interactions; therefore, a comprehensive study is required to understand the interaction between different types of engineered nanomaterials and different plant species, including phytotoxicity, uptake and translocation of engineered nanomaterials by the plant at the whole plant and cellular level (Wang *et al.*, 2012; Koelmel *et al.*, 2013).

### 9.15.1 Reasons for toxicity

The toxicity of nanoparticles can be attributed to the features below.

1. Surface area to volume ratio of the particles, which increases their interaction with the surrounding molecules.
2. The reactivity and chemical constituents of the particle.
3. The surface charge of the particle is responsible for electrostatic interactions.
4. Lipophilic groups causing hydrophobicity permits the interaction with membranes and proteins.
5. Complementarity of the nanostructure could cause inhibition of enzyme activity, either competitive or non-competitive.
6. Accumulation of an inert particle in the body could also trigger tissue formation around the foreign entity, thus leading to formation of scar tissue.

### 9.15.2 Phytotoxicity mechanism of ENPs

Toxicity of the ecosystem (Illuminato, 2009), potential residue carry-over into foodstuffs (Chaudhry and Castle, 2011), and nanomaterial phytotoxicity are some of the major concerns for the application of nanomaterials in agriculture. From a toxicological perspective, surface area and particle size are important material characteristics. As the size of the particles decreases, its surface area ratio increases, and this allows a greater proportion of its atoms or molecules to be displayed on the surface rather than the interior of the ENPs (Service, 2003). The change in the structural and physicochemical properties of ENPs, with a decrease in size, could be responsible for a number of material interactions that could result in toxicological effects. Multiple studies have shown that nanosized particles are more toxic than microsized particles (Judy *et al*., 2010; Glenn *et al*., 2012). Intrinsic surface reactivity is another factor that determines the toxicity of ENPs (Navarro *et al*., 2008).

Manufactured metal-based nanoparticles aggregate in the soil and interfere with soil biota causing ecotoxicity; for example, bacteria in contact with AgNPs have a detrimental effect (Choi *et al*., 2008), and ROS (reactive oxygen species) generation causes cell membrane damage (Cabiscol *et al*., 2000). In bacterial metabolism, enzymatic activity is lost or reduced when enzymes such as protease, catalase and peroxidase interact with nanoparticles such as ZnO and $TiO_2$ (Du *et al*., 2016). Similarly, nanoparticles such as $CeO_2$ eliminate the $N_2$ fixation of root nodule bacteria (Priester *et al*., 2012), and fullerene ($C_{60}$) disrupts the membrane lipid and DNA of the bacteria through producing ROS, and also shows an antioxidant property (Foley *et al*., 2002; Sayes *et al*., 2005).

There is evidence that some nanoparticles causing toxicity during silver–nanoparticle interactions affect the soil physicochemical properties (Shoults-Wilson *et al*., 2011; Cornelis *et al*., 2012; Benoit *et al*., 2013) and also disrupt the soil's physical and chemical parameters, such as soil texture, pH, cation exchange capacity and soil organic matter (Navarro *et al*., 2008) (Table 9.1).

Phytotoxicity studies using the higher plants are an important criterion for understanding the toxicity of ENPs (Table 9.2). The vast majority of research dedicated to the potential toxicity of ENPs to plants and both negative and positive or inconsequential effects have been reported (Ankamwar *et al*., 2005; Phenrat *et al*., 2007). The majority of the reports available in the literature indicate the phytotoxicity of ENPs (Zhao *et al*., 2005; Galloway, 2008). For example, $Al_2O_3$ nanomaterials inhibit root elongation of cucumber, maize, soybeans, carrot and cabbage (Nagarkar *et al*., 2014), while ZnO nanomaterials were reported to be among the most toxic nanomaterials that could terminate root growth of test plants (Lin and Xing, 2007, 2008). Similar studies were carried out on the toxicology of $Al_2O_3$, $SiO_2$, ZnO and $Fe_3O_4$ on *Arabidopsis thaliana*, with the results showing ZnO nanomaterials at 400 mg/l capable of inhibiting germination (Sheteiwy *et al*., 2016). Overall, the current phytotoxicity profile of ENPs is highly speculative and preliminary, and the effects of their unique characteristics are poorly understood and more studies on toxicity are required, especially on commercial food crops.

Some studies have indicated that the phytotoxicity observed on the exposure to ZnO nanoparticles may be attributed solely to dissolved Zn, which was similar to the conclusion drawn regarding Au nanoparticles. Another study discovered

**Table 9.1.** Effect of nanomaterials on soil microbes.

| Microbes | Toxicity | Nanomaterial | Reference |
|---|---|---|---|
| *E. coli* | Cell wall pitting | Ag | Choi *et al.*, 2008 |
| *E. coli* | Inhibition of bacterial growth, bactericidal action | Ag | Pal *et al.*, 2007 |
| *E. coli, P. aeruginosa, Staphylococcus aureus* and *Salmonella typhimurium* | Antibacterial activity | Ag | Sahu *et al.*, 2013 |
| *E. coli, S. aureus* | Low toxicity to bacteria | Au | Zhou *et al.*, 2012 |
| Nitrogen-fixing root nodules | Decrease of $N_2$ fixation potentials | $CeO_2$ | Klanjscek *et al.*, 2017 |
| *B. sutbilis, S. aureus* | Antibacterial activity | MgO | Huang *et al.*, 2005 |
| *E. coli* | Solar disinfection through photocatalytic activity and reactive oxygen species (ROS) | $TiO_2$ | Rincon and Pulgarin, 2004 |
| *Micrococcus luteus, B. subtilis* and *Aspergillus niger* | Photocatalytic oxidation | $TiO_2$ | Wolfrum *et al.*, 2002 |
| *B. subtilis, E. coli* | Mild toxicity due to ROS production | $TiO_2$, $SiO_2$, ZnO | Ge *et al.*, 2011 |
| Rhizobiales, Bradyrhizobiaceae, Bradyrhizobium, Methylobacteriaceae | Decline in bacterial communities and reduced diversity | $TiO_2$, ZnO | Holden *et al.*, 2012 |
| *Pseudomonas putida* | Inhibition of bacterial growth | ZnO | Li *et al.*, 2010 |

that the toxic effect by ZnO is more significant in seed germination, root elongation, and number of leaves, rather than other nanoparticles (Stampoulis *et al.*, 2009; Dimkpa *et al.*, 2012) (Fig. 9.4).

Nair *et al.* (2010) highlighted that nanomaterials have different effects on various agricultural plants and if not quickly dealt with, will also hamper alternative cropping systems. Studies are needed and their implications should be understood thoroughly before using the nanomaterials in agricultural production system. Major concerns associated with the application of nanomaterials in agriculture and crop protection are (FAO/WHO meeting report, 2010): (i) accurate characterization of nanomaterials in biological matrices to minimize their toxicity in biological systems; (ii) interaction of nanomaterials; (iii) dose considerations; (iv) exposure assessment; (v) product life duration; (vi) background levels in food and feed matrices; and (vii) nanomaterials residue and formation in foodstuffs due to their use in agricultural production and crop protection. Additionally, an IFPRI [International Food Policy Research Institute] policy brief recommended to 'conduct risk analysis so decision makers understand the cost effectiveness of using certain nanotechnology applications to improve food and water safety compared to other technologies'.

**Table 9.2.** Detrimental effect of engineered nanoparticles (ENPs) on plants.

| Serial no. | Plant | NPs | Effect | Reference |
|---|---|---|---|---|
| 1. | *Vicia faba* | Ag | Decreased rate of mitotic index, chromosomal aberrations, irreversible DNA damage | Patlolla *et al*., 2012 |
| 2. | *Allium cepa* | Ag | Generation of ROS, cell death, mitotic index, micronucleus and mitotic aberrations, DNA damage | Panda *et al*., 2011 |
| 3. | *Spinacia oleracia* | $CeO_2$ | Enhancement in SOD (superoxide dismutase) activity and chloroplast ROS – scavenging activity | Giraldo *et al*., 2014 |
| 4. | Squash | Ag, Cu | Reduction in the biomass | Musante and White, 2012 |
| 5. | Maize, tomato, cucumber, spinach | $CeO_2$ | Reduced seed germination | |
| 6. | *Lolium rigidum*, *Lolium peerenne*, *Raphanus sativus* | CuO | Damages DNA | Atha *et al*., 2012 |
| 7. | Zucchini (courgette) and onion | Cu | Reduced root growth | Stampoulis *et al*., 2009<br>Nagaonkar *et al*., 2015 |
| 8. | *Zea mays* | Fe | Impact on structure of photosynthetic enzymes: small concentration increases growth of plantlets, high concentration decreases growth of plantlets | Racuciu and Creanga, 2007 |
| 9. | *Mentha piperita* | $TiO_2$ | Toxic to seed germination and decreases the shoot, root length and also shoot biomass | Samadi *et al*., 2014 |
| | *Spinacia oleracea* | $TiO_2$ | Increases Hill reaction, chloroplast activity, photosynthesis rate and non-cyclic photophosphorylation | Hong *et al*., 2005 |
| 10. | *Spinacia oleracea* | $TiO_2$ | Increase in protein expression of Rubisco enzyme by 40% | Xuming *et al*., 2008 |
| 11. | Onions, wheat, tobacco | $TiO_2$ | Reduced root growth | Larue *et al*., 2012; Feizi *et al*., 2012 |
| 12. | Onion, tobacco, maize and beans | $TiO_2$ | Produces ROS (reactive oxygen species), damage DNA | Ghosh *et al*., 2010; Castiglione *et al*., 2011 |
| 13. | Wheat | $TiO_{2,}$ ZnO | Reduction in biomass production | Du *et al*., 2011 |
| 14. | *Lolium multiforum* | Zn | Inhibits seed germination and root growth | Lin and Xing, 2007 |

*Continued*

**Table 9.2.** Continued.

| Serial no. | Plant | NPs | Effect | Reference |
|---|---|---|---|---|
| 15. | *Zea mays* | ZnO | Inhibits seed germination and root growth | Lin and Xing, 2007 |
| 16. | *Lolium perenne* | ZnO | Shrunken root tips, collapsed cells in root epidermis and cortex | Lin *et al*., 2008 |
| 17. | *Vicia faba* beans | Au | Concentration-dependent decrease in oxidative enzyme activity, growth reduction, decreased antioxidative enzyme activity (e.g. catalase and ascorbate peroxidase) and greater electrolyte leakage | Anjum *et al*., 2013;<br>Anjum *et al*., 2014 |
| 18. | Lettuce, cabbage, red spinach and tomato | Au | Reduced plant growth, biomass, number and size of leaves, and increased ROS along with necrotic symptoms | Begum *et al*., 2011 |
| 19. | Tobacco | WS-C70 | Cell boundary disruption, growth inhibition, possible adsorption of WS-C70 to the cell wall through hydrostatic interaction with the carboxylic groups of fullerenes | Liu *et al*., 2013 |
| 20. | Mustard | MWCNT | Reduced germination and dry biomass | Mondal *et al*., 2011 |

## 9.16 Toxicity of Nanoparticles in Aquatic Ecosystem

Literature on ecotoxicology reveales the toxic effect of nanoparticles on invertebrates and fish even at lower concentrations (mg/l) as the aggregation of nanoparticles often occurs in seawater and hard water. It has been reported that ecotoxicity of nanoparticles is altered by state of dispersion and factors such as salinity, pH and presence of organic matter in water. Uptake of nanoparticles in fish occurs through dietary exposure and via absorption through gill epithelia, intestinal epithelia and through skin (Handy *et al*., 2008). Utilization of nanoparticles for different aquaculture practices has led to its accumulation and penetration in aquatic animals. Several studies showed the toxic effect of engineered nanoparticles (ENPs), such as biomagnification, biotransformation and migration along food web (Krysanov *et al*., 2010). Submission to ENPs produces health risks in fish by causing oxidative DNA damage in different tissues. Silver nanoparticle treatment in zebrafish has resulted in slow blood flow, twisted notochord, abnormal body axes, pericardial oedema and cardiac arrhythmia (Asha Rani *et al*., 2008). $C_{60}$ fullerenes have been reported to be toxic to fish and invertebrates such as *Daphnia magna* (water flea), in which there is a higher mortality rate for higher

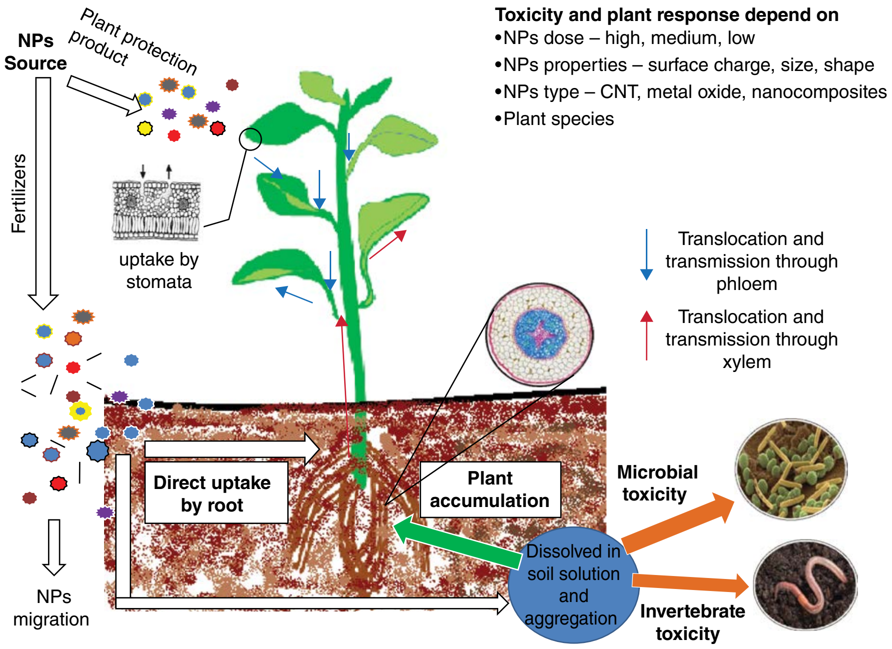

**Fig. 9.4.** Interaction and fate of nanoparticles in agroecosystem.

concentrations (Oberdörster *et al.*, 2006). Smith *et al.* (2007) have reported that single-walled carbon nanotubes act as a respiratory toxicant in rainbow trout, leading to swellings or aneurysms on the ventral surface of the cerebellum in the brain and apoptotic bodies and cells in abnormal nuclear division in liver cells and aggressive behaviour. It has been reported that silver nanoparticles produce irrecoverable toxic effects on biological and physiological properties of fish in freshwater, exceeding those in the saline water ecosystem (Kalbassi *et al.*, 2011). Environmental health news in the USA in November 2009 reported an experiment by a University of Utah researcher, Darin Furgeson, who reported on effect of exposure to silver nanoparticles on embryo of zebrafish and found that some fishes were dead while those left were deformed by mutation in swim bladders, tails, eyes and heart (Shetler, 2009). Federici and co-workers in 2007 reported that brain injury by exposure of rainbow trout to $TiO_2$ nanoparticles depends on particle nature (Federici *et al.*, 2007). $TiO_2$ nanoparticles are widely used in industries and they enter the aquatic ecosystem through industrial effluent. A study was conducted on bioaccumulation, sub-acute toxicity and the effect of $TiO_2$ nanoparticles on tissues such as gills, intestine, muscle and brain of goldfish. It was reported that an increase in $TiO_2$ level in water from 10 mg kg$^{-1}$ to 100 mg kg$^{-1}$ caused abnormal behavioural and physiological changes. It also leads to reduced growth rate in fishes and increased oxidative stress (Ates *et al.*, 2013). Still, there is need for toxicological studies on distribution, absorption, metabolism, excretion and localization of nanomaterial in the body, and its effects on organ systems, spleen, skeletal muscles, bones and kidney need to be explored (Handy *et al.*, 2008).

## 9.17 Risk Assessments

Standard development activities are crucial for proper functioning of nanotechnology market and product development. Standardization plays a key role in guiding, supporting and augmenting the nanotechnology industry, both at local and international levels. The international Organization for Standardization (ISO) Technical Committee (TC) 229 is responsible for developing international guidelines for nanotechnology. In the USA, government initiated a multi-agency nanotechnology programme called the 'National Nanotechnology Initiative' (NNI) in 2000, which provided a comprehensive framework for developing nanoscience and nanotechnology (Table 9.3). In India, the key regulatory body is the Department of Science and Technology (DST), with other bodies such as the Department of Information and Technology (DIT), Department of Bio-technology (DBT), Council of Scientific and Industrial Research (CSIR), Defence Research and Development Organizationn (DRDO), Indian Council of Medical Research (ICMR), Indian Space Research Organization (ISRO) and Digital Audio Extraction Community (DAE) (Jayanthi *et al*., 2012). In 2010, the DST appointed a task force which has been asked to advise the Nano Mission Council to develop a regulatory body for nanotechnology.

## 9.18 Conclusion

The industrial sector comprising nanotechnology is expanding rapidly and it has been predicted that sale of nanoproducts may reach a remarkable level in the coming years. The rapid increase in development and consumption rate in ENP products will also enhance the release and involvement of these nanoparticles in the environment. There are various benefits of nanotechnology, but a major concern remains regarding the long-term risks of ENPs to the environment. The

**Table 9.3.** Coordinating body in different countries for addressing nanotechnology risk.

| Countries | Supporting bodies | Key legislation |
|---|---|---|
| USA | Multi-agency governance at various levels. command and control mode;<br>Nanoscale Science Engineering and Technology Subcommittee | All aspects of nanotechnology |
| China | National Steering Committee for Nanoscience and Nanotechnology | Nanomaterials and ICT applications |
| India | Multi-agency DST (initiation and implementation of Nano Science and Technology Institute and Nano Mission); DIT, DBT, CSIR, DRDO, ICMR, ISRO, DAE | Nanomaterials, biomedical, electronics, energy (solar), water |
| Taiwan | National Science Council, Department of Industrial Technology | ICT applications, primarily to electronics |
| Japan | National Institute of Advance Industrial Sciences, National Institute of Material Sciences | Chemical Screening and Regulation Law |

crucial demand of the current scenario is for models to predict the nanomaterial exposure limits, with details of transport, transformation and toxicity assessment of each particular nanomaterial, as some nanoparticles may be beneficial for flora but can be hazardous to fauna. The crucial role of concentration also cannot be ignored, as nanoparticles can be beneficial at low concentration but may harm the environment at high concentrations. The potential benefits of nanotechnology for agriculture, food, fisheries and aquaculture need to be balanced against concerns for the soil, water, environment and the occupational health of workers. The development of nanomaterials with good dispersion, wettability, less toxicity, more photogenerative, easily biodegradable in soil and the environment, with well-defined toxicology, ease of fabrication and application in agriculture, would be an ideal approach towards their effective use in increasing agricultural production.

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# 10

# Global Market of Nanomaterials and Colloidal Formulations for Agriculture: An Overview

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## 10.1 Introduction

The increase in the growth rate of the global population, together with the need to produce greater amounts of high-quality food in smaller areas, has contributed to an expansion of the agricultural sector in recent years. New tools and farming policies have emerged, ranging from sustainable agriculture to mechanization, biotechnology and nanotechnology (Dethier, 2011; Unsworth *et al.*, 2016). In this chapter, we will focus on nanotechnology, whose activity is related to the creation, processing, characterization and application of materials at the nanoscale (Khan and Asmatulu, 2013).

The development of nanomaterials and colloidal formulations is very promising, with new investments in this area every day, reaching approximately US$ 1.08 billion per year (Sabourin and Ayande, 2015), which shows that this sector will have a significant impact on the world's economy in the next few years (Khan and Asmatulu, 2013). According to Sabourin and Ayande (2015), nanotechnological developments could transform the entire agri-food sector, with the potential to increase agricultural productivity, food security and industrial economic growth by at least 30%.

Many nanomaterials and colloidal formulations have been studied by agricultural science in recent years, as can be seen from the growing number of peer-reviewed journal articles and patents (Fig. 10.1). Recent reviews describe interesting applications in this area (Kah *et al.*, 2013; Kah and Hofmann, 2014; Sekhon, 2014; Campos *et al.*, 2014; Parisi *et al.*, 2015; Fraceto *et al.*, 2016; Grillo *et al.*, 2016; Mishra *et al.*, 2017a,b). These include precision farming (such as the use of nano- and biosensors able to determine the growth of plants and identify

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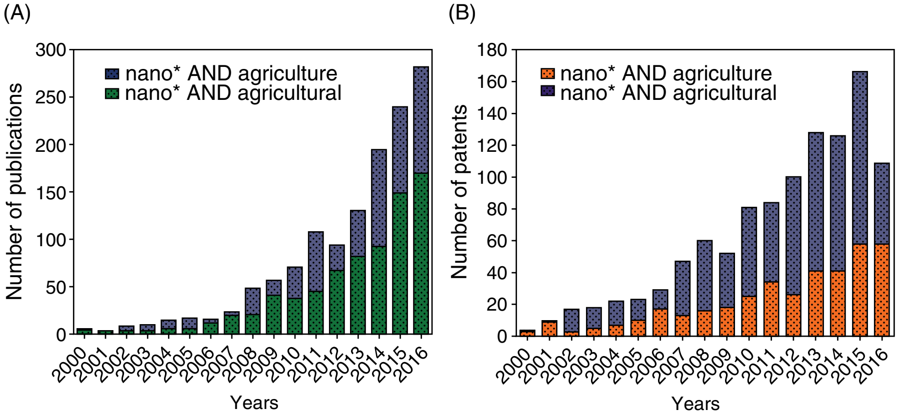

**Fig. 10.1.** Growth rates of peer-reviewed journal articles (A) and patents (B), obtained using the search terms 'nano* and agriculture' and 'nano* and agricultural' in the ISI Web of Knowledge database and the Global Patent Index (the tool used to search the EPO worldwide bibliographic database). The data were obtained by applying the search terms only to the title and abstract sections.

problems related to crops), nanodelivery systems (for example, colloidal nanoparticles developed to promote the controlled release of pesticides, fertilizers and DNA vectors), plant growth regulators, and soil management agents. However, the use of such products in the agricultural sector is still in its infancy, with improvements required in relation to scale-up and the need for valid methodologies to evaluate the potential toxic effects of these materials on the environment and human health. Hence, this area is receiving more attention from academic researchers worldwide, although there is already a range of products available on the market.

The aim of the present work is to provide an overview of the main nanomaterials and colloidal formulations available on the global market or undergoing patent processes, related to the agricultural sector. In this survey, an extensive search was conducted using scientific databases including the Web of Science, Science Direct and PubMed, as well as the web pages of different commercial agricultural companies. The Nanotechnology Products Database (NPD) was also used as an important source of information concerning the nanotechnology-based products already available on the market (Nanotechnology Products Database, 2017). The goal of this chapter is not to consider all products, but to give an overview of those products that are being produced and used in the agricultural sector.

## 10.2 Applications of Nanomaterials and Colloidal Formulations in Agricultural Science

### 10.2.1 Sustained release formulations

A major consequence of the excessive use of agrochemicals has been their uncontrolled release into the environment due to losses by leaching, volatilization and degradation processes (Miyamoto *et al.*, 2013). As a result, agrochemicals have contaminated aquatic resources and have accumulated in plants and animals, consequently affecting human health (Kim *et al.*, 2017). The development of new agrochemical formulations is intended to address such problems. Conventional formulations (CFs) usually consist of inert ingredients plus the active ingredient (the chemical responsible for control of the target pest). Inert ingredients (also called adjuvants) include solvents, surfactants, emulsifiers and water, which are added to the formulation in order to improve its stability and efficacy (Lamichhane *et al.*, 2016). On the other hand, sustained release formulations (SRFs) consist of an active ingredient (AI, an agrochemical or a bioactive agent) incorporated into a matrix that may be synthetic or natural. These systems are able to release the AI slowly and continuously into the environment, promoting extended control and concentrations of the AI that are more sustained, compared to the CF, as shown in Fig. 10.2. The great advantages of using these systems are: (i) minimization of impacts on the environment and non-target organisms; (ii) the need for smaller amounts of active agent; and (iii) improved efficiency (Nuruzzaman *et al.*, 2016).

Curiously, several formulations available on the market, despite containing nanometric compounds, are marketed using the terms ‘microencapsulation’, ‘microemulsion’ and ‘miniemulsion’. According to McClements (2012), the main reason for this confusion in terminology is a result of the historical development of colloid science, since the terms ‘microencapsulation’, ‘microemulsion’, ‘nanoencapsulation’ and ‘nanoemulsion’ became widespread before being clearly delimited or distinguished from each other. On the other hand, the term ‘nano’ has not been correctly employed in the case of commercial products, due to considerable public uncertainty concerning the fate of nanomaterials and their effects on human and environmental health (Kah *et al.*, 2013). Therefore, up to now there has been disagreement about the critical particle size that should be used to distinguish these formulations. However, it is legitimate to classify these products as new formulations in the field of nanotechnology, since their main characteristics are different to those of the bulk materials. In order to demonstrate these characteristics, several commercial nanoproducts are described below, together with their main applications and the benefits for agriculture.

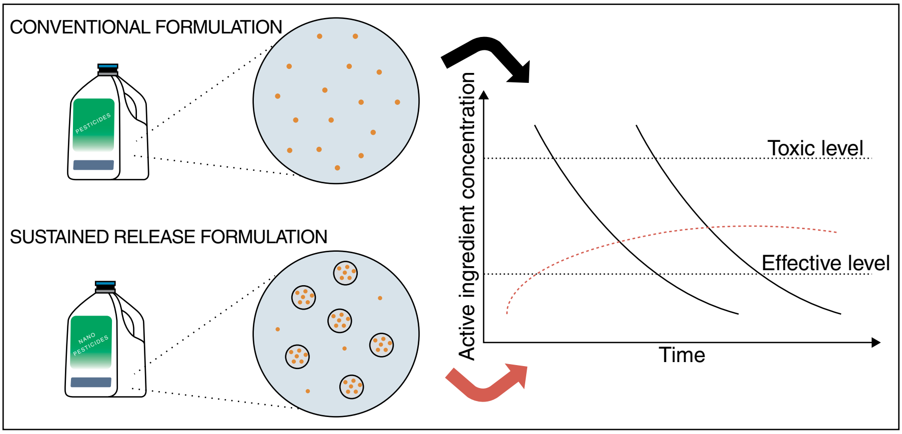

**Fig. 10.2.** Schematic illustration comparing conventional formulations (CFs) and sustained release formulations (SRFs) used in agricultural applications.

The multinational company Syngenta (Syngenta, 2017) offers some products described as microemulsions. Banner Maxx® II is a microemulsion of a systemic fungicide that provides control of a broad spectrum of diseases in turf, with sustained release and better root absorption resulting in effective control of fungi. The fungicide Subdue Maxx®, also described as a microemulsion, offers control of *Pythium* rust. According to the manufacturer, the formulation provides excellent compatibility and is stable in tank mixtures. The company has also developed a product for plant growth regulation, called Primo Maxx®, based on a microemulsion. According to the manufacturer, this product provides sustained release of the ingredients, improves absorption, and promotes a denser and healthier turf that is able to withstand a variety of stresses, including heat, drought, disease and traffic.

The German company Bayer (Bayer, 2017) markets the Thumper® insecticide, also described as a microemulsion, which provides reliable control of mites. Due to its properties, this low-odour formulation provides extended residual control. The manufacturer states that after application, the Thumper® insecticide penetrates the foliar tissue, where its translaminar activity and sustained release capacity provide control of mites that feed on the upper and lower surfaces of the leaf.

The Canadian company Vive Crop Protection (Vive Crop Protection, 2017) has patented a technology called the Allosperse™ Delivery System. According to the manufacturer, this system uses polymer ‘shuttles’ to transfer a crop protection chemical to the target location. These ‘shuttles’ provide control and assist mixing in application tanks, and also enhance interactions with the soil matrix. According to the company, Allosperse polymer transport can be adjusted to be compatible with various crops and/or with different active ingredients, hence creating new products. The first Vive Crop Protection products are: (i) the market-leading broad-spectrum fungicide AZteroid™, an azoxystrobin-based product designed to be compatible with liquid fertilizers; (ii) Bifender™ insecticide, which contains bifenthrin, an excellent broad-spectrum insecticide; and (iii) Fenstro™, a product that combines bifenthrin with azoxystrobin.

The German company Neufarm GmbH (Neufarm, 2017) has developed nanotechnology-based formulations across all its product lines. According to the company, efficient technology has contributed to reducing environmental problems, since it aims at the maximum possible effect using the minimum possible amount of active agent. The sustained release of the active ingredients promotes greater control and also provides a residual control effect, hence reducing the number of applications required. A total of ten insecticides, four herbicides and one fungicide are described in the product catalogue.

The American company Max Systems LLC (Max Systems, 2017) has developed the NanoRevolution™ 3.0 product. This is an adjuvant for herbicide formulations, which, when added to a conventional formulation, improves efficiency and performance. The company does not provide any specific size details, but notes that adding the NanoRevolution™ 3.0 adjuvant to a formula is like putting the herbicide ‘on steroids’. It can therefore be understood that the main advantage of use of the product is the sustained release of an agrochemical.

The Chinese company Nanjing High Technology Nano Material Co. Ltd. (HtNano, 2017) has also developed products that function as adjuvants in pesticide formulations. The products Pesticide deflocculant® and Pesticide synergist® are composed of nanoscale catalytic inorganic materials that increase pesticide efficacy, improve toxicity, promote dispersion, reduce the amount used, and prolong the effect. The company is also a manufacturer of Pesticide antibacterial agent®, which is composed of an inorganic nanocarrier loaded with a variety of metal ions with antibacterial properties. The properties of the product include resistance to water, acid and washing, as well as long-term antimicrobial action due to sustained release.

The Indian company Nano Green Sciences Inc. (Nano Green Sciences, 2017) is the manufacturer of the NanoGreen® product. This is based on nanoscale micelles that act as cleaning, emulsifying, degreasing and encapsulating agents. The company points out that NanoGreen® is a true 'green' product, since it consists of extracts of maize, grains, soybeans, potatoes, coconut and palm. Due to its high content of fatty acids, the product presents antibacterial, antimicrobial and fungicidal properties. The company also notes that the product has an FDA (Food and Drug Administration) certification.

In addition to the products already marketed by the companies mentioned above, the scientific community and industries have made considerable efforts, through the development of patents, in order to solve the problems caused by the excessive use and physicochemical properties of conventional formulations. As a result, many different release systems and encapsulated compounds have been proposed.

Different types of emulsions, such as nanoemulsions (US20020112131 20020329A1), miniemulsions (US201161565245P), and microemulsions (US201261640423P), have been proposed mainly in order to provide the solubilization of compounds that are insoluble in water. In addition, one or more compounds may be combined, resulting in a broad-spectrum action of formulations. Due to the release properties of these formulations, a smaller amount of active ingredient is used for pest control, resulting in a reduction in the number of treatments. Semiconductor materials, such as quantum dots, are already being studied as systems for the release of agrochemicals at the required locations. It has been observed that the use of quantum dots results in better absorption of the active ingredient in target organisms, due to their reduced size (Treseder and Whiteside, 2011).

Nanoparticles produced from a wide variety of materials, such as unspecified polymers (AU2014201945B2), silica (WO2010068275A1), clay (WO2015155585A1) and metal (WO2009153231A2), among others, have been proposed in order to reduce pesticide decomposition caused by sunlight (especially UV radiation), as well as to increase pesticidal activity and improve stability during storage and/or after application in the environment. Nanoencapsulation permits very slow release of the active agent and reduces environmental pollution since smaller quantities of pesticides are used. Table 10.1 lists several examples of commercial products and patents related to environmentally friendly and/or sustained release formulations designed for agricultural applications.

### 10.2.2 Plant growth and soil management

Fertilizers and growth regulators are very important for plant development. Conventionally, these products are used in large quantities in order to have the

**Table 10.1.** Examples of commercial products and patents related to environmentally friendly/sustained release formulations for agricultural use.

| Type | Name/patent no. | Company | Innovation |
|---|---|---|---|
| Commercial products | | | |
| Microemulsion | Plenum 160 ME® | Dow AgroSciences, 2017 | Systemic microemulsion to release herbicides in the environment. The technology allows the use of smaller amounts of herbicides. |
| Sulfur nanoparticles (unspecified size) | Nanosulf Drenching®<br>Nanosulf Foliar Spray® | Alert Biotech, 2017 | The product is based on sulfur nanoparticles. Sulfur is essential for healthy growth, with deficiency causing leaves to turn yellow or light green in colour. The product dissolves completely in water and acts as fertilizer, fungicide and insecticide. |
| Unspecified nano content | Nano-5® | Uno Fortune Inc., 2017 | Nano-5 is an environmentally friendly product applicable for controlling pests and diseases in all plants in any environment. It contains the ingredient G-protein. Due to its nanometric size, it can penetrate the cells of plants and pests, providing greater effectiveness. |
| Unspecified nano content | AlgaeStop® | Dennerle, 2017 | DennerleAlgaeStop is made from renewable raw materials (humic peat, oak bark and alder fruit). This system reduces and regulates pH, filters algae-promoting UV light, and prevents new algal growth. |
| Inorganic nanocarrier (unspecified) | Antibacterial pesticide agent | HtNano, 2017 | This product is composed of an inorganic nanocarrier loaded with a variety of metal ions possessing antibacterial properties. The product presents broad-spectrum action, with high ability to kill bacteria and viruses. It is acid resistant, wash resistant, light resistant, and shows long-term antimicrobial activity. |
| Silver (Ag) nanoparticles (size around 20 nm) | Nanosept®<br>Nanosept® Aqua<br>Nanosept® Aqua Super | Nanosept, 2017 | These products are a new generation of nanotechnology-based disinfectants. They contain hydrogen peroxide, silver nanoparticles, non-ionic surfactant and distilled water. They present a broad spectrum of bactericidal action, with both immediate and long-term effects. |
| Copper (Cu) and Silver (Ag) nanoparticles (unspecified size) | SomGuard®silcop | AgriLife Company, 2017 | SomGuard®silcop is prepared by a unique process in which nano ions of silver and copper are mixed, bonded, and interlocked to give anoligodynamic, stable and long-lasting effect. It is highly toxic to microorganisms. |

*Continued*

Table 10.1. Continued.

| Type | Name/patent no. | Company | Innovation |
|---|---|---|---|
| Patents | | | |
| Polymeric nanoparticles | AU2014201945B2 | – | Increased aqueous solubility and sustained release of active ingredients used in agriculture. |
| Silica nanoformulation | WO2010068275A1 | – | Nanoenvironment to host antibacterial and antifungal agents, with sustained release kinetics. |
| Nanoporouscarbon | CN102210301B | – | Nanoporous activated carbon-supported agricultural antibiotics in order to improve antibiotic stability, avoid premature degradation and promote sustained release. |
| Hollow nanoparticles | US20150033418A1 | – | This invention provides different kinds of nanoparticles in order to treat plants with agrochemicals. The hollow nanoparticles have an encapsulating coating or shell comprising a polymer, together with a carrier comprising inert or biodegradable woven or non-woven fibres, to which the nanoparticles are bound or in which the nanoparticles are suspended. The nanoparticles contain an active agrochemical agent. |
| Nanofibres and mesofibres | US20120270942A1 | – | Product designed to direct the release of agricultural chemicals towards specific sites, improving effectiveness and reducing losses to the environment. |
| Nanoemulsion | US6638994B2 | – | Aqueous suspension of nanoparticles consisting of small particles with a high concentration of the active ingredient, providing sustained release. |
| Quantum dots (2–10 nm) | WO2011031487A2 | – | A new composite nanoparticle (quantum dots) for delivery of agrochemicals (fungicides, herbicides, etc.) to desired locations. Due to the reduced size, the formulation allows better absorption of active ingredients in the target organisms and/or cells (e.g. fungal cells). |
| $SiO_2$ nanoparticles | CN1695446A | – | $SiO_2$ nanoparticles containing a pesticide active ingredient, with predominantly radially arranged pore walls. The technology offers good release properties, without affecting the active agent. |

| | | | |
|---|---|---|---|
| Leucite – Potassium aluminum silicate nanoparticles | US8911526B2 | – | Slow release of nitrogenous fertilizers in order to reduce nutrient losses due to leaching, hence decreasing groundwater contamination. |
| Nanofabrication of phosphorus on kaolin mineral receptacles | WO2015155585A1 | – | New nanophosphorus products in plant-available forms. Phosphate ions are intercalated in kaolin mineral clay, which acts as a receptacle. The invention provides sustained release and enhanced uptake of nutrient phosphorus. |
| Nanocomposite for slow pesticide release | CN101773112B | – | In this invention, a herbicide is encapsulated in hydroxyapatite nanoparticles coated with calcium alginate hydrogel. This technology provides very slow release of pesticides and decreases environmental pollution, since smaller quantities of pesticides are used. |
| Nanosilicon carrier (1–100 nm) | US20130225412A1 | – | Nanosilicon carrier composed of diatom frustules that can be loaded with pesticides for crop protection. |
| Emulsifiable concentrate | WO2006002984 A1 | – | Stable concentrate formulation for organic pesticides that present low solubility in water. The technology provides protection from premature degradation. |
| Nanosized self-assembled structure | WO2011138701 A1 | – | Aqueous-based formulation with low amounts of organic solvents, which presents a high pesticide loading and is stable during storage or after dilution with water. |
| Metal oxide nanoparticles | WO2009153231A2 | – | The formulation reduces the decomposition of pesticides due to sunlight, especially UV light. Stability is increased during storage and/or after application in the environment, and the pesticidal activity is increased. |
| Miniemulsion (<800 nm) | WO2013082016A1 | – | Stable miniemulsions that include two or more agriculturally active ingredients, thus creating a broad-spectrum activity formulation, reducing the number of times that a particular field must be treated. |
| Polymeric nanoparticles (1–500 nm) | WO2013093578A1 | – | Strobilurin formulations that can be easily mixed with fungicides that have other modes of action, in order to minimize the spread of strobilurin-resistant strains. |

*Continued*

**Table 10.1.** Continued.

| Type | Name/patent no. | Company | Innovation |
|---|---|---|---|
| Oil-in-water emulsion (<800 nm) | WO2013165793A1 | – | Emulsion composed of oily globules that are provided with a lamellar liquid crystal coating and are dispersed in an aqueous phase; each oily globule contains at least one agrochemical. |
| Oil-in-water emulsion (<800 nm) | WO2012097149A1 | – | Oil-in-water emulsion containing oily globules that include at least one agrochemical agent and are coated with a polymeric adsorption layer. |
| Quaternary ammonium nanomaterial | US20140308330A1 | – | Quaternary ammonium nanomaterials as an alternative to Cu-based fungicides for managing or controlling citrus canker. This technology has the ability to attenuate quaternary ammonium phytotoxicity, while maintaining superior biocidal properties. |
| Chemical microemulsion | US20050220834A1 | – | The microemulsion contains one agricultural active ingredient and one or more of different natural high molecular weight materials (fulvic acid, humic acid, chitosan and dextran). This technique provides sustained release and reduces the dosage and application frequency of agricultural chemicals. |
| Water-dispersible agrochemical formulations (180–400 nm) | WO2010051607A1 | – | Solubilization medium for biocidal active agents, providing stable concentrations and improving water-solubility. The particle size distribution is smaller than 400 nm. The reduction of particle size enhances the effect of the active ingredient, decreases the application dosage, and improves the agronomic effectiveness. |
| Calcium alginate nanoparticles | CN102823585B | – | Nanoparticles for loading with water-soluble pesticides in order to control the rate of pesticide release, extend the duration of action, decrease the quantity of pesticide required, and reduce environmental pollution. |
| Silicon carbide nanoparticles | CN104310402B | - | Production of carbide nanoparticles from agricultural waste biomass. The invention aims to take advantage of the low cost of agricultural waste biomass, using simple technology for large-scale production of small silicon carbide nanoparticles with uniform size distribution. |

desired effect in cultivations. Intensive use is frequently necessary due to the numerous processes, such as leaching, degradation (photolysis, hydrolysis) and decomposition, which make these substances less available to plants (Gellings, 2009). Hence, it is necessary to take steps to minimize losses and increase crop productivity, and nanotechnology has emerged as an innovative and effective tool for this purpose (Nair, 2016).

According to Mastronardi *et al.* (2015), the application of nanotechnology to fertilizers and growth regulators can be divided into three categories: (i) nanoscale fertilizer inputs, in which various methods are employed to reduce fertilizers or supplements to the nanoscale, with release typically in the form of nanoparticles; (ii) nanoscale additives, where nanomaterials with different properties (such as water retention or the control of pathogens in plants or soil) are added to the bulk product; (iii) nanoscale coatings or host materials for fertilizers, where nanomaterials (including nano-thin films, nanoporous materials, and nanoparticles) are used for the sustained release of nutrients. Some products and patents combine these categories.

The main advantage of nanoscale fertilizer use is related to improved nutrient absorption and consequently better efficiency, with smaller amounts required. Another advantage is related to a higher dissolution rate of these compounds in water/soil solution, contributing to a faster release of soluble ions (Mukhopadhyay and Kaur, 2016). Nonetheless, despite these benefits, nanotechnology is still not widely used for agricultural purposes, including fertilization.

Some products currently available on the market cite the use of nanotechnology in their formulations. However, most of these products do not provide specifications concerning the nanoscale content (such as size and synthesis route, among others), and many times the terminology is used generically.

The Nanotechnology Products Database (NPD) lists a number of nanotechnology products that are already being marketed. In the area of fertilizers, there are 77 listed products, manufactured by 16 companies from 9 different countries (Nanotechnology Products Database, 2017). In the case of products intended for plant growth regulation, there are 73 products listed, manufactured by 10 companies from 8 countries.

The UK company Plant Vitality Ltd (Plant Vitality, 2017), in collaboration with experts and scientists from UK universities, has used nanotechnology to develop products for different cultures (Soil: grow®; Soil: flower®; Coco: grow®; and Humic 101®, among others). The manufacturing process is based on a reactor that can produce nanoscale particles suitable for improving absorption in plants.

The Indian company Kanak Biotech (Kanak Biotech, 2017), which produces nanoscale fertilizers, is described as one of the pioneers in the manufacture of such formulations. An eco-friendly organic synthesis technique is described for the conversion of elements to the nanoscale. Biogenic routes are used for the synthesis of these nanoproducts intended to replace existing chemicals.

The American company Agro Nanotechnology Corporation (Agro Nanotechnology Corporation, 2017) has developed the product Nano-Gro™, which contains different quantities of micronutrients (iron, cobalt, manganese and magnesium) at nanomolar concentrations. These elements are contained in sugar pellets with diameters smaller than ⅛". On the company website, the product is described as a revolutionary cultivation enhancer, acting to increase crop yields, improve product quality, and increase the immunity of the plant to diseases and extreme weather conditions.

The German company Zeovita GmbH (Zeovita, 2017) manufactures the product Lithovit, which is sold for various different applications. The product components (limestone, boron oxide, amino acids, urea and others) are submitted to a reduction process known as Tribodynamic Activation, producing particles with sizes between 200 nm and 10 μm. The product provides an increase in the $CO_2$ concentration available to the plant, hence increasing yield, improving the quality and storage properties of the crop, reducing water requirements, and intensifying growth and green pigmentation.

The Indian company Richfield Fertilisers Pvt. Ltd (Richfield Fertilisers Ltd, 2017) has also used the Tribodynamic Activation process to produce fertilizers (Rich Vitaflora and Rich Herba Green) for different crops. Due to the nanoscale size of the micronutrients, these products cause an increase of the foliage of the plant, increasing the formation of flowers and fruits. They stimulate tolerance to stress in plants and improve the shelf life of the product. The formulations can be applied to both soil and the plant (by foliar application).

The Chinese company Taiyuan Mapon Humic Acid Development Co. Ltd (Mapon Humic, 2017) manufactures organic products composed of humic acid extracted from leonardite mineraloid. The products (HumiMix® and HumiTE®) contain micronutrients as well as nanoscale organic components. According to the manufacturer, the product stimulates plant enzymatic activity, accelerates plant metabolism, regulates stomatal openings, and enhances crop drought resistance. In addition, it reduces nutrient losses, increasing crop yield and quality.

Considering the listing of patents, nanotechnology has been used in formulations capable of improving the development of plants by increasing nutrient uptake by the cells and decreasing nutrient loss. The encapsulation of different macro- or micronutrients in nanoparticulate systems can increase plant development, due to decreased degradation and leaching losses, as well as increased nutrient uptake by plants (CN102217480A, CN101096329A, CN103081928B). In addition, many patents have shown that certain types of nanomaterials, by themselves, are capable of triggering better development of plants. Examples are silver nanoparticles (WO2014062079A1), carbon nanotubes (US20150007496A1), nanochitin whiskers (CN105746520A), and nanocrystalline cellulose (WO2015145442A2). Table 10.2 shows more examples of commercial products and patents related to plant growth and soil management.

### 10.2.3 Nanosensors/nanobiosensors

Nanosensors are compact analytical devices in which at least one of the sensing dimensions is no greater than 100 nm (Turner, 2000). These devices allow the effective detection of a wide variety of agrochemicals, including fertilizers and pesticides. They can also be used for sensing pathogens, moisture, soil pH, lack of nutrients, temperature, and plant stress due to drought (Baruah and Dutta, 2009; Khot *et al.*, 2012; Rai *et al.*, 2012). The first report concerning a biosensor

**Table 10.2.** Examples of commercial products and patents related to plant growth and soil management.

| Type | Name/patent no. | Company | Innovation |
|---|---|---|---|
| Commercial products | | | |
| Microemulsion | PrimoMaxx® | Syngenta, 2017 | Plant growth regulator that slows the production of gibberellic acid and stimulates lateral and below-ground growth. The formulation technology ensures complete mixing with water. |
| Microemulsion | Clipless® | Cheminova, 2017 | Turf growth regulator that inhibits cell elongation by blocking the production of gibberellic acid and promotes lateral and root growth. |
| Nanoscale sulfur (S) (<100 nm particle size) | Nanosulf Foliar®Spray | Alert Biotech, 2017 | Nanosulf contains elemental sulfur on nanoparticles, which dissolves completely in water. Nanosulf works as a fertilizer and an insecticide. |
| Nanonutrients (unspecified size) | Nanomol (F) Micronutrient<br>Nano Zinc (Chelated)<br>NanoBor 20%<br>Nano Ferrous<br>Nanomag | Alert Biotech, 2017 | These nanotechnology products provide micronutrients at the nanoscale. Their main features are pH control, high dispersion in water, and better absorption by the plant. |
| Nanonutrients (unspecified size) | GreenEarth-NanoPlant Concentrated Organic Liquid Fertilizer | GreenEarth NanoPlant, 2017 | New generation liquid organic fertilizer produced by the dispersion of biological humus, with simultaneous water activation. The nanonutrients in the product provide optimal conditions for the growth and development of plants, improving the ecology and fertility of soil. |
| Nanonutrients (unspecified size) | Nano Potassium Chelate Fertilizer<br>Nano Calcium Chelate Fertilizer<br>Nano Iron Chelate Fertilizer<br>Nano Zinc Chelate Fertilizer | AFME Trading Group, 2017 | Chelated fertilizers provide one or more nutrient metal elements to plants in cases where deficiencies result in yellowing of leaves, retarded growth and general low crop quality. According to the manufacturer, the reduced size scale means that use of these types of fertilizers can increase plant growth, ensure proper development, and provide efficient crop production. |
| Nanonutrients (unspecified size) | Agriklik®<br>Floriklik®<br>Hortiklik®<br>Teaklik® | Nano Solutions, 2017 | These products feature essential nanoscale micronutrients for plants and soil microorganisms, providing faster quantitative absorption by the plant. The formulations are 'biologically activated products from plant extracts' and are completely natural and organic, containing 'no chemicals'. |

*Continued*

**Table 10.2.** Continued.

| Type | Name/patent no. | Company | Innovation |
|---|---|---|---|
| Nanonutrients (size 150–300 nm) | Nano Fertilizer | Lazuriton Nano Biotechnology, 2017 | Nanoscale fertilizer molecules are rapidly absorbed by plants, increasing crop yield and quality. According to the manufacturer, the formulation can also shorten the production period. |
| Nanonutrients (size 5–100 nm) | Nano Nutrients for Crops | NanoLandBaltic, 2017 | According to the manufacturer, the product contains nanonutrients at particle sizes of 5–1000 nm. Due to the large surface area, when sprayed on the leaves, the product provides all the nutrients for chlorophyll directly. It improves the efficiency of photosynthesis, enhances plant growth, and stimulates high yields. |
| Patents | | | |
| Nanoparticulate foliar fertilizer | WO2012116417A1 | – | Nanocrystalline compounds containing essential nutrients. A high contact surface area/total surface area ratio provides maximal leaf surface contact, limited mobility and improved solubility. |
| Antimicrobial beads | WO2013162163A1 | – | This invention increases plant growth and yield by applying antimicrobial beads consisting of silica nanotubes containing metal nanoparticles and zeolite powder. Unlike conventional treatments, these antimicrobial beads are applied to the soil. |
| Silver nanoparticles | WO2014062079A1 | – | Stimulation of the growth and development of plants by treatment of the seeds or growing plants with a solution containing silver nanoparticles and particles consisting of polyhexamethylene biguanide or polyhexamethylene guanidine, or at least one salt of polyhexamethylene biguanide and polyhexamethylene guanidine. |
| Inorganic films | CN1358791A | – | Resin-based films to improve infrared barriers, enhancing the thermal insulation properties of agricultural films and enabling increases in crop production. |
| Thin films | CN101654532A | – | Polyethylene agricultural films containing nanopowders of $TiO_2$ or $SiO_2$, or a combination thereof, which are more resistant to degradation, more stable towards light, absorb ultraviolet light more easily, and are more environmental friendly when compared with PVC films. |
| Single- and multi-walled carbon nanotubes | US20150007496A1 | – | Carbon nanotubes are employed as biostimulants, nanominerals or nanofertilizers, which are incorporated into soil, seeds, plants, water, or any media containing plants and microorganisms, stimulating RNA, DNA, and anion exchange capacity and/or cation exchange capacity. |

| | | | |
|---|---|---|---|
| Nano-bio-organic composite liquid fertilizer | CN1451636A | – | Nanofertilizer produced from food industry wastewater, offering a broad spectrum of nutrients, easy assimilation, and a strong influence on increasing plant yields. |
| Chitosan nanoparticles | CN103081928B | – | Biological pesticide composed of chitosan nanoparticles containing biological materials (dsRNA) in order to control pine wilt. The technology provides efficient control of pine wilt and also improves the *in vitro* stability of dsRNA. |
| Nano-chitin whiskers (100–150 nm) | CN105746520A | – | Aqueous nano-chitin suspensions improve tobacco seed germination and increase the height, stem diameter, number of leaves, and maximum leaf area of the plants. |
| Carbon nanotubes (powder) | CN102217480A | – | This invention increases the potassium content in tobacco leaves by mixing carbon nanotubes with commonly used fertilizers for cured tobaccos, including compound fertilizers, potassium sulfate and nitrate fertilizers. The size and high surface energy of the carbon nanotubes enables binding with NPK nutrient ions to form a polymer, improving the efficiency of fertilizer use and preventing losses. |
| Nanocrystalline cellulose | WO2015145442A2 | – | Nanocrystalline cellulose is a fibrous nanomaterial able to absorb and retain aqueous media as well as organic or inorganic agents, in liquid, solid or solution form. This material, employed as a growth medium in combination with soil, can reduce the amount of irrigation required, due to its water retention capacity. It can incorporate fertilizers and provide sustained release. |
| Carbon nanotubes | US20150296793A1 | – | Utilization of carbon nanotubes to treat seeds in order to improve the probability and rate of seed germination, increase vegetative biomass, and increase water uptake in seeds. |
| Silver nanoparticles | CN103302307A | – | Application of silver nanoparticles to increase germination of cucumber plants. |
| Nano super fertilizer | CN101096329A | – | Nano super fertilizer contains large amounts of nitrogen, phosphorus, potassium, magnesium, calcium and silicon. It also contains molybdenum, boron, zinc, iron and enzymes. This technology provides the sustained release of fertilizers, overcoming concentration problems and environmental pollution. |

*Continued*

**Table 10.2.** Continued.

| Type | Name/patent no. | Company | Innovation |
|---|---|---|---|
| Nanocomposite (resin/inorganic nanoparticles) | CN101712785A | – | This invention is a new highly water-absorbent resin/inorganic nanocomposite. It shows excellent absorption and thermal properties, making it a good candidate to replace conventional super-absorbent resin employed for seed protection. |
| Silver and gold nanoparticles | US20120108425A1 | – | Silver and gold nanoparticles synthesized from microbes provide effective biocontrol/biofertilizer agents in the field. The selected microbes were indigenous organisms isolated from tea fields, which can control various diseases, both individually and in combination with other microbes used as biofertilizers. |
| Hydroxyapatite phosphate nanoparticles | US8361185B2 | – | Plant fertilizer nanocomposite comprising a nitrogen-containing macronutrient adsorbed on the surface of hydroxyapatite phosphate. The resulting complex is intercalated within the inter-layers of nanoclay by adsorption onto surface active hydroxyl groups. |
| Nanofertilizer | CN102701844A | – | Fertilizer composed of nanometric selenium (Nano-Se) for application in soilless cultivations. |
| Carbon nanomaterials | US20110174032A1 | – | Complex fertilizer containing carbon selected from ammonium bicarbonate, urea, or a combination thereof, which could reduce greenhouse gas emissions. |
| Hydroxyapatite phosphate nanoparticles (30 nm) | WO2014087202A1 | – | A nitrogen-containing macronutrient is adsorbed on hydroxyapatite phosphate nanoparticles and used as fertilizer. Slow release improves the effectiveness of the fertilizer, providing sufficient quantities of macronutrients for higher crop yields. |
| Nanopowders | US20060079410A1 | – | Nanopowders doped with molybdenum present high surface area and small particle size, enabling them to permeate through and/or reside in the pores/internal surfaces and the external surface topography of seeds or soil. |
| Nanobiofertilizer | CN101113120A | – | Control of urea degradation in order to accelerate the decomposition of organic molecules and enhance the resistance of plants. |

was published in 1962, when Clark and Lyons developed a sensor based on the specific catalytic interaction of the glucose oxidase enzyme with glucose (Clark and Lyons, 1962).

With the advancement of science and technology, many studies have combined different approaches (nanoscience, electronics, computing and biology) in order to develop highly sensitive sensors that offer greater resolution and reliability (Baruah and Dutta, 2009; Rai *et al.*, 2012). In the agricultural area, nanosensors can help farmers to utilize inputs more efficiently by indicating the nutrient or water status of a crop. They can be used in the control of plant growth and the efficient use of natural resources, as biomarkers, for soil analysis, and as fast diagnostic tools for the detection of bacterial, viral and fungal plant pathogens (Yao *et al.*, 2009; Boonham *et al.*, 2008; Antonacci *et al.*, 2016).

There are many different types of nanosensor that can be grouped roughly into three main categories: (i) optical nanosensors; (ii) electromagnetic nanosensors; and (iii) mechanical and/or vibrational nanosensors (Lim and Ramakrishna, 2014). According to Rai *et al.* (2012), the main nanosensors employed in agriculture are as follows: (i) mechanical nanobiosensors; (ii) optical nanobiosensors; (iii) nanowire biosensors; (iv) ion channel switch biosensors; (v) electronic nanobiosensors; (vi) viral nanobiosensors; (vii) nanobiosensor probes encapsulated by biologically localized embedding; and (viii) nanoshell biosensors.

Agriculture is one of the main activities responsible for the release of contaminants to the environment. At the same time, one of the main challenges for the monitoring of contaminants in the food chain is the lack of fast and simple monitoring systems. Hence, it is necessary to develop new detection tools. The German company ttz Bremerhaven (ttz Bremerhaven, 2017) has developed sensitive nanosensors (NanoDetect® and Toxsens®) based on immunoassays in order to monitor products in the food chain. According to the company, the nanobiosensors can provide efficiencies in terms of cost and time, as well as simultaneous evidence of diverse substances.

The North American company C2Sense (C2Sense, 2017) has developed a nanosensor also called C2Sense®. The company suggests that around one-third of the world's food supply is wasted, and that this food waste has substantial environmental and social costs. The nanosensor can be used in the various stages of the food chain (from farm to table), monitoring volatile substances associated with meat/poultry/fish freshness and the ripeness of fruit. This could help to improve food quality, reduce waste, and allow producers, storage facilities, distributors, retailers and consumers to make dynamic decisions.

RipeSense (RipeSense, 2017), a New Zealand company, has marketed the RipeSense® nanosensor. According to the manufacturer, this product is the world's first intelligent sensor label that changes colour to indicate fruit ripeness. The company points out that many types of fruit do not change colour as they mature, and that visible signs of ripening may vary among different varieties of a particular fruit. Not knowing whether or when the fruit has reached its preferred state of maturity is frustrating for consumers and constitutes a barrier to purchase. The RipeSense® sensor works by reacting to the aromas released by the fruit as it matures. The sensor is initially red, and progresses to orange and finally to yellow. RipeSense suggests that the device makes the selection process simple and precise, in addition to providing hygienic safety since it avoids the fruit being handled or squeezed by other potential consumers.

Precision agriculture is dependent on real-time collection of data concerning climate, soil and air quality, and crop maturity, in order to perform predictive analyses and make better-informed decisions. To this end, the South African company PST Sensors (PST Sensor, 2017) has developed the product Heater-Sensor Stage, a nanosensor intended for temperature sensing. This type of device could be integrated into precision farming systems and used for soil monitoring.

In precision agriculture, nanosensors are an important source of data concerning the nutritional status of the plants, soil parameters, management conditions, yield mapping, diseases and pest infestations. Sensors are being developed to detect pesticide residues (WO2016145300A1), to improve seed germination (US20110000411A1), and to detect the nutritional state of the plant (US20120282594A1).

It is known that most fungal pathogens, when they attack plants, release volatile substance signatures. In the same way, plants produce phytochemical defences characterized by chemical signatures. The patent WO2016168585A1 proposes the development of an electrochemical sensor to detect both target stress-induced plant volatile compounds and/or target pathogen-emitted volatile compounds. The sensor is composed of an electrode substrate and a bionanocomposite detection element. Results have shown that this electrochemical biosensor provides high sensitivity and a low limit of detection, enabling short sample-collection times.

Table 10.3 lists some of the products and patents related to precision farming.

## 10.3 Concluding Remarks and Future Perspectives

Developments in nanotechnology are providing new tools to support the growth of modern agriculture, with many promising applications. Due to the wide range of potential uses, the global agricultural nanotechnology market is expected to grow significantly in the next decades (Ozmen, 2016), associated with a series of new technological developments designed to provide new opportunities in agricultural production and food marketing. As a recent example, several techniques have been developed for the sustained release of pesticides, which have shown lower toxicity in cell cultures (Grillo *et al.*, 2012; Clemente *et al.*, 2013; Grillo *et al.*, 2014; Campos *et al.*, 2015; Maruyama *et al.*, 2016) and enhanced activity of the active agent in plants (de Oliveira *et al.*, 2015), compared to conventional formulations.

However, regulatory protocols related to nanomaterials and colloidal formulations are still not well defined, leading to inaccurate information on the labels of products, which can create a degree of caution in the use of this technology. Furthermore, the fate and behaviour of nanomaterials in the environment (including soils and the hydrosphere) remain uncertain, and there are many doubts concerning possible toxic effects and the impact on human health (Mukhopadhyay and Kaur, 2016). These issues reveal the need to develop new studies and protocols concerning the use of nanomaterials and colloidal formulations

**Table 10.3.** Examples of commercial products and patents related to precision farming.

| Type | Name/patent no. | Company | Innovation |
|---|---|---|---|
| Commercial products | | | |
| Nanosensor | AquaDx® | MyDx, Inc., 2017 | Determination of residual pesticides in crops, soil and water to support sustainable farming. According to the manufacturer, the product enables rapid and accurate detection of a wide range of heavy metals as well as pesticides. |
| Integrated circuit (based on a nanosensor) | Ultralow Power Light Recognition System for Smart Agriculture | Analog Devices, Inc., 2017 | According to the manufacturer, the integrated circuit system contains nanosensors capable of detecting different wavelengths, especially those that identify photosynthetically active plants. The measurement of photosynthetic activity allows users to optimize the efficiency of their lighting systems. |
| Nanosensor | Wireless NanoSensor Networks Monitor | Linear Technology Corporation, 2017 | Sensors are used to monitor soil moisture, water stress and electrical conductivity, and to provide information to growers on cropping conditions such as soil, climate and crop status. |
| Patents | | | |
| Nanochip | US20110000411A1 | – | Porous nanochip to accommodate nanoparticles of biologically active substances for the treatment of seeds of agricultural plants in order to improve seed germination. |
| Electrochemiluminescence sensor | CN101995402A | – | The technology enables the rapid, highly sensitive and specific screening of trace amounts of pesticides in agricultural products. |
| Chemical sensor | WO2016145300A1 | – | The invention provides a nanomaterial-based chemical sensor chip to detect chemicals in gas, vapour, liquid and aerosol phases. The sensor is also able to determine the chemical concentration. |
| Electrochemical sensor | WO2016168585A1 | – | The technology provides an electrochemical sensor that allows the detection of target stress-induced plant volatile compounds and/or target pathogen-emitted volatile compounds in order to monitor the condition of the plant. |

*Continued*

**Table 10.3.** Continued.

| Type | Name/patent no. | Company | Innovation |
|---|---|---|---|
| Molecular sensor | US20120282594A1 | – | Sensor based on single-walled carbon nanotubes for the detection of gaseous molecules such as NO and $NO_2$, which play very important roles in the chemistry of the atmosphere. |
| Organophosphorus pesticide molecular probe | CN105646349A | – | A molecular probe with surface modified by a rare earth nanomaterial and Tween 80 (surfactant) can determine the concentrations of organophosphorus pesticides. |
| Nanosensor | US20100330686A1 | – | A tool to detect and quantify carbohydrates in sugar-containing agricultural products under laboratory conditions or in a processing plant. The nanosensor comprises nanoparticles conjugated to one or more boronic acid molecules and one or more pH-sensitive materials. |
| Biosensor | CN101893596A | – | Highly sensitive silicon nanowire biosensor for detection of organophosphorus and carbamate pesticides. |

in agriculture, in order to clarify information about the benefits and, at the same time, the potential hazards of these systems.

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## Conflict of Interest Statement

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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# 11

# The Responsible Development of Nanoproducts – Lessons from the Past

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## 11.1 Highlights of Nanotechnology Development across the Globe

Ever since Richard Feynman talked about molecular building with atomic precision in 1959, there has been no setback for nanotechnology. Soon after that, in 1974, Professor Norio Taniguchi coined the term 'nanotechnology'. Although evidence suggests that nano-based techniques have been used unwittingly for centuries (Walter *et al.*, 2006; Wittstock, 2012; Schaming and Remita, 2015), the first use of a nanomaterial in an industrial application was titanium dioxide, which was first accepted for cosmetic sunscreen in 1988. Since then, many research institutes have started working towards the development of nanotech products. In the 1990s Japan, China and the US were the pioneers in initiating regulations in nanotech research. Following them, several countries created government agencies to fund and regulate the development and application of nanotechnology. By the end of 1991, Dr Sumio Ijiima had invented carbon nanotubes, which became the base materials for many nanotech products (Iijima, 1991). In 1999, safety guidelines for nanotech were released for the first time by the Foresight institute in the US, the basic objective of which was to provide guidelines for the responsible development of nanotechnology. This guideline has been updated six times since then; the current version was last updated in April 2006. In 2000, the UK government published a White paper entitled 'Excellence and Opportunity: A Science and Innovation Policy for the 21st Century' (DTI, 2000). In this White paper, the UK government committed to invest £250 million for the development of new areas of science, including nanotechnology, which was defined as a technology with the potential to lead economic growth in the 21st century. In the same

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year, the then US president Bill Clinton created the US National Nanotechnology Initiative (NNI). The basic aim of NNI was to initiate, develop and promote world class R&D programmes for the development of nanotechnology (NNI, n.d.). Many other countries started investing in the development of nanotechnology by 2000.

All the technologies come with risks and uncertainties and during the rapid development of a budding technology, risks are often ignored. To assess the risks that could potentially be posed by nanotechnology, major initiatives were taken in 2002–3. In 2002, the Centre for Responsible Nanotechnology (CRN) was founded in the US. CRN was founded to make people aware of both benefits and risks of nanotechnology, and to thoroughly study its effects on societies, economies and environment, in order to plan for the responsible development of nanotechnology. The first paper, named 'Safe Utilization of Advanced Nanotechnology' was published by CRN in 2003. In the same year, ETC, an Ottawa-based group, published a report, *From Genome to Atom: The Big Down*, in which the group reported their concerns about the wobbly regulation of intellectual property rights and the power of corporates to control the researches, the possibilities of biological warfare using this technology and the rapid and uncontrolled development of synthetic biology; they argued to ban any further research temporarily before strict regulatory policies were implemented (ETC, 2003). Later in 2003, the Joint Centre for Bioethics in Toronto proposed to increase investment in studying the economic, legal, social and regulatory aspects of nanotechniques. These were the highlights of the initial developments of nanotechnological research over the past few years. A lot of developments have been made since then and the regulatory bodies change the policy from time to time to keep the research under control in their respective countries. A lot needs to be done in developing countries like India. This chapter focuses on the need for responsible development of nanotechnology and how this can be achieved.

## 11.2 The Nanotechnology Initiatives in India – NSTI and Nano Mission

Since the launch of the American National Nanotechnology Initiative (NNI) in 2000, nanotechnology has been publicized as a technology that could bring the 'next industrial revolution' (Roco, 2007). Subsequently, in 2001, the Government of India (GOI) launched the Nano Science and Technology Initiative (NSTI), as a part of the tenth five-year plan of India, with a budget of 60 million INR (US$936,000) (MST, n.d.). Since then, the GOI has consistently prioritized investment in nanotechnology. Succeeding the NSTI, Nano Mission was launched in 2007, with an increased budget outlay of 10 billion INR (US$156 million) for the next five years (Nano Mission, n.d.). In their annual report of 2008–9, the planning commission of India advocated that investment in nanotechnology could enhance agricultural productivity (Planning Commission, n.d.). In the 12th five-year plan (2012–17), Nano Mission has been continued with an allocation of a further 6.5 billion INR (US$101 million) to Phase II of the mission (PIB, 2014). The Nano Mission has clear mandates to promote research and development in nanoscience, but industrial participation is not apparent yet.

Currently, there are 19 centres of excellence established all across India supported by Nano Mission. In addition to providing financial aid for the establishment and running of the nanotechnology centres of excellence, the Mission also supports the launch of postgraduate teaching programmes in this area of study (Mishra *et al.*, 2014). International collaborations are among the core objectives of Nano Mission, to ease the exchange of breakthrough scientific knowledge generated by nanotechnologists in India and abroad. Although industrial participation in the development of this technology in India is not yet apparent, the number of nanotechnology research projects sanctioned by the GOI since 2002 are indeed the telltale signs that nanotechnology is indisputably gaining momentum in India (see Fig. 11.1). But, in terms of regulation and risk assessment, it seems nanotechnology is still at a nascent stage in India. The risks and potential negative impacts of nanoparticles have not been acknowledged much in scientific and technical literature. Taking the first step towards a systematic regulation, Nano Mission constituted a Nano-Regulatory Task Force in 2010.

An effective and comprehensive risk assessment is fundamental to the regulation of this revolutionary technology. This chapter highlights and reviews the crucial traits of nanotechnology, including the concerns and potential risks posed by nanotechnology. In most instances, we aim to provide possible ways to minimize the risks or at least call for appropriate measures to be taken in the relevant fields by the regulatory and decision-making bodies.

## 11.3 Standard Definitions: Are We Using Them Appropriately?

The term nanotechnology was first used by Taniguchi in 1974 for a technology which has the ability to engineer materials precisely at the nanometer (nm) level. Since then, the term nanotechnology has been redefined by many scientists over decades. There are still many versions of the definition.

Eric Drexler, the founding father of nanotechnology, shares his memories of the early 1990s in his book *Radical Abundance* (Drexler, 2013). He says, 'a well-known

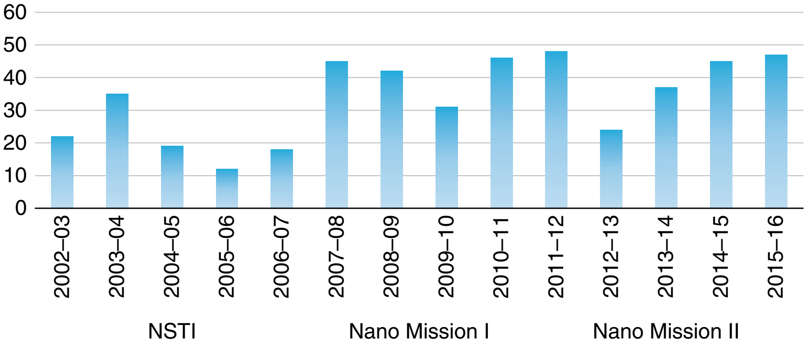

**Fig. 11.1.** Government-led nanotechnology projects sanctioned in India since 2002. (Graph plotted using data obtained from: 'Projects sanctioned' section of Nanomission website: http://nanomission.gov.in.)

tactic for winning funding' used to be the use of the term 'nanotechnology'. He further writes:

> People joked about this at conferences and asked a question that has never gone away – 'What is nanotechnology, anyway?' I know of no other field pasted together from pieces that had so little in common, and certainly none defined by a criterion as generic as size.
>
> (Drexler, 2013)

Even today, the working definitions used by nanotechnology experts across the world do not follow a consensus, which makes the understanding of this multidisciplinary technology ambiguous. It is clear that conceptual understanding demands much more clarity and precision in the way this technology and its products are defined. Further, an unambiguous comprehension of the terminology is also desired in legal and regulatory contexts. In the current scenario, a tougher scrutiny is needed for the approval of nanoproducts with special surveillance on how the products and their various ingredients are defined and presented to consumers. To facilitate international scientific communications between individuals and organizations, the International Organization for Standardization (ISO) has specified some standard definitions (see Table 11.1). It is important to note that some of the terms – for example, nanomaterial, nano-object, nanoparticle, etc. – might seem similar, but there are major differences in what these terms mean. A mutual agreement on definitions is vital for research as well as legal purposes.

## 11.4 Interdisciplinary Nature of Nanotechnology

Science and engineering at nanoscale is highly cross-disciplinary, involving knowledge from diverse disciplines converged with a broader perspective. Nanotechnology incorporates knowledge, principles and practices of basic technology of a wide range of disciplines, including physics, chemistry, biology, mathematics, different branches of engineering, materials science and biotechnology. For the development and regulation of such an integrative technology, education, research and infrastructure all are equally important (Roco and Bainbridge, 2003; Roco and Bainbridge, 2005). Highly qualified experts of their respective disciplines from all over the world should collaborate for a responsible and regulated research and development of nanotechnology. For teaching purposes, curricula should be designed accordingly, aimed at giving a good theoretical background of each discipline, teaching the students the basics of interdisciplinary integration and innovation. To provide a high-quality teaching environment, the teachers involved must be trained appropriately.

## 11.5 Public Acceptability

Since the mid-1990s, the value of the organic food sector has constantly increased in India and elsewhere. The promises made by the pro-GM community

**Table 11.1.** Commonly used terms in nanotechnology and their standard definitions.

| Term | Definition |
|---|---|
| Nanoscale | Anything ranging between 1 nm to 100 nm in size |
| Nanomaterial (NM) | A material with one of its external or internal dimensions in the nanoscale |
| Nano-object | A material with a single, two or three of its dimensions in the nanoscale |
| Nanoparticle | A nanomaterial of which all the external dimensions are in the nanoscale and in which there is no significant difference between the lengths of the longest and the shortest dimensions |
| Structure of a nanomaterial | This includes key structural features of a nanoparticle including its crystallinity, the structure of its crystals, its molecular structure and microstructure |
| Crystallinity of a nanomaterial | The potential of a nanomaterial to possess a crystalline structural order at the atomic level; this governs the optical, magnetic and electrical properties of a nanomaterial |
| Crystal structure of a nanomaterial | An ordered arrangement of atoms constituting a nanomaterial in a three-dimensional space |
| Microstructure of a nanomaterial | The manner in which each crystal or amorphous phase is arranged in a polycrystalline or multiphasic nanomaterial |
| Nano-enhanced | A function or purpose that has been improved and escalated by the use of nanotechnology |
| Nano-object release rate | The number of nano-objects released in a second under the influence of a disturbance |
| Incidental nano-object | An involuntarily developed nano-object generated merely as a product of a process |
| Fluid nanodispersion | A heterogeneous material composed of a nanomaterial dispersed in one or more compositionally varied fluid phase(s) |
| Nano-emulsion | A fluid nanodispersion in which one or more liquid phase(s) are in nanodimensions |

(those that strongly advocate the use of genetically modified crops) are also alluring. However, despite the increased public advocacy of organic farming and GM crops, a growing segment of the public is still not in favour of these modern agricultural practices (Lucht, 2015; Twardowski and Małyska, 2015). No wonder that nanotechnology-based products in agriculture and the food sector will be hard to swallow for many (Roco and Bainbridge, 2005). Public responses to nanotechnology-based products and their applications in different realms of life could be influenced by several social and ethical factors. Public awareness and acceptability of nanotechnology, being the key determinants of the future of nanotechnology, need to be systematically assessed (Mishra *et al*., 2017). The mass media and campaigning could help the public understand the potential of nanotechnology. Such schemes should give potential consumers an assurance that the research, development and manufacturing processes in the area of nanotechnology are all being performed in a highly regulated manner. This will help to reduce fears about nanotechnology to some extent.

## 11.6 Nano-divide

As we embark on a ‘nanotechnology boom’, we need to realize how this technology could irrevocably change the world as we know it. The way we are heading for an arms race in nanotechnology, the world could rapidly polarize and cause a ‘nano-divide’, widening the socioeconomic gap between the countries that have limitless access to this technology and the least privileged or underdeveloped countries of the world. As projected by experts, the use of nanotechnology in agriculture will increase agricultural productivity (Handford *et al.*, 2014; Sekhon, 2014), but at the same time, it could make many of the natural products redundant as they could potentially be replaced by nano-based products with enhanced qualities. This could also mean that nano-based agriculture, which supposedly requires lesser resources and workforce, could bring some sort of financial instability among those who rely on agriculture for their regular wage income. There is also an increased risk of ‘brain-drain’ from the developing countries to the industrialized and technologically advanced nations. To prevent the global nano-divide, experts recommend that the industrialized and developed nations should engage in making specialized policies addressing the transition from ‘a pre-nano to a post-nano world’ and suggestions are being made that the impact of rapid development of nanotechnology will vary based on how these policies are implemented across the world (Flament, 2013; Ionescu, 2016).

## 11.7 Early Warnings and Recommendations

### 11.7.1 Risk assessment of nanoproducts

A risk assessment plan should always be a part of good manufacturing practices. In the case of nanotechnology-based agricultural products, more extensive and comprehensive health and safety risk assessments should be followed. Not only the professionals who are involved in the development of a product, but also the farmers who will be potentially handling the product in bulk amounts, should be trained and taught to make their own risk assessments on a product. Every nanomaterial is chemically unique and, thus, each product containing a different nanomaterial should be assessed independently. In general, it is important to consider the size of the nano-ingredients when discussing about the safety of the farmers and other workforces who are working in agricultural industries. It is the responsibility of scientists and product developers to educate agricultural personnel about the potential hazards of nanoparticles and to recommend proper safety measures. Government and non-government agencies can play a key role in providing financial aid to farmers who cannot afford proper safety equipment to keep themselves protected from any potential hazards. Following are some key criteria based on which all nanoparticles should be treated as potential hazards.

### 11.7.2 Size and surface area

Stephan Herrera, in *The Big Science of Nanomedicine*, writes on the size of nanoparticles:

> Let's take a trip down the powers of ten: a dime is 1,000 microns thick, a human egg cell is a tenth of that, a red blood cell is a tenth of that, a nerve axon is a tenth thinner still, and you can fit ten viruses along that axon's diameter. Now we're down to 100 nanometers.
>
> (Herrera, 2000)

A particle at nanoscale changes its physicochemical and biological properties that it would have in its native form. For example, gold, a naturally inert metal, when broken down to about 5 nm, starts behaving as a catalyst (Campbell, 2004). Similarly, when the effect of pure carbon and pure titanium dioxide were studied, no damage was found to the lungs. But, when the same compounds were converted into nanosize, they were found potent enough to cause damage (Oberdörster *et al.*, 1994). Apart from enabling novel applications due to enhanced properties, quantum mechanics also evokes a challenge to control the self-assembly of nanoparticles and the potential dangers posed by them. Since the nanoparticle has a relatively large surface area, nanoparticles may readily adsorb other toxins and transport them to the organs of the body. Also, owing to their large surface area, they can readily form free radicals in the lungs, leading to lung and cardiovascular diseases. Nanoparticles also adsorb hydrocarbons and metals and carry them to the lungs, which can cause some serious problems like asthma and even cancer (Lu *et al.*, 2009).

## 11.8 Amount of Nanomaterial in a Nanoproduct

It is the next big concern that we don't know how much nanomaterial is being generated every year. According to the Nanotechnology Company & Laboratories Directory, an online nanotechnology web-portal published by Nanowerk (Nanowerk, n.d.), currently there are at least 1906 companies around the world, that are working on nanotechnology. Among these are 28 companies functional in India. These companies include multinational, medium size, small and university spinoffs. They cover many sectors and markets, including food packaging. In 2006, the Woodrow Wilson International Center for Scholars launched PEN (Project for Emerging Nanotechnologies) to maintain an online Consumer Product Inventory (PEN, n.d.). This inventory contains approximately 1317 products from 30 countries. The inventory contains the information about the product. There are other online and offline databases available which give massive information about the global development of nanotechnologies. Unfortunately, an important piece of information that is lacking in these databases is the amount of nanomaterial present in individual products, and also the units of individual products being produced and sold. The nano-based products that are available in the market do not give such information on the product labels. Consumers are largely unaware of the hazards of individual nano-based products.

## 11.9 Environmental Hazard

It is evident that almost all kinds of airborne ultrafine particles can potentially increase the morbidity and mortality rates of cardiovascular and lung diseases (Pekkanen *et al.*, 1997; Semmler *et al.*, 2004). The danger of the diseases is inversely proportionate to the size of the particles, i.e. the smaller the size of the particle, the more severe or lethal the disease. Thus, concerns on the health hazards posed by airborne nanoparticles are being raised. Several pieces of evidence, reported prior to the development and popularization of nanotechnology as a separate branch of science, suggested the presence of a wide range of nanoparticles in the pollutants generated from various industries, such as power plants, incinerators or cement factories. Such pollutants claim thousands of lives every year.

## 11.10 Occupational Hazard

On hearing the word ‘nanotechnology’, one always thinks of high-tech labs equipped with sophisticated instruments, but, in reality, it is quite different. Research and development facilities of the organizations might have sophisticated labs, as they deal with small quantities of nanomaterials on a laboratory scale. But, the scenario is not the same in manufacturing plants, and therefore there is a strong need to protect the workers from the hazards. Similarly, when agricultural nanoproducts are being applied, in bulk quantities, to a large field by a farmer, the farmer needs to take special protective measures. For those who handle any type of nano-based product in bulk quantities as a part of their occupation, risk assessment is of utmost importance. They must be aware of the possible routes by which nanoparticles can enter a human body and pose a hazard. According to the experts, there are four possible routes by which nanoparticles can enter the human body.

1. Skin absorption – some of the dry or liquid suspension of nanomaterial can pass through the skin and enter the bloodstream and reach different organs. If the material is toxic, it might cause damage to the body.
2. Ingestion – highly unlikely, but ingestion may occur if the hands are exposed to the nanomaterial and not washed properly.
3. Inhalation – dry nanopowder can be absorbed by the respiratory tract and reach deep into the lungs and then can be circulated through the blood. This only can happen when the nanomaterials are airborne. Therefore, it is recommended to use nanoparticles in the form of liquid suspension or attached to a substrate whenever possible.
4. Injection – injecting the nanomaterial into the body or exposure of nanomaterial to the wounded skin. This could happen accidentally, especially when working with needles.

To prevent these exposures during research, manufacturing and usage, it is essential to follow good laboratory, manufacturing and consumer practices as when working with any other biomaterial, such as the following.

(i) Wearing double gloves, using safety glasses and suitable lab coats.
(ii) Using respiratory filter masks, made up of NIOSH-approved cartridges, when working with nanopowder.
(iii) Risk assessment of the potential hazards of each nanomaterial/nanoproduct to be performed by all the researchers and manufacturing personnel on an individual basis.
(iv) Legitimate training on the handling of nanomaterials for all the workers and researchers.
(v) Awareness among all those who are handling nanomaterials, about the material safety data sheet (MSDS) of any new nanomaterials when purchased.

Not much is known about the real dangers of nanomaterials and therefore, just applying the current standards may not fully eliminate the risks. Thus, strategic planning and regulations, to control and manage the hazards, needs to be in place to at least guarantee as little exposure as possible.

## 11.11 Marketing of Nanoproducts

### 11.11.1 Increasing research in agri-nanotechnology, but no apparent commercially available products

The use of nanotechnology in agriculture is projected as a solution to increase the productivity of agricultural products, improve soil quality and quality of the produce, for a better and sustainable agriculture. For example, nano-emulsions can be used to reduce the amount of fertilizers and chemicals sprayed on the crop by efficiently delivering the active ingredient directly to the target part of the plant. Realizing the overwhelming advantages and tremendous potential of agricultural nanotechnology in India, it seems that the centres of excellence, research institutes, have been working hard since the conception of this technology in India. A high number of research papers on nanotechnology have been published to date and the number continues to rise. But nanoproducts are not able to make their way to the market. Clearly, there is a gap between academia and industries. Most of the discoveries in agricultural nanotechnology are claimed by the academic sector or small enterprises only. Some small companies launched their products in the market, but unfortunately their commercial scale application has not been achieved so far, due to high development and manufacturing costs. Therefore, there is no noticeable revenue generation in return for the agricultural nanotechnology research work. In contrast to the small enterprises, large agrochemical companies usually patent their products instead of bringing them to the market. The number of patents applied for nanotech-based products by the agrochemical industries are continuously increasing, suggesting that the big market players are keeping a close eye on the nanotechnology market and keeping their options open to exploit their patents or redevelop their products, according to the requirements of the commercial market.

### 11.11.2 Concerns of the industries regarding labelling of nanotech-based products

The other concern, according to some industries, is labelling of the product as a nanotechnology-based product. The industries foresee that the consumers may reject the products labelled as 'nanotech-based'. To overcome this problem, nanotech products with potentially high benefits and low rejection risks could be launched prior to those products that are prone to public rejection. This might help in gaining the confidence of the consumer, after which other nano-based agricultural products can be introduced to the market.

## 11.12 Mistakes Made and Lessons to be Learned

### 11.12.1 The asbestos case study

If we look back to the past, we can find many examples of materials with high industrial potential but also safety concerns; these early warnings were ignored and the material became a killer of thousands. Asbestos is one of them. Before anyone could understand the risks and hazards of asbestos and take the suitable protection or ban the material, it had already claimed 10,000 lives. Although some countries started banning asbestos from 1983 (Iceland being the first), it is said that the regulatory warnings regarding the potential hazards of asbestos first surfaced in the early 1900s, when many cases of severe illness due to lung dysfunction and deaths were reported and noticed in the towns where asbestos-mining factories were located. The first official death due to asbestosis was reported in Britain in 1924 (Cooke, 1924). The unfortunate fact is that asbestos-based products are still widely manufactured and used in India, which is currently the second-largest consumer of asbestos and the leading importer (Asbestos.com, n.d.).

### 11.12.2 Hazardous carbon nanotubes that resemble asbestos

Asbestos is compared with carbon nanotubes by many scientists because the shape of individual nanotubes resembles asbestos fibres. So, the asbestos case can be used as a good example to understand the hazard of carbon nanotubes. Several studies provide evidence of the toxicity of carbon nanotubes. In one such study, when mice were exposed to multi-walled carbon nanotubes (MWCNT) via inhalation, it was observed that the MWCNTs were deposited in their nasal cavity, larynx and trachea, causing inflammation and alveolar lipoproteinosis (Muller *et al.*, 2005).

### 11.12.3 Carcinogenic titanium dioxide nanoparticles

A study conducted more than two decades ago found a significant increase in malignant lung tumours in rats after chronic inhalation of nano $TiO_2$ (Heinrich *et al.*, 1995). The National Institute for Occupational Safety and Health (NIOSH) recently concluded that $TiO_2$ is not a direct-acting carcinogen and the genotoxicity exhibited by its particles is mainly because of the size and surface area of its nanoparticle and not due to the general properties of $TiO_2$ (NIOSH, 2011). Thus, one can say that all particles at nanoscale could be hazardous, regardless of their actual chemical composition.

### 11.12.4 Silver nanoparticles

Another type of nanoparticles widely used in everyday consumer products includes silver nanoparticles. Due to their antibacterial properties, silver nanoparticles are widely used in food packaging, kitchenwares and water purification. A big concern is that for such products containing silver nanoparticles, there is no regulatory labelling requirement and therefore the amount of nanomaterial in the product is not known to consumers (Boxall *et al.*, 2007). Many products which use nano-silver involve direct exposure to humans. Therefore, concerns have been raised to check the potential risk of nano-silver to human health. Silver metal in its original form is considered to be very low in toxicity. However, studies suggest that an exposure to nano-silver particles can cause liver damage and lung inflammation and altered lung function as observed in rats (Cha *et al.*, 2008; Wijnhoven *et al.*, 2009). Research suggests that, although the silver metal is not toxic to humans, nanoparticles of silver could be potentially hazardous.

## 11.13 Concluding Remarks

As the members of the scientific community, we always feel proud in predicting the future of an emerging science or technology. We love to forecast ‘where will we stand in the next 50 years’. But, the reality is that there is a long list of wrong predictions we have made in the past. It is certain that the wonders of science and technology are countless, but they may come up with good or bad. From steam turbines to gasoline-powered automobiles, from wireless telegraphy to the internet and mobiles, from X-ray machines to magnetic-resonance imaging, from advanced farm machinery to agricultural drones, from digital cameras to 3D-biomaterial printers, the list of breakthroughs goes on, and encompasses every aspect of life on earth. No one ever thought that science would change our world so dramatically. There are predictions from experts all over the world on how nanotechnology will change the world even further in the next 50 years or so. Keeping these predictions in mind and learning from the past, we need to consider the safety and regulatory aspect of this technology. Nanotechnology is at a budding stage currently, but is growing at an extremely fast pace.

First and foremost, we need to construct the foundation of this nanotechnology in an eco-friendly manner, so that the technology is developed in harmony with the natural resources for a healthy planet. All the products should be analysed and regulated appropriately before their marketing to assess the possible environmental and human hazards. It is also important to study appropriate disposal measures for the nanomaterials and any byproducts generated during the process of their synthesis. Such studies need to be conducted at a small scale before scaling-up the technology for commercial production. The next concern is the responsible and constructive use of the technology for the benefit of mankind. Antisocial individuals or organizations could use this technology for devastating causes, and this can only be curbed by strict regulations and monitoring.

One thing is certain and that is ‘revolution will happen’, but, it is uncertain whether it will happen in a way that we have predicted or in its own surprising ways. Our job is to be prepared for any challenges that such revolutionary modern technologies bring.

The internationally influential thinker, E.F. Schumacher, well known for his critique of modern technologies wrote in his famous book, *Small is Beautiful*:

> I have no doubt that it is possible to give a new direction to technological development, a direction that shall lead it back to the real needs of man, and that also means: to the actual size of man. Man is small, and, therefore, small is beautiful …
>
> (Schumacher, 1973)

Nanotechnology is a technology of small wonders, and small is, indeed, beautiful.

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# 12 Nanotechnology Application and Emergence in Agriculture

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## 12.1 Introduction

Nanotechnology basically can be defined as the science of manufacturing materials that have at least one dimension below 100 nanometer (nm) in size, while it can also be described as the study of physical matter and organized structures at the 1–100 nm physical range and also incorporation of these nanostructures into applications (Fig. 12.1). There are lots of differentiations between physical, chemical and biological properties when the scale turns from the micro- to the nanoscale. The major differentiation is larger surface/volume ratio of nanoscale materials. Additionally, nanomaterials reaction to mechanisms, thermodynamics and optical and magnetic properties are different from the same materials at macro levels. Nanoparticles have a different surface structure and composition via different reactivity, according to redox reactions and adsorption mechanisms. Similarly, there are lots of extraordinary examples that can be shown at nanoscale range, such as cation exchange capacity, complexation, ion adsorption, etc. These types of differentiation make possible the development and improvement of new applications on nanoscales (Kostoff, 2007; Maurice and Hochella, 2008; Gruère, 2012; Mukhopadhyay, 2014; Otles and Yalcin Sahyar, 2016).

Apart from classic agricultural technologies, modern agricultural techniques and technologies give direction to future agricultural production, improvement, development, transportation, smart delivery systems for traceability of crop improvement, nanomaterials for improving fertilizer efficiency, nanosensors for track delivery systems and many more. Nanoscale product development has evolved novel applications in agriculture (Scrinis and Lyons, 2007; Nair *et al.*, 2010; Mishra *et al.*, 2016; Mishra *et al.*, 2017).

Nanotechnology and nanosciences have many directions for potential improvement and development, and have opened up new perspectives to many industrial and consumer sectors, while there are also some concerns about and drawbacks to

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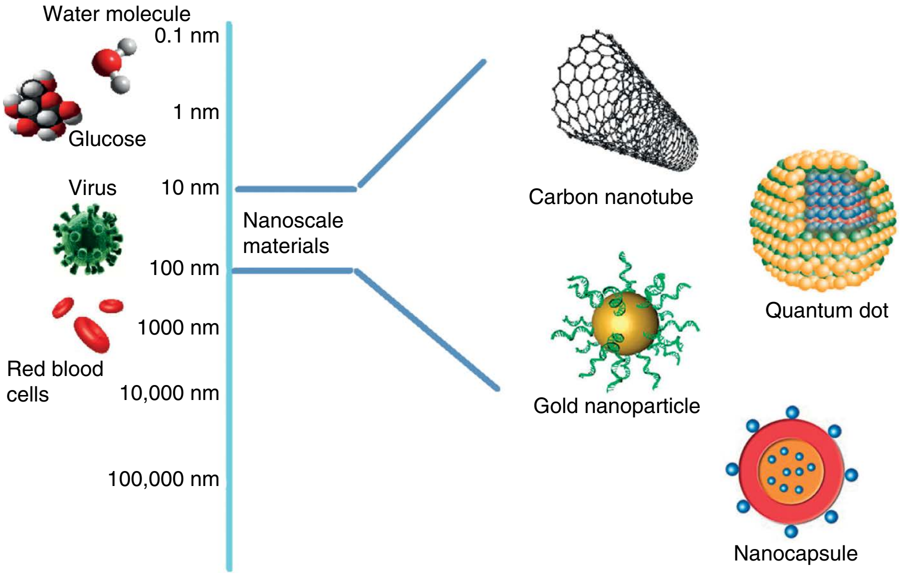

**Fig. 12.1.** Examples of nanoscale materials.

nanomaterial properties, reactions and impacts on human health (Chaudhry, 2011). Generally, nanotechnology applications in the agricultural system focus on nutrients, water sanitation and purification, nanopesticides and herbicides.

## 12.2 Nanotechnology Application on Agriculture

Nanoagricultural studies are mainly focused on the development and control of input such as water and nutrients to manage and eliminate waste. While developing and controlling nanoherbicides and nanopesticides to cover excessive usage of these materials for consumer and environmental health, and also increasing production yield (Robinson and Morrison, 2009). There are other interesting applications such as nanofertilizer (nanoporous zeolites indicate the release and increased efficiency of fertilizers); nanosensors (detection of soil quality, enzyme immobilization) and smart delivery systems (nanoherbicides, nanopesticides encapsulated in nanomaterials) in order to control and trace food and agricultural system (Moraru *et al.*, 2003; Kim *et al.*, 2006; Chau *et al.*, 2007; Chinnamuthu and Boopathi, 2009; Gruère, 2012); genetic development of plants (Kuzma, 2007); drug molecules and gene delivery mechanism (Maysinger, 2007); gene expression in plants via nanoarray-based technologies (Evans, 2009; Ahmed *et al.*, 2013); early detection of contaminants and pathogens in food products. These functions support the development of precision farming by minimizing pollution and maximizing the value of farming practice (Ghormade *et al.*, 2011; Mukhopadhyay, 2014).

The popularity of protein-based diets, the human population increase, and changes in environmental conditions (e.g. decreasing of green area, deformation of ozone layer, atmosphere pollution) affect the demand for agricultural product quantity, services, safety, functionality and sustainability practices. Food safety hazards such as BSE (mad cow disease) and FMD (footh and mouth disease) in livestock can be overcome via agricultural biotechnology and/or nanobiotechnology applications to improve human wellbeing. Furthermore, consumer demands are also focused on the origin/sources of agricultural products, especially in terms of sustainability and minimal impact on the environment. Organic produce is rapidly growing in popularity, perceived as 'green' and environmentally friendly. Thus, the market needs traceable agricultural supply chains, and we need to integrate bioengineering, biotechnology and nanotechnology into agricultural systems. These can be easily used to solve critical problems of agriculture; for example, agricultural biotechnology can create genetically modified species for crop and animal production (see Austin *et al.*, 2002 on DNA cell control), nanofabrication of plants and animals, disease control, nutrient deficiency and developmental abnormalities (Opara, 2004).

## 12.3 Water Sources

Water sources and clean water are very important for all production areas; availability of clean water is also necessary for all aspects of agricultural application. Clean water resources are being depleted and polluted, potentially leading to a water-related crisis. Nanotechnology shows great promise in providing clean water resources, via enabling technologies such as desalination of seawater to increase the water supply (Brame and Alvarez, 2011). Nanotechnology enables efficient water treatment and recycling systems for disinfection and microbial control: numerous natural and engineered nanomaterials have shown strong antimicrobial properties. These nanomaterials have diverse mechanisms, including photocatalytic production of reactive oxygen species, which damage viruses and cell components using $TiO_2$- and ZnO-like materials (compromising the bacterial cell envelope via peptides, chitosan, carboxyfullerene, carbon nanotubes), ZnO and silver nanoparticles (deduction of energy transduction via silver nanoparticles and aqueous fullerene nanoparticles), and inhibition of enzyme activity and DNA synthesis via chitosan-like materials. In this context, these systems, as a new technological development, have a great positive impact concerning clean water resources (Li *et al.*, 2008).

Currently, providing clean water to meet human needs poses a serious challenge. The worldwide water supply needs to be sustainable to meet fast-growing demand due to population growth, global climate change, and water quality deterioration. Water sources should be controlled and managed through integrated studies. Nanotechnology holds great potential in water and wastewater treatment to enhance and/or improve treatment efficiency and also for the safe use of unconventional water sources (Qu *et al.*, 2013).

## 12.4 Nanosensors and Smart Delivery Systems

Nanotechnology and its usability in agricultural areas accounts for a wide variety of research and advance studies such as reproductivity, recycling of food and agricultural waste as energy, byproduct reuse in enzymatic nanobioprocessing, nanocides or biocides as plant disease treatment and/or prevention (Carmen *et al.*, 2003). Thus, systems including and/or consisting of nanomaterials/devices can be called 'smart' because of the benefits of nanoscale usage in agricultural systems. These devices have been found helpful in areas such as nanodrug delivery in humans due to their capability of delivering chemicals in a targeted and controlled manner (Roco, 2003; Lu *et al.*, 2008). The smart delivery system in agriculture can be briefly defined as the combination of specifically targeted, timed, highly controlled, preprogrammed, regulated/self-regulated, multifunctional characteristics to avoid biological barriers for successful targeting (Nair *et al.*, 2010).

One smart delivery system example is nanopesticide, which can 'involve either very small particles of pesticidal active ingredients or other small engineered structures with useful pesticidal properties' (Bergeson, 2010a), while another definition is: 'nanopesticides which can enhance the dispersion and wettability of agricultural formulations, and unwanted pesticide movement' (Bergeson, 2010b). Nanopesticide formulation should demonstrate permeability, thermal stability, stiffness, solubility, crystallinity and biodegradability properties (Bordes *et al.*, 2009; Bouwmeester *et al.*, 2009). Nanomaterials have a relatively large surface area, and thus enhance affinity to the target compound (Jianhui *et al.*, 2005). Nanopesticide delivery techniques include nanoemulsions, nanoencapsulates, nanocontainers and nanocages (Bouwmeester *et al.*, 2009; Lyons and Scrinis, 2009; Bergeson, 2010b) for plant protection (Khot *et al.*, 2012).

Actually, there are some nanoformulation examples in plant-based foodstuffs. One of them is reported as a development of sodium dodecyl sulfate (SDS) modified photocatalytic $TiO_2$/Ag nanomaterial conjugated with dimethomorph (DMM), a commonly used pesticide in agricultural production as a nanopesticide. These nanoformulations, which have 96 nm average granularities, should degrade faster in the soil and slowly in plants with residue levels below the regulatory criterion for foodstuffs, and also show increased decomposition and dispersivity of the pesticide in soil, while increasing its effectiveness in vegetable seedlings (Jianhui *et al.*, 2005). Another example can be given as encapsulated nano-imidacloprid, which contains pest-control properties, during vegetable production (Guan *et al.*, 2010). According to Jianhui *et al.* (2005) and Guan *et al.* (2010), SDS is modified with $TiO_2$/Ag imidacloprid nanoformulation and then microencapsulated using alginate and chitosan. This nanoformulation was tested on soybean plants, and it was observed that photodegradation of SDS is increased using this encapsulation. Additionally, highly photodegradable $TiO_2$/Ag particles (5–7 nm) were synthesized by using polyoxyethylene lauryl ether (POL), and tested under visible and UV radiation by comparison with SDS. The results showed that POL-synthesized nanoparticles photodegraded faster during the same exposure period (Mohamed and Khairou, 2011). Pesticide residue detection can be performed using nanosensor technology via high sensitivity, low detection limits, super selectivity and fast responses (Liu *et al.*, 2008). Furthermore, enzyme-based biosensors can be used to detect organophosphate, organochlorine and carbamate residues. Nanoparticles (gold (Au), titanium (Ti), Au-platinum (Pt), nanostructured lead dioxide ($PbO_2$)/$TiO_2$/Ti) can be used to increase biosensor sensitivity. However, random test of all pesticides is impossible; this is why nanomaterials are needed for selectivity, stability and sensitivity (Dyk and Pletschke, 2011). Furthermore, nano-$TiO_2$ film in photocatalytic degradation of organochlorine pesticides was studied, and then electron transfers on the surface of $TiO_2$, permitting photolytic degradation of pesticide (Yu *et al.*, 2007; Khot *et al.*, 2012).

Nanosensors (consisting of smart nanomaterials) can be used to detect major residuals which are extremely harmful to human health (Bergeson, 2010a), via an advanced alert system (such as colour change), to enable farmers to decide upon the dosage rate and frequency.

## 12.5 Genetically Developed Plants

Whenever the terms ‘genetic’ and ‘plant’ come together, there are a lot of questions and a negative impression is created. That is why we always need to think about technical terms carefully before using them. There are numerous comments on the health effects of these modifications, starting with genetic development and enhancement with addition of nano term. In the scientific perspective, first, the necessity for genetically developed plants, organisms and/or cells needs to be identified, then scientifically developed, and then the benefits and drawbacks can be considered.

Recently, numerous research has been published related to the effect of nanomaterials on plant growth, germination and application to agricultural areas. The effect of micro- and nano-$TiO_2$ on naturally aged spinach seed growth has been studied. There are some clear benefits of the nanomaterial, such as 73% more dry weight, 45% increase in chlorophyll formation, and three times higher photosynthetic rate compared to the control over a germination period of 30 days. Thus, it can be concluded that the smaller the nanomaterial, the better the seed germination. The main reason for the growth rate increase in spinach seed can be said to be nano-$TiO_2$, as this can increase the seed stress resistance and promote capsule penetration for intake of water and oxygen needed for fast germination. Additionally, accelerated breakdown of organic substances, increase in the absorption of inorganic nutrients, and increased photosynthetic rate are nano-$TiO_2$ properties (Zheng *et al.*, 2005; Khot *et al.*, 2012). Other related studies show that nanoparticle-mediated plant transformation has the potential for genetic modification of plants for further improvement. Specifically, the application of nanoparticle technology in plant pathology targets specific agricultural problems in plant–pathogen interactions and provides new ways for crop protection in safe use of this technology and improvement of crops (Nair *et al.*, 2010).

Nanomaterials as engineered nanoparticles (ENPs) have been developed rapidly and found potential applications because of their unique properties. ENPs’ impact on and interactions with plants should also be considered according to the assessment of risk to the ecosystem. The impact of ENPs on plants varies depending on concentration, composition, size and other related physical, chemical and biochemical properties of the plant and the ENPs. ENPs might potentially be taken up by the plant roots and transported to shoots through vascular systems depending on the shape, size and composition of ENPs, and on plant anatomy. Phytotoxicity, accumulation and uptake of ENPs should be studied and clarified.

According to existing scientific studies, the phytotoxicity of nanoparticles should be researched to identify connections between the characteristics of nanoparticles, such as surface area, particle size and surface activity. There are some studies about the uptake kinetics of ENPs and investigations into how the composition, particle size and aggregation state affect uptake kinetics and transportation of nanoparticles within plant system, but studies are lacking on the impact of environmental factors in correlation with ENP uptake and accumulation by plants. There are some methods to detect nanoparticles, such as optical detection for fluorescent nanoparticles (quantum dots) or on nanoparticles functionalized with fluorescent markers (Gonzalez- Melendi *et al.*, 2008), while scanning (SEM) and transmission (TEM) electron microscopy can be used for surface functionalization (de Jonge *et al.*, 2009; Ma *et al.*, 2010).

## 12.6 Drug and Gene Delivery Systems

Nanotechnology offers solutions for agricultural-related biomedicine, drug and gene delivery systems, such as the transformation of biosystems as a molecular medicine to detect and treat illness, nanoscale surgery, synthesis and targeted delivery of drugs (Bugunia-Kubik and Susisaga, 2002; Schmidt and Montemagno, 2002); to investigate the health effect of nanostructures in the environment (Keanea *et al.*, 2002) and eco-toxicology (Borm, 2002; Moore, 2002; Roco, 2003). Additionally, there are other solutions for nanotechnological drug and gene delivery system, which can be classified as green manufacturing (biocomplexity and biocompatibility aspects) as biochips, sensors for astronauts and soldiers, as biofluidics to handle DNA and other molecules, designing pharmaceuticals as a function of patient genotypes, synthesis of biodegradable and effective chemicals for sustainable agriculture (Roco, 2003).

Nanotechnology's application to medicine can be designed to interact with tissues and cells at a molecular level with high functional individuality, thus enabling a degree of integration between biological systems and technology not previously accessible. Finally, it can be concluded that nanotechnology is a multidisciplinary and emerging science, which can be combined with traditional sciences, such as physics, chemistry, biology and materials science, bringing together the collective expertise to develop novel technologies (Silva, 2004).

## 12.7 Benefits and Drawbacks of Nanotechnology Applications in Agriculture

Nanotechnology benefits and drawbacks should be clearly identified for the sake of customers, producers and users. According to researchers, there are numerous ethical issues in nanotechnology and agrifood, linked to the ethical concepts of autonomy, beneficence, non-malfeasance and justice (ensuring safety, effective risk assessment, transparency, consumer benefits and choice, animal welfare and environmental protection) (Coles and Frewer, 2013). The same researchers conclude that risk assessment procedures are in most cases not specific to nanomaterials for agrifood, resulting in uncertainty regarding the nature and extent of potential risks. There are currently no labelling requirements for usage of nanomaterials in agrifood production (Coles and Frewer, 2013). As well as labelling, there should be substantial investment in agricultural nanotechnology applications to address and identify limitations and challenges of this technological application to the farming system.

On the other hand, there are some benefits of this technological development, such as improvement of soil efficiency (fertility and capacity), targeted delivery systems (nutrients and pesticides) (Scrinis and Lyons, 2007) and nanomaterials (such as nano-iron and carbon nanotubes) used for water and soil purification and remediation (Karn *et al.*, 2009). These products can be supplemented by formulating new substances for more effective pesticide control (smart pesticides) via smart sensors and/or smart delivery systems (Rai and Ingle, 2012). Further benefits would accrue from incorporating nanosensors into livestock (facilitating drug delivery systems, animal tracking) (Nguyen *et al.*, 2012); from encapsulated vaccines (released into water from microcapsules once ingested by fish) (Nielsen *et al.*, 2011); and from genetically modified seeds (Scrinis and Lyons, 2007). More examples are: slow release of nanomaterial-assisted fertilizers, macronutrients and biofertilizers for efficient use; nanomaterial-assisted delivery of genetic materials for crop improvement; immobilization of enzyme on nanostructures increasing effective concentration of the preparation (Kim *et al.*, 2006). Thus, nanotechnology applications in agricultural systems can reduce vulnerability to climate, over-dependence on supplementary irrigation, energy conversion and poor input impact (Karn *et al.*, 2009). With the beneficial examples, there are some limitations also, such as that nanomaterial-based sensors used for pesticide residue detection are restricted due to the large number of pesticides used in agricultural production (Liu *et al.*, 2008; Dyk and Pletschke, 2011).

## 12.8 Conclusion

Nanotechnology has great potential in terms of agriculture. Applications have numerous benefits and some drawbacks which cannot be ignored, emerging as they do from gaps in knowledge of nanotechnology, nanomaterials, physical, chemical and biochemical mechanisms and interactions. Even if there are numerous studies, lab-scale trials, production and usage of nanomaterials and nanoscience, this technology is still in its early ages. The main objective now is that when the topic is related to human health, knowledge gaps should be filled and unknown points should be clarified.

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# 13 Positive and Negative Effects of Nanotechnology

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## 13.1 Introduction

New technologies are always applied in an area such as agriculture to improve the production of crops. For the last decade or so, nanomaterials have been widely used in the world, such as the use of nanoparticles in agriculture, with the particles having certain valuable effects on the crops (Morla *et al.*, 2011; Mishra *et al.*, 2014). Nanoparticles have enhanced interaction, due to an increase in each of the following: reactive area; specific surface area; or responsiveness of these particles along the particle surfaces. Nanotechnology can provide solutions to increasing agricultural productivity and decreasing environmental problems (Mishra and Singh, 2015; Mishra *et al.*, 2017). With the use of nanoparticles and nanopowders, researchers can produce controlled- or delayed-release fertilizers (Roghayyeh *et al.*, 2010; Kottegoda *et al.*, 2011). On the other hand, there is now extensive argument about the hazards of releasing nanomaterials into the environment (USEPA, 2007), so many researchers are operating with increasing awareness of this topic in order to evaluate the potentially negative effects on the environment and on human health (Ruffini and Roberto, 2009). Therefore, this chapter highlights the importance of nanotechnology in improving agricultural productivity, and its ability to improve plant growth under normal and environmental stresses. Further, it will also shed light on some of the negative effects of nanotechnology that affect plants in particular and the environment in general.

## 13.2 Positive Effects of Nanotechnology

### 13.2.1 Effect of nanoparticles (NPs) in improving plant growth and its chemical composition under normal conditions

Many studies have reported that the application of nanoparticles on plants can enhance seedling growth and chemical composition. Navarro *et al.*

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(2008) reported that in the presence of appropriate organic compounds, NPs will have a longer residence time in aquatic systems, or enhanced mobility in soils, and may thus interact more efficiently with algae or with plant roots. As a result of their remarkably high surface area to volume ratio, ENPs may adsorb pollutants, which might change the transport and bioavailability of both the ENPs and the pollutants in natural systems, and alter their toxic effects. Trace-metal ion speciation might be altered by NPs (especially oxide and oxide-coated NPs), therefore altering their bioavailability and potential toxicity (Fig. 13.1).

Lu *et al.* (2002) observed that soybean seeds treated with a mixture of N-$SiO_2$ and N-$TiO_2$ had increased germination and the activity of nitrate reductase, superoxide dismutase, catalase and peroxidase of germinating seeds were increased significantly. In another study, Bao-Shan *et al.* (2004) tested TMS (nanostructured silicon dioxide) on the growth of Changbai larch (*Larix olgensis*) seedlings. They observed that TMS-treated *Larix* seedlings showed improved growth and quality. The 500 μL $L^{-1}$ concentration of TMS showed enhanced mean height, root collar diameter, main root length and the number of lateral roots of seedlings. Zhang *et al.* (2005) analysed the effects of nano-$TiO_2$ and nonnano-$TiO_2$ (control) on the germination and growth of naturally aged seeds of *Spinacia oleracea* by measuring the germination rate and the vigour index, finding an increase in this index of 0.25–4% nano-$TiO_2$ treatments. During the development phase, the plant dry weight was increased, as was the chlorophyll formation, the ribulose bisphosphate

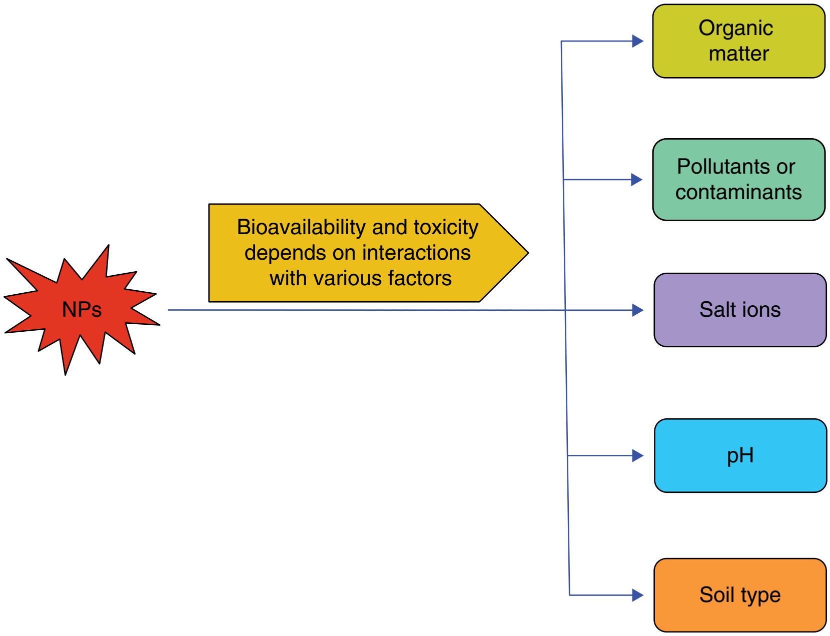

**Fig. 13.1.** Schematic representation of interactions of nanoparticles (NPs) with various components determining their bioavailability and toxicity behaviour.

carboxylase/oxygenase activity, and the photosynthetic rate. These results demonstrated that the physiological effects were linked to the size of nanomolecules. The authors also reported that the effects of nonnano-$TiO_2$ particles were not significant. Furthermore, Liu *et al.* (2005) reported that treatment with nano-iron oxide facilitated the transfer of photosynthate and iron to the leaves of groundnut, whereas no such effects were observed in the case of treatment with organic materials and iron citrate. At the same time, the use of nano-calcium carbonate compared to humic acid and organic fertilizer caused more tillering in groundnut, and low concentrations of nano-calcium carbonate caused an increase in the number of leaves, leaf area, dry weight, soluble sugar and groundnut protein (Liu *et al.*, 2005). Similarly, Doshi *et al.* (2008) investigated the environmental impacts of nano-aluminum on plants, and found that the presence of nano-aluminum particles did not have an adverse effect on the growth of a California red kidney bean (*Phaseolus vulgaris*) or rye grass (*Lolium perenne*) plants. California red beans did not show an uptake of aluminum, while the situation was different from rye grass, where a 2.5-fold increase in Al concentration in the leaves was observed as compared with control tests. Nano-aluminum particles in suspension do not appear to have an impact on the metabolic activity of *Vibrio fischeri*. In summation, the application of nano-iron oxide significantly affected groundnut and caused an increase in growth (plant height, plant diameter, number of sub-branches, number of filled pod/plant, hollow pod number/plant, total number of grains per plant, total grain weight, shoot weight, leaf + pod weight, 100 grain weight, pod dry weight yield) and photosynthesis (Sheykhbaglou *et al.*, 2010). Also, Srinivasan and Saraswathi (2010) concluded that the carbon nanotubes (CNTs) are significant in the rapid germination, growth rates, increased biomass and yield of tomatoes and are not toxic to plants. Meanwhile, the presence of ZnO nanoparticles gave maximum effects on the growth of mung (*Vigna radiata*) at 20 ppm and gram (*Cicer arietinum*) seedlings at 1 ppm (Mahajan *et al.*, 2011). Furthermore, El-Kereti *et al.* (2013) reported that ZnO NPs foliar spray had a significant enhancement on the plant growth characteristics (branches and leaves number/plant, fresh and dry weight), total chlorophyll, total carbohydrate, essential oil content, iron content, and consequently, will increase the total yield of sweet basil. Similarly, Elfeky *et al.* (2013) concluded that $Fe_3O_4$ nanoparticles had significant effects on the total chlorophyll, total carbohydrate, essential oil content, iron content and plant growth characteristics (branches and leaves number per plant, fresh and dry weight) of sweet basil. Also, micronutrient nanoparticles (MN-NPs), such as Fe and Mn NPs have shown positive indications in terms of enhancing plant growth, metabolism or nutrient accumulation from the NPs (Alidoust and Isoda, 2014; Kim *et al.*, 2014; Pradhan *et al.*, 2014; Monreal *et al.*, 2016). In addition, Liu and Lal (2015) indicated that N and P macronutrient nanofertilizers can enhance plant growth in certain concentration ranges and could be used as nanofertilizers in agriculture to increase agronomic yields of crops and/or minimize environmental pollution. Also, hydroxyapatite nanoparticles (nHA) foliar application played a critical role in the significant increase of phosphorus availability to the plant, which led to improved growth parameters, chemical compositions, good scavengers for DPPH radicals and anticancer activity of *Adansonia digitata*, especially under new area (sandy soil) compared to control plants (no fertilizer application) (Soliman *et al.*, 2016).

### 13.2.2 Effect of nanoparticles on plant growth and its chemical composition under environmental stresses

Several environmental factors (drought, salinity, nutrient imbalances) adversely affect plant growth, development and the final yield of a crop (Dudal, 1976; Batool *et al.*, 2014). Therefore, reviewers try to improve plant tolerance to abiotic stresses by using nanoparticles (NPs), which may help satisfy the growing food demands of developing and underdeveloped countries. In addition, the alleviation of environmental stress can be attributed to the properties of NPs (larger specific surface area and more reactive areas) that help in enhanced enzyme activity related to salt tolerance (Soliman *et al.*, 2015).

Application of the $SiO_2$ nanoparticles increased shoot fresh and dry weight of maize under salinity stress (Gao *et al.*, 2006) and these results are in agreement with the findings of Corredor *et al.* (2009), who reported nanoparticles improving growth and chemical composition of pumpkin plants. Also, salinity stress affects crop growth due to the toxicity of sodium ions, but the application of nano-$Sio_2$ can decrease its toxicity and so improve crop growth (Savvas *et al.*, 2009). Furthermore, Sheykhbaglou *et al.* (2010) found that the nano-iron oxide had significant effects on the dry pod weight, leaf with the dry pod and yield of soybean compared to other treatments. In pumpkin, iron oxide NPs increased root elongation, which was attributed to Fe dissolution (Wang *et al.*, 2011). At the same time, Haghighi *et al.* (2012) reported that one mM nano-silicon (N-Si) under different salinity levels showed great enhancement of germination characteristics such as germination rate, root length and dry weight. Also, nano-silicon (N-Si) improved photosynthesis rate, mesophyll conductance, and plant water use efficiency of cherry tomatoes (*Solanum lycopersicum* L.) under saline stress conditions (Haghighi and Pessarakli, 2013). Although the sodium ion concentration increased in the crop-shoot as a result of salinity stress, an application of $SiO_2$ nanoparticles can decrease its concentration in plant tissues (Kalteh *et al.*, 2014). Similarly, Soliman *et al.* (2015) concluded that salt stress can be alleviated in Moringa plants using foliar applications of ZnO and $Fe_3O_4$ NPs mixed with a Hoagland solution in comparison to spraying only with the normal solution. Growth parameters and chemical composition related to salt tolerance were enhanced when nano-forms of Fe and Zn were used in Hoagland solution (60 mg/l). Application of $SiO_2$ nanoparticles was beneficial in improving salinity tolerance in the lentil seedling and its application may stimulate the defence mechanisms of a plant against salinity (Sabaghnia and Janmohammadi, 2015). Similarly, the harmful effect of salt stress on vegetative growth and relative water content (RWC) was also alleviated by the addition of nanoparticles-Si which caused significant increases in plant height, fresh and dry weights, RWC and total yield. Seed quality, represented by nutrient elements, was also improved by application of nanoparticles-Si (Abdul-Qados and

Ansary, 2015). *Brassica napus* L. plants treated with $CeO_2$ NPs had higher plant biomass, exhibiting the higher efficiency of the photosynthetic apparatus and less stress in both freshwater and saline water irrigation conditions (Rossi *et al.*, 2016).

## 13.3 Non-Beneficial Effect of Nanoparticles on Plant Growth and Its Chemical Composition Under Normal and Stressed Conditions

Many studies reported that the toxicity of ENPs may be partly due to their release of toxicants (Brunner *et al.*, 2006; Franklin *et al.*, 2007; Navarro *et al.*, 2008). At the same time, the literature on the ecotoxicity of nanoparticles and nanomaterials as well as the chemistry of both manufactured and natural NSPs is summarized in reports (Handy *et al.* 2008a,b; Yu-Nam and Lead, 2008). Because of their widespread use in consumer products, it is expected that NSPs will find their way into aquatic, terrestrial and atmospheric environments, where their fate and behaviour are largely unknown.

There are many knowledge gaps regarding the ecotoxicological aspect of NPs and many of these gaps are still unresolved problems and hence there are new challenges concerning the biological effects of these NPs. It is worth mentioning here that nanoparticles can be synthesized from a variety of bulk materials and their activity totally depends on both the chemical composition and on the size and/or shape of the particles. Compared to other contaminant, nanoparticle size plays an important role in the behaviour, reactivity and toxicity of NPs. Considering these aspects, it is unsurprising to find both positive and negative effects of nanoparticles on higher plants. Given that the nanotechnology industry is growing fast, it is crucial to perform further studies on the subject, in order to establish regulation of nanomaterials regarding their use, confinement, and disposal (Ruffini and Roberto, 2009). Also, Maynard *et al.* (2006) and Wiesner *et al.* (2006) concluded the unique properties of NPs (high specific surface area, abundant reactive sites on the surface as a consequence of a large fraction of atoms located on the exterior rather than in the interior of NPs, as well as their mobility) could potentially lead to unexpected health or environmental hazards, especially organisms that interact strongly with their immediate environments such as algae, plants and fungi.

In contrast, Stampoulis *et al.* (2009) studied the effects of five nanomaterials (multi-walled carbon nanotubes (MWCNTs), Ag, Cu, ZnO, Si) and their corresponding bulk counterparts on seed germination, root elongation, and biomass of *Cucurbita pepo* (zucchini/courgette). They further demonstrated that considering parameters such as germination and root elongation do not provide accurate data to evaluate nanoparticle toxicity to terrestrial plant species.

Written reports on the toxicity of nanomaterials are still coming out and show several negative effects on growth and development of plantlets. Results are reported by USEPA (1996) that consider studies on seed germination, stem elongation, often accompanied by other evaluations on biomass changes and anatomical histological studies, useful to demonstrate *in situ* symptoms of potential toxicity. Meanwhile, Lin and Xing (2007) reported phytotoxicity of five types of multi-walled nanoparticles in six higher plant species (*Raphanus sativus*, *Brassica napus*, *Lolium multiflorum*, *Lactuca sativa*, *Zea mays* and *Cucumis sativus*) based on parameters of seed germination and root growth, and found that the seed germination was not affected except for the inhibition of nanoscale zinc on *Lolium multiflorum* and nanoscale zinc oxide on *Zea mays*. They also reported that the inhibition of root growth varied greatly among nanoparticles and plants, and it is partially correlated to nanoparticle concentration. Finally, the authors concluded that the inhibition occurred during the seed incubation process rather than the seed-soaking stage.

A similar trend was found by Zhu *et al.* (2008), who concluded that iron oxide nanoparticles prevented the root growth of pumpkin plants. In addition, Harris and Bali (2008) investigated the limits of uptake and the distribution of silver nanoparticles in *Brassica juncea* and *Medicago sativa*. Lee *et al.* (2008) analysed the toxicity and bioavailability of copper nanoparticles for *Phaseolus radiatus* and *Triticum aestivum* using a soilless system, i.e. plant agar, for homogeneous exposure of nanoparticles. Plant agar, which is a soft gel, allows dispersion of NSPs, hardly water-soluble, avoiding their precipitation. Due to their exposure to nanoparticles, the growth rates of both the plants were inhibited, whereas it was also found that seedling lengths of test species were negatively related to the exposure concentration of nanoparticles. Furthermore, Lee *et al.* (2010) reported toxicity of nano-$SiO_2$ on *Arabidopsis thaliana*, but this toxicity was not as strong as other nanoparticles, such as nano-ZnO and nano-$Fe_3O_4$. In addition, Adhikari *et al.* (2012) concluded that the increasing concentration of copper oxide nanoparticles severely inhibited the elongation of the roots of soybean and chickpea. Massive adsorption of Cu oxide nanoparticles (above 200 ppm Cu) into the root system was responsible for the toxicity. Da Costa and Sharma (2016) demonstrated the toxic effect of Cu accumulation in roots and shoots of rice (*Oryza sativa*, var. Jyoti) that resulted in the loss of photosynthesis.

## 13.4 Conclusion

As evidenced by the abovementioned reports, remarkable progress has been made in the rapid development of a great variety of nanoparticles (NPs) and the effects of these inorganic and organic nanosized materials may result sometimes in enhancing crop quantity and quality (speeding up germination, better development and chemical composition, or increase in plant endurance under environmental stresses) and that has led to improvements in the economics of food production. Nanotechnology has also resulted in an intelligent nanofertilizer for efficient delivery of the nutrients needed by the plant, which may help to get rid of or decrease the use of chemical fertilizers, leading to a reduction in pollution of the agricultural environment and thus to improved human health worldwide.

Meanwhile, some showed deleterious effects of nanoparticles (NPs) into the higher plant (toxicity of the plant, delay in germination, decrease plant growth and chemical composition under normal or environmental stresses) or into the environment (soil, water etc.).

Considering these effects, it is crucial and urgent to undertake further studies on the uses of nanotechnology in society and to establish the correct regulation of each type of nanomaterial separately over their use, confinement, and discharge of each material to the plants and the environment.

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# 14 Vanguard Nano(bio)sensor Technologies Fostering the Renaissance of Agriculture

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## 14.1 Introduction

In the report, *The State of the World's Land and Water Resources for Food and Agriculture*, published in 2011, the Food and Agriculture Organization of the United Nations (FAO) stated:

> Land and water resources are central to agriculture and rural development, and are intrinsically linked to global challenges of food insecurity and poverty, climate change adaptation and mitigation, as well as degradation and depletion of natural resources that affect the livelihoods of millions of rural people across the world.
>
> (FAO, 2011)

In recent years, the challenge of assuring adequate food worldwide has never been harder due to demographic pressure, climate change, and the increased competition for resources, especially in developing countries such as Africa and Asia, where almost 1 billion people are undernourished. The agricultural industry has handled these increasing constraints producing massive food volumes by immoderately exploiting practices that have been used without considering their impact on the environment and human wellbeing. In fact, farming techniques have been oriented towards the indiscriminate use of labour and resources, high-tech machinery, and pesticides in the cultivation of crops to achieve an augmented profit, causing an abuse of the soil and at the same time triggering huge pollution levels in different environmental segments. Watercourses and related ecosystems are facing worrying levels of pollution and degradation due to intense farming that is causing reduced quality, biodiversity injury, water scarcity, damage to territories,

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and increased greenhouse gas emissions (Buckley and Carney, 2013). Indeed, in the dawn of the Green Revolution, based on research and development initiatives aimed to augment agricultural production worldwide (1930–60), the widespread use of irrigation and agrochemicals largely increased production yields but it turned in the course of time in a wrong direction, resulting in land degradation, loss in soil fertility, and water pollution, directly and indirectly affecting human health.

Recently, the National Economic and Development Authority (NEDA) reported that 37% of the total water pollution in the Philippines geographic area originates from agricultural practices, which include animal waste, fertilizer and pesticide runoff. Moreover, the Greenpeace Organization analysed groundwater in the Benguet and Bulacan Provinces of the Philippines, revealing that 30% of the tested artesian wells showed nitrate levels above the safety limits provided by World Health Organization (WHO) for drinking water. Nitrate groundwater contamination is a worldwide problem, especially in agricultural countries, where the exposure to high levels of nitrate may contribute to adverse health effects in humans (Chica-Olmo *et al*., 2016; Zirkle *et al*., 2016). The greatest risk of nitrate poisoning is considered to be the 'blue baby syndrome' or methaemoglobinaemia, which occurs in infants given nitrate-laden water, and affects particularly babies under 4 months of age (Saigal *et al*., 2014; Sadler *et al*., 2016). Moreover, drinking from nitrate contaminated wells could induce long-term effects on human health, including cancers (Inoue Choi *et al*., 2015; Jones *et al*., 2016).

The extensive use of phytosanitary products and pesticides in massive cultivation has also polluted groundwater and soil, resulting in hazardous effects on the ecosystems, as well as on non-target species such as humans and animals (Willhite, 2001; Plaza-Bolaños *et al*., 2012). These pollutants are persistent and can be transported to other environmental systems, such as ground and surface waters, the atmosphere and crops (Mirbagheri and Hashemi-Monfared, 2009). Of course, pesticides are indispensable in agricultural production. Worldwide, approximately 9000 species of insects and mites, 50,000 species of plant pathogens, and 8000 species of weeds damage crops, causing loss of fruit, vegetables and cereals productivity from pest injury levels of 78%, 54% and 32% respectively (Cai, 2008). For this reason, 4.6 million tons of pesticides are annually sprayed worldwide with mass applications of carbamate, organophosphorus and organochlorine insecticides, and also some herbicides and fungicides containing varying levels of mercury, arsenic and lead. Of that, only 1% of the sprayed pesticides are effective, while 99% are released to non-target soils, water bodies and the atmosphere (Zhang *et al*., 2011b). In Fig. 14.1, the worldwide pesticide consumption intensification in the period 1960–2010 is shown.

Besides crucial issues related to the pollution of air, water and soil, according to the Bulletin of the World Health Organization (WHO), there are more than 26 million human pesticide poisonings with about 220,000 deaths per year worldwide (Thundiyil *et al*., 2008). For these reasons, many organizations, such as the European Union, the United States Environmental Protection Agency and the United Nations, have released several recommendations to regulate the use and occurrence of pesticides in soil and water (USEPA, 1979; Stockholm, 2001; EU, 2004; Spanish Ministry of Environment, 2005).

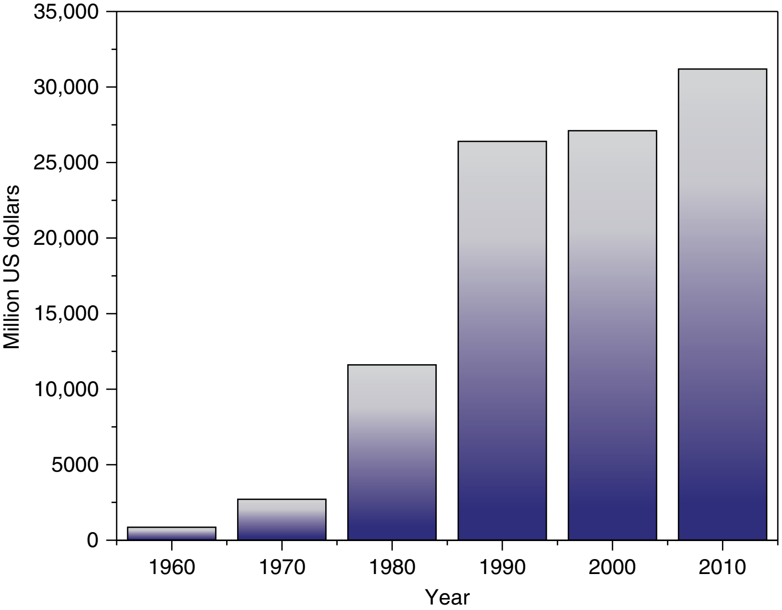

**Fig. 14.1.** Change of pesticide consumption reported as worldwide sale.

Another critical question related to the intensive farming system is freshwater use; in fact, agricultural production is currently responsible for 85% of global water consumption (Shiklomanov and Rodda, 2003) and is expected to double in 2050 (Tilman *et al.*, 2002). Moreover, the irrigated area might increase by a factor of 1.9 in the next 30 years, and climate change will probably aggravate water availability by modifying its geographic distribution worldwide (Lobell *et al.*, 2008). Unquestionably, the benefits of irrigation were uncountable, such as lower food prices, improving the quality of life for rural populations, higher employment and more rapid agricultural and economic development (Lü *et al.*, 2014). However, the sustainability of irrigated agriculture has been questioned, being correlated with negative environmental and economic effects. The agriculture intensification and the massive irrigation may generate: (i) soil erosion; (ii) worsening of water quality due to increased chemical levels; and (iii) proliferation of aquatic weeds and eutrophication (Galbraith *et al.*, 2005; Le *et al.*, 2010; Nyenje *et al.*, 2010; Pfister *et al.*, 2011; Misra *et al.*, 2016). The last, in particular, may generate loss of productivity due to low dissolved oxygen concentrations in water; however, the explosive growth of algae (cyanobacteria) and its production of toxin is of particular concern (Paerl *et al.*, 2001).

The detrimental effects of intense farming on the environment have raised severe concerns among environmentalists, and consequently spread the idea worldwide to encourage green policies to help develop and support more sustainable agriculture practices where high nature and/or conservation value are guaranteed by specific custom-made farming approaches. Starting from 1992, the United Nations Framework Convention on Climate Change (UNFCCC) was commissioned to reduce greenhouse gas emissions due to human activity, with the definitive objective of stabilizing greenhouse gas concentrations in the atmosphere at a level that would not interference with the climate system (United Nations, 1992). In particular, activities like the abuse of forested land for agricultural purposes and the expansion of agriculture based on intensive exploitations of resources/chemicals, among others, have been able in the last decades to emit increasingly huge amounts of carbon dioxide, methane and nitrous oxide in the atmosphere, contributing massively to increasing global temperatures. As an example, despite scientific uncertainty, from 600 million to 2.6 billion tons of carbon are estimated to be globally released from deforestation every year (Houghton *et al.*, 1992).

Subsequently, many other international agreements have been drawn up by the United Nations, including the Kyoto Protocol in 1997 and the Conference of Paris in 2015, setting a goal of limiting global warming to less than 2°C (3.6°F), compared to pre-industrial levels.

Hence, this issue was critically analysed by Sutter and colleagues, which asserted that only zero net anthropogenic greenhouse gas emissions, between 2030 and 2050, would reach the goal (Sutter and Berlinger, 2015). Nowadays, crop agriculture exploits 12% (1.6 billion ha) of the world's land. This caused a decline of about 3.3% (135 million ha) of forested area between 1990 and 2010, a misuse of 70%, of all water resources, a soil quality constraint in several regions (sub-Saharan Africa, Southern America, Southeast Asia, and Northern Europe) comprising ~ 50 % of the cultivated lands, and a massive pollution extent due to intensified use of fertilizers (FAO, 2011).

For these reasons, there is scope for governments and private sectors to foster the adoption of novel actions, including smart agriculture, for a wise use of resources. Smart agriculture entails the exploitation of multifarious approaches based on more energy efficient and environmentally friendly cross-cutting technologies, including: (i) the use of nanoformulations to increase the dispersion and wettability of agricultural formulations; (ii) crop growth control and soil analysis; and (iii) remote sensing, yield mapping and positioning systems. These technologies are pivotal to optimize the sustainability of farming processes and reduce their impacts on the environment and human health. Among them, sensor technology is gaining prominence in supporting sustainable agricultural practices, being able to:

- provide high-tech systems to evaluate crop maturity and their status health by *in situ* sensing of plant photosynthetic activity;
- detect and tune the amount of fertilizers and pesticides;
- monitor the physicochemical parameters of the soil;
- sense soil humidity and tailor irrigation, avoiding water misuse.

The last trends of nanotechnology in the design of innovative nanomaterials and nanodevices fulfils the needs of agriculture and the food industry. Indeed, nanotechnology proved its potential to revolutionize the farming system through the development of novel tools for accelerating disease detection, enhancing the ability of plants to absorb nutrients or pesticides, increasing yields and nutritional values, while conferring potential benefits that range from improved food quality and safety to reduced environmental impacts (Prasad *et al.*, 2014). It also furnishes the opportunity to realize smart sensors and delivery systems able to help the agricultural industry monitor chemical and physical parameters, tailor pesticide/fertilizer delivery to increase their efficiency, as well as combat pathogens.

The aim of this chapter is to provide an overview on the innovative and positive effects of nanotechnology in the agri-food sector in general, and specifically for agriculture application, with a main focus on nano(bio)sensors developed for the detection of soil humidity; nutrient/pesticide residues in water, soil, and crop; plant pathogens and pests.

## 14.2 Nanotechnology in the Agri-food Sector

In 2015, Parisi and co-workers asserted that:

> Nanotechnology is recognised by the European Commission as one of its six Key Enabling Technologies that contribute to sustainable competitiveness and growth in several industrial sectors. The current challenges of sustainability, food quality and safety, food security, and climate change are engaging researchers in exploring nanotechnology as a smart source for key improvements of the agrifood sector practices.
>
> (Parisi *et al.*, 2015)

The truthfulness of this statement has been largely demonstrated by the numerous types of nanomaterials that have been exploited in the last years in the agri-food sector, along with the whole food supply chain, from primary food production to final consumption, encompassing seed selection (Kagan, 2016), soil preparation (Majeed and Taha, 2013), pest management (Rai and Ingle, 2012; Grillo *et al.*, 2016), packing (Mahalik and Nambiar, 2010; Silvestre *et al.*, 2011), as well as raw material handling and control, transport and storage (Will, 2003). Some of the benefits of nanotechnology for the food sector are the development of new tools in molecular and cellular biology to enhance reproductive science and technology, conversion of agricultural and food wastes into energy, useful byproducts obtained by enzymatic nanobioprocessing, and disease prevention and treatment of plants and animals (Shrivastava and Dash, 2012).

Smart monitoring of food nutrients, as well as fast screening of biological and chemical contaminants, are also some of the key evolving issues challenging the assessment of food quality and safety that can be faced by nanotechnology in the development of custom-made sensors (Buonasera *et al.*, 2009; Scognamiglio *et al.*, 2010; Scognamiglio *et al.*, 2014). Several sensing systems exploiting nanomaterials have been described in the literature as valid alternatives towards conventional methodologies for:

- the analysis of food constituents (sugars, alcohols, vitamins and minerals) and contaminants (pathogens and toxins, heavy metals, pesticides, phenolic compounds);
- the evaluation of freshness and traceability (putrescin and cadaverine);
- the continuous monitoring of industrial process indicators (sugars, alcohols, amino acids).

The exploitation of nanotechnology in food logistics has also delivered several advantages to both farmers and consumers, thanks to effective advances in

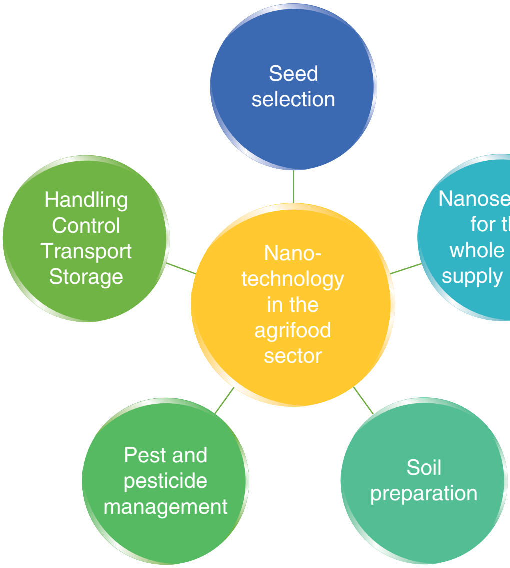

**Fig. 14.2.** Main applications of nanotechnology in the agri-food sector.

processes along the entire food supply chain from the food production, to processing, preservation, packaging, tracking, storage and distribution (Bowles and Lu, 2012). Figure 14.2 gives an overview of the most relevant applications of nanotechnology in the agri-food sector.

## 14.3 Nanotechnology in Smart Agriculture

The use of nanomaterials in the rural system is relatively new and the related literature is still sparse, needing further research efforts. The main applications of nanomaterials for agricultural purposes include plant breeding/genetic transformation (Ohadi Rafsanjani *et al.*, 2012), protection/production and germination/growth (Khandelwal *et al.*, 2016), pests and pathogen detection (Ghormade *et al.*, 2011; Rai and Ingle, 2012), and pesticide/herbicide residue monitoring (Patel, 2002; Khandelwal *et al.*, 2016), soil physicochemical parameter control (Stone *et al.*, 2010) and water purification (Khot *et al.*, 2012; Dervin *et al.*, 2016; Fraceto *et al.*, 2016). Nanomaterials, such as nanotubes, nanowires, nanoparticles or nanocrystals, can help in the realization of intelligent nanosystems for the controlled release in soil of nutrients and pesticides, minimizing leaching and improving their uptake by plants. They can improve the structure and function of pesticides by increasing solubility and enhancing resistance against hydrolysis, or as agents to stimulate plant growth (Fraceto *et al.*, 2016). These trials seek to diminish the amount of chemicals using smart delivery systems of both fertilizers and pesticides, decrease at the same time nutrient losses, and increment yields through optimized resources administration (Parisi *et al.*, 2015). Figure 14.3 provides an overview of the most relevant agricultural applications of nanotechnology.

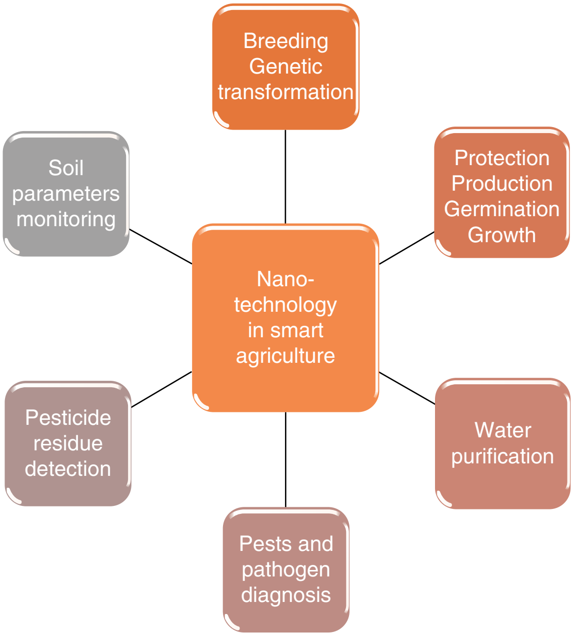

**Fig. 14.3.** Main applications of nanotechnology in the smart agriculture sector.

## 14.4 Nano(bio)sensors

Progress in nanotechnology has paved the way for the design of nano(bio)sensors with improved features in terms of sensitivity and versatility, thanks to the wonders of functional materials at the nanoscale. Nanobiosensors are biosensors in which nanomaterials are exploited or the immobilization of the biological recognition element over a transducer, generating an amplification of the analytical signal produced by the event occurring between the bioelement and its target analyte. Furthermore, the use of nanomaterials to functionalize bioelements can dramatically improve the stability and sensitivity of the bioelements, yielding also reproducibility and reliability. Finally, nanotechnology allows the miniaturization and the integration of biocomponents, transduction systems, electronics and microfluidics in complex architectures, able to perform continuous and in field monitoring, high throughput analyses as lab-on-a-chip devices, rapid and low-cost screening of chemicals in complex matrices using small sample volumes.

To date, modern nanomaterials have achieved a high degree of complexity, in terms of synthesizing functional tools with custom-made properties and controlled nanoscale dimensions. Numerous types of nanomaterials have been employed for biosensor development, including metal nanoparticles, magnetic nanobeads, quantum dots, nanotubes, nanowires, nanorods, nanofibres, as well as nanocomposites, nanofilms, nanopolymers and nanoplates. These materials are able to enhance the performance of detection systems, thanks to their unique and special chemical, mechanical, magnetic and optical properties, such as strong absorption band in the visible region, high electrical conductivity, and good mechanical features (Scognamiglio, 2013; Arduini *et al.*, 2016).

This led to the development of nano(bio)sensors with enhanced analytical performances in terms of response time, higher storage/operational stability, resistance towards environmental conditions, improved sensitivity, reduced sample volumes and easy sampling.

As affirmed by Pérez-de-Luque and co-workers (Pérez de Luque and Hermosín, 2013), 'The potential applications of nanosensors in agriculture are limited only by imagination'. Indeed, a huge literature documents the efforts and the challenges to realize nano(bio)sensors for agricultural commitments, with manifested advantages for the farmers, including simple use, low cost, miniaturization and portability, and effective operation in complex matrices without or with minimized sample preparation (Scognamiglio *et al.*, 2016).

Foremost applications of nano(bio)sensors for crop field sensing mainly include real-time control of crop growth, monitoring of field conditions (e.g. moisture level, soil fertility, temperature, crop nutrient status, insects, and plant diseases), and controlled release of fertilizers/pesticides via nanoscale carriers avoiding their overdose, improving productivity and reducing waste.

In combination with tailored nano(bio)sensors, wireless sensor networks positioned across cultivated fields can deliver spatio-temporal data on crop maturity and level of water and chemicals, prompting improved agronomic practices with reduced use of resources as well as maximized yields. In addition, robotics as satellites or drones for remote sensing can provide information on soil conditions, plant growth and weed infestation, as well as automated irrigation systems that, coupled with sensor technology, may have the potential to maximize the efficiency of water use.

In the following sections, an overview of the nano(bio)sensors developed and realized for agriculture has been provided, with special focus on the detection of soil humidity, soil nutrients, agrochemicals as residues in final products or in water and soils, and plant pathogens.

### 14.4.1 Nanosensors to detect soil humidity

Soil texture, moisture and water content are highly mutable parameters in space and time; however, the effects of such spatio-temporal variations on agricultural yields have scarcely been addressed in literature. Conventional approaches for the measurement of soil moisture can be classified into the following categories: (i) gravimetric; (ii) nuclear-based; (iii) electromagnetic; (iv) tensionmeter-based; and (v) hygrometric (Petropoulos *et al.*, 2013). Alternative analyses of surface soil water content are based on remotely determining the thermal and vegetation index by multispectral measurements performed by aircraft and satellites. These technologies are able to evaluate a wide range of surface radiant temperature and vegetation fractions to obtain data about surface humidity (Carlson *et al.*, 1994; Carlson, 2007). Nevertheless, these techniques display several drawbacks in terms of extensive time response and labour, low accuracy, need for individual calibrations, questionable long-term stability, environmental sensitivity, among others. In this context, nanotechnology is able to furnish amazing functional materials with humidity-sensing properties that have been widely exploited for the development of innovative humidity sensors for agricultural applications. Humidity sensors play an important role in quality management of the soil, environmental condition control, plant cultivation, greenhouse air conditioning, plantation protection, soil moisture monitoring and cereal storage.

Humidity analysis is based on the measure of amount of water vapour present in a gas mixture, such as air, that is usually expressed in relative humidity (RH), which is the ratio of the partial pressure of water vapour present in a gas to the saturation vapour pressure of the gas at a given temperature (Chen and Lu, 2005). Humidity sensors utilize changes in the physical and electrical properties of the sensitive elements when exposed to the different atmospheric humidity conditions of the surrounding environment, and provide a measure of the humidity due to some amount of adsorption and desorption of water vapour molecules.

Humidity sensors are mainly based on electrical transduction (impedance ionic or impedance electronic or capacitance type) (Farahani *et al.*, 2014) and exploit a hygroscopic material whose dielectric properties alter upon the absorption of water molecules. In particular, the sensing mechanism of these materials relays on the adsorption of the surrounding water vapour that enhances the surface electrical conductivity or the dielectric constant (Lee and Lee, 2005). In combination with these sensors, different materials including polymers, ceramics and composites have proven their advantages for humidity sensor application. Indeed, they hold virtuous properties such as chemical and thermal stability, high sensitivity, environmental adaptability, small humidity hysteresis and simple technique, and a wide range of working temperature.

However, investigations on the synthesis of novel materials are still required. Many efforts have been provided in the last years to improve the sensing properties in terms of response values, response/recovery speed, the long-term stability, by exploiting nanomaterials with excellent humidity sensing power, able to minimize the humidity hysteresis and to increase the sensitivity and repeatability. These include $Ba_{0.7}Sr_{0.3}TiO_3$ (Xiao *et al.*, 2008), $Na_2Ti_3O_7$ (Zhang *et al.*, 2008), $Bi_{0.5}K_{0.5}TiO_3$ (Zhang *et al.*, 2010), v-doped nanoporous $Ti_{0.9}Sn_{0.1}O_2$thin film (Anbia *et al.*, 2012), graphene oxide films (Zhao *et al.*, 2011), $Bi_{0.5}Na_{0.5}TiO_3$–$Bi_{0.5}K_{0.5}TiO_3$ (Zhang *et al.*, 2011a), Sr(II)-added $BaAl_2O_4$ composites (Vijaya *et al.*, 2007), single crystalline $Zn_2SnO_4$ nanorods, $Mn_{0.2}Ni_{0.8}Fe_2O_4$ nanoparticles (Köseoğlu *et al.*, 2013).

To take one example, Liu and co-workers synthesized $Na_2Ti_3O_7$ nanotubes and coated them on $Al_2O_3$ ceramic substrate to fabricate an impedance sensor for humidity using Ag-Pd as interdigitated electrodes. This sensor showed high humidity sensitivity in the range from 11% to 95% relative humidity, with a maximum hysteresis of less than 3% RH, and a quick response-recovery time (2 and 4 seconds, respectively) (Liu *et al.*, 2011b). Wang and colleagues also showed the high performance of a composite material made of nanocrystal $BaTiO_3$ and acrylic resin in developing an impedance sensor, obtaining a maximum humidity hysteresis of 3% RH in the range 7–98%, response and recover time of 15 and 120 s, respectively, in 33–98% RH, and a long-term stability up to 14 months (Wang *et al.*, 2002).

The use of graphene oxide films rather than others as sensing material significantly also showed its capability of improving the sensitivity and the response time of humidity sensors. For example, Zhao and colleagues described the resistive humidity-sensing properties of graphene oxide films. They fabricated a humidity sensor with complementary metal-oxide-semiconductor fabrication technology and microelectro-mechanical systems post-processing step by using different graphene oxide films dispersion concentrations, obtaining high sensing capacitance as well as fast response and good repeatability (Dai *et al.*, 2007; Zhao *et al.*, 2011).

Optical sensors have also showed tremendous advantages over their electrical counterpart, being capable of operating without interference from nearby electric or magnetic fields, and in a fast response time. The interaction of the water vapour with the sensitive material leads to a change in the optical parameters such as reflectance (Jen *et al.*, 2010), refractive index (Mohan *et al.*, 2012), wavelength shift (Liu *et al.*, 2011a) and photoluminescence (Zhang *et al.*, 2012). In this regard, opto-electronic sensors (Yadav *et al.*, 2010), surface plasmon resonance (SPR) sensors (Sharma and Gupta, 2013), fibreoptical chemical sensors (FOCSs) (Shukla *et al.*, 2004), and near-field Fabry-Perot (NFFP)-based optical fibre sensors (Consales *et al.*, 2011) have been reported in literature for humidity monitoring.

Many smart materials at the nanoscale have been exploited to develop optical sensors for humidity measurements. A composite material made from multi-walled carbon nanotubes and Nafion was synthesized by Lei *et al.* (Lei *et al.*, 2011) to design a surface acoustic wave resonator (SAWR) with high resonance frequency. This nanocomposite, used as humidity-sensitive film, was deposited on the surface of SAWR by drop-casting, being able to improve sensitivity and dynamic characteristic due to its large specific area and special ionic conductivity. Indeed, this sensor showed a high sensitivity up to 260 kHz/% RH, good linearity with $R^2 > 0.99$, high precision of 0.3% RH at low humidity level below 10% RH. The remarkable characteristics of graphene oxide as sensing material were also explored to design optical humidity sensors. In particular, Lim and colleagues (Lim *et al.*, 2014) coated a graphene oxide film onto a SU8 polymer channel waveguide using the drop-casting technique, obtaining a linear response of 0.553 dB/% RH in the range of 60% to 100% RH in less than 1 second.

Humidity sensors based on mechanical effects have been also widely described in literature. They are mainly mass-sensitive humidity sensors and micro-electro-mechanical resonant humidity sensors and are based on the changes in their electro-mechanical behaviour due to adsorption of water vapour. Major advantages of mechanical sensors are simplicity of construction and operation, low weight, small power requirement, and their ability to operate on highly reliable phenomenon. To cite one example, Wu and colleagues (Wu *et al.*, 2008) reported a highly sensitive humidity sensor configured by a 128YX-$LiNbO_3$ based surface acoustic wave (SAW) resonator with an operating frequency of 145 MHz. In detail, they synthesized camphor sulfonic acid doped polyaniline nanofibres and further deposited these on the SAW resonator as a selective coating. They showed that the nanostructured material possesses a high surface-to-volume ratio, large penetration depth and fast charge diffusion rate, providing relative humidities in the range 5–90%, excellent sensitivity and short-term repeatability. Finally, nanotechnology offers also the advantage to realize the miniaturization of sensor devices with numerous advantages such as low hysteresis batch fabrication, and ease of packaging/integration along with the corresponding cost reductions.

### 14.4.2 Nano(bio)sensors to detect soil nutrients

The use of fertilizers in agriculture has the main purpose of increasing productivity (Delgadillo-Vargas *et al.*, 2016). Many products are nowadays commonly used by farmers, who discovered their remarkable attributes as high performance, cost-effective products promoting plant growth, magnification and stabilization of fertilizers, and potent stimulation of soil life. Most fertilizers contain the three basic plant nutrients such as nitrogen, phosphorus, and potassium, as well as certain micronutrients such as zinc and other metals necessary for plant growth.

However, fertilizers have significant environmental implications being able, once released into the environment, to contaminate surface and surface-/groundwaters. Furthermore, industrial waste materials are often used in fertilizers as a source of zinc and other micronutrients, but they may contain also measurable levels of heavy metals such as lead, arsenic and cadmium. Comparable data at the European level on consumption of fertilizers in 2010 highlighted that France was the largest user of fertilizers in agriculture among EU countries (4.1 million tons), followed by Germany, Poland, Spain and the United Kingdom. Italy was sixth with just over 1.1 million (ISTAT, 2012). In Fig. 14.4, a worldwide picture of the use of nitrogen-, potassium- and phosphorus-based fertilizers is shown.

For these reasons, there is a crucial demand for carefully controlled fertilizer release by means of agricultural and environmental policies, but also through effective monitoring tools as sensors. Moreover, losses to the environment can be

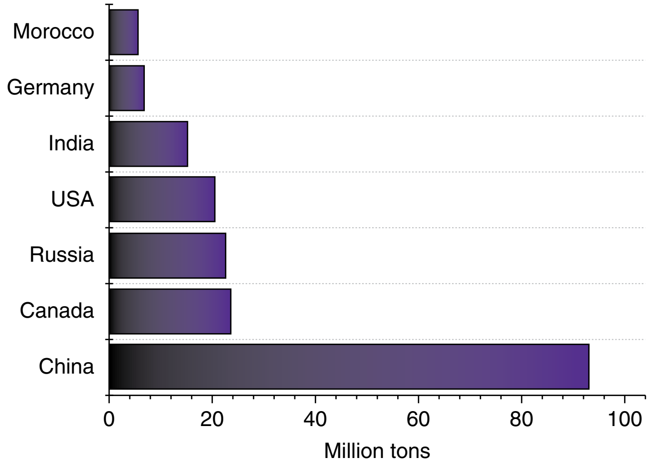

**Fig. 14.4.** Worldwide use of fertilizers (N-P-K World, 2016).

minimized if a reasoned fertilization is used, together with sustainable agricultural practices, such as crop rotation, planting cover crops and ploughing in crop residues. Here, reasoned fertilization means application of fertilizers in the correct weather conditions (to avoid runoff) at the appropriate stage in crop growth (so that plants take up the nitrogen quickly) and at the correct doses. In this context, nano(bio) sensors can assist these sustainable practices by accurately monitoring fertilizers in water and soil. Indeed, if soil analysis is combined with data on nutrients available to crops, a reliable basis for planning intelligent fertility programmes can be established. Nano(bio)sensors represent a precision technology able to support farmers to obtain information about spatial and temporal variations of fertilizer concentrations within the field in order to match inputs to site-specific field conditions.

Several electrochemical and optical sensors have been developed to evaluate soil organic matter or total carbon content, soil salinity, sodium content, residual nitrate, or total nitrogen content. Being fertilizer's major sources of nitrates, phosphates and urea in agriculture, this section focuses on the nano(bio)sensors described in the research literature for nitrates, phosphates and urea detection in both water, soil and plants.

Nitrates are mainly determined by the spectrometric, colorimetric and ion chromatography methods (Moo *et al.*, 2016). In the last years, sensor technologies showed their high potential in helping nitrate monitoring with advantages of in-the-field analysis, cost-effectiveness, and eco-friendly procedures (Birrell and Hummel, 1997; Badea *et al.*, 2001; Álvarez-Romero *et al.*, 2007; Yunus and Mukhopadhyay, 2011). However, the development of nano(bio)sensors for nitrate detection in agriculture is still restricted to very few examples. Gutés and colleagues (Gutés *et al.*, 2013) described an amperometric nitrate sensor based on an epoxy-copper electrode modified with palladium nanoparticles. They evaluated the effect of the palladium nanoparticles deposition towards nitrate electroreduction, highlighting the importance of these nanomaterials as a good candidate for nitrate monitoring in the range from 2 to 35 ppm in the field.

Also for phosphate detection, a huge number of sensors and biosensors have been designed and realized (Boyle *et al.*, 2016), while the realization of phosphate nano(bio)sensors are still restricted to environmental applications. A recent example is reported by Cinti and colleagues (Cinti *et al.*, 2016), who manufactured a novel reagentless paper-based electrochemical sensor for phosphate determination. This sensor provided the detection of phosphate ions using heptamolybdate as a reagent, with high reproducibility and long storage stability, achieving a detection limit of 4 μM over a wide linear range up to 300 μM. The authors challenged this cheap and green sensor in both standard solutions and real samples (river water), demonstrating its suitability for *in situ* phosphate determination and thus for soil quality control application in agricultural field. The same group (Talarico *et al.*, 2015) reported an automatable flow system for the continuous and long-term monitoring of the phosphate level using an amperometric miniaturized sensor. This sensor was based on screen-printed electrodes modified with carbon black nanoparticles for the monitoring of an electroactive complex obtained by the reaction between phosphate and molybdate that is consequently reduced at the electrode surface. The use of carbon black nanoparticles led to the quantification of the complex at low potential, being the carbon black nanoparticles capable of electrocatalytically enhancing the phosphomolybdate complex reduction at +125 mV versus Ag/AgCl without fouling problems. These enhanced analytical performances permitted the detection of phosphate at a low detection limit (6 μM), without significant interference, and good recovery percentages were between 89 and 131.5%.

Urea biosensors have been widely reported based on various analytical methods such as conductometry, spectrometry, potentiometry, coulometry, inductometry and amperometry (Dhawan *et al.*, 2009; Ali *et al.*, 2016). A huge number of urea nano(bio)sensors have been also reported in literature based on different nanomaterials including ZnO nanorods (Zhang *et al.*, 2004), multi-walled carbon nanotubes combined with tin oxide ($SnO_2$) nanoparticles (Zhang *et al.*, 2005), nickel nanoelectrodes (Hubalek *et al.*, 2007), iron oxide ($Fe_3O_4$) nanoparticles-chitosan (CH) based nanobiocomposite films (Kaushik *et al.*, 2009; Ali *et al.*, 2013), magnetic nanoparticles ($Fe_3O_4$ and $Co_3O_4$) (Ali *et al.*, 2016), graphene (Srivastava *et al.*, 2011). Nevertheless, these nano(bio)sensors are still in early stage applications since they have been challenged only in standard solutions, or they have been realized for biomedical field and *in vitro* diagnostics.

### 14.4.3 Nano(bio)sensors to detect pesticides

The increased use of pesticides has become necessary in the last decades to maximize agricultural productivity in order to meet demand from the growing population. The worldwide consumption of pesticides is estimated to be 2 million tonnes per year, capable of supporting around one-third of agricultural global production (Rapini and Marrazza, 2016). However, although their role is helpful in agriculture, pesticides are hazardous compounds affecting humans, non-targeted organisms and ecosystems (de Oliveira *et al.*, 2014). For this reason, nano(bio)sensor applications in pesticide detection are extremely timely, due to the requirement to support healthy agriculture by monitoring these compounds in the environment. Recent advances in the application of nanomaterials such as gold nanoparticles, carbon nanotubes, magnetic nanoparticles and graphene support ultra-sensitive and ultra-fast biosensing systems development, thanks to their superior electrical, mechanical, chemical and structural properties. Compared to most commercially available (bio)sensors, nanomaterial-based (bio)sensors have great advantages, e.g. high sensitivity, due to high surface-to-volume ratio; fast response time; ability to mediate fast electron-transfer kinetics; highly stability and longer lifetime (Scognamiglio, 2013).

Several kinds of nano(bio)sensors have been described in the research literature for the detection of pesticides (Table 14.1) in water and soil for agricultural applications, including:

- insecticides: mostly organophosphates, carbamates and organochlorines, they are very important for eliminating insects and maintaining high agriculture productivity;
- herbicides: mostly diazine, triazine and ureic herbicides, they are essential for weed growth control to implement agricultural crop production;

- fungicides: mostly dithiocarbamates, dicarboximide and organomercurials, they are crucial to control fungal disease on crops when applied on pre- or postharvest cultivations.

Pesticide monitoring in agriculture is a challenging task and requires cutting-edge technologies, due to the high complexity of the agricultural matrices as soil, water and crops. A huge number of nano(bio)sensors have been designed and realized for pesticide residue detection in water and food samples exploiting different types of nanomaterials, including carbon nanotubes (Yang *et al.*, 2010; Cesarino *et al.*, 2012; Liu *et al.*, 2012a; Zhang *et al.*, 2015), poly(3-hexylthiophene)-functionalized $TiO_2$ nanoparticles (Li *et al.*, 2011b), quantum dots (Zheng *et al.*, 2011), gold nanoparticles (Liu *et al.*, 2012b), nanometre-sized titanium (Li *et al.*, 2011a), silver dendrite nanostructure (Pang *et al.*, 2014), Prussian blue nanoparticles (Arduini *et al.*, 2015), poly-o-toluidine zirconium (IV) phosphate nanocomposite (Khan and Akhtar, 2011), nano $TiO_2$/Nafion composite (Kumaravel and Chandrasekaran, 2011), nano-$ZrO_2$/graphite/paraffin (Parham and Rahbar, 2010), carbon black (Talarico *et al.*, 2016).

Soil is also a crucial resource in agriculture, but due to its ability to retain chemicals such as pesticides, it absorbs these compounds into soil particles. These compounds can be persistent or degraded into secondary products, causing pollution of subterranean aquatic systems and living organisms. Being a complex matrix retaining pesticides and other residues, soil analysis is a difficult procedure, since pre-treatment procedures are required to extract pesticides for their quantification. Several extraction methods have been described in the literature, including matrix solid-phase dispersion (Shen *et al.*, 2007), single-drop micro extraction and solid-liquid extraction with low temperature partitioning (Soares

**Table 14.1.** Classification of the main exploited pesticides in agriculture. (Adapted from Rapini and Marrazza, 2016.)

| Groups | Class | Main examples |
|---|---|---|
| Insecticides | Organophosphates | Malathion, parathion, acephate, azinphos-methyl, chlorpyrifos, diazinon, dimethoate, phosmet |
| | Carbamates | Aldicarb, carbaryl, carbofuran, fenoxycarb, methiocarb, methomyl, oxamyl, primicarb |
| | Organochlorines | DDT, chlordane, dicofol, endosulfan, endrin, heptachlor, lindane, methoxychlor |
| Herbicides | Diazines | Bromacil, lenacil, cloridazon, piridate, bentazone |
| | Ureas | Chlorotoluron, diuron, fenuron, isoproturon, linuron, metoxuron, monolinuron, neburon, chlorimuron-ethyl, chlorsulfuron, metsulfuron-methyl, sulfometuron-methyl, triasulfuron |
| | Triazines | Atrazine, ametryn, cyanazine, prometryn, propazine, simazine, terbutryn |
| Fungicides | Dithiocarbamates | Mancozeb, ferbam, maneb, metiram, propineb, thiram, zineb, ziram |
| | Dicarboximides | Chlozolinate, iprodione, procymidone, vinclozolin |
| | Organomercurials | Methyl-mercury, phenyl-mercuric-acetate |

*et al.*, 2015), QuEChERS (Wilkowska and Biziuk, 2011), as well as pressurized liquid extraction or microwave-assisted extraction, headspace solid-phase micro extraction, solid-phase micro-extraction (Andreu and Picó, 2004).

Once extracted, pesticide analysis is generally accomplished by means of gas or liquid chromatography coupled to mass spectrometers, as well as capillary electrophoresis. These techniques show many advantages in terms of high sensitivity and multiple detection. On the other hand, disadvantages such as long extraction time, large consumption of organic solvents, and requirement of expensive and complex instrumentation, can make these procedures less helpful for sustainable, fast and in-field analysis. Very few examples of nano(bio)sensors for soil analysis of pesticides have been described in the literature, probably due to the difficulties related to sample preparation.

To take one example, Yu and colleagues (Yu *et al.*, 2010) described a tyrosinase/$TiO_2$ nanotube-based biosensor for the detection of atrazine in soil samples (Fig. 14.5). The authors realized a biocompatible tubular structure by vertically growing $TiO_2$ nanotubes and immobilizing tyrosinase enzyme at the interface, resulting in a sensitive, robust and rapid response to atrazine in the ppt range. Indeed, the presence of highly ordered and vertically aligned nanotubes allowed for a larger surface area for the enzyme loading in the inner nanospaces, as well as a better electron transfer, resulting in a higher sensitivity. In addition, $TiO_2$ nanotubes possess excellent characteristics as biomaterial, thus permitting biocompatibility, as well as a better robustness of the immobilized biological recognition elements. Furthermore, the authors challenged the present nanobiosensor in soil by simply diluting samples with buffer until atrazine was comprised in the linearity range, with a standard deviation less than 5% when compared with HPLC data.

A similar nanobiosensor was described by Dong and colleagues (Dong *et al.*, 2013) for ultra-trace detection of pesticides in water and soil samples. They fabricated an amperometric biosensor by immobilizing acetylcholinesterase enzyme on multi-walled carbon nanotubes-chitosan nanocomposites modified glassy carbon electrode (Fig. 14.6).

The pesticide was measured evaluating its inhibition capacity on the enzyme using 5,5-dithiobis(2-nitrobenzoic) acid (DTNB) as electrochemical mediator.

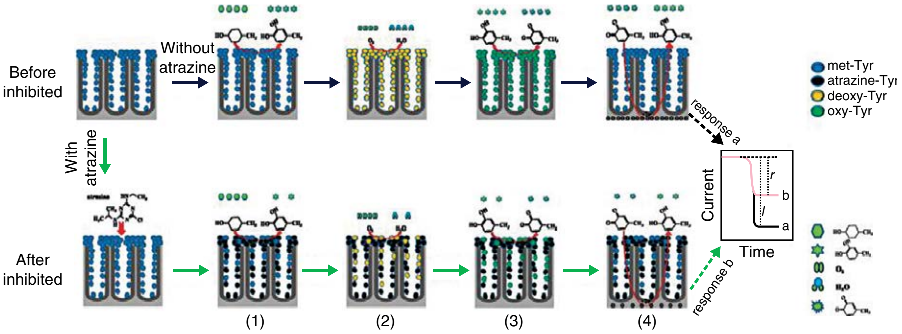

**Fig. 14.5.** Schematic illustration of the nanobiosensor proposed by Yu and colleagues (Yu *et al.*, 2010). Reprinted with permission from Environmental Science Technology. Copyright (2016) American Chemical Society.

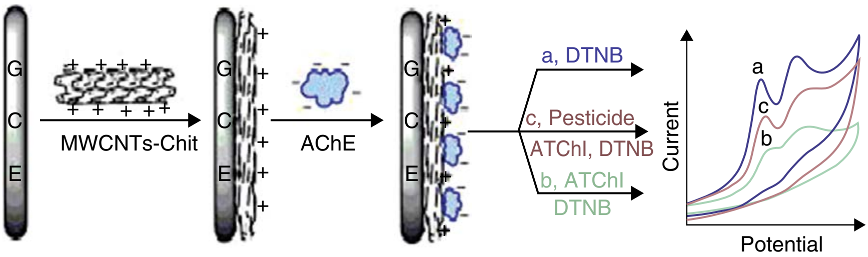

**Fig. 14.6.** Schematic diagram of the nanobiosensor proposed by Dong and colleagues (Dong *et al*., 2013). Reprinted with permission from *Analytica Chimica Acta*. Copyright (2016) Elsevier.

The excellent conductivity and favourable biocompatibility of the realized nanocomposite allowed for a high sensitivity towards methyl parathion in a concentration range between $1.0 \times 10^{-12}$ and $5.0 \times 10^{-7}$M and a detection limit of $7.5 \times 10^{-13}$ M. In addition, the authors further demonstrated the practicality of the proposed nanobiosensor by means of recovery tests carried out on spiked soil samples, after a simple pre-treatment to homogenate, sieve and air-dry the soil at room temperature, with results in agreement with the given concentration and recoveries from 93.8% to 103.2%.

### 14.4.4 Nano(bio)sensors to detect plant pathogens and pests

Productivity of crops is daily threatened by the incidence of pests, especially weeds, pathogens and animal pests; the relative impact on farm economy is closely related to these harmful pests and for this reason crops must be protected with appropriate measures.

In this context, nano(bio)sensors recently demonstrated their helpfulness even in the detection and quantification of minute amounts of contaminants such as viruses, bacteria, toxins in agriculture and food products (Boonham *et al.*, 2008; López *et al.*, 2009; Sharon *et al.*, 2010). This novel class of biosensors may positively affect the economic aspect of the farm, due to its contribution in smart agriculture methods, in particular monitoring in real-time soil conditions and crop growth over vast areas and detecting infectious diseases in plants before visible symptoms appear. In addition, nanotechnology powerfully supports the design of innovative autonomous/robotic biosensors linked into the GPS system for extensive, continuous and remote control.

More generally, the 'nano-know-how' influence in research outcomes has become an important reality (Khot *et al.*, 2012). Indeed, despite the use of smart nanomaterials for labelling and/or immobilization of the biological recognition elements on tailored supports, nanotechnology can be also helpful for the construction of nanodevices capable of operating on the structure of sensor systems, including microfluidics and instrumentation. As evidence, we cite nano-chips, which represent the state of the art in microarray technology, being able to detect several molecules by electrochemical and optical multi-analysis platforms.

Nucleic acid-based nano-chips, for example, show high sensitivity and specificity in the detection of bacteria and viruses, since single nucleotide changes can be revealed after target analyte binding (López *et al.*, 2009). In comparison with conventional methodologies, nanotechnology-based sensors for pathogen detection show important advantages in terms of speed, efficiency, sensitivity and portability, as shown in Table 14.2.

Quantum dots are one of the most utilized nanomaterials; they are a class of luminescent semiconductor nanocrystal that offers several advantages over organic dye-based broad excitation spectra (Medina-Sánchez *et al.*, 2012; Edmundson *et al.*, 2014; Syed, 2014; Kashyap *et al.*, 2015). Several nano(bio) sensors have been recently designed exploiting quantum dots to detect virus, fungi and plant pathogens. Safarpour and colleagues developed a quantum dots FRET-based biosensor for an efficient detection of *Polymyxa betae*, a vector of beet necrotic yellow vein virus responsible for Rhizomania disease in sugar beet (Safarpour *et al.*, 2012). Instead, Rad *et al.* created an immunosensor FRET-based with quantum dots for the detection of *Candidatus Phytoplasma aurantifolia*. This immunosensor presented 100% specificity with a detection limit of 5 *Ca. P. aurantifolia* $\mu l^{-1}$ (Rai and Ingle, 2012). Bakhori and colleagues exploited the same FRET technology for the detection of synthetic oligonucleotide of *Ganoderma boninense*, an oil palm pathogen (Bakhori *et al.*, 2013). They modified quantum dots with carboxylic groups and conjugated them with a DNA probe, obtaining high sensitivity with a LOD of $3.55 \times 10^{-9}$ M.

Recently, metal nanoparticles have been also used in biosensor design (Kashyap *et al.*, 2016). For example, gold nanoparticles have been utilized for sensor functionalization in several examples of sensing systems for pathogen detection, thanks to their high surface-to-volume ratios, offering lower LODs and higher specificity than conventional strategies (Wang *et al.*, 2010; Singh *et al.*, 2010). Zhao and colleagues presented an electrochemical enzyme-linked immunoassay using gold nanoparticle tags with antibodies of horseradish peroxidase to detect *Pantoea stewartii subsp. stewartii* plant bacterial pathogen. Their analyses revealed that, in comparison to conventional ELISA assay, the detection was 20 times more sensitive, reaching a detection limit of $7.8 \times 10^3$ CFU/ml (Zhao *et al.*, 2014).

Gold nanorods have been also exploited, as reported by Lin and colleagues (Lin *et al.*, 2014). They developed a label-free SPR immunosensor for the quantification of two viruses of orchid Cymbidium mosaic virus (CymMV) or Odontoglossum ringspot virus (ORSV). They obtained LODs of 48 and 42 pg/ml for CymMV and

**Table 14.2.** Main diagnostic techniques for plant pathogen detection. (Adapted from Kashyap *et al.*, 2016.)

| Technique | Time to results | LOD | Specificity | Sensitivity | Portability |
|---|---|---|---|---|---|
| Plating | 1–3 days | 1 CFU $ml^{-1}$ | Good | Poor | Poor |
| Immunoassays | 1–2 h | 1 pg $ml^{-1}$ | Moderate | Moderate | Very good |
| Nucleic acid assays | 6–12 h | $10^3$ CFU $ml^{-1}$ | Very good | Good | Moderate |
| Nano(bio)sensors | 0.5–1 h | 1 fmol $l^{-1}$ | Excellent | Very good | Excellent |

ORSV in leaf saps, respectively, much lower than the LODs of 1200 pg/ml obtained for both viruses by ELISA. The authors reported that the device was able to discriminate between healthy and infected plants in a few minutes, and further quantitatively analyse the infection level.

Recently, an electrochemical DNA biosensor for the identification of a soil-borne fungus *Trichoderma harzianum* and crude DNA taken from real samples was successfully developed by using a ZnO nanoparticles/chitosan nanocomposite modified gold electrode (Siddiquee *et al.*, 2014). This nanobiosensing system was capable of detecting the target analyte at concentration ranges of $1.0 \times 10^{-18}$–$1.82 \times 10^{-4}$ mol $l^{-1}$, with a LOD of $1.0 \times 10^{-19}$ mol $l^{-1}$.

Apart from nanoparticles, nanomaterials such as carbon nanotubes, graphene, nanowires and nanocomposites have widely helped the development of nanosensing platforms for the detection of pathogens and mycotoxins (Malhotra *et al.*, 2014). Indeed, a plethora of nanostructures has been synthesized for sensor development, with different properties and applications (Khiyami *et al.*, 2014; Savaliya *et al.*, 2015), providing to the farmers easy-to-use, fast and portable nano-diagnostic kits in support of effective prevention and management of epidemic diseases.

In recent years, the use of nanosilica has opened a novel research sector for the monitoring of plant health. In particular, nanosilica is able to control insects by absorbing them into cuticular lipids, without altering the genetic character of insects (Mewis and Ulrichs, 2001; Barik *et al.*, 2008). For example, Yao and colleagues combined nanosilica-based fluorescent probes with antibodies to identify *Xanthomonas axonopodis* pv. vesicatoria, which is responsible for bacterial spot disease in Solanaceae plants (Yao *et al.*, 2009). In this study, the organic dye tris-2,2'-bipyridyl dichlororuthenium (II) hexahydrate was included as a label in the core of silica nanoparticles to perform fluorescence tests.

Furthermore, nanochannels and nanopores have been also utilized for the design of innovative and sensitive nano(bio)sensing systems for the detection of pathogens and pests (de la Escosura-Muñiz and Merkoçi, 2016; Khater *et al.*, 2017). The natural selective transport in nanochannels and nanopores (protein-based ion channels), common in living systems, is a new approach for the application in nano(bio)sensors. In particular, new advances in this context and the integration of nanochannels with biomolecules and synthetic receptors can be fundamental for the design of smart nano(bio)sensors useful in environmental analyses.

In Fig. 14.7, the most exploited nanomaterials for the design of nano(bio)sensors involved in the diagnosis of plant pathogens are shown.

## 14.5 The Nanobiosensor Trade

The global market for biosensors was valued at US$12.963 million in 2014, and it is expected to grow at a compound annual growth rate (CAGR) of 9.7% during 2015 to 2020, to reach $22.490 million by 2020. In particular, applications of sensors for biomedicine and life sciences dominate the market, accounting for 99%, followed by agri-food analysis, environmental control and

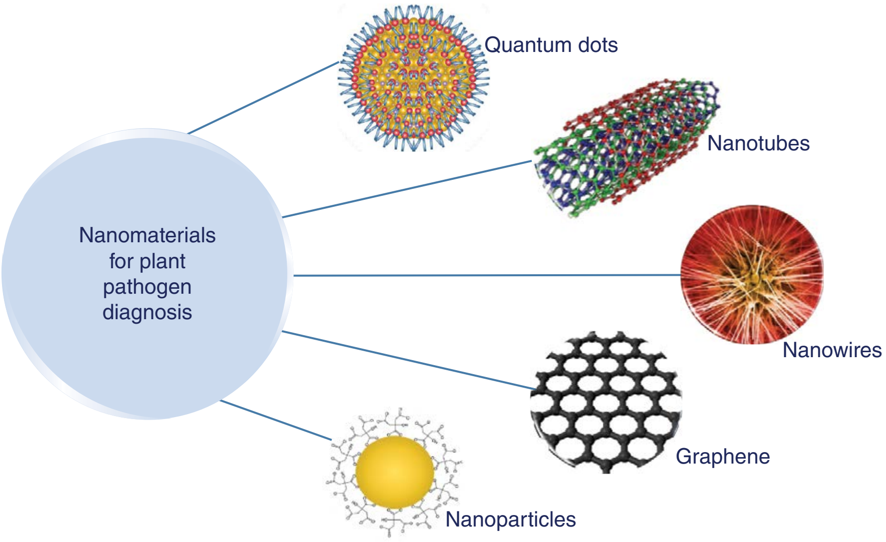

**Fig. 14.7.** Main nanomaterials exploited for the development of nano(bio)sensors for plant pathogen diagnosis. (Adapted from Kashyap *et al.*, 2016.)

remediation applications. Many companies worldwide have commercialized biosensing devices for agri-food applications for the evaluation of food quality and safety, for food process control, or for the realization of intelligent food packaging (Antonacci *et al.*, 2016).

Several companies invested their resources also in the development of sensing systems for sustainable farming, including open platform sensors capable of plant health measurement, water-quality assessment, vegetation index calculation, and plant counting, as well as systems for aerial mapping and imaging by means of unmanned aerial systems (UAVs) or drones. These efforts aim to support farmers to adopt an effective use of products for plant protection and fertilization, as well as to provide data on soil parameters, increasing productivity, reducing inputs and maximizing yield potential.

From this viewpoint, nanotechnology could pave the way to provide innovative nano(bio)sensors custom-made according to the requirements of the farmers, to foster more sustainable and concrete agricultural practices and to augment crop yields without impacting on the environment and human/animals health. However, there is a potential market still to be established. A search for articles and reviews on Google Scholar combining the terms ‘commercial’ and ‘nano(bio)sensors’ revealed 5 items, in comparison with ‘commercial’ and ‘biosensors’ terms, which revealed 913 items (accessed November 2016). This great discrepancy highlights how R&D on nano(bio)sensors is still constrained at an early stage, perhaps due to the lack of academic research and the industrial institutions to deal with arguments on the realization of commercial nano(bio)sensors. Nevertheless, to face the real need of the market in the realization of automated integrated systems the convergence of cross-cutting technologies like bioinformatics and rational design, microfluidics, robotics, Internet of Things, and nanotechnology, will make real the industrial manufacture of nano(bio)sensors for smart agriculture.

## 14.6 Future Perspectives and Conclusions

Failure to obtain data about soil characteristics and crop quality in a rapid and inexpensive manner remains one of the biggest limitations of precision agriculture. Several research efforts have been attempted to develop sensors for measuring mechanical, physical and chemical properties of water and soil as well as plants. Applications of nanotechnology as a high multi-scattered and cross-sector discipline in the agri-food sector may help to obtain innovative analytical tools with high reproducibility and controlled properties, scalability and affordable cost. The discovery of remarkable functional materials at the nanoscale led to the development of next-generation nano(bio)sensors with numerous advantages beyond their cognate biosensors, in terms of highest efficiency, ultra-sensitivity, augmented surface-to-volume ratio, stable under storage/working conditions, minimal reaction time, accuracy, reproducibility, biocompatibility, portability, low cost and so on. However, nano(bio)sensors are still in their infancy. In this sense, the convergence of cutting-edge technologies, including novel sustainable functional materials (e.g. nano-cellulose), microfluidics, 3D printing, Internet of Things, and solar cells will have a giant impact on nano(bio)sensor progress for smart agriculture. Indeed, in the face of rising pressure from climate change, growing populations and decreasing crop yields, nano(bio)sensors will have a significant role in the future of food and agriculture, being able to: (i) improve the quality of crops by maximizing the farmer/customer satisfaction and at the same time the environmental protection; (ii) use the most modern hardware and software technologies according to standards to reduce delivery times; (iii) allow continuous and real-time monitoring of critical parameters for enhancing the productivity and ensuring compliance with mandatory hygiene and traceability rules.

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# 15 Current Trends and Future Priorities of Nanofertilizers

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## 15.1 Introduction

The current view of environments and how to fertilize them is based on reductionist models, where each part of the environment is studied separately. In other words, the soil is seen as a separate entity; the amount of fertilizer required is another block; the root systems of the crop are another; and so on. A good way to understand this scenario is to visualize how phosphorus is used today and what its fate is.

Being a macroelement indispensable to agriculture, phosphorus has no substitute in food production (Cordell *et al.*, 2011) and is a chemical element that is also essential to life, since it is a key component in cellular communication, cell membranes, ATP, DNA and so on. Currently, agriculture is based on the use of chemical fertilizers, which are applied indiscriminately and at large volumes. Without them, it is nearly impossible to produce enough food to feed the growing world population, mainly because of soil exhaustion and degradation. However, how are phosphorus-based fertilizers used? Let's consider a simplified view of what occurs today. Plants extract phosphorus from the soil, through aqueous soil solution. If 100% of a given dose of phosphorus is applied, only 15% goes to the plant; i.e. 85% is lost. This lost portion goes into the soil, ending its journey in the water bodies, resulting in environments with extra phosphorus, which leads to eutrophication. Something is wrong there: it is easy to see that the actual habits of fertilizer usage are unsustainable. Nearly 80% of each dose of phosphorus is lost due to lack of technology used with our current fertilizers and also because we are not thinking of the crops holistically (Carpenter *et al.*, 1998; Sims *et al.*, 2000; Schmid Neset *et al.*, 2008; Cordell *et al.*, 2009; Cordell *et al.*, 2011; Dawson and Hilton, 2011). Here it is important to highlight that the source of phosphorus used on agriculture today is basically extracted from mines, and has a limited life

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span. Phosphorus is becoming increasingly scarce (Gilbert, 2009) and the fact we are wasting nearly 85% of what we extract, it is urgent to produce phosphate fertilizers that are more efficient.

At this point, we may ask ourselves questions like 'How does nature build things?', and especially 'How does nature build things with 100% effectiveness, in low temperatures, without hazardous chemicals?' Fortunately, some of our developments seem to be going in this direction and some created products already exist in nature in a more elegant form. Janine Benyus once said that sometimes engineers challenge her to solve the problem of crusting pipes with 'natural tools' (Benyus, 2002). Crusting is a build-up of minerals inside pipes, which block them up after a certain amount of time. Because of this tendency, engineers must flush the pipes with toxins or hazardous chemicals, or even dig them up. What causes this problem is the accumulation of calcium carbonate inside pipes. At this point, Benyus reminded them that a seashell is made of calcium carbonate as well. But, in fact, nobody sees a seashell in a state of uncontrolled growth, because it is controlled by the exudation of a protein that stops crystallization: a simple self-assembly of proteins, which occurs at the nanoscale. Indeed, today we have an environmentally friendly way to stop scaling in pipes: TPA (Tissue Plasminogen Activator), a product that bio-mimicks that seashell protein. This example translates the future priorities of nanotechnology to agriculture: the search for information and integration of research fields to work on agrosystems practices based on nano-inspired biomaterials that possess levels of adaptivity, multi-functionality and that are eco-friendly.

By these means, this chapter proposes that we realize and accept, once and for all, nature's challenges and, therefore, see and take advantage of the time-tested ideas on how nature builds things, and find a way to reproduce them in our laboratories and, ultimately, use in our agricultural systems. In this context, it is proposed here that nanotechnology must be seen as an adaptive gene, a tool to build things bottom-up, learning from nature.

## 15.2 Current Trends

Due to the low efficiency of conventional chemical fertilizers (as pointed out in the previous section) and their outdated management on crops, nanotechnology approaches to agriculture play an important role in the efficiency of transport, delivery and plant uptake of nutrients. In the same scenario, there is a growing concern around water and soil contamination by toxic metals and organic molecules. However, it is a little-known fact that our water bodies and soils contain significant levels of pollution caused by fertilizers that exceed the baseline established by environmental and even regulation authorities.

### 15.2.1 Controlled and efficient delivery of nutrients

Harvests of many crops have begun to decrease as a consequence of excessive fertilization and reduction in soil organic matter and structure. Because of this, the trend in agricultural systems is to changing the situation by accelerating plant growth and productivity using new approaches. Researchers and agronomists are accomplishing these goals by usage and application of nanofertilizers, opening perspectives to the development of new products and practices in order to assess the evolution of plant nutrient uptake and response. In spite of this, fertilizers and nanotechnology embrace three major areas of research: (i) encapsulated fertilizers inside nanoporous cores; (ii) fertilizers coated with thin polymer film; and (iii) fertilizers as nanoparticle or nanoemulsions (El-Bendary and El-Helaly, 2013). Here, it should be pointed that there are several pathways to promote an encapsulation of polymeric materials (such as polymers and dendrimers), fullerenes, carbon nanotubes, nanosponges and other fabrication methods for the safe storage and transportation of active ingredients of a formulation. By using the fertilizers in encapsulated systems, the chemicals can be protected against biotic and abiotic factors, reducing the initial amount of fertilizer applied and the waste to the environment, allowing, at the same time, the sustainable release of the active principles (Chen and Yada, 2011).

Through these pathways, nanofertilizers have the potential to combine several features of nanoscale materials with the controlled, sustainable and efficient release of fertilizer, so avoiding unwanted nutrient leaching to soil and water. However, attention should be paid to the fact that the effects of nanofertilizers in plants change with the plant species, the plant stage and the characteristics of the nanomaterial (Abdel-Aziz *et al*., 2016).

Faced with a wide range of applications and possibilities, researchers are still discovering the differences between fertilizers in bulk form and their nanoparticulated form. Recently, Abdel-Aziz and collaborators found that chitosan nanoparticles loaded with nitrogen, phosphorus and potassium (NPK) applied to leaves are able to enter via the stomata and have no need to interact with the soil. Also, the authors showed that after treatments with chitosan-NPK nanoparticles, some species of wheat plants on sandy soil show an increase in harvest, crop and mobilization indexes. Surprisingly, the authors also discovered that the life cycle of the nanofertilized wheat plants was reduced in relation to the controls using NPK in bulk form. The nanofertilizer reduces the period to 130 days, compared with 170 days, for yield production from the period of the beginning of the wheat crop. Consequently, it is possible to conclude that for *Triticum aestivum*, NPK nanoparticles were responsible for accelerating plant development and productivity (Abdel-Aziz *et al*., 2016).

Nanofertilizers as nanomaterials applied to the crops can also influence plant growth in synergistic or antagonistic ways, or even show no effect on crop development (Fageria, 2001). As an example, the effect of biologically transformed ZnO nanoparticles on clusterbean (*Cyamopsis tetragonoloba* L.) can be cited, since its influence on the improvement of native phosphorous mobilizing enzymes and nanoinduced gum production has been investigated (Raliya and Tarafdar, 2013). The ZnO nanoparticles were used via a foliar route (10 ppm) on the leaf in plants with 14-day clusterbean. A noteworthy enhancement in plant biomass, root length, rhizospheric microbial population, alkaline phosphatase and other parameters was detected over the control in 6-week-old plants, due to application of nano-ZnO (Fig. 15.1).

**Fig. 15.1.** Effect of nanofertilizer on growth of clusterbean. Reproduced with permission of Springer from Raliya and Tarafdar (2013) ZnO nanoparticle biosynthesis and its effect on phosphorous-mobilizing enzyme secretion and gum contents in clusterbean (*Cyamopsis tetragonoloba* L.).

Nanoparticles as fertilizers, their structure and function at nanoscale, plays an important role in the macroscopic expression of phenotype of clusterbean plant (4-week old) under treatment with O ZnO (ordinary zinc oxide) and n ZnO (nano zinc oxide).

Besides the encapsulated techniques, the bulk form of fertilizers can be modified with engineered nanoparticles, giving them new properties and usages. In this context, Cai and collaborators introduced the term 'loss control fertilizer' (LCF) for controlling nitrogen loss to the soil environment. The authors added a specific amount of modified attapulgite to the nitrogen fertilizer in bulk form and they observed that nitrogen can self-assemble into 3D micro- or nano-networks through hydrogen bonds and other molecular forces. This self-assembly mechanism actually increases the nitrogen spatial scale (Cai *et al.*, 2014). This finding is a great example of how practical nanotechnology can be when applied in the agricultural context. Smart modifications can produce huge improvements in the usage and efficiency of a fertilizer.

Because soil and organisms are both living things, the pharmacology sector is sometimes able to exchange information and models with the food and agriculture sectors. Monreal and collaborators proposed a model of an intelligent nanofertilizer platform for efficient delivery of microelements into the soil of agrosystems. The model proposes an understanding between the communications from living cells in the crop rhizosphere by the signalling networks established under microelements deficiency. Their approach may support development systems that can improve crop yield and decrease the environmental impacts of agriculture worldwide (Monreal *et al.*, 2016).

### 15.2.2 Nanotechnology for recovery of nutrients

Typically, technologies of water and soil decontamination are employed to remove several pollutants, including the excess of nutrients, mainly phosphate.

These technologies include methods of adsorption, precipitation, mineral-based sorbents (microporous), as well as filtration. Due to their low efficiency, generally, researchers and stakeholders are now using nanotechnology to remove high and low concentrations of nutrient pollutants from the environment. Inside nanotechnology, the most common methods known are sorbent microporous nanoparticles and nano-filtration. However, despite the fact that nanoparticles are known as a suitable sorbent, they possess an unknown environmental fate and toxicity. Nano-filtration, on the other hand, has a high cost for nutrient removal.

The use of magnetic nanoparticles has already been reported (Tu *et al.*, 2015) for phosphate removal from waste- and freshwater. Tu and collaborators (2015) showed that $Fe_3O_4$ nanoparticles, generated from the ferrite process, spontaneously and successfully removed phosphate through the adsorption of ions from aqueous solutions. The authors also showed that magnetic nanoparticles, under specific conditions, promote desorption of phosphate from the magnetic adsorbents. The desorption mechanism makes the removal and recovery process of nutrients feasible, since the adsorbent and nutrient can be recovered.

The removal of nitrogen and phosphate of effluent from anaerobically digested swine wastewater (anaerobic bioreactors) by nanozeolites was report by Chen and collaborators (Chen *et al.*, 2012). The authors reach a removal efficiency of N and P of 51% and 98% respectively for all experiments done, showing that the nanostructures of zeolite synthesized from fly ash particle increased the levels of specific surface area and cation exchange capacity at times of 40 and 104, compared to raw fly ash (bulk form).

Recently, materials science and environmental researchers united their knowledge and started combining technologies and methods to improve the features of nanoparticles to work as a nano-adsorbent and nano-absorbent of pollutants. These nanocleaners are commonly built to have hydrophilic and hydrophobic layers (generally surfactants) in order to promote the solubilization and/or (ad/ab)sorption of the target pollutant, low degree of sorption onto soils and high dispersion stability in the water medium (Kim, 2012). Despite the existence of just a few publications in this area of knowledge, this path should be urgently explored, since mineral exploitation is almost exhausted; scientists and engineers need to give the nanocleaners specific jobs, to find, remove and recover nutrients in pollutant form.

## 15.3 Trends in Nanofertilizers

### 15.3.1 Back to the basics: reverse-engineering nature

In the age of technology, access to information is as simple as a mouse-click. However, this readiness of information has influenced how we see the world, how we view science and how we manage the world over the last decades. One of the consequences is the distance between humans and the environment. This leads us to the agricultural model and system: the prioritization of volume, the quantity of harvests as a priority over the environment or the agrosystem as a whole entity. Nowadays it is crystal clear that this model of industrial agriculture is no longer sustainable and is forcing man to search for another approach, another technology based on nature.

There is a recent and growing trend supporting the idea that man must search for new patterns modelled on nature. Nature, by itself, has selected materials, mechanisms and machineries through billions years of development, discovering how to work at a maximum achievement of operation with a minimum input of energy.

Fertilizer research and application should lead to an age whose foundations are based not only on what can be extracted from nature, as the previous section showed, but also on what can be learned and built from it. Doing things the way nature does, researchers have the possibility to change the way in which food is produced, since we have the ability to not only deliver things, but to deliver them by interaction of smart structures with a specific surrounding environment. Reverse engineering is pointed out as a primary endeavour to explore how a biomachine was designed, atom by atom, to accomplish its function, whether inside a cell or its expression on the macroscale.

### 15.3.2 Prospect of nanofertilizer

Several studies have documented that soil properties vary across farm fields, causing spatial variability in crop productivity (Khosla *et al.*, 2002; Fleming *et al.*, 2004; Mzuku *et al.*, 2005). This non-uniform variability can vary from three to four paces in length (assuming that 1 pace = 0.75 m) (Fig. 15.2), depending on the place, and it can be attributed to agricultural production practices, parent material of the soil, microbiology diversity, temperature, moisture and nutrient levels. In other words, soil variability occurs due to changes in properties over space and time as a result of continuous interactions between the lithosphere, biosphere and atmosphere (Robert, 1993); and with a variability of properties so accentuated over the majority of soils, it is very difficult and expensive to establish, across farm fields, specific and well delineated zones of custom management of soil treatment and application of fertilizers. The current solution to this issue is to do a mathematical interpolation and generalize the nutrition treatment of an environment in order to obtain an average yield of crops. However, instead

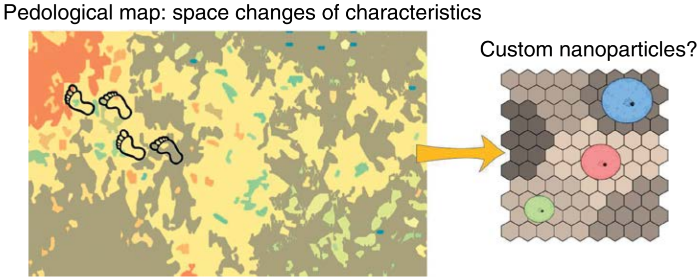

Fig. 15.2. Variability map illustrating the changes on physical, chemical and biological characteristics of the soil: in some places, soils can vary every three to four paces (assuming that 1 pace = 0.75 m).

of searching for an average result, agriculture should be seen as an accounting project to create materials that can care, heal, rebuild and nourish the soil while producing food. This is the real concept of fertilizer.

But how can we design this accounting project to apply fertilizers to soil for plant growth without compromising soil health? Would it mean the application of custom nanoparticles in every little piece of soil? This would be an expensive and unfeasible path from the point of view of farm and crop management. Here, it appears there is a need for a material containing the key concepts and processes from a biological archetype: the cell. Cells are the essential unit of life, having specific molecular properties and biological needs. In a living organism, each cell is capable of reacting to its environment and assembling molecular machinery to produce a response to its surroundings. Nevertheless, a cell cannot be built, since it holds the ultimate secrets of life, exhibiting an elegant and fundamental organizational level of properties and networks. However, it is possible to conceive of a nanobiotechnology which illustrates how specific interactions can be induced and constructed through the synthesis and self-assembly of nanostructures by mimicking templates of biological molecules and organisms.

In this context, the way to promote fertilization of soil and crops will be with an intelligent fertilizer material which can deal with, recognize and work according to the response of the surrounding medium: biomimetic cells, as units of bioinorganic nanosystems that exhibit sensing, adaptability and response properties. In other words, a nanobiotechnology which will converge and bring together all the advances obtained in different research areas of knowledge.

The new understanding on what a fertilizer is really about and what role it plays in soil and plants will depend on the integration of nanosystems and knowledge generated to date and the biotechnology advances prospects. The fertilizer should be an intelligent nanosystem that works as cells (Fig. 15.3), being a compartmentalized entity with design, patterns of structure, multiple functions

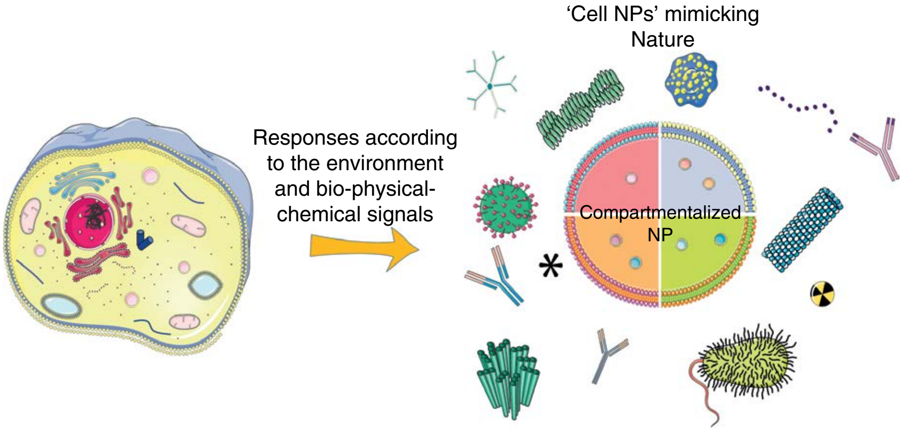

**Fig. 15.3.** Nanosystems as cells: compartmentalized entity with design, patterns of structure and mechanism of interaction, which acts as a material that recognizes and responds to the environment in which it is inserted: cell nanofertilizer.

and a mechanism of interaction, which acts as a material that recognizes and responds to the environment in which it is inserted. Its fate in the soil should follow what it is already known about nanoparticles' mobility in soils, which is dependent on many factors, such as particle size, shape and coating, medium pH, ionic strength, mineral composition, porous and water flow rate.

In fact, this task has already been begun, with many practical researches on nanobiotechnology. Researchers have already developed nanotubes able to select mass transport, allowing them to mimic the features of natural pores (Zhou *et al*., 2012). In this study, the authors showed an array that can act as a filter for some molecules and ions. With this feature, they demonstrated the building of self-assembling nanopores that are also size-specific, allowing for the manufacture of nanotubes for particular functions, such as to set up the pores to block or allow the transport of specific molecules and ions through changes in the nanopore proportions. Because of that, it is already known that the replication of cellular processes such as endocytosis, exocytosis, phagocytosis, and so on, is a reality in nanoscience, with a huge potential to transform nanotechnology through several striking properties and applications (Fig. 15.4).

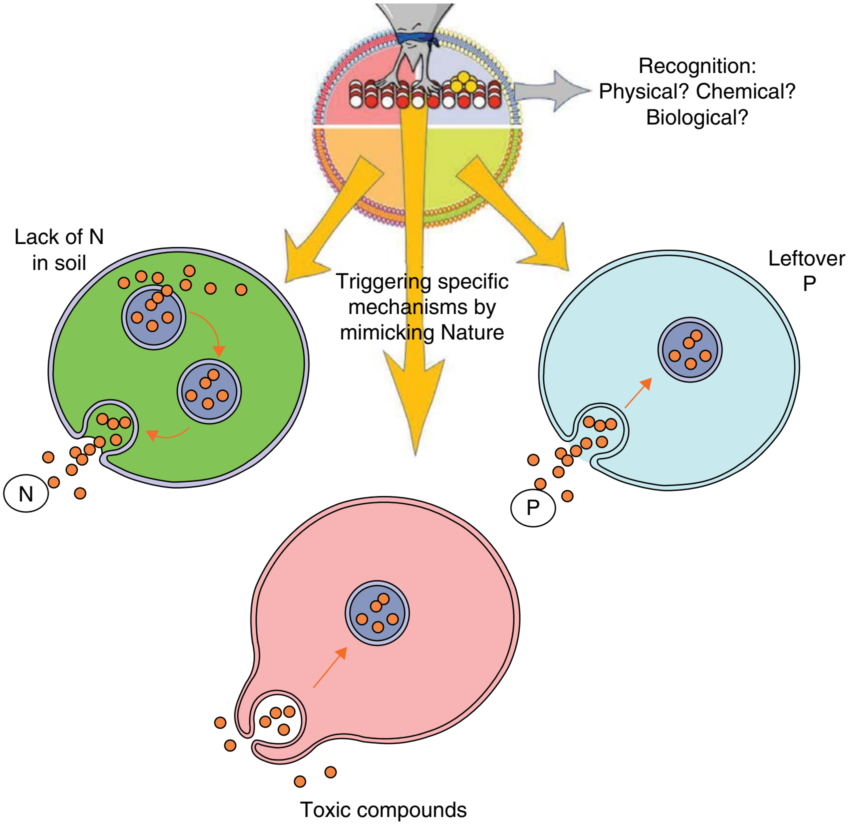

**Fig. 15.4.** Accounting project for interactive fertilization based on the response and molecule traffic through the cellular membrane of a cell nanofertilizer.

High-order levels of building and operation of such structures can be achieved using self-assembly inorganic and organic nanoparticles, proteins and surface distribution of specific amino acids. In fact, proteins are major candidates for template growth of nanomaterials and systems, since they are viewed as highly evolved structuring agents that self-assemble superstructures in the form of hierarchical architectures (Dujardin and Mann, 2007). Here, the protein–polymer hybrid structures are a promising template to build the nanofertilizer as a cell, since its structures are able to exploit the enhanced permeability and retention (EPR) effect in order to mimic the cellular membrane, to turn the nanosystem capable of performing complex tasks of opening and closing ion channels to specific signals (gating) and allowing specific ions to pass through (selectivity). These features can be achieved by the incorporation of lab-on-a-chip (LOC) devices, constructed at a nanoscale that works with nanofluidic and/or even by functionalization of the surface with nanowires that work as sensing devices which are capable of turning a physical signal into a chemical response. Actually, there is significant progress in the research field of biomimetic ion transport through ion channels. These channels, currently, are already applied in biosensors and molecular recognition (Cornell *et al.*, 1997; Husaru *et al.*, 2005; Steller *et al.*, 2012; de la Escosura-Muñiz and Merkoçi, 2016), antibacterial activity (Negin *et al.*, 2013; Leevy *et al.*, 2005a,b) and as an ion-selective electrode to monitor the concentration of ions in a medium (DiFrancesco *et al.*, 2015; Göpfrich *et al.*, 2015; Gilles *et al.*, 2016), showing that this nanotechnology is possible for application and working in the environment.

## 15.4 Perspectives, Gaps and Obstacles

Research has revealed that the current trend in agriculture is the investigation and usage of nanofertilizer in order to enhance plant growth, comparing their new properties with their behaviour on the macroscale form. The results so far are very favourable for the use of nanofertilizers and these will evolve further with the advancement of technology and accumulation of information. Finally, the perception of nanotechnology on agriculture, especially with respect to fertilizers, inclines towards the biomimetic pathway. Mechanisms able to mimic nature are already a reality and present signs of further evolution. Thus, it is possible to predict a future in which fertilizer research relies on flatter pathways and mechanisms of creation with simple building blocks, as in nature, inside a lab called the Molecular Self-Assembly Studio, where nanotechnology supports the conditions to encourage life in an efficient way.

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# 16

# Biosafety and Regulatory Aspects of Nanotechnology in Agriculture and Food

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## 16.1 Introduction

Nanotechnologies have opened the door of innovation and promises for the development of new products in almost all industrial, agricultural and food-based sectors. They have increased the efficacy of agrochemicals, enhanced nutrient availability, created efficient machinery for drug delivery, improvised food processing and product storage. They have unique properties due to their high surface-to-mass ratio, which results in a higher reactivity for interactions, ion delivery or contact. However, due to such small dimensions, characteristics such as shape, composition, charge and solubility can change their physicochemical behaviour in an unpredictable way. Therefore, they may pose a risk to human health and the environment due to widespread and irrational use, either directly, or via exposure to animals or residues in soil by the virtue of their enhanced delivery potential (Amenta *et al*., 2015; Mishra *et al*., 2017).

As new nano-based products are entering the market, their proper assessment and appropriateness require regulatory frameworks for dealing with the unintended biosafety risk posed to the consumer and the environment. Direct use of nanoparticles in various products, as well as the uptake from the environment, can lead to the presence of such materials in the processed product also. Limited data about their safety and potential impact on the consumer's health is available. The biggest concerns about their use are that they might cross biological barriers and, due to the increased surface-to-mass ratio and surface reactivity, they might also have a potential toxicological impact (Nel *et al*., 2006). In fact, many nanoparticles have distinctly different physicochemical properties, behaviour and interactions, compared to their conventional form, which makes assessing their

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potential toxic effects even more difficult (Gallocchio *et al.*, 2015). Therefore, it is problematic to predict the effects and impacts of these nanomaterials by just measuring the risk of the conventional stable form. They can even aggregate with time, depending upon their chemical properties and surroundings. In this context, certain detection methods for the characterization of nanomaterials in complex final products or food substances, and toxicological data, need to be assessed before products reach consumers (Gallocchio *et al.*, 2015). With its wide range of applications in food, medicine, nutraceuticals and agriculture, there is an urgent need for a regulatory basis to assess the efficacy and risk involved (Mishra *et al.*, 2014).

Although there is currently no legislation dedicated to the use of nanomaterials, there are isolated efforts to regulate their production and use either by legislation or by recommendations and guidelines (van der Meulen *et al.*, 2014; Amenta *et al.*, 2015). Currently, legislation on nanoparticles and nanotechnology is in place in many countries (European Commission, 2012; OECD, 2013); however, amendments have been suggested by stakeholders and non-governmental organizations. The definition of the term 'nanomaterial' itself requires regulation. Other issues include authorization procedures, specific information linked to the nano-based product, risk assessment and management, and provisions to increase the transparency and traceability of commercial products, e.g. labelling and coding (Aschberger *et al.*, 2014). In this chapter, we provide an overview of the use of nanoparticles in agriculture and the food sector, biosafety issues related to nanoparticles, and existing legislation and guidelines for risk assessment with regard to their use.

## 16.2 Nanotechnology in Agriculture and Food

Nanotechnology has promising applications in the food and agricultural sectors at different stages (Fig. 16.1). Food products containing nano-based additives are already commercially available. Likewise, a number of pesticides formulated at the nanoscale have been researched and even released into the environment.

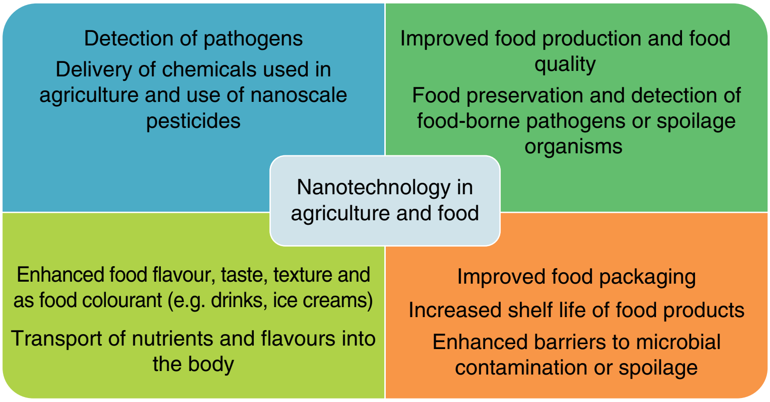

**Fig. 16.1.** Applications of nanotechnology in the agriculture and food sectors.

They are used in the delivery of chemicals applied in agriculture and for detection of animal and plant pathogens in the agricultural sector. These nanosensors work through a variety of mechanisms, such as by the use of nanoparticles tailor-made to fluoresce different colours or nanoparticles containing magnetic material which can selectively attach themselves to food pathogens. Companies like Monsanto, Syngenta and BASF are already developing nanoparticle-based pesticides. Nanoparticles are used for providing food colour and enhanced flavour (interactive drinks and ice creams), as food supplements and food with novel structure (e.g. nanoemulsion to reduce fat content), as well as for removal of contaminants and pathogens from food. Certain nanoparticles with antimicrobial or antioxidant characteristics are used in food preservation and detection of chemicals or food-borne pathogens, whereas biodegradable nanosensors are used to monitor temperature and moisture. Nanoclays or nanoflakes are also available as barrier materials. Their suspensions or encapsulated forms are used as food supplements (Gallocchio *et al.*, 2015).

## 16.3 Biosafety Issues Regarding the Use of Nanoparticles

The rapidly expanding horizon of nanotechnologies has applications in all the sectors, including agriculture, food and water. The use of certain nanoscale materials in agriculture and food may have intrinsic risks associated with human health and/or for the environment (Davies, 2010). Research has started investigating these risks (Bhattacharya *et al.*, 2012). The high surface reactivity of nanoparticles and the ability to cross cell membranes poses a risk to human health, though not all nanoparticles or nanotechnologies are a threat. Therefore, a systematic risk assessment and risk management approach is required to allow the use of nanoparticles to decrease probability of exposure or toxicity. Nano-based fertilizers have not been linked to increased phytotoxicity to date. As far as nanopesticides are concerned, their release should be highly regulated and risk assessments are required before product registration.

The broad range of applications of nanoparticles has thus increased the possibilities of risk associated with it. The important ones are as follows.

- The major risk involved is the release of nanoparticles to the environment and the possible deleterious effect they may cause to the surroundings and to consumers.
- Safety risks for workers involved in their production and packaging.
- Future risks such as enhancement of an affected living organism and self-replication of nanoparticles.

The application of nanotechnology for assessing food safety, monitoring nutritional equivalence and water safety are limited within a medium and thus contribute to low environmental exposure unless they are physically or chemically damaged (Gruère *et al.*, 2011). The intentional addition of synthetic nanominerals to bind to water-borne contaminants, such as arsenic, or use of magnetic nanoparticles or other substances to absorb or aggregate harmful substances could result in risk to human health if they are not removed from drinking water prior to its consumption. This risk could be taken care of by designing a closed system that does not allow access to unfiltered water. Most research on risk assessment is currently on non-food nanomaterials, which indicates a need for risk assessment in food-based nanomaterials (Byrne, 2010). The risks are heterogeneous and include environmental, health, occupational and socioeconomic risks. The ‘free nanoparticles’ can enter the human body directly by inhalation, ingestion or absorption through the skin, or indirectly via dispersion into the environment. Nanomaterials could reach various parts of the body, where they may exert adverse effects. Nanoparticles might disrupt cellular, enzymatic and other organ-related functions, posing potential health hazards. They might also be non-biodegradable and thus may pose a threat to the environment (TERI, 2010). Life cycle analysis (LCA) has been proposed as a first step to understand the risks from the use of nanoparticles, from their production to disposal. Adequate funding, along with robust research, is required to fill the knowledge gaps to address the safety issues. Thus, it is important to develop a regulatory framework to understand the underlying risks involved and their implications on human health and the environment.

## 16.4 Regulation

Currently, there is no specific framework for regulation of nanoparticles. In fact, most of the developed countries have not introduced specific regulations on nanotechnology (OECD, 2010), relying mainly on existing legislation to regulate nanomaterials. The issue of risk associated with nanotechnology has called for entirely new regulation at national (Patra *et al.*, 2009; Sharma, 2010) and international level (Bürgi and Pradeep, 2006). In the UK, the Science and Technology Committee of the House of Lords (House of Lords, 2010) has suggested a voluntary code of conduct, a mandatory pre-commercialization risk assessment for new nano-based food. They also recommended the revision of existing risk regulations every three years. The European Food Safety Agency supports the use of conventional risk assessment methods and guidance, acknowledging the limited data and knowledge on exposure from nano-based applications (Kuzma, 2010). Other countries provide more detailed recommendations on definitions and regulatory approaches (Chau *et al.*, 2007; Walsh and Medley, 2008) and regulatory codes of conduct (Bowman and Hodge, 2009). The Biocidal Products Regulation definition of nanomaterials (European Parliament and Council, 2012) incorporates most of the EC Recommendation criteria, without mentioning the criteria about specific surface area ($>60\ m^2/cm^3$), which is required in specific legislation. Pesticides containing nanoparticles of approved active substances require a separate risk assessment and authorization guidelines (European Parliament and Council, 2009). Similarly, the type of nanomaterial or the purpose of its use as food/feed necessitates specific legislation. The proposal for ‘novel food regulation’ (European Commission, 2013) will provide a basis for covering foods modified by processes such as nanotechnology or those consisting of ‘engineered nanomaterials’ (Amenta *et al.*, 2015). The food production concerning ‘novel foods’ and ‘novel food ingredients’ is currently covered by EC Regulation No. 258/97 (European Parliament and Council, 1997).

Addressing environmental health and safety concerns in the use and disposal of nanoparticles is still one of the biggest challenges to the development of nanotechnology. A regulatory framework is required to fine-tune regulatory capacity, coordination and information asymmetry. A comprehensive framework has to be applied for complete development and application of the technology. The legislation applicable to nanomaterials is too complex to be described in brief. The first legal definition of nanoparticles was given by the EU Commission (Recommendation 2011/696/EU) describing it thus:

> nanomaterial means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm–100 nm.

The definition of 'engineered nanomaterials' has been included in Reg. 1169/2011 (EFSA, 2011) on the provision of food information to consumer, where the labelling of food products containing nanomaterials is made mandatory. They defined the engineered nanoparticle as

> any material that is deliberately created such that it is composed of discrete functional and structural parts, either internally or at the surface, many of which will have one or more dimensions of the order of 100 nm or less.

If they are to be used as primary ingredients (e.g. nanoemulsions), they fall within the scope of 'Novel Food' Regulation (258/97) as 'foods and food ingredients with a new or intentionally modified primary molecular structure' and they are subjected to a risk assessment procedure before market approval. If they are used as food additives, a different procedure is applied (Reg. 1333/2008) and they are expected to be inserted in the EU register before use. Both developed and developing countries must be encouraged to undertake research and develop standardized protocols, reference materials and other databases to assess the risk.

## 16.5 Conclusion

Applications of nanotechnologies in agriculture and food are currently in speedy development and a large number of nano-based products are expected to enter the market in the near future. Despite these great promises, the use of nanotechnologies should be regulated carefully to avoid any unintentional deleterious effect posed by nanomaterials, several of which are already in use. Therefore, it is important to understand the biosafety issues linked to the use of nanoparticles and to have regulatory frameworks to manage the potential risks of nanotechnology. Studies should be focussed on development of analytical methods, data collection and response evaluation techniques to guarantee consumer protection. The future of agriculture relies on the development of nanoparticles, with a potential shift from inorganic materials, such as silver, to organic materials, such as nanoencapsulates and nanocomposites, with wider applications in novel foods, feed additives, biopesticides or bioherbicides. Nanotechnology thus requires the development of reliable methods for the characterization of nanomaterials in different matrices, along with the assessment of potential hazards on the environment (Servin and White, 2016) and human beings (EFSA, 2011). Furthermore, it is very important that countries across the world exchange information, engage stakeholders and non-governmental organizations, ensuring a high level of risk management and public support for nanotechnology.

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# 17

# Implication of Nanotechnology for the Treatment of Water and Air Pollution

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## 17.1 Introduction

Due to the revolution in the development of science and technology at the nanoscale, there has been an increase in the ability to fabricate and manipulate the nanosized materials; by which we mean particles smaller than 100 nm. Interest in these nanomaterials has increased tremendously because they produce many opportunities to improve the performance of material. Metal-based nanoparticles, consisting of Cu, Au, Ag, etc., have been generally used as industrial electrode, magnetic materials, chemicals, catalysts and optical media. In agriculture, the use of nanoparticles has just started, but is increasing its dimensions. With the help of nanosciences, plant growth has been enhanced by using a wide range of applications of nanotechnology (Nair *et al.*, 2010).

Nanoparticles often exhibit many useful properties which are commonly not observed in their bulk counterparts. Their applications have been reported in many fields ranging from catalysts and sensing to optics, antibacterial activity, as well as data storage (Sun *et al.*, 2000; Salata, 2004; Lu *et al.*, 2007; Zhang *et al.*, 2008; Mody *et al.*, 2010). Nanoparticles have useful applications in life sciences as well as environmental sciences. Their particle size could be compared with the small molecular dimensions (about 1–10 nm) or of viruses (about 10–100 nm). This property helps nanoparticles to combine with biological entities in such a way that their functions are not changed. Nanoparticles have a large surface area, which creates a strong association with surfactant molecules. Due to their small size and large surface area, nanoparticles become very sensitive in the detection of a specific pollution-causing contaminant in the environment. Also nanoparticles can be manipulated or engineered to interact actively with a specific pollutant and produce reactions in order to degrade the pollutant.

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Nanotechnology offers a potential application to clean the environment by detection, prevention and removal of pollutants and thus is being integrated in cleaner industrial processes and creating environmentally friendly products. For example, iron nanoparticles have the ability to remove contaminants present in soil and groundwater; whereas nanosized sensors can potentially detect and track the contaminants.

In today's world, due to modernization and advancement of industries, various types of pollutants are emitted in the environment by anthropogenic activities and industrial processes. Examples of such pollutants are chlorofluorocarbons (CFCs), heavy metals (arsenic, chromium, lead, cadmium, mercury and zinc), carbon monoxide (CO), hydrocarbons, nitrogen oxides (NOx), organic compounds (volatile organic compounds and dioxins), sulfur dioxide ($SO_2$) and particulates. Human activities, such as combustion of fossil fuels (oil, coal and gas), have great potential to create air pollution (Yunus *et al.*, 2012). Along with air pollution, water is also polluted by various factors, such as waste disposal, oil spills, leakage of fertilizers, herbicides and pesticides, byproducts of industrial processes and combustion and extraction of fossil fuels (Krantzberg *et al.*, 2010).

Mostly, the contaminants are observed to be mixed in the air, water and soil. Therefore, a technology is needed which could monitor, detect and clean the contaminants present in the air, water and soil. In such situations, nanotechnology has a wide range of properties for improving the quality of the polluted environment. Nanotechnology could also be used for preventing the generation of pollutants or contaminants by the processes of material technology, industrial methods and others. Therefore, in the field of environment, three important applications of nanotechnology can be categorized: (i) restoration (remediation) and purification of contaminated material; (ii) pollution detection (sensing and detection); and (iii) pollution prevention.

The contaminated water and polluted air substantially harm the development of plants. Several studies have reported the reduction in crop yield when irrigated with wastewater. High concentration of various air pollutants also lead to injury in agricultural crops. The processes of nanotechnology involved in the treatment of wastewater and polluted air have been described below.

## 17.2 Nanoparticles in Wastewater Treatment

Due to advancement of science and technology at the nanoscale, various problems involving the quality of water could be greatly minimized by the help of non-absorbent, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes, submicron, nanopowder, nanotubes, magnetic nanoparticles, granules, flake, micromolecules, colloids and high surface area metal particle having supramolecular assemblies (Mamadou and Savage, 2005). Nanotechnology has the potential to be used for detecting pesticides (Nair and Pradeep, 2004) and other biological materials including metals (e.g. cadmium, copper, lead, mercury, nickel, zinc), nutrients (e.g. phosphate, ammonia, nitrate, nitrite), cyanide organics, algae (e.g. cyanobacterial toxins), viruses, bacteria, parasites, antibiotics and biological agents used for terrorism. Currently, the challenges of the application of nanomaterials for the purification of surface water, groundwater and industrial wastewater streams are given much consideration.

Figure 17.1 shows a schematic presentation of a composite nanomaterial packed bed reactor for purification of water contaminated by mixtures of metal ions, organic solutes and bacteria. For purification of water, the four categories of nanosized materials generally considered as functional materials are: (i) dendrimers; (ii) metal-containing nanoparticles; (iii) zeolites; and (iv) carbonaceous nanomaterials. These nanoparticles have a wide range of physicochemical properties, which make them specifically attractive as separation and reactive media for the water purification. Characterization of the interactions of the water contaminated by harmful bacteria with nanoparticles by atomic force microscopy (AFM), transmission electron microscopy (TEM) and laser confocal microscopy exhibits changes in the cell membrane structure, which leads to the death of the bacteria in many cases.

### 17.2.1 Dendrimers in water treatment

Dendrite polymers consist of monodispersed and highly branched macromolecules such as dendrons, dendrimers, dendrigraft polymers and random hyperbranched polymers with controlled composition and structure containing three components: a core, interior branch cells and terminal branch cell (Frechet and Tomalia, 2001) and silver level composition of 10% in the tissue. The structure of dendrimer macromolecules is symmetrical and spherical, consisting of a relatively dense shell containing a core, branching sites and terminal groups which generally form a well-defined surface. The interior part could be similar or significantly different from the outer surface of the molecule. Chemical and/or physical characteristics, such as reactivity, complex or formation of salt, and hydrophilicity can be modified and optimized. As a proof of concept study, Diallo *et al*. (2005) detected the feasibility of applying dendron-enhanced ultrafiltration (DEUF) and

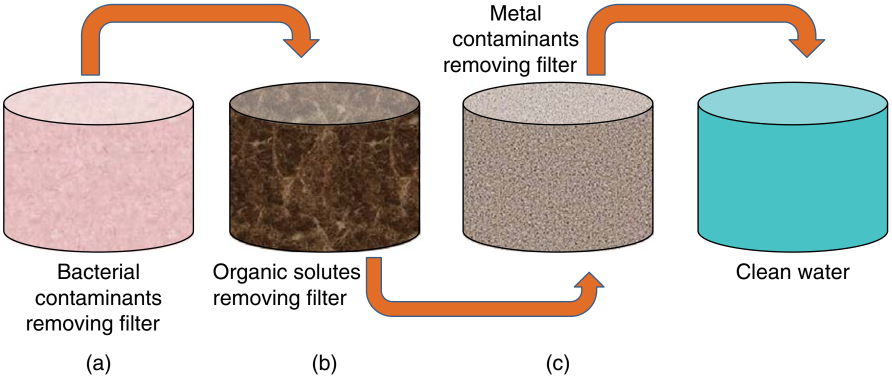

**Fig. 17.1.** Schematic presentation of a bed reactor with nanomaterial for purification of water contaminated by mixtures of (a) metal ions, (b) organic solutes and (c) bacteria.

poly (amidoamine) (PAMAM) dendrimers with ethylene diamine (EDA) core and terminal $NH_2$ groups for the recovery of Cu (II) ions from aqueous solutions. On the basis of mass, the Cu (II) binding abilities of the PAMAM dendrimers are very high and much more sensitive to solution pH compared to linear polymers with amine groups.

Dendritic polymers have also been observed to successfully deliver antimicrobial agents such as Ag (I) and quaternary ammonium chlorides (Balogh *et al.*, 2001; Chen *et al.*, 2003). Poly (amidoamine) dendrimer (PAMAM)-based silver complexes and nanocomposites have been observed to be effective in *in vitro* antimicrobial agents. In the macroscopic view, the silver is found conjugated to the dendrimer as ions, stable metallic silver clusters or silver compounds. Due to the soluble nature of the dendrimer host, it diffuses and delivers the immobilized silver in the agar medium. Extremely high surface area allows the silver clusters to remain active. The diffusion of the silver is neither blocked by reaction with chloride and sulfate ions nor by the activity against *Staphylococcus aureus, Pseudomonas aeruginosa* and *Escherichia coli*. In several situations, the protected silver and silver compounds have exhibited high antimicrobial activity without losing the solubility. However, the common cellulose membranes could prevent the diffusion of dendrimers.

### 17.2.2 Metal nanoparticle

MgO nanoparticles and magnesium (Mg) nanoparticles have been found to exhibit highly biocidal activity against Gram-positive and Gram-negative bacteria and bacterial spores, notably *Escherichia coli*, *Bacillus megaterium* and *Bacillus subtillus* (Stoimenov *et al.*, 2002). Magnesium oxide nanoparticles or magnesia nanoparticles (MgO) exhibit high surface area and are typically 5–100 nanometers (nm) with specific surface area (SSA) in the 25–50 $m^2 g^{-1}$ range. Interestingly, magnesium (Mg) nanoparticles, nanodots or nanopowder are spherical black high surface area particles. Magnesium nanoparticles are typically 20–60 nanometres (nm) with specific surface area (SSA) in the 30–70 $m^2 g^{-1}$ range.

Ag (I) and silver compounds have been observed as the effective antimicrobial compounds for coliform present in wastewater (Jain and Pradeep, 2005). The structure of silver (Ag) nanoparticles, nanodots or nanopowder is spherical and contains high surface area having high antibacterial activity (Furno *et al.*, 2004; Moran *et al.*, 2005). In general, silver nanoparticle size range includes 1–40 nanometres (nm), averaging 2–10 micron range with an estimated specific surface area of 1 $m^2 g^{-1}$. It has been observed that Ag nanoparticles act as active biocides against Gram-positive and Gram-negative bacteria, including *Escherichia coli, Staphylococcus aureus, Klebsiella pneumoniae* and *Pseudomonas aeruginosa* (Sons *et al.*, 2004; Jain and Pradeep, 2005). Gold (Au) nanoparticles, nanodots and nanopowder are brown, spherical with high surface area of metal particles. Typically, the size range of gold nanoparticles is 20–100 nanometres (nm) with specific surface area (SSA) in the 1–3 $m^2 g^{-1}$. The gold nanoparticles coated with palladium have been observed to be very effective catalysts for the removal of trichloroethane (TCE) from groundwater, which is 2200 times better than palladium alone.

Zinc oxide nanoparticles have been commonly used for the removal of arsenic from water, even though bulk zinc oxide is unable to absorb arsenic. The treatment of wastewater using some adsorption processes apply ferrites and other different forms of iron containing minerals, such as akaganeite, feroxyhyte, ferrihydrite, goethite, hematite, lepidocrocite, maghemite and magnetite. Adsorption of organics to the nanoparticle media have been observed extremely rapid. More than 90% of the organics could be adsorbed within 30 minutes. The isotherm studies showed that, on the basis of surface area, the adsorption capacities of the media containing nanoparticles were significantly (>twofold) greater than the ferric oxide media, which is typically used for the treatment of water (Yang *et al.*, 2013). Due to the smaller size of magnetic nanoparticles (about 2–3 times smaller than a bacterium), it provides extra benefits as observed by magnetic beads. When their surface area is appropriately increased, magnetic nanoparticles can also exhibit efficient binding to the bacteria due to their high surface/volume ratio offering more contact area. Nanoscale iron particles are typically 20–40 nanometres (nm) with specific surface area (SSA) in the 30–50 $m^2$ $g^{-1}$ range. Many recent studies have reported the enhanced magnetic removal of cobalt and iron from contaminated groundwater. The magnetic field-enhanced filtration/sorption process shows significant difference from magnetic separation processes, commonly applied in the processing of minerals and currently, for water treatment. For the treatment of wastewater, the use of iron ferrite and magnetite has been proved to have advantages over the conventional flocculent precipitation techniques for the removal of metal ion.

### 17.2.3 Zeolite

Zeolites are considered to be effective sorbents and ion exchange media for metal ions. NaP1 zeolites (Na6Al6Si10O32, 12$H_2O$) contain a high density of $Na^+$ ion exchange sites. NaP1 zeolites have been considered as ion exchange media for the heavy metal removal from acid mine wastewaters. Synthetic NaP1 zeolites have been observed to successfully remove Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II) from metal electroplating wastewater (Alvarez *et al.*, 2003). Non-porous ceramic oxides having very large surface areas (1000 $m^2g^{-1}$) and numerous sorption sites can be utilized to increase their specificity towards target pollutants. Experimentally, it has been observed that nanoparticles exhibit a wide range of size and morphology. Large nanoparticles (>200nm) are generally irregularly shaped crystals of zeolite, lipoteichoic acid (LTA), whereas small nanoparticles (<50 nm) are commonly spherical, dense and amorphous, which indicates destruction of the original LTA crystal structure.

### 17.2.4 Carbonaceous nanoparticle

Carbonaceous nanomaterials are used as high capacity and selective sorbents, especially for organic solutes in aqueous solutions. For this purpose, a number of polymers exhibiting antibacterial properties were developed including soluble and insoluble pyridinium-type polymers, which are generally involved in surface coating (Li, 2000), azidated poly (vinyl chloride) (Lakshmi *et al.*, 2002), which are applied to prevent bacterial adhesion of medical devices, poly(ethylene glycol) PEG polymers that can be applied on polyurethane surfaces and also prevent the initial adhesion of bacteria to the biomaterial surfaces (Lin, 2002) and polyethyleneimine (PEI) (Park, 1998) that shows high antibacterial and antifungal activity. High activity of polycationic agents is associated with absorption of positive charged nanostructures onto negatively charged bacterial cell surfaces. This process is supposed to be responsible for increasing cell permeability and disrupting the cell membranes.

Studies of PEI nanostructured compounds analyse their antibacterial properties as a character of hydrophobicity, particle size, molecular weight and charge, which can play an important role in antibacterial effect of the investigated compound. The antibacterial activity is investigated against *Streptoccocus mutans* cariogenic bacteria. Various PEI nanoparticles from 100 nm to 1 micron in diameter have been prepared exhibiting different degree of cross-linking, particle size and zeta potential which are achieved by alkylation with a bromo alkane followed by methylation. Their antibacterial effects are analysed against *Streptoccocus mutans* in direct contact with bacteria. One of the major features of the antibacterial agent is the maintenance of antibacterial activity for a long time. However, only the PEI nanoparticles containing long chain alkyls exhibited high antibacterial effect against *Streptoccocus mutans* for more than 4 weeks (Park, 1998).

## 17.3 Nanoparticles for the Adsorption of Toxic Gases

Besides water remediation, nanotechnology can also be applied for removing toxic gases from the ambient air. For example, nanotechnology is applied in the cleaning of toxic gas by the process of carbon nanotubes (CNTs) and gold particle adsorption. The structure of CNTs is a hexagonal arrangement of carbon atoms in graphene sheets, surrounding the tube axis. In this structure, a strong interaction exists between the two benzene rings of dioxin and the surface of CNTs. Besides this, dioxin molecule interaction is found with the entire surface of nanotubes having a porous wall, i.e. 2.9 nm, and the probability of overlapping events which increase the potential of adsorption inside the pores. Strong oxidation resistance of CNTs at high temperatures has also been observed beneficial for the regeneration of the adsorbent.

CNTs are unique macromolecules, both single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs), and have a one-dimensional structure, stability for temperature change and exceptional chemical properties. These nanomaterials have been observed to have more potential as superior adsorbents for removing various types of organic and inorganic pollutants, present both in air streams and in an aqueous environment. The adsorption ability of pollutants by CNTs is mainly due to the pore structure and the presence of a broad spectrum of surface functional groups of CNTs, which can be achieved by manipulating the chemical or thermal treatment to tune the CNTs for obtaining an optimal performance for a specific purpose.

The unique electronic properties and structures of CNTs have attracted researchers and gave them the idea to enhance the potential applications of SWNTs and MWNTs. For example, SWNTs have been observed to be a chemical sensor for $NO_2$ and $NH_3$. After exposing SWNTs to $NO_2$ or $NH_3$ gas, their electrical resistance was observed to change significantly, either up or down. SWNTs and MWNTs could also be used as storage for hydrogen gas. In addition, CNTs have also been used as electron field emitters, quantum nanowires, catalyst supports, etc.

### 17.3.1 Adsorption of dioxins

Dioxin and other related compounds such as polychlorinated dibenzofuran and polychlorinated biphenyls are considered stable and highly toxic pollutants. Dibenzo-p-dioxins are a family of compounds with a characteristic feature of two benzene rings which are joined together by two oxygen atoms. With the ring, about 0–8 chlorine atoms are attached. Dibenzofuran is a similar but somewhat different compound as only one of the bonds between two benzene rings are joined by oxygen. The toxicity of dioxins varies on the basis of the number of chlorine atoms. The dioxins with no or a single chlorine atom have no toxic property, while the dioxins containing more than one chlorine atom are toxic.

Since 1991, adsorption with the help of activated carbon has been commonly adopted to remove dioxins from waste incinerators in Europe and Japan. Since dioxin is an extremely toxic compound, to reduce its emission to a much lower level, a more efficient adsorbent than activated carbon is required. Regarding this, Long and Yang (2001a) have observed that the interaction of dioxin with CNTs is about three times stronger compared to the interaction of dioxin with activated carbon. This property of CNTs is probably due to the curved surface of nanotubes compared to those for flat sheets leading to strong interaction with dioxin (Bhushan, 2010).

### 17.3.2 NOx adsorption

Currently, a major effort has been put into the development of technologies for the elimination of the emissions of NOx (mixture of NO and $NO_2$) from the combustion of fossil fuels. The adsorbent commonly used for the removal of NOx at low temperatures comprises activated carbon, ion exchange zeolites FeOOH dispersed on active carbon fibre. NOx can be effectively adsorbed by the activated carbon due to reactions of surface functional groups; however, the amount of adsorption is not significant. Long and Yang (2001b) observed that CNTs could act as an adsorbent for the elimination of NO. The quantity of NOx absorption was about 78 mg $g^{-1}$ CNTs.

NOx adsorption might be influenced by the electronic properties, unique structures and surface functional groups of CNTs. After passing NO and $O_2$ through CNTs, NO is oxidized to $NO_2$, which further gets adsorbed on the outer surface of nitrate species. This process is similar to the study by Mochida *et al.* (1997), who observed the oxidation of NO to $NO_2$ at room temperature on the activated carbon fibre. Similar to NO or $NO_2$, $SO_2$ could also be adsorbed on CNTs, although the rate of adsorption is not so high, whereas $CO_2$ adsorption has been observed much less on CNTs.

### 17.3.3 $CO_2$ capture

Since the Kyoto Protocol on 16 February 2005, the sequestration of carbon dioxide ($CO_2$) produced from power plants running on fossil fuels has gained significant attention. Thus, investigations of various $CO_2$-capture technologies such as absorption, adsorption, cryogenic, membrane, etc. started to increase in number (White *et al.*, 2003; Aaron and Tsouris, 2005). The most developed process among these technologies is the adsorption–regeneration technology. In this process, amine-based absorption or ammonia absorption is the main governing principle.

Since the energy requirement for the absorption process is very high, scientists across the world are still involved in the investigation of better technologies. The Intergovernmental Panel on Climate Change (IPCC) suggested that a large-scale adsorption process design might be appropriate, and the production of a new generation of material capable of adsorbing $CO_2$ in a more efficient way will undoubtedly increase the competition for adsorptive separation in a flue gas application (Metz *et al.*, 2005). Among those adsorbents, activated carbon, zeolite, silica adsorbents, SWNTs and nanoporous silica-based molecular baskets are commonly used.

It has been suggested that the chemical modification of CNTs could have a greater potential for capture of the greenhouse gas $CO_2$. Further, the values of $CO_2$ adsorption efficiency (qe) significantly increased when the CNT was modified/combined with the chemical solutions, such as ethylene diamine (EDA), 3-aminopropyltriethoxysilane (APTS) and polyethyleneimine (PEI). The amine groups present in the solution react with $CO_2$ to produce carbamate in the absence of water, leading to enhancement in the value of qe. It has been observed that the CNTs modified by APTS increased qe by a higher amount than the CNTs modified by EDA and PEI. Commonly, the process of $CO_2$ adsorption on the modified CNTs becomes greater as the relative humidity increases; however, it becomes lower as the temperature increases.

### 17.3.4 Removal of volatile organic compounds from air

In addition to NOx and $SO_2$, many chemicals are produced by reactions in the atmosphere, such as soot (Indarto, 2009), nitrous acid (Indarto, 2012), polyaromatic compounds (Santiago and Indarto, 2008; Natalia and Indarto, 2008; Indarto *et al.*, 2009) and volatile organic compounds (VOCs). Clean air regulations currently have become more stringent, as the contaminated air is potentially damaging to human health. Conventional air purification systems are commonly based on photocatalysts, and adsorbents such as activated carbon or ozonolysis. However, these systems are not considered good for the removal of organic pollutants at room temperature. A new purification system has been developed by Japanese researchers, which looks very promising for removing VOCs, nitrogen and sulfur oxides present in air at room temperature (Sinha and Suzuki, 2007). This process involves highly porous manganese oxide containing gold nanoparticles grown into it.

For the improvement of the purification capacity of this catalyst, Sinha and Suzuki (2007) used a precursor of metal nitrate salt, a mixed non-aqueous, ethylene glycol-propanol medium and poly(alkylene oxide) block copolymers as templates, to prepare a highly stable 3D mesoporous structure. The results of the study indicated that compared to the conventional catalyst systems, this modified catalyst was very efficient in removing and degrading the three organic indoor pollutants present in the air (viz. acetaldehyde, toluene and hexane).

The important reason for the success of porous manganese oxide is its much larger surface area compared to the previously known compounds. The large surface area is very efficient in adsorption of volatile molecules. Furthermore, there is effective decomposition of the adsorbed pollutants. The degradation of the pollutants on the surface is very effective due to the presence of free radicals. This process produces a large amount of free radicals, creating a barrier, and these are reduced by the gold nanoparticles. This process of air purification has given an insight for the application of other nano-metal components.

## 17.4 Conclusions

In the current scenario of environmental degradation and increasing pollution, the development of nanotechnology has proved its importance for the purpose of maintaining environmental sustainability. Technologies that are being developed include those that can improve the performance of conventional technologies and produce of better technologies which could replace the conventional ones.

With the help of nanotechnology, the water purification process can apply iron nanoparticles, ferritin, polymeric nanoparticles, nanofibres, nanobiocides, nanoenzymes and nanofiltration techniques. Despite the application of nanotechnology for cleaning and water purification, nanotechnology can also be used for cleaning the air of toxic gaseous contaminants such as CO, VOCs and dioxins, using CNTs, gold nanoparticles and other adsorbents.

Further research is warranted using nanoscale science and technology for the identification of opportunities and applications for environmental problems, and evaluation of the potential impact of nanoparticles on the environment. Also, investigations are needed which could offer new capabilities for the prevention or treatment of highly toxic or persistent pollutants.

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# 18 Role of Nanotechnology in Insect Pest Management

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## 18.1 Introduction

A chief consideration for population development is the pertinent need for a boost in food production. A huge proportion of people living in developing countries face the problem of food scarcity as a consequence of ecological forces, namely, rainstorms, floods and droughts on agriculture (Joseph and Morrison, 2006). Correspondingly, farming and agricultural production are hampered by a number of abiotic and biotic factors. For example, insect pests, diseases and weeds cause substantial injury to prospective agricultural production. Conversely, herbivorous insects, one of the major obstacles in sustainable food production, are said to be accountable for devastating one-fifth of the world's total crop production annually and losses can occur in the field as well as during storage (Oerke, 2006). Insects are the largest group of creatures, with an extraordinary evolutionary history and found in all habitats throughout the world. Their adaptability and diversity in terms of wings, reproductive potential, behaviour, exoskeleton, eggs resistant to drought and diversification in feeding habits make them highly successful. Many species are vectors of deadly diseases, destructive as pests of agricultural and horticultural crops, structural items like wood, inimical to human health, and economically important. To offset these human conflicts and various losses that are caused, several chemicals have been employed with a view to destroy them or hinder their feeding habits and reproduction (Mogul *et al.*, 1996). The ineffective traditional methods have led to new and recent advances for management, and currently, there is an urgent need of adopting new technology for pest management. These include developments in the form of more efficient pesticides for use in lower quantities, and attributes of persistence, and versatility in application methods, such as controlled release formulations and improved devices.

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These have led to the development of new formulations, deploying the new and promising micro- and nanotechnology with a new assemblage of compounds, with the core material being protected against adverse reactions in air and light. There has been opposition to the use of pesticides, due to their harmful effects on humans as well as the environment (Sparks *et al.*, 2012). Use of nanomaterials will result in the progress of proficient and potential approaches towards management of insect pests and thus application of nanotechnology in agriculture is highly relevant (Mishra *et al.*, 2017a).

## 18.2 What is Nanotechnology?

The term nanotechnology was coined in 1974 by Norio Taniguichi of Tokyo Science University to depict semiconductor procedures such as thin-film deposition with the scale in the order of a nanometre. Nanoparticles and other nanostructured materials are often manufactured using chemical methods. The target nanoparticles can be identified with the scanning tunnelling microscope (STM) and atomic force microscope (AFM). Nanoscale science possibly began with the groundbreaking invention of the scanning tunnelling microscope, for which Gerd Binnig and Heinrich Rohrer of IBM were awarded the Nobel Prize in Physics in 1986. Nanotechnology has previously revealed huge potential for environmental safety usage (Nowack, 2009; Ying, 2009). Thus, nanotechnology refers to the science and technology of the objects that are <100 nm; one nm is $10^{-9}$ m or about 3 atoms long; for comparison, a human hair is 60,000–80,000 nm in breadth.

In 1959, physicist and Nobel laureate Richard Feynman gave what has become a classic science lecture of the 20th century – ‘There’s plenty of room at the bottom’. In it he discussed the large tools that could create miniature tools appropriate for making even smaller tools and so on, until tools fit for directly manipulating atoms and molecules were attained. Scientists have concluded that sources at minute size, like those of small particles or thin films, are similar to those from substances at larger scale. There is thus a never-ending potential for developing apparatus, composition and matter, if we can be trained how to manage diminutive structures. There are several different ways of defining what characterizes nanotechnology. The essential aspects are as follows.

1. Small size: 100s of nanometres or less.
2. Distinct properties due to small size.
3. Structure and composition are on the nm scale and properties need to be managed accordingly.

The prefix ‘nano’ is from the Greek word meaning ‘dwarf’, and is used in nanotechnology to mean $10^{-9}$ or one-billionth part of a metre. This term is solely for materials limited to 1–100 nm that exhibit properties different from bulk materials as a result of size. These discrepancies include element reactivity, material strength, magnetism, electrical conductance and ocular consequences. Nanoscience is the depiction, plan, construction and function of structures, devices and systems by controlling shape and size at the nanometre scale. Nanobiotechnology is the multidisciplinary combination of nanotechnology, biotechnology, material science, chemical processing and system engineering into biochips, molecular motors, nanocrystals and nanobiomaterials (Huang *et al.*, 2007). Solid state physics, chemistry, electrical engineering, chemical engineering, biochemistry and biophysics, and materials science are integrated here. Thus, it is an interdisciplinary science involving ideas from many disciplines. While some universities consider it a separate degree subject, others do so in the existing academic areas. In both cases, trained scientists, engineers and technicians will be required in these areas in the ensuing decades, since nanotechnology is a likely field of interdisciplinary investigation. It has modernized diverse fields like drugs, medicine, food, electronics, pharmaceuticals and agriculture. The possibilities of nanotechnology are enormous, and it is now regarded as one of the most vigorously growing research areas in modern science. It is the science of invention, planning and function of materials with size ranging from less than a micron to that of individual atoms. There are some drawbacks associated with current approaches used for pest management.

## 18.3 Nanoparticles

Nano-silica, a type of nanomaterial, is (as its name suggests) prepared from silica. It has many applications in medicine and drug advancement, most importantly, that it can be used as a pesticide. Barik *et al.* (2008) reassessed the utilization of nano-silica as nanopesticide. The use of nano-silica for pest control is based on the fact that insect pests used an array of cuticular lipids for retaining their water barrier and preventing desiccation. Physio-sorption means that nano-silica is absorbed with the cuticular lipids and leads to insect mortality when applied on stem and leaves surface (Ulrichs *et al.*, 2005). Yang *et al.* (2009) demonstrated the insecticidal activity of polyethylene glycol-coated nanoparticles packed with garlic essential oil against adult *Tribolium castaneum* in stored products. It was observed that the control efficiency against adult *T. castaneum* was about 80%, apparently due to the deliberate and determined release of the active elements from the nanoparticles. Rouhani *et al.* (2013) evaluated the efficiency of silica nanoparticles (SNP) and silver nanoparticles (AgNP) on larvae and adults of *Callosobruchus maculatus* in the seeds of cowpea. Nanoparticles of silica and silver were produced with a solvothermal method at various concentrations (1, 1.5, 2 and 2.5 g kg$^{-1}$) and evaluated. In these experiments, the $LC_{50}$ value of $SiO_2$ and Ag nanoparticles were observed to be 0.68 and 2.06 g kg$^{-1}$ on adults and 1.03 and 1.00 g kg$^{-1}$ on larvae, respectively. Goswami *et al.* (2010) explored the applications of diverse kind of nanoparticles – silver nanoparticles (SNP), aluminium oxide (ANP), zinc oxide and titanium dioxide – against the rice weevil *Sitophilus oryzae* and grasserie disease in silkworm (*Bombyx mori*) caused by baculo virus Bm NPV (*B. mori* nuclear polyhedrosis virus). Solid and liquid formulations were used in a plastic box with 20 adults of *S. oryzae* and observed for 7 days. It was found that hydrophilic SNP was most successful on the first day. On day 2, more than 90% mortality was found with SNP and ANP. After 7 days of exposure, 95 and 86% mortality were observed with hydrophilic and hydrophobic SNP and nearly 70% of the insects were killed when the rice was treated with lipophilic SNP. On the other hand, 100% mortality was detected in the case of ANP. Likewise, in the bioassay against grasserie disease, a considerable decline in viral load was obtained when food of *B. mori* was treated with ethanolic suspension of hydrophobic alumina-silicate nanoparticles. Chakravarthy *et al.* (2012) evaluated the efficiency of the DNA-tagged gold nanoparticles on the major polyphagous pest, *Spodoptera litura* (F.) (Lepidoptera: Noctuidae). The dilutions of 200, 300, 400 and 500 ppm in 10 μl of the suspension were distributed on the chickpea (*Cicer arietinum*) based semi-synthetic diet filled in 5 ml glass vials. Second instar *S. litura* larvae of identical age and size were left to feed on the diet 20 min after surface treatment. Twenty larvae of *S. litura* were exposed to each concentration of DNA-tagged gold nanoparticles for 30 s. The mortality data sets subjected to ANOVA revealed that the particles were effective and caused 50% mortality above 500 ppm.

Zahir *et al.* (2012) reported that silver nanoparticles (AgNPs) were produced by using aqueous leaf extracts of *Euphorbia prostrate* as a simple, non-toxic and ecological green material. To find out the pesticidal activity of aqueous extracts of leaves of *E. prostrata*, silver nitrate ($AgNO_3$) solution (1 mM) and synthesized AgNPs were used against the adults of *Sitophilus oryzae*. No fresh insect infestation was found in the AgNPs treated stored rice, even after 2 months of treatment. Nanoparticles thus have been shown to possess potential for new proficient and successful control of pests, but we are very short of information on how to proceed and how these can be enclosed to allow their liberation into the environment (Khot *et al.*, 2012). Nanopesticides hold surety for reducing the environmental footprint left by the conventional pesticides (Mishra and Singh, 2015). In contrast to insecticides, nanostructure alumina might provide a cheap and reliable substitute for control of insect pests, and such studies may enlarge the frontiers for nanoparticles based technologies in pest management (Table 18.1).

## 18.4 Nanoencapsulation

Nanoencapsulation is a practice through which a chemical is gradually but economically liberated to the targeted host for insect pest control. The release mechanisms comprise suspension, dispersal, biodegradation and osmotic pressure with specific pH (Vidyalakshmi *et al.*, 2009).The release rate depends upon the safety time; subsequently a decline in release rate can extend mosquito protection time (Sakulk *et al.*, 2009). Nanopesticides, nanofungicides and nanoherbicides are being applied economically in agriculture (Owolade *et al.*, 2008). Bhagat *et al.* (2013) concluded that social management of fruit flies involving pheromones is useful in managing the detrimental pest populations accountable for lessening the yield and the crop value. Nanoencapsulation comprises the use of a diverse type of nanoparticles with insecticide. Here an insecticide is gradually but economically liberated to a targeted host plant for insect pest control. Nanoencapsulation with nanoparticles in form of pesticide permits for appropriate inclusion of the chemical into the plants unlike the case of larger particles (Scrinis and Lyons, 2007). Teodoro *et al.* (2010) pioneered the study of insecticidal activity of nanostructured alumina against two insect pests, *S. oryzae* and *Rhyzopertha dominica*, which are major insect pests in stored food supplies throughout the world. These

**Table 18.1.** Insecticidal activity of various nanoparticles/nanoformulation for potential application in agriculture.

| Nanoparticles/ Nanoformulations | Efficacy | References |
|---|---|---|
| Silica nanoparticles | Insecticidal activity against *Rhyzopertha dominica* F. and *Tribolium confusum* Jacquelin du Val<br>Insecticidal activity against *Callosobruchus maculatus* | Ziaee and Ganji, 2016<br>Arumugam *et al*., 2016<br>Rouhani *et al*., 2013 |
| Nanocrystalline palladium nanoparticles | Acaricidal, insecticidal and larvicidal efficacy | Roopan *et al*., 2012 |
| Nanoformulations of β-cyfluthrin | Bioefficacy against *Callosobruchus maculatus* | Loha *et al*., 2012 |
| Silver nanoparticles | Pesticidal activity against *Sitophilus oryzae* | Zahir *et al*., 2012 |
| Nicotine carboxylate nanoemulsion | Insecticidal activity against *Drosophila melanogaster* | Casanova *et al*., 2005 |
| Nanoformulation of polyethylene glycol (PEG)-coated nanoparticles loaded with garlic essential oil | Insecticidal activity against adult *Tribolium castaneum* | Yang *et al*., 2009 |
| Nanoformulations of aluminium oxide, zinc oxide and titanium dioxide nanoparticles | Insecticidal activity against rice weevil *Sitophilus oryzae* | Goswami *et al*., 2010 |

studies reported significant mortality after 3 days of continuous exposure to nanostructured alumina-treated wheat.

Syngenta, the world's prime agrochemical company, is using nano-emulsions in its pesticide products. One of its successful development regulating products is the Primo MAXX® plant growth regulator, which, if applied prior to the beginning of pressure such as drought, heat, disease or traffic, can build up the physical configuration of turf grass and allow it to endure ongoing stress all through the growing season. A further encapsulated product from Syngenta provides a broad control spectrum on primary and secondary insect pests of rice, cotton, soybean and groundnut. Marketed under the name Karate® ZEON is a rapid discharge microencapsulated product restraining the active compound lambda-cyhalothrin (a synthetic insecticide) which ruptures open on contact with leaves. In comparison, the encapsulated product 'gutbuster' only ruptures open to release its substances when it comes into contact with alkaline surroundings, such as the stomach of certain insects.

## 18.5 Application of Nanotechnology

The currently investigated nanotechnology-based applications in food technology, from agriculture to food processing, packaging and food supplements have been illustrated in Fig. 18.1. Based on studies to date and ongoing research,

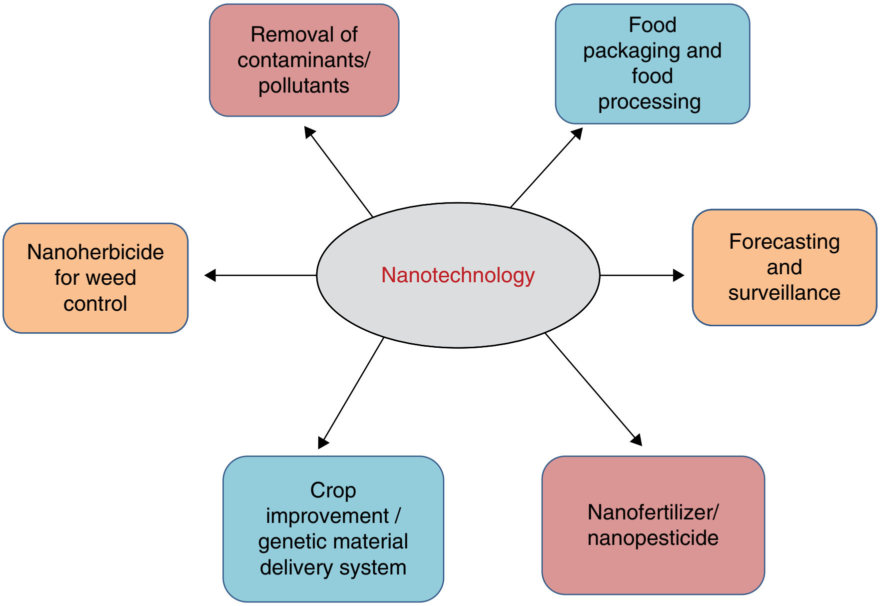

**Fig. 18.1.** Multifarious applications of nanotechnology in agriculture.

it is clear that nanotechnology has revolutionized the agricultural sector. Nanotechnology-based approaches have efficiently been used in different sectors, such as agriculture, food processing/packaging and feed sectors. Remarkable applications of nanotechnology include encapsulation of agrochemicals as a smart delivery system, nanopesticides for plant disease management, crop improvement through delivery of genetic materials and appropriate food packaging system for food protection (Kah and Hofmann, 2014; Mishra *et al.*, 2014; Mishra *et al.*, 2017b). Besides that, nanosensors and nanochips have also been developed for monitoring soil conditions and detecting pathogens (Gogos *et al.*, 2012).

In the food sector, nanotechnology has offered potential applications that involve supplements and food additives in order to enhance the stability of foods during storage. Likewise, for better storage of food, nanoclays and nanofilms are applied which act as a barrier to retard oxygen assimilation. Moreover, food surface coatings with antimicrobial nanoparticles improve shelf life and protect the food from deterioration and damage. Furthermore, various ecological nanosensors and antibody-linked nanoparticles have been developed to identify food-borne pathogens and for monitoring the temperature and moisture level (Amenta *et al.*, 2015).

### 18.5.1 Other applications of nanotechnology

A team of researchers led by Zhang and Liu (2006) have used the wings of cicadas, ubiquitous insects best known for their acoustic skills, as stamps to pattern polymer films with nanometre-sized structures. The wings of these insects are characterized by extremely ordered arrangements of regularly spaced microscopic pillars.

The researchers were inspired by the natural world to conceive their nanolithography procedure, which could produce helpful light-scattering or water-repelling characteristics. Cicada-inspired nanosurfaces could be utilized in precision lenses, where light-reflecting properties are essential. Silk fibroin (SF) nanofibre non-woven materials made by an electro-spinning process are used in wound dressing.

Ganeshprabhu *et al.* (2012) observed that the feed efficiency of larvae (5th instar) was enhanced by 25% silver nanoparticles in comparison to control and others (50%, 75% and 100%). The green production of silver nanoparticles was done by using silver originator (silver nitrate – $AgNO_3$) with *Morus sinensis* leaf extract as a stabilizing and reducing agent. The different concentrations (25%, 50%, 75% and 100%) of prepared silver nanoparticles were applied to evaluate the larval period. This study has revealed that the silver nanoparticles have definite expansion stimulant activity and could be utilized to enlarge the silk yield in commercial sericulture.

### 18.5.2 Areas of nanoscience research in agriculture and food science

Involvement of nanoscience research in agriculture is in the areas of:

- food safety and biosecurity;
- materials science;
- food processing and product development.

### 18.5.3 Natural nanoparticles in insects

Naturally occurring nanostructures are very few, but these are a rich resource of products that meet definite specifications (Watson and Watson, 2004). The trades supported by nanotechnology have so far made little use of ‘free’ technology accessible in nature (Ehrlich *et al.*, 2008). The hexagonal patterns in the wings of the cicada, *Psaltoda claripennis* Ashton, and termites in the Rhinotermitidae family are good examples (Zhang and Liu, 2006). The size of nanoparticles varies from 200 to 1000 nm, and they have an encircled shape at the apex and protrude some 150–350 nm from the surface plane. These wing nanoparticles help in aerodynamic effectiveness. The size of isolated nanoparticles measure about 12 nm diameter in abdomen with petiole whereas they measure 11 nm diameter in head with antennae. Nanostructure elements are also present in the compound eyes of insects. Wings of butterflies acquire bright colour elements and these are nothing but nanoparticles. Recently, a novel photodegradable insecticide containing nanoparticles was brought out (Guan *et al.*, 2008).

### 18.5.4 Nanotechnology in migrational studies

Nano-tagged insects can gather prohibited biological, chemical or radiological materials from the surroundings they move through and convey them for investigation, giving both composition and source of these hazards. The procedure begins when nano-taggants, comprising metallic nanoparticles bound to fluorescent semiconductor quantum dots, are scattered on the wings of captured insects. The metallic nanoparticles are definite alloy concentrations, which permit the categorized insects to be recognized after recapture. The insects are liberated into the region to be monitored for a chosen period of time, and are afterwards recaptured. The captured insects are exposed to ultraviolet or visible light that formulates the nano-taggant quantum dots glow, allowing the tagged insects to be recognized with hand-operated portable detectors that are commercially accessible and usable by field-grade personnel. The composition of the metallic nanoparticles connected to the quantum dots is then read like a barcode, using laser-induced breakdown spectroscopy, representing the precise batch insects and connecting them with the environment that they tested.

### 18.5.5 Nanopesticides

Over the last decade, nanotechnology has been presented as having the potential to modernize agricultural functions (e.g. Scott and Chen, 2003; Royal Society and Royal Academy of Engineering, 2004). The proposals such as genetically modified crops (using nanoparticles, nanofibres, or nanocapsules as vectors for DNA) or expansion of precision farming devices (e.g. nanosensors) are still in the early stages of development. The nanopesticides are those that in any formulation essentially contain ingredients in the nanometre size range and/or states having novel possessions correlated with this small size range. Thus it would come out that some nanopesticides have already been in the market for several years. Nanotechnology is a current discipline which has been utilized in pest control. The inventiveness of nanotechnology is the ability to specifically form matter to atomic level specificity. Thus, the most important benefit of employing nano-based pesticides is the chance to improve properties such as specificity and efficiency. The possible application and advantages of nanotechnology are vast. These comprise insect pest management by the formulation of nanomaterial-based pesticides and insecticides, bioconjugated nanoparticles for deliberate discharge of nutrients and insecticides. Nanotechnology has potential application in nanoparticle-mediated gene transfer. It can be applied to deliver DNA and other necessary chemicals into the plant tissues for the safety of host plants but without benefit to insect pests (Torney, 2009). Worldwide, insect pests cause a huge crop loss of 14% and plant pathogens cause an estimated loss up to 13% with a value of US$2,000 billion per year (Pimentel, 2009). Nanomaterials are exploited economically for safe application of pesticides, herbicides and fertilizers at lower doses (Kuzma and Verhage, 2006). Pesticides cause undesirable consequences on human health and on pollinating insects. So, nanomaterials play an imperative role in diminishing toxicity and aiding the efficiency of pesticides (Mousavi and Rezaei, 2011). Nanopesticide formulations liberate the active ingredient gradually and essentially enhance the solubility of poorly soluble active ingredient. Nanopesticides are thus formulations that intentionally consist of elements in the nm size range and/or display novel characteristics connected with this small size range. Some nanopesticides have been on the market for several years. Nanopesticides include an immense range of products and cannot be regarded as a single class; these could consist of organic (e.g. active ingredient (a.i.), polymers) and/or inorganic ingredients (e.g. metal oxides) in different forms (e.g. particles and micelles). The nanoformulations must have the following properties.

**1.** Enhancing the perceptible solubility of poorly soluble active ingredient.
**2.** Discharging the active ingredient in a deliberate/targeted way and/or defending the active ingredient against spontaneous deficiency.

Rotenone, a water-insoluble botanical insecticide which has been used to control thrips, aphids and mites for decades, is inadequate due to its poor water solubility, degradation, permanence, and isomerization when in sunlight. Lao *et al.* (2010) effectively produced nanoparticles by attaching octadecanol-1glycidyl ether to amino groups and sulfate to hydroxyl groups with novel amphiphilic chitosan derivatives N(octadecanol-1-glycidyl ether)-O sulphate chitosan (NOSCS), with particle sizes of 167.7 to 214.0 nm and zeta potential of –45.0 to –51.9 mV. This study showed a way to allow slow release of water-insoluble agrochemicals. Nanostructured alumina was successfully employed in controlling two major stored insect pests, *Sitophilus oryzae* and *Rhyzopertha dominica* on wheat (Stadler *et al*., 2010). Debnath *et al.* (2011) explored the effectiveness of surface-utilized silica nanoparticle against rice weevil, *Sitophilus oryzae*, and they observed that the silica nanoparticle-treated stored rice was not attacked by pests after 2 months of treatment.

The nanopesticide formulations are usually related to those of other pesticide formulations, but the objective of these being: (i) to raise the perceptible solubility of poorly soluble a.i.; or (ii) to liberate the a.i. in a deliberate/marked way and/or defend the a.i. alongside impulsive degradation. Nanopesticides were first categorized according to the planned function, with the object of analysing potential outcomes influencing ecological fortune.

## 18.6 Categories of Nanopesticides

**a) Microemulsions:** The atom size in microemulsions is about 250 times smaller than typical pesticide elements (ETC, 2004) and numerous ones have been proposed with diameters less than 100 nm (ETC, 2004; Observatory Nano, 2010). Microemulsions are thermodynamically stable water-based formulations comprising: (i) suspended a.i. in oil; (ii) surfactant solubilizers (blend); (iii) a co-surfactant (often medium chain aliphatic alcohol); and (iv) water (Lawrence and Warisnoicharoen, 2006; Green and Beestman, 2007). Many microemulsion formulations are available in the market (e.g. 12 different a.i. listed in Tomlin, 2009). For illustration, Syngenta has been marketing Primo MAXX since 1993: this product is currently the plant growth regulator extensively exploited by golf course superintendents and other professional turf managers (Observatory Nano, 2010). Former products by Syngenta also promoted as microemulsion concentrate formulations include Subdue MAXX (systemic fungicide), Banner MAXX (systemic fungicide for broad-spectrum disease control in turf and ornamentals), and Apron MAXX (disease protection for soybean; Observatory Nano, 2010).

In contrast to other formulations (e.g. emulsifiable concentrations, or ECs) the improvements of microemulsions included: (i) advanced tank mix compatibility; (ii) developed stability; (ii) decreased wear on equipment (e.g. preventing spray tank filters from clogging); and (iv) low flammability (due to low solvent content in a continuous water phase, ETC, 2004; Observatory Nano, 2010). Microemulsions can improve herbicidal efficiency due to the developed penetration or uptake of the a.i. that results from the high solubilizing power of surfactants (Green and Beestman, 2007). Disadvantages of microemulsions comprise: (i) a small a.i. content (<30%); (ii) a high concentration of surfactants (usually in the region of 20%, Tadros *et al.*, 2004; Lawrence and Warisnoicharoen, 2006); and (iii) the restricted number of appropriate surfactant systems. Finally, an increased uptake is confirmed through microemulsion formulations and these might also present phytotoxicity and toxicity issues.

**b) Nanoemulsions:** Nanoemulsions (also referred to as miniemulsions, ultrafine emulsions, and submicron emulsions; Lawrence and Warisnoicharoen, 2006; Anton *et al.*, 2008; Song *et al.*, 2009) are emulsions with a droplet size that can be related with those of microemulsions. Even though there still appears to be some disagreement between authors regarding the appropriate terminology (e.g. Mason *et al.*, 2006; Gutierrez *et al.*, 2008), the main difference between microemulsions and nanoemulsions is usually based on stability status. As microemulsions are thermodynamically constant, nanoemulsions have the affinity to divide into the component phases. Nanoemulsions may however acquire a comparatively high kinetic (meta-) strength (Gutierrez *et al.*, 2008) and are often said to be metastable.

**c) Nanodispersion:** Diffusion of nanocrystals (crystalline or unstructured particles consisting of 100% a.i.) in fluid media directly related to the development of nanodispersions (also called nanosuspensions; Muller and Junghanns, 2006). This advance plans to make the most of the surface area in order to increase the dissolution speed and solubility diffusion due to poor water solubility of the a.i. The maximum dissolving strength is expected for crystals <50 nm (Muller and Junghanns, 2006).

## 18.7 Safety of Nanoinsecticides

**a) Potential human health concerns:** (i) dermal assimilation (so small they may go through cell membranes); (ii) inhalation (go to the deep lung and may translocate to the brain, i.e. could cross the blood–brain barrier), and **potential environmental concerns:** (iii) high durability or reactivity of some nanomaterials raises issues of their fate in the environment; (iv) lack of information to assess environmental exposure to engineered nanomaterials.

**b) Socioeconomic issues of agricultural nanotechnology:** the appearance of nanotechnology applications in user products has also produced moral and communal unease in some countries, primarily from the health and ecological safety point of view, to user awareness and ethical usage. There are many sociopsychological issues that influence the public response to the beginning of a new technology. In the case of nanotechnology, it is essential to identify these issues among different stakeholder groups. Different studies about consumer acceptance of nanotechnology products show that the public view is commonly not negative. As for many rising technologies, the common and valid characteristics of nanotechnology and securing freedom to function are matters that must be dealt with before developing new products. The number of patent applications in nanotechnology has increased more than tenfold during the last 20 years, representing a huge potential for commercial applications. Copyrighting on nanotechnology in common presents some essential concerns. Nanotechnology has been developed for different fields of application and nano-based creations could infringe patents in those fields. This threat of overlapping patents can also have effects for the agri-food sector. Furthermore, patent containers could lock up enormous areas of technology. There are already over 3000 patents globally for potential agrochemical usage of nanotechnology, but they are most likely patents with broad claims. In developing countries, nanotechnologies can have imperative applications in several agri-food areas, such as food security, input delivery, rice production systems, agri-biotechnology, healthcare of animals, precision farming, the food industry and water use. The key factors limiting the expansion of these applications are low investments in manpower training and in research infrastructure.

## 18.8 Conclusion

Nanotechnology has the potential to modernize the existing technologies used in various divisions together with agriculture. Nanotechnology may have actual solutions alongside many agriculture-interrelated problems like insect pest management via conventional means, expansion of advanced crop varieties, undesirable consequences of chemical pesticides, etc. Nanomaterials in diverse forms can be applied for proficient management of insect pests and formulations of potential insecticides and pesticides. Nanoparticle-mediated gene transfer would be helpful for the improvement of new insect-resistant varieties. Consequently, it can also be concluded that nanotechnology can provide green and ecological substitutes for insect pest management without damaging the environment.

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